

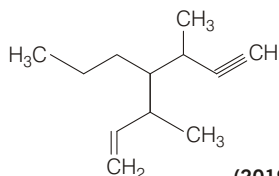
# 21

# Organic Chemistry Basics

## Topic 1 Nomenclature and Isomerism

### Objective Questions I (Only one correct option)

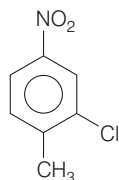
1. The IUPAC name for the following compound is



(2019 Main, 12 April II)

- (a) 3-methyl-4-(3-methylprop-1-enyl)-1-heptyne  
(b) 3, 5-dimethyl-4-propylhept-6-en-1-yne  
(c) 3-methyl-4-(1-methylprop-2-ynyl)-1-heptene  
(d) 3, 5-dimethyl-4-propylhept-1-en-6-yne

2. The correct IUPAC name of the following compound is



(2019 Main, 9 April I)

- (a) 2-methyl-5-nitro-1-chlorobenzene  
(b) 3-chloro-1-methyl-1-nitrobenzene  
(c) 2-chloro-1-methyl 1-4-nitrobenzene  
(d) 5-chloro-4-methyl 1-1-nitrobenzene

3. Which of the following compounds will show the maximum 'enol' content? (2019 Main, 8 April II)

- (a)  $\text{CH}_3\text{COCH}_3$   
(b)  $\text{CH}_3\text{COCH}_2\text{COCH}_3$   
(c)  $\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5$   
(d)  $\text{CH}_3\text{COCH}_2\text{CONH}_2$

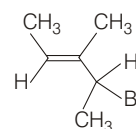
4. The IUPAC name of the following compound is



(2019 Main, 8 April I)

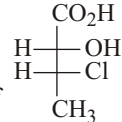
- (a) 4,4 - dimethyl -3-hydroxybutanoic acid  
(b) 2-methyl-3-hydroxypentan-5-oic acid  
(c) 3- hydroxy -4- methylpentanoic acid  
(d) 4-methyl-3-hydroxypentanoic acid

5. What is the IUPAC name of the following compound?



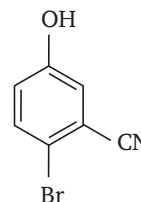
(2019 Main, 10 Jan II)

- (a) 3-bromo-3-methyl-1,2-dimethylprop-1-ene  
(b) 3-bromo-1,2-dimethylbut-1-ene  
(c) 2-bromo-3-methylpent-3-ene  
(d) 4-bromo-3-methylpent-2-ene

6. The absolute configuration of  is (2016 Main)

- (a) (2S, 3R) (b) (2S, 3S)  
(c) (2R, 3R) (d) (2R, 3S)

7. The IUPAC name of the following compound is



(2009)

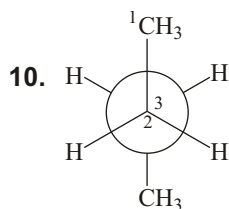
- (a) 4-bromo-3-cyanophenol  
(b) 2-bromo-5-hydroxybenzonitrile  
(c) 2-cyano-4-hydroxybromobenzene  
(d) 6-bromo-3hydroxybenzonitrile

8. The number of stereoisomers obtained by bromination of *trans*-2-butene is (2007, 3M)

- (a) 1 (b) 2 (c) 3 (d) 4

9. The IUPAC name of  $\text{C}_6\text{H}_5\text{COCl}$  is (2006, 3M)

- (a) benzoyl chloride  
(b) benzene chloro ketone  
(c) benzene carbonyl chloride  
(d) chloro phenyl ketone



$C_2$  is rotated anti-clockwise  $120^\circ$  about  $C_2-C_3$  bond. The resulting conformer is (2004, 1M)

- (a) partially eclipsed (b) eclipsed  
(c) gauche (d) staggered
11. Which of the following compounds exhibits stereoisomerism? (2002, 3M)  
(a) 2-methylbutene-1 (b) 3-methylbutyne-1  
(c) 3-methylbutanoic acid (d) 2-methylbutanoic acid
12. The number of isomers for the compound with molecular formula  $C_2BrClFI$  is (2001, 1M)  
(a) 3 (b) 4 (c) 5 (d) 6
13. Which of the following compounds will exhibit geometrical isomerism? (2000, 1M)  
(a) 1-phenyl-2-butene (b) 3-phenyl-1-butene  
(c) 2-phenyl-1-butene (d) 1,1-diphenyl-1-propene
14. The optically active tartaric acid is named as D-(+)-tartaric acid because it has a positive (1999, 2M)  
(a) optical rotation and is derived from D-glucose  
(b) pH in organic solvent  
(c) optical rotation and is derived from D-(+)-glyceraldehydes  
(d) optical rotation when substituted by deuterium
15. How many optically active stereoisomers are possible for butane-2, 3-diol? (1997, 1M)  
(a) 1 (b) 2 (c) 3 (d) 4
16. Isomers which can be interconverted through rotation around a single bond are (1992, 1M)  
(a) conformers (b) diastereomers  
(c) enantiomers (d) positional isomers
17. The enolic form of acetone contains (1990, 1M)  
(a) 9 sigma bonds, 1 pi bond and 2 lone pairs  
(b) 8 sigma bonds, 2 pi bonds and 2 lone pairs  
(c) 10 sigma bonds, 1 pi bond and 1 lone pair  
(d) 9 sigma bonds, 2 pi bonds and 1 lone pair
18. The number of isomers of  $C_6H_{14}$  is (1987, 2007, 3M)  
(a) 4 (b) 5 (c) 6 (d) 7
19. If two compounds have the same empirical formula but different molecular formulae, they must have (1987, 1M)  
(a) different percentage composition  
(b) different molecular weight  
(c) same velocity  
(d) same vapour density
20. Which of the following will have least hindered rotation about carbon-carbon bond? (1987, 1M)  
(a) Ethane (b) Ethylene  
(c) Acetylene (d) Hexachloroethane

21. The IUPAC name of the compound  $CH_2=CH-CH(CH_3)_2$  is (1987, 1M)  
(a) 1,1-dimethyl-2-butene (b) 3-methyl-1-butene  
(c) 2-vinyl propane (d) None of these

22. An isomer of ethanol is (1986, 1M)  
(a) methanol (b) diethyl ether  
(c) acetone (d) dimethyl ether

23. The IUPAC name of the compound having the formula is  $CH_3$



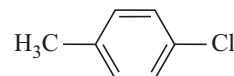
$CH_3$  (1984, 1M)

- (a) 3, 3, 3-trimethyl-1-propene  
(b) 1, 1, 1-trimethyl-2-propene  
(c) 3, 3-dimethyl-1-butene  
(d) 2, 2-dimethyl-3-butene
24. Which of the following compounds will exhibit *cis-trans* (geometrical) isomerism? (1983, 1M)  
(a) 2-butene (b) 2-butyne  
(c) 2-butanol (d) butanal
25. The compound which is not isomeric with diethyl ether is (1981, 1M)  
(a) *n*-propyl methyl ether (b) butane-1-ol  
(c) 2-methyl propane-2-ol (d) butanone

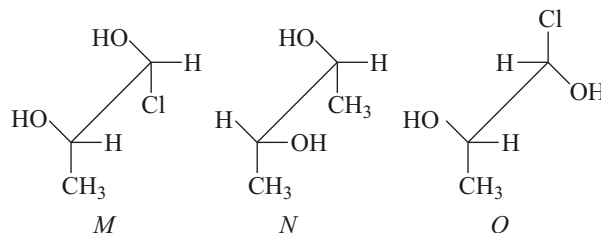
## Objective Questions II

(One or more than one correct option)

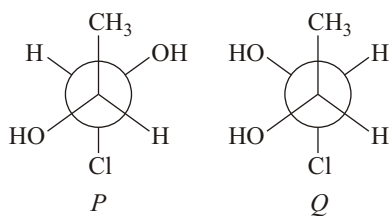
26. The IUPAC name(s) of the following compound is (are) (2017 Adv.)



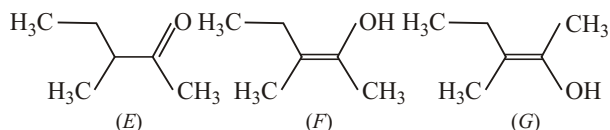
- (a) 4-methylchlorobenzene  
(b) 4-chlorotoluene  
(c) 1-chloro-4-methylbenzene  
(d) 1-methyl-4-chlorobenzene
27. The correct combination of names for isomeric alcohols with molecular formula  $C_4H_{10}O$  is/are (2014 Adv.)  
(a) *tert*-butanol and 2-methylpropan-2-ol  
(b) *tert*-butanol and 1,1-dimethylethan-1-ol  
(c) *n*-butanol and butan-1-ol  
(d) *iso*-butyl alcohol and 2-methylpropan-1-ol
28. Which of the given statement(s) about *N*, *O*, *P* and *Q* with respect to *M* is/are correct? (2012)



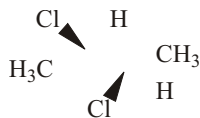
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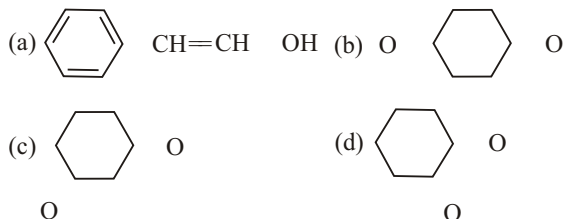
- (a) *M* and *N* are non-mirror image stereoisomers  
 (b) *M* and *O* are identical  
 (c) *M* and *P* are enantiomers  
 (d) *M* and *Q* are identical
29. The correct statement(s) about the compound (2009)  
 $\text{H}_3\text{C}(\text{HO})\text{HC}=\text{CH}-\text{CH}=\text{CH}(\text{OH})\text{CH}_3$  (*X*) is/are  
 (a) The total number of stereoisomers possible for *X* is 6  
 (b) The total number of diastereomers possible for *X* is 3  
 (c) If the stereochemistry about the double bond in *X* is *trans*, the number of enantiomers possible for *X* is 4  
 (d) If the stereochemistry about the double bond in *X* is *cis*, the number of enantiomers possible for *X* is 2
30. The correct statement(s) concerning the structures *E*, *F* and *G* is/are



- (a) *E*, *F* and *G* are resonance structures  
 (b) *E*, *F* and *E*, *G* are tautomers  
 (c) *F* and *G* are geometrical isomers  
 (d) *F* and *G* are diastereomers
31. The correct statement(s) about the compound given below is/are

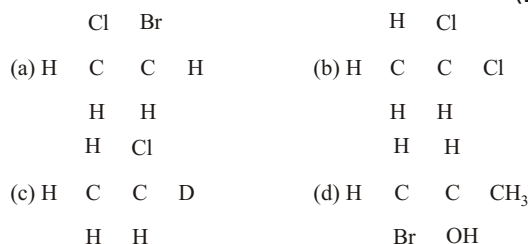


- (a) the compound is optically active  
 (b) the compound possesses centre of symmetry  
 (c) the compound possesses plane of symmetry  
 (d) the compound possesses axis of symmetry
32. Tautomerism is exhibited by (1998, 2M)

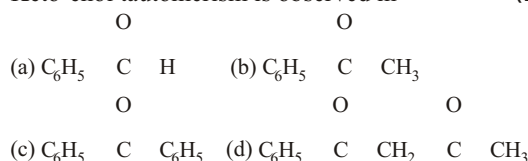


33. Which of the following compounds will show geometrical isomerism? (1998, 2M)  
 (a) 2-butene  
 (b) propene  
 (c) 1-phenyl propene  
 (d) 2-methyl-2-butene

34. Which of the following have asymmetric carbon atom? (1989, 1M)



35. Keto-enol tautomerism is observed in (1988, 2M)

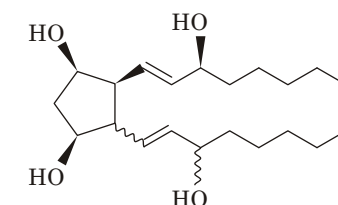


36. Only two isomeric monochloro derivatives are possible for (1986, 1M)



### Numerical Value Based Question

37. For the given compound *X*, the total number of optically active stereoisomers is .....



- ▶ This type of bond indicates that the configuration at the specific carbon and the geometry of the double bond is fixed  
 ~~~ This type of bond indicates that the configuration at the specific carbon and the geometry of the double bond is not fixed

(2018 Adv.)

### Assertion and Reason

Read the following questions and answer as per the direction given below :

- (a) Statement I is correct; Statement II is correct; Statement II is the correct explanation of Statement I  
 (b) Statement I is correct; Statement II is correct; Statement II is not the correct explanation of Statement I  
 (c) Statement I is correct; Statement II is incorrect  
 (d) Statement I is incorrect; Statement II is correct
38. **Statement I** Molecules that are non-superimposable on their mirror images are chiral.  
**Statement II** All chiral molecules have chiral centres.  
 (2007, 3M)

### Fill in the Blanks

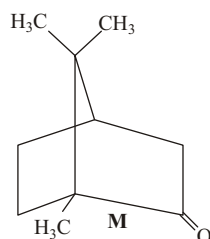
39. Isomers which are ..... mirror images are known as ..... (superimposable, non-superimposable, enantiomers, diastereomers, epimers) (1988, 1M)

## True/False

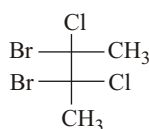
40. 2, 3, 4-trichloropentane has three asymmetric carbon atoms. (1990, 1M)
41. *m*-chlorobromobenzene is an isomer of *m*-bromochlorobenzene. (1985,  $\frac{1}{2}$ M)

## Integer Answer Type Questions

42. The total number of stereoisomers that can exist for *M* is (2015 Adv.)



43. The total number(s) of stable conformers with non-zero dipole moment for the following compound is/are



(2014 Adv.)

## Subjective Questions

44. Give the total number of cyclic structural as well as stereoisomers possible for a compound with the molecular formula  $C_5H_{10}$ . (2009)

45.  $\text{obs} = \sum_i f_i X_i$   
where  $f_i$  is the dipole moment of stable conformer and  $x_i$  is the mole fraction of that conformer.

(a) Write stable conformer for  $Z$   $\text{CH}_2 = \text{CH}_2$   $Z$  in Newman's projection.

If solution 1.0 D and mole fraction of *anti* form 0.82, find *gauche*

(b) Write most stable *meso* conformer of  $(\text{CHDY})_2$ . If

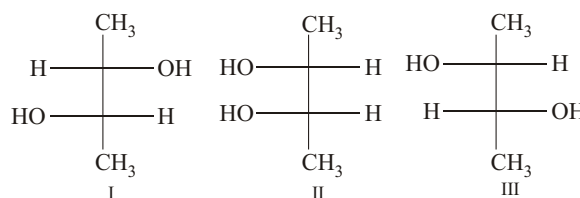
(i)  $Y = \text{CH}_3$  about  $C_2-C_3$  rotation and

(ii)  $Y = \text{OH}$  about  $C_1-C_2$  rotation. (2005, 6M)

46. (a) Draw Newman's projection for the less stable staggered form of butane.  
(b) Relatively less stability of the staggered form is due to  
(i) Torsional strain  
(ii) van der Waals' strain  
(iii) Combination of the above two (2004, 5M)

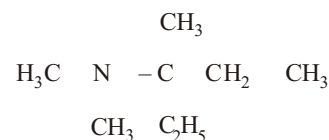
47. Glycerine contain one ..... hydroxy group. (2004)

48. Identify the pairs of enantiomers and diastereomers from the following (2000, 2M)



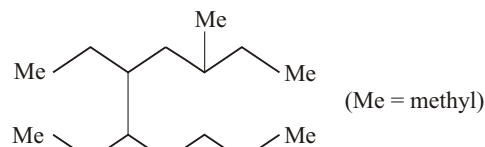
49. Write tautomeric forms of phenol. (1992, 1M)

50. Write the IUPAC name of the following compound:



(1991, 1M)

51. Give the IUPAC name of the following compound :



(1990, 1M)

52. Write the IUPAC name of  $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCOOH}$ . (1986, 1M)

53. Write the structure of all the possible isomers of dichloroethene. Which of them will have zero dipole moment ? (1985, 2M)

54. Write structural formulae for the isomeric alcohols having the molecular formula  $C_4H_{10}O$ . (1984, 2M)

## Topic 2 General Organic Chemistry

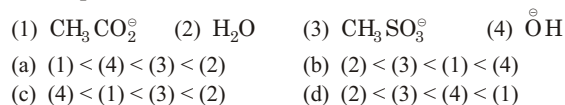
## Objective Questions I (Only one correct option)

1. 25 g of an unknown hydrocarbon upon burning produces 88 g of  $\text{CO}_2$  and 9 g of  $\text{H}_2\text{O}$ . This unknown hydrocarbon contains (2019 Main, 12 April II)
- (a) 20 g of carbon and 5 g of hydrogen  
(b) 22 g of carbon and 3 g of hydrogen  
(c) 24 g of carbon and 1 g of hydrogen  
(d) 18 g of carbon and 7 g of hydrogen

2. An organic compound *A* is oxidised with  $\text{Na}_2\text{O}_2$  followed by boiling with  $\text{HNO}_3$ . The resultant solution is then treated with ammonium molybdate to yield a yellow precipitate. Based on above observation, the element present in the given compound is (2019 Main, 12 April I)
- (a) nitrogen  
(b) phosphorus  
(c) fluorine  
(d) sulphur

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3. The increasing order of nucleophilicity of the following nucleophiles is (2019 Main, 10 April II)



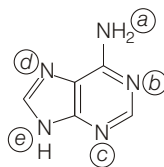
4. In chromatography, which of the following statements is incorrect for  $R_f$ ? (2019 Main, 10 April II)

- (a)  $R_f$  value depends on the type of chromatography  
 (b) Higher  $R_f$  value means higher adsorption  
 (c)  $R_f$  value is dependent on the mobile phase  
 (d) The value of  $R_f$  can not be more than one

5. The principle of column chromatography is (2019 Main, 10 April I)

- (a) differential absorption of the substances on the solid phase  
 (b) differential adsorption of the substances on the solid phase  
 (c) gravitational force  
 (d) capillary action

6. In the following compound,



the favourable site/s for protonation is/are

(2019 Main, 11 Jan II)

- (a) (a) and (e) (b) (b), (c) and (d)  
 (c) (a) and (d) (d) (a)

7. The correct match between items I and II is

| Item - I<br>(Mixture)             | Item II<br>(Separation method) |
|-----------------------------------|--------------------------------|
| A. $\text{H}_2\text{O}$ : Sugar   | P. Sublimation                 |
| B. $\text{H}_2\text{O}$ : Aniline | Q. Recrystallisation           |
| C. $\text{H}_2\text{O}$ : Toluene | R. Steam distillation          |
|                                   | S. Differential extraction     |

(2019 Main, 11 Jan I)

- (a) (A) (Q); (B) (R); (C) (S)  
 (b) (A) (Q); (B) (R); (C) (P)  
 (c) (A) (S); (B) (R); (C) (P)  
 (d) (A) (R); (B) (P); (C) (S)

8. An organic compound is estimated through Dumas method and was found to evolved 6 moles of  $\text{CO}_2$ , 4 moles of  $\text{H}_2\text{O}$  and 1 mole of nitrogen gas. The formula of the compound is

(2019 Main, 11 Jan I)

- (a)  $\text{C}_6\text{H}_8\text{N}$  (b)  $\text{C}_{12}\text{H}_8\text{N}$  (c)  $\text{C}_{12}\text{H}_8\text{N}_2$  (d)  $\text{C}_6\text{H}_8\text{N}_2$

9. If dichloromethane (DCM) and water ( $\text{H}_2\text{O}$ ) are used for differential extraction, which one of the following statements is correct? (2019 Main, 10 Jan I)

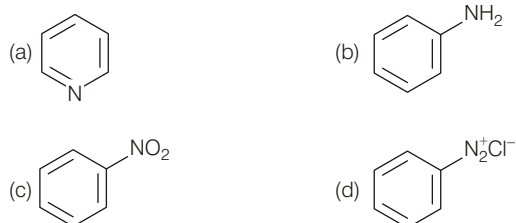
- (a) DCM and  $\text{H}_2\text{O}$  would stay as lower and upper layer respectively in the S.F.  
 (b) DCM and  $\text{H}_2\text{O}$  would stay as upper and lower layer respectively in the separating funnel (S.F.)  
 (c) DCM and  $\text{H}_2\text{O}$  will be miscible clearly  
 (d) DCM and  $\text{H}_2\text{O}$  will make turbid/colloidal mixture

10. Which amongst the following is the strongest acid?

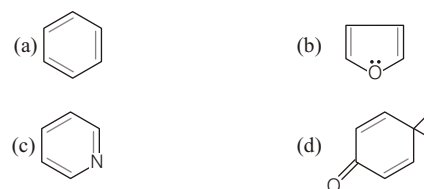
(2019 Main, 9 Jan I)

- (a)  $\text{CHBr}_3$  (b)  $\text{CHI}_3$   
 (c)  $\text{CHCl}_3$  (d)  $\text{CH}(\text{CN})_3$

11. Which of the following compounds will be suitable for Kjeldahl's method for nitrogen estimation? (2018 Main)



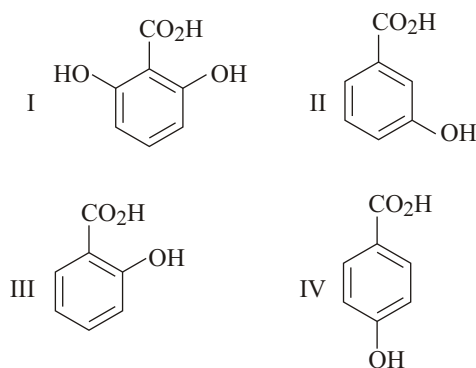
12. Which of the following molecules is least resonance stabilised? (2017 Main)



13. The distillation technique most suited for separating glycerol from spent lye in the soap industry is (2016 Main)

- (a) fractional distillation  
 (b) steam distillation  
 (c) distillation under reduced pressure  
 (d) simple distillation

14. The correct order of acidity for the following compounds is (2016 Adv.)



- (a)  $\text{I} > \text{II} > \text{III} > \text{IV}$   
 (b)  $\text{III} > \text{I} > \text{II} > \text{IV}$   
 (c)  $\text{III} > \text{IV} > \text{II} > \text{I}$   
 (d)  $\text{I} > \text{III} > \text{IV} > \text{II}$

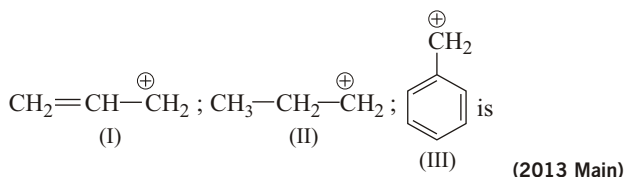
15. For the estimation of nitrogen, 1.4 g of an organic compound was digested by Kjeldahl's method and the evolved ammonia was absorbed in 60 mL of  $M/10$  sulphuric acid. The unreacted acid required 20 mL of  $M/10$  sodium hydroxide for complete neutralisation. The percentage of nitrogen in the compound is

- (a) 6% (b) 10% (2014 Main)  
 (c) 3% (d) 5%

16. A gaseous hydrocarbon gives upon combustion 0.72 g of water and 3.08 g of  $\text{CO}_2$ . The empirical formula of the hydrocarbon is (2013 Main)

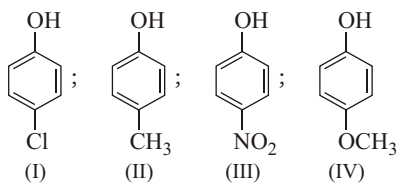
(a)  $\text{C}_2\text{H}_4$  (b)  $\text{C}_3\text{H}_4$  (c)  $\text{C}_6\text{H}_5$  (d)  $\text{C}_7\text{H}_8$

17. The order of stability of the following carbocations



(a)  $\text{III} > \text{II} > \text{I}$  (b)  $\text{II} > \text{III} > \text{I}$   
 (c)  $\text{I} > \text{II} > \text{III}$  (d)  $\text{III} > \text{I} > \text{II}$

18. Arrange the following compounds in the order of decreasing acidity (2013 Main)



(a)  $\text{II} > \text{IV} > \text{I} > \text{III}$  (b)  $\text{I} > \text{II} > \text{III} > \text{IV}$   
 (c)  $\text{III} > \text{I} > \text{II} > \text{IV}$  (d)  $\text{IV} > \text{III} > \text{I} > \text{II}$

19. A solution of (I) 1-chloro-1-phenylethane in toluene racemises slowly in the presence of a small amount of  $\text{SbCl}_5$ , due to the formation of (2013 Main)

(a) carbanion (b) carbene  
 (c) carbocation (d) free radical

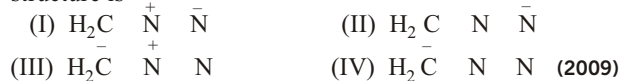
20. In allene ( $\text{C}_3\text{H}_4$ ), the type(s) of hybridisation of the carbon atoms, is (are) (2012)

(a)  $sp$  and  $sp^3$  (b)  $sp$  and  $sp^2$   
 (c) only  $sp^3$  (d)  $sp^2$  and  $sp^3$

21. Among the following compounds, the most acidic is (2011)

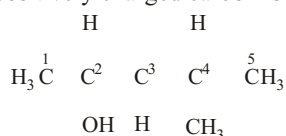
(a) *p*-nitrophenol (b) *p*-hydroxybenzoic acid  
 (c) *o*-hydroxybenzoic acid (d) *p*-toluic acid

22. The correct stability order of the following resonance structure is



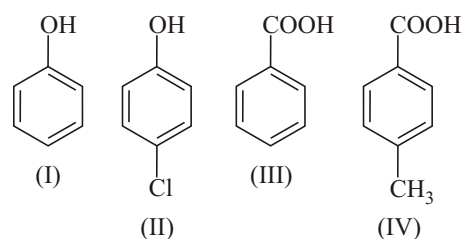
(a)  $\text{I} > \text{II} > \text{IV} > \text{III}$   
 (b)  $\text{I} > \text{III} > \text{II} > \text{IV}$   
 (c)  $\text{II} > \text{I} > \text{III} > \text{IV}$   
 (d)  $\text{III} > \text{I} > \text{IV} > \text{II}$

23. In the following carbocation;  $\text{H}/\text{CH}_3$  that is most likely to migrate to the positively charged carbon is (2009)



(a)  $\text{CH}_3$  at C-4 (b) H at C-4  
 (c)  $\text{CH}_3$  at C-2 (d) H at C-2

24. The correct acidity order of the following is (2009)

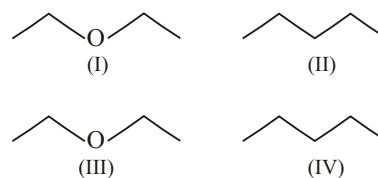


(a)  $\text{III} > \text{IV} > \text{II} > \text{I}$  (b)  $\text{IV} > \text{III} > \text{I} > \text{II}$   
 (c)  $\text{III} > \text{II} > \text{I} > \text{IV}$  (d)  $\text{II} > \text{III} > \text{IV} > \text{I}$

25. Hyperconjugation involves overlap of the following orbitals (2008, 3M)

(a) - (b)  $-p$  (c)  $p-p$  (d) -

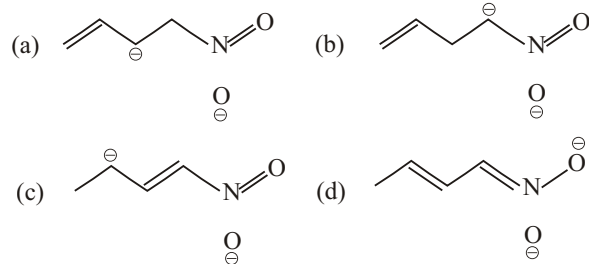
26. The correct stability order for the following species is



(2008, 3M)

(a)  $\text{II} > \text{IV} > \text{I} > \text{III}$  (b)  $\text{I} > \text{II} > \text{III} > \text{IV}$   
 (c)  $\text{II} > \text{I} > \text{IV} > \text{III}$  (d)  $\text{I} > \text{III} > \text{II} > \text{IV}$

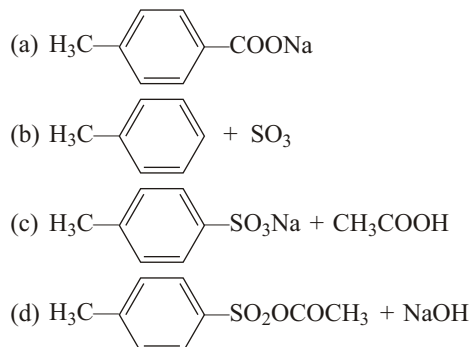
27. Among the following, the least stable resonance structure is (2007, 3M)



28. When benzene sulphonic acid and *p*-nitrophenol are treated with  $\text{NaHCO}_3$ , the gases released respectively are (2006)

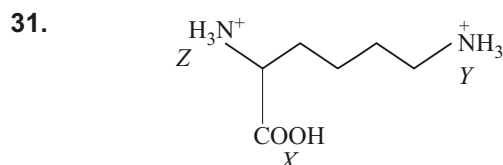
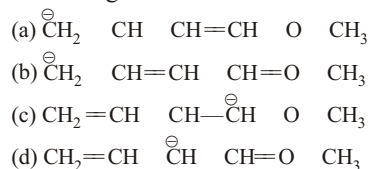
(a)  $\text{SO}_2, \text{NO}_2$  (b)  $\text{SO}_2, \text{NO}$   
 (c)  $\text{SO}_2, \text{CO}_2$  (d)  $\text{CO}_2, \text{CO}_2$

29. Which of the following is obtained when 4-methylbenzene sulphonic acid is hydrolysed with excess of sodium acetate? (2005, 1M)



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30. For 1-methoxy-1,3-butadiene, which of the following resonating structure is least stable? (2005, 1M)



Arrange in order of increasing acidic strength (2004, 1M)

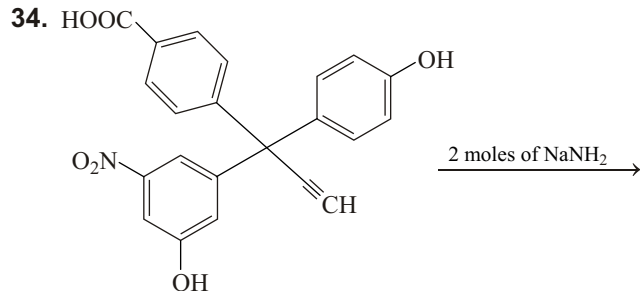
- (a)  $X > Z > Y$  (b)  $Z > X > Y$   
 (c)  $X > Y > Z$  (d)  $Z > X > Y$

32. Among the following, the molecule with the highest dipole moment is (2003, 1M)

- (a)  $\text{CH}_3\text{Cl}$  (b)  $\text{CH}_2\text{Cl}_2$  (c)  $\text{CH}_2\text{Cl}_2$  (d)  $\text{CCl}_4$

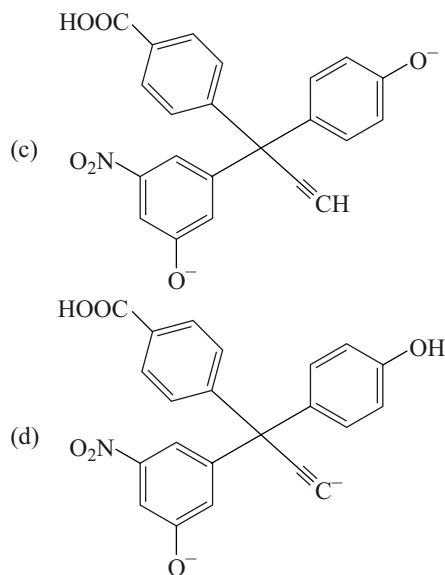
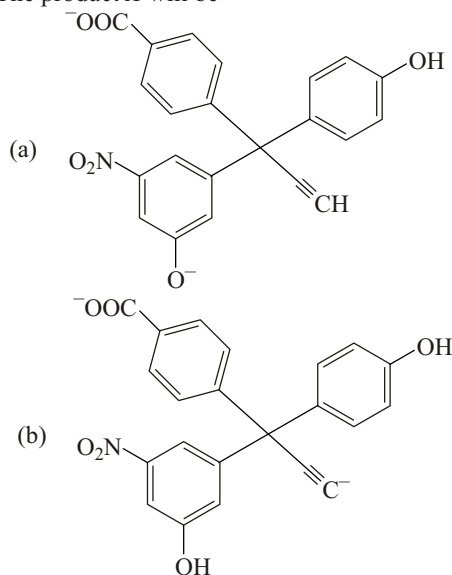
33. Which of the following represent the given mode of hybridisation  $sp^2$   $sp^2$   $sp$   $sp$  from left to right? (2003, 1M)

- (a)  $\text{H}_2\text{C}=\text{CH}-\text{C}\equiv\text{N}$  (b)  $\text{HC}\equiv\text{C}-\text{C}\equiv\text{CH}$   
 (c)  $\text{H}_2\text{C}=\text{C}=\text{C}=\text{CH}_2$  (d)



The product A will be

(2003)



35. Which of the following acids has the smallest dissociation constant? (2002)

- (a)  $\text{CH}_3\text{CHFCOOH}$   
 (b)  $\text{FCH}_2\text{CH}_2\text{COOH}$   
 (c)  $\text{BrCH}_2\text{CH}_2\text{COOH}$   
 (d)  $\text{CH}_3\text{CHBrCOOH}$

36. Identify the correct order of boiling points of the following compounds:



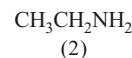
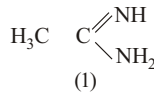
(2002)

- (a)  $1 > 2 > 3$  (b)  $3 > 1 > 2$   
 (c)  $1 > 3 > 2$  (d)  $3 > 2 > 1$

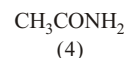
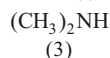
37. Which of the following hydrocarbons has the lowest dipole moment? (2002)

- (a) *cis*-2-butene (b) 2-butyne  
 (c) 1-butyne (d)  $\text{H}_2\text{C}=\text{CH}-\text{C}\equiv\text{CH}$

38. The correct order of basicities of the following compounds is



(2001)



- (a)  $2 > 1 > 3 > 4$  (b)  $1 > 3 > 2 > 4$   
 (c)  $3 > 1 > 2 > 4$  (d)  $1 > 2 > 3 > 4$

39. Among the following, the strongest base is (2000)

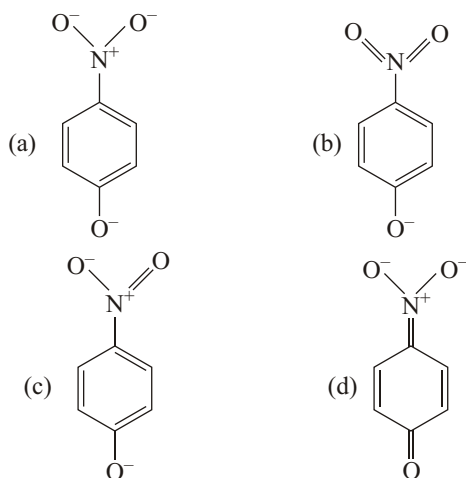
- (a)  $\text{C}_6\text{H}_5\text{NH}_2$   
 (b)  $p\text{-NO}_2\text{C}_6\text{H}_4\text{NH}_2$   
 (c)  $m\text{-NO}_2\text{C}_6\text{H}_4\text{NH}_2$   
 (d)  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$

40. Which of the following, has the most acidic hydrogen? (2000)

- (a) 3-hexanone  
 (b) 2,4-hexanedione  
 (c) 2,5-hexanedione  
 (d) 2,3-hexanedione



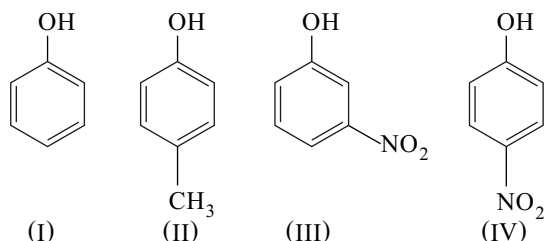
41. The most unlikely representation of resonance structures of *p*-nitrophenoxide ion is (1999)



42. Among the following compounds, the strongest acid is (1998)



43. In the following compounds (1997)



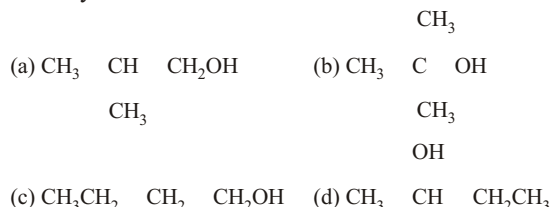
The order of acidity is

- (a) III > IV > I > II  
(b) I > IV > III > II  
(c) II > I > III > IV  
(d) IV > III > I > II
44. What is the decreasing order of strength of the bases?  
 $\text{OH}^-$ ,  $\text{NH}_2^-$ ,  $\text{H}^-$ ,  $\text{C}^-$  and  $\text{CH}_3^-$  (1997)
- (a)  $\text{CH}_3^- > \text{CH}_2^- > \text{NH}_2^- > \text{H}^- > \text{C}^- > \text{OH}^-$   
(b)  $\text{H}^- > \text{C}^- > \text{CH}_3^- > \text{CH}_2^- > \text{NH}_2^- > \text{OH}^-$   
(c)  $\text{OH}^- > \text{NH}_2^- > \text{H}^- > \text{C}^- > \text{CH}_3^- > \text{CH}_2^-$   
(d)  $\text{NH}_2^- > \text{H}^- > \text{C}^- > \text{OH}^- > \text{CH}_3^- > \text{CH}_2^-$
45. The hybridisation of carbon atoms in  $\text{C} \equiv \text{C}$  single bond  $\text{H} - \text{C} - \text{C} - \text{CH} = \text{CH}_2$  is (1991, 1M)
- (a)  $sp^3$   $sp^3$  (b)  $sp^2$   $sp^3$   
(c)  $sp$   $sp^2$  (d)  $sp^3$   $sp$
46. Amongst the following, the most basic compound is (1990, 1M)
- (a) benzylamine (b) aniline  
(c) acetanilide (d) *p*-nitroaniline

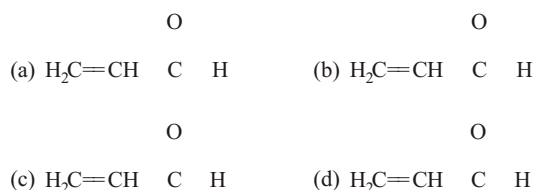
47. The number of sigma and pi-bonds in 1-butene 3-yne are (1989, 1M)



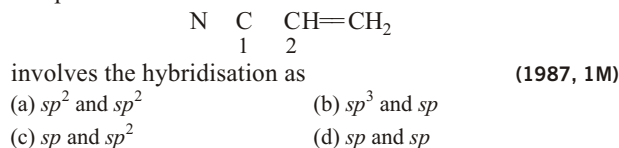
48. The compound which gives the most stable carbonium ion on dehydration is (1989, 1M)



49. Polarisation of electrons in acrolein may be written as (1988, 1M)



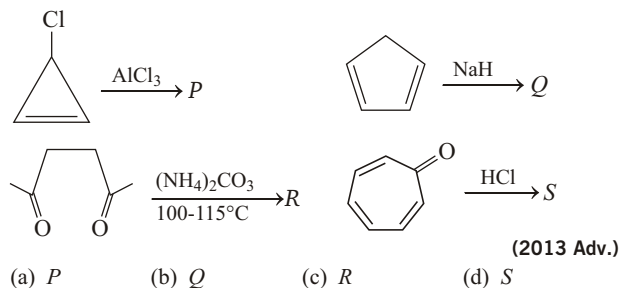
50. The bond between carbon atom (1) and carbon atom (2) in compound



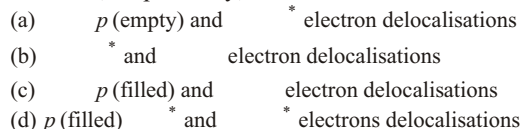
## Objective Questions II

(One or more than one correct option)

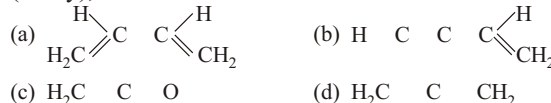
51. Among *P*, *Q*, *R* and *S*, the aromatic compound(s) is/are



52. The hyperconjugative stabilities of *tert*-butyl cation and 2-butene, respectively, are due to (2013 Adv.)



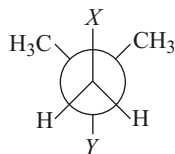
53. Amongst the given options, the compound(s) in which all the atoms are in one plane in all the possible conformations (if any), is/are (2011)





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54. In the Newman's projection for 2,2-dimethylbutane



$X$  and  $Y$  can respectively be

(2010)

- (a) H and H
- (b) H and  $C_2H_5$
- (c)  $C_2H_5$  and H
- (d)  $CH_3$  and  $CH_3$

55. The molecules that will have dipole moment are (1992, 1M)

- (a) 2, 2-dimethyl propane
- (b) *trans*-2-pentene
- (c) *cis*-3-hexene
- (d) 2,2,3,3-tetramethyl butane

56. The compound in which C uses its  $sp^3$ -hybrid orbitals for bond formation is (2000, 1M)

- (a)  $HCOOH$
- (b)  $(H_2N)_2CO$
- (c)  $(CH_3)_3COH$
- (d)  $CH_3CHO$

57. Phenol is less acidic than

(1986)

- (a) acetic acid
- (b) *p*-methoxy phenol
- (c) *p*-nitrophenol
- (d) ethanol

### Assertion and Reason

Read the following questions and answer as per the direction given below :

- (a) Statement I is correct; Statement II is correct; Statement II is the correct explanation of Statement I
- (b) Statement I is correct; Statement II is correct; Statement II is not the correct explanation of Statement I
- (c) Statement I is correct; Statement II is incorrect
- (d) Statement I is incorrect; Statement II is correct

58. **Statement I** *p*-hydroxybenzoic acid has a lower boiling point than *o*-hydroxybenzoic acid.

**Statement II** *o*-hydroxybenzoic acid has intramolecular hydrogen bonding.

59. **Statement I** *p*-nitrophenol is a stronger acid than *o*-nitrophenol.

**Statement II** Intramolecular hydrogen bonding make the *o*-isomer weaker acid than *p*-isomer.

### Match the Columns

60. Match the reactions in Column I with appropriate types of steps/reactive intermediate involved in these reactions as given in Column II. (2011)

|    | Column I |    | Column II                  |
|----|----------|----|----------------------------|
| A. |          | p. | Nucleophilic substitution  |
| B. |          | q. | Electrophilic substitution |
| C. |          | r. | Dehydration                |
| D. |          | s. | Nucleophilic addition      |
|    |          | t. | Carbanion                  |

61. Match the reaction in Column I with appropriate options in Column II.

(2010)

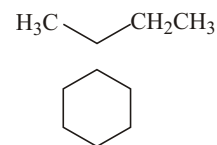
| Column I |  | Column II                   |
|----------|--|-----------------------------|
| A.       |  | p. Racemic mixture          |
| B.       |  | q. Addition reaction        |
| C.       |  | r. Substitution reaction    |
| D.       |  | s. Coupling reaction        |
|          |  | t. Carbocation intermediate |

## Fill in the Blanks

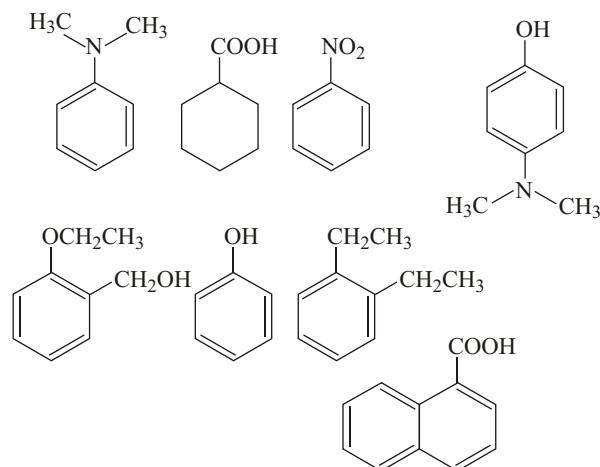
62. The kind of delocalisation involving sigma bond orbitals is called..... (1994, 1M)
63. The bond dissociation energy needed to form the benzyl radical from toluene is ..... than the formation of the methyl radical from methane. (1994, 1M)
64. The structure of the enol form of  
 $\text{CH}_3\text{COCH}_2\text{COCH}_3$   
 with intermolecular hydrogen bonding is ..... (1993, 1M)
65. The IUPAC name of succinic acid is ..... (1990, 1M)
66. The shape of  $(\text{CH}_3)_4$  is ..... (1990, 1M)
67. A..... diol has two hydroxyl groups on ..... carbon atoms. (1985, 1M)
68. The terminal carbon atom in butane is ..... hybridised. (1985, 1M)
69. .... ring is most strained. (cyclopropane, cyclobutane, cyclopentane) (1981, 1M)
70. The compound having both  $sp$  and  $sp^2$ -hybridised carbon atoms is ..... (propane, propene, propadiene). (1981, 1M)
71. In acidic medium, ..... behaves as the strongest base. (nitrobenzene, aniline, phenol) (1981, 1M)
72. Among the given cations, ..... is most stable. (*sec*-butyl carbonium ion, *tert*-butyl carbonium ion, *n*-butyl carbonium ion) (1981, 1M)

## Integer Answer Type Questions

73. The total number of contributing structures showing hyperconjugation (involving C—H bonds) for the following carbocation is (2011)



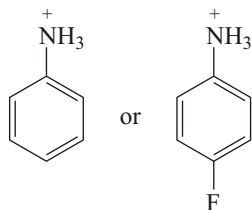
74. Amongst the following, the total number of compounds soluble in aqueous NaOH is (2010)



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### Subjective Questions

75. Which of the following is more acidic and why?



(2003)

76. Draw the resonating structures of  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{OH}$ . (2003)

77. You have an ether solution containing 4-hydroxybenzoic acid and 4-aminobenzoic acid. Explain, how will you separate the two in not more than 3 steps? Give confirmatory tests with reagents and conditions for functional groups of each. (2003)

78. Match the following with their  $K_a$  values

|                              |                      |
|------------------------------|----------------------|
| Benzoic acid                 | $4.2 \times 10^{-5}$ |
| <i>p</i> -nitrobenzoic acid  | $3.3 \times 10^{-5}$ |
| <i>p</i> -chlorobenzoic acid | $6.4 \times 10^{-5}$ |

|                               |                       |
|-------------------------------|-----------------------|
| <i>p</i> -methylbenzoic acid  | $36.2 \times 10^{-5}$ |
| <i>p</i> -methoxybenzoic acid | $10.2 \times 10^{-5}$ |

(2003)

79. Give reasons for the following:

$\text{CH}_2=\text{CH}-$  is more basic than  $\text{HC}\equiv\text{C}-$ . (2000)

80. Explain, why *o*-hydroxybenzaldehyde is a liquid at room temperature while *p*-hydroxybenzaldehyde is a high melting solid? (1999)

81. Discuss the hybridisation of carbon atoms in allene ( $\text{C}_3\text{H}_4$ ) and show the  $\pi$ -orbital overlaps. (1999, 3M)

82. Give reasons for the following in one or two sentences. The central carbon-carbon bond in 1, 3-butadiene is shorter than that of *n*-butane. (1998)

83. Although phenoxide ion has more number of resonating structures than benzoate ion, benzoic acid is a stronger acid than phenol. Why? (1997)

84. Arrange the following in the order of their increasing basicity.

*p*-toluidine, *N,N*-dimethyl-*p*-toluidine, *p*-nitroaniline, aniline. (1985, 1M)

## Answers

### Topic 1

- |                                     |             |             |             |
|-------------------------------------|-------------|-------------|-------------|
| 1. (d)                              | 2. (c)      | 3. (b)      | 4. (c)      |
| 5. (d)                              | 6. (a)      | 7. (b)      | 8. (a)      |
| 9. (c)                              | 10. (c)     | 11. (d)     | 12. (d)     |
| 13. (a)                             | 14. (c)     | 15. (b)     | 16. (a)     |
| 17. (a)                             | 18. (b)     | 19. (b)     | 20. (a)     |
| 21. (b)                             | 22. (d)     | 23. (c)     | 24. (a)     |
| 25. (d)                             | 26. (b,c)   | 27. (a,c,d) | 28. (a,b,c) |
| 29. (a,d)                           | 30. (b,c,d) | 31. (a,d)   | 32. (a,c,d) |
| 33. (a,c)                           | 34. (c,d)   | 35. (b,d)   | 36. (d)     |
| 37. (7)                             | 38. (c)     |             |             |
| 39. Non-superimposable, Enantiomers |             | 40. False   |             |
| 41. False                           | 42. (2)     | 43. (3)     | 44. (7)     |

### Topic 2

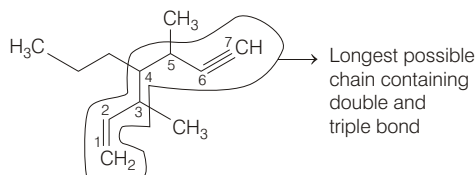
- |         |         |         |         |
|---------|---------|---------|---------|
| 1. (c)  | 2. (b)  | 3. (c)  | 4. (b)  |
| 5. (b)  | 6. (b)  | 7. (a)  | 8. (d)  |
| 9. (a)  | 10. (d) | 11. (b) | 12. (d) |
| 13. (c) | 14. (a) | 15. (b) | 16. (d) |

- |                                       |                   |                      |             |
|---------------------------------------|-------------------|----------------------|-------------|
| 17. (d)                               | 18. (c)           | 19. (c)              | 20. (b)     |
| 21. (c)                               | 22. (b)           | 23. (d)              | 24. (a)     |
| 25. (b)                               | 26. (d)           | 27. (a)              | 28. (d)     |
| 29. (c)                               | 30. (c)           | 31. (a)              | 32. (a)     |
| 33. (a)                               | 34. (a)           | 35. (c)              | 36. (b)     |
| 37. (b)                               | 38. (b)           | 39. (d)              | 40. (b)     |
| 41. (b)                               | 42. (d)           | 43. (d)              | 44. (a)     |
| 45. (d)                               | 46. (a)           | 47. (b)              | 48. (b)     |
| 49. (d)                               | 50. (c)           | 51. (a,b,c,d)        | 52. (a)     |
| 53. (b,c)                             | 54. (b,d)         | 55. (b,c)            | 56. (c,d)   |
| 57. (a,c)                             | 58. (d)           | 59. (a)              |             |
| 60. A r, s, t; B p, s; C r, s; D q, r |                   |                      |             |
| 61. A r, s; B t; C p, q; D r          |                   |                      |             |
| 62. hyperconjugation                  |                   |                      |             |
| 63. less                              | 64. cyclic        | 65. butanedioic acid |             |
| 66. triangular planar                 | 67. geminal, same |                      |             |
| 68. $sp^3$                            | 69. cyclopropane  | 70. propene          | 71. aniline |
| 72. <i>tert</i> -butyl carbonium ion, | 73. (6)           | 74. (4)              |             |

# Hints & Solutions

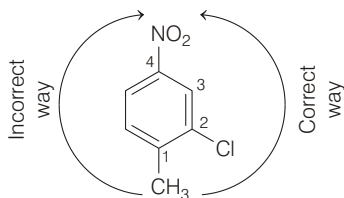
## Topic 1 Nomenclature and Isomerism

1. The IUPAC name for the given compound is 3, 5-dimethyl-4-propylhept-1-en-6-yne.



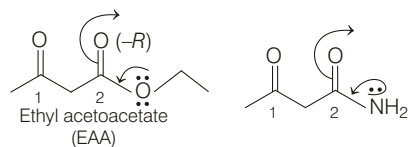
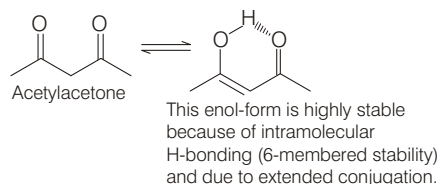
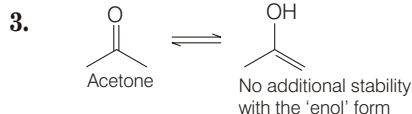
If both double and triple bonds are present in the compound, the endings like-en-yne, a (numeral) dien-(numeral)-yne etc., are used. Numbers as low as possible are given to double and triple bonds as a set.

2. The IUPAC name of the given compound is



2-chloro-1-methyl-4-nitrobenzene

Here, the given compound contains two or more functional groups. So, the numbering is done in such a way that the sum of the locants is the lowest.

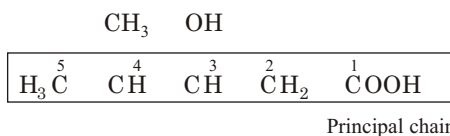


In both of the compounds, C-2 of  $C=O$  group is a part of the acid

derivative (ester,  $C-OEt$  and acid amide,  $C-NH_2$ ). So,

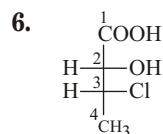
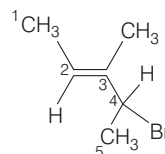
$C^2=O$  does not take part in enolisation, because it is already in resonance ( $-R$ ) with the derivative group itself.

4. The IUPAC name of the given compound is 3-hydroxy-4-methylpentanoic acid.



While naming the compound, the longest chain that have principal functional group  $COOH$  is chosen and numbered in such a manner that the principal functional group gets the lowest possible number.  $OH$  act as substituent and used as prefix in nomenclature.

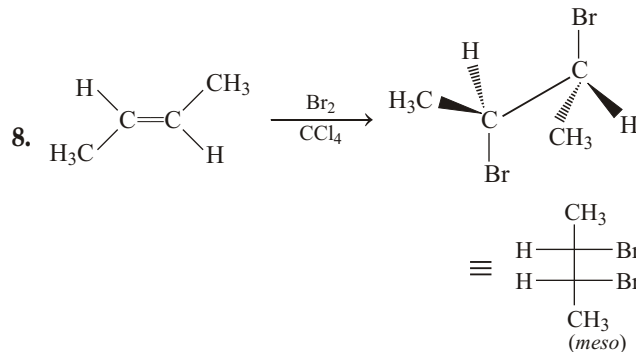
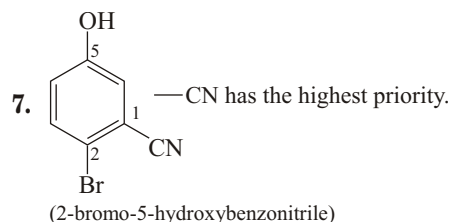
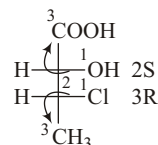
5. While naming the compound, alkene gets priority over functional group ( $Br$ ) and numbering starts from alkene side. Hence, IUPAC name: 4-bromo-3-methyl pent-2-ene



For C-2, order of priority of substituents is  $OH > CH(Cl)(CH_3) > COOH$

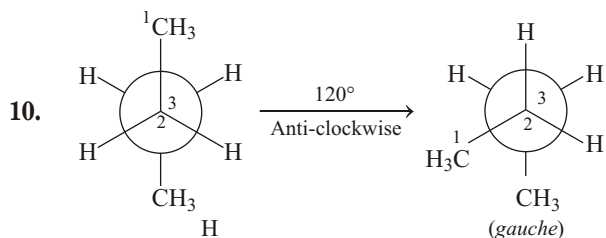
For C-3, order of priority of substituents is  $Cl > CH(OH)COOH > CH_3$

Hence, according to CIP rules,

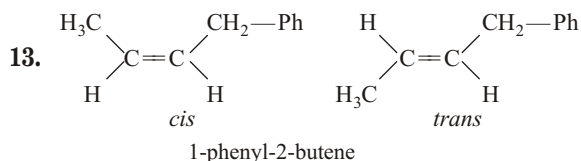
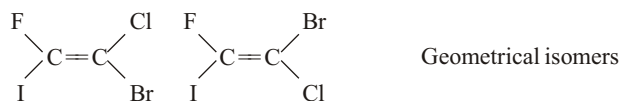
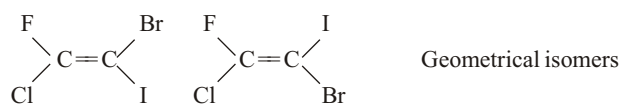
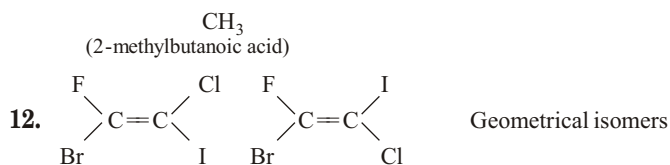


9.  $C_6H_5-COCl$ : Benzene carbonyl chloride

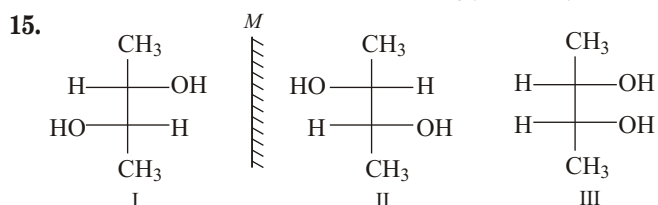
## 298 Organic Chemistry Basics



11.  $\text{CH}_3\text{—CH}_2\text{—C}^*\text{—COOH}$ : Has a chiral carbon, optically active.



14. The 'D' term in name is derived from D-glyceraldehyde.



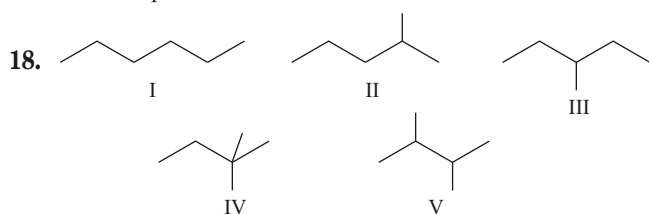
16. Conformers can be interconverted through rotation about C—C bond.



17.  $\text{H—C—C—CH}_3$ :

H  
Enol of acetone

It has 9 (6 with H, two C—C and one C—O), one  $\pi$ -bond and two lone-pairs.



19. Compounds with same empirical formula but different molecular formula have same percentage composition of elements but different molecular weight.



20.  $\text{H—C—C—H}$ ; Ethane has the smallest sized group (H)



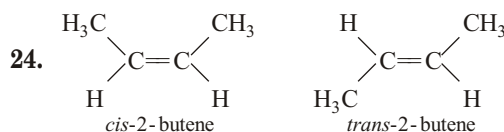
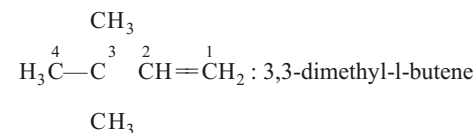
bonded to carbons, hence there will be least hindered rotation about C—C bond.

21.  $\text{CH}_2=\text{CH}^1\text{—CH}^2\text{—CH}_3^3$ ; 3-methyl-1-butene

22. Ethers and alcohols (saturated, acyclic) with same number of carbons are always isomeric.

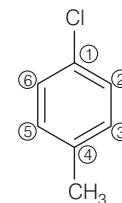
$\text{CH}_3\text{—O—CH}_3$  and  $\text{CH}_3\text{—CH}_2\text{—OH}$  are functional isomers.

23. Double bond has preference over alkyl group hence:



25. Diethyl ether ( $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ ) will be isomeric with all 4-carbon saturated alcohols. Butanone ( $\text{CH}_3\text{CH}_2\text{COCH}_3$ ) is unsaturated, has two hydrogen less than the diethylether.

26. Since, there is no principal functional groups, numbering of disubstituted benzene is done in alphabetical order as



Hence IUPAC name of this compound is 1-chloro-4-methylbenzene.

Also, toluene is an acceptable name in IUPAC, hence this compound can also be named as 4-chloro toluene.

27. **PLAN** This problem is based on structure and nomenclature of organic compound.

Draw structure of each compound and write IUPAC name of the given compound.

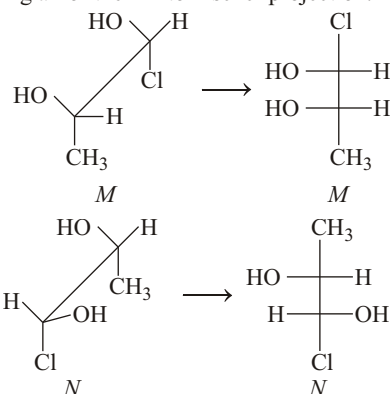
Match the molecular formula of given compound with molecular formula of compound given in choices.

The combination of names for possible isomeric alcohols with molecular formula  $\text{C}_4\text{H}_{10}\text{O}$  is/are

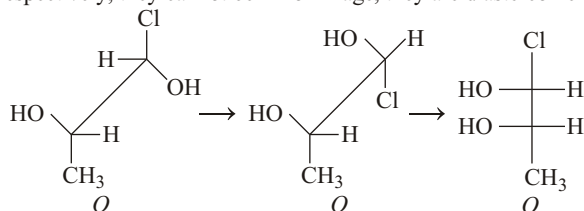
| Formula                                                                                                                    | Names                                                               |
|----------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------|
| $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$                                                                    | <i>n</i> -butyl alcohol / <i>n</i> -butanol / butan-1-ol            |
| $\begin{array}{cccc}\text{CH}_3 & \text{CH} & \text{CH}_2 & \text{OH} \\ &   & & \\ & \text{CH}_3 & & \end{array}$         | <i>Iso</i> -butyl alcohol / 2-methyl propan-1-ol                    |
| $\begin{array}{cccc}\text{CH}_3 & \text{CH}_2 & \text{CH} & \text{OH} \\ & &   & \\ & & \text{CH}_3 & \end{array}$         | Secondary butyl alcohol / butan-2-ol                                |
| $\begin{array}{ccc}\text{CH}_3 & & \\   & & \\ \text{CH}_3 & \text{C} & \text{OH} \\   & & \\ \text{CH}_3 & & \end{array}$ | Tertiary butyl alcohol / <i>tert</i> butanol / 2-methyl propan-2-ol |

Hence, choices (a), (c) and (d) are correct.

28. Converting all of them into Fischer projection.



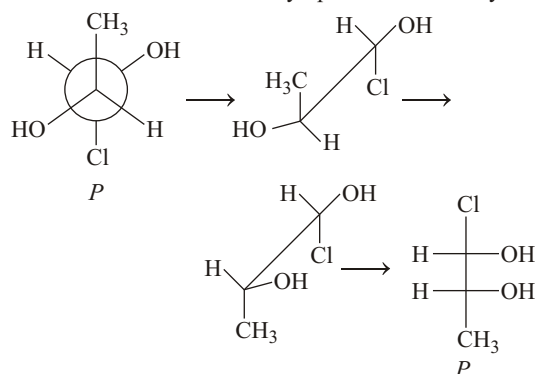
Since, *M* and *N* have OH on same side and opposite side respectively, they cannot be mirror image, they are diastereomers.



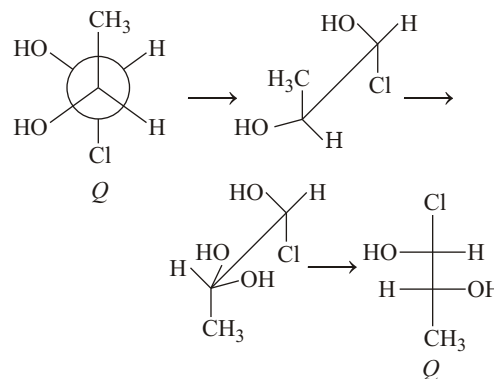
*M* and *O* are identical.

**NOTE** Fischer projection represents eclipse form of Sawhorse projection.

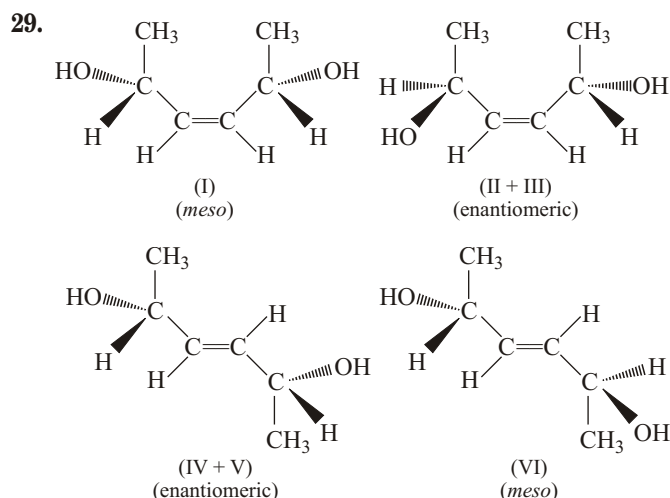
For comparison purpose, similar types of eclipse conformers must be drawn i.e. both vertically up or both vertically down.



*M* and *P* are non-superimposable mirror images, hence, enantiomers.



*M* and *Q* are non-identical they are diastereomers.



Total six isomers. In both *cis* and *trans* forms, there are two enantiomers each.

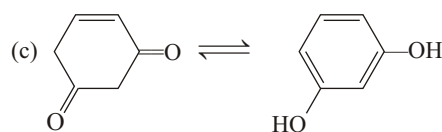
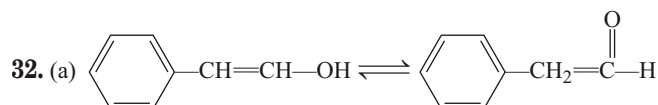
30. *E*, *F* and *G* are not resonance structures because movement of hydrogen between *E* and *F* are involved.

*E*, *F* and *E*, *G* are tautomers in which *E* is keto form and both *F* and *G* are enol form of the same *E*.

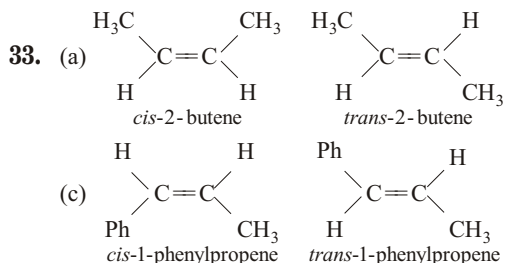
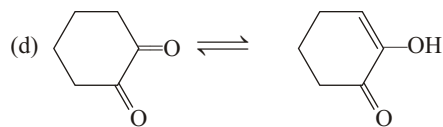
*F* and *G* are geometrical isomers.

*F* and *G* are diastereomers as they are stereo isomers but not related by mirror image relationship.

31. The compound is optically active as well as it possesses a two-fold axis of symmetry.



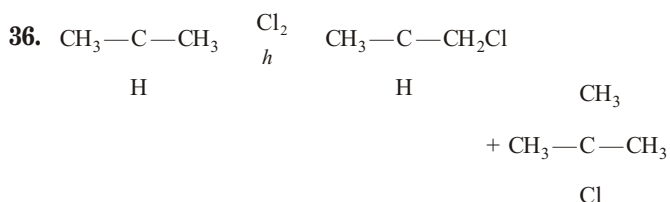
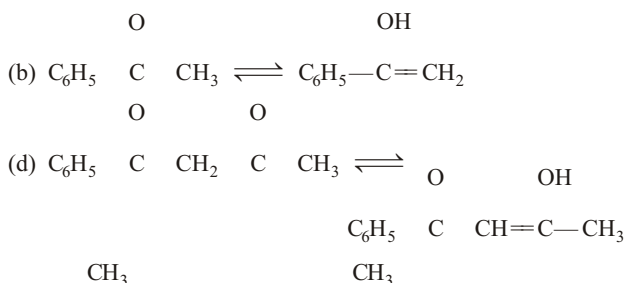
## 300 Organic Chemistry Basics



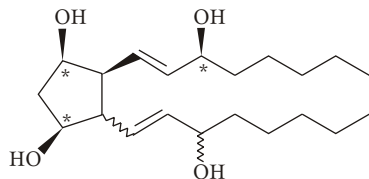
34. A carbon bonded to four different atoms or groups is called asymmetric carbon :



35. Carbonyl compounds containing  $\alpha\text{-H}$  show keto-enol tautomerism.

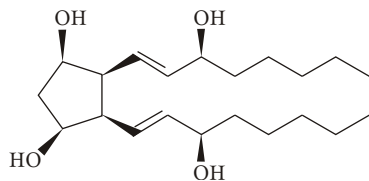


37. (7) As given in the question 3 stereocentres are visible, i.e.



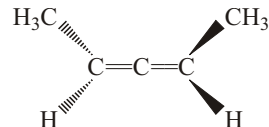
Hence, the total number of stereoisomers  $2^3 = 8$

But out of these the following one is optically inactive due to symmetry



Hence, total number of optically active stereoisomers = 7

38. Molecules that are non-superimposable on its mirror image are optically active and known as chiral molecule. However, for chirality of molecule, presence of chiral centre is not essential, e.g.

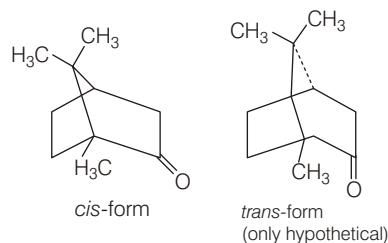


Molecule is chiral but does not possess any chiral carbon.

39. Non-superimposable, Enantiomers.

### True / False

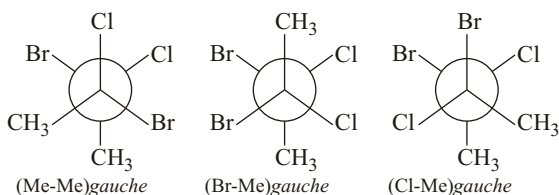
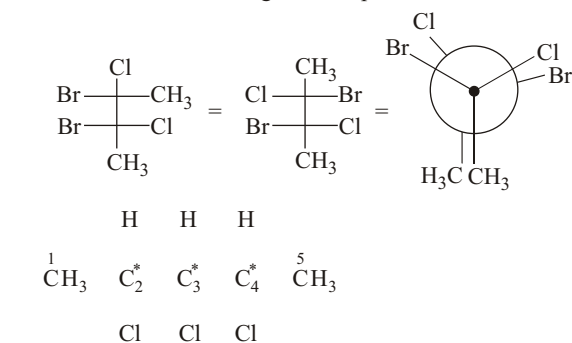
40. It has only two asymmetric carbon, carbon no.3 is not asymmetric.
41. They are identical.
42. Although the compound has two chiral carbons (indicated by stars), it does not have four optically active isomers as expected. It is due to its existence in *cis*-form only.



The above shown transformation does not exist due to restricted rotation about the bridge head carbons, hence only *cis*-form and its mirror image exist.

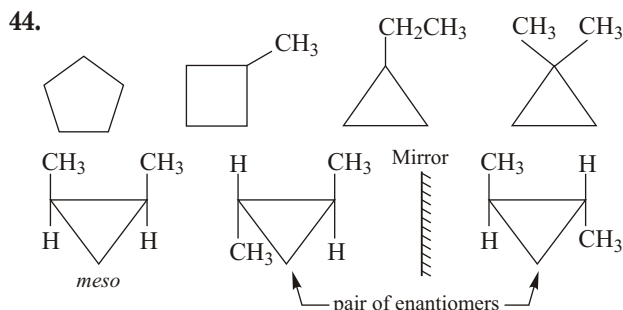
43. **PLAN** This problem can be solved by using concept of conformational analysis of given organic compound. To solve the question draw the stable conformational structures of organic compound and determine the net resultant dipole moment.

The conformations of the given compound are as follows

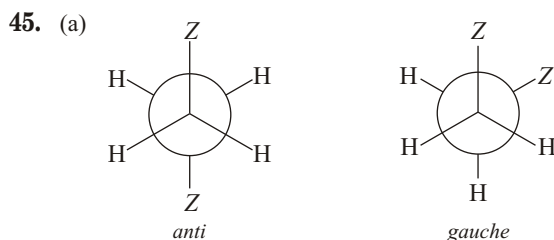




These three have non-zero dipole moment due to non-cancellation of all dipole moment created by C—Cl and C—Br bond.



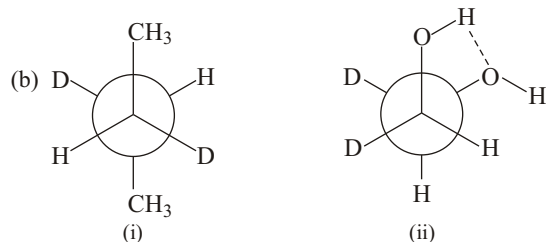
Total seven isomers



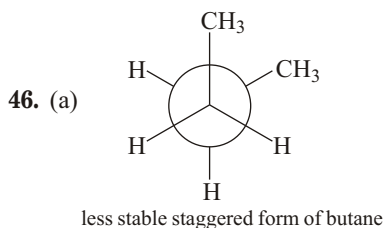
Mole fraction of *anti* form = 0.82

Mole fraction of *gauche* form = 0.18

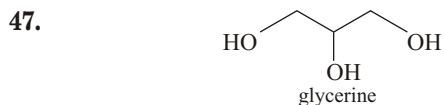
$$\begin{aligned} \therefore \frac{\text{obs}}{1} &= \frac{1 \text{ D}}{\text{anti}} = 0.82 + \frac{\text{gauche}}{1} = 0.18 \\ \frac{\text{gauche}}{0.18} &= \frac{1}{5.55 \text{ D}} \end{aligned}$$



Structure (ii) is more stable than its *anti* conformer because of intramolecular H-bonding.



(b) The less stability of above mentioned conformer is due to van der Waals' repulsion between the adjacent methyl groups.

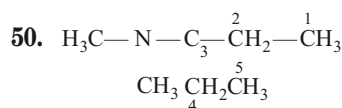
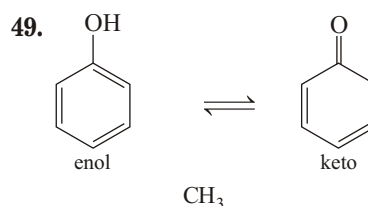


It contains a secondary ( $2^\circ$ ) hydroxy group.

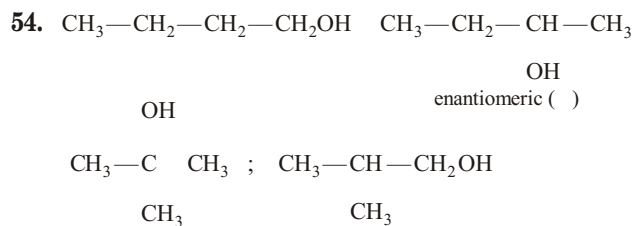
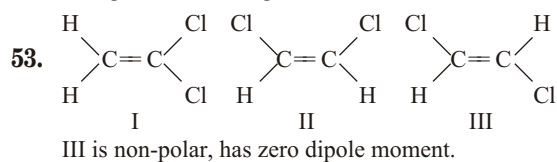
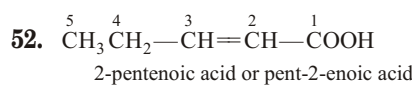
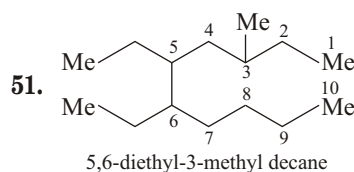
48. I and III are mirror images of one another as well as they are non-superimposable while II is a *meso* form.

(I + III) = Enantiomers

I + II and II + III = Diastereomers



3-(N, N-dimethyl)-3-methyl pentanamine  
or 3-methyl-3-(N, N-dimethyl) pentanamine



Total number of isomers (including stereoisomers) = 5

## Topic 2 General Organic Chemistry

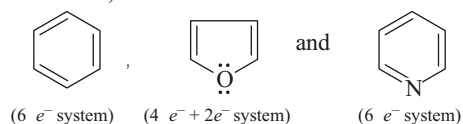
1. Hydrocarbon containing C and H upon burning produces CO<sub>2</sub> and water vapour respectively. The equation is represented as

$$\begin{aligned} \text{C}_x\text{H}_y + (x + y/4)\text{O}_2 &\rightarrow x\text{CO}_2 + (y/2)\text{H}_2\text{O} \\ \text{Mass of carbon} &= \frac{12}{44} \times \text{mass of CO}_2 \\ &= \frac{12}{44} \times 88 \text{ g} = 24 \text{ g} \\ \text{Mass of hydrogen} &= \frac{2}{18} \times \text{mass of H}_2\text{O} \\ &= \frac{2}{18} \times 9 \text{ g} = 1 \text{ g} \end{aligned}$$

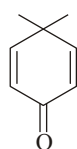
So, the unknown hydrocarbon contains 24 g of carbon and 1 g of hydrogen.



11. Estimation of nitrogen through Kjeldahl's method is not suitable for organic compounds containing nitrogen in ring or nitrogen in nitro or azo groups. It is because of the fact that nitrogen of these compounds does not show conversion to Ammonium sulphate  $(\text{NH}_4)_2\text{SO}_4$  during the process. Hence, among the given compounds only aniline can be used suitably for estimation of nitrogen by Kjeldahl's method.
12. Aromatic compounds are stable due to resonance while non-aromatics are not. According to Huckel's rule (or  $4n + 2$  rule), "For a planar, cyclic compound to be aromatic, its cloud must contain  $(4n + 2)$  electrons, where,  $n$  is any whole number." Thus,



are aromatic and stabilised by resonance. They follow Huckel's rule.

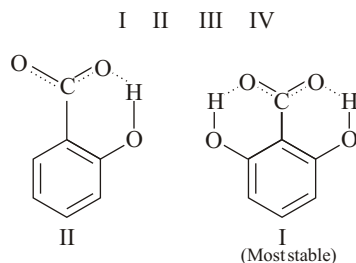


13. Glycerol with high boiling point ( $290^{\circ}\text{C}$ ) can be separated from spent lye by distillation under reduced pressure. This process is used to purify liquids having very high boiling points. By this process, liquid is made to boil at lower temperature than its boiling point by lowering the pressure on its surface.

14. OH group displays both kinds of effect; an electron withdrawing acid-strengthening inductive effect from the *meta*-position and an electron-releasing acid weakening resonance effect from the *para*-position (at this position, resonance effect overweighs the inductive effect). Thus, III > IV.

*o*-hydroxybenzoic acid (II) is far stronger than the corresponding *meta* and *para* isomers as the carboxylate ion is stabilised by intramolecular H-bonding.

2,6-dihydroxybenzoic acid (I) forms carboxylate ion which is further stabilised by intramolecular H-bonding. Thus, correct order is



- 15. THINKING PROCESS** This problem is based on the estimation of percentage of N in organic compound using Kjeldahl's method. Use the concept of stoichiometry and follow the steps given below to solve the problem.

- (a) Write the balanced chemical reaction for the conversion of N present in organic compound to ammonia, ammonia to

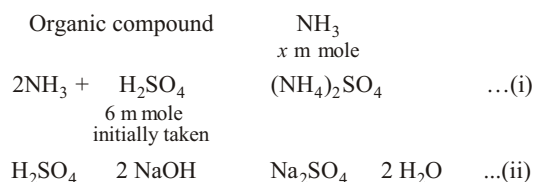
ammonium sulphate and ammonium sulphate to sodium sulphate.

- (b) Calculate millimoles ( $m$  moles) of N present in organic compound followed by mass of N present in organic compound using the concept of stoichiometry.
- (c) At last, calculate % of N present in organic compound using formula

$$\% \text{ of N} = \frac{\text{Mass of N}}{\text{Mass of organic compound}} \times 100$$

Mass of organic compound    1.4 g

Let it contain  $x$  m mole of N atom.



2 m mole NaOH reacted.

Hence,  $m$  moles of  $\text{H}_2\text{SO}_4$  reacted in Eq. (ii) 1

m moles of  $\text{H}_2\text{SO}_4$  reacted from Eq. (i)      6      1

5 m moles

$$\frac{\text{m moles of NH}_3 \text{ in Eq. (i)}}{\text{m moles of N atom in the organic compound}} = \frac{2}{10} = \frac{5}{10} \text{ m moles}$$

|           |    |        |    |        |
|-----------|----|--------|----|--------|
| Mass of N | 10 | $10^3$ | 14 | 0.14 g |
|-----------|----|--------|----|--------|

$$\% \text{ of N} = \frac{\text{Mass of N present in organic compound}}{\text{Mass of organic compound}} \times 100$$

$$\begin{array}{rcl} \text{\% of N} & \frac{0.14}{1.4} & 100 \\ & 10\% & \end{array}$$

- 16.** 18 g  $\text{H}_2\text{O}$  contains 2g H

0.72 g H<sub>2</sub>O contains 0.08 g H

44 g  $\text{CO}_2$  contains 12 g C

3.08 g CO<sub>2</sub> contains 0.84 g C

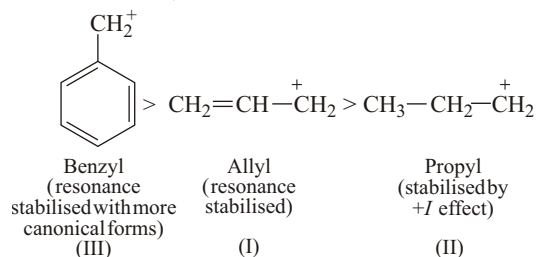
$$\text{C : H} \quad \frac{0.84}{12} : \frac{0.08}{1}$$

$$0.07 : 0.08$$

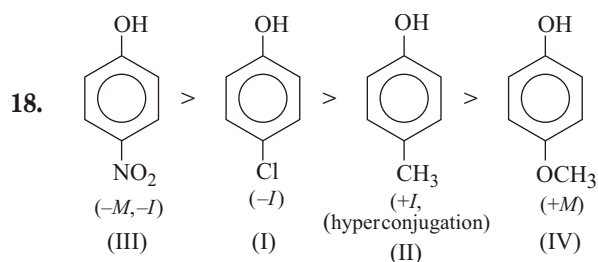
$$0.07 : 0.08 \quad 7 : 8$$

Empirical formula  $\text{C}_7\text{H}_8$

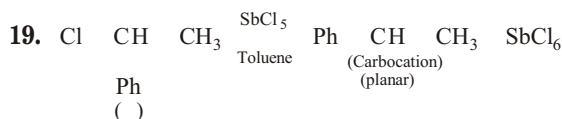
17. The order of stability of carbocation will be



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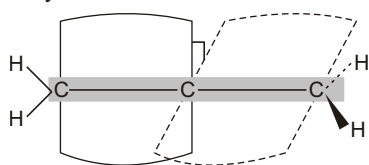


Electron releasing group decreases while electron withdrawing group increases acidic strength by destabilising and stabilising the phenoxide ion formed respectively.



Hybridisation of an atom is determined by determining the number of hybrid orbitals at that atom which is equal to the number of sigma ( ) bonds plus number of lone pairs at the concerned atom.

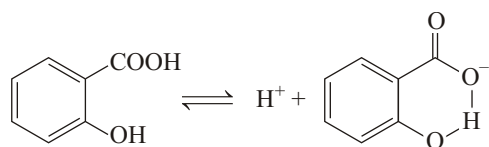
Pi ( ) bonds are not formed by hybrid orbitals, therefore, not counted for hybridisation.



Here, the terminal carbons have only three sigma bonds associated with them, therefore, hybridisation of terminal carbons is  $sp^3$ . The central carbon has only two sigma bonds associated, hence hybridisation at central carbon is  $sp$ .

21. A mono-substituted benzoic acid is stronger than a mono-substituted phenol as former being a carboxylic acid. Among the given substituted benzoic acid, *ortho*-hydroxy acid is strongest acid although  $-\text{OH}$  causes electron donation by resonance effect which tends to decrease acid strength.

It is due to a very high stabilisation of conjugate base by intramolecular H-bond which outweigh the electron donating resonance effect of  $-\text{OH}$ .

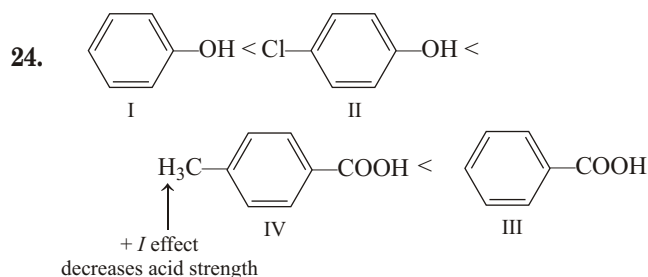
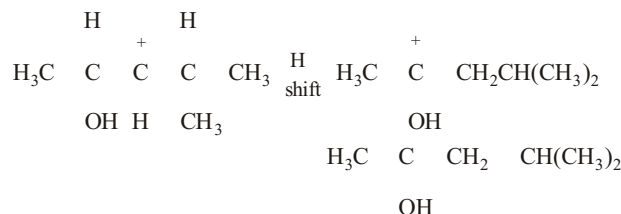


The overall order of acid-strength of given four acids is *ortho*-hydroxybenzoic acid ( $pK_a = 2.98$ ) > Toluic acid ( $pK_a = 4.37$ ) > *p*-hydroxybenzoic acid ( $pK_a = 4.58$ ) > *p*-nitrophenol ( $pK_a = 7.15$ )

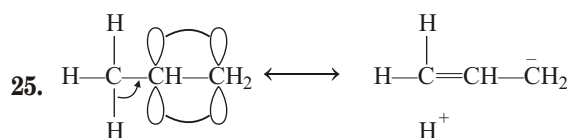
22. I is most stable because it has more covalent bonds and negative charge on electronegative nitrogen. III is more stable than II and IV due to greater number of covalent bonds. Between II and IV, II is more stable since, it has negative charge on electronegative atom and positive charge on electropositive atom. Hence, overall stability order is



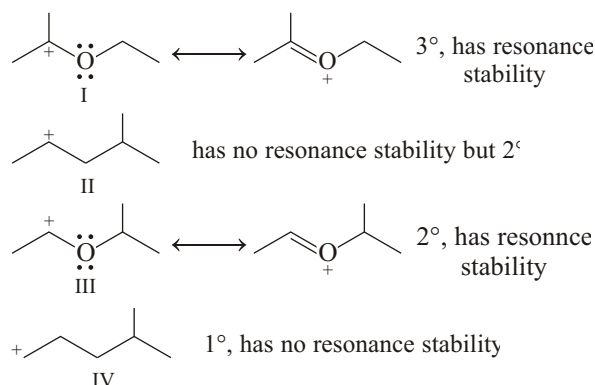
23. H at  $\text{C}_2$  will migrate giving resonance stabilised carbocation.



Cl has overall electron withdrawing effect, increases acid strength.

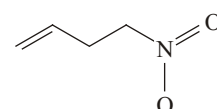


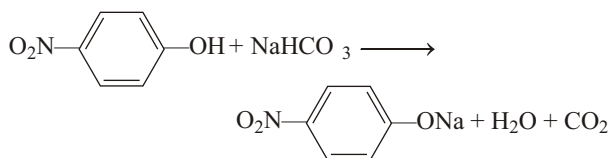
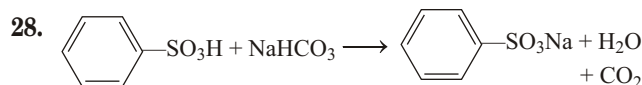
26. The  $\pi$ -electron of C—H bond is delocalised with  $p$ -orbitals of  $\pi$ -bond.



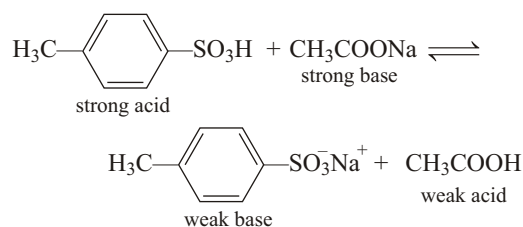
Therefore, overall stability order is : I > III > II > IV

27. The following structure has like charge on adjacent atoms, therefore, least stable





29. A spontaneous neutralisation will occur between strong acid and strong base as



30.  $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}-\text{O}-\text{CH}_3$

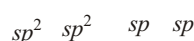
Lone pair of oxygen is not the part of this mode of delocalisation.

31. Carboxylic acid is stronger acid than ammonium ion, hence  $-\text{COOH}(X)$  is most acidic.  $Z(\text{NH}_3^+)$  is more acidic than  $Y(\text{NH}_3^+)$  due to  $-I$  effect of  $-\text{COOH}$  on  $Z$ . Hence, overall acid strength order is

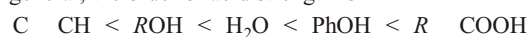


32.  $\text{CH}_3\text{Cl}$  has highest dipole moment.

33.  $\text{H}_2\text{C}=\text{CH}-\text{C}\equiv\text{N}$

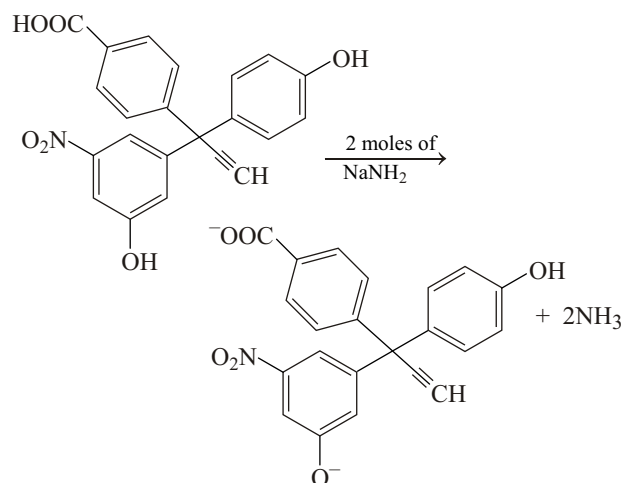


34. In general, the order of acid strength is



Therefore, during stepwise neutralisation of given acid,  $-\text{COOH}$  will be neutralised first.

In the second step, the phenolic  $-\text{OH}$ , assisted by  $-I$  effect of  $\text{NO}_2$  at *meta* position will be neutralised.

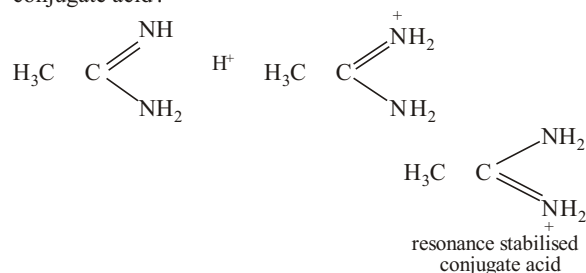


35. Weakest acid  $\text{BrCH}_2\text{CH}_2\text{COOH}$  has smallest dissociation constant.

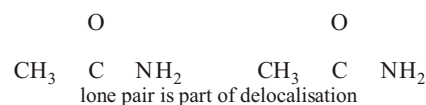
36. Butanoic acid forms more exhaustive H-bonds than butanol and butanal do not form intermolecular H-bonds. Hence, boiling point order will be  $3 > 1 > 2$ .

37.  $\text{CH}_3-\text{C}(\text{CH}_3)_2-\text{C}(\text{CH}_3)_2-\text{CH}_3$   
symmetric

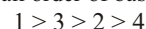
38. I is most basic due to formation of resonance stabilised conjugate acid.



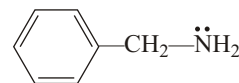
IV is amide, least basic.



Also, among alkyl amines,  $2^\circ$  is more basic than  $1^\circ$  amine. Hence, overall order of basic strength is

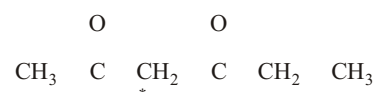


- 39.

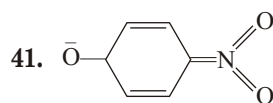


Lone pair is not taking part in resonance, most basic. In other cases, lone pair of nitrogen is part of delocalisation which decreases Lewis base strength.

40. A methylene ( $-\text{CH}_2-$ ) with carbonyl on both side is highly acidic.



has very acidic H.



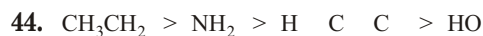
octet of nitrogen is violated.

42. Although alcohols are weaker acid than water, it is stronger than ammonia and terminal alkynes.

43. Nitro group from *para* position exert electron withdrawing resonance effect, increases acidity of phenol the most. This is followed by *meta* nitrophenol in which nitro group exert electron withdrawing effect on acidity.  $\text{CH}_3-$  is an electron donating group, decreases acid strength. Hence, the overall order is



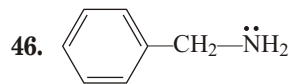
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It is because the order of acid-strength of their conjugate acid is  $\text{CH}_3\text{CH}_3 < \text{NH}_3 < \text{H} \quad \text{C} \quad \text{C} \quad \text{H} < \text{H}_2\text{O}$ : Acid strength.

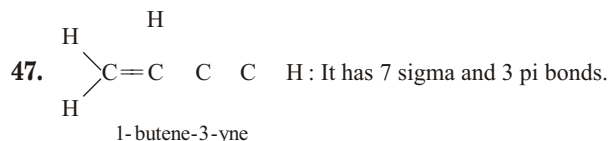


$sp \quad sp^3$

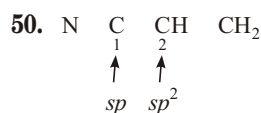
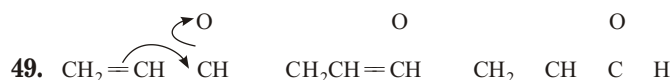
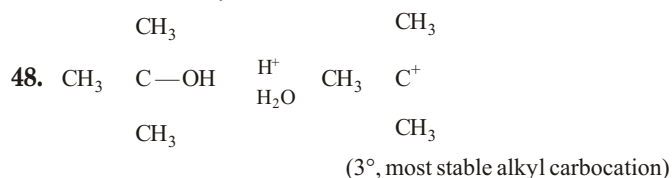


benzylamine

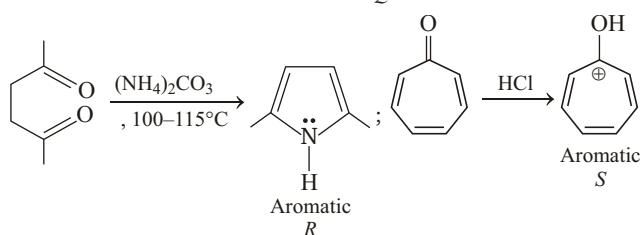
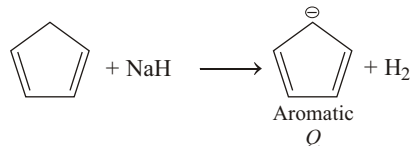
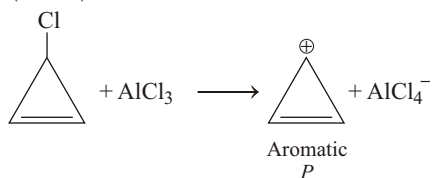
Lone pair is not involved in resonance, most basic. In all other cases, lone pair of nitrogen is involved in resonance, less basic.



1-butene-3-yne



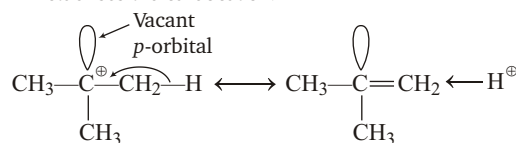
51. **PLAN** A species is said to have aromatic character if  
 (a) ring is planar  
 (b) there is complete delocalisation of  $\pi$ -electrons  
 (c) Huckel rule i.e.  $(4n + 2)$  rule is followed.  
 where,  $n$  is the number of rings  
 $(4n + 2)$  electron delocalised.



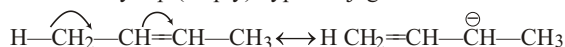
|   | $n$ | $(4n + 2)$ | electrons                    |
|---|-----|------------|------------------------------|
| P | 0   | 2          | 2                            |
| Q | 1   | 6          | 6 (including lone pair)      |
| R | 1   | 6          | 6 (including lone pair on N) |
| S | 1   | 6          | 6                            |

In all cases there is complete delocalisation of  $\pi$ -electrons.

52. **PLAN** Spreading out charge by the overlap of an empty  $p$ -orbital with an adjacent  $\pi$ -bond is called hyperconjugation. This overlap (the hyperconjugation) delocalises the positive charge on the carbocation, spreading it over a larger volume, and this stabilises the carbocation.

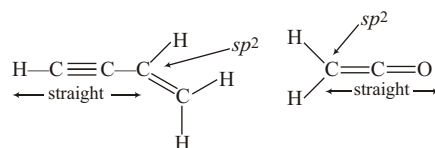


tertiary butyl carbocation has one vacant  $p$ -orbital, hence, it is stabilised by  $\pi$ - $p$  (empty) hyperconjugation.



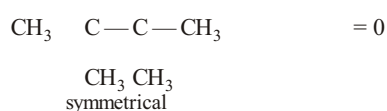
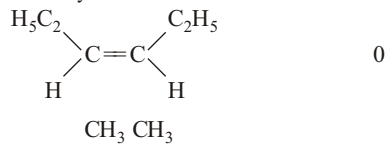
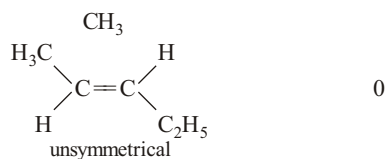
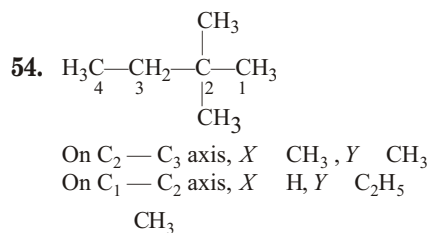
In 2-butene, stabilisation is due to hyperconjugation between  $\pi$ - $\sigma^*$  electron delocalisation.

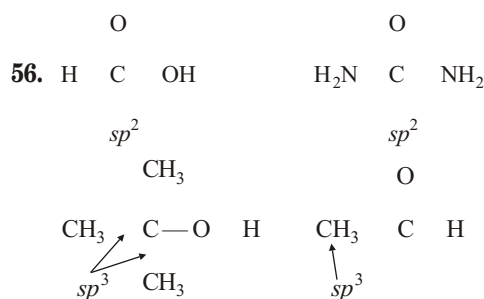
53. In both (b) and (c), all the atoms are present in one single plane



In (a) 1, 3-butadiene, conformational change is possible between  $\text{C}_2 - \text{C}_3$  bond in which atoms will be present in more than one single plane.

In (d) allene, the terminals  $\text{H}-\text{C}-\text{H}$  planes are perpendicular to one another.





57. Phenol is less acidic than a carboxylic acid (acetic acid). Nitro group from *para* position exert electron withdrawing resonance effect, increases acid strength. Therefore, phenol is less acidic than *p*-nitro phenol.

On the other hand, methoxy group from *para* position, donate electrons by resonance effect, decreases acid strength of phenol. Also ethanol is weaker acid than phenol due to resonance stabilisation in phenoxide ion.

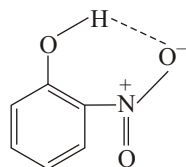
Hence,

ethanol < *p*-methoxyphenol < phenol < *p*-nitrophenol < acetic acid  
increasing acid strength

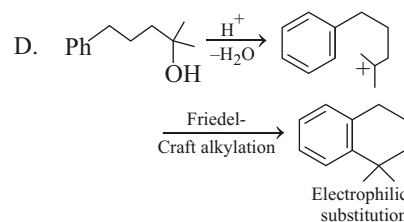
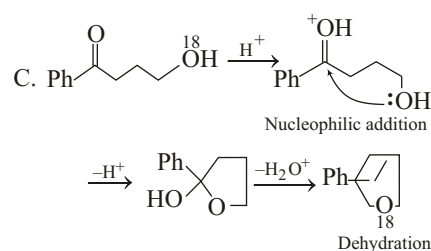
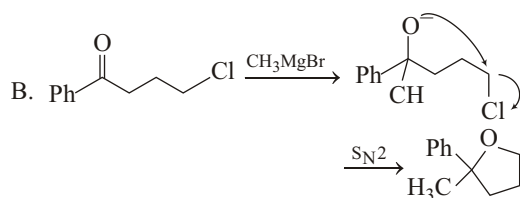
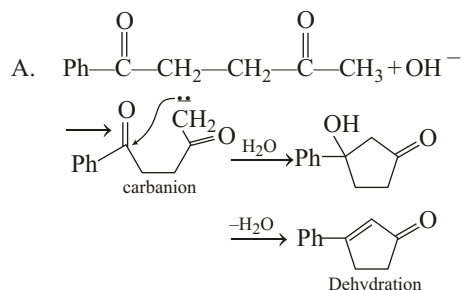
58. Statement I is incorrect; Statement II is correct. Intramolecular H-bonding in *ortho*-hydroxy benzoic acid lowers the boiling point.

59. Statement I is correct; Statement II is correct; Statement II is the correct explanation of Statement I.

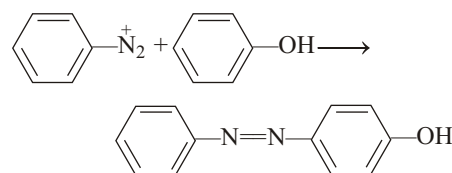
Intramolecular H-bonding discourage release of H to some extent, hence weaker acid than its *para* isomer.



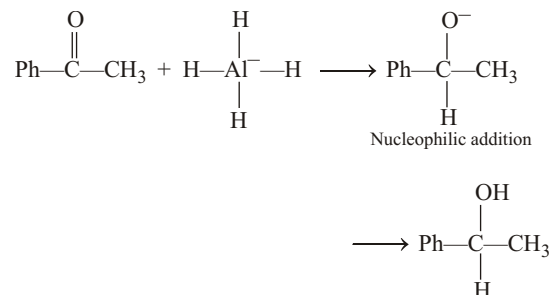
60.



61.

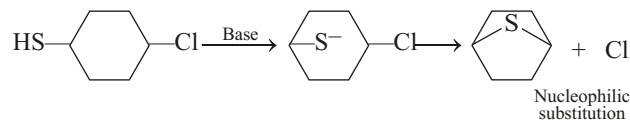


this is an example of electrophilic substitution at *para* position of phenol, giving a coupling product.



Pianacol-pinacolone rearrangement, occur through carbocation intermediate.

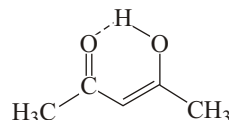
Nucleophilic addition occur at  $sp^2$  (planar) carbon, generating a chiral centre, hence product will be a racemic mixture.



62. Hyperconjugation.

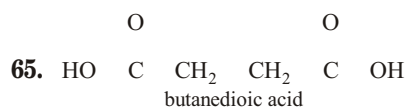
63. Less, stable free radical is formed.

64. Cyclic





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66. Triangular planar; carbon is  $sp^2$ -hybridised

67. geminal, same

68.  $sp^3$ -hybridised

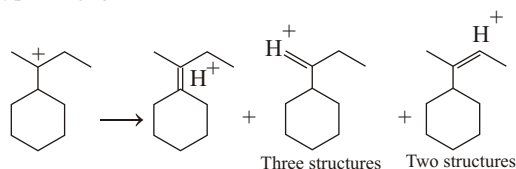
69. Cyclopropane: here the C—C—C bond angle is  $60^\circ$  while the requirement is  $109^\circ$ .

70. Propene :  $\text{CH}_2=\text{CH}-\text{CH}_3$   
 $sp^2 \quad sp^3$

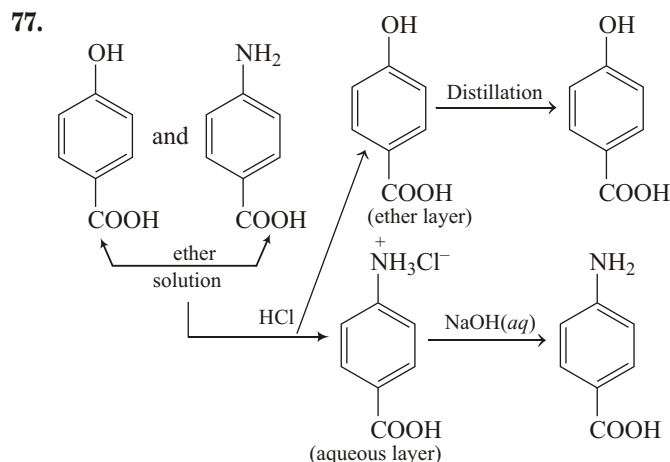
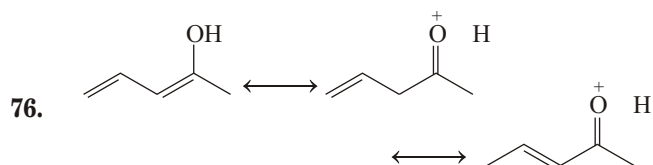
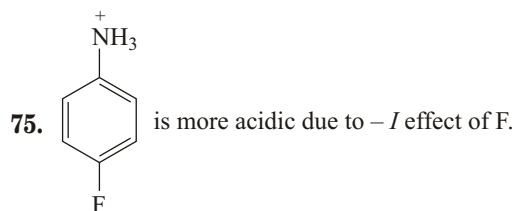
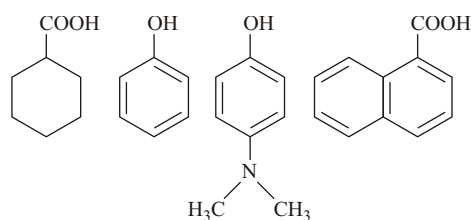
71. Aniline

72. *Tert*-butyl carbonium ion because the three methyl group stabilises carbocation by +I effect.

73. These are total 6 -H to  $sp^2$  carbon and they all can participate in hyperconjugation.

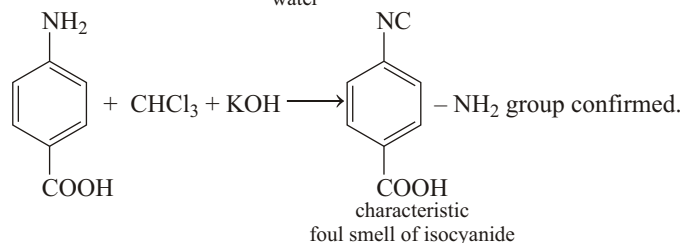


74. Aromatic alcohols and carboxylic acids forms salt with NaOH, will dissolve in aqueous NaOH :



**Tests of functional groups**

$\text{FeCl}_3$       violet colouration confirm phenolic group  
 $\text{NaHCO}_3$        $\text{CO}_2$       lime water      milky      —COOH



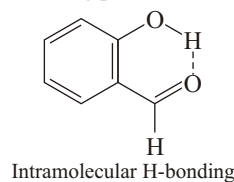
78. *p*-methoxy benzoic acid is the weakest and *p*-nitrobenzoic acid is the strongest acid among these acids. Chloro group has overall electron withdrawing effect on ring, therefore, increases acid strength of benzoic acid. Methyl group decreases acid strength of benzoic acid by +I effect. Therefore,

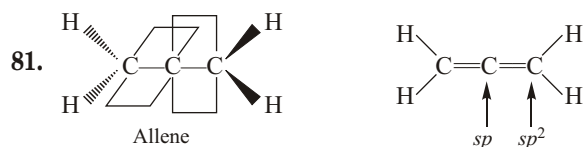
|                                | $K_a$ | $10^5$ |
|--------------------------------|-------|--------|
| <i>p</i> -methoxy benzoic acid | 3.3   | $10^5$ |
| <i>p</i> -methyl benzoic acid  | 4.2   | $10^5$ |
| benzoic acid                   | 6.4   | $10^5$ |
| <i>p</i> -chlorobenzoic acid   | 10.2  | $10^5$ |
| <i>p</i> -nitrobenzoic acid    | 36.2  | $10^5$ |

79.  $\text{H}-\text{C}(\text{H})=\text{C}(\text{H})-\text{H}$  is more acidic than  $\text{CH}_2=\text{CH}_2$ .

80. Intramolecular H-bonding in *ortho*-hydroxybenzaldehyde decreases its melting point as well as boiling point.

Molecules of *p*-hydroxybenzaldehyde is symmetrical, associated together by intermolecular H-bonds, has higher boiling point and melting point.

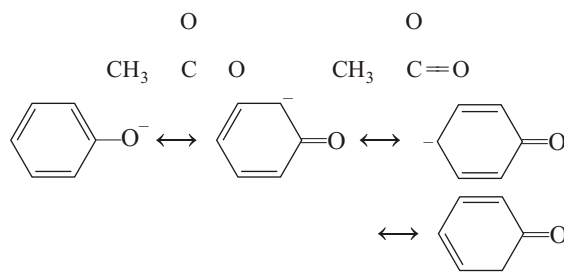




The above shown resonance introduces some double bond character to central C—C bond. Therefore, the central C—C bond in 1, 3-butadiene is shorter (stronger) than C—C bond in butane.

83. In case of acetate ion, both the resonance structures are equivalent and negative charge always remains on electronegative oxygen. These factors makes acetate ion more

stable than phenoxide ion in which negative charge also moves on carbon atoms.



84. *p*-nitroaniline < aniline < *p*-toluidine < N,N-dimethyl-*p*-toluidine. Nitro group, by electron withdrawing resonance effect decreases the basic strength. Methyl group by electron donating inductive effect, increases basic strength.

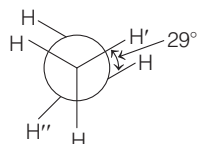
# 22

# Hydrocarbons

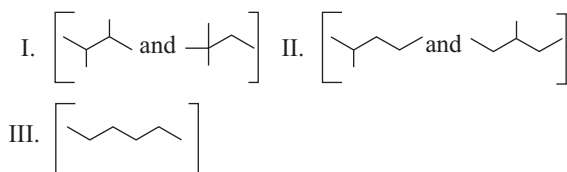
## Topic 1 Saturated Hydrocarbons

### Objective Questions I (Only one correct option)

1. In the following skew conformation of ethane,  $H'-C-C-H''$  dihedral angle is (2019 Main, 12 April II)



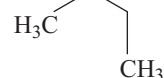
- (a)  $58^\circ$  (b)  $149^\circ$  (c)  $151^\circ$  (d)  $120^\circ$
2. Which of these factors does not govern the stability of a conformation in acyclic compounds? (2019 Main, 10 April II)
- (a) Electrostatic forces of interaction  
(b) Torsional strain  
(c) Angle strain  
(d) Steric interactions
3. Isomers of hexane, based on their branching, can be divided into three distinct classes as shown in the figure. (2014 Adv.)



The correct order of their boiling point is

- (a)  $I > II > III$   
(b)  $III > II > I$   
(c)  $II > III > I$   
(d)  $III > I > II$

4.  $\xrightarrow{Cl_2, h\nu}$   $N$  (isomeric products)  $C_5H_{11}Cl$



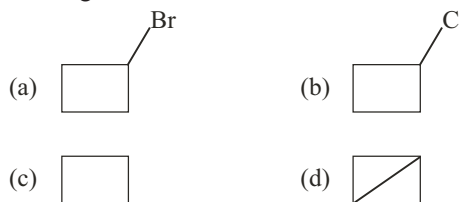
Fractional distillation  $\rightarrow M$  (isomeric products)

What are  $N$  and  $M$ ?

- (a) 6, 6 (b) 6, 4  
(c) 4, 4 (d) 3, 3

(2006, 5M)

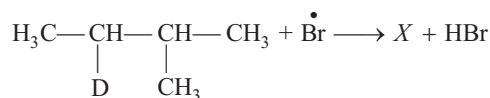
5. 1-bromo-3-chlorocyclobutane when treated with two equivalents of Na, in the presence of ether which of the following will be formed? (2005, 1M)



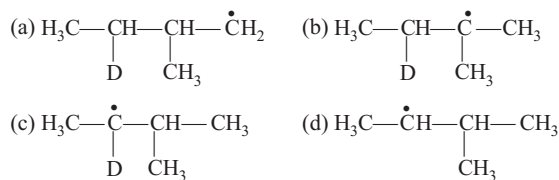
6. How many chiral compounds are possible on mono chlorination of 2-methyl butane? (2004, 1M)

- (a) 2 (b) 4  
(c) 6 (d) 8

7. Consider the following reaction



Identify the structure of the major product  $X$  (2002, 3M)



8. Benzyl chloride ( $C_6H_5CH_2Cl$ ) can be prepared from toluene by chlorination with (1998)

- (a)  $SO_2Cl_2$  (b)  $SOCl_2$   
(c)  $Cl_2$  (d)  $NaOCl$

9.  $(CH_3)_3CMgCl$  on reaction with  $D_2O$  produces (1997)

- (a)  $(CH_3)_3CD$  (b)  $(CH_3)_3OD$   
(c)  $(CD_3)_3CD$  (d)  $(CD_3)_3OD$

10. When cyclohexane is poured on water, it floats because

- (a) cyclohexane is in 'boat' form (1997, 1M)  
(b) cyclohexane is in 'chair' form  
(c) cyclohexane is in 'crown' form  
(d) cyclohexane is less dense than water

11. The C—H bond distance is the longest in (1989, 1M)

- (a)  $C_2H_2$  (b)  $C_2H_4$   
(c)  $C_2H_6$  (d)  $C_2H_2Br_2$

12. The compound which has one isopropyl group, is (1989, 1M)  
 (a) 2,2,3,3-tetramethyl pentane (b) 2,2-dimethyl pentane  
 (c) 2,2,3-trimethyl pentane (d) 2-methyl pentane
13. The highest boiling point is expected for (1986, 1M)  
 (a) *iso*-butane (b) *n*-octane  
 (c) 2, 2, 3, 3-tetramethyl butane (d) *n*-butane
14. Which of the following compounds does not dissolve in conc.  $\text{H}_2\text{SO}_4$  even on warming? (1983, 1M)  
 (a) Ethylene (b) Benzene  
 (c) Hexane (d) Aniline
15. The compound with highest boiling point is (1982, 1M)  
 (a) 2-methyl butane (b) *n*-pentane  
 (c) 2, 2-dimethyl propane (d) *n*-hexane
16. Marsh gas mainly contains (1980, 1M)  
 (a)  $\text{C}_2\text{H}_2$  (b)  $\text{CH}_4$   
 (c)  $\text{H}_2\text{S}$  (d) CO

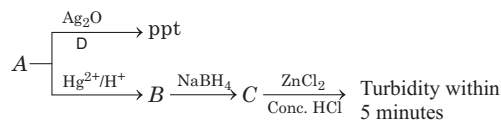
### Integer Answer Type Question

17. The maximum number of isomers (including stereoisomers) that are possible on mono-chlorination of the following compound, is  $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2$  (2011)

## Topic 2 Unsaturated Hydrocarbons

### Objective Questions I (Only one correct option)

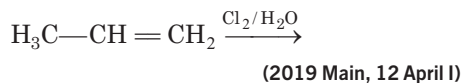
1. Consider the following reactions,



- $A$  is (2019 Main, 12 April II)  
 (a)  $\text{CH}\equiv\text{CH}$  (b)  $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3$   
 (c)  $\text{CH}_3-\text{C}\equiv\text{CH}$  (d)  $\text{CH}_2=\text{CH}_2$
2. But-2-ene on reaction with alkaline  $\text{KMnO}_4$  at elevated temperature followed by acidification will give (2019 Main, 12 April I)

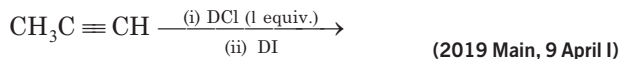
- (a)  $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\underset{\text{OH}}{\text{CH}}-\text{CH}_3$   
 (b) one molecule of  $\text{CH}_3\text{CHO}$  and one molecule of  $\text{CH}_3\text{COOH}$   
 (c) 2 molecules of  $\text{CH}_3\text{COOH}$   
 (d) 2 molecules of  $\text{CH}_3\text{CHO}$

3. The major product of the following addition reaction is



- (a)  $\text{CH}_3-\underset{\text{Cl}}{\text{CH}}-\underset{\text{OH}}{\text{CH}_2}$   
 (b)  $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\underset{\text{Cl}}{\text{CH}_2}$   
 (c)  $\text{H}_3\text{C}-\text{C}(\text{O})-\text{CH}_2$   
 (d)  $\text{H}_3\text{C}-\text{C}(\text{O})-\text{CH}_3$

4. The major product of the following reaction is



- (a)  $\text{CH}_3\text{CD}(\text{Cl})\text{CHD}(\text{I})$  (b)  $\text{CH}_3\text{CD}_2\text{CH}(\text{Cl})\text{I}$   
 (c)  $\text{CH}_3\text{CD}(\text{I})\text{CHD}(\text{Cl})$  (d)  $\text{CH}_3\text{C}(\text{I})(\text{Cl})\text{CHD}_2$

5. Which one of the following alkenes when treated with HCl yields majorly an anti Markownikov product? (2019 Main, 8 April II)

- (a)  $\text{Cl}-\text{CH}=\text{CH}_2$  (b)  $\text{H}_2\text{N}-\text{CH}=\text{CH}_2$   
 (c)  $\text{CH}_3\text{O}-\text{CH}=\text{CH}_2$  (d)  $\text{F}_3\text{C}-\text{CH}=\text{CH}_2$

6. The correct order for acid strength of compounds

$\text{CH}\equiv\text{CH}$ ,  $\text{CH}_3-\text{C}\equiv\text{CH}$  and  $\text{CH}_2=\text{CH}_2$  is as follows : (2019 Main, 12 Jan I)

- (a)  $\text{CH}_3-\text{C}\equiv\text{CH} > \text{CH}_2=\text{CH}_2 > \text{HC}\equiv\text{CH}$   
 (b)  $\text{CH}_3-\text{C}\equiv\text{CH} > \text{CH}\equiv\text{CH} > \text{CH}_2=\text{CH}_2$   
 (c)  $\text{HC}\equiv\text{CH} > \text{CH}_3-\text{C}\equiv\text{CH} > \text{CH}_2=\text{CH}_2$   
 (d)  $\text{CH}\equiv\text{CH} > \text{CH}_2=\text{CH}_2 > \text{CH}_3-\text{C}\equiv\text{CH}$

7. The *trans*-alkenes are formed by the reduction of alkynes with (2018 Main)

- (a)  $\text{H}_2$ -Pd/C,  $\text{BaSO}_4$  (b)  $\text{NaBH}_4$   
 (c)  $\text{Na/liq. NH}_3$  (d)  $\text{Sn-HCl}$

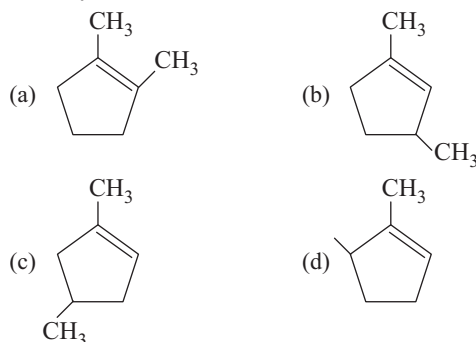
8. The reaction of propene with  $\text{HOCl}$  ( $\text{Cl}_2 + \text{H}_2\text{O}$ ) proceeds through the intermediate (2016 Main)

- (a)  $\text{CH}_3-\overset{+}{\text{C}}\text{H}-\text{CH}_2-\text{Cl}$  (b)  $\text{CH}_3-\text{CH}(\text{OH})-\overset{+}{\text{C}}\text{H}_2$   
 (c)  $\text{CH}_3-\text{CHCl}-\overset{+}{\text{C}}\text{H}_2$  (d)  $\text{CH}_3-\overset{+}{\text{C}}\text{H}-\text{CH}_2-\text{OH}$

9. Which of the following compounds will exhibit geometrical isomerism? (2015 Main)

- (a) 1-phenyl-2-butene (b) 3-phenyl-1-butene  
 (c) 2-phenyl-1-butene (d) 1, 1-diphenyl-1-propane

10. Which compound would give 5-keto-2-methyl hexanal upon ozonolysis? (2015 Main)

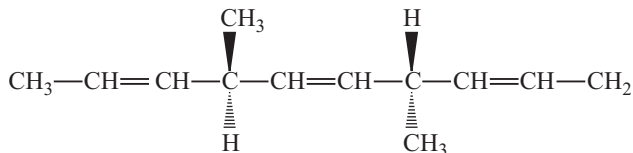


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11. The major organic compound formed by the reaction of 1,1,1-trichloroethane with silver powder is (2014 Main)

(a) acetylene (b) ethene  
(c) 2-butyne (d) 2-butene

12. The number of optically active products obtained from the complete ozonolysis of the given compound, is (2012)



(a) 0 (b) 1 (c) 2 (d) 4

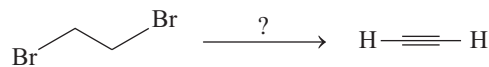
13. The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and an alkyne. The bromoalkane and alkyne respectively are (2010)

(a)  $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  and  $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$   
(b)  $\text{BrCH}_2\text{CH}_2\text{CH}_3$  and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$   
(c)  $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  and  $\text{CH}_3\text{C}\equiv\text{CH}$   
(d)  $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  and  $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$

14. The number of stereoisomers obtained by bromination of *trans*-2-butene is (2007)

(a) 1 (b) 2  
(c) 3 (d) 4

15. The reagent(s) for the following conversion,



is/are

(a) alcoholic KOH  
(b) alcoholic KOH followed by  $\text{NaNH}_2$   
(c) aqueous KOH followed by  $\text{NaNH}_2$   
(d)  $\text{Zn}/\text{CH}_3\text{OH}$

(2007, 3M)

16.  $\text{CH}_3-\text{CH}=\text{CH}_2 + \text{NOCl} \longrightarrow \text{P}$ ; Identify the adduct.

(2006, 3M)

(a)  $\text{CH}_3-\underset{\text{Cl}}{\text{CH}}-\underset{\text{NO}}{\text{CH}_2}$  (b)  $\text{CH}_3-\underset{\text{NO}}{\text{CH}}-\underset{\text{Cl}}{\text{CH}_2}$   
(c)  $\text{CH}_3-\text{CH}_2-\underset{\text{NO}}{\overset{\text{Cl}}{\text{CH}}}$  (d)  $\underset{\text{NO}}{\text{CH}_2}-\text{CH}_2-\underset{\text{Cl}}{\text{CH}_2}$

17. Cyclohexene is best prepared from cyclohexanol by which of the following? (2005)

(a) conc.  $\text{H}_3\text{PO}_4$  (b) conc.  $\text{HCl} / \text{ZnCl}_2$   
(c) conc.  $\text{HCl}$  (d) conc.  $\text{HBr}$

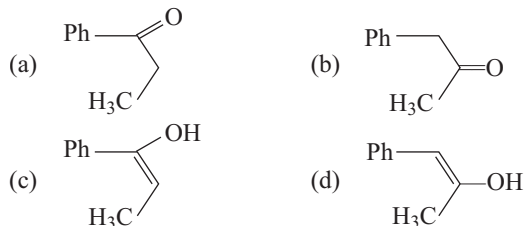
18. 2-hexyne gives *trans*-2-hexene on treatment with (2004, 1M)

(a)  $\text{Li}/\text{NH}_3$  (b)  $\text{Pd}/\text{BaSO}_4$   
(c)  $\text{LiAlH}_4$  (d)  $\text{Pt}/\text{H}_2$

19. 2-phenyl propene on acidic hydration, gives (2004, 1M)

(a) 2-phenyl-2-propanol  
(b) 2-phenyl-1-propanol  
(c) 3-phenyl-1-propanol  
(d) 1-phenyl-2-propanol

20.  $\text{Ph}-\text{C}\equiv\text{C}-\text{CH}_3 \xrightarrow[\text{H}^+]{\text{Hg}^{2+}} \text{A}$ ; A is (2003, 3M)



21. Identify a reagent from the following list which can easily distinguish between 1-butyne and 2-butyne. (2002, 3M)

(a) bromine,  $\text{CCl}_4$  (b)  $\text{H}_2$ , Lindlar catalyst  
(c) dilute  $\text{H}_2\text{SO}_4$ ,  $\text{HgSO}_4$  (d) ammoniacal  $\text{CuCl}_2$  solution

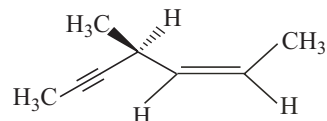
22. In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markownikoff's addition to alkenes because (2001, 1M)

(a) both are highly ionic  
(b) one is oxidising and the other is reducing  
(c) one of the steps is endothermic in both the cases  
(d) all the steps are exothermic in both the cases

23. The reaction of propene with  $\text{HOCl}$  proceeds *via* the addition of (2001)

(a)  $\text{H}^+$  in the first step (b)  $\text{Cl}^+$  in the first step  
(c)  $\text{OH}^-$  in the first step (d)  $\text{Cl}^+$  and  $\text{OH}^-$  single step

24. Hydrogenation of the adjoining compound in the presence of poisoned palladium catalyst gives



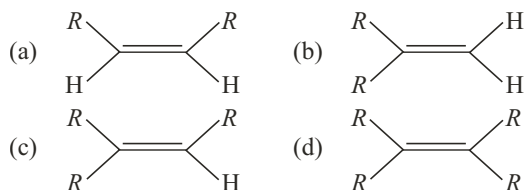
(2001, 1M)

(a) an optically active compound  
(b) an optically inactive compound  
(c) a racemic mixture  
(d) a diastereomeric mixture

25. Propyne and propene can be distinguished by (2000)

(a) conc.  $\text{H}_2\text{SO}_4$  (b)  $\text{Br}_2$  in  $\text{CCl}_4$   
(c) dil.  $\text{KMnO}_4$  (d)  $\text{AgNO}_3$  in ammonia

26. Which one of the following alkenes will react fastest with  $\text{H}_2$  under catalytic hydrogenation condition? (2000, 1M)



27. The product(s) obtained *via* oxymercuration ( $\text{HgSO}_4 + \text{H}_2\text{SO}_4$ ) of 1-butyne would be (1999, 2M)

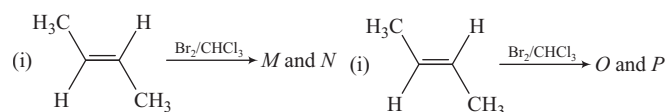
(a)  $\text{CH}_3-\text{CH}_2-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\text{CH}_3$   
(b)  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CHO}$   
(c)  $\text{CH}_3-\text{CH}_2-\text{CHO} + \text{HCHO}$   
(d)  $\text{CH}_3-\text{CH}_2-\text{COOH} + \text{HCOOH}$

28. In the compound,  $\text{CH}_3\text{CH}=\text{CH}-\text{C}\equiv\text{CH}$ , the C2-C3 bond is of the type (1999, 2M)  
 (a)  $sp-sp^2$  (b)  $sp^3-sp^3$  (c)  $sp-sp^3$  (d)  $sp^2-sp^3$
29. The reaction of  $\text{CH}_3\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{OH}$  with HBr gives (1998, 2M)  
 (a)  $\text{CH}_3\text{CHBrCH}_2-\text{C}_6\text{H}_4-\text{OH}$   
 (b)  $\text{CH}_3\text{CHBrCH}_2-\text{C}_6\text{H}_4-\text{Br}$   
 (c)  $\text{CH}_3\text{CH}_2\text{CHBr}-\text{C}_6\text{H}_4-\text{OH}$   
 (d)  $\text{CH}_3\text{CH}_2\text{CHBr}-\text{C}_6\text{H}_4-\text{Br}$
30. Which one of the following has the smallest heat of hydrogenation per mole? (1993, 1M)  
 (a) 1-butene (b) *trans*-2-butene  
 (c) *cis*-2-butene (d) 1, 3-butadiene
31. The number of structural and configurational isomers of a bromo compound,  $\text{C}_5\text{H}_9\text{Br}$ , formed by the addition of HBr to 2-pentyne respectively, are (1988, 1M)  
 (a) 1 and 2 (b) 2 and 4 (c) 4 and 2 (d) 2 and 1
32. Acidic hydrogen is present in (1985, 1M)  
 (a) ethyne (b) ethene (c) benzene (d) ethane
33. Baeyer's reagent is (1984, 1M)  
 (a) alkaline permanganate solution  
 (b) acidified permanganate solution  
 (c) neutral permanganate solution  
 (d) aqueous bromine solution
34. When propyne is treated with aqueous  $\text{H}_2\text{SO}_4$  in the presence of  $\text{HgSO}_4$ , the major product is (1983, 1M)  
 (a) propanal (b) propyl hydrogen sulphate  
 (c) acetone (d) propanol
35. The compound 1, 2-butadiene has (1983, 1M)  
 (a) only  $sp$ -hybridised carbon atoms  
 (b) only  $sp^2$ -hybridised carbon atoms  
 (c) both  $sp$  and  $sp^2$ -hybridised carbon atoms  
 (d)  $sp$ ,  $sp^2$  and  $sp^3$ -hybridised carbon atoms
36. Which of the following will decolourise alkaline  $\text{KMnO}_4$  solution? (1980, 1M)  
 (a)  $\text{C}_3\text{H}_8$  (b)  $\text{CH}_4$  (c)  $\text{CCl}_4$  (d)  $\text{C}_2\text{H}_4$

## Objective Questions II

(One or more than one correct option)

37. The correct statement(s) for the following addition reactions is (are) (2017 Adv.)



- (a) (*M* and *O*) and (*N* and *P*) are two pairs of enantiomers  
 (b) Bromination proceeds through *trans*-addition in both the reactions  
 (c) *O* and *P* are identical molecules  
 (d) (*M* and *O*) and (*N* and *P*) two pairs of diastereomers

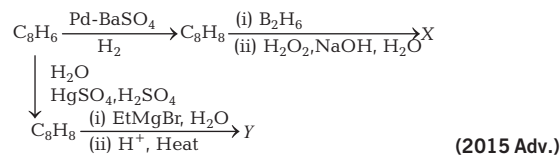
## Assertion and Reason

Read the following questions and answer as per the direction given below :

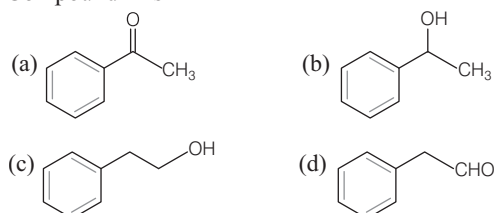
- (a) Statement I is correct Statement II is correct Statement II is a correct explanation of Statement I.  
 (b) Statement I is correct Statement II is correct Statement II is not the correct explanation of Statement I.  
 (c) Statement I is correct Statement II is incorrect.  
 (d) Statement I is incorrect Statement II is correct.
38. **Statement I** Addition of bromine to *trans*-2-butene yields *meso*-2, 3-dibromo butane.  
**Statement II** Bromine addition to an alkene is an electrophilic addition. (2001, 1M)
39. **Statement I** Dimethyl sulphide is commonly used for the reduction of an ozonide of an alkene to get the carbonyl compound.  
**Statement II** It reduces the ozonide giving water soluble dimethyl sulfoxide and excess of it evaporates. (2001, 1M)
40. **Statement I** 1-butene on reaction with HBr in the presence of a peroxide produces 1-bromobutane.  
**Statement II** It involves the formation of a primary radical. (2000, 1M)
41. **Statement I** Addition of  $\text{Br}_2$  to 1-butene gives two optical isomers.  
**Statement II** The product contains one asymmetric carbon. (1998, 1M)

## Passage Based Questions

### Passage 1

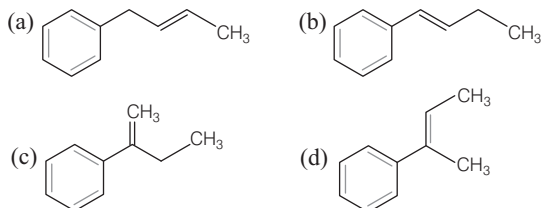


42. Compound *X* is



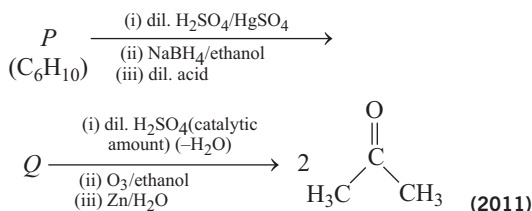
## 314 Hydrocarbons

43. The major compound *Y* is

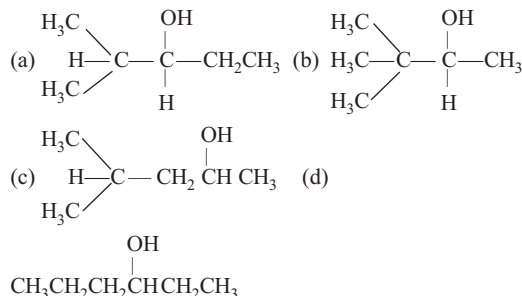


### Passage 2

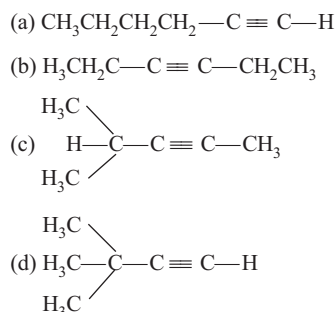
An acyclic hydrocarbon *P*, having molecular formula  $C_6H_{10}$ , gave acetone as the only organic product through the following sequence of reactions, in which *Q* is an intermediate organic compound.



44. The structure of the compound *Q* is

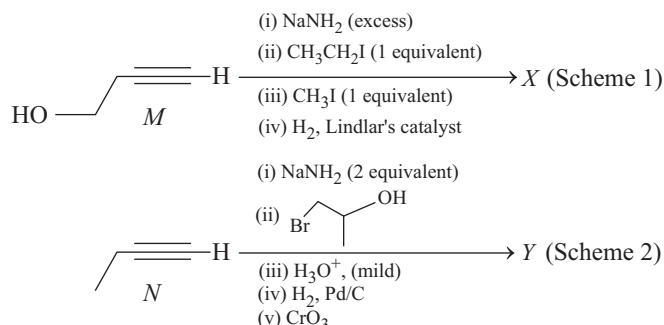


45. The structure of compound *P* is



### Passage 3

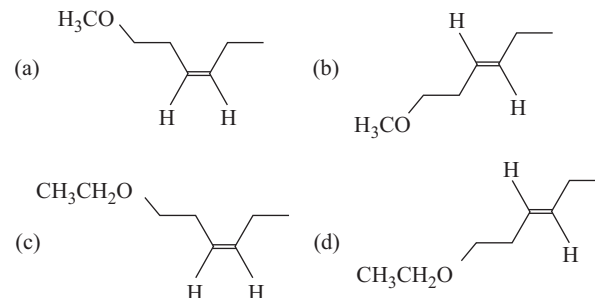
Schemes 1 and 2 describe sequential transformation of alkynes *M* and *N*. Consider only the major products formed in each step for both schemes.



46. The correct statement with respect to product *Y* is

- (a) it gives a positive Tollen's test and is a functional isomer of *X*  
(b) it gives a positive Tollen's test and is a geometrical isomer of *X*  
(c) it gives a positive iodoform test and is a functional isomer of *X*  
(d) it gives a positive iodoform test and is a geometrical isomer of *X*

47. The product *X* is



### Fill in the Blanks

48. 1,3-butadiene with bromine in molar ratio of 1 : 1 generate predominantly ..... . (1997, 1M)
49. Addition of water to acetylene compounds is catalysed by ..... and ..... (1993, 1M)
50. Kolbe's electrolysis of potassium succinate gives  $CO_2$  and ..... (1993, 1M)
51. The terminal carbon atom in 2-butene is ..... hybridised. (1985, 1M)
52. Acetylene is treated with excess sodium in liquid ammonia. The product is reacted with excess methyl iodide. The final product is ..... (1983, 1M)
53. .... is most acidic. (Ethane, Ethene, Ethyne) (1981, 1M)

### True/False

54. Moist ethylene can be dried by passing it through concentrated sulphuric acid. (1981)

### Integer Answer Type Question

55. The total number of cyclic isomers possible for a hydrocarbon with the molecular formula  $C_4H_6$  is (2010)



## Subjective Questions

56. Monomer *A* of a polymer on ozonolysis yields two moles of HCHO and one mole of CH<sub>3</sub>COCHO.

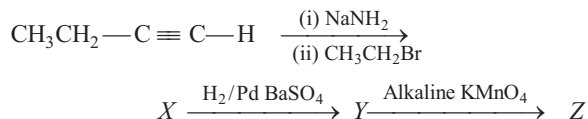
(a) Deduce the structure of *A*.  
 (b) Write the structure of all *cis* form of polymer of compound *A*. (2005, 2M)

57. A biologically active compound, Bombykol (C<sub>16</sub>H<sub>30</sub>O) is obtained from a natural source. The structure of the compound is determined by the following reactions.

- (a) On hydrogenation, Bombykol gives a compound *A*, C<sub>16</sub>H<sub>34</sub>O, which reacts with acetic anhydride to give an ester.  
 (b) Bombykol also reacts with acetic anhydride to give another ester, which on oxidative ozonolysis (O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>) gives a mixture of butanoic acid, oxalic acid and 10-acetoxy decanoic acid.

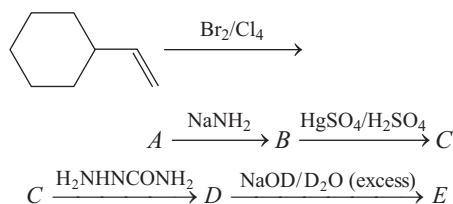
Determine the number of double bonds in Bombykol. Write the structures of compound *A* and Bombykol. How many geometrical isomers are possible for Bombykol?

58. Identify *X*, *Y* and *Z* in the following synthetic scheme and write their structures.

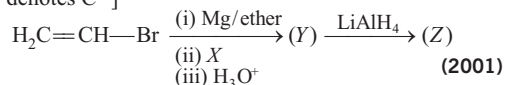


Is the compound *Z* optically active? Justify your answer. (2002)

59. (a) Identify (*A*), (*B*), (*C*), (*D*) and (*E*) in the following schemes and write their structures :



- (b) Identify (*X*), (*Y*) and (*Z*) in the following synthetic scheme and write their structures. Explain the formation of labelled formaldehyde (H<sub>2</sub>C\*O) as one of the products when compound (*Z*) is treated with HBr and subsequently ozonolysed. Mark the C\* carbon in the entire scheme. BaC\*O<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub> → (*X*) gas [C\* denotes C<sup>14</sup>]

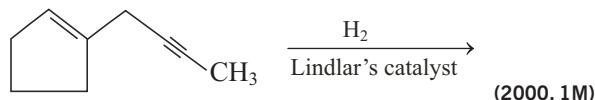


60. An alkene (*A*) C<sub>16</sub>H<sub>16</sub> on ozonolysis gives only one product (*B*) C<sub>8</sub>H<sub>8</sub>O. Compound (*B*) on reaction with NaOH/I<sub>2</sub> yields sodium benzoate. Compound (*B*) reacts with KOH/NH<sub>2</sub>NH<sub>2</sub> yielding a hydrocarbon (*C*) C<sub>8</sub>H<sub>10</sub>. Write the structures of compounds (*B*) and (*C*). Based on

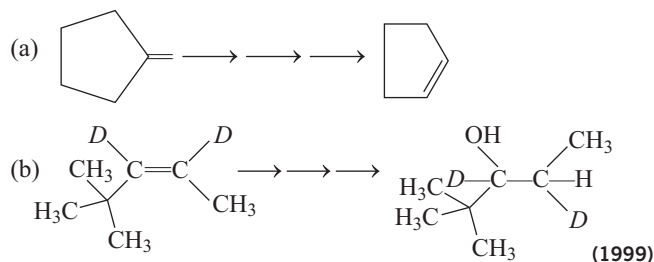
this information two isomeric structures can be proposed for alkene (*A*). Write their structures and identify the isomer which on catalytic hydrogenation (H<sub>2</sub>/Pd - C) gives a racemic mixture.

(2001)

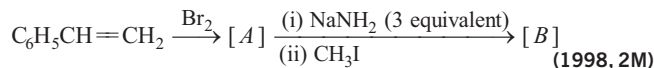
61. What would be the major product in the following reaction?



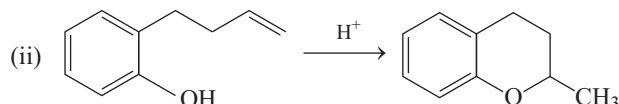
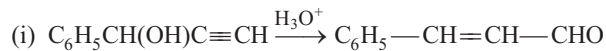
62. Complete the following reactions with appropriate reagents :



63. Complete the following reactions with appropriate structures of products/reagents :

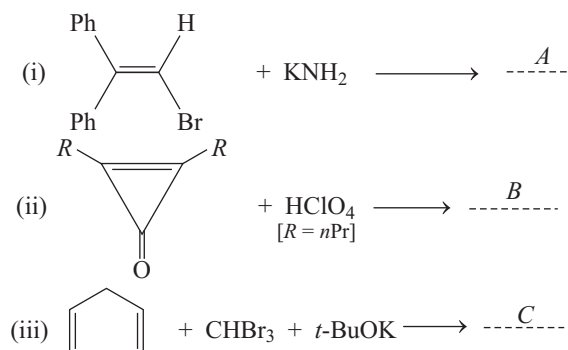


64. Write the intermediate steps for each of the following reactions :



65. The hydrocarbon *A*, adds one mole of hydrogen in the presence of a platinum catalyst to form *n*-hexane. When *A* is oxidised vigorously with KMnO<sub>4</sub>, a single carboxylic acid, containing three carbon atoms, is isolated. Give the structure of *A* and explain.

66. Complete the following, giving the structures of the principal organic products :



67. An alkyl halide, *X*, of formula C<sub>6</sub>H<sub>13</sub>Cl on treatment with potassium tertiary butoxide gives two isomeric alkenes *Y* and *Z* (C<sub>6</sub>H<sub>12</sub>). Both alkenes on hydrogenation gives 2, 3-dimethyl butane. Predict the structures of *X*, *Y* and *Z*. (1996, 3M)

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68. Give the structure of the major organic products obtained from 3-ethyl-2-pentene under each of the following reaction conditions : (1996)
- HBr in the presence of peroxide
  - $\text{Br}_2 / \text{H}_2\text{O}$
  - $\text{Hg}(\text{OAc})_2 / \text{H}_2\text{O}, \text{NaBH}_4$
69. Write down the structure of the stereoisomers formed when *cis*-2-butene is reacted with bromine. (1995)
70. An organic compound *E* ( $\text{C}_5\text{H}_8$ ) on hydrogenation gives compound *F* ( $\text{C}_5\text{H}_{12}$ ). Compound *E* on ozonolysis gives formaldehyde and 2-keto propanal. Deduce the structure of compound *E*. (1995)
71. When gas *A* is passed through dry KOH at low temperature, a deep red coloured compound *B* and a gas *C* are obtained. The gas *A*, on reaction with but-2-ene, followed by treatment with  $\text{Zn} / \text{H}_2\text{O}$  yields acetaldehyde. Identify *A*, *B* and *C*. (1994, 3M)
72. Give the structures of *A*, *B* and *C* (explanation are not required)
- A* ( $\text{C}_4\text{H}_8$ ) which adds on HBr in the presence and in the absence of peroxide to give same product.
  - B* ( $\text{C}_4\text{H}_8$ ) which when treated with  $\text{H}_2\text{O} / \text{H}_2\text{SO}_4$  gives  $\text{C}_4\text{H}_{10}\text{O}$  which cannot be resolved into optical isomers.
  - C* ( $\text{C}_6\text{H}_{12}$ ), an optically active hydrocarbon which on catalytic hydrogenation gives an optically inactive compound  $\text{C}_6\text{H}_{14}$ . (1993, 1M  $\times$  3 = 3M)
73. Write the balanced chemical equation for the following  
“Ethylene glycol is obtained by the reaction of ethylene with potassium permanganate.” (1991, 1M)
74. Give a chemical test and the reagents used to distinguish between cyclohexane and cyclohexene. (1991, 1M)
75. A white precipitate was formed slowly when silver nitrate was added to compound *A* with molecular formula  $\text{C}_6\text{H}_{13}\text{Cl}$ . Compound *A* on treatment with hot alcoholic potassium hydroxide gave a mixture of two isomeric alkenes *B* and *C*, having formula  $\text{C}_6\text{H}_{12}$ . The mixture of *B* and *C*, on ozonolysis, furnished four compounds
- $\text{CH}_3\text{CHO}$
  - $\text{C}_2\text{H}_5\text{CHO}$
  - $\text{CH}_3\text{COCH}_3$
  - $\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{CHO}$
- What are the structures of *A*, *B* and *C*? (1986, 4M)
76. How would you convert acetylene to acetone? (1985, 1M)
77. Give the chemical test to distinguish between 2-butyne and 1-butyne. (1985, 1M)
78. Following statements are true, only under some specific conditions. Write the condition for each subquestion in not more than two sentences :
- 2-methyl propene can be converted into isobutyl bromide by hydrogen bromide.
  - Ethyne and its derivatives will give white precipitate with ammoniacal silver nitrate solution. (1984, 1M  $\times$  2 = 2M)
79. Give reasons for the following in one or two sentences :
- Methane does not react with chlorine in the dark.
  - Propene reacts with HBr to give isopropyl bromide but does not give *n*-propyl bromide. (1983, 1M  $\times$  2 = 2M)
80. State with balanced equation, what happens when “propene is bubbled through a hot aqueous solution of potassium permanganate.”? (1982, 1M)
81. One mole of a hydrocarbon *A* reacts with one mole of bromine giving a dibromo compound,  $\text{C}_5\text{H}_{10}\text{Br}_2$ . Compound *A* on treatment with cold dilute alkaline potassium permanganate solution forms a compound,  $\text{C}_5\text{H}_{12}\text{O}_2$ . On ozonolysis *A* gives equimolar quantities of propanone and ethanal. Deduce the structural formula of *A*. (1981, 1M)
82. Write the structural formula of the major product in each of the following cases
- Ethene mixed with air is passed under pressure over a silver catalyst.
  - The compound obtained by hydration of ethyne is treated with dilute alkali. (1981, 2  $\times$  1 / 2 M = 1M)
83. Outline the reaction sequence for the conversion of ethene to ethyne (the number of steps should not be more than two). (1981, 1M)
84. Give one characteristic test which would distinguish  $\text{CH}_4$  from  $\text{C}_2\text{H}_2$ . (1979, 1M)

## Answers

### Topic 1

- |         |         |         |         |
|---------|---------|---------|---------|
| 1. (b)  | 2. (c)  | 3. (b)  | 4. (b)  |
| 5. (d)  | 6. (c)  | 7. (b)  | 8. (c)  |
| 9. (a)  | 10. (d) | 11. (c) | 12. (d) |
| 13. (b) | 14. (c) | 15. (d) | 16. (b) |
| 17. (8) |         |         |         |

### Topic 2

- |         |         |         |         |
|---------|---------|---------|---------|
| 1. (c)  | 2. (c)  | 3. (b)  | 4. (d)  |
| 5. (d)  | 6. (c)  | 7. (c)  | 8. (a)  |
| 9. (a)  | 10. (b) | 11. (c) | 12. (a) |
| 13. (d) | 14. (a) | 15. (b) | 16. (a) |

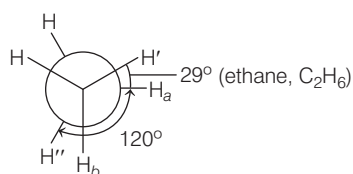
- |                              |                                            |              |         |
|------------------------------|--------------------------------------------|--------------|---------|
| 17. (a)                      | 18. (a)                                    | 19. (a)      | 20. (a) |
| 21. (d)                      | 22. (c)                                    | 23. (b)      | 24. (b) |
| 25. (d)                      | 26. (a)                                    | 27. (a)      | 28. (d) |
| 29. (c)                      | 30. (b)                                    | 31. (b)      | 32. (a) |
| 33. (a)                      | 34. (c)                                    | 35. (d)      | 36. (d) |
| 37. (a,b,d)                  | 38. (b)                                    | 39. (a)      | 40. (c) |
| 41. (a)                      | 42. (c)                                    | 43. (d)      | 44. (b) |
| 45. (d)                      | 46. (c)                                    | 47. (a)      |         |
| 48. 3,4-dibromo-1-butene     | 49. $\text{H}_2\text{SO}_4, \text{HgSO}_4$ |              |         |
| 50. ethene                   | 51. $sp^3$                                 | 52. 2-butyne |         |
| 53. Terminal alkyne (ethyne) | 54. False                                  | 55. (5)      |         |

# Hints & Solutions

## Topic 1 Saturated Hydrocarbons

1. A dihedral angle is the angle between two C—H bonds projected on a plane orthogonal to the C—C bond. In the given skew conformation, having Newman's projection the dihedral angle is

$$\begin{aligned} & \text{H}'-\text{C}-\text{C}-\text{H}'' \\ &= (\text{H}'-\text{C}-\text{C}-\text{H}_a) + (\text{H}_a-\text{C}-\text{C}-\text{H}'') \\ &= 29^\circ + 120^\circ = 149^\circ \end{aligned}$$



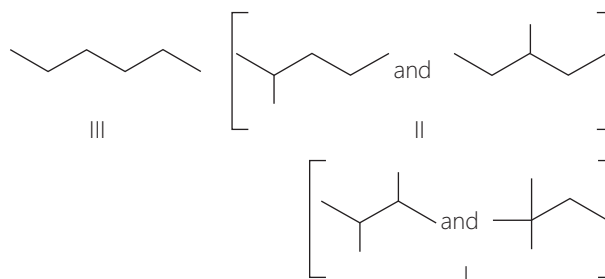
2. The four types of strains viz (a) electrostatic force of attraction, (b) torsional strain, (c) angle strain, (d) steric strain, are responsible for the stability or energy barriers of conformers. In cyclic compounds, all types of strains may be present.

| Compound | Type of strains/forces |
|----------|------------------------|
|          | a + c                  |
|          | a + b + c              |
|          | a + b + c + d          |

In a cyclic or open-chain compounds, angle strain (c) is absent. e.g.

| Compound | Types of strains/forces |
|----------|-------------------------|
|          | a                       |
|          | a + b                   |
|          | a + b + d               |

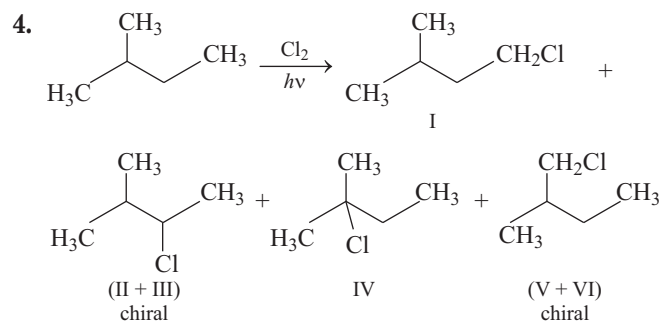
3. **PLAN** This problem is based on boiling point of isomeric alkanes. As we know more the branching in an alkane, lesser will be its surface area and lesser will be the boiling point



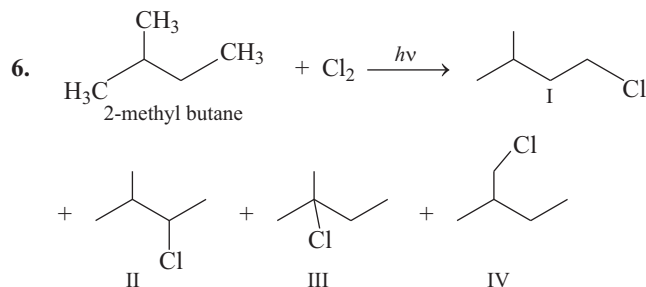
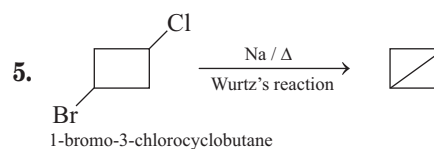
**On moving left to right (III to I)**

- branching increases
- surface area decreases
- boiling point decreases

Hence, correct choice is (b).



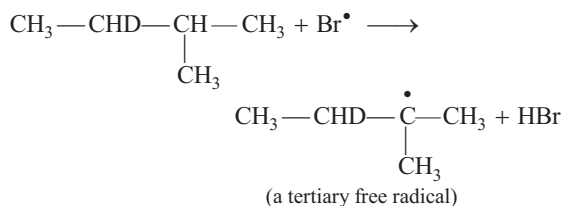
Since, fractional distillation cannot separate enantiomers (II + III and V + VI),  $M = 4$  and  $N = 6$ .



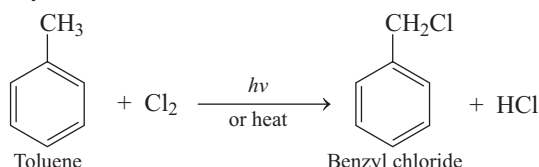
Out of the four products formed above, II and IV are chiral, produced in pairs, giving total of six mono-chlorination products.

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7. Bromination is highly selective, occur at the carbon, where the most stable free radical is formed :



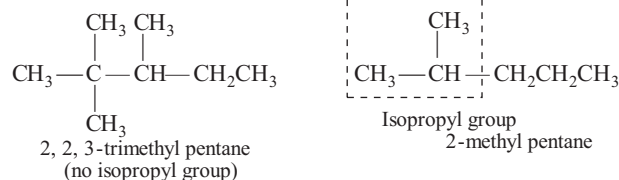
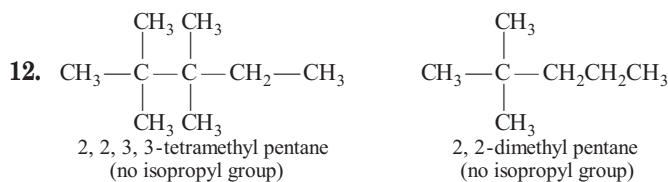
8. Toluene on treatment with  $\text{Cl}_2$  in the presence of heat or light undergo free-radical chlorination at benzylic position, giving benzyl chloride



9.  $(\text{CH}_3)_3\text{CMgCl} + \text{D}_2\text{O} \longrightarrow \text{CH}_3 - \underset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}} - \text{D} + \text{Mg}(\text{OD})\text{Cl}$

10. Alkanes are all less dense than water, floats over water.

11. C—H bond with  $sp^3$ -C will be longest in  $\text{C}_2\text{H}_6$ .



13. Boiling point of alkane increases with molar mass. Among isomeric alkanes, branching decreases boiling point. Therefore, *n*-octane has highest boiling point, higher than 2, 2, 3, 3-tetramethyl-butane (an isomer of *n*-octane).

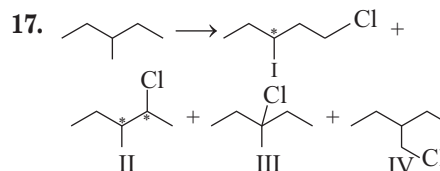
14. Ethylene absorb  $\text{H}_2\text{SO}_4$  forming  $\text{CH}_3 - \text{CH}_2\text{OSO}_3\text{H}$  and dissolve. Benzene, with warm  $\text{H}_2\text{SO}_4$ , undergo sulphonation and dissolve.

Aniline, with  $\text{H}_2\text{SO}_4$ , forms anilinium sulphate salt and dissolve. Hexane, a hydrophobic molecule, does not react with  $\text{H}_2\text{SO}_4$ , remains insoluble.

15. Among alkanes, boiling point increases with molar mass. Among isomeric alkanes, branching decreases boiling point. Therefore, *n*-hexane has highest boiling point among these.

16. Methane is produced due to the decay of vegetables or animal organisms present in swamps and marsh, by the action of bacteria.

Due to this method of formation, methane is also known as marsh gas.



I has one chiral carbon = two isomers

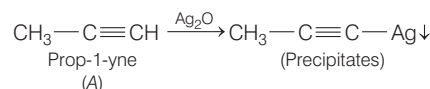
II has two chiral carbons and no symmetry = four isomers.

III and IV have no chiral carbon, no stereoisomers.

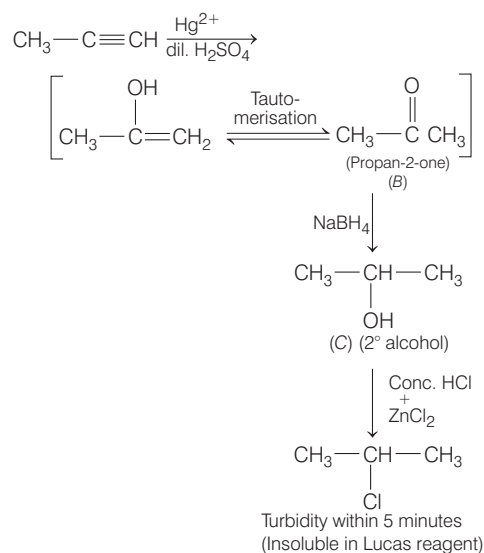
## Topic 2 Unsaturated Hydrocarbons

1. According to the given conditions, the compound should be alkyne with triple bond present at the terminal. The chemical reactions involved are as follows:

### Step 1



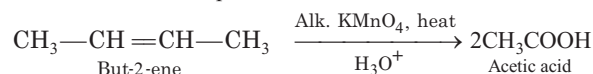
### Step 2



In step-1, prop-1-yne reacts with  $\text{Ag}_2\text{O}$  to form  $\text{CH}_3 - \text{C} \equiv \text{C} - \text{Ag}$ , that forms white precipitates.

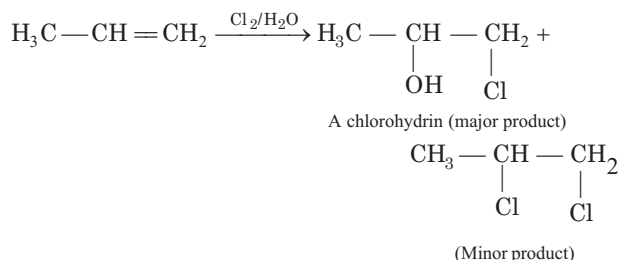
In step 2, prop-1-yne in presence of mercuric sulphate and dil.  $\text{H}_2\text{SO}_4$  produces carbonyl compound  $(\text{CH}_3)_2\text{C} = \text{O}$  which produces  $(\text{CH}_3)_2\text{CH} - \text{OH}$  in presence of  $\text{NaBH}_4$ . 2°alcohol on reaction with Lucas reagent produces turbidity in about 5 min.

2. But-2-ene on reaction with alkaline  $\text{KMnO}_4$  at elevated temperature followed by acidification will give acetic acid ( $\text{CH}_3\text{COOH}$ ). Hot alkaline solution of potassium permanganate followed by acidification oxidatively cleaved alkenes. The reaction proceed as follows :

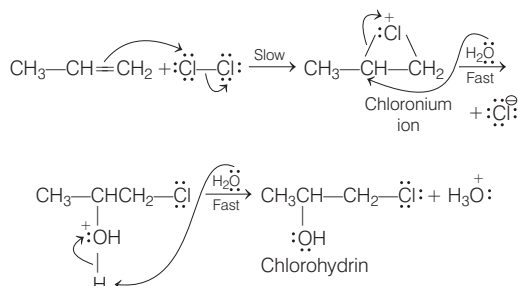


3. The major product of the given addition reaction is
- $$\text{H}_3\text{C}-\underset{\text{OH}}{\text{CH}}-\underset{\text{Cl}}{\text{CH}_2}$$

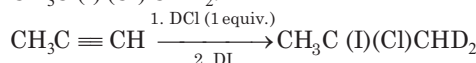
In this reaction,  $\text{H}_2\text{O}$  is used as a solvent and the major product of the reaction will be a *vicinal* halohydrin. A halohydrin is an organic molecule that contains both OH group and a halogen. In a *vicinal* halohydrin, the OH and halogen are bonded to adjacent carbons.



The reaction proceeds through following mechanism :

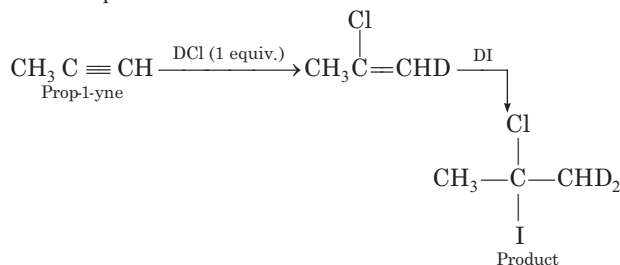


4. The major product obtained in the given reaction is  $\text{CH}_3\text{C}(\text{I})(\text{Cl})\text{CHD}_2$ .



Addition in unsymmetrical alkynes takes place according to Markovnikov's rule.

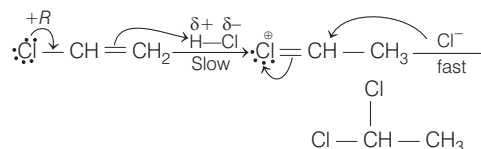
Reaction proceed as follows :



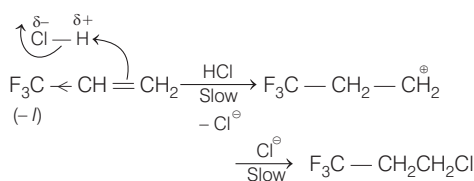
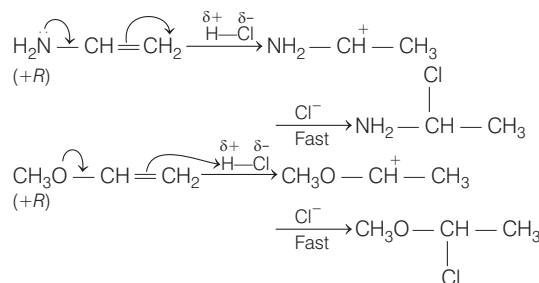
5. Attachment of electron donating group (+R or +I) with  $sp^2$ -carbon of an unsymmetrical alkene supports Markownikov's addition rule through electrophilic-addition-pathway.

But, attachment of electron-withdrawing group (−R or −I) for the same will follow anti-Markownikov's pathway (even in absence of organic peroxide which favours free radical addition) through electrophilic addition pathway.

The product formed by given alkenes when treated with HCl.

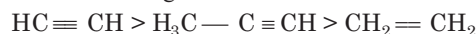


Similarly,



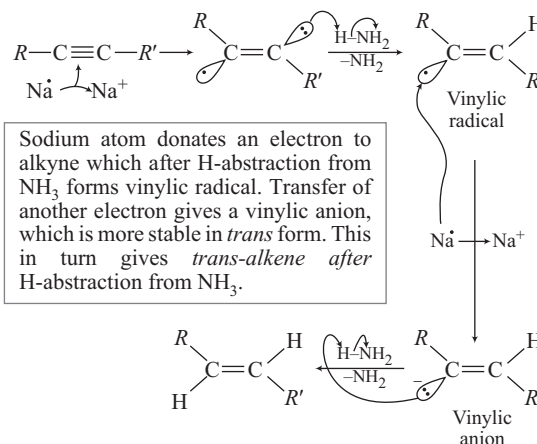
6. Ethene ( $\text{H}_2\text{C}=\text{CH}_2$ ) is  $sp^2$ -hybridised and ethyne ( $\text{HC}\equiv\text{CH}$ ) is  $sp$ -hybridised. In ethyne, the  $sp$ -hybridised carbon atom possesses maximum s-character and hence, maximum electronegativity. Due to which, it attracts the shared electron pair of C—H bond to a greater extent and makes the removal of proton easier. Hence, alkyne is much more acidic than alkene.

Presence of electron donating group in alkyne ( $\text{H}_3\text{C}-\text{C}\equiv\text{CH}$ ) decreases the acidic strength of compound. Hence, the correct order of acidic strength is:

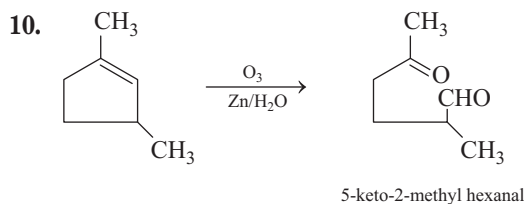
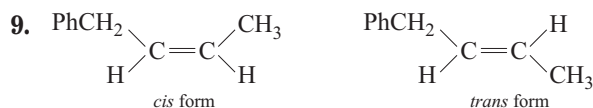
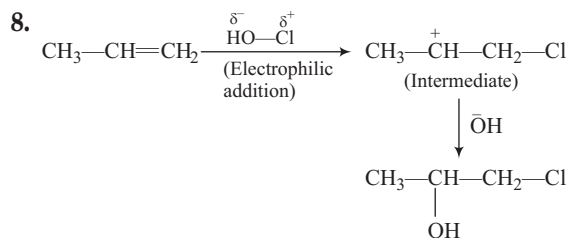


7. Sodium metal in liquid ammonia reduces alkynes with anti stereochemistry to give *trans* alkenes. The reduction is selectively *anti* since the vinyl radical formed during reduction is more stable in *trans* configuration.

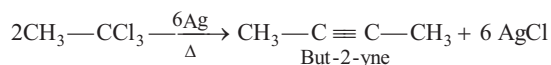
#### Mechanism



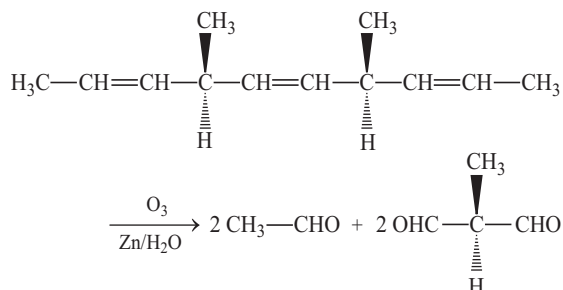
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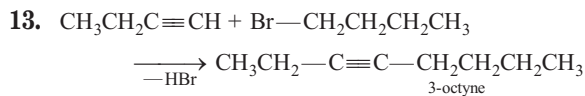
11. The reaction is



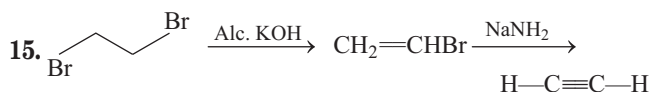
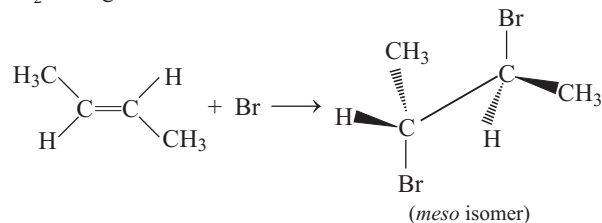
12. Ozonolysis of the given triene occur as follows :



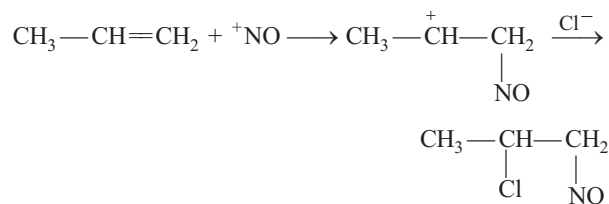
Since, none of the above dial is chiral, no optically active product is obtained.



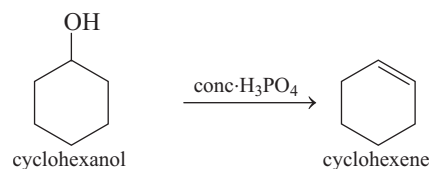
14. Br<sub>2</sub> undergo anti-addition on C=C bonds as:



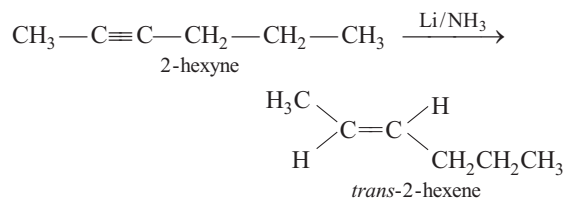
16. NOCl undergo electrophilic addition on alkene as:



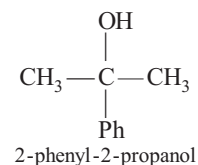
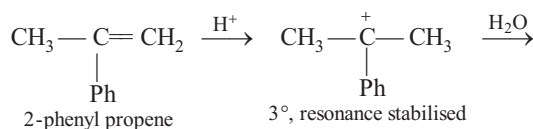
17. Cyclohexanol on treatment with concentrated H<sub>3</sub>PO<sub>4</sub> undergo acid catalysed dehydration giving cyclohexene.



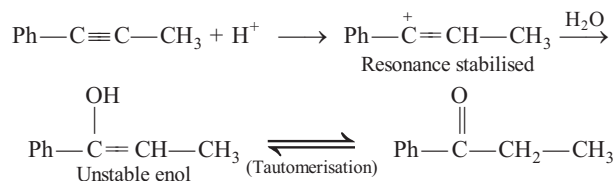
18. Alkynes on treatment with alkali metals in liquid ammonia gives *trans* hydrogenation product:



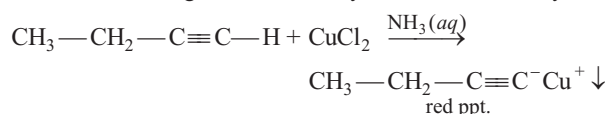
19. Reaction proceeds through carbocation intermediate:



20. Reaction proceeds through carbocation intermediate :



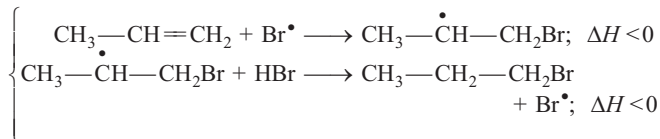
21. Ammoniacal CuCl<sub>2</sub> forms red precipitate with terminal alkynes, can be used to distinguish terminal alkynes from internal alkynes:



22. In addition of HBr to an alkene, in the presence of peroxide, both the propagation steps are exothermic :

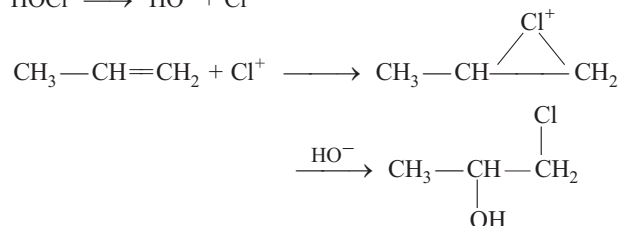


Propagation



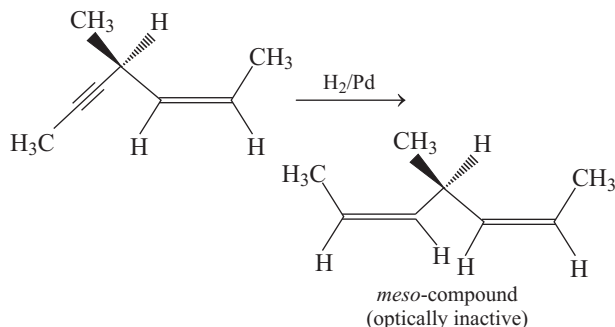
In case of addition of HCl and HI, one of the propagation step is endothermic, reaction fail to occur.

23.  $\text{HOCl} \longrightarrow \text{HO}^- + \text{Cl}^+$

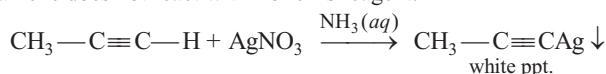


i.e. reaction is initiated by  $\text{Cl}^+$  (chloronium ion electrophile)

24. Hydrogenation with poisoned palladium brings about *cis* hydrogenation of alkyne and does not affect double bonds :



25. Terminal alkynes forms silver salt with Tollen's reagent while alkene does not react with Tollen's reagent.

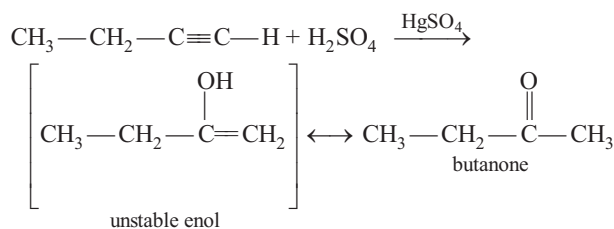


Therefore, Tollen's reagent can be used to distinguish a terminal alkyne like propyne from alkene as well as from internal alkynes.

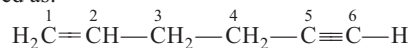
26. Ease of catalytic hydrogenation depends upon the size of groups present at the doubly bonded carbon. Larger the size of groups, difficult the hydrogenation. Therefore, in the given situation, disubstituted reacts at faster rate than tri and tetra substituted alkenes. Among disubstituted, the stability order is :

*cis* < *geminal* < *trans*.

27. Oxymercuration-demercuration brings about Markownikoff's addition of water as :

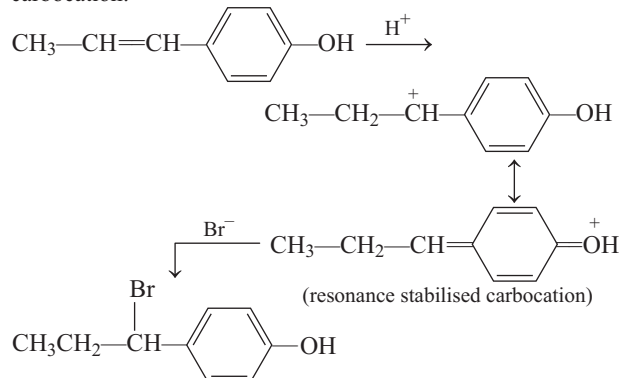


28. According to the IUPAC conventions, compound can be numbered as:



Here, C-2 is  $sp^2$  and C-3 is  $sp^3$ -hybridised.

29. Electrophilic addition on  $\text{C}=\text{C}$  is governed by stability of carbocation:



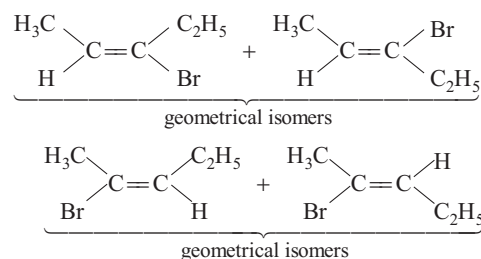
30. Among alkenes-heat of hydrogenation depends on :

- (a) The number of double bonds-greater, greater the amount of heat evolved in hydrogenation.

Hence, 1, 3-butadiene has highest heat of hydrogenation among these.

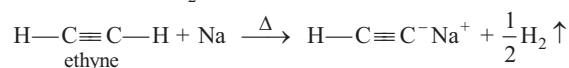
- (b) Relative stability of alkenes-greater the stability, smaller the heat evolved in hydrogenation. *trans*-2-butene is most stable among three given butenes, has least heat of hydrogenation.

31.  $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_2\text{CH}_3 + \text{HBr} \longrightarrow$



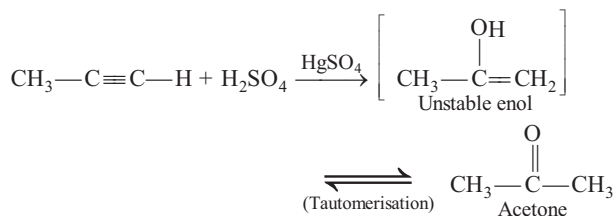
Therefore, two structural and four configurational isomers.

32. Terminal alkynes are slightly acidic, forms salt with very strong base like Na,  $\text{NaNH}_2$  etc.



33. Baeyer's reagent is cold, dilute, alkaline permanganate solution, used to detect presence of olefinic bonds.

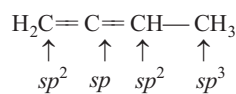
34. Alkynes undergo Markownikoff's addition of water in the presence of  $\text{H}_2\text{SO}_4 / \text{HgSO}_4$  :



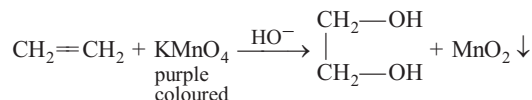


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35. Structural formula of 1, 2-butadiene is :

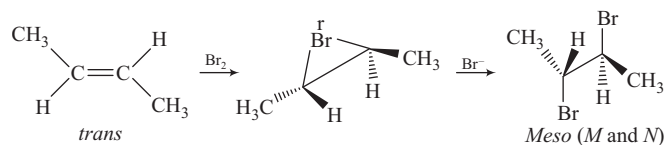


36. Unsaturated compounds which contain  $\text{C}=\text{C}$  or  $\text{C}\equiv\text{C}$ , decolourises the purple colour of alkaline  $\text{KMnO}_4$  solution.

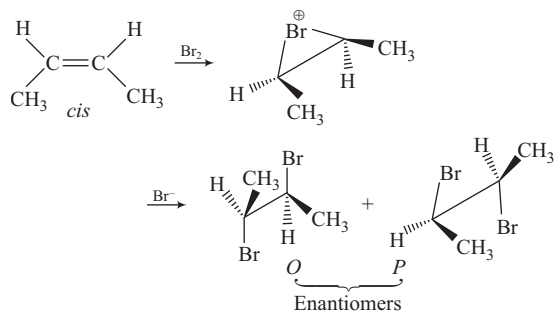


37. Addition of halogen at double bond occur in antiorientation via cyclic halonium ion intermediate.

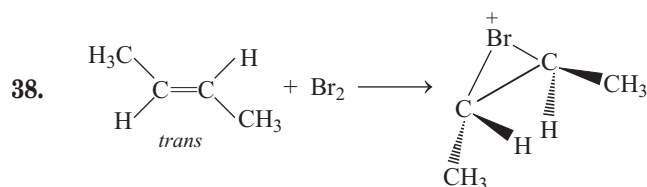
(i)



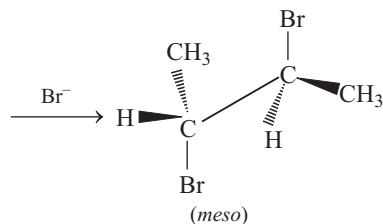
(ii)



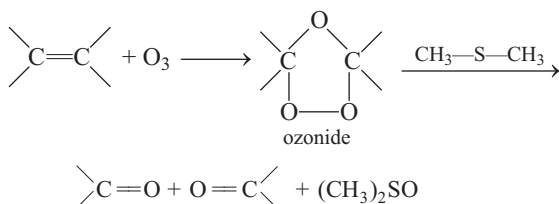
Here,  $(M + O)$  and  $(N + P)$  are pair of diastereomers.



Statement I is correct. Statement II is also correct. *Meso* form of the product is due to *anti* addition of  $\text{Br}^-$  on cyclic bromonium ion intermediate, hence Statement II is not correct explanation of Statement I.

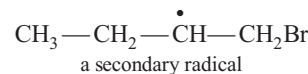


- 39.



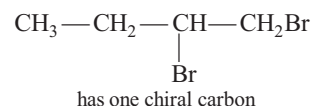
Both Statement I and Statement II are correct and Statement II is correct explanation of Statement I.

40.  $\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2 + \text{Br}^\bullet \longrightarrow$



Therefore, Statement I is correct but Statement II is incorrect.

41.  $\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2 + \text{Br}_2 \longrightarrow$

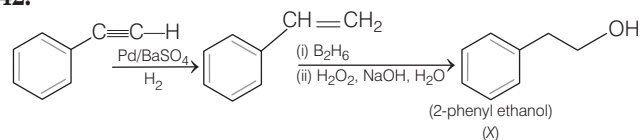


Both Statement I and Statement II are correct and Statement II is correct explanation of Statement I.

### Passage 1

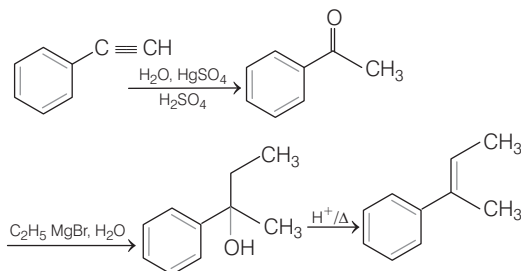
The reaction condition indicates that starting compound is phenyl acetylene.

- 42.



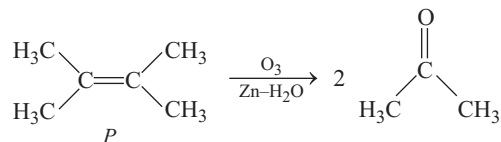
Hydroboration oxidation brings about anti-Markonikoff's hydration of alkene.

- 43.

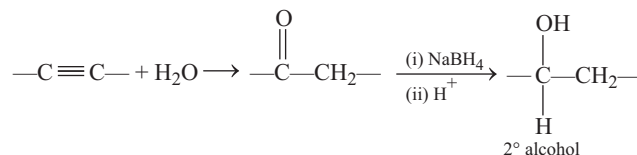


### Passage 2

The final ozonolysis product indicates that the alkene before ozonolysis is

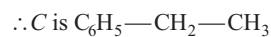
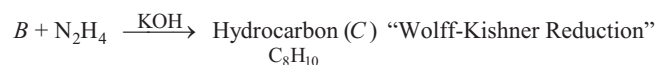
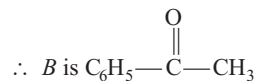
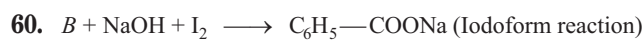
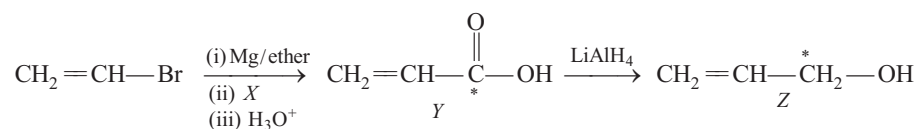
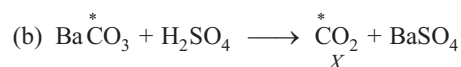
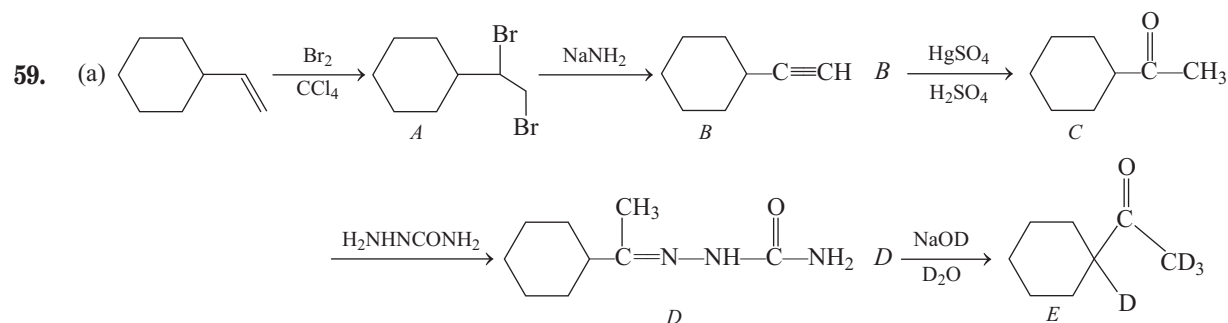
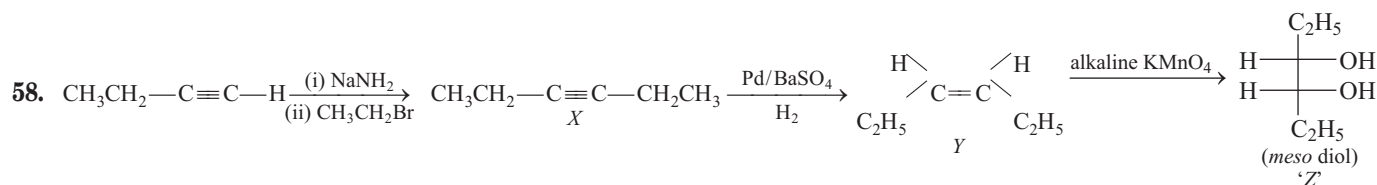


Also  $P(\text{C}_6\text{H}_{10})$  has two degree of unsaturation and oxymercuration demercuration hydration indicates that it is an alkyne. As alkyne, on hydration, gives a carbonyl compound which on reduction with  $\text{NaBH}_4$  gives a  $2^\circ$  alcohol.

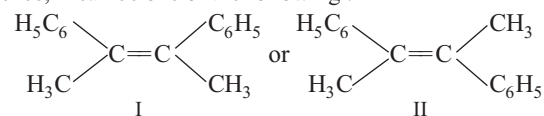




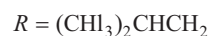
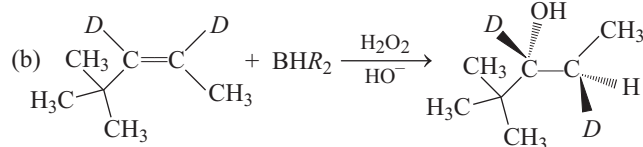
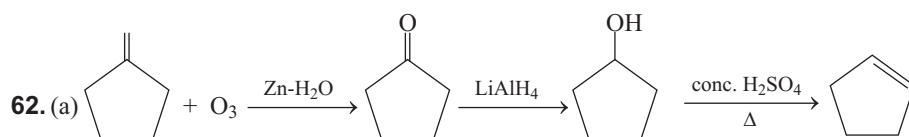
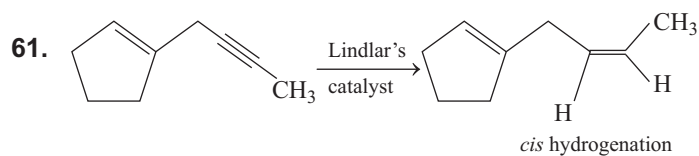
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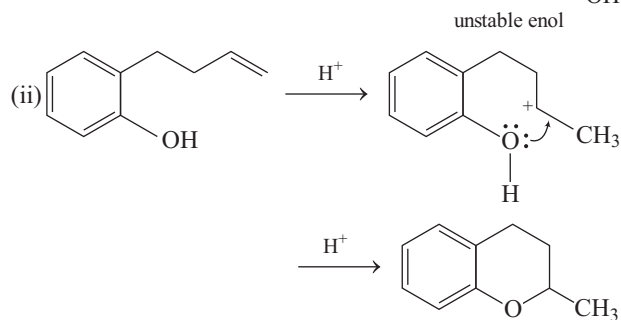
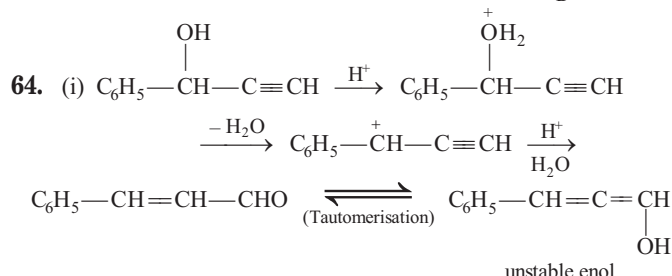
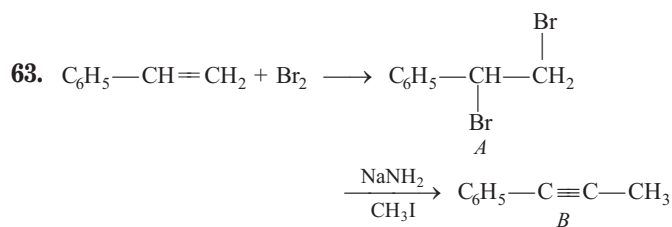


Hence,  $A$  can be one of the following :

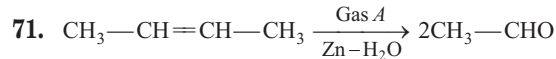
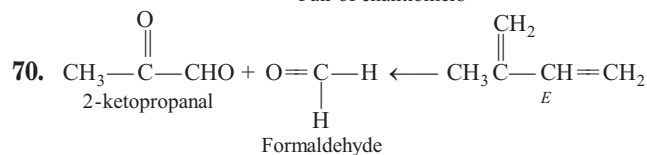
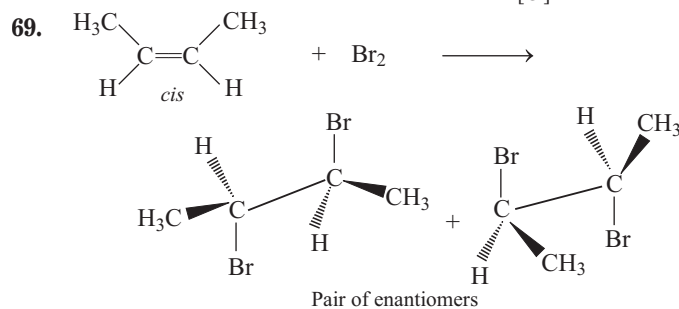
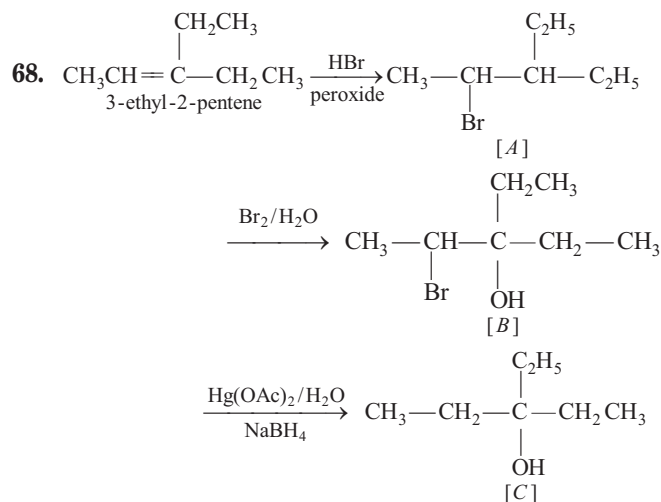
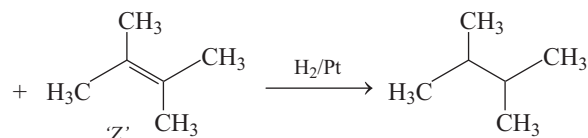
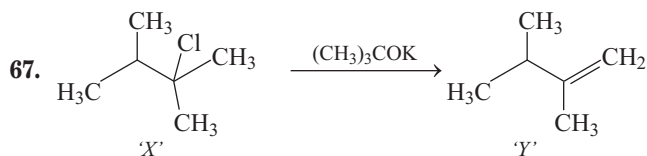
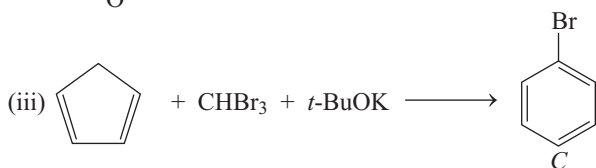
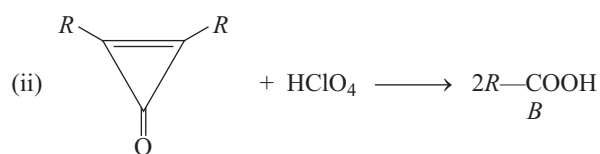
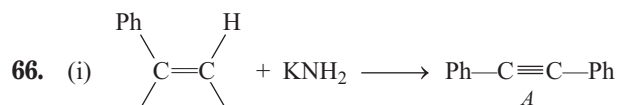
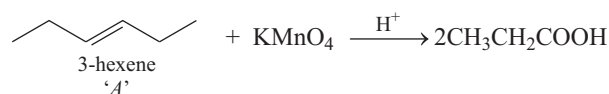


I on catalytic hydrogenation, would give *meso* compound while II on catalytic hydrogenation, would produce racemic mixtures.



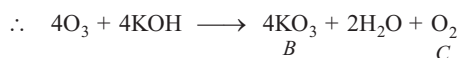


65. Oxidation product indicates that alkene is symmetrical :

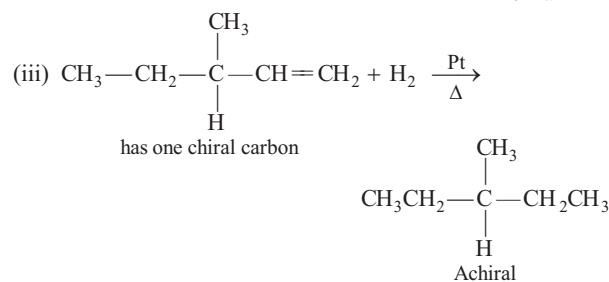
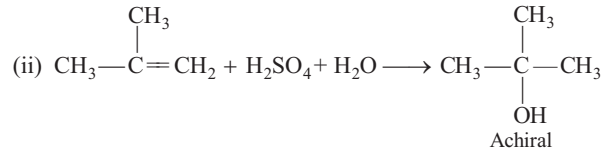
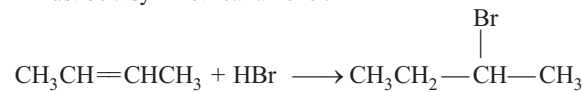


$\therefore$  Gas A is ozone ( $\text{O}_3$ )

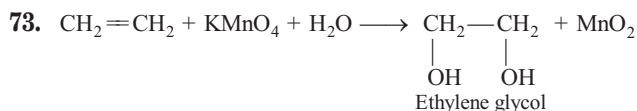
Also; Gas A + KOH (dry)  $\longrightarrow$  B + Gas C  
 deep red coloured



72. (i) A must be a symmetrical alkene :

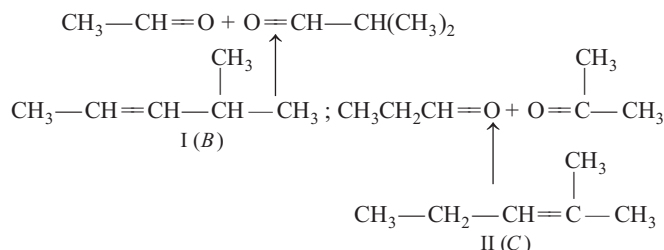


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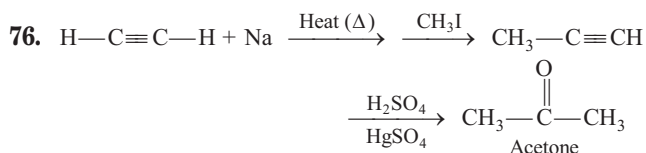
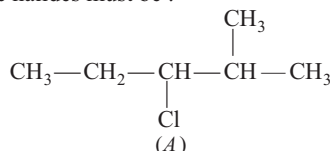


74. Baeyer's reagent (cold, dilute, alkaline permanganate) can be used to distinguish between alkanes and alkenes. Alkenes decolourise purple colour of Baeyer's reagent while alkanes do not.

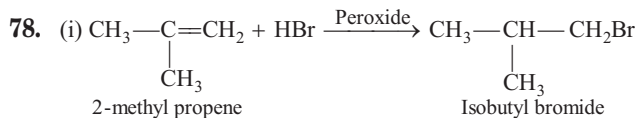
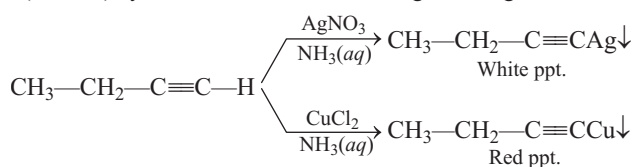
75. The alkenes are :



Since, both alkenes I and II are obtained by  $\beta$ -elimination of same halides, the halides must be :

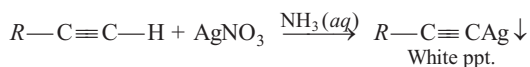


77. 1-butyne (terminal) can be distinguished from 2-butyne (internal) by either Tollen's test or through Fehling's test.



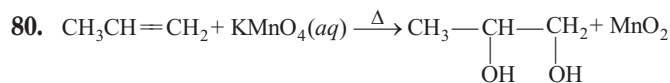
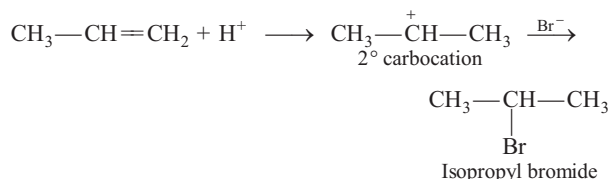
In the absence of peroxide, HBr would be added giving tertiary butyl bromide.

(ii) Tertiary alkynes are slightly acidic, forms silver salt with ammoniacal solution of silver nitrate :

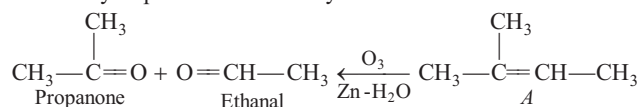


79. (i) Free radical chlorination of alkane require energy which is supplied either in the form of heat or radiation.

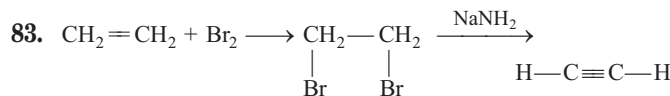
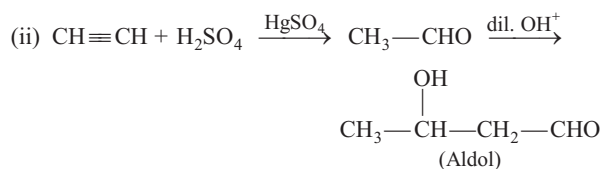
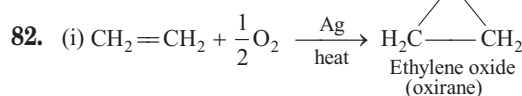
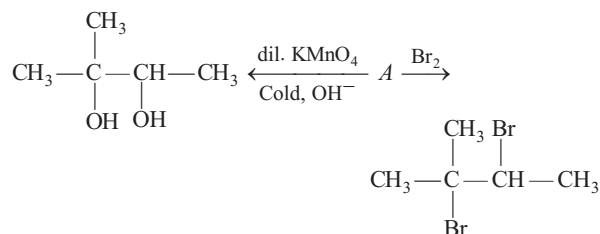
(ii) Addition of HBr proceeds through carbocation intermediates.



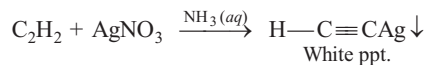
81. Ozonolysis products are the key of identification :



Other products are:



84. Acetylene can be distinguished from methane using Tollen's reagent :



No such reaction occur with methane.

Download Chapter Test  
<http://tinyurl.com/yyjzocvw>

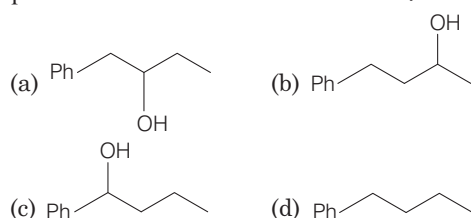
or



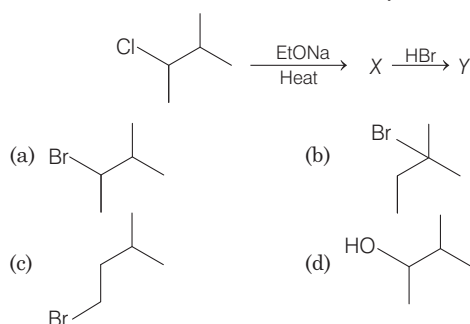
# 23

## Alkyl Halides

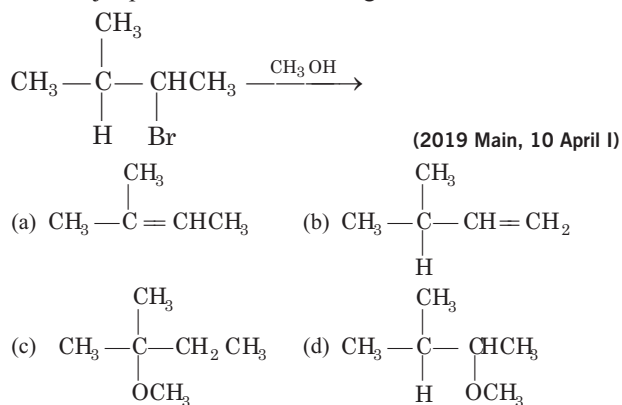
1. Heating of 2-chloro-1-phenyl butane with EtOK/EtOH gives  $X$  as the major product. Reaction of  $X$  with  $\text{Hg}(\text{OAc})_2 / \text{H}_2\text{O}$  followed by  $\text{NaBH}_4$  gives  $Y$  as the major product.  $Y$  is (2019 Main, 12 April II)



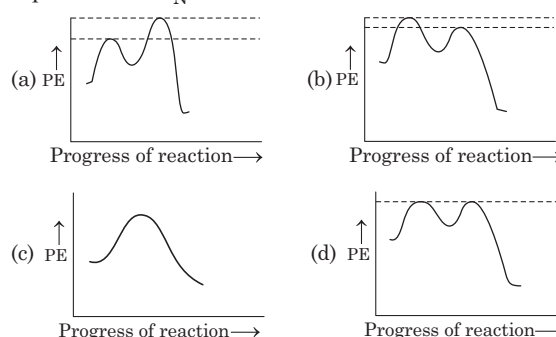
2. Which one of the following is likely to give a precipitate with  $\text{AgNO}_3$  solution? (2019 Main, 12 April II)
- (a)  $\text{CH}_2=\text{CH}-\text{Cl}$  (b)  $\text{CCl}_4$   
(c)  $\text{CHCl}_3$  (d)  $(\text{CH}_3)_3\text{CCl}$
3. The major product  $Y$  in the following reaction is (2019 Main, 10 April II)



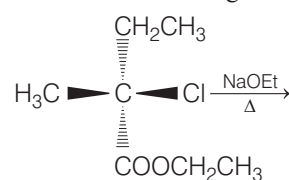
4. The major product of the following reaction is



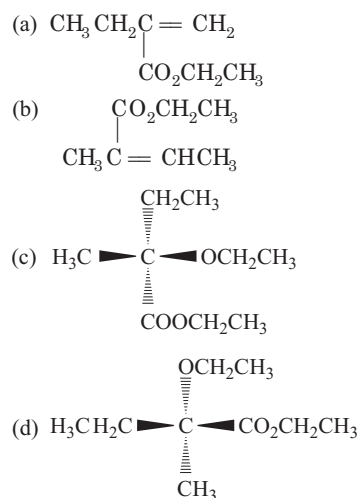
5. Which of the following potential energy (PE) diagrams represents the  $\text{S}_{\text{N}}1$  reaction? (2019 Main, 9 April II)



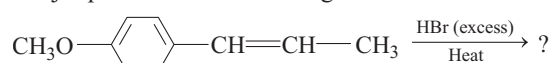
6. The major product of the following reaction is



(2019 Main, 12 Jan II)

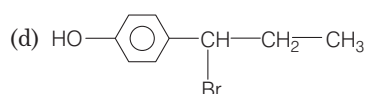
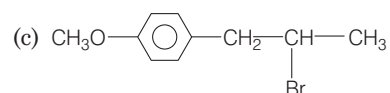
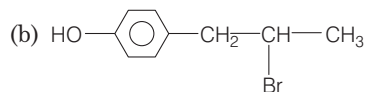
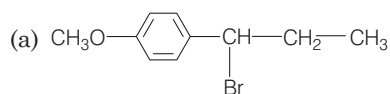


7. The major product in the following conversion is

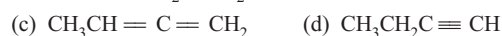
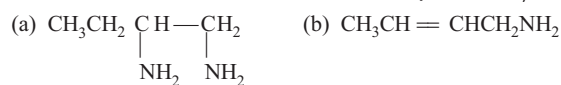
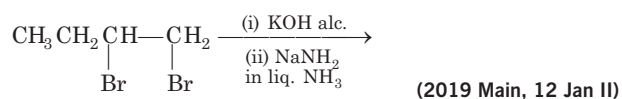


(2019 Main, 12 Jan II)

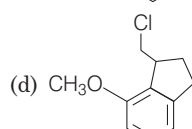
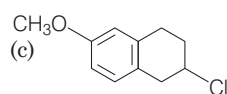
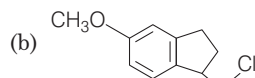
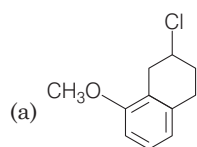
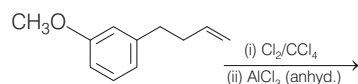
## 328 Alkyl Halides



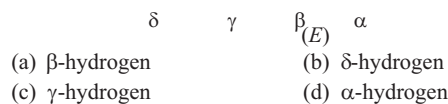
8. The major product of the following reaction is



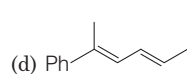
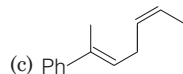
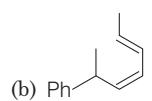
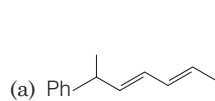
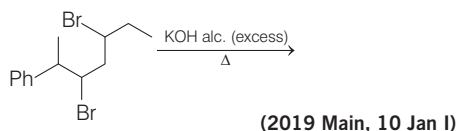
9. The major product of the following reaction is  
(2019 Main, 12 Jan I)



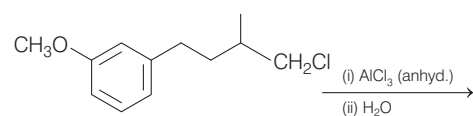
10. Which hydrogen in compound (E) is easily replaceable during bromination reaction in presence of light?



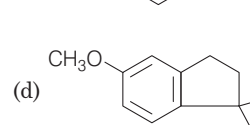
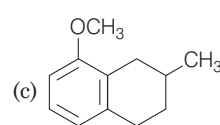
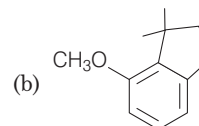
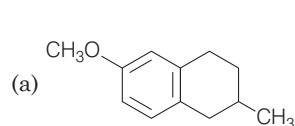
11. The major product of the following reaction is



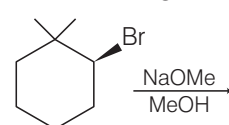
12. The major product of the following reaction is



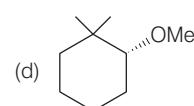
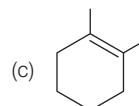
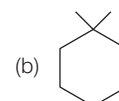
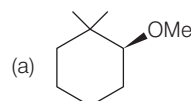
(2019 Main, 10 Jan I)



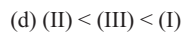
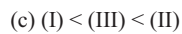
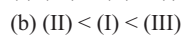
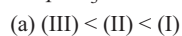
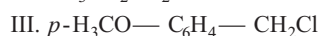
13. The major product of the following reaction is



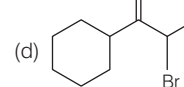
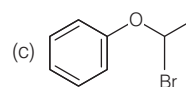
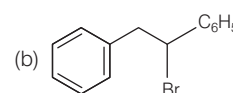
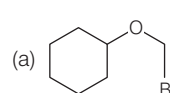
(2018 Main)



14. The increasing order of reactivity of the following halides for the  $\text{S}_\text{N}1$  reaction is  
(2017 Main)



15. Which of the following, upon treatment with *tert*-BuONa followed by addition of bromine water, fails to decolourise the colour of bromine ?  
(2017 Main)

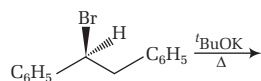


16. 3-methyl-pent-2-ene on reaction with HBr in presence of peroxide forms an addition product. The number of possible stereoisomers for the product is  
(2017 Main)



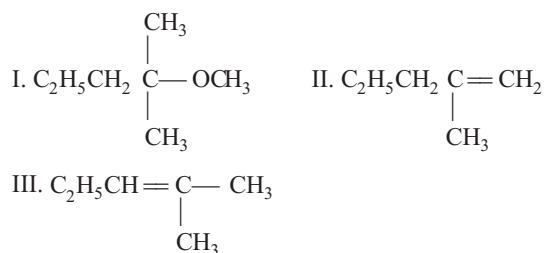


17. The major product obtained in the following reaction is

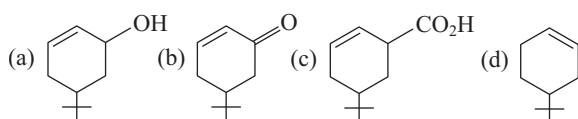
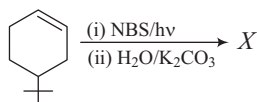


(2017 Main)

- (a)  $(\pm)$   $\text{C}_6\text{H}_5\text{CH}(\text{O}^t\text{Bu})\text{CH}_2\text{C}_6\text{H}_5$   
 (b)  $\text{C}_6\text{H}_5\text{CH}=\text{CHC}_6\text{H}_5$   
 (c)  $(+)$   $\text{C}_6\text{H}_5\text{CH}(\text{O}^t\text{Bu})\text{CH}_2\text{C}_6\text{H}_5$   
 (d)  $(-)$   $\text{C}_6\text{H}_5\text{CH}(\text{O}^t\text{Bu})\text{CH}_2\text{C}_6\text{H}_5$
18. 2-chloro-2-methylpentane on reaction with sodium methoxide in methanol yields (2016 Main)



- (a) Both I and III (b) Only III  
 (c) Both I and II (d) All of these
19. The product of the reaction given below is (2015 Adv.)



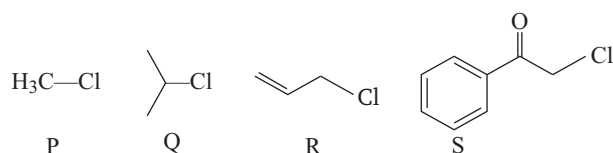
20. The synthesis of alkyl fluorides is best accomplished by (2015 Main)

- (a) free radical fluorination (b) Sandmeyer's reaction  
 (c) Finkelstein reaction (d) Swarts reaction

21. In  $\text{S}_{\text{N}}2$  reactions, the correct order of reactivity for the following compounds  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{CH}_2\text{Cl}$ ,  $(\text{CH}_3)_2\text{CHCl}$  and  $(\text{CH}_3)_3\text{CCl}$  is (2014 Main)

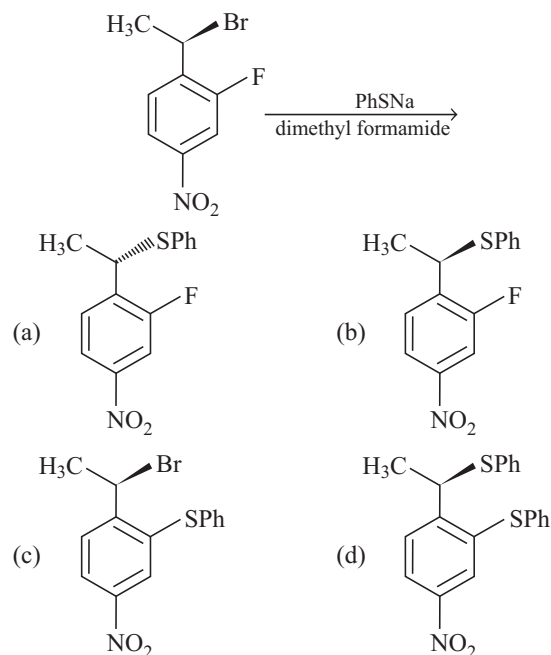
- (a)  $\text{CH}_3\text{Cl} > (\text{CH}_3)_2\text{CHCl} > \text{CH}_3\text{CH}_2\text{Cl} > (\text{CH}_3)_3\text{CCl}$   
 (b)  $\text{CH}_3\text{Cl} > \text{CH}_3\text{CH}_2\text{Cl} > (\text{CH}_3)_2\text{CHCl} > (\text{CH}_3)_3\text{CCl}$   
 (c)  $\text{CH}_3\text{CH}_2\text{Cl} > \text{CH}_3\text{Cl} > (\text{CH}_3)_2\text{CHCl} > (\text{CH}_3)_3\text{CCl}$   
 (d)  $(\text{CH}_3)_2\text{CHCl} > \text{CH}_3\text{CH}_2\text{Cl} > \text{CH}_3\text{Cl} > (\text{CH}_3)_3\text{CCl}$

22. KI in acetone, undergoes  $\text{S}_{\text{N}}2$  reaction with each P, Q, R and S. The rates of the reaction vary as (2013 Adv.)

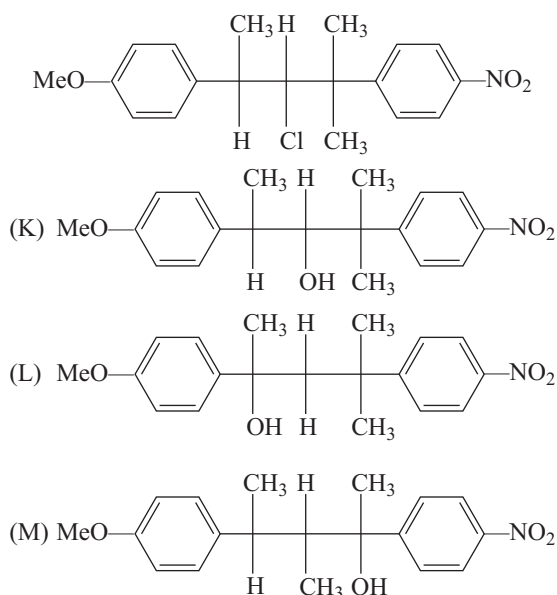


- (a)  $P > Q > R > S$  (b)  $S > P > R > Q$   
 (c)  $P > R > Q > S$  (d)  $R > P > S > Q$

23. The major product of the following reaction is (2008, 3M)



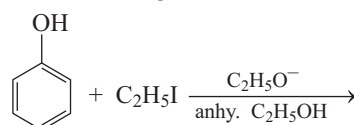
24. The following compound on hydrolysis in aqueous acetone will give (2005, 1M)



It mainly gives

- (a) K and L (b) only K  
 (c) L and M (d) only M

25. The product of following reaction is

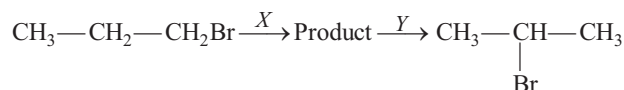


(2003, 1M)

- (a)  $\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$  (b)  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$   
 (c)  $\text{C}_6\text{H}_5\text{OC}_6\text{H}_5$  (d)  $\text{C}_6\text{H}_5\text{I}$

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26. Identify the set of reagents/reaction conditions  $X$  and  $Y$  in the following set of transformations— (2002, 3M)



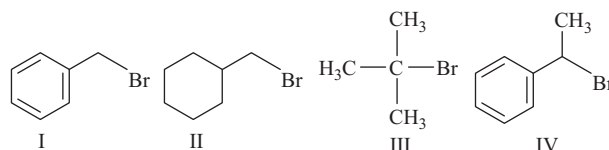
- (a)  $X$  = dilute aqueous NaOH,  $20^\circ\text{C}$ ,  $Y$  = HBr/acetic acid,  $20^\circ\text{C}$   
 (b)  $X$  = concentrated alcoholic NaOH,  $80^\circ\text{C}$ ,  $Y$  = HBr/acetic acid,  $20^\circ\text{C}$   
 (c)  $X$  = dilute aqueous NaOH,  $20^\circ\text{C}$ ,  $Y$  =  $\text{Br}_2/\text{CHCl}_3$ ,  $0^\circ\text{C}$   
 (d)  $X$  = concentrated aqueous NaOH,  $80^\circ\text{C}$ ,  $Y$  =  $\text{Br}_2/\text{CHCl}_3$ ,  $0^\circ\text{C}$
27. The compound that will react most readily with NaOH to form methanol is (2001, 1M)
- (a)  $(\text{CH}_3)_4\text{N}^+\text{I}^-$  (b)  $\text{CH}_3\text{OCH}_3$   
 (c)  $(\text{CH}_3)_3\text{S}^+\text{I}^-$  (d)  $(\text{CH}_3)_3\text{Cl}$
28. An  $\text{S}_\text{N}2$  reaction at an asymmetric carbon of a compound always gives (2001)
- (a) an enantiomer of the substrate  
 (b) a product with opposite optical rotation  
 (c) a mixture of diastereomers  
 (d) a single stereoisomer
29. The order of reactivities of the following alkyl halides for a  $\text{S}_\text{N}2$  reaction is— (2000, 1M)
- (a)  $\text{RF} > \text{RCl} > \text{RBr} > \text{RI}$  (b)  $\text{RF} > \text{RBr} > \text{RCl} > \text{RI}$   
 (c)  $\text{RCl} > \text{RBr} > \text{RF} > \text{RI}$  (d)  $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$
30. Which of the following has the highest nucleophilicity? (2000)
- (a)  $\text{F}^-$  (b)  $\text{OH}^-$  (c)  $\text{CH}_3^-$  (d)  $\text{NH}_2^-$
31. A solution of (+)-2-chloro-2-phenylethane in toluene racemises slowly in the presence of small amount of  $\text{SbCl}_5$ , due to the formation of (1999)
- (a) carbanion (b) carbene  
 (c) free-radical (d) carbocation
32. Which of the following is an organometallic compound?
- (a) Lithium methoxide (b) Lithium acetate (1997)  
 (c) Lithium dimethylamide (d) Methyl lithium
33.  $(\text{CH}_3)_3\text{CMgCl}$  on treatment with  $\text{D}_2\text{O}$  produces (1997, 1M)
- (a)  $(\text{CH}_3)_3\text{CD}$  (b)  $(\text{CH}_3)_3\text{COD}$  (c)  $(\text{CD})_3\text{CD}$  (d)  $(\text{CD})_3\text{COD}$
34. 1-chlorobutane on reaction with alcoholic potash gives (1991, 1M)
- (a) 1-butene (b) 1-butanol  
 (c) 2-butene (d) 2-butanol
35.  $n$ -propyl bromide on treatment with ethanolic potassium hydroxide produces (1987, 1M)
- (a) propane (b) propene (c) propyne (d) propanol
36. The reaction condition leading to the best yield of  $\text{C}_2\text{H}_5\text{Cl}$  are— (1986, 1M)

- (a)  $\text{C}_2\text{H}_6(\text{excess}) + \text{Cl}_2 \xrightarrow{\text{UV light}}$   
 (b)  $\text{C}_2\text{H}_6 + \text{Cl}_2(\text{excess}) \xrightarrow[\text{room temp.}]{\text{dark}}$   
 (c)  $\text{C}_2\text{H}_6 + \text{Cl}_2(\text{excess}) \xrightarrow{\text{UV light}}$   
 (d)  $\text{C}_2\text{H}_6 + \text{Cl}_2 \xrightarrow{\text{UV light}}$

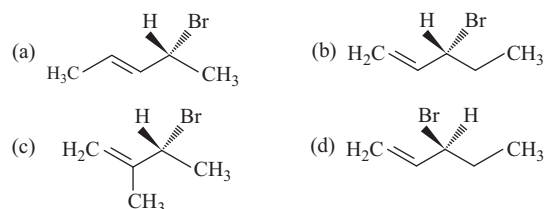
## Objective Questions II

(One or more than one correct option)

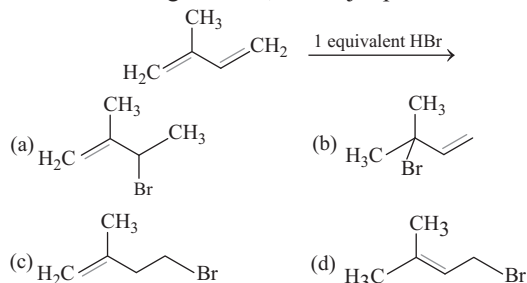
37. For the following compounds, the correct statement(s) with respect to nucleophilic substitution reaction is(are) (2017 Adv.)



- (a) Compound IV undergoes inversion of configuration  
 (b) The order of reactivity for I, III and IV is :  $\text{IV} > \text{I} > \text{III}$   
 (c) I and III follow  $\text{S}_\text{N}1$  mechanism  
 (d) I and II follow  $\text{S}_\text{N}1$  mechanism
38. Compound(s) that on hydrogenation produce(s) optically inactive compound (s) is/are (2015 Adv.)



39. In the following reaction, the major product is (2015 Adv.)



40. The compounds used as refrigerant are (1990, 1M)
- (a)  $\text{NH}_3$  (b)  $\text{CCl}_4$  (c)  $\text{CF}_4$  (d)  $\text{CF}_2\text{Cl}_2$   
 (e)  $\text{CH}_2\text{F}_2$

## Assertion and Reason

41. An **Assertion** and a **Reason** are given below. Choose the correct answer from the following options.

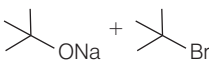
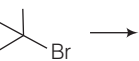
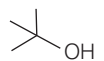
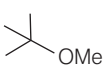
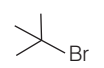
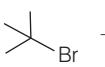
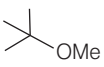
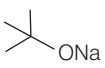
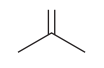
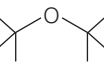
**Assertion** (A) Vinyl halides do not undergo nucleophilic substitution easily.

**Reason** (R) Even though the intermediate carbocation is stabilised by loosely held  $\pi$ -electrons, the cleavage is difficult because of strong bonding. (2019 Main, 12 April II)

- (a) Both (A) and (R) are wrong statements.  
 (b) Both (A) and (R) are correct statements and (R) is correct explanation of (A).  
 (c) Both (A) and (R) are correct statements but (R) is not the correct explanation of (A).  
 (d) (A) is a correct statement but (R) is a wrong statement.

## Match the Columns

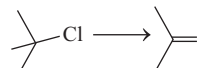
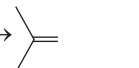
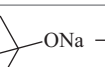

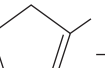
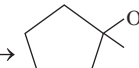
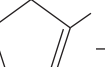

42. List-I contains reactions and List-II contains major products.

| List-I                                                                                                                                                                     | List-II                                                                              |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|
| P.  +  → | 1.  |
| Q.  + HBr →                                                                               | 2.  |
| R.  + NaOMe →                                                                             | 3.  |
| S.  + MeBr →                                                                              | 4.  |
|                                                                                                                                                                            | 5.  |

Match each reaction in List-I with one or more products in List-II and choose the correct option. (2018 Adv.)

- (a) P → 1, 5; Q → 2; R → 3; S → 4  
 (b) P → 1, 4; Q → 2; R → 4; S → 3  
 (c) P → 1, 4; Q → 1, 2; R → 3, 4; S → 4  
 (d) P → 4, 5; Q → 4; R → 4; S → 3, 4

43. Match the chemical conversion in Column I with the appropriate reagents in Column II and select the correct answer using the code given below the lists. (2013 Adv.)

| Column I                                                                                                                                                                     | Column II                                                             |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------|
| P.  →  | 1. (i) Hg(OAc) <sub>2</sub> ;<br>(ii) NaBH <sub>4</sub>               |
| Q.  →  | 2. NaOEt                                                              |
| R.  →  | 3. Et-Br                                                              |
| S.  →  | 4. (i) BH <sub>3</sub> ;<br>(ii) H <sub>2</sub> O <sub>2</sub> / NaOH |

## Codes

|     | P | Q | R | S |
|-----|---|---|---|---|
| (a) | 2 | 3 | 1 | 4 |
| (b) | 3 | 2 | 1 | 4 |
| (c) | 2 | 3 | 4 | 1 |
| (d) | 3 | 2 | 4 | 1 |

44. Match the following : (2006, 3M)

| Column I                                                                                                                                                                                      | Column II               |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------|
| A. CH <sub>3</sub> —CHBr—CD <sub>3</sub> on treatment with alc. KOH gives CH <sub>2</sub> =CH—CD <sub>3</sub> as a major product.                                                             | p. E1 reaction          |
| B. Ph—CHBr—CH <sub>3</sub> reacts faster than Ph—CHBr—CD <sub>3</sub>                                                                                                                         | q. E2 reaction          |
| C. Ph—CH <sub>2</sub> —CH <sub>2</sub> Br on treatment with C <sub>2</sub> H <sub>5</sub> OD / C <sub>2</sub> H <sub>5</sub> O <sup>−</sup> gives Ph—CD=CH <sub>2</sub> as the major product. | r. E1CB reaction        |
| D. PhCH <sub>2</sub> CH <sub>2</sub> Br and PhCD <sub>2</sub> CH <sub>2</sub> Br react with same rate.                                                                                        | s. First order reaction |

## Fill in the Blanks

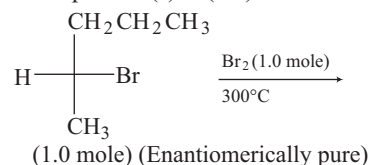
45. Vinyl chloride on reaction with the dimethyl copper gives ..... (1997)  
 46. The starting material for the manufacture of polyvinyl chloride is obtained by reacting HCl with ..... (1983, 1M)  
 47. The halogen which is most reactive in the halogenation of alkanes under sunlight is ... (1981, 1M)

## True/False

48. Photobromination of 2-methylpropane gives a mixture of 1-bromo-2-methyl propane and 2-bromo-2-methyl propane in the ratio 9 : 1. (1993, 1M)  
 49. During S<sub>N</sub>1 reactions, the leaving group leaves the molecule before the incoming group is attached to the molecule. (1990, 2M)  
 50. The reaction of vinyl chloride with hydrogen iodide to give 1-chloro-1-iodoethane is an example of anti-Markownikoff's rule. (1989, 2M)  
 51. Iodide is better nucleophile than bromide. (1985)  
 52. Carbon tetrachloride is inflammable. (1985, 1/2M)  
 53. Carbon tetrachloride burns in air when lighted to give phosgene. (1983, 1M)

## Integer Answer Type Question

54. In the following monobromination reaction, the number of possible chiral product(s) is (are)...

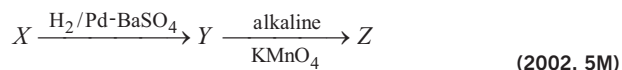
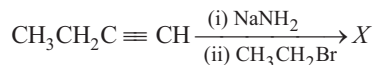


55. The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH is (2011)

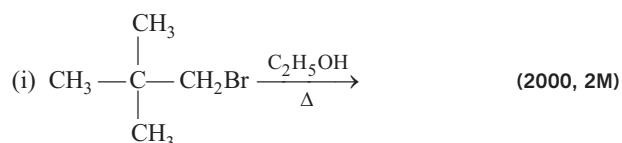
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### Subjective Questions

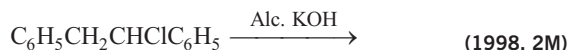
56. Identify *X*, *Y* and *Z* in the following synthetic scheme and write their structures



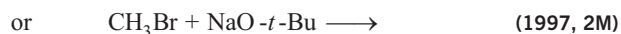
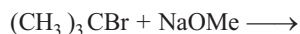
57. What would be the major product in each of the following reactions?



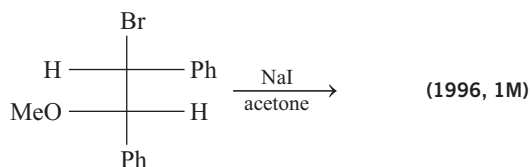
58. Write the structures of the products :



59. Which of the following is the correct method for synthesising methyl-*t*-butyl ether and why?

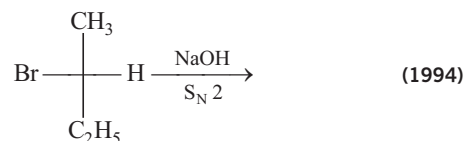


60. Predict the structure of the product in the following reaction



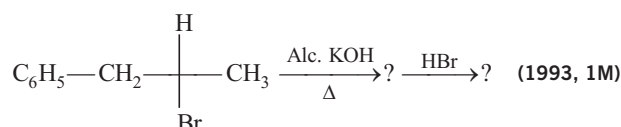
61. Optically active 2-iodobutane on treatment with NaI in acetone gives a product which does not show optical activity. Explain briefly. (1995, 2M)

62. Draw the stereochemical structure of product in the following reaction

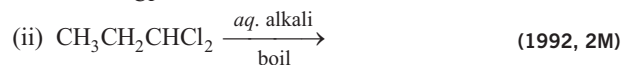
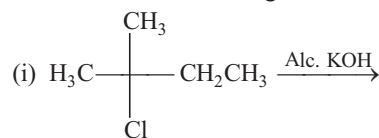


63. Aryl halides are less reactive than alkyl halides towards nucleophilic reagents. Give reason. (1994, 2M)

64. Identify the major product in the following reaction.



65. Write the structures of the major organic product expected from each of the following reactions :



66. Arrange the following in order of their

- (i) Increasing basicity



- (ii) Increasing reactivity in nucleophilic substitution reactions



67. Chloroform is stored in dark coloured bottles. Explain in not more than two sentences. (1980, 1M)

68. Show by chemical equations only, how would you prepare the following from the indicated starting materials? Specify the reagents in each step of the synthesis. (1979, 2M)

- (i) Chloroform from carbon disulphide.

- (ii) Hexachloroethane ( $\text{C}_2\text{Cl}_6$ ) from calcium carbide.

## Answers

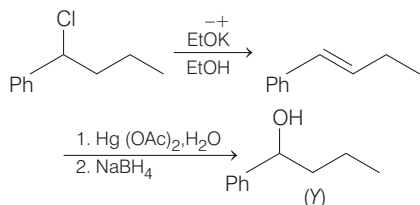
- |         |         |         |         |                                                                                                                                     |            |              |            |
|---------|---------|---------|---------|-------------------------------------------------------------------------------------------------------------------------------------|------------|--------------|------------|
| 1. (c)  | 2. (d)  | 3. (b)  | 4. (c)  | 33. (a)                                                                                                                             | 34. (a)    | 35. (b)      | 36. (a)    |
| 5. (b)  | 6. (b)  | 7. (d)  | 8. (d)  | 37. (a, d)                                                                                                                          | 38. (b, d) | 39. (d)      | 40. (a, d) |
| 9. (c)  | 10. (c) | 11. (d) | 12. (d) | 41. (c)                                                                                                                             | 42. (b)    | 43. (a)      |            |
| 13. (b) | 14. (b) | 15. (a) | 16. (d) | 44. $\text{A} \rightarrow \text{q}, \text{B} \rightarrow \text{q}, \text{C} \rightarrow \text{r}, \text{D} \rightarrow \text{p, s}$ |            |              |            |
| 17. (b) | 18. (d) | 19. (a) | 20. (d) | 45. propene                                                                                                                         | 46. ethyne | 47. chlorine | 48. False  |
| 21. (b) | 22. (b) | 23. (a) | 24. (a) | 49. True                                                                                                                            | 50. True   | 51. True     | 52. False  |
| 25. (a) | 26. (b) | 27. (a) | 28. (d) | 53. False                                                                                                                           | 54. (5)    | 55. (5)      |            |
| 29. (d) | 30. (c) | 31. (d) | 32. (d) |                                                                                                                                     |            |              |            |

# Hints & Solutions

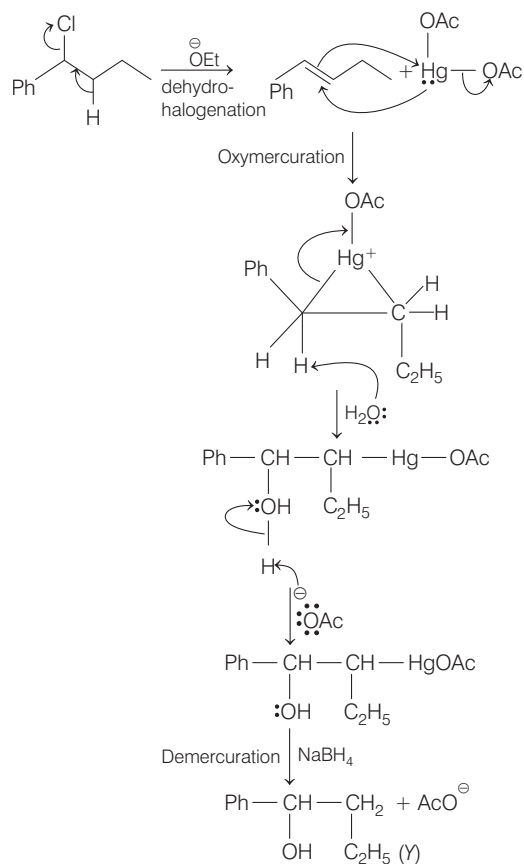
1. Heating of 2-chloro-1-phenylbutane with EtOK/EtOH gives 1-phenyl but-1-ene(X).

Reaction of X with  $\text{Hg}(\text{OAc})_2 / \text{H}_2\text{O}$  followed by  $\text{NaBH}_4$  gives 1-phenyl butan-1-ol (Y).

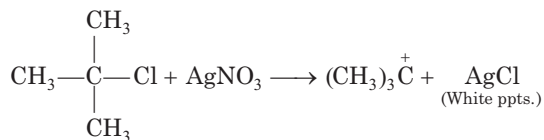
Reaction involved is as follows:



## Mechanism

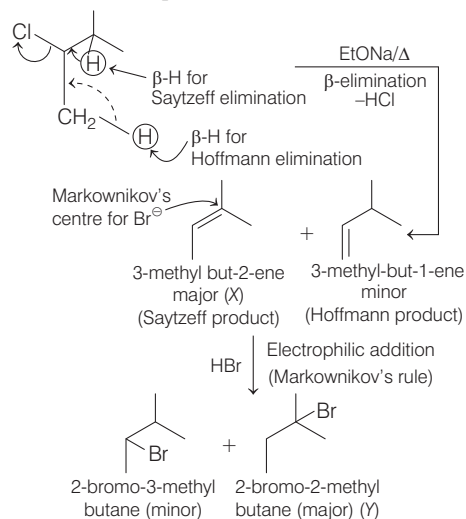


2.  $(\text{CH}_3)_3\text{CCl}$  gives a precipitate with  $\text{AgNO}_3$  solution because it forms stable carbocation. (i.e. tertiary) that readily combines with  $\text{AgNO}_3$  to give precipitates of  $\text{AgCl}$ .

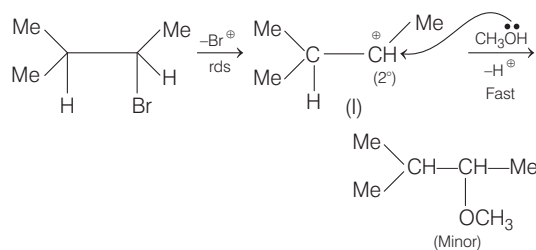


$\text{CH}_2=\text{CH}-\text{Cl}$  forms unstable carbocation. Hence, it does not readily react with  $\text{AgNO}_3$ .

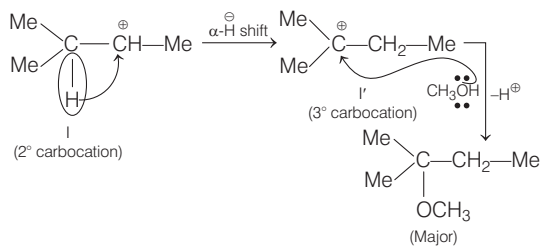
3. The given reaction takes place as follows :



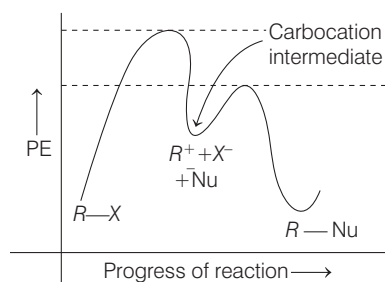
4. In the given question, the substrate is a 2°-halide (bromide) and the medium,  $\text{CH}_3\text{OH}$  (as well as a poor nucleophile) is protic in nature, So, the reaction will follow mainly  $\text{S}_{\text{N}}1$  pathways *via* the formation of a carbocation intermediate (I).



The intermediate, I can be rearranged into the more stable form I' ( $3^\circ$ ) by  $\alpha$ -hydride shift. I' will give the major product.



5. The potential energy (PE) diagram for  $\text{S}_{\text{N}}1$  reaction is

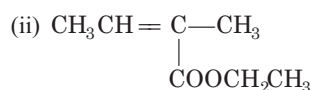
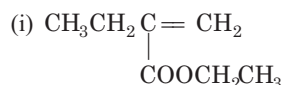


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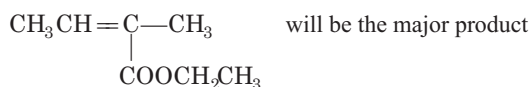
$S_N1$  reaction has two steps. In the first step, the carbon halogen bond breaks heterolytically, with the halogen retaining the previously shared pair of electron. In the second step, the nucleophile reacts rapidly with the carbocation formed in the first step.

In the above graph, the alkyl halide is the only species that participates in the rate limiting step. Here, the rate of reaction depends on the concentration of the alkyl halide and does not depend on the concentration of nucleophile.

6. Presence of strong base ( $\text{EtO}^-$ ) and heat indicates elimination. Thus, the compound undergo dehydrohalogenation and alkene is produced. As per the position of Cl in substrate, following 2 alkenes are formed as product:



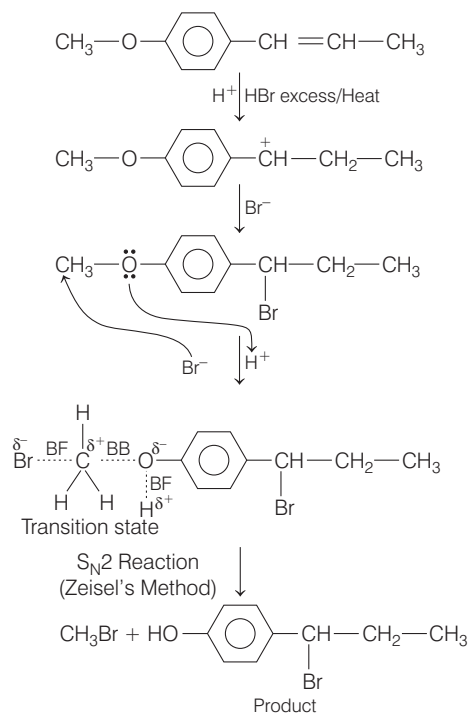
In accordance with Saytzeff rule



7. **Key Idea** The excess of HBr and high temperature in given reaction serves for dual purpose:

- (i) Hydrolysis of ether *via*  $S_N2$  mechanism, i.e. Zeisel's method.  
 (ii) Markownikoff addition at double bond of the branch.

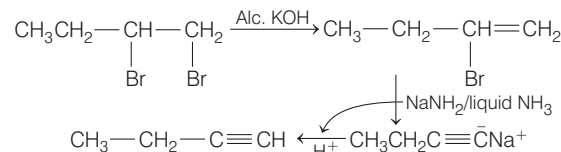
The road map of complete reaction is as follows:



Here, BB = Bond breakage  
 BF = Bond formation

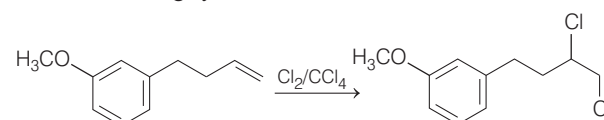
8. **Key Idea** Both alc. KOH and  $\text{NaNH}_2$  in liquid  $\text{NH}_3$  are dehydrohalogenating reagents. On comparative terms  $\text{NaNH}_2/\text{liquid NH}_3$  is stronger in action.

The reaction proceeds as :

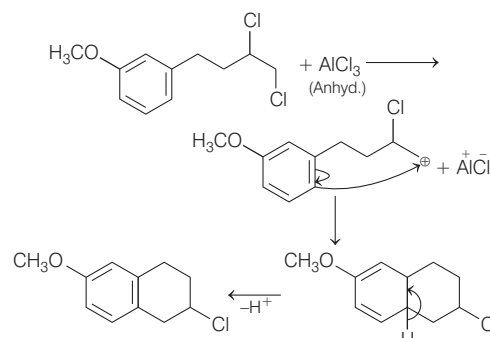


Thus, option (d) is the correct answer.

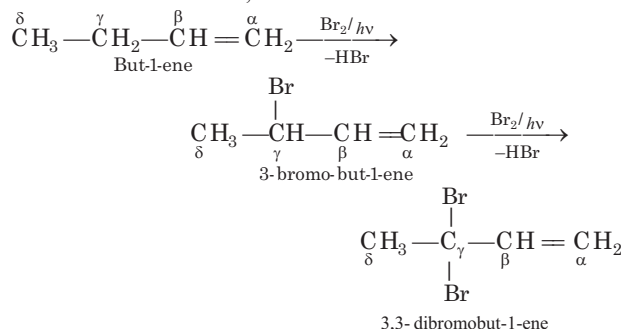
9. The given reactant in presence of  $\text{Cl}_2/\text{CCl}_4$ , given *vicinal* dihalide. Chlorine adds up to alkene *via* electrophilic addition reaction involving cyclic chloronium ion formation.



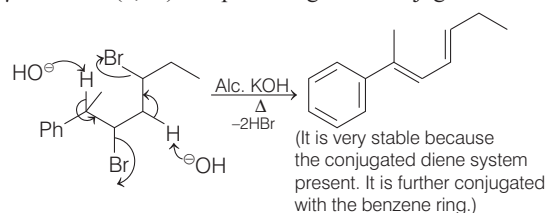
The vicinal dihalide in presence of anhyd.  $\text{AlCl}_3$  results in the formation of carbocation that rearranges itself to form a cyclic compound.



10. The compound (E) has two allyl-hydrogen atoms ( $\gamma$ ). When E reacts with  $\text{Br}_2/h\nu$ , it readily undergoes allylic free radical substitution and forms 3, 3-dibromobut-1-ene



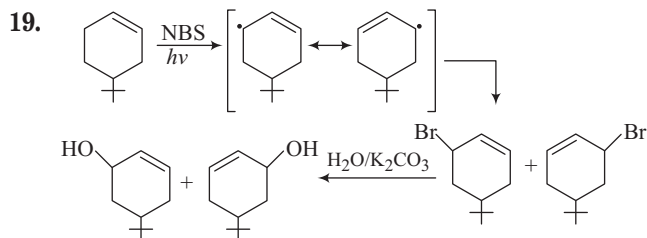
11. The reaction follows  $\alpha, \beta$ -elimination mechanism to give a more substituted stable alkene as a major product. As the substrate is a  $\alpha, \gamma$ -dibromo (1, 3-) compound it gives a conjugated diene.



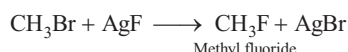




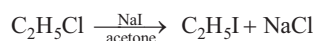
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20. Alkyl fluorides can be prepared by action of mercurous fluoride or antimony trifluorides (inorganic fluorides) on corresponding alkyl halide. This reaction is known as Swarts reaction.



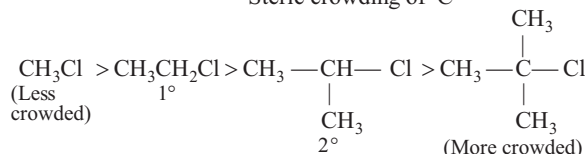
But, when action of NaI/acetone takes place on alkyl chloride or bromide, alkyl iodide forms. This reaction is called 'Finkelstein reaction'



Free radical fluorination is highly explosive reaction, so not preferred for the preparation of fluoride.

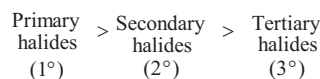
21. Steric hindrance (crowding) is the basis of  $\text{S}_{\text{N}}2$  reaction, by using which we can arrange the reactant in correct order of their reactivity towards  $\text{S}_{\text{N}}2$  reaction.

$$\text{Rate of } \text{S}_{\text{N}}2 \propto \frac{1}{\text{Steric crowding of 'C'}}$$

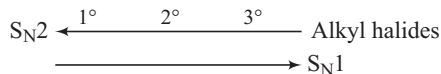


As steric hindrance (crowding) increases, rate of  $\text{S}_{\text{N}}2$  reaction decreases.

**Note** The order of reactivity towards  $\text{S}_{\text{N}}2$  reaction for alkyl halides is



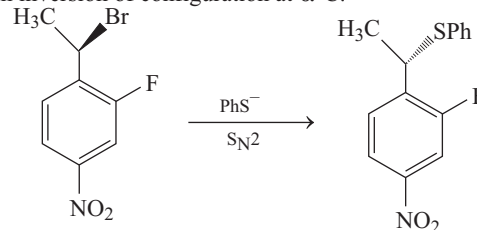
22. **PLAN** Acetone is an aprotic solvent and can dissolve both the nucleophile and the substrate and thus  $\text{S}_{\text{N}}2$  reaction is favoured. Also



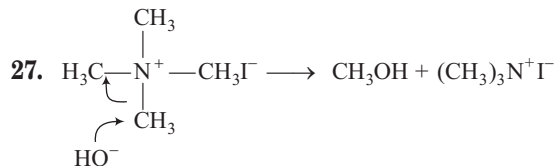
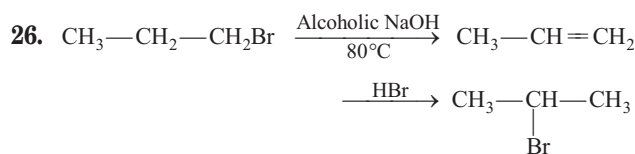
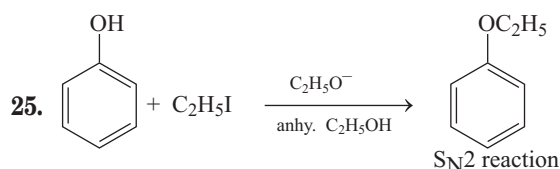
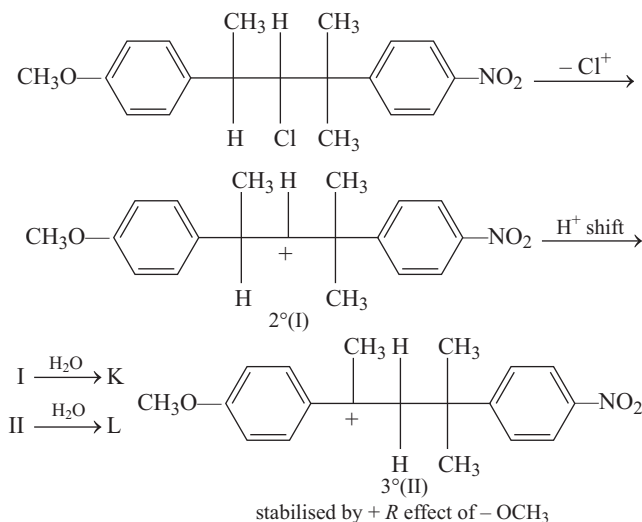
|    |                         |                                                                                                                                                                                                      |
|----|-------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| S. |                         | $1^\circ$ alkyl halide but (C—Cl). B.E. is decreased by electron withdrawing $[\text{C}_6\text{H}_5\text{CO}]$ group, (a case of $I$ -effect). Thus, maximum rate in $\text{S}_{\text{N}}2$ reaction |
| Q. |                         | $2^\circ$ alkyl halide, rate is minimum                                                                                                                                                              |
| P. | $\text{CH}_3-\text{Cl}$ | $1^\circ$ alkyl halide                                                                                                                                                                               |
| R. |                         | $1^\circ$ allylic halide but allylic $1^\circ$ carbocation is resonance stabilised in $\text{S}_{\text{N}}1$ reaction                                                                                |

Thus, reactivity order is  $S > P > R > Q$

23. Nucleophile  $\text{PhS}^-$  substitute the  $\text{Br}^-$  through  $\text{S}_{\text{N}}2$  mechanism with inversion of configuration at  $\alpha$ -C.



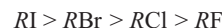
24. Reaction proceed through carbocation intermediate



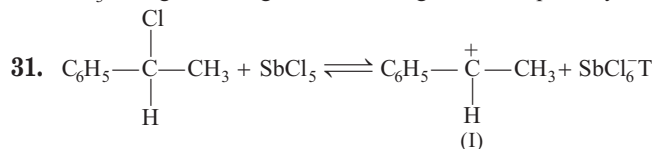
Lack of  $\beta$ -H on quaternary ammonium iodide leads to  $\text{S}_{\text{N}}2$  reaction otherwise  $\text{E}2$  elimination usually takes place.

28.  $\text{S}_{\text{N}}2$  reaction at asymmetric carbon occur with inversion of configuration and a single stereoisomer is formed because the reactant and product are not enantiomer. Therefore the sign of optical rotation may or may not change.

29. If alkyl groups are same, the order of leaving ability of halides in  $\text{S}_{\text{N}}2$  reaction is

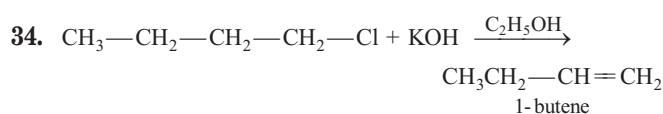
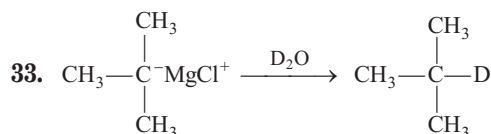


30.  $\text{CH}_3^-$ , being the strongest base, has highest nucleophilicity.



he planar carbocation (I), when return back, forms racemic mixture of the starting compounds.

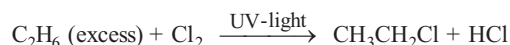
32. Compound in which metal is directly bonded to carbon, is known are organometallic compound, e.g.  $\text{CH}_3\text{Li}$ .



35. An alkyl halide containing at least one  $\beta$ -H, on treatment with ethanolic KOH, undergoes dehydrohalogenation, giving alkene.

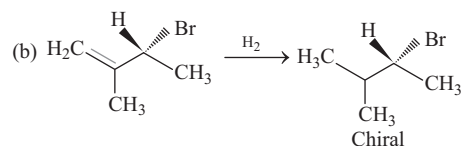
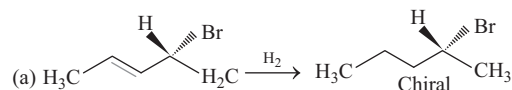


36. During chlorination of alkane, if excess of alkane is treated with  $\text{Cl}_2(\text{g})$  in presence of light or heat, chance of mono-chlorination predominate.

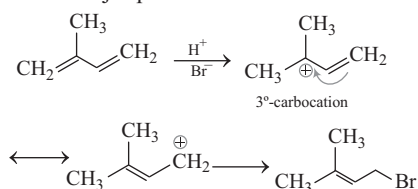


37. (a) Both I and II are  $1^\circ$  halide, undergoes  $\text{S}_\text{N}2$  reaction.  
(d) III is a tertiary halide, undergoes  $\text{S}_\text{N}1$  reaction. I is benzylic bromide, it is very reactive in  $\text{S}_\text{N}1$  also as it produces stable benzylic carbocation.

38. In both cases, hydrogenation of olefinic bond will render compound achiral as two identical ethyl group will come at the  $\alpha$ -carbon which was earlier chiral carbon. However, in (a) and (c), chirality will be retained even after hydrogenation.

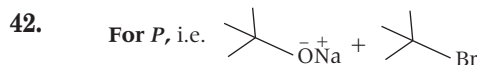
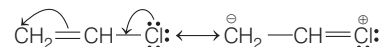


39. Since, there is no mention of temperature, room temperature will be considered and thermodynamically controlled product would be the major product as:



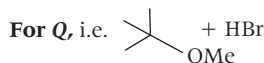
40. Both  $\text{NH}_3$  and  $\text{CF}_2\text{Cl}_2$  are used as refrigerant.

41. Vinyl halide ( $\text{CH}_2=\text{CH}-\text{Cl}$ ) do not undergo nucleophilic substitution reactions. This is because it forms highly unstable carbocation ( $\text{CH}_2=\overset{\oplus}{\text{CH}}$ ). It cannot delocalise its  $\pi$ -electron. In vinyl halide C—Cl bond possess double bond character also.

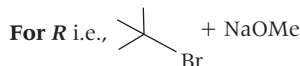
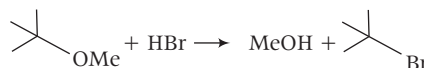


For this reaction 1 and 4 are probable products.

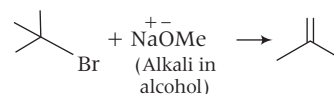
Product 1 i.e.,  $\text{CH}_3-\text{C}(\text{CH}_3)_2-\text{OH}$  is formed due to substitution while product 4 i.e.,  $\text{CH}_3-\text{C}(\text{CH}_3)=\text{CH}_2$  is formed due to elimination. A tertiary carbocation i.e.,  $\text{CH}_3-\text{C}^+(\text{CH}_3)_2$  formed during the reaction. Remember for  $3^\circ$  carbocation ions elimination product predominates.



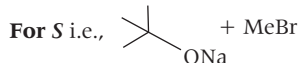
Correctly matched product for this reaction is 2 i.e.,  $\text{CH}_3-\text{C}(\text{CH}_3)_2-\text{Br}$ . The reaction proceeds as



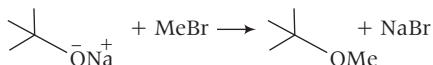
Correctly matched product is 4 i.e.,  $\text{CH}_3-\text{C}(\text{CH}_3)=\text{CH}_2$ . It is a normal elimination reaction and proceeds as



$3^\circ$  alkyl halide prefers elimination.



The correct match is 3 i.e.,  $\text{CH}_3-\text{C}(\text{CH}_3)_2-\text{OMe}$ . The reaction proceeds as



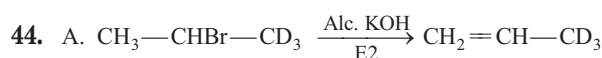
43.

|    | Column I                                                                                                    | Column II         | Explanation                                                                                      |
|----|-------------------------------------------------------------------------------------------------------------|-------------------|--------------------------------------------------------------------------------------------------|
| P. | $\text{CH}_3-\text{C}(\text{CH}_3)_2-\text{Cl} \rightarrow \text{CH}_3-\text{C}(\text{CH}_3)=\text{CH}_2$   | $\text{NaOEt}(2)$ | $\text{O}^- \text{Et}$ (strong nucleophile) causes dehydrohalogenation of $3^\circ$ alkyl halide |
| Q. | $\text{CH}_3-\text{C}(\text{CH}_3)_2-\text{ONa} \rightarrow \text{CH}_3-\text{C}(\text{CH}_3)_2-\text{OEt}$ | $\text{EtBr}(3)$  | $3^\circ$ butoxide undergoes $\text{S}_\text{N}$ reaction with $1^\circ$ alkyl halide            |

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|    |  |                                                                     |                                                                                                   |
|----|--|---------------------------------------------------------------------|---------------------------------------------------------------------------------------------------|
| R. |  | (i) $\text{Hg}(\text{OAc})_2$<br>(ii) $\text{NaBH}_4$<br>(1)        | Mercuriation-demercuration adds $\text{H}_2\text{O}$ by Markownikoff's rule without rearrangement |
| S. |  | (i) $\text{BH}_3$<br>(ii) $\text{H}_2\text{O}_2/\text{OH}^-$<br>(4) | Hydroboration-oxidation adds $\text{H}_2\text{O}$ by anti-Markownikoff's rule                     |

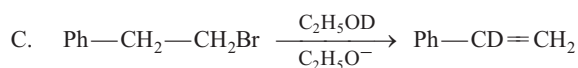
Thus, P — (2), Q — (3), R — (1), S — (4)



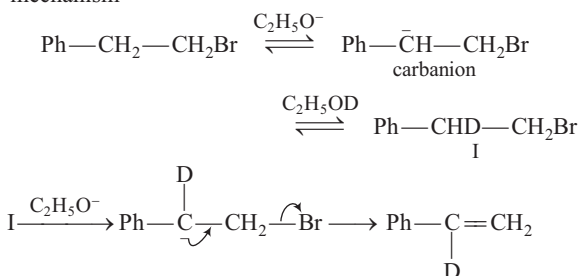
E2 reaction is a single-step reaction in which both deprotonation from  $\beta\text{-C}$  and loss of leaving group from  $\alpha\text{-C}$  occur simultaneously in the rate-determining step.

C—D bond is stronger than C—H bond, C—H is preferably broken in elimination.

B.  $\text{Ph—CHBr—CH}_3$  reacts faster than  $\text{Ph—CHBr—CD}_3$  in E2 reaction because in latter case, stronger C—D bond is to be broken in the rate determining step.



Deuterium incorporation in the product indicates E1CB mechanism



D. Both  $\text{PhCH}_2\text{CH}_2\text{Br}$  and  $\text{PhCD}_2\text{CH}_2\text{Br}$  will react at same rate in E1 reaction because C—H bond is broken in fast non rate determining step. Also E1 reaction follow first order kinetics.

45. Propene is produced



46. Vinyl chloride is obtained by the reaction of HCl with ethyne.

47. Chlorine is most reactive.

48. 2-bromo-2-methylpropane is formed as major product.

49. In  $\text{S}_\text{N}1$  reaction, leaving group is detached in the first step forming carbocation intermediate.

50. True

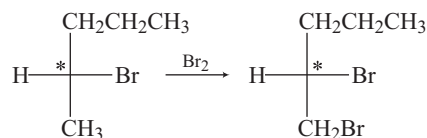
51. Larger the size of donor atom, greater is its polarisability, stronger is the nucleophile.

52. False

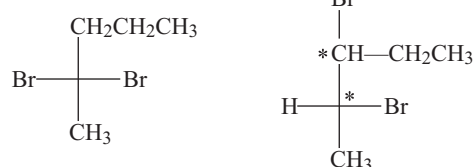
53.  $\text{CCl}_4$  is fire retardant, used as fire-extinguisher.

54. Given compound undergoes free-radical bromination under given conditions, replacing H by Br.

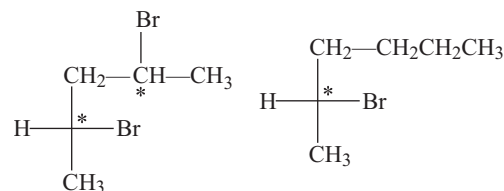
$\text{C}^*$  is chiral carbon.



I. Chiral



II. Achiral

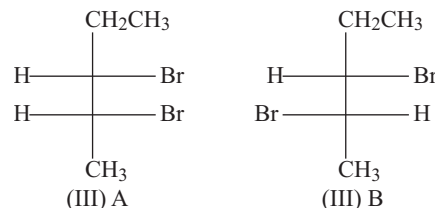


III. Chiral

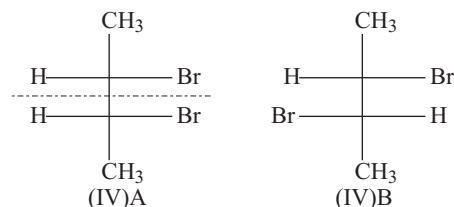
IV. Chiral

V. Chiral

(III) has two chiral centres and can have two structures.



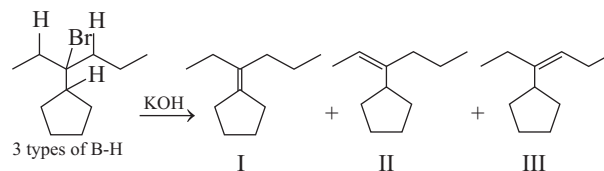
(IV) has also two chiral centres and can have two structures.



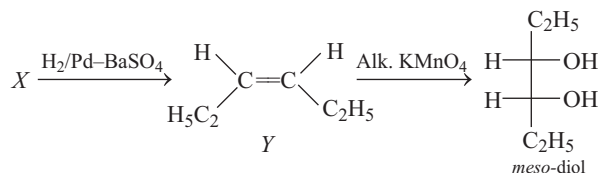
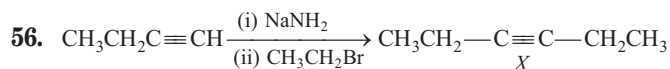
It has plane of symmetry thus, achiral.

Thus, chiral compounds are five. I, III A, III B, IV B and V.

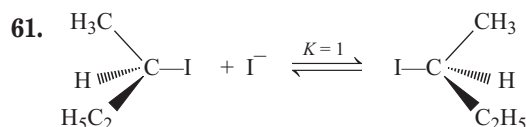
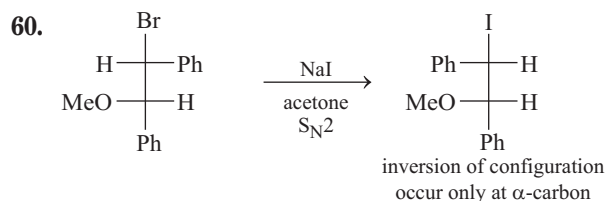
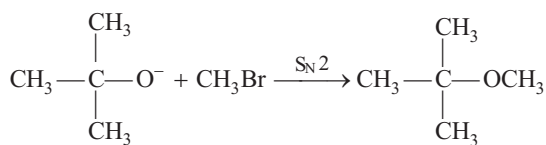
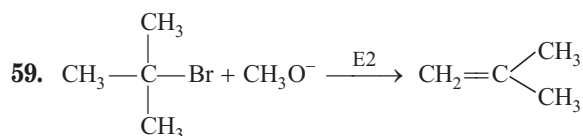
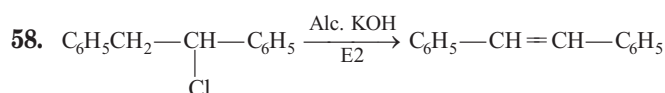
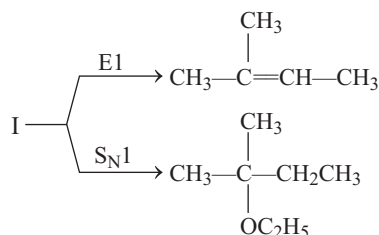
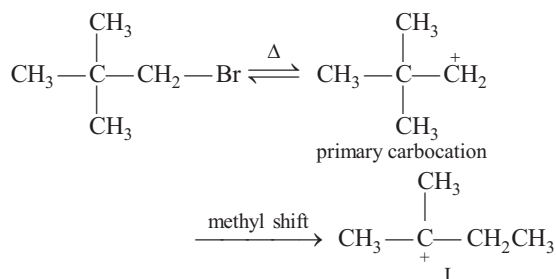
55. The substrate has three different types of B—H, therefore, first three structural isomers of alkenes are expected as :



The last two alkenes II and III are also capable of showing geometrical isomerism, hence two geometrical isomers for each of them will be counted giving a total of five isomers.

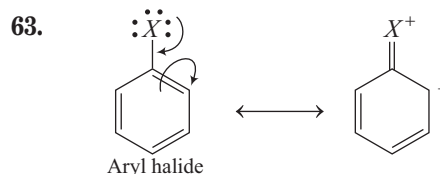
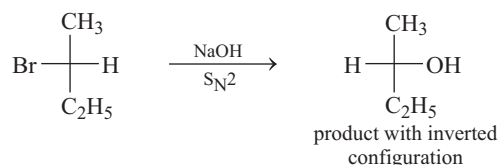


57. Unimolecular reaction occur

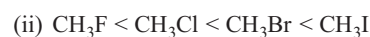
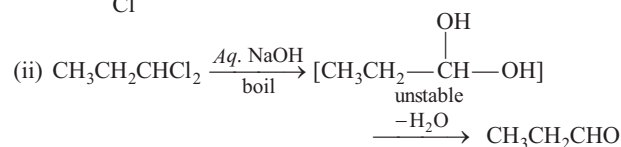
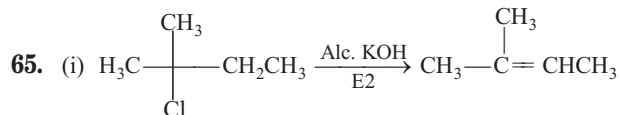
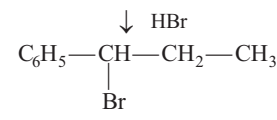
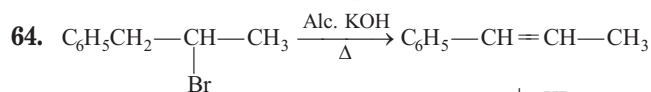


Above equilibrium is established which has equilibrium constant equal to 1. Therefore, equilibrium mixture will have both the enantiomers in equal amount giving racemic mixture.

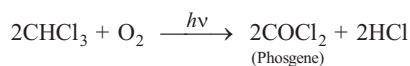
62.  $\text{S}_{\text{N}}2$  reactions leads to inversion of configuration at  $\alpha$ -C



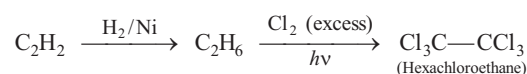
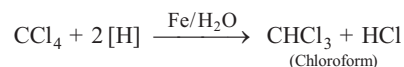
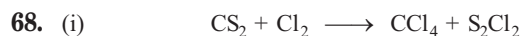
Due to the above resonance phenomena, C—X bond acquire partial double bond character and becomes difficult to break in the rate determining step of  $\text{S}_{\text{N}}2$  reaction.



67. Chloroform in presence of air and sunlight, oxidises slowly to form a highly poisonous compound called phosgene



To prevent the above oxidation reaction, chloroform is kept in dark bottles.



Download Chapter Test

<http://tinyurl.com/y54uy6l6>

or

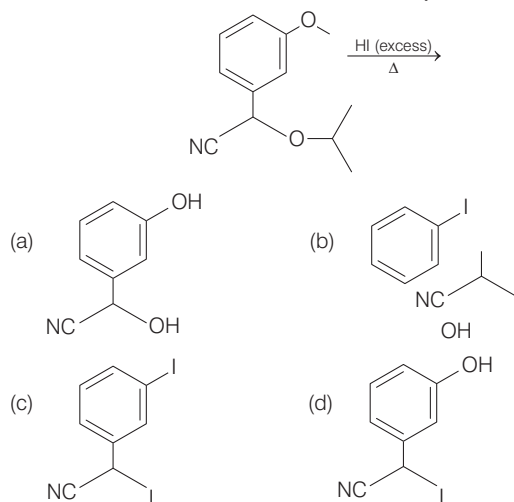


# 24

## Alcohols and Ethers

### Objective Questions I (Only one correct option)

1. The major product of the following reaction is  
(2019 Main, 10 April I)



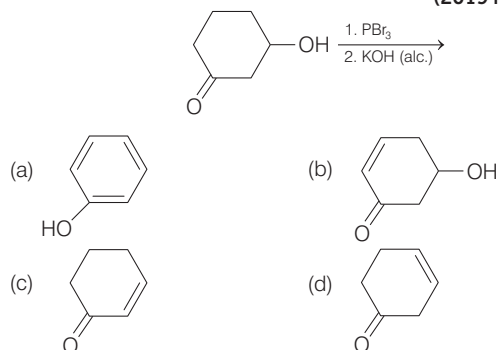
2. The synonym for water gas when used in the production of methanol is  
(2019 Main, 10 April I)

- (a) natural gas (b) laughing gas  
(c) *syn* gas (d) fuel gas

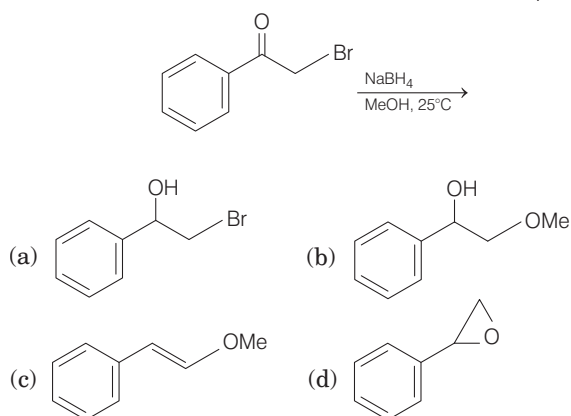
3. The major product of the following reaction is  
CH3CH=CHCO2CH3  $\xrightarrow{\text{LiAlH}_4}$  (2019 Main, 9 April I)

- (a) CH3CH=CHCH2OH (b) CH3CH2CH2CH2OH  
(c) CH3CH2CH2CO2CH3 (d) CH3CH2CH2CHO

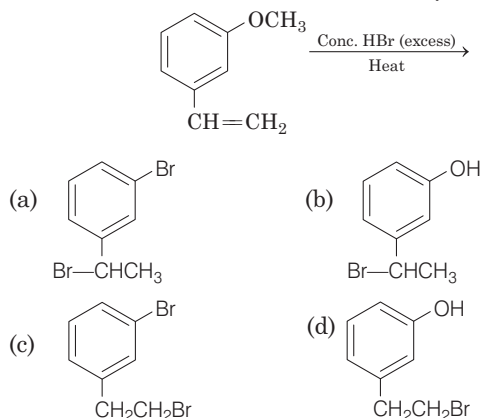
4. The major product of the following reaction is  
(2019 Main, 9 April I)



5. The major product of the following reaction is  
(2019 Main, 8 April I)



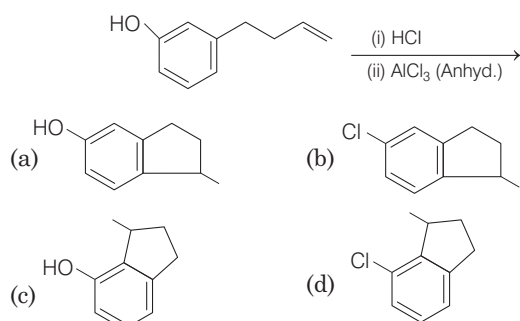
6. The major product of the following reaction is  
(2019 Main, 8 April I)



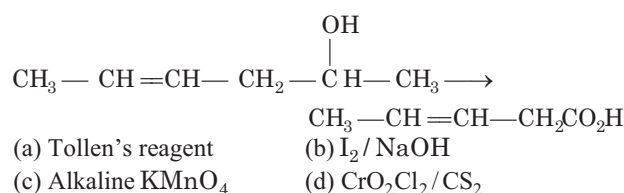
7. CH3CH2C(OH)(Ph)CH3 cannot be prepared by  
(2019 Main, 12 Jan I)

- (a) CH3CH2COCH3 + PhMgX  
(b) PhCOCH3 + CH3CH2MgX  
(c) PhCOCH2CH3 + CH3MgX  
(d) HCHO + PhCH(CH3)CH2MgX

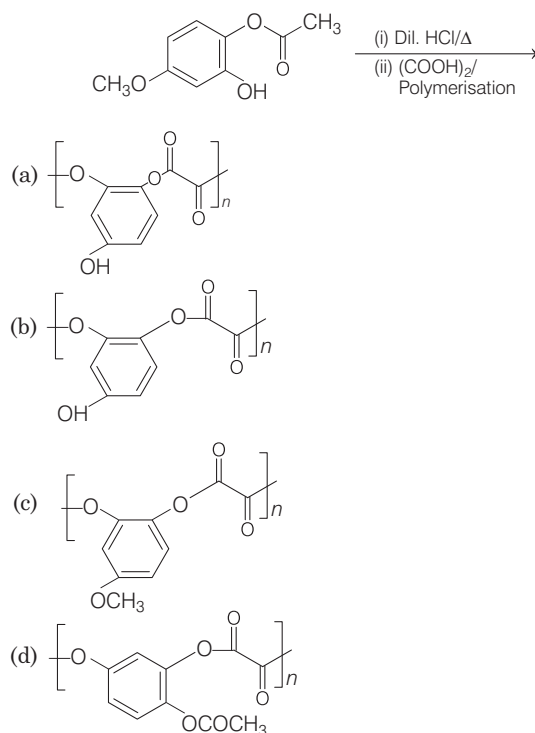
8. The major product of the following reaction is  
(2019 Main, 11 Jan II)



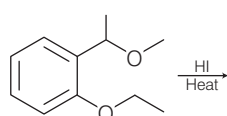
9. Which is the most suitable reagent for the following transformation?  
(2019 Main, 10 Jan II)



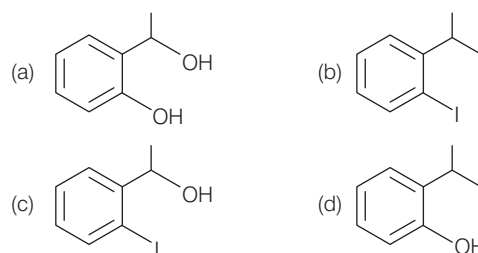
10. The major product of the following reaction is  
(2019 Main, 10 Jan II)



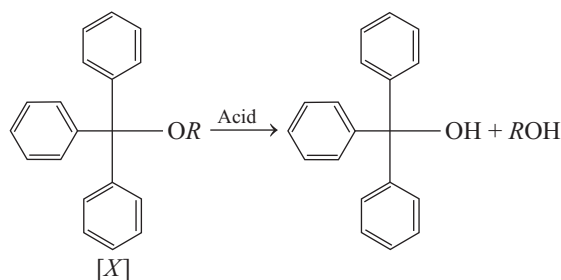
11. The major product formed in the following reaction is



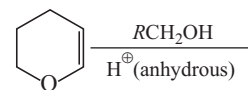
(2018 Main)



12. The acidic hydrolysis of ether (X) shown below is fastest when  
(2014 Adv.)



- (a) one phenyl group is replaced by a methyl group  
 (b) one phenyl group is replaced by a *para*-methoxyphenyl group  
 (c) two phenyl groups are replaced by two *para*-methoxyphenyl groups  
 (d) no structural change is made to X
13. An unknown alcohol is treated with the "Lucas reagent" to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism?  
(2013 Main)
- (a) Secondary alcohol by  $\text{S}_{\text{N}}1$   
 (b) Tertiary alcohol by  $\text{S}_{\text{N}}1$   
 (c) Secondary alcohol by  $\text{S}_{\text{N}}2$   
 (d) Tertiary alcohol by  $\text{S}_{\text{N}}2$
14. The major product of the following reaction is

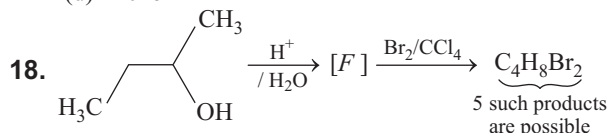


- (a) a hemiacetal (b) an acetal  
 (c) an ether (d) an ester
15. (I) 1, 2-dihydroxy benzene  
 (II) 1, 3-dihydroxy benzene  
 (III) 1, 4-dihydroxy benzene  
 (IV) Hydroxy benzene
- The increasing order of boiling points of above mentioned alcohols is  
(2006, 3M)
- (a)  $\text{I} < \text{II} < \text{III} < \text{IV}$  (b)  $\text{I} < \text{II} < \text{IV} < \text{III}$   
 (c)  $\text{IV} < \text{I} < \text{II} < \text{III}$  (d)  $\text{IV} < \text{II} < \text{I} < \text{III}$
16. The best method to prepare cyclohexene from cyclohexanol is by using  
(2005, 1M)
- (a) conc.  $\text{HCl} + \text{ZnCl}_2$  (b) conc.  $\text{H}_3\text{PO}_4$   
 (c)  $\text{HBr}$  (d) conc.  $\text{HCl}$

## 342 Alcohols and Ethers

17. When phenyl magnesium bromide reacts with *tert* butanol, which of the following is formed? (2005, 1M)

(a) *Tert* butyl methyl ether  
(b) Benzene  
(c) *Tert* butyl benzene  
(d) Phenol



How many structures of *F* is possible? (2003, 1M)

(a) 2 (b) 5 (c) 6 (d) 3

19. Compound 'A' (molecular formula  $\text{C}_3\text{H}_8\text{O}$ ) is treated with acidified potassium dichromate to form a product 'B' (molecular formula  $\text{C}_3\text{H}_6\text{O}$ ) 'B' forms a shining silver mirror on warming with ammoniacal silver nitrate. 'B' when treated with an aqueous solution of  $\text{H}_2\text{NCONHNH}_2$  and sodium acetate gives a product 'C'. Identify the structure of 'C'.

(a)  $\text{CH}_3\text{CH}_2\text{CH}=\text{NNHCONH}_2$  (2002, 3M)

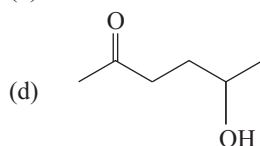
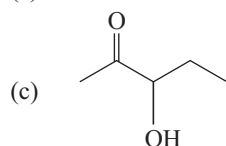
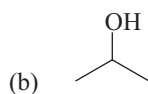
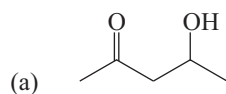
(b)  $\text{H}_3\text{C}-\text{C}(\text{CH}_3)=\text{NNHCONH}_2$

(c)  $\text{H}_3\text{C}-\text{C}(\text{CH}_3)=\text{NCONHNH}_2$

(d)  $\text{CH}_3\text{CH}_2\text{OH} + \text{NCONHNH}_2$

20. 1-propanol and 2-propanol can be best distinguished by  
(a) oxidation with alkaline  $\text{KMnO}_4$  followed by reaction with Fehling solution (2001, 1M)  
(b) oxidation with acidic dichromate followed by reaction with Fehling solution  
(c) oxidation by heating with copper followed by reaction with Fehling solution  
(d) oxidation with concentrated  $\text{H}_2\text{SO}_4$  followed by reaction with Fehling solution

21. Which one of the following will most readily be dehydrated in acidic condition? (2000, 1M)



22. The products of combustion of an aliphatic thiol ( $\text{RSH}$ ) at 298 K are (1992)

(a)  $\text{CO}_2(\text{g})$ ,  $\text{H}_2\text{O}(\text{g})$  and  $\text{SO}_2(\text{g})$   
(b)  $\text{CO}_2(\text{g})$ ,  $\text{H}_2\text{O}(\text{l})$ , and  $\text{SO}_2(\text{g})$   
(c)  $\text{CO}_2(\text{l})$ ,  $\text{H}_2\text{O}(\text{l})$  and  $\text{SO}_2(\text{g})$   
(d)  $\text{CO}_2(\text{g})$ ,  $\text{H}_2\text{O}(\text{l})$  and  $\text{SO}_2(\text{l})$

23. In  $\text{CH}_3\text{CH}_2\text{OH}$ , the bond that undergoes heterolytic cleavage most readily is (1988, 1M)

(a)  $\text{C}-\text{C}$  (b)  $\text{C}-\text{O}$   
(c)  $\text{C}-\text{H}$  (d)  $\text{O}-\text{H}$

24. Hydrogen bonding is maximum in (1987, 1M)

(a) ethanol (b) diethyl ether  
(c) ethyl chloride (d) triethyl amine

25.  $\text{HBr}$  reacts fastest with (1986, 1M)

(a) 2-methyl propan-2-ol (b) propan-1-ol  
(c) propan-2-ol (d) 2-methyl propan-1-ol

26. An industrial method of preparation of methanol is (1984, 1M)

(a) catalytic reduction of carbon monoxide in presence of  $\text{ZnO}-\text{Cr}_2\text{O}_3$   
(b) by reacting methane with steam at  $900^\circ\text{C}$  with nickel catalyst  
(c) by reducing formaldehyde with  $\text{LiAlH}_4$   
(d) by reacting formaldehyde with aqueous sodium hydroxide solution

27. Diethyl ether on heating with conc.  $\text{HI}$  gives two moles of

(a) ethanol (b) iodoform (1983, 1M)  
(c) ethyl iodide (d) methyl iodide

28. The compound which reacts fastest with Lucas reagent at room temperature is (1981, 1M)

(a) butan-2-ol (b) butan-1-ol  
(c) 2-methyl propan-1-ol (d) 2-methyl propan-2-ol

29. Ethyl alcohol is heated with conc.  $\text{H}_2\text{SO}_4$ . The product formed is

(a)  $\text{CH}_3\text{COOC}_2\text{H}_5$  (b)  $\text{C}_2\text{H}_2$  (1980, 1M)  
(c)  $\text{C}_2\text{H}_4$  (d)  $\text{C}_2\text{H}_6$

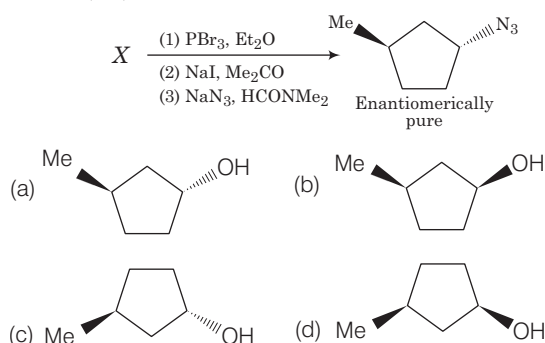
30. Which of the following is soluble in water? (1980, 1M)

(a)  $\text{CS}_2$  (b)  $\text{C}_2\text{H}_5\text{OH}$   
(c)  $\text{CCl}_4$  (d)  $\text{CHCl}_3$

## Objective Questions II

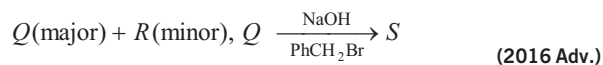
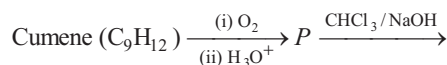
(One or more than one correct option)

31. In the following reaction sequence, the correct structure (s) of *X* is (are) (2018 Adv.)





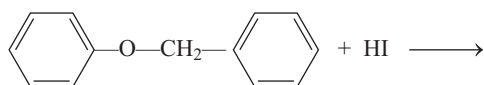
32. The correct statement(s) about the following reaction sequence is (are)



(2016 Adv.)

- (a) *R* is steam volatile  
 (b) *Q* gives dark violet colouration with 1% aqueous  $\text{FeCl}_3$  solution  
 (c) *S* gives yellow precipitate with 2, 4-dinitrophenylhydrazine  
 (d) *S* gives dark violet colouration with 1% aqueous  $\text{FeCl}_3$  solution

33. The following ether, when treated with HI produces (1999, 3M)



- (a) c1ccccc1CI (b) c1ccccc1CO  
 (c) c1ccccc1I (d) c1ccccc1O

34. The products of reaction of alcoholic silver nitrate with ethyl bromide are (1991, 1M)

- (a) ethane (b) ethene  
 (c) nitroethane (d) ethyl alcohol  
 (e) ethyl nitrite

### Assertion and Reason

Read the following question and answer as per the direction given below :

- (a) Statement I is correct; Statement II is correct; Statement II is a correct explanation of Statement I.  
 (b) Statement I is correct; Statement II is correct; Statement II is not the correct explanation of Statement I.  
 (c) Statement I is correct; Statement II is incorrect.  
 (d) Statement I is incorrect; Statement II is correct.
35. **Statement I** Solubility of *n*-alcohol in water decreases with increase in molecular weight.

**Statement II** The relative proportion of the hydrocarbon part in alcohols increases with increasing molecular weight which permit enhanced hydrogen bonding with water.

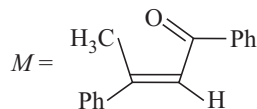
(1988, 2M)

### Passage Based Questions

#### Passage 1

A tertiary alcohol *H* upon acid catalysed dehydration gives a product *I*. Ozonolysis of *I* leads to compounds *J* and *K*.

Compound *J* upon reaction with KOH gives benzyl alcohol and a compound *L*, whereas *K* on reaction with KOH gives only *M*.



(2008, 3 × 4M = 12M)

36. The structures of compounds *J*, *K* and *L* respectively, are

- (a)  $\text{PhCOCH}_3$ ,  $\text{PhCH}_2\text{COCH}_3$  and  $\text{PhCH}_2\text{COO}^-\text{K}^+$   
 (b)  $\text{PhCHO}$ ,  $\text{PhCH}_2\text{CHO}$  and  $\text{PhCOO}^-\text{K}^+$   
 (c)  $\text{PhCOCH}_3$ ,  $\text{PhCH}_2\text{CHO}$  and  $\text{CH}_3\text{COO}^-\text{K}^+$   
 (d)  $\text{PhCHO}$ ,  $\text{PhCOCH}_3$  and  $\text{PhCOO}^-\text{K}^+$

37. The structure of compound *I* is

- (a) (b)   
 (c) (d)

38. Compound *H* is formed by the reaction of

- (a) ;  $\text{PhMgBr}$   
 (b) ;  $\text{PhCH}_2\text{MgBr}$   
 (c) ;  $\text{PhCH}_2\text{MgBr}$   
 (d) ;

### Fill in the Blanks

39. Glycerine contains one ..... hydroxyl group. (1997, 1M)  
 40. Aliphatic ethers are purified by shaking with a solution of ferrous salt to remove ..... which are formed on prolonged standing in contact with water. (1992, 1M)  
 41. A ..... diol has two hydroxyl groups on ..... carbon atoms. (1986, 1M)  
 42. Ethanol vapour is passed over heated copper and the product is treated with aqueous NaOH. The final product is ..... (1983, 1M)

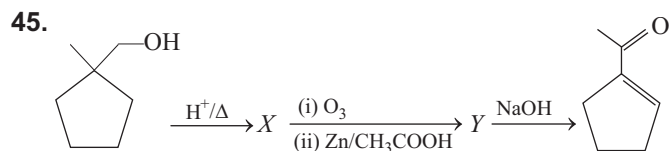
### True or False

43. Sodium ethoxide is prepared by reacting ethanol with aqueous sodium hydroxide. (1985, 1M)

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44. The yield of a ketone when a secondary alcohol is oxidised is more than the yield of aldehyde when a primary alcohol is oxidised. (1983, 1M)

### Subjective Questions

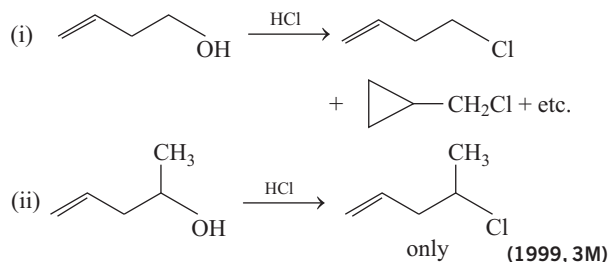


Identify *X* and *Y*. (2005, 2M)

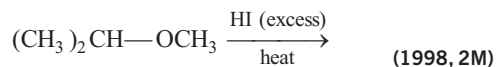
46. An organic compound *P* having the molecular formula  $C_5H_{10}O$  when treated with dil  $H_2SO_4$  gives two compounds, *Q* and *R* both gives positive iodoform test. The reaction of  $C_5H_{10}O$  with dil.  $H_2SO_4$  gives reaction  $10^{15}$  times faster than ethylene. Identify organic compound of *Q* and *R*. Give the reason for the extra stability of *P*. (2004)

47. Cyclobutylbromide on treatment with magnesium in dry ether forms an organometallic compound (*A*). The organometallic reacts with ethanal to give an alcohol (*B*) after mild acidification. Prolonged treatment of alcohol (*B*) with an equivalent amount of  $HBr$  gives 1-bromo-1-methylcyclopentane (*C*). Write the structures of (*A*), (*B*) and explain how (*C*) is obtained from (*B*). (2001, 5M)

48. Explain briefly the formation of products giving the structures of the intermediates.



49. Write the structures of the products :



50. Give reasons for the following in one or two sentences.  
“Acid catalysed dehydration of *t*-butanol is faster than that of *n*-butanol. (1998, 2M)

51. 2, 2-dimethyloxirane can be cleaved by acid ( $H^+$ ). Write mechanism. (1997, 2M)

52. A compound *D* ( $C_8H_{10}O$ ) upon treatment with alkaline solution of iodine gives a yellow precipitate. The filtrate on acidification gives a white solid *E* ( $C_7H_6O_2$ ). Write the structures of *D*, *E* and explain the formation of *E*. (1996, 2M)

53. 3, 3-dimethylbutan-2-ol losses a molecule of water in the presence of concentrated sulphuric acid to give tetramethylethylene as a major product. Suggest a suitable mechanism. (1996, 2M)

54. When *t*-butanol and *n*-butanol are separately treated with a few drops of dilute  $KMnO_4$  in one case only, the purple colour disappears and a brown precipitate is formed. Which of the two alcohols gives the above reaction and what is the brown precipitate? (1994, 2M)

55. Compound *X* (molecular formula,  $C_5H_8O$ ) does not react appreciably with Lucas reagent at room temperature but gives a precipitate with ammoniacal silver nitrate with excess of  $MeMgBr$ , 0.42 g of *X* gives 224 mL of  $CH_4$  at STP. Treatment of *X* with  $H_2$  in presence of Pt catalyst followed by boiling with excess  $HI$ , gives *n*-pentane. Suggest structure for *X* and write the equation involved. (1992, 5M)

56. Arrange the following in increasing order of boiling point : *n*-butane, *n*-butanol, *n*-butylchloride, *iso*-butane. (1988, 1M)

57. How may be the following transformation be carried out (in not more than six steps)?  
“Ethyl alcohol to vinyl acetate.” (1986, 3M)

58. Write down the main product of the following reaction :



59. Give a chemical test to distinguish between methanol and ethanol. (1985, 1M)

60. Suggest a reason for the large difference between the boiling points of butanol and butanal, although they have almost the same solubility in water. (1985, 2M)

61. An alcohol *A*, when heated with conc.  $H_2SO_4$  gives an alkene *B*. When *B* is bubbled through bromine water and the product obtained is dehydrohalogenated with excess of sodamide, a new compound *C* is obtained. The compound *C* gives *D* when treated with warm dilute  $H_2SO_4$  in presence of  $HgSO_4$ . *D* can also be obtained either by oxidising *A* with  $KMnO_4$  or from acetic acid through its calcium salt. Identify *A*, *B*, *C* and *D*. (1983, 4M)

62. State the conditions under which the following preparations are carried out. Give necessary equations which need not be balanced.

- Ethanol from acetylene
- Lead tetraethyl from sodium-lead alloy
- Methyl chloride from aluminium carbide (1983, 3M)

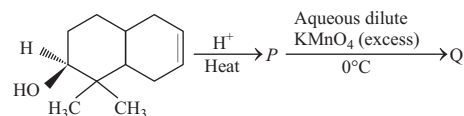
63. A compound ‘*X*’ containing C, H and O is unreactive towards sodium. It does not add with bromine. It also does not react with Schiff’s reagent. On refluxing with an excess of  $HI$ , ‘*X*’ yields only one organic product ‘*Y*’. ‘*Y*’ on hydrolysis yields a new compound ‘*Z*’ which can be converted into ‘*Y*’ by reaction with red phosphorus and iodine. The compound ‘*Z*’ on oxidation with potassium permanganate gives a carboxylic acid. The equivalent weight of acid is 60. What are the compounds ‘*X*’, ‘*Y*’ and ‘*Z*’? Write chemical equations leading to the conversion of ‘*X*’ to ‘*Y*’. (1981, 3M)

64. An organic liquid 'A' containing C, H and O with boiling point  $78^{\circ}\text{C}$ , possessing a rather pleasant odour, on heating with concentrated sulphuric acid gives a gaseous product 'B' with the empirical formula,  $\text{CH}_2$ . 'B' decolourises bromine water as well as alkaline permanganate solution and takes up one mole of  $\text{H}_2$  (per mole of B) in presence of finely divided nickel at high temperature. Identify the substances A and B.

(1979, 2M)

## Integer Type Question

65. The number of hydroxyl group(s) in Q is (2015 Adv.)

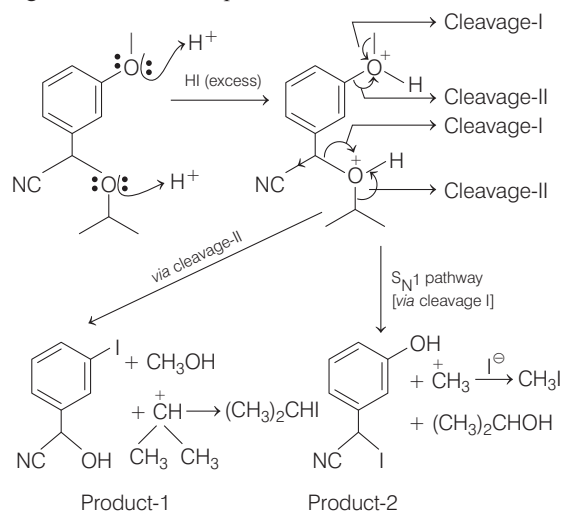


## Answers

- |         |         |         |         |                   |           |               |               |
|---------|---------|---------|---------|-------------------|-----------|---------------|---------------|
| 1. (d)  | 2. (c)  | 3. (a)  | 4. (c)  | 25. (a)           | 26. (a)   | 27. (c)       | 28. (d)       |
| 5. (d)  | 6. (b)  | 7. (d)  | 8. (a)  | 29. (c)           | 30. (b)   | 31. (b)       | 32. (b,c)     |
| 9. (b)  | 10. (c) | 11. (d) | 12. (c) | 33. (a,d)         | 34. (c,e) | 35. (c)       | 36. (d)       |
| 13. (b) | 14. (b) | 15. (c) | 16. (b) | 37. (a)           | 38. (b)   | 39. secondary | 40. Peroxides |
| 17. (b) | 18. (d) | 19. (a) | 20. (c) | 41. vicinal; same | 42. aldol | 43. False     | 44. False     |
| 21. (a) | 22. (b) | 23. (d) | 24. (a) | 65. (4)           |           |               |               |

## Hints &amp; Solutions

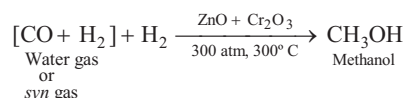
1. The given reaction takes place as follows:



Product-2 is formed because

- Cleavage-I will give more stable aryl carbocation.
- Cleavage-I will give intermediate which is in conjugation with ring.

2. The production of methanol from water gas is as follows:

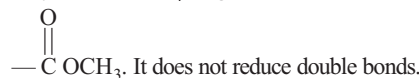


It is an industrial process used for the production of methanol where volume ratio of the reactant gases is maintained as:

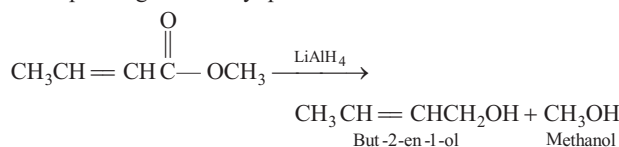
syn gas :  $\text{H}_2 = 2 : 1$  and  $\text{ZnO}-\text{Cr}_2\text{O}_3$  act as catalysts

Thus, water gas is also called *syn* gas because it is used for synthesis of methanol.

3. **Key Idea**  $\text{LiAlH}_4$  reagent is used for the reduction of  $-\text{CHO}$ ,

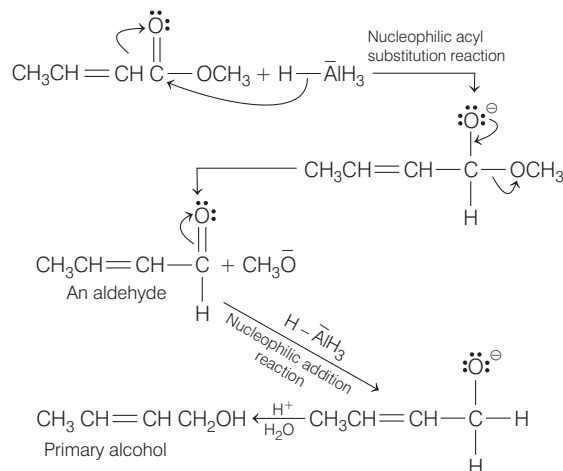


The reaction of an ester with  $\text{LiAlH}_4$  produces two alcohols, one corresponding to the acyl portion of the ester and one corresponding to the alkyl portion.



Thus, the major product of the given reactant

$\text{CH}_3\text{CH}=\text{CH}\overset{\text{O}}{\parallel}\text{C—OCH}_3$  in presence of  $\text{LiAlH}_4$  is  $\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}$  and  $\text{CH}_3\text{OH}$ . The reaction proceeds through following mechanism.

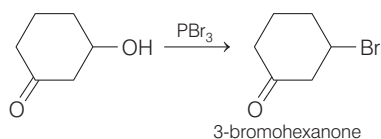
**Mechanism**

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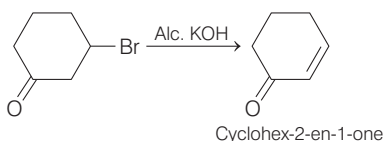
4. **Key Idea**  $\text{PBr}_3$  reagent is used for the substitution of  $-\text{OH}$  group while alc.  $\text{KOH}$  reagent is used to carry out elimination reaction.

The given reaction proceed in following manner:

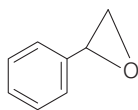
**Step I** In presence of  $\text{PBr}_3$ , alcohols undergo substitution reactions to give halides. Reagent  $\text{PBr}_3$  is usually generated *insitu* by the reaction of red phosphorus with bromine.



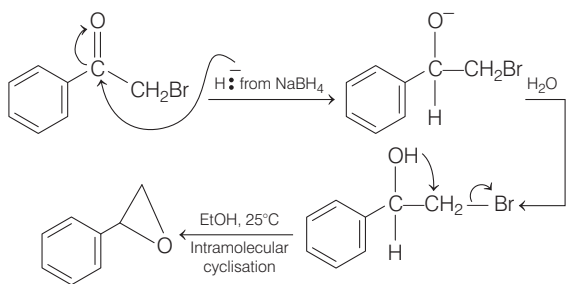
**Step II** 3-bromocyclohexanone in presence of alc.  $\text{KOH}$  undergoes elimination reaction and gives cyclohex-2-en-1-one.



5. Major product obtained in the given reaction is

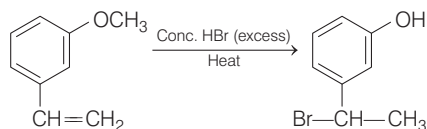


$\text{NaBH}_4$  in the reaction is used for the reduction by addition of a hydride ion and a proton. Carbon-oxygen double bonds are easily reduced by sodium borohydride. The actual reducing agent in these reductions is hydride ion ( $\text{H}^-$ ). Hydride ion adds to the carbonyl carbon and the alkoxide ion that is formed is subsequently protonated by water. In other words, the carbonyl group is reduced by adding an  $\text{H}^-$  followed by an  $\text{H}^+$ . The mechanism of the given reaction is as follows :



6. **Key Idea** Ethers are least reactive functional groups. The cleavage of  $\text{C}-\text{O}$  bond in ethers take place under drastic conditions with excess of  $\text{HX}$ .

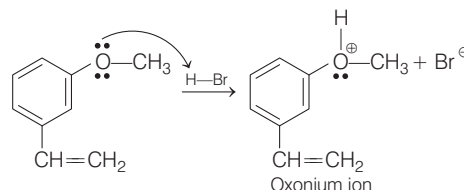
The major product obtained in the reaction is as follows :



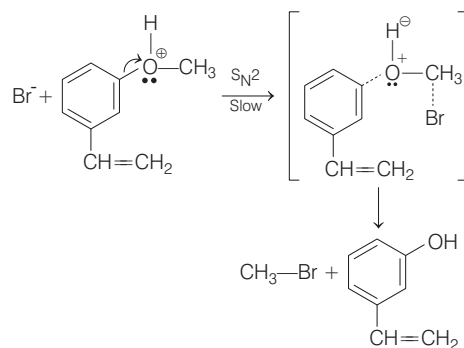
As conc.  $\text{HBr}$  is in excess. So, reaction will take place at both the substituents.

### Mechanism

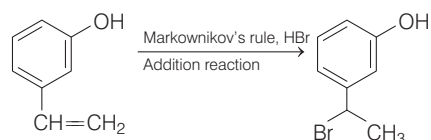
**Step 1** Protonation of ether to form oxonium ion.



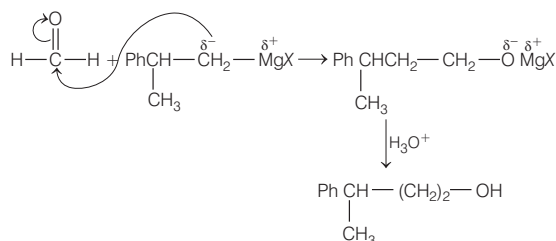
**Step 2** Attack of nucleophile at the protonated ether.



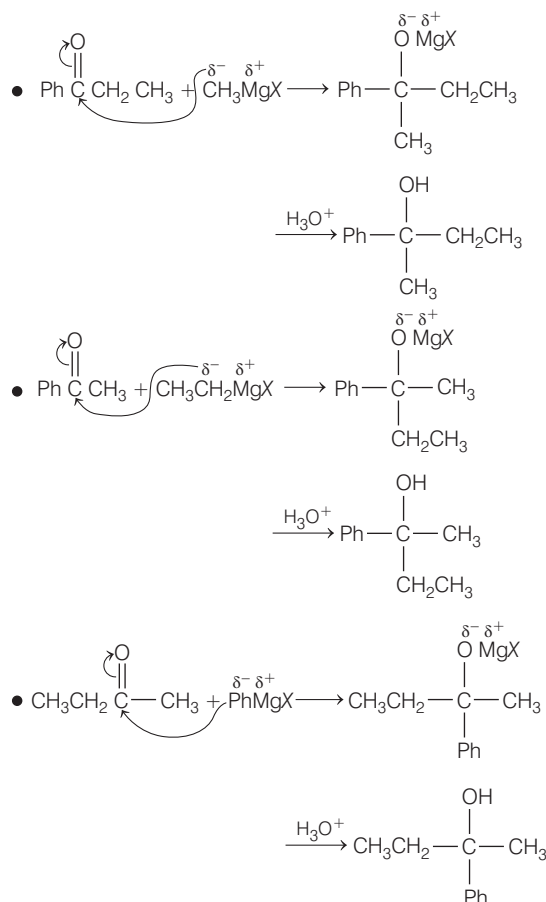
**Step 3** As  $\text{HBr}$  is in excess, so, reaction will also take place at alkene.



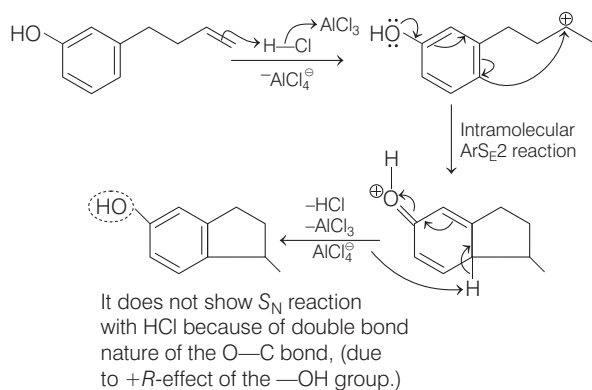
7.  $\text{CH}_3\text{CH}_2-\overset{\text{OH}}{\underset{\text{Ph}}{\text{C}}}-\text{CH}_3$  cannot be prepared by  $\text{HCHO}$  and  $\text{PhCH}(\text{CH}_3)\text{CH}_2\text{MgX}$ . This can be easily illustrated by following reaction.



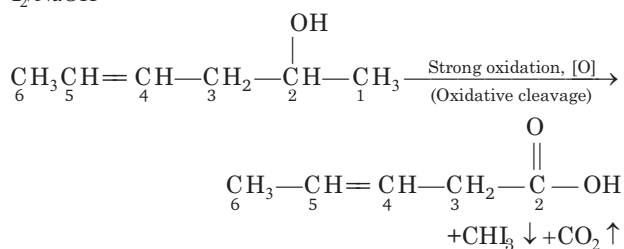
The obtained product is not the required substance. While option (a), (b) and (c) can readily prepare the required substance. The reactions are as follows :



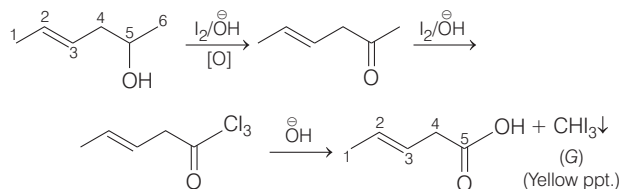
8. In the given reaction,  $\text{AlCl}_3$  helps in the generation of electrophile that further undergoes  $\text{ArS}_{\text{E}}2$  reaction to give the required product.



9. The most suitable reagent to carry out given transformation is  $\text{I}_2/\text{NaOH}$



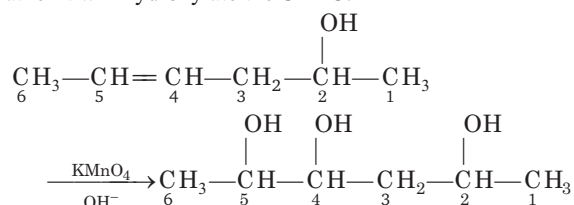
Here, the haloform reaction will give following reaction:



- (i) Tollen's reagent ( $\text{AgNO}_3 + \text{NH}_4\text{OH}$ ) is a mild oxidising agent. It does not react with  $-\overset{\text{OH}}{\mid}{\text{CH}}-\text{CH}_3$  group

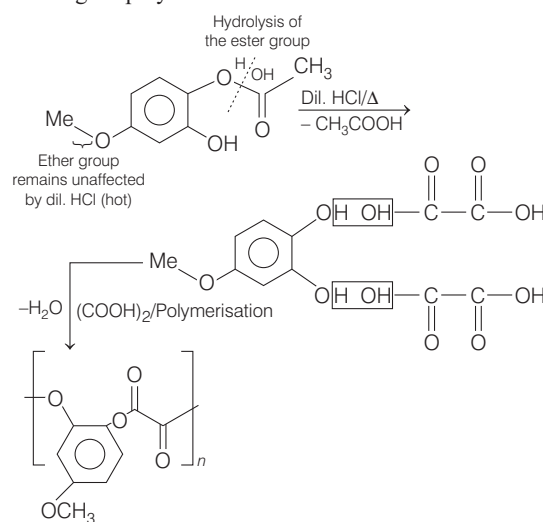
(2°-alcohol).

- (ii) Alkaline  $\text{KMnO}_4$  cannot perform the oxidative cleavage, rather it will hydroxylate the  $\text{C}=\text{C}$ .

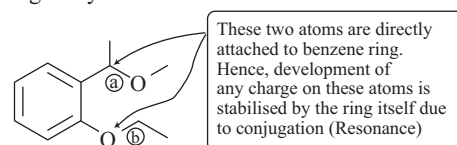


- (iv)  $\text{CrO}_2\text{Cl}_2 / \text{CS}_2$  will not react here.

10. In the given reaction, ester get cleaved in presence of dil.  $\text{HCl}$  and readily forms alcohol. This alcohol on reaction with oxalic acid undergoes polymerisation reaction.



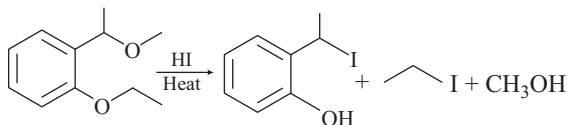
11. **Key idea** The reaction given is a nucleophilic substitution reaction in which cleavage at  $\text{C}-\text{O}$  bond is visible. The product formation can be visualised with the help of following analysis.



If any one properly visualise the fact written with figure above, than a conclusion can be made that  $\text{C}-\text{O}$  bonds marked (a) and (b) in the figure will undergo heterolysis during the reaction.

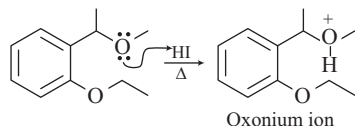
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The reaction can be represented as

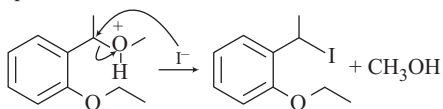


### Mechanism

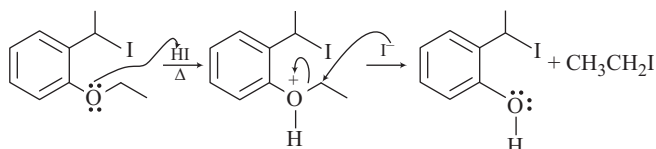
**Step I** The reaction begins with the attack of  $\text{H}^+$  of HI on oxygen to form oxonium ion as



**Step II** This oxonium ion undergoes lysis and addition of  $\text{I}^-$  to form two products as



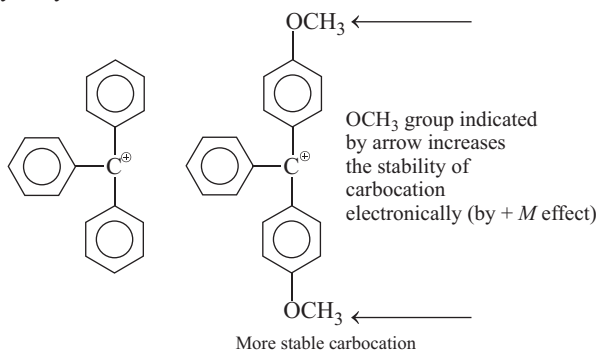
**Step III** Similar pathway is followed at the other oxygen atom, which can be visualised as



**Note** Mechanism of a reaction is always a logical sequencing of events which may occur simultaneously as well.

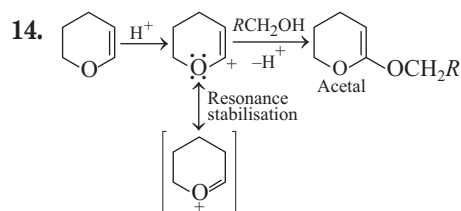
- 12. PLAN** This problem can be solved by using the concept of stability of carbocation and  $\text{S}_{\text{N}}1$  reaction.

When two phenyl groups are replaced by two *para* methoxy group, carbocation formed will be more stable. As the stability of carbocation formed increases, rate of acidic hydrolysis increases.

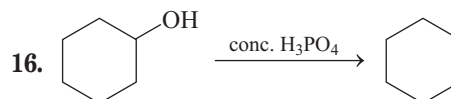
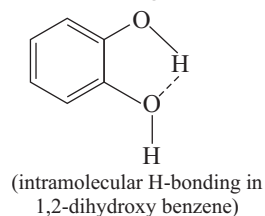


Hence, (c) is the correct choice.

- 13.** The reaction of alcohol with Lucas reagent is mostly an  $\text{S}_{\text{N}}1$  reaction and the rate of reaction is directly proportional to the stability of carbocation formed in the reaction. Since  $3^\circ$   $\text{R}-\text{OH}$  forms  $3^\circ$  carbocation (most stable), hence it will react fastest.

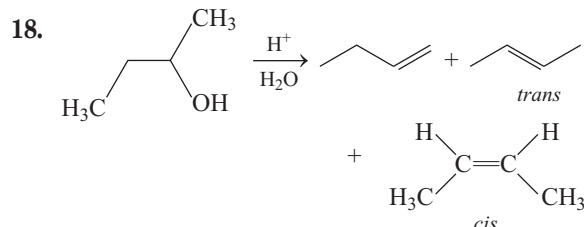


- 15.** All dihydroxy benzene will have higher boiling points than monohydroxy benzene. Also, among dihydroxy benzenes, 1, 2,-di-hydroxy benzene has lowest boiling point due to intramolecular H-bonding.

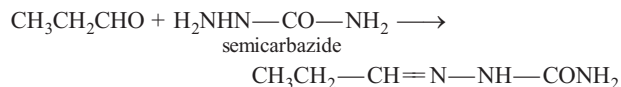


Concentrated  $\text{H}_3\text{PO}_4$  solution does not involve any substitution product while with others, substitution products are also formed.

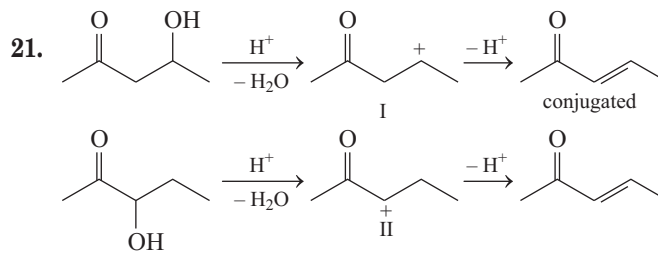
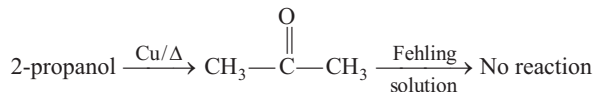
- 17.**  $\text{C}_6\text{H}_5\text{MgBr} + (\text{CH}_3)_3\text{COH} \longrightarrow \text{C}_6\text{H}_6 + \text{Mg}[(\text{CH}_3)_3\text{CO}]\text{Br}$



- 19.** A is an alcohol and its oxidation product gives Tollen's test, i.e. B must be an aldehyde ( $\text{CH}_3\text{CH}_2\text{CHO}$ ).



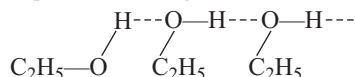
- 20.** 1-propanol  $\xrightarrow{\text{Cu}/\Delta}$   $\text{CH}_3-\text{CH}_2-\text{CHO}$   $\xrightarrow[\text{red}]{\text{Fehling solution}}$   $\text{Cu}_2\text{O} \downarrow$



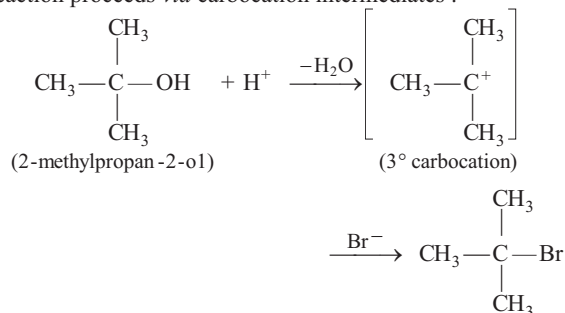


Although both reactions are giving the same product, carbocation I is more stable than II.

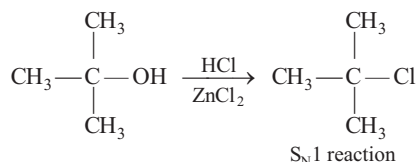
22. Thiol, (RSH), on combustion produces  $\text{CO}_2$  (g),  $\text{SO}_2$  (g) and  $\text{H}_2\text{O}$  (l). At 298 K,  $\text{H}_2\text{O}$  will be in liquid phase.
23.  $\text{OH}^- \longrightarrow \text{O}^- + \text{H}^+$  (has maximum electronegativity difference)
24. Ethanol is capable in forming intermolecular H-bonds :



25. Reaction proceeds via carbocation intermediates :



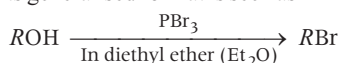
26.  $\text{CO} + \text{H}_2 \xrightarrow[\text{heat}]{\text{ZnO-Cr}_2\text{O}_3} \text{CH}_3\text{OH}$
27.  $\text{CH}_3 - \text{CH}_2 - \text{O} - \text{CH}_2 - \text{CH}_3 + \text{HI} \longrightarrow 2\text{C}_2\text{H}_5\text{I}$
28. 2-methyl propan-2-ol is a tertiary alcohol, will react fastest with Lucas reagent :



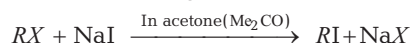
29. On heating with concentrated  $\text{H}_2\text{SO}_4$ , ethanol would undergo dehydration to produce ethene.
30. Ethanol is soluble in water due to its ability to form intermolecular H-bonds with water :
31. **Key idea** All the reactions involved in the problem are Nucleophilic substitution of second order i.e.,  $\text{S}_{\text{N}}2$  which have the speciality of inversion of configuration at the carbon atom involved.

Of the reactions given

**Reaction 1** in its generalised format is seen as



**Reaction 2** is simple halogen exchange reaction called **Finkelstein reaction**. Its generalised format is

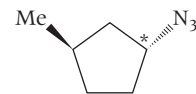


where  $\text{X} = \text{Cl}$  or  $\text{Br}$

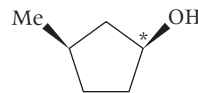
**Reaction 3** in its generalised format seen as



Now if the given product is

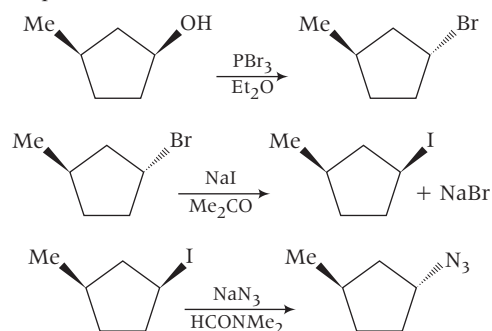


and which is too enantiomerically pure i.e. 100% either dextrorotatory or levorotatory form, then the 'X' must be

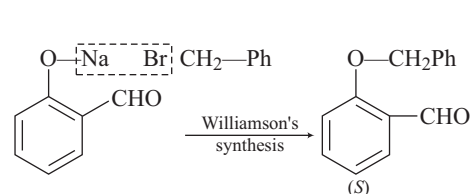
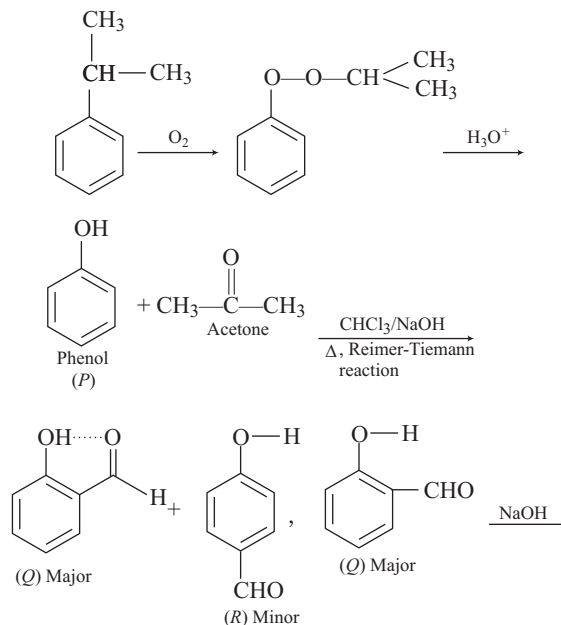


**Note** The configuration at carbon \* atom in 'X' becomes inverted due to  $\text{S}_{\text{N}}2$  mechanism which is visible in the product as well.

Thus, the probable reactions will be



32.



- (a)  $R$  is not steam volatile, but  $Q$  is steam volatile thus, incorrect.
- (b)  $Q$  has enolic group thus, gives violet colour with 1% aqueous  $\text{FeCl}_3$  solution thus, correct.

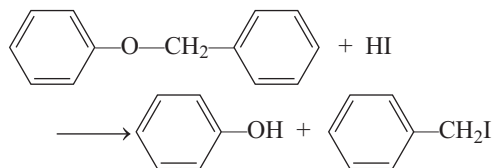


## 350 Alcohols and Ethers

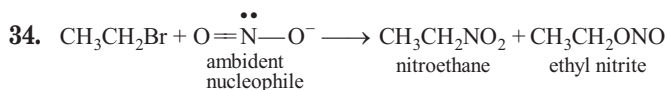
(c) *S* has carbonyl group hence, gives yellow precipitate with 2, 4-DNP thus, correct.

(d) *S* does not give colour with  $\text{FeCl}_3$  thus, incorrect.

33.



Phenol does not react further with HI.



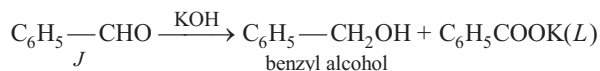
35.  $\text{R}-\text{OH} \leftarrow$  Hydrophilic

Hydrophobic

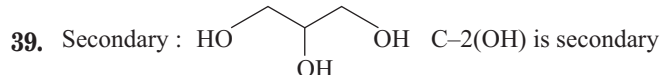
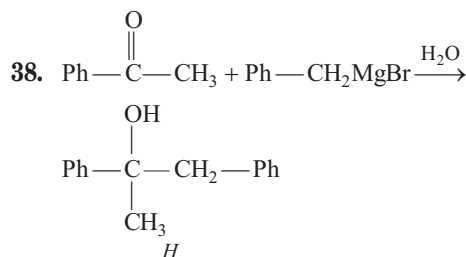
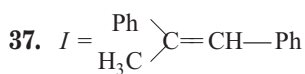
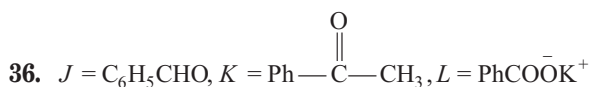
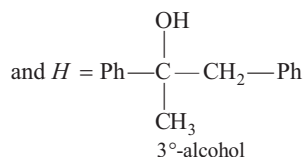
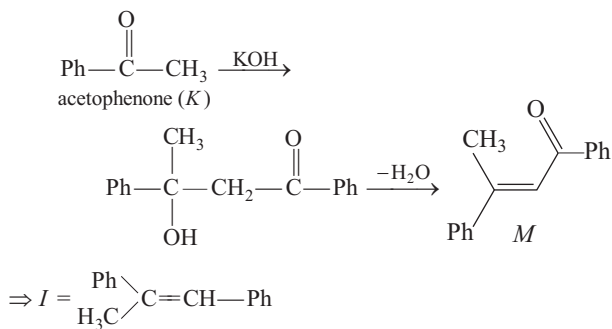
Increasing molecular weight increases hydrocarbon (*R*) proportion that lowers the solubility in water.

### Passage 1

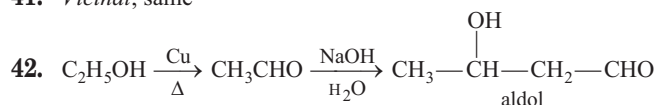
Compound *J* must be benzaldehyde because it on treatment with KOH undergoing Cannizzaro's reaction producing benzyl alcohol and pot-benzoate (*L*).



Also *M* is aldol condensation product formed from acetophenone

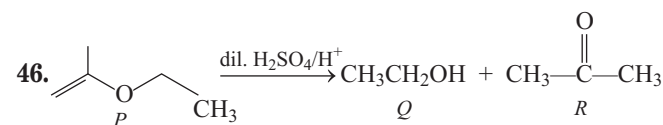
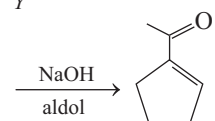
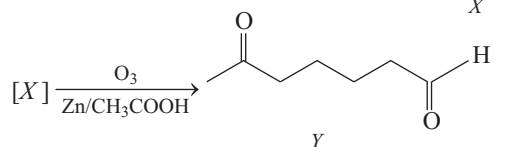
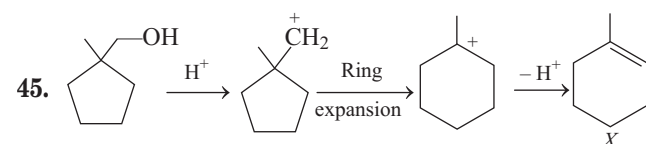


41. Vicinal, same

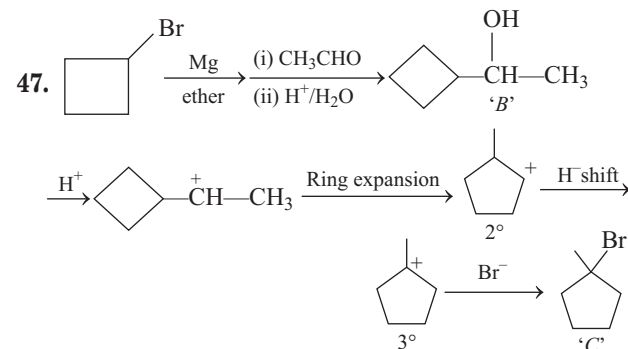


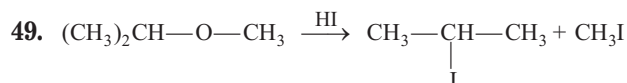
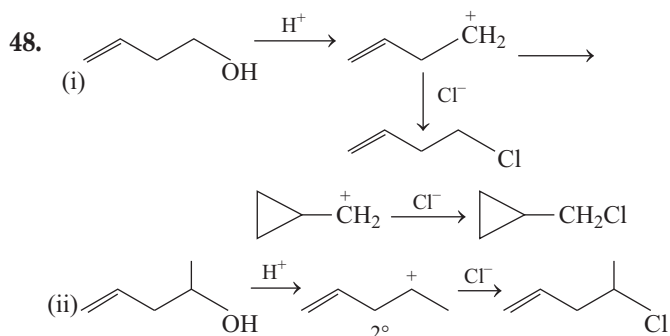
43. Ethanol is weaker acid than water, not neutralised with NaOH.

44. 2°-alcohol on oxidation yields ketone while 1°alcohol on oxidation produces aldehyde which can further be oxidised to acid.

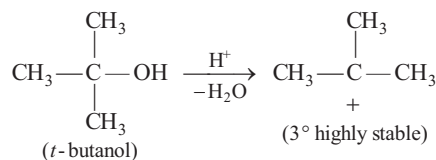


$\xrightarrow{\text{I}_2/\text{NaOH}}$  Both gives positive iodoform test.

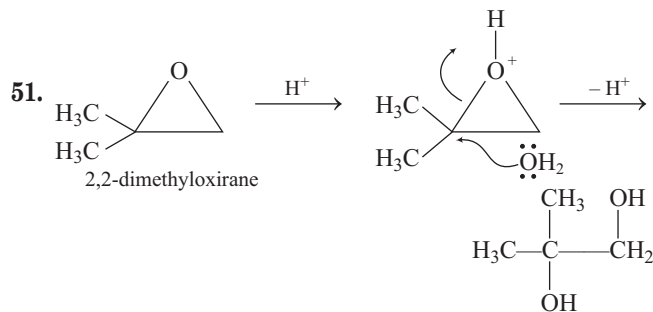




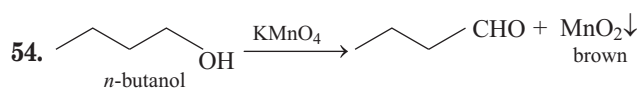
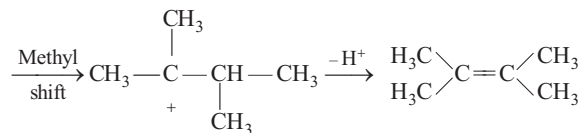
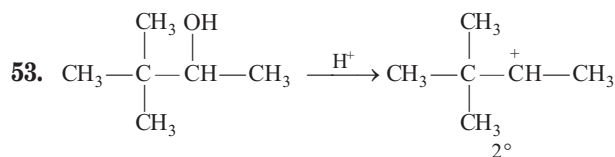
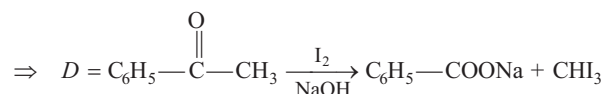
50. Acid catalysed dehydration proceeds *via* carbocation intermediate. Also, greater the stability of reactive intermediate, faster the reaction :



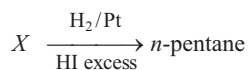
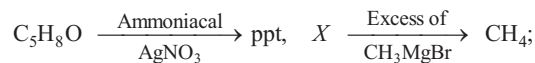
*n*-butanol forms less stable ( $1^\circ$ ) carbocation.



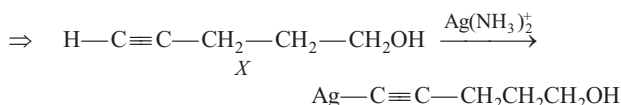
52.  $E = \text{C}_6\text{H}_5\text{COOH}$  (benzoic acid)



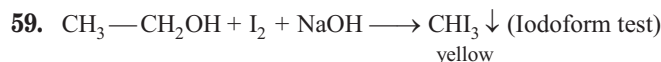
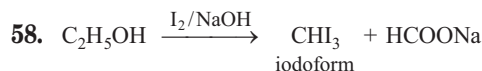
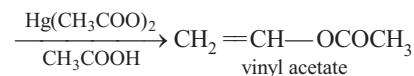
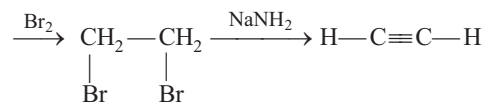
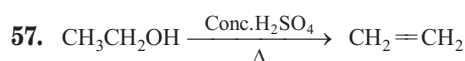
55. Compound 'X'  $\xrightarrow{\text{Lucas reagent}}$  No reaction at room temperature.



Above information suggest that X has a terminal triple bond and it contain primary  $-\text{OH}$  group.

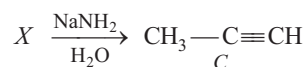
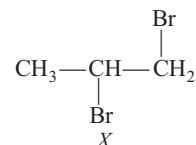
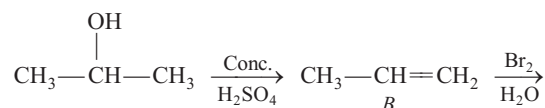
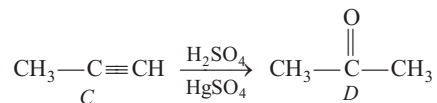
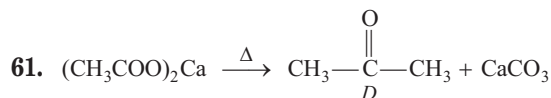


56. Isobutane < *n*-butane < *n*-butylchloride < *n*-butanol

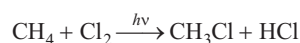
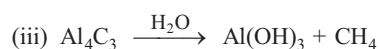
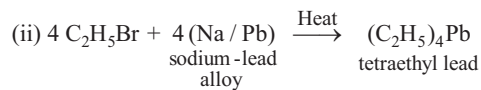
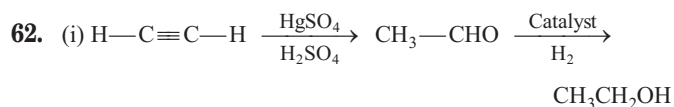


Iodoform test is not given by methanol.

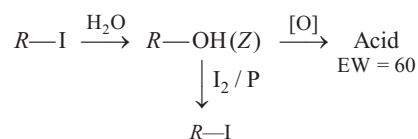
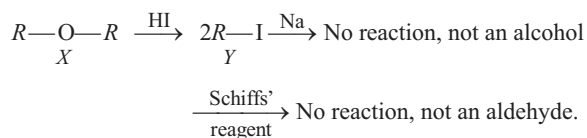
60. Butanol forms intermolecular H-bonds, has higher boiling point than butanal.



## 352 Alcohols and Ethers

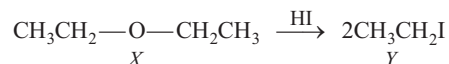


63. Compound *X* must be a symmetrical ether :

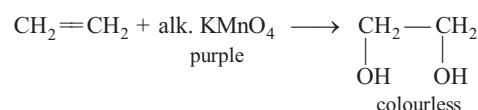
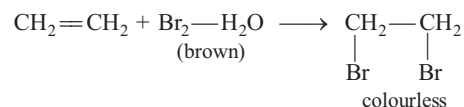
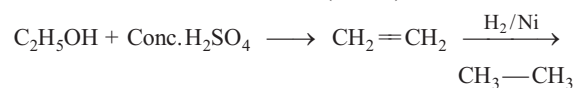


$\Rightarrow$  Acid is  $\text{CH}_3\text{COOH}$  and  $\text{Z} = \text{CH}_3\text{CH}_2\text{OH}$

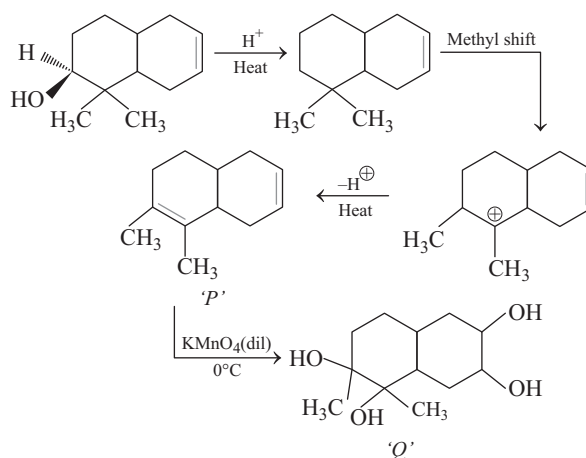
$\Rightarrow \text{X} = \text{C}_2\text{H}_5-\text{O}-\text{C}_2\text{H}_5, \text{Y} = \text{CH}_3-\text{CH}_2-\text{I}$



64. *A* is ethanol because *B* is an alkene (ethene).



65.



**Download Chapter Test**

<http://tinyurl.com/yy5jdmfu> or

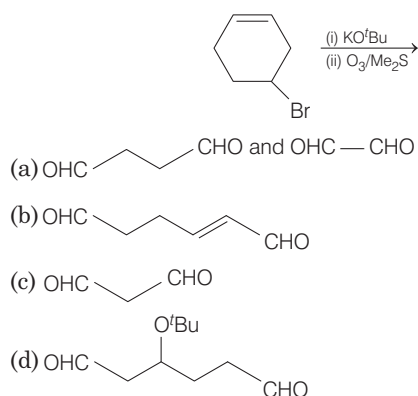


# 25

## Aldehydes and Ketones

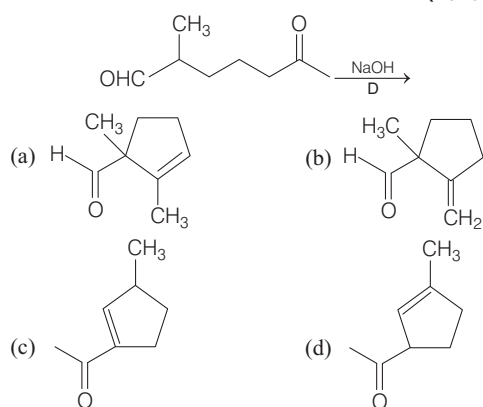
### Objective Questions I (Only one correct option)

1. The major product(s) obtained in the following reaction is/are  
(2019 Main, 12 April I)

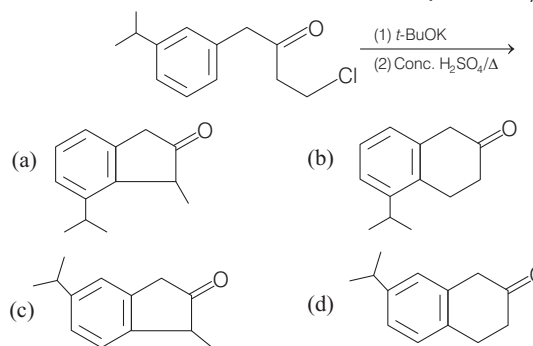


2. In the following reaction,  
 $\text{Carbonyl compound} + \text{MeOH} \xrightleftharpoons{\text{HCl}} \text{acetal}$   
 Rate of the reaction is the highest for: (2019 Main, 9 April II)
- (a) Acetone as substrate and methanol in excess  
 (b) Propanal as substrate and methanol in stoichiometric amount  
 (c) Acetone as substrate and methanol in stoichiometric amount  
 (d) Propanal as substrate and methanol in excess

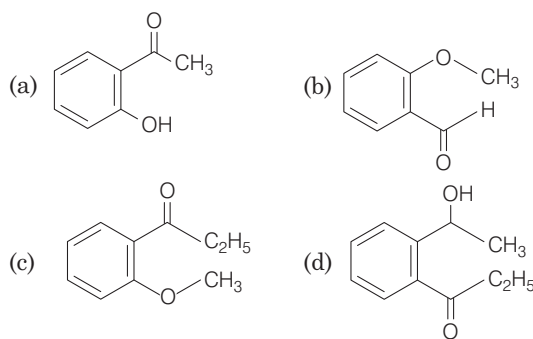
3. The major product obtained in the following reaction is  
(2019 Main, 8 April II)



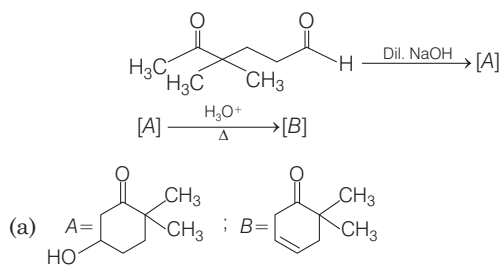
4. The major product of the following reaction is  
(2019 Main, 8 April II)



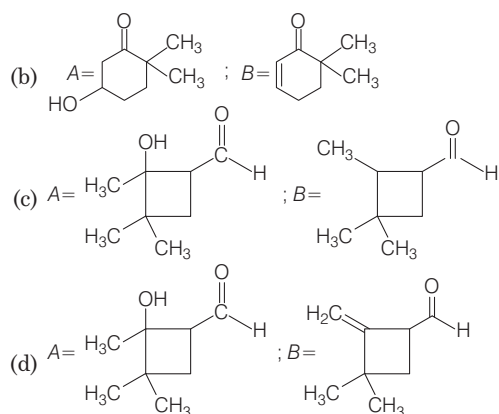
5. An organic compound neither reacts with neutral ferric chloride solution nor with Fehling solution. It however, reacts with Grignard reagent and gives positive iodoform test. The compound is  
(2019 Main, 8 April I)



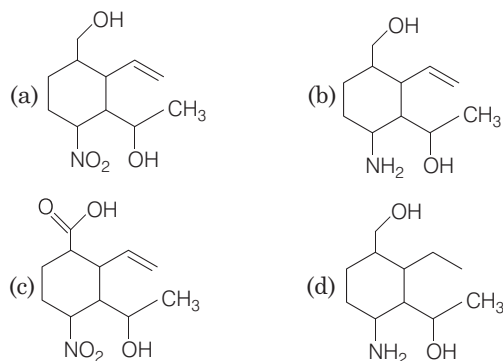
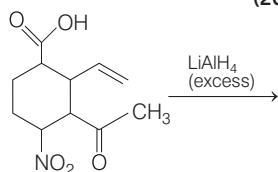
6. In the following reactions, products A and B are  
(2019 Main, 12 Jan I)



## 354 Aldehydes and Ketones



7. The major product obtained in the following reaction is  
(2019 Main, 11 Jan II)



8. The correct match between item 'I' and item 'II' is

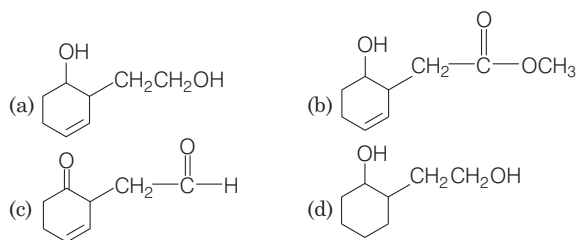
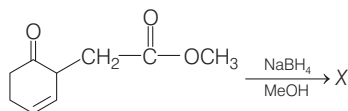
| Item 'I'<br>(Compound) | Item 'II'<br>(Reagent)     |
|------------------------|----------------------------|
| (A) Lysine             | (P) 1-naphthol             |
| (B) Furfural           | (Q) Ninhydrin              |
| (C) Benzyl alcohol     | (R) $\text{KMnO}_4$        |
| (D) Styrene            | (S) Ceric ammonium nitrate |

(2019 Main, 10 Jan II)

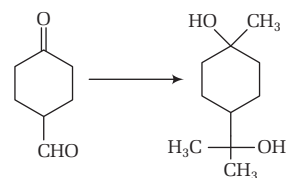
### Codes

|       |   |   |   |
|-------|---|---|---|
| A     | B | C | D |
| (a) Q | R | S | P |
| (b) R | P | Q | S |
| (c) Q | P | S | R |
| (d) Q | P | R | S |

9. The major product 'X' formed in the following reaction is  
(2019 Main, 10 Jan I)

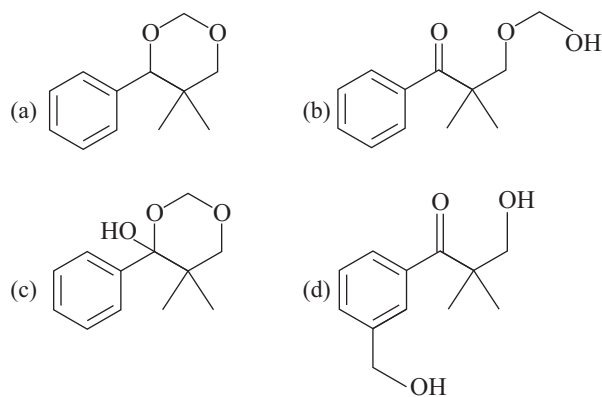
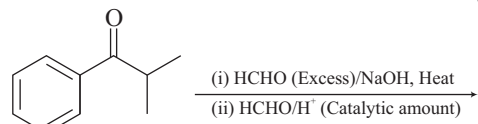


10. The correct sequence of reagents for the following conversion will be  
(2017 Main)

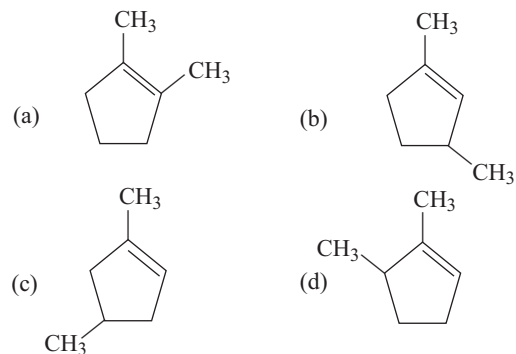


- (a)  $[\text{Ag}(\text{NH}_3)_2]^+ \text{OH}^-$ ,  $\text{H}^+$  /  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{MgBr}$   
 (b)  $\text{CH}_3\text{MgBr}$ ,  $\text{H}^+$  /  $\text{CH}_3\text{OH}$ ,  $[\text{Ag}(\text{NH}_3)_2]^+ \text{OH}^-$   
 (c)  $\text{CH}_3\text{MgBr}$ ,  $[\text{Ag}(\text{NH}_3)_2]^+ \text{OH}^-$ ,  $\text{H}^+$  /  $\text{CH}_3\text{OH}$   
 (d)  $[\text{Ag}(\text{NH}_3)_2]^+ \text{OH}^-$ ,  $\text{CH}_3\text{MgBr}$ ,  $\text{H}^+$  /  $\text{CH}_3\text{OH}$

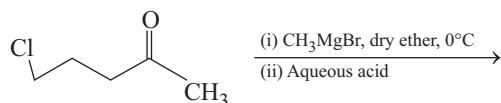
11. The major product of the following reaction sequence is  
(2016 Adv.)

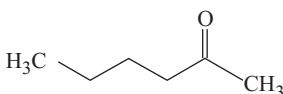
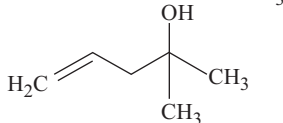
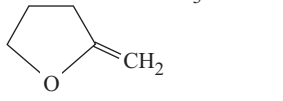
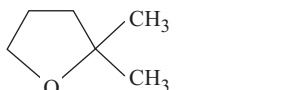


12. Which compound would give 5-keto-2-methyl hexanal upon ozonolysis?  
(2015 Main)



13. The major product in the following reaction is (2014 Adv.)

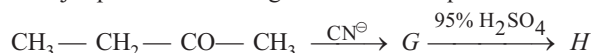


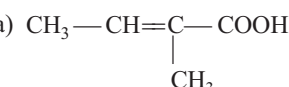
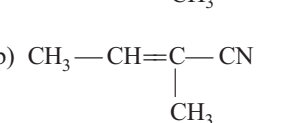
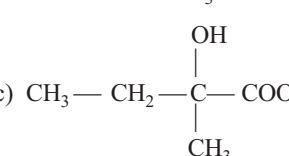
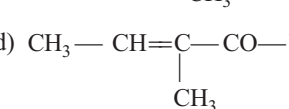
- (a)   
 (b)   
 (c)   
 (d) 

14. The most suitable reagent for the conversion of  $R-\text{CH}_2-\text{OH} \rightarrow R-\text{CHO}$  is (2014 Main)

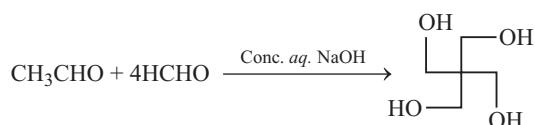
- (a)  $\text{KMnO}_4$   
 (b)  $\text{K}_2\text{Cr}_2\text{O}_7$   
 (c)  $\text{CrO}_3$   
 (d) PCC (pyridinium chlorochromate)

15. The major product H in the given reaction sequence is



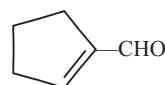
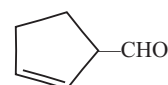
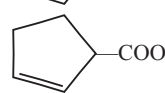
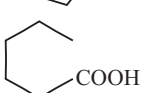
- (a)   
 (b)   
 (c)   
 (d) 

16. The number of aldol reaction(s) that occurs in the given transformation is (2012)



- (a) 1  
 (b) 2  
 (c) 3  
 (d) 4

17. Cyclohexene on ozonolysis followed by reaction with zinc dust and water gives compound E. Compound E on further treatment with aqueous KOH yields compound F. Compound F is (2007, 3M)

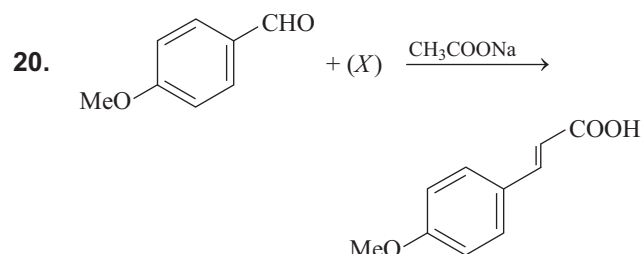
- (a)   
 (b)   
 (c)   
 (d) 

18. The smallest ketone and its next homologue are reacted with  $\text{NH}_2\text{OH}$  to form oxime (2006)

- (a) two different oximes are formed  
 (b) three different oximes are formed  
 (c) two oximes are optically active  
 (d) all oximes are optically active

19. Butan-2-one can be converted to propanoic acid by which of the following? (2006)

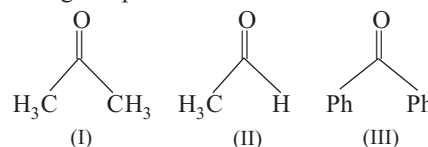
- (a)  $\text{NaOH}$ ,  $\text{NaI}/\text{H}^+$   
 (b) Fehling's solution  
 (c)  $\text{NaOH}$ ,  $\text{I}_2/\text{H}^+$   
 (d) Tollen's reagent



What is X?

- (a)  $\text{CH}_3\text{COOH}$   
 (b)  $\text{BrCH}_2\text{COOH}$   
 (c)  $(\text{CH}_3\text{CO})_2\text{O}$   
 (d)  $\text{HOC}-\text{COOH}$

21. The order of reactivity of phenyl magnesium bromide with the following compounds is (2004, 1M)



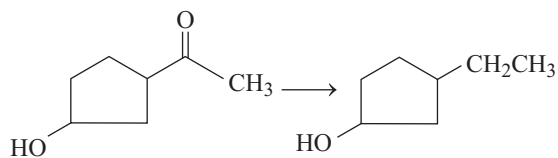
- (a) (II) > (III) > (I)  
 (b) (I) > (III) > (II)  
 (c) (II) > (I) > (III)  
 (d) All of the above

22. A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives (2001, 1M)

- (a) benzyl alcohol and sodium formate  
 (b) sodium benzoate and methyl alcohol  
 (c) sodium benzoate and sodium formate  
 (d) benzyl alcohol and methyl alcohol

## 356 Aldehydes and Ketones

23. The appropriate reagent for the following transformation:

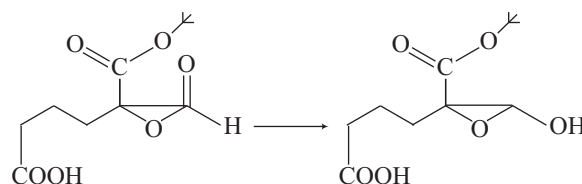


- (a) Zn (Hg), HCl (b)  $\text{NH}_2\text{NH}_2$ ,  $\text{OH}^-$   
 (c)  $\text{H}_2/\text{Ni}$  (d)  $\text{NaBH}_4$
24. Which of the following has the most acidic hydrogen? (2000, 1M)  
 (a) 3-hexanone (b) 2, 4-hexanedione  
 (c) 2, 5-hexanedione (d) 2, 3-hexanedione
25. The enol form of acetone, after treatment with  $\text{D}_2\text{O}$ , gives (1999, 2M)  
 (a)  $\text{H}_3\text{C}-\text{C}(\text{OD})=\text{CH}_2$  (b)  $\text{D}_3\text{C}-\text{C}(\text{OD})=\text{CD}_3$   
 (c)  $\text{H}_2\text{C}=\text{C}(\text{OH})-\text{CH}_2\text{D}$  (d)  $\text{D}_2\text{C}=\text{C}(\text{OD})-\text{CD}_3$
26. Which of the following will react with water? (1998, 2M)  
 (a)  $\text{CHCl}_3$  (b)  $\text{Cl}_3\text{CCHO}$   
 (c)  $\text{CCl}_4$  (d)  $\text{ClCH}_2\text{CH}_2\text{Cl}$
27. Which of the following compounds is oxidised to prepare methyl ethyl ketone? (1987, 1M)  
 (a) 2-propanol (b) 1-butanol  
 (c) 2-butanol (d) *t*-butyl alcohol
28. The compound that will not give iodoform on treatment with alkali and iodine is (1985, 1M)  
 (a) acetone (b) ethanol  
 (c) diethyl ketone (d) isopropyl alcohol
29. The Cannizzaro's reaction is not given by (1983, 1M)  
 (a) trimethyl acetaldehyde  
 (b) acetaldehyde  
 (c) benzaldehyde  
 (d) formaldehyde
30. When acetaldehyde is treated with Fehling's solution, it gives a precipitate of (1983, 1M)  
 (a) Cu (b) CuO  
 (c)  $\text{Cu}_2\text{O}$  (d)  $\text{Cu} + \text{Cu}_2\text{O} + \text{CuO}$
31. A compound that gives a positive iodoform test is (1982, 1M)  
 (a) 1-pentanol (b) 3-pentanone  
 (c) 2-pentanone (d) pentanal
32. The reagent with which both acetaldehyde and acetone react easily is (1981, 1M)  
 (a) Tollen's reagent (b) Schiff's reagent  
 (c) Grignard's reagent (d) Fehling's reagent

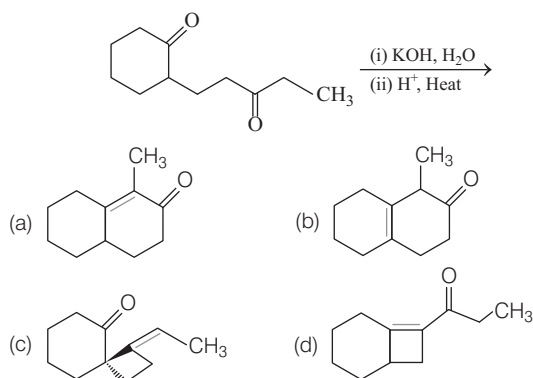
## Objective Questions II

(One or more than one correct option)

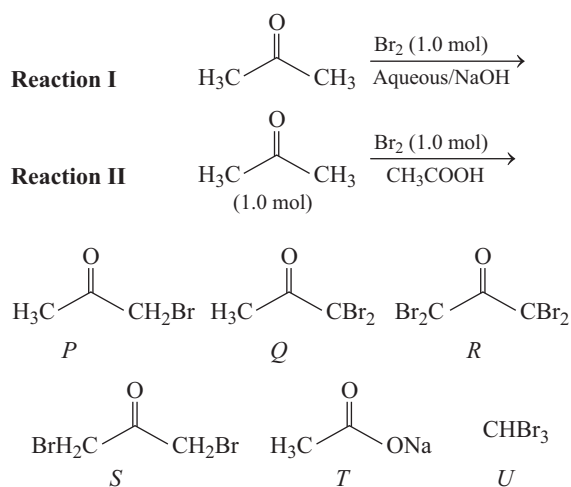
33. Reagent(s) which can be used to bring about the following transformation is (are) (2016 Adv.)



- (a)  $\text{LiAlH}_4$  in  $(\text{C}_2\text{H}_5)_2\text{O}$  (b)  $\text{BH}_3$  in THF  
 (c)  $\text{NaBH}_4$  in  $\text{C}_2\text{H}_5\text{OH}$  (d) Raney Ni/ $\text{H}_2$  in THF
34. The major product of the following reaction is (2015 Adv.)



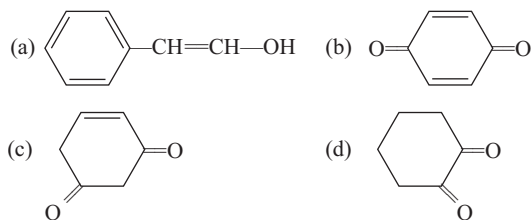
35. After completion of the reactions (I and II), the organic compound (s) in the reaction mixtures is/are (2013)



- (a) reaction I : *P* and reaction II : *P*  
 (b) reaction I : *U*, acetone and reaction II : *Q*, acetone  
 (c) reaction I : *T*, *U*, acetone and reaction II : *P*  
 (d) reaction I : *R*, acetone and reaction II : *S*, acetone



36. Tautomerism is exhibited by (1998)



37. A new carbon-carbon bond formation is possible in (1998, 2M)

- (a) Cannizzaro's reaction  
(b) Friedel-Crafts' reaction  
(c) Clemmensen's reduction  
(d) Reimer-Tiemann reaction

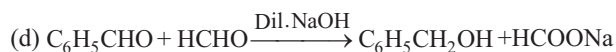
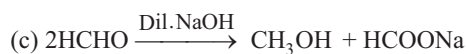
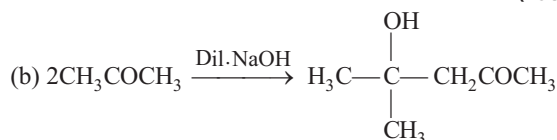
38. Which of the following will undergo aldol condensation? (1998, 2M)

- (a) Acetaldehyde  
(b) Propanaldehyde  
(c) Benzaldehyde  
(d) Trideutero acetaldehyde

39. Among the following compounds, which will react with acetone to give a product containing  $\text{>C=N-}$ ?

- (a)  $\text{C}_6\text{H}_5\text{NH}_2$  (b)  $(\text{CH}_3)_3\text{N}$  (1998, 2M)  
(c)  $\text{C}_6\text{H}_5\text{NHC}_6\text{H}_5$  (d)  $\text{C}_6\text{H}_5\text{NHNH}_2$

40. Which of the following is an example of aldol condensation?



41. Which of the following compounds will react with ethanolic KCN? (1984, 1M)

- (a) Ethyl chloride (b) Acetyl chloride  
(c) Chlorobenzene (d) Benzaldehyde

42. Which of the following compounds will give a yellow precipitate with iodine and alkali? (1984, 1M)

- (a) 2-hydroxy propane  
(b) Acetophenone  
(c) Methyl acetate  
(d) Acetamide

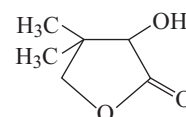
43. Base catalysed aldol condensation occurs with (1984, 1M)

- (a) propionaldehyde  
(b) benzaldehyde  
(c) 2-methyl propionaldehyde  
(d) 2, 2-dimethyl propionaldehyde

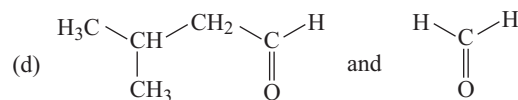
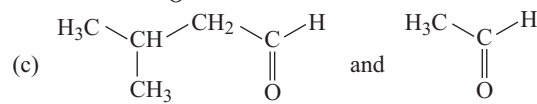
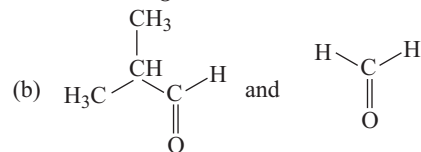
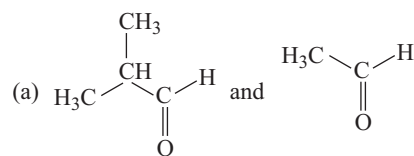
## Passage Based Questions

### Passage 1

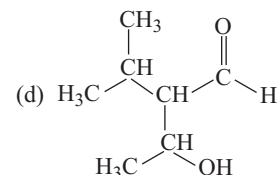
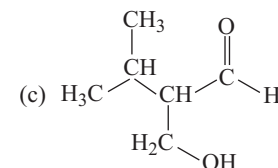
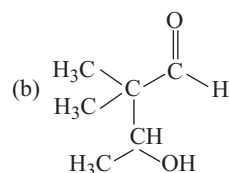
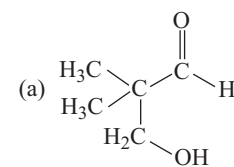
Two aliphatic aldehydes *P* and *Q* react in the presence of aqueous  $\text{K}_2\text{CO}_3$  to give compound *R*, which upon treatment with HCN provides compound *S*. On acidification and heating, *S* gives the product shown below : (2010)



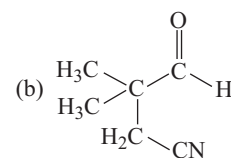
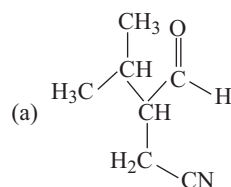
44. The compounds *P* and *Q* respectively are



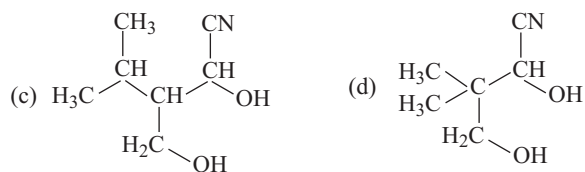
45. The compound *R* is



46. The compound *S* is

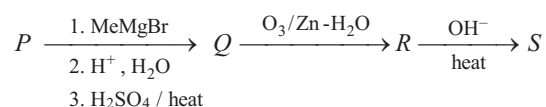


## 358 Aldehydes and Ketones

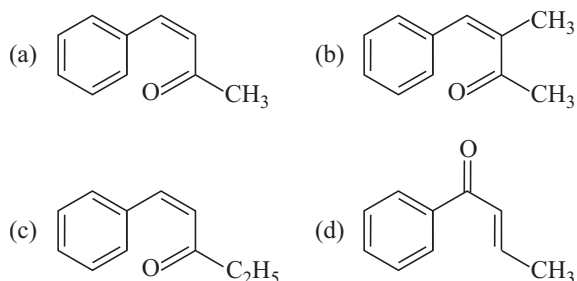


### Passage 2

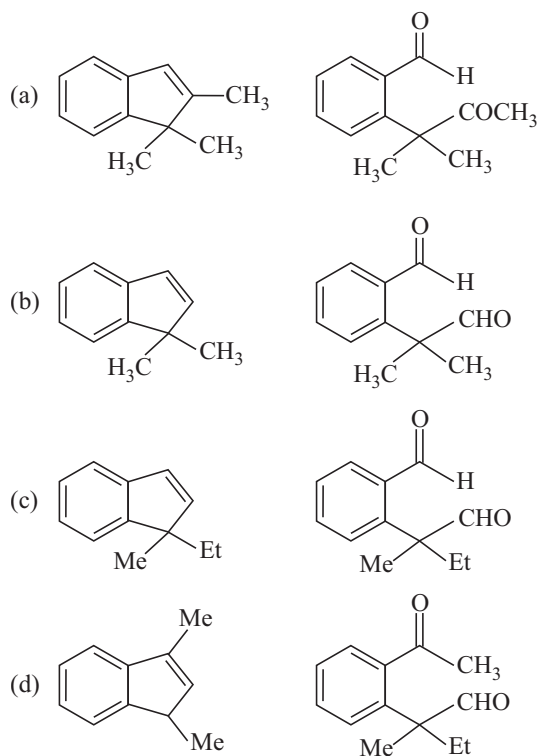
A carbonyl compound *P*, which gives positive iodoform test, undergoes reaction with  $\text{MeMgBr}$  followed by dehydration to give an olefin *Q*. Ozonolysis of *Q* leads to a dicarbonyl compound *R*, which undergoes intramolecular aldol reaction to give predominantly *S*. (2009)



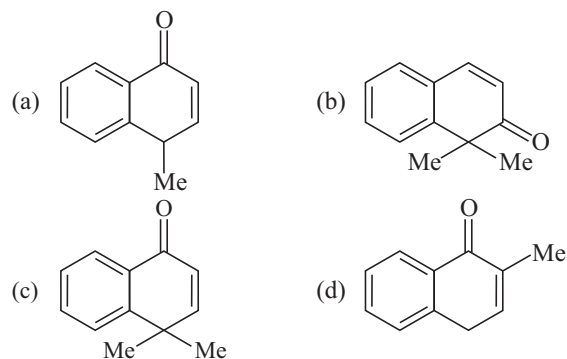
47. The structure of the carbonyl compound *P*, is



48. The structures of the products *Q* and *R*, respectively, are

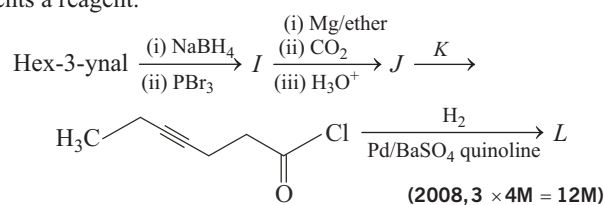


49. The structure of the product *S*, is

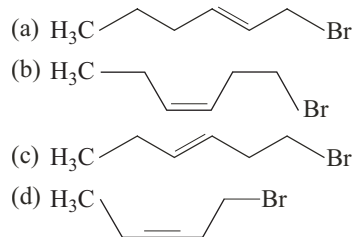


### Passage 3

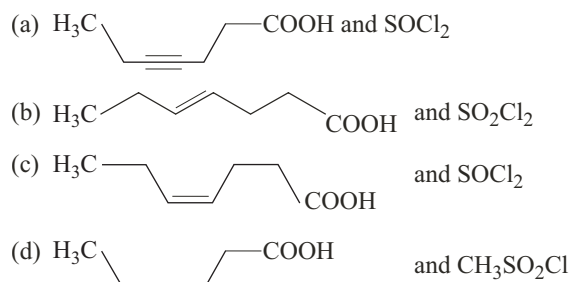
In the following sequence, product *I*, *J* and *L* are formed. *K* represents a reagent.



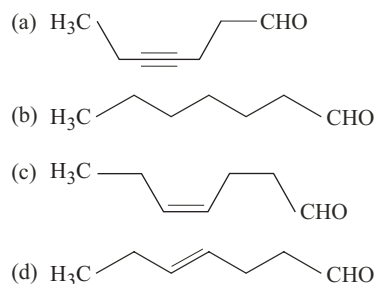
50. The structure of the product *I* is



51. The structures of compounds *J* and *K*, respectively, are

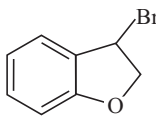
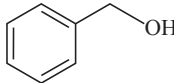
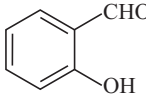
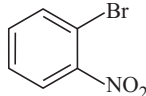


52. The structure of product *L* is



## Match the Column

53. Match each of the compounds given in Column I with the reaction(s) that they can undergo, given in Column II.

| Column I                                                                             | Column II                               |
|--------------------------------------------------------------------------------------|-----------------------------------------|
| A.  | p. Nucleophilic substitution            |
| B.  | q. Elimination                          |
| C.  | r. Nucleophilic addition                |
| D.  | s. Esterification with acetic anhydride |
|                                                                                      | t. Dehydrogenation                      |

54. Match the compounds/ions in Column I with their properties/reactions in Column II. (2007, 6M)

| Column I            | Column II                                             |
|---------------------|-------------------------------------------------------|
| A. $C_6H_5CHO$      | p. gives precipitate with 2, 4-dinitrophenylhydrazine |
| B. $CH_3C\equiv CH$ | q. gives precipitate with $AgNO_3$                    |
| C. $CN^-$           | r. is a nucleophile                                   |
| D. $I^-$            | s. is involved in cyanohydrin formation               |

## Fill in the Blanks

55. Fehling's solution *A* consists of an aqueous solution of copper sulphate, while Fehling's solution *B* consists of an alkaline solution ..... (1990, 1M)

## True or False

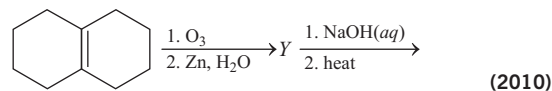
56. The reaction of methyl magnesium iodide with acetone followed by hydrolysis gives secondary butanol. (1987, 1M)
57. Benzaldehyde undergoes aldol condensation in an alkaline medium. (1982, 1M)

## Integer Answer Type Questions

58. Consider all possible isomeric ketones including stereoisomers of MW = 100. All these isomers are independently reacted with  $NaBH_4$ . The total number of ketones that gives a racemic product(s) is/are

NOTE (Stereoisomers are also reacted separately). (2014 Adv.)

59. In the scheme given below, the total number of intramolecular aldol condensation products formed from *Y* is



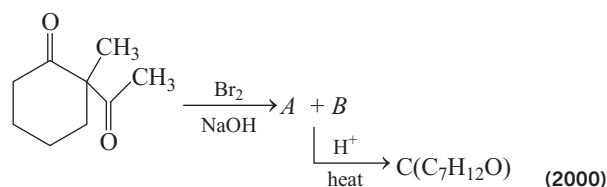
## Subjective Questions

60. (*A*),  $C_6H_{12} \xrightarrow{HCl}$  (*B*),  $C_6H_{13}Cl$  + (*C*),  $C_6H_{13}Cl$   
 (*B*)  $\xrightarrow{\text{Alcoholic KOH}}$  (*D*), (an isomer of (*A*))  
 (*D*)  $\xrightarrow{\text{Ozonolysis}}$  (*E*), (positive iodoform and negative Fehling's solution test)  
 (*A*)  $\xrightarrow{\text{Ozonolysis}}$  (*F*) + (*G*), (positive Tollen's test for both)  
 (*F*) + (*G*)  $\xrightarrow{\text{Conc. NaOH}}$   $HCOONa$  + A primary alcohol  
 Identify the compounds (*A*) to (*D*). (2003)

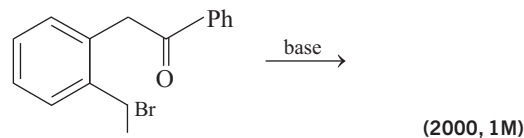
61. A compound  $C_9H_7O_2Cl$  exists predominantly in enol form (*A*) and also in keto form (*B*). On oxidation with  $KMnO_4$  it gives *m*-chlorobenzoic acid as one of the products. Identify the compounds (*A*) and (*B*). (2003)

62. An alkene (*A*)  $C_{16}H_{16}$  on ozonolysis gives only one product (*B*)  $C_8H_8O$ . Compound (*B*) on reaction with  $NaOH / I_2$  yields sodium benzoate. Compound (*B*) reacts with  $KOH / NH_2NH_2$  yielding a hydrocarbon (*C*)  $C_8H_{10}$ . Write the structures of compounds (*B*) and (*C*). Based on this information two isomeric structures can be proposed for alkene (*A*). Write their structures and identify the isomer which on catalytic hydrogenation ( $H_2 / Pd-C$ ) gives a racemic mixture. (2001, 5M)

63. Identify *A*, *B* and *C*, and give their structures.



64. An organic compound *A*,  $C_6H_{10}O$ , on reaction with  $CH_3MgBr$  followed by acid treatment gives compound *B*. The compound *B* on ozonolysis gives compound *C*, which in presence of a base gives 1-acetyl cyclopentane *D*. The compound *B* on reaction with  $HBr$  gives compound *E*. Write the structures of *A*, *B*, *C* and *E*. Show, how *D* is formed from *C*. (2000, 5M)
65. What would be the major product in the following reaction ?



66. (a) Compound *A* ( $C_8H_8O$ ) on treatment with  $NH_2OH \cdot HCl$  given *B* and *C*. *B* and *C* rearrange to give *D* and *E*, respectively, on treatment with acid. *B*, *C*, *D* and *E* are all

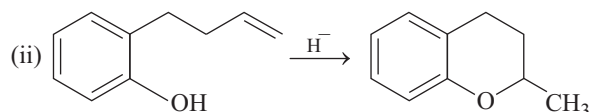
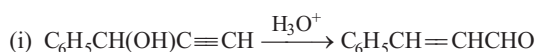
## 360 Aldehydes and Ketones

isomers of molecular formula ( $C_8H_9NO$ ). When  $D$  is boiled with alcoholic KOH, an oil  $F$  ( $C_6H_7N$ ) separates out.  $F$  reacts rapidly with  $CH_3COCl$  to give back  $D$ . On the other hand,  $E$  on boiling with alkali followed by acidification gives a white solid  $G$  ( $C_7H_6O_2$ ). Identify  $A-G$ .

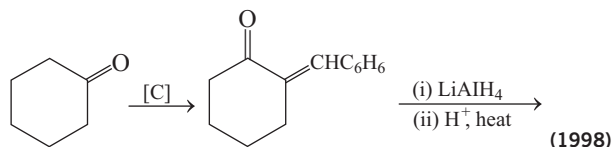
- (b) Carry out the following transformation in not more than three steps.



67. Write the intermediate steps for each of the following reactions



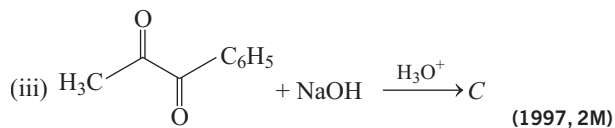
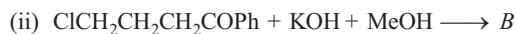
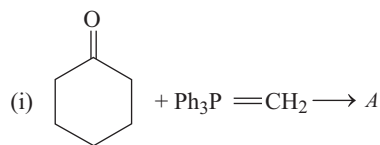
68. Complete the following reactions with appropriate structures of products/reagents.



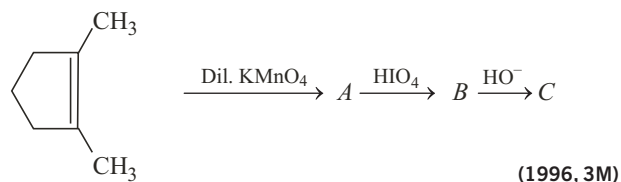
69. An aldehyde  $A$  ( $C_{11}H_8O$ ), which does not undergo self aldol condensation, gives benzaldehyde and two moles of  $B$  on ozonolysis. Compound  $B$ , on oxidation with silver ion gives oxalic acid. Identify the compounds  $A$  and  $B$ . (1998, 2M)

70. Acetophenone on reaction with hydroxylamine hydrochloride can produce two isomeric oximes. Write structures of the oxime. (1997, 2M)

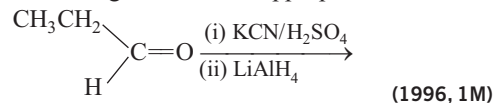
71. Complete the following, giving the structures of the principal organic products,



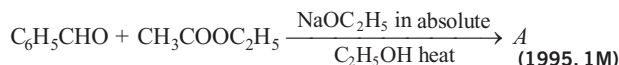
72. Suggest appropriate structures for the missing compounds. (the number of carbon atoms remains the same throughout the reaction)



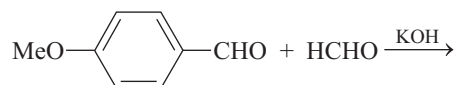
73. Complete the following reaction with appropriate structure :



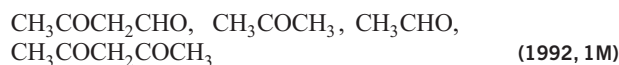
74. Complete the following reaction with appropriate structure.



75. Write the structure of the major organic product expected from the following reaction. (1992, 1M)



76. Arrange the following in the increasing order of expected enol content.



77. Give reason in one or two sentences :

"Iodoform is obtained by the reaction of acetone with hypoiodite but not with iodide". (1991)

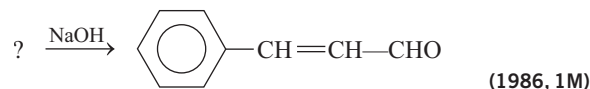
78. A ketone  $A$ , which undergoes haloform reaction, gives compound  $B$  on reduction.  $B$  on heating with sulphuric acid gives compound  $C$ , which forms mono-ozonide  $D$ .  $D$  on hydrolysis in the presence of zinc dust gives only acetaldehyde. Identify  $A$ ,  $B$  and  $C$ . Write down the reactions involved. (1989, 4M)

79. Answer the followings with suitable equations wherever necessary

(i) suggest a reagent to distinguish acetaldehyde from acetone.

(ii) what happens when excess chlorine is passed through boiling toluene in the presence of sunlight? (1987, 2M)

80. Complete the following with appropriate structures



81. How may the following transformation be carried out (in not more than six steps) "benzaldehyde to cyanobenzene"?

(1986, 2M)

82. Give reason in one or two sentences for the following:

"Hydrazone of aldehydes and ketones are not prepared in highly acidic medium". (1986, 1M)

83. Write down product of the following reaction



84. Arrange the following in order of their increasing reactivity towards HCN :



85. Write down the reactions involved in the preparation of the following using the reagents indicated against in parenthesis:

“Acetoxime from acetaldehyde.”



86. Show with balanced equation, what happens, when the following are mixed :

“Chloral is heated with aqueous hydroxide” (1984, 2M)

87. An alkene *A* on ozonolysis yields acetone and an aldehyde. The aldehyde is easily oxidised to an acid *B*. When *B* is

treated with bromine in presence of phosphorus yields a compound *C* which on hydrolysis gives a hydroxyl acid *D*. This acid can also be obtained from acetone by the reaction with hydrogen cyanide followed by hydrolysis. Identify the compounds *A*, *B*, *C* and *D*. (1982, 2M)

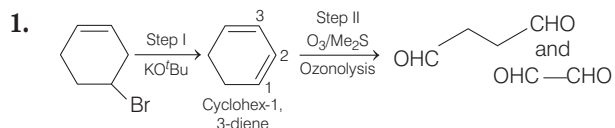
88. Outline the reaction sequence for the conversion of methanal to ethanol (the number of steps should not be more than three). (1981, 2M)

89. Write the structural formula of the main organic product formed when methanal reacts with ammonia. (1981, 1/2M)

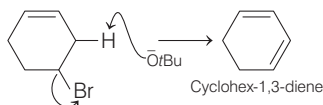
## Answers

- |         |         |         |             |                                                                                                 |             |           |           |
|---------|---------|---------|-------------|-------------------------------------------------------------------------------------------------|-------------|-----------|-----------|
| 1. (a)  | 2. (d)  | 3. (c)  | 4. (d)      | 37. (b,d)                                                                                       | 38. (a,b,d) | 39. (a,d) | 40. (a,b) |
| 5. (d)  | 6. (b)  | 7. (b)  | 8. (c)      | 41. (a,b,d)                                                                                     | 42. (a,b)   | 43. (a,c) | 44. (b)   |
| 9. (b)  | 10. (a) | 11. (a) | 12. (b)     | 45. (a)                                                                                         | 46. (d)     | 47. (b)   | 48. (a)   |
| 13. (d) | 14. (d) | 15. (a) | 16. (c)     | 49. (b)                                                                                         | 50. (d)     | 51. (a)   | 52. (c)   |
| 17. (a) | 18. (b) | 19. (c) | 20. (c)     | 53. $A \rightarrow p, q, t$ $B \rightarrow p, s, t$ $C \rightarrow r, s$ $D \rightarrow p$ .    |             |           |           |
| 21. (c) | 22. (a) | 23. (b) | 24. (b)     | 54. $A \rightarrow p, q, s$ $B \rightarrow q, r$ $C \rightarrow q, r, s$ $D \rightarrow q, r$ . |             |           |           |
| 25. (b) | 26. (b) | 27. (c) | 28. (c)     | 55. Sodium potassium tartarate                                                                  |             |           |           |
| 29. (b) | 30. (c) | 31. (c) | 32. (c)     | 56. False                                                                                       | 57. False   |           |           |
| 33. (c) | 34. (a) | 35. (c) | 36. (a,c,d) | 58. (5)                                                                                         | 59. (1)     |           |           |

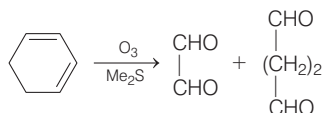
## Hints & Solutions



In step-1 dehydrohalogenation reaction takes place. Here, hydrogen is eliminated from  $\beta$ -carbon and the halogen is lost from  $\alpha$ -carbon atom. As a result diene is formed.

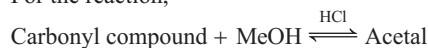


Cyclohex-1,3-diene on ozonolysis gives butane-1,4-dial and ethane-1,2-dial.



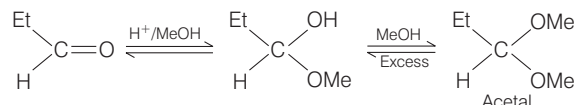
2. **Key Idea** Aldehydes are more reactive than ketones in nucleophilic addition reactions.

For the reaction,

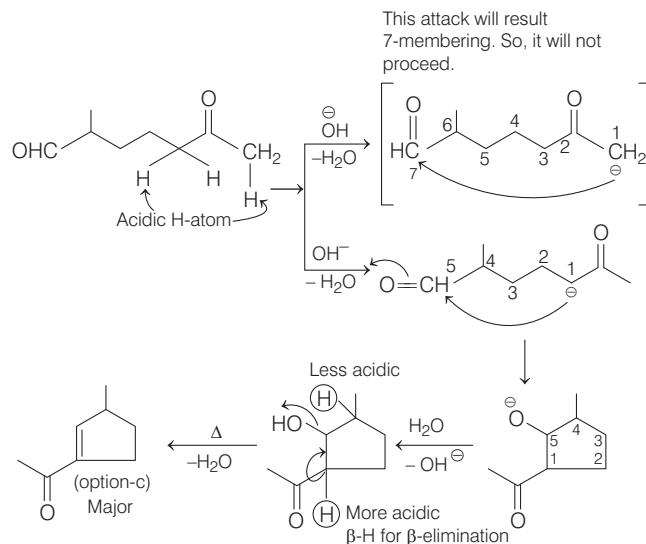


Rate of reaction is the highest for propanal as substrate and methanol in excess. Propanal is an aldehyde and more reactive than ketones. When MeOH is taken in excess then reaction

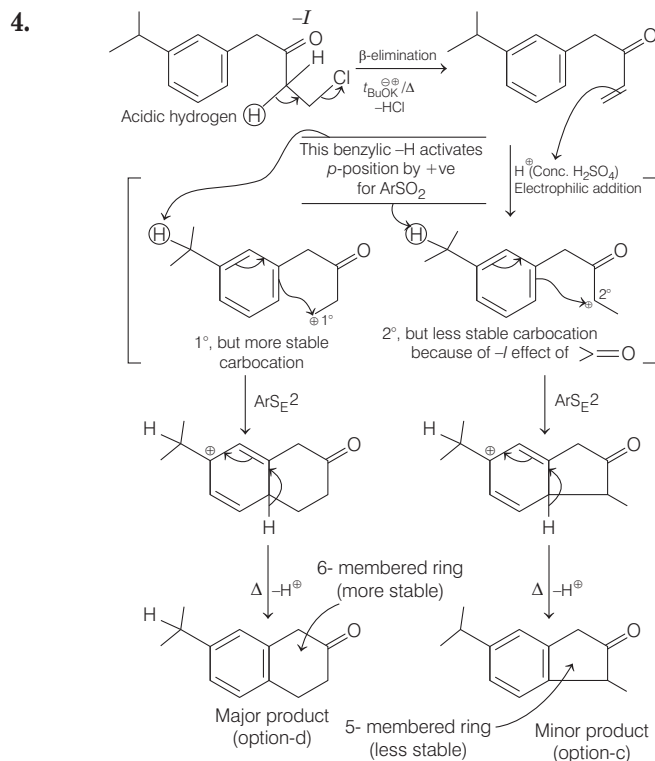
moves in the forward direction that results in the formation of acetal. Reaction involved is as follows :



3. It is an intramolecular aldol condensation reaction.

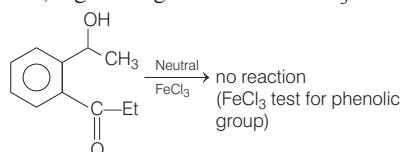


## 362 Aldehydes and Ketones

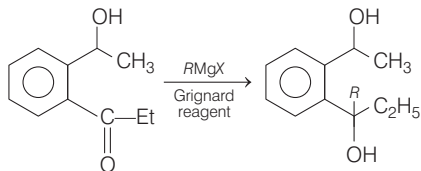


5. According to the given conditions, compound (d) neither reacts with neutral ferric chloride solution nor with Fehling solution. It however reacts with Grignard reagent and gives positive iodoform test.

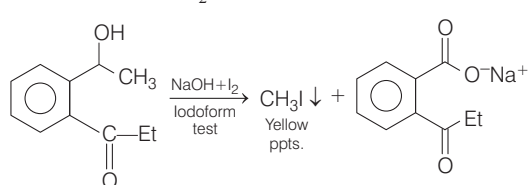
- As the compound does not contain any phenolic  $\text{—OH}$  group. Hence, it gives negative neutral  $\text{FeCl}_3$  test.



- Compound gives reaction with  $\text{RMgX}$  as it contains  $\text{—C(=O)—Et}$ .

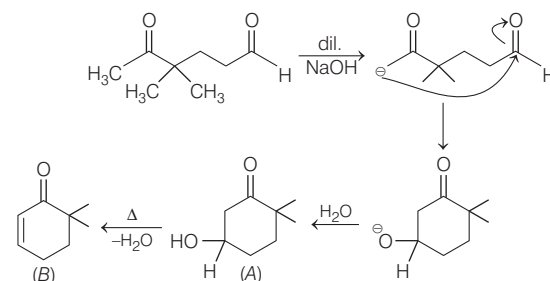


Compound with  $\text{CH}_3\text{CH—OH}$  group undergoes iodoform test in presence of  $\text{NaOH}$  and  $\text{I}_2$ .

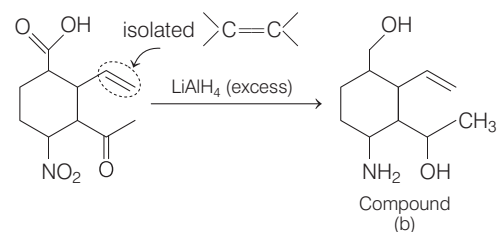


6. The reactant in presence of  $\text{dil. NaOH}$  undergoes intramolecular aldol condensation reaction.

As a result of this,  $\beta$ -hydroxyketone (A) is obtained which on hydrolysis followed by heating produces  $\alpha, \beta$ -unsaturated ketone (B)

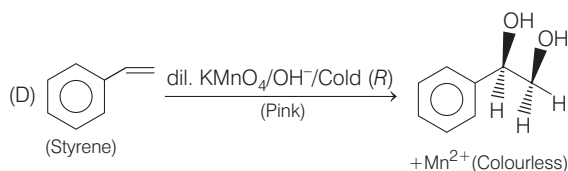
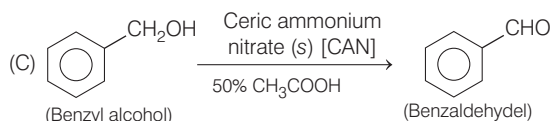
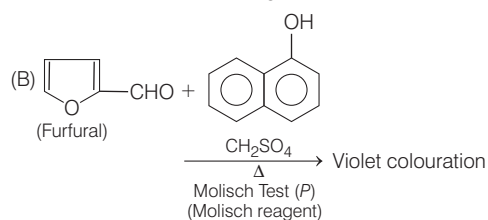
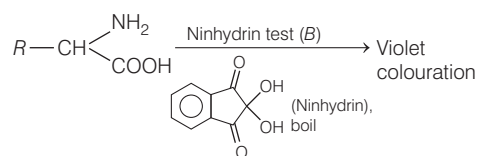


7.  $\text{LiAlH}_4$  acts as a nucleophilic reducing agent that can reduce  $\text{—COOH}$  to  $\text{—CH}_2\text{OH}$ ,  $\text{—C(=O)—}$  into  $\text{—CH—OH}$  and  $\text{—NO}_2$  into  $\text{—NH}_2$ , but it cannot reduce isolated  $\text{>C=C<}$

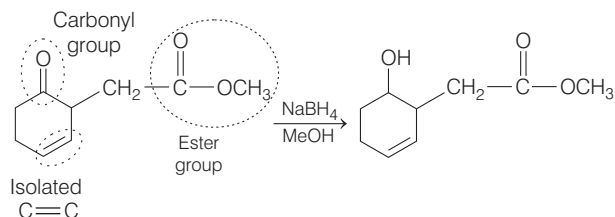


8. (A)  $\rightarrow$  Q; B  $\rightarrow$  (P) ; C  $\rightarrow$  (S), D  $\rightarrow$  (R)

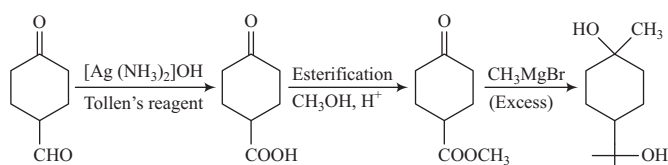
(A) Lysine ( $\text{R} = \text{—(CH}_2\text{)}_4\text{—NH}_2$ )



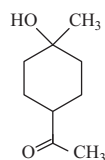
9.  $\text{NaBH}_4$  is a selective reducing agent. It reduces carbonyl ( $>\text{C}=\text{O}$ ) group into an alcohol but cannot reduce an isolated  $\text{C}=\text{C}$  and an ester group too.



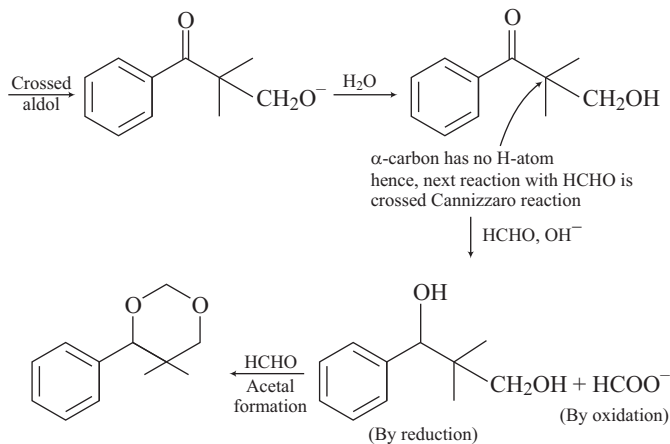
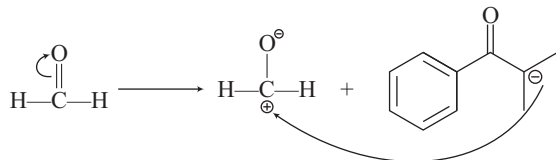
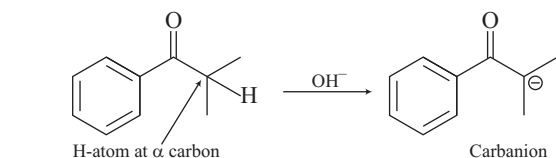
10.



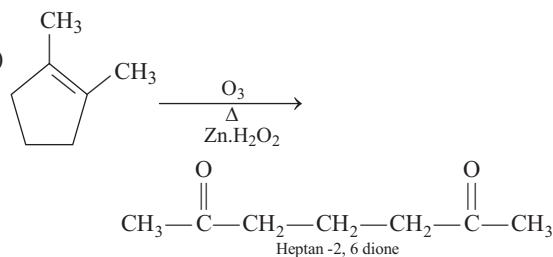
Before final product is formed, intermediate is



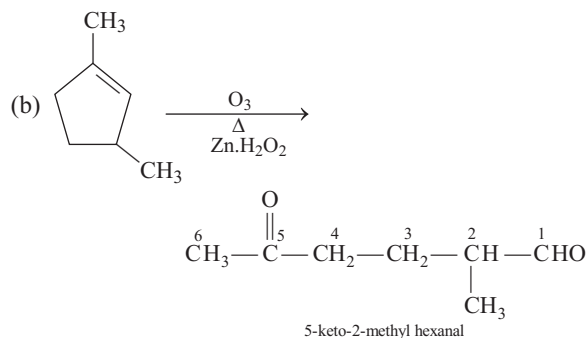
11.



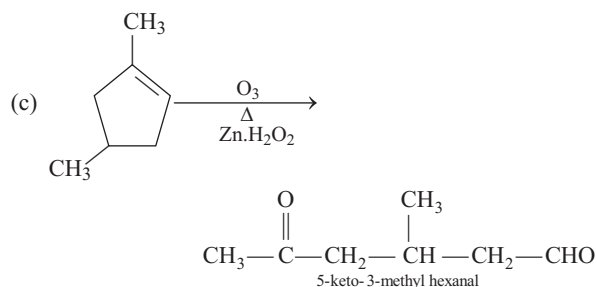
12. (a)



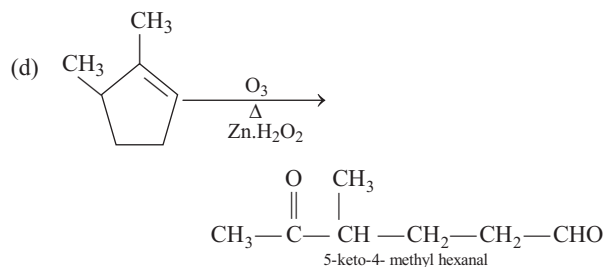
(b)



(c)

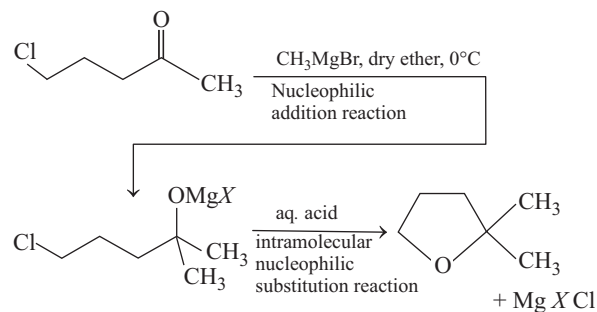


(d)



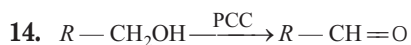
13. **PLAN** This problem includes concept of nucleophilic addition reaction to carbonyl compound (ketone here) and intramolecular nucleophilic substitution reaction.

Complete reaction sequence is as shown below:



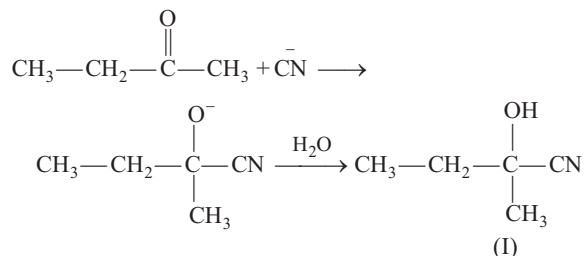


## 364 Aldehydes and Ketones

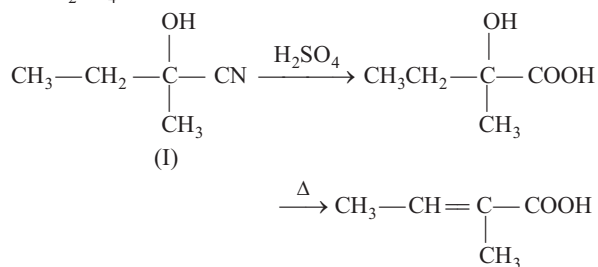


Pyridinium chlorochromate is the mild oxidising agent which causes conversion of alcohol to aldehyde stage. While others causes conversion of alcohol to acid.

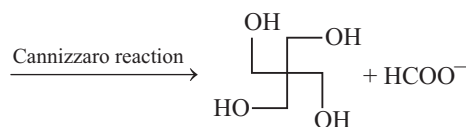
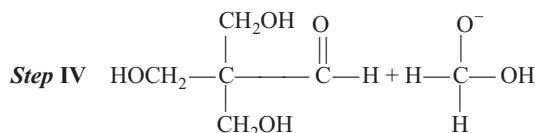
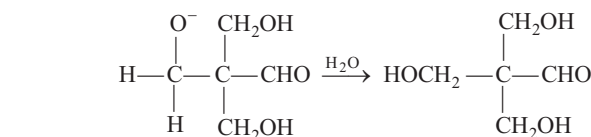
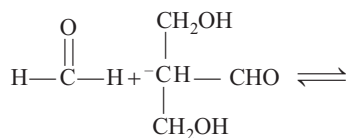
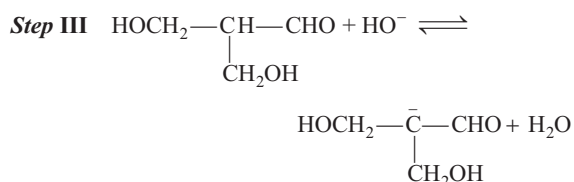
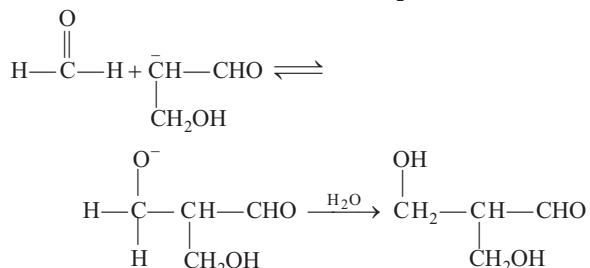
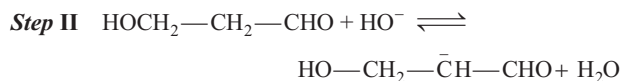
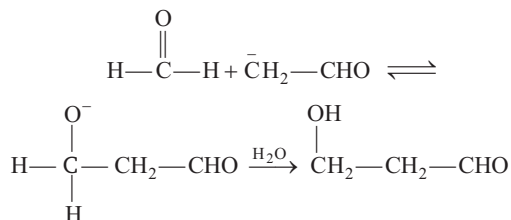
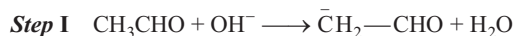
15. The first step is cyanohydrin reaction



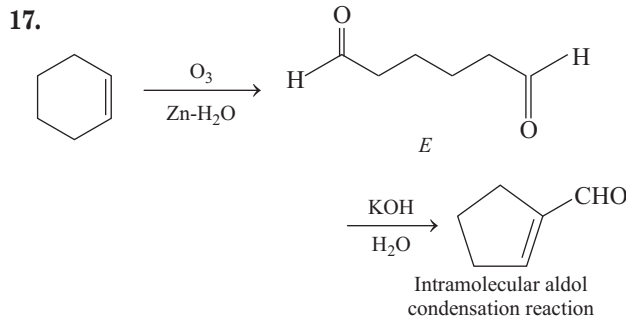
In the second step the  $-CN$  of intermediate (I) is first hydrolysed and then dehydrated on heating in the presence of conc.  $H_2SO_4$ .



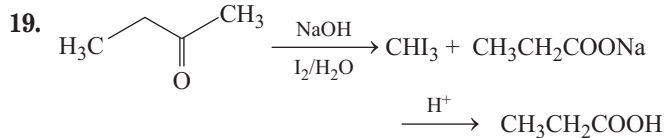
16. The given reaction is an example of repeated aldol condensation followed by Cannizzaro reaction.



In the last step, formaldehyde is oxidised and the other aldehyde is reduced giving the desired products.

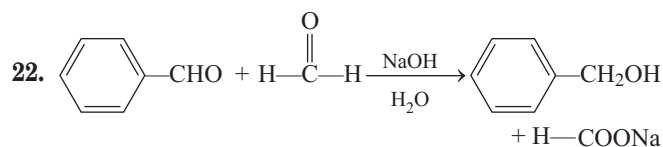
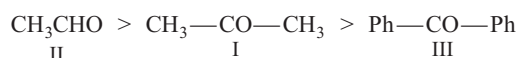


18. Three different oximes are formed out of which two are optically active i.e. exists as a pair of enantiomers while other is optically inactive.

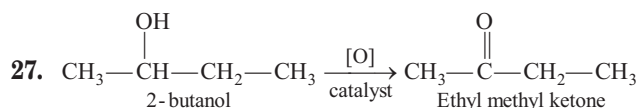
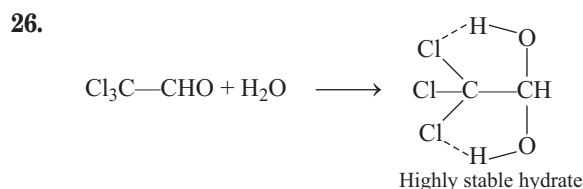
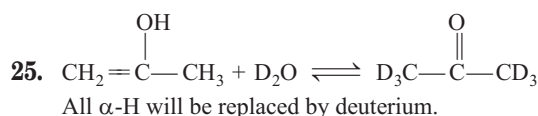
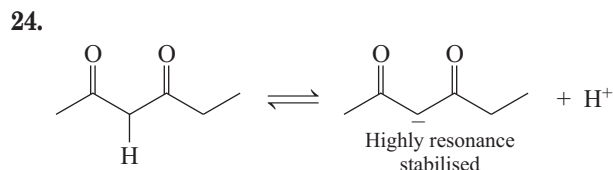
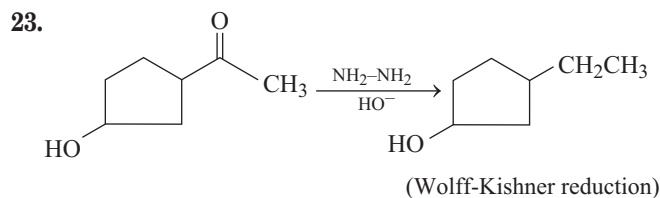


20.  $X$  is  $(CH_3CO)_2O$  and it is an example of Perkin's reaction.

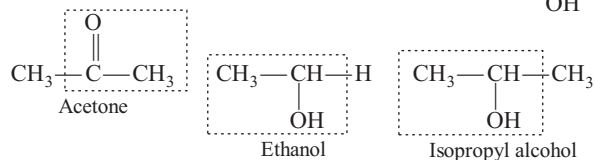
21. The reactivity of carbonyl compound towards nucleophilic addition of Grignard's reagent depends on extent of steric hindrance at  $\alpha$ -carbon. Greater the steric hindrance smaller the reactivity. Hence, reactivity order is



This is an example of cross Cannizzaro reaction in which formaldehyde is always oxidised.



28. Compounds that contain either  $\text{CH}_3-\text{CO}$  or  $\text{CH}_3-\text{CH}(\text{OH})$  group gives iodoform test :

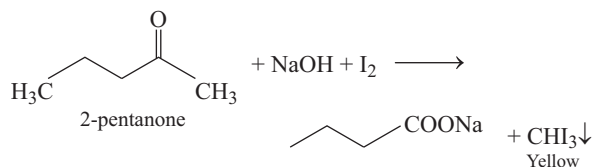


Above three compounds has the desired group for iodoform test. Diethyl ketone does not has the required group for iodoform test.

29. Aldehydes lacking presence of  $\alpha$ -H undergo Cannizzaro reaction. When treated with aqueous base  $\text{CH}_3\text{CHO}$  does not undergo Cannizzaro reaction because it has  $\alpha$ -H and in the presence of aqueous base it undergoes aldol condensation.



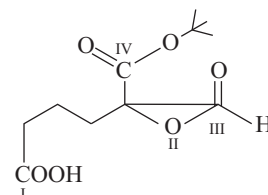
31. For iodoform test,  $\text{CH}_3-\text{C}(=\text{O})$  group is required



32. Grignard's reagent reacts with both aldehydes and ketones while other three reagents reacts only with aldehydes, not with ketones.

33. Only  $-\text{CHO}$  group is to be reduced to  $-\text{CH}_2\text{OH}$ .

It can be done using  $\text{NaBH}_4$  in  $\text{C}_2\text{H}_5\text{OH}$ .

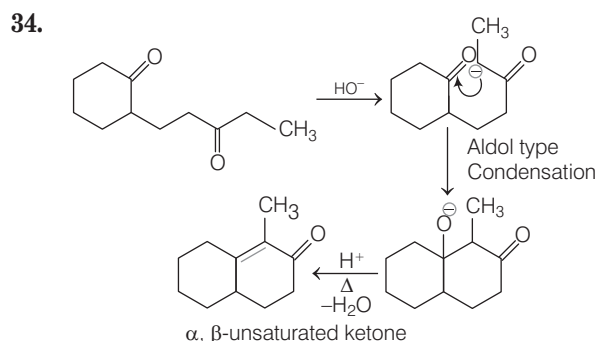


(a)  $\text{LiAlH}_4 / (\text{C}_2\text{H}_5)_2\text{O}$  reduces I, II and III into  $-\text{CH}_2\text{OH}$ , and IV into diol.

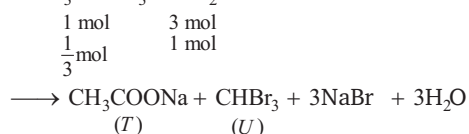
(b)  $\text{BH}_3 / \text{THF}$  show same properties as (a).

(c)  $\text{NaBH}_4 / \text{C}_2\text{H}_5\text{OH}$  reduces III into  $-\text{CH}_2\text{OH}$ .

(d) Raney nickel, same as (a) and (b), thus (c) is correct reagent.



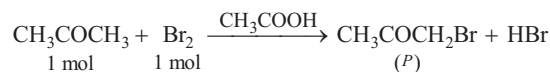
35. **Plan** When acetone reacts with  $\text{Br}_2$  in basic medium, bromoform is formed.



When  $\text{CH}_3\text{COCH}_3$  and  $\text{Br}_2$  are in equimolar quantity, all the  $\text{Br}_2$  (limiting reactant) is converted into desired products and  $2/3$  mole of  $\text{CH}_3\text{COCH}_3$  remains unreacted, being in excess.

When acetone reacts with  $\text{Br}_2$  in acidic medium, there is monobromination of acetone.

**Reactions II**

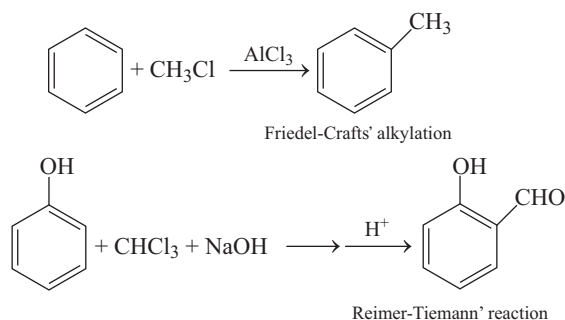


$\text{CH}_3\text{COCH}_3$  and  $\text{Br}_2$  react in 1 : 1 mole ratio and (P) is formed. In reaction I, (U) and (T) are formed and acetone (reactant) remains unreacted. In reaction II, (P) is formed.

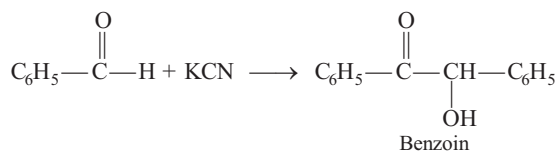
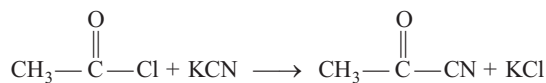
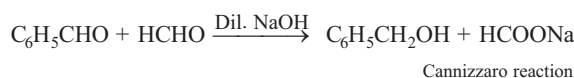
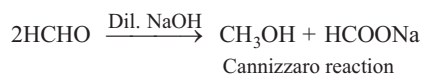
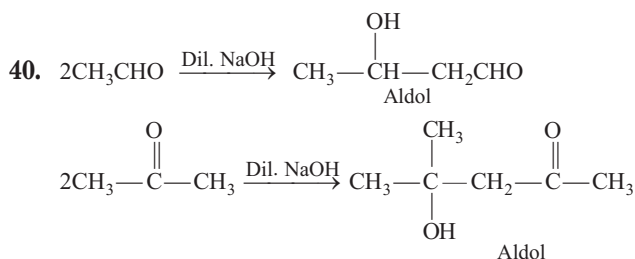
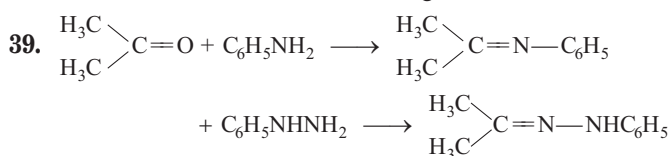
36. All those carbonyl compounds containing  $\alpha$ -H to  $sp^2$  carbon show keto-enol tautomerism.

## 366 Aldehydes and Ketones

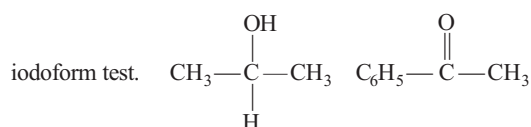
37. In both Friedel-Craft's reaction and Reimer-Tiemann reaction new carbon-carbon bond is formed.



38. All carbonyl compounds containing  $\alpha$ -H or  $\alpha$ -D undergo aldol condensation. In given example, benzaldehyde does not contain  $\alpha$ -H to  $-\text{CHO}$ , hence does not undergo aldol condensation.

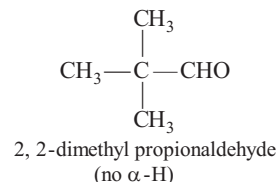
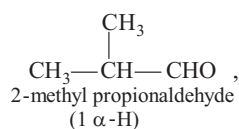
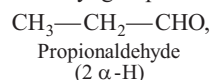


42. Aldehyde, ketones containing  $\text{CH}_3-\text{C}(=\text{O})-$  group gives iodoform test. Also alcohol containing  $\text{CH}_3-\text{CH}(\text{OH})-$  group gives



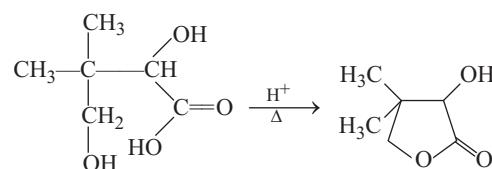
Both gives positive iodoform test  
Esters and amides do not give iodoform test.

43. For base catalysed aldol condensation, there must be at least one  $\alpha$ -H to carbonyl group.

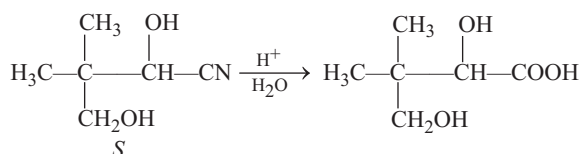


### Passage 1 (For Q. Nos. 44-46)

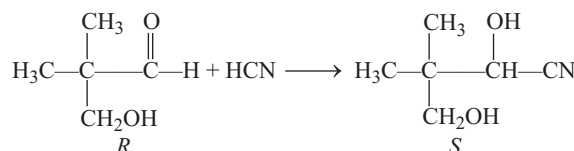
The given product is an ester, obtained by condensation of a hydroxy acid obtained through hydrolysis of a cyanohydrin :



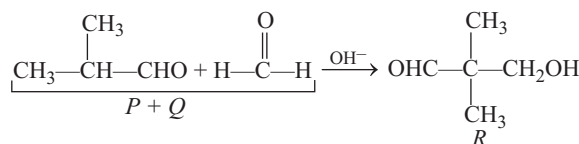
Acid above is obtained by acid hydrolysis of cyanohydrin *S* as



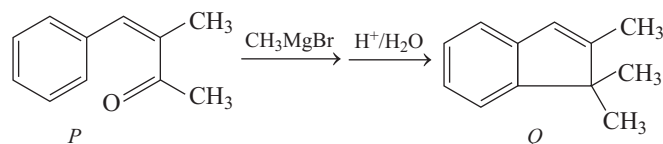
*S* is obtained by nucleophile addition of HCN on *R*, hence *R* is



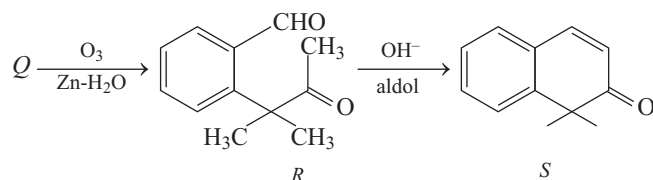
*R* is obtained by treatment of *P* and *Q* with aqueous  $\text{K}_2\text{CO}_3$  through aldol condensation reaction as



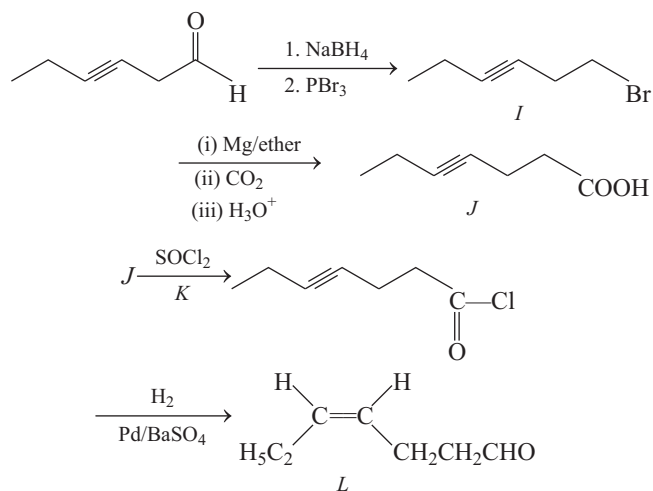
### Passage 2 (For Q. Nos. 47-49)



(gives positive iodoform test)



## Passage 3 (For Q. Nos. 50-52)

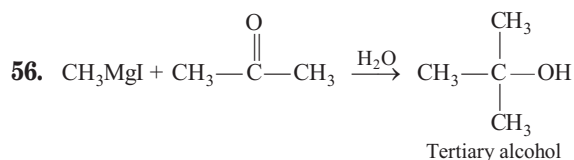


| 53. | Column I | Column II                                                                                                                                                                                                                                                           |
|-----|----------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| A.  |          | Undergo nucleophilic substitution of $\text{Br}^-$ . Undergo elimination of $\text{HBr}$ . Does not undergo nucleophilic addition. Does not esterify with acetic anhydride, can be dehydrogenated.                                                                  |
| B.  |          | Undergo nucleophilic substitution with $\text{SOCl}_2$ , $\text{PCl}_5$ etc. Does not undergo elimination. Does not undergo nucleophilic addition. Undergo esterification with acetic anhydride. Undergo dehydrogenation to give $\text{C}_6\text{H}_5\text{CHO}$ . |
| C.  |          | Does not undergo nucleophilic substitution, there is no leaving group. Does not undergo elimination. Undergo nucleophilic addition at carbonyl carbon of $-\text{CHO}$ . Undergo esterification with acetic anhydride. Does not undergo dehydrogenation.            |
| D.  |          | Undergo aromatic nucleophilic substitution ( $\text{S}_{\text{N}}\text{Ar}$ ) Does not undergo elimination, nucleophilic addition, esterification or dehydrogenation.                                                                                               |

54.

| Column I                                 | Column II                                                                                                                           |
|------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------|
| A. $\text{C}_6\text{H}_5\text{CHO}$      | Gives phenyl hydrazone with 2, 4-dinitrophenyl hydrazine. Gives precipitate with $\text{AgNO}_3$ , Tollen's test forms cyanohydrin. |
| B. $\text{CH}_3-\text{C}\equiv\text{CH}$ | Gives precipitate ( $\text{CH}_3-\text{C}\equiv\text{CAg}$ ) with $\text{AgNO}_3$ . A nucleophile, undergo electrophilic attack.    |
| C. $\text{CN}^-$                         | Forms $\text{AgCN}$ with $\text{AgNO}_3$ . A nucleophile is involved in cyanohydrin formation.                                      |
| D. $\text{I}^-$                          | Gives $\text{AgI}$ precipitate with $\text{AgNO}_3$ and it is a nucleophile.                                                        |

55. Sodium potassium tartarate

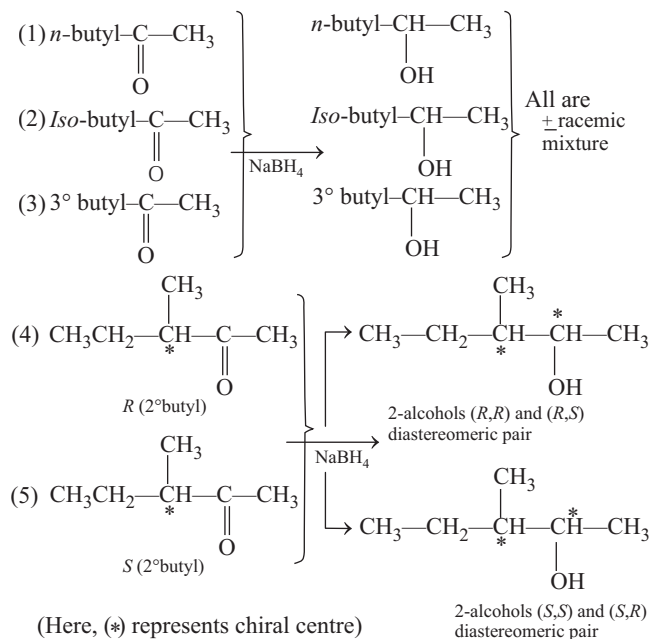
57. Benzaldehyde, lacking  $\alpha$ -H does not undergo aldol condensation, rather it undergoes Cannizzaro reaction.

58. Molecular weight of the ketone is 100

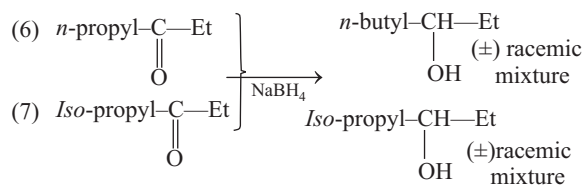
So, molecular formula =  $\text{C}_6\text{H}_{12}\text{O}$ 

$$\text{Degree of unsaturation} = (6 + 1) - \frac{12}{2} = 1$$

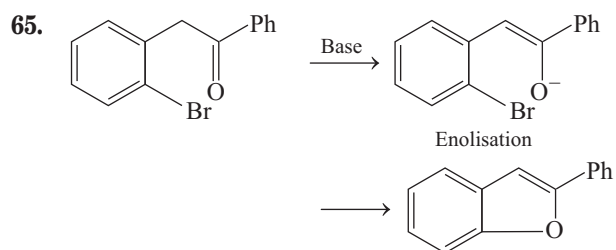
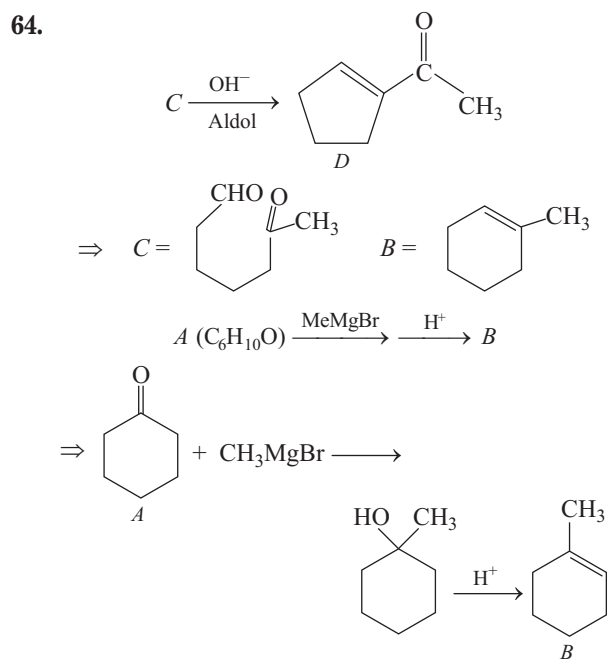
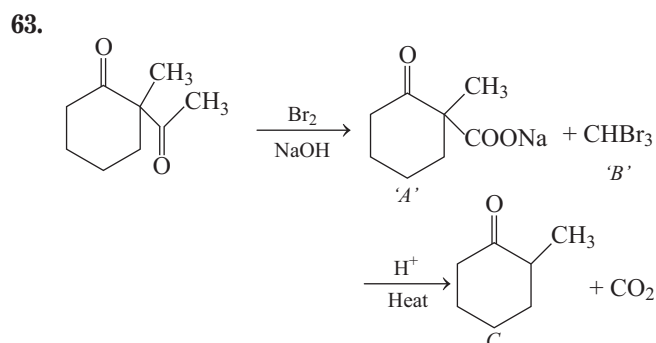
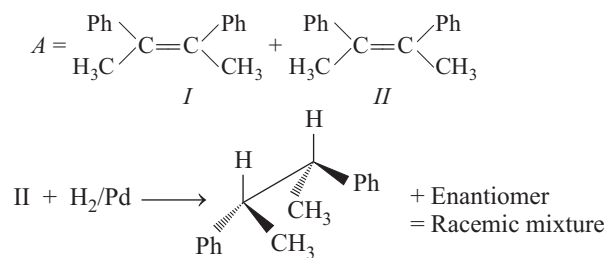
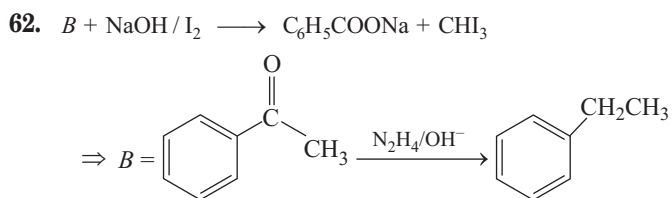
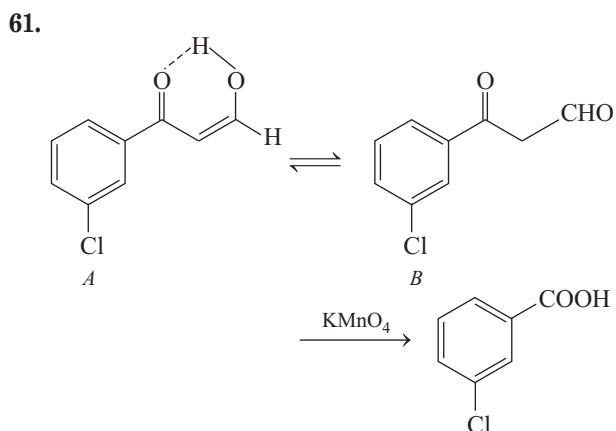
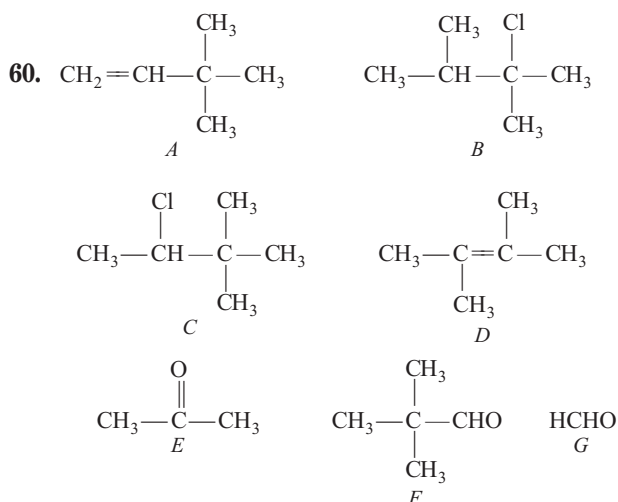
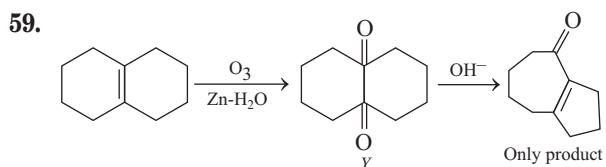
According to question, compound contains ketone group. Since, the compound which contain chiral centre lead to the formation of diastereomer while other produces enantiomers. Various isomers and their possible reduced product are as shown below.



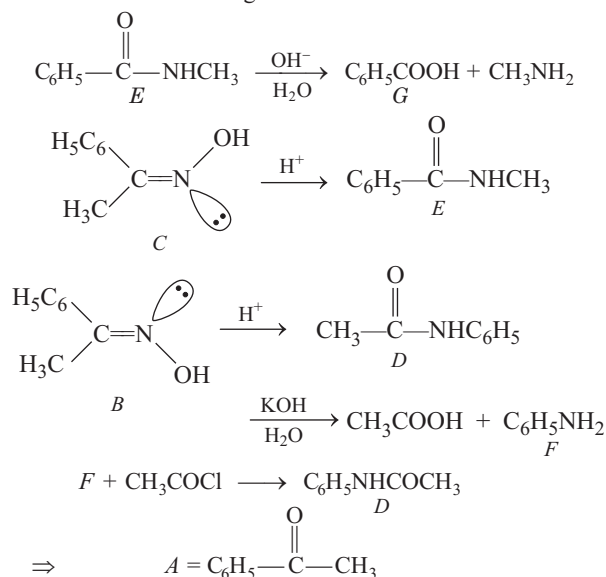
## 368 Aldehydes and Ketones



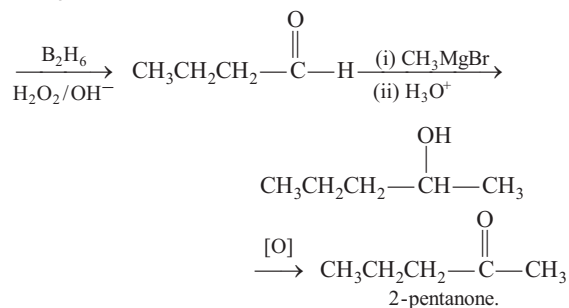
While in case of (4) and (5) they do not produce enantiomer due to the presence of stereogenic centre on ketone.



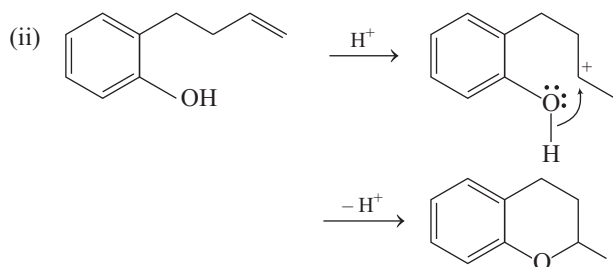
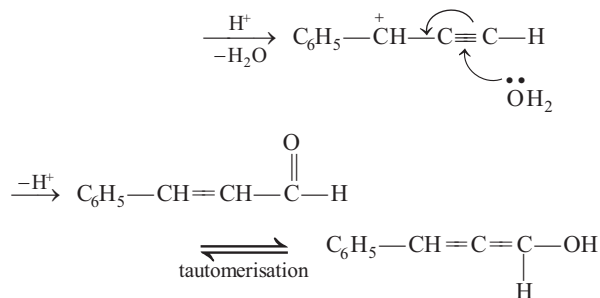
66. (a)  $G$  is benzoic acid  $\text{C}_6\text{H}_5\text{—COOH}$ ,  $B$  and  $C$  are two stereomeric oximes which undergo Beckmann's rearrangement on treatment with acid to give amides  $D$  and  $E$ .



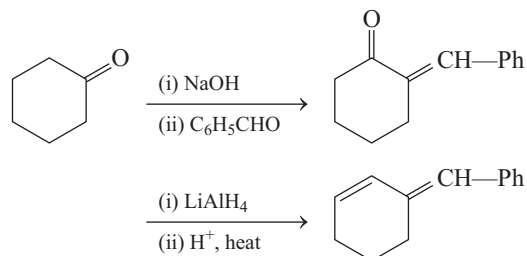
- (b)  $\text{CH}_3\text{—CH}_2\text{—C}\equiv\text{CH}$



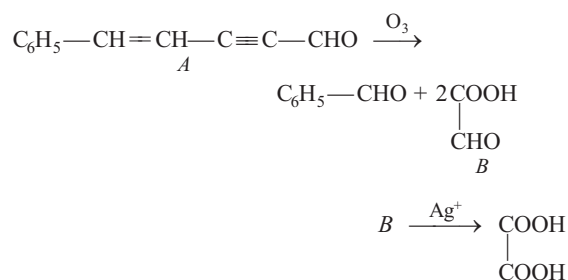
67. (i)  $\text{C}_6\text{H}_5\text{—}\underset{\text{OH}}{\text{CH}}\text{—C}\equiv\text{C—H}$



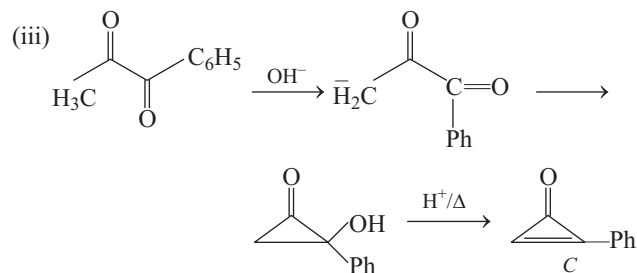
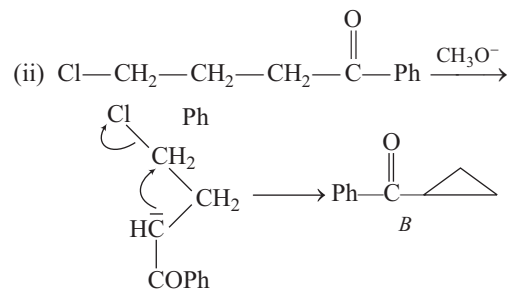
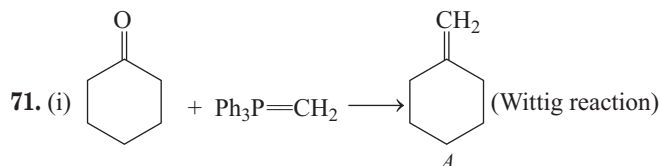
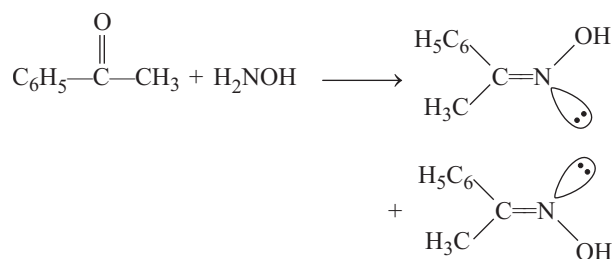
- 68.



69. Aldehyde  $A$  does not have any  $\alpha$ -H but undergoes ozonolysis to give two moles of compound  $B$  and benzaldehyde. Compound  $B$  on oxidation gives oxalic acid, so  $A$  is

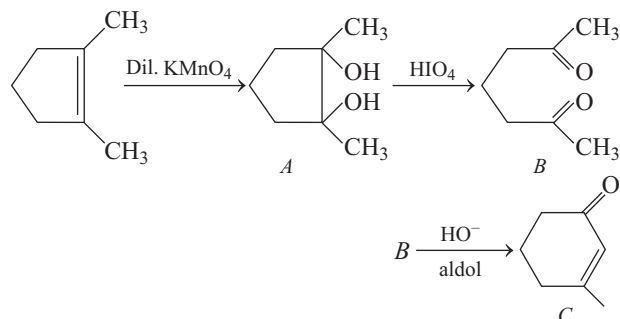


- 70.

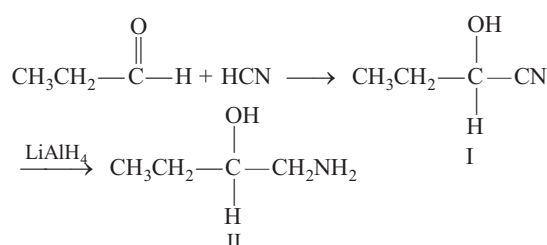


## 370 Aldehydes and Ketones

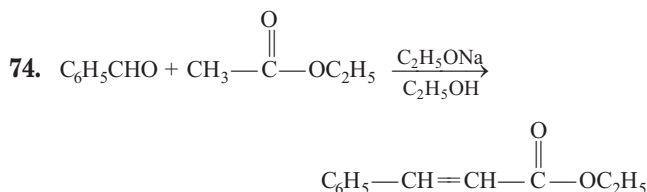
72.



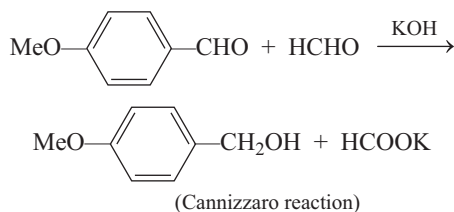
73.  $\text{KCN} + \text{H}_2\text{SO}_4 \longrightarrow \text{KHSO}_4 + \text{HCN}$



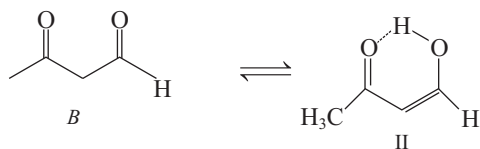
I is formed as racemic mixture.



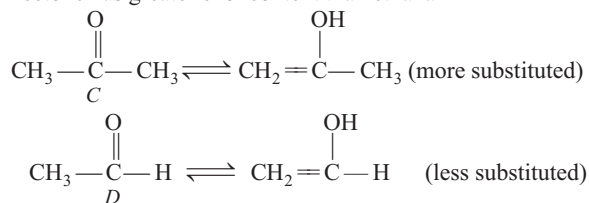
75.



In cross-Cannizzaro reaction, methanal is always oxidised.

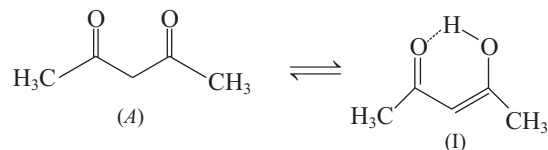


II is less stable than I because II is less substituted enol. Acetone has greater enol content than ethanal



Therefore, overall enol-content order is  $D < C < B < A$

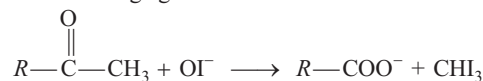
76.  $\text{CH}_3\text{—CO—CH}_2\text{—COCH}_3$  has highest enol content due to resonance and formation of six membered ring through intramolecular H-bonding



Also, enol content depends upon the number of substituents on double bond, greater the number of substituents, greater the stability, higher the enol content.

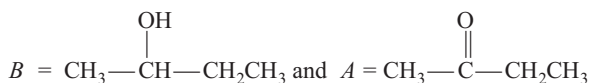
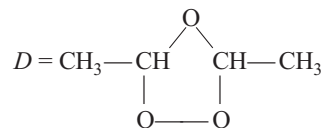
Therefore,  $\text{CH}_3\text{COCH}_2\text{CHO}$  forms next most stable enol

77. Iodoform reaction is an oxidation reaction in which hypoiodite  $\text{OI}^-$  acts as oxidising agent :

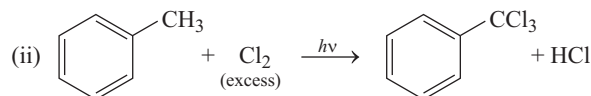


Iodide ( $\text{I}^-$ ) is a reducing agent, does not give iodoform reaction.

78.  $D \xrightarrow{\text{O}_3} \xrightarrow[\text{H}_2\text{O}]{\text{Zn}} \text{CH}_3\text{CHO}$  (only)



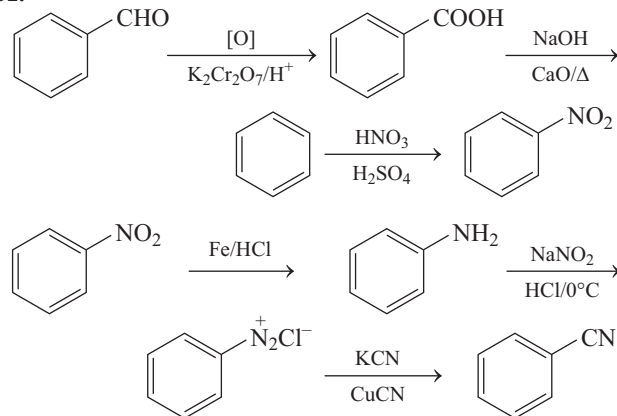
79. (i) Tollen's reagent gives grey precipitate of Ag, acetone does not.



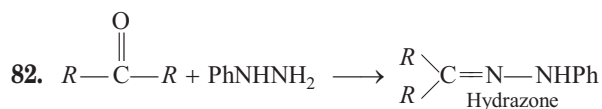
80.  $\text{C}_6\text{H}_5\text{CHO} + \text{CH}_3\text{CHO} \xrightarrow{\text{NaOH}} \text{C}_6\text{H}_5\text{—CH=CH—CHO}$

Cross-aldol condensation

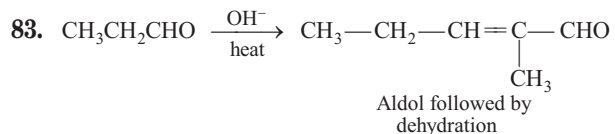
81.



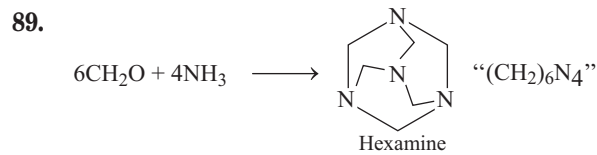
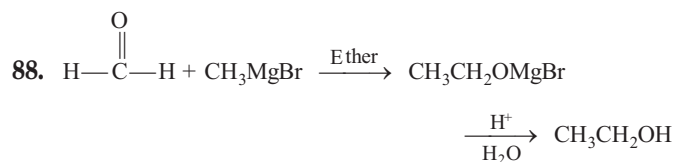
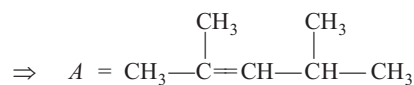
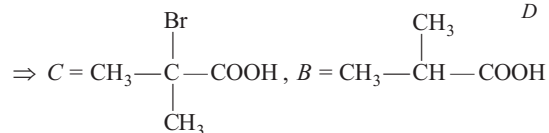
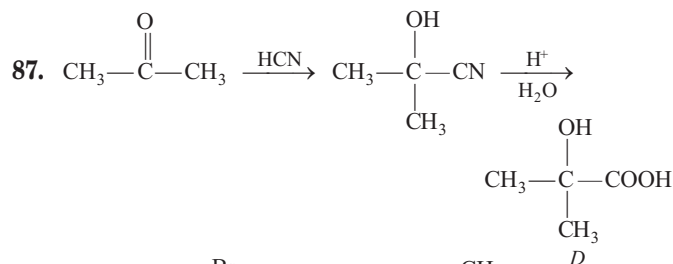
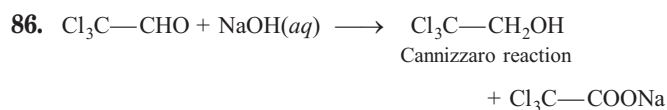
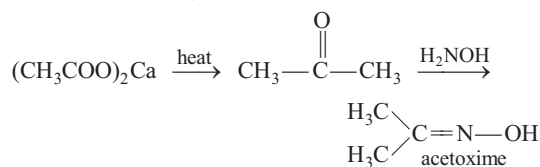




In acidic medium, hydrazine reacts to form salt and hydrazone is hydrolysed back to aldehyde/ketone.



84. Steric hindrance at carbonyl carbon determine the reactivity towards nucleophilic addition reaction. Greater the steric hindrance, smaller the reactivity.



**Download Chapter Test**  
<http://tinyurl.com/yx9d32yd>

or



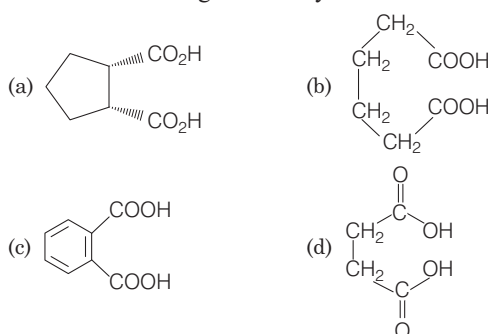
# 26

## Carboxylic Acids and Their Derivatives

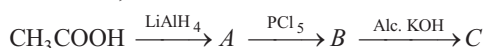
### Topic 1 Carboxylic Acids

#### Objective Questions I (Only one correct option)

1. Which dicarboxylic acid in presence of a dehydrating agent is least reactive to give an anhydride? (2019 Main, 10 Jan I)



2. In the reaction,



The product *C* is

(2014 Main)

- (a) acetaldehyde (b) acetylene  
(c) ethylene (d) acetyl chloride

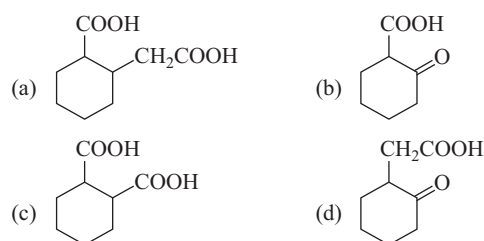
3. The compound that does not liberate  $\text{CO}_2$ , on treatment with aqueous sodium bicarbonate solution, is (2013 Adv.)

- (a) benzoic acid  
(b) benzenesulphonic acid  
(c) salicylic acid  
(d) carbolic acid (Phenol)

4. An organic compound *A* upon reacting with  $\text{NH}_3$  gives *B*. On heating, *B* gives *C*. *C* in the presence of  $\text{KOH}$  reacts with  $\text{Br}_2$  to give  $\text{CH}_3\text{CH}_2\text{NH}_2$ . *A* is (2013 Main)

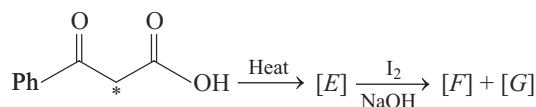
- (a)  $\text{CH}_3\text{COOH}$   
(b)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$   
(c)  $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{COOH}$   
(d)  $\text{CH}_3\text{CH}_2\text{COOH}$

5. The compound that undergoes decarboxylation most readily under mild condition is (2012)

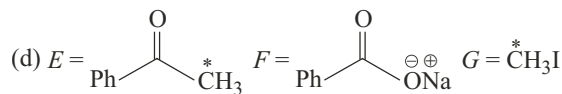
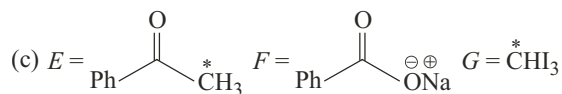
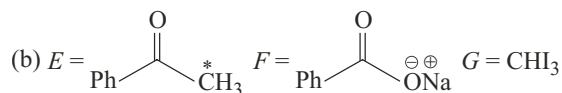
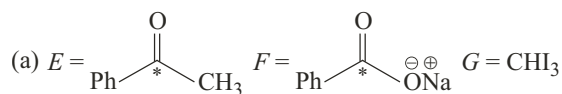


6. The carboxyl functional group ( $-\text{COOH}$ ) is present in (2012)  
(a) picric acid  
(b) barbituric acid  
(c) ascorbic acid  
(d) aspirin

7. In the following reaction sequence, the correct structures of *E*, *F* and *G* are



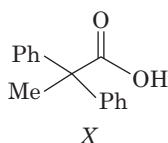
(\* implies  $^{13}\text{C}$  labelled carbon) (2008, 3M)



8. When benzene sulphonic acid and *p*-nitrophenol are treated with  $\text{NaHCO}_3$ , the gases released respectively, are (2006, 3M)  
(a)  $\text{SO}_2$ ,  $\text{NO}_2$  (b)  $\text{SO}_2$ ,  $\text{NO}$  (c)  $\text{SO}_2$ ,  $\text{CO}_2$  (d)  $\text{CO}_2$ ,  $\text{CO}_2$
9. An enantiomerically pure acid is treated with racemic mixture of an alcohol having one chiral carbon. The ester formed will be (2003, S, 1M)  
(a) optically active mixture (b) pure enantiomer  
(c) *meso* compound (d) racemic mixture
10. Benzoyl chloride is prepared from benzoic acid by  
(a)  $\text{Cl}_2$ ,  $h\nu$  (b)  $\text{SO}_2\text{Cl}_2$  (2000, S, 1M)  
(c)  $\text{SOCl}_2$  (d)  $\text{Cl}_2$ ,  $\text{H}_2\text{O}$
11. When propionic acid is treated with aqueous sodium bicarbonate,  $\text{CO}_2$  is liberated. The C of  $\text{CO}_2$  comes from  
(a) methyl group (1999, 2M)  
(b) carboxylic acid group  
(c) methylene group  
(d) bicarbonate group
12. Which of the following is basic? (1980, 1M)  
(a)  $\text{CH}_3\text{CH}_2\text{OH}$  (b)  $\text{H}_2\text{O}_2$   
(c)  $\text{HOCH}_2\text{CH}_2\text{OH}$  (d)  $\text{CH}_3\text{COOH}$

### Matching Type Questions

13. The desired product *X* can be prepared by reacting the major product of the reactions in List-I with one or more appropriate reagents in List-II.  
(given, order of migratory aptitude : aryl > alkyl > hydrogen)



(2018 Adv.)

| List-I | List-II                                  |
|--------|------------------------------------------|
| P.     | 1. $\text{I}_2$ , $\text{NaOH}$          |
| Q.     | 2. $[\text{Ag}(\text{NH}_3)_2]\text{OH}$ |
| R.     | 3. Fehling solution                      |
| S.     | 4. $\text{HCHO}$ , $\text{NaOH}$         |
|        | 5. $\text{NaOBr}$                        |

The correct option is

- (a)  $\text{P} \rightarrow 1$ ;  $\text{Q} \rightarrow 2, 3$ ;  $\text{R} \rightarrow 1, 4$ ;  $\text{S} \rightarrow 2, 4$   
(b)  $\text{P} \rightarrow 1, 5$ ;  $\text{Q} \rightarrow 3, 4$ ;  $\text{R} \rightarrow 4, 5$ ;  $\text{S} \rightarrow 3$   
(c)  $\text{P} \rightarrow 1, 5$ ;  $\text{Q} \rightarrow 3, 4$ ;  $\text{R} \rightarrow 5$ ;  $\text{S} \rightarrow 2, 4$   
(d)  $\text{P} \rightarrow 1, 5$ ;  $\text{Q} \rightarrow 2, 3$ ;  $\text{R} \rightarrow 1, 5$ ;  $\text{S} \rightarrow 2, 3$

### Subjective Questions

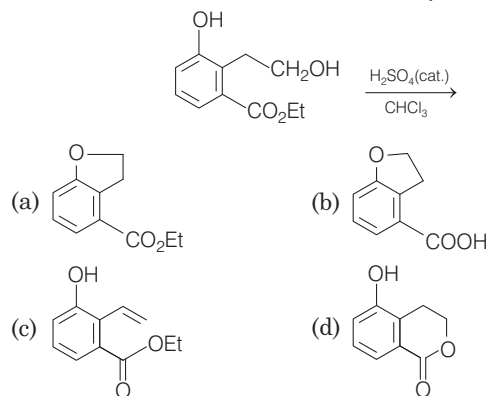
14. How will you bring about the following conversion?  
"Ethanal to 2-hydroxy-3-butenic acid." (1990, 2M)

## Topic 2 Acid Derivatives

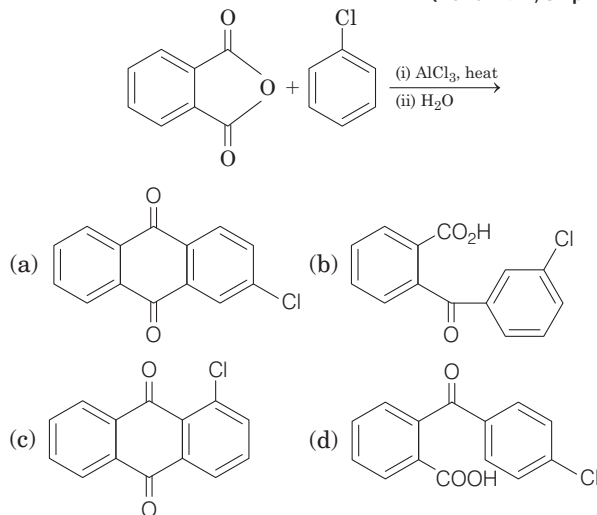
### Objective Questions I

(Only one correct option)

1. The major product of the following reaction is (2019 Main, 9 April II)

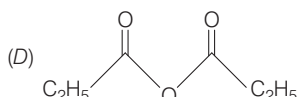
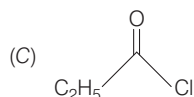
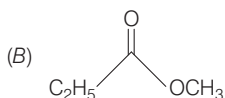
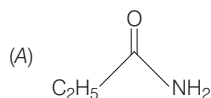


2. The major product of the following reaction is (2019 Main, 8 April I)



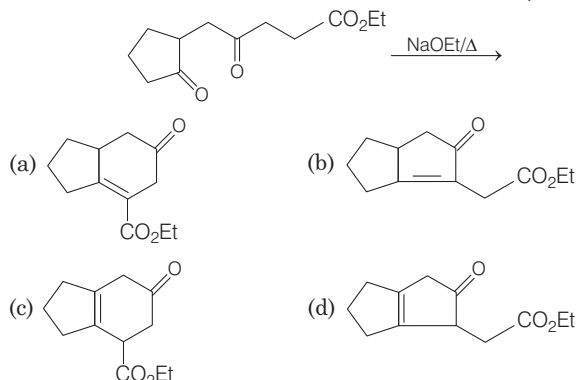
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- 3.** The increasing order of the reactivity of the following with  $\text{LiAlH}_4$  is (2019 Main, 12 Jan II)

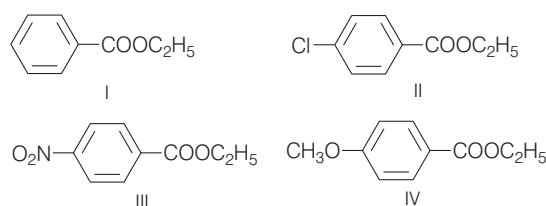


- (a)  $(A) < (B) < (D) < (C)$   
 (b)  $(A) < (B) < (C) < (D)$   
 (c)  $(B) < (A) < (D) < (C)$   
 (d)  $(B) < (A) < (C) < (D)$

- 4.** The major product obtained in the following reaction is  
(2019 Main, 10 Jan II)

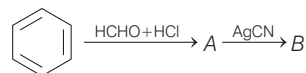


- 5.** The decreasing order of ease of alkaline hydrolysis for the following esters is (2019 Main, 10 Jan I)



- (a)  $\text{III} > \text{II} > \text{IV} > \text{I}$       (b)  $\text{III} > \text{II} > \text{I} > \text{IV}$   
(c)  $\text{II} > \text{III} > \text{I} > \text{IV}$       (d)  $\text{IV} > \text{II} > \text{III} > \text{I}$

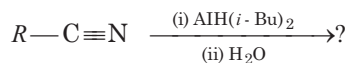
6. The compounds *A* and *B* in the following reaction are, respectively



(2019 Main, 9 Jan I)

- (a)  $A$  = Benzyl alcohol,  $B$  = Benzyl isocyanide  
(b)  $A$  = Benzyl alcohol,  $B$  = Benzyl cyanide  
(c)  $A$  = Benzyl chloride,  $B$  = Benzyl isocyanide  
(d)  $A$  = Benzyl chloride,  $B$  = Benzyl cyanide

7. The major product of following reaction is

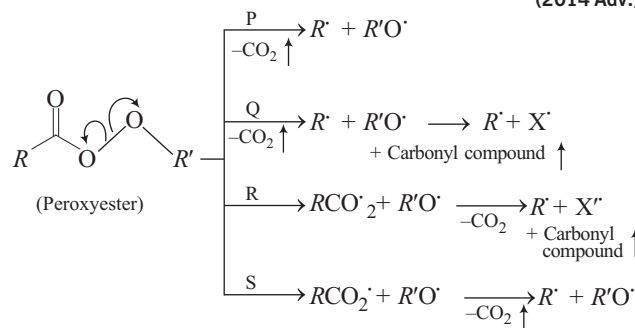


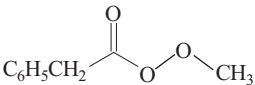
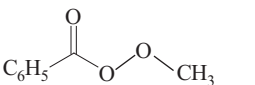
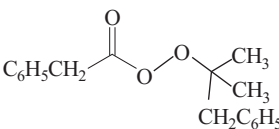
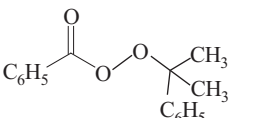
(2019 Main, 9 Jan I)

- (a)  $RCHO$  (b)  $RCONH_2$   
(c)  $RCOOH$  (d)  $RCH_2NH_2$

8. Different possible thermal decomposition pathways for peroxyesters are shown below. Match each pathway from Column I with an appropriate structure from Column II and select the correct answer using the code given below the lists.

(2014 Adv.)



|    | Column I         | Column II                                                                                |
|----|------------------|------------------------------------------------------------------------------------------|
| P. | Pathway <i>P</i> | 1.    |
| Q. | Pathway <i>Q</i> | 2.   |
| R. | Pathway <i>R</i> | 3.  |
| S. | Pathway <i>S</i> | 4.  |

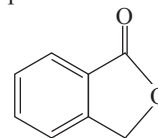
## Codes

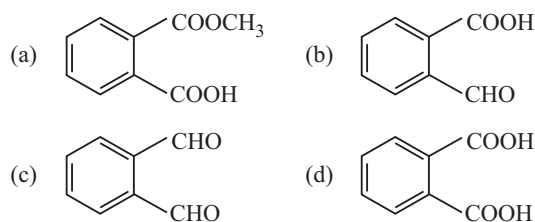
|     | P | Q | R | S |
|-----|---|---|---|---|
| (a) | 1 | 3 | 4 | 2 |
| (b) | 2 | 4 | 3 | 1 |
| (c) | 4 | 1 | 2 | 3 |
| (d) | 3 | 2 | 1 | 4 |

9. A compound with molecular mass 180 is acylated with  $\text{CH}_3\text{COCl}$  to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is (2013 Main)

- (a) 2 (b) 5  
(c) 4 (d) 6

10. Which of the following reactants on reaction with conc. NaOH followed by acidification gives the following lactone as the only product? (2006, 5M)

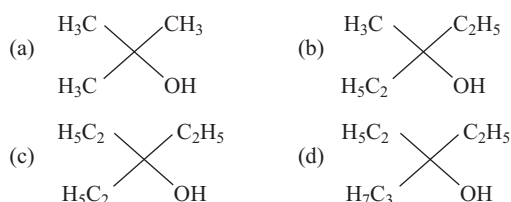




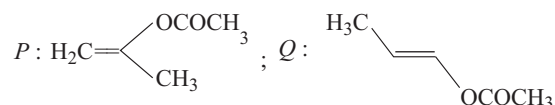
11. Benzamide on treatment with  $\text{POCl}_3$  gives (2004, S, 1M)

- (a) aniline (b) benzonitrile  
(c) chlorobenzene (d) benzyl amine

12. Ethyl ester  $\xrightarrow[\text{(excess)}]{\text{CH}_3\text{MgBr}}$   $P$ , the product ' $P$ ' will be (2003, S, 1M)



13. The product of acid hydrolysis of  $P$  and  $Q$  can be distinguished by (2003, S, 1M)



- (a) Lucas reagent (b) 2, 4-DNP  
(c) Fehling's solution (d)  $\text{NaHSO}_3$

14. Hydrogenation of benzoyl chloride in the presence of Pd on  $\text{BaSO}_4$  gives (1992, 1M)

- (a) benzyl alcohol (b) benzaldehyde  
(c) benzoic acid (d) phenol

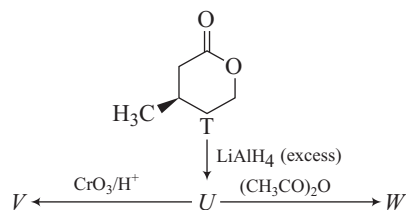
15. Acetamide is treated separately with the following reagents. Which one of these would give methyl amine? (1983, 1M)

- (a)  $\text{PCl}_5$  (b)  $\text{NaOH} + \text{Br}_2$   
(c) Sodalime (d) Hot conc.  $\text{H}_2\text{SO}_4$

## Objective Questions I

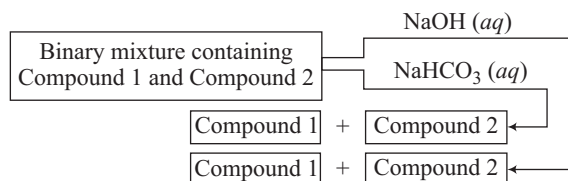
(One or more than one correct options)

16. With reference to the scheme given, which of the given statement(s) about  $T$ ,  $U$ ,  $V$  and  $W$  is/are correct? (2012)



- (a)  $T$  is soluble in hot aqueous  $\text{NaOH}$   
(b)  $U$  is optically active  
(c) Molecular formula of  $W$  is  $\text{C}_{10}\text{H}_{18}\text{O}_4$   
(d)  $V$  gives effervescence on treatment with aqueous  $\text{NaHCO}_3$

17. Identify the binary mixture(s) that can be separated into individual compounds, by differential extraction, as shown in the given scheme. (2012)



- (a)  $\text{C}_6\text{H}_5\text{OH}$  and  $\text{C}_6\text{H}_5\text{COOH}$   
(b)  $\text{C}_6\text{H}_5\text{COOH}$  and  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$   
(c)  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$  and  $\text{C}_6\text{H}_5\text{OH}$   
(d)  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$  and  $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$

18. Reaction of  $\text{RCONH}_2$  with a mixture of  $\text{Br}_2$  and  $\text{KOH}$  gives  $\text{R}-\text{NH}_2$  as the main product. The intermediates involved in this reaction are (1992, 1M)

- (a)  $\text{RCONHBr}$   
(b)  $\text{RNHBr}$   
(c)  $\text{R}-\text{N}=\text{C}=\text{O}$   
(d)  $\text{RCONBr}_2$

## Assertion and Reason

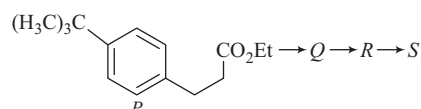
Read the following questions and answer as per the direction given below :

- (a) Statement I is true; Statement II is true; Statement II is a correct explanation of Statement I.  
(b) Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I.  
(c) Statement I is true; Statement II is false.  
(d) Statement I is false; Statement II is true.
19. **Statement I**  $p$ -hydroxybenzoic acid has a lower boiling point than  $o$ -hydroxybenzoic acid.  
**Statement II**  $o$ -hydroxybenzoic acid has intramolecular hydrogen bonding. (2007, 3M)
20. **Statement I** Acetic acid does not undergo haloform reaction.  
**Statement II** Acetic acid has no  $\alpha$  hydrogen. (1998, 2M)

## Passage Based Questions

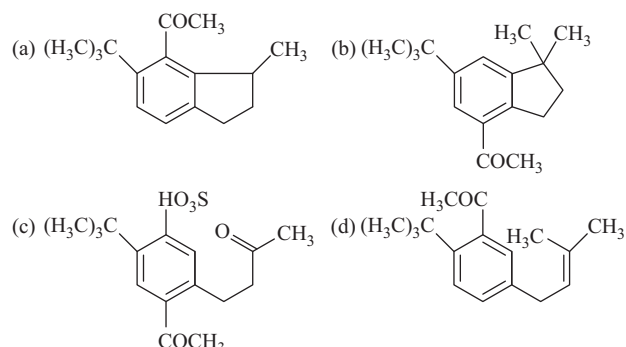
### Passage 1

The reaction of compound  $P$  with  $\text{CH}_3\text{MgBr}$  (excess) in  $(\text{C}_2\text{H}_5)_2\text{O}$  followed by addition of  $\text{H}_2\text{O}$  gives  $Q$ . The compound  $Q$  on treatment with  $\text{H}_2\text{SO}_4$  at  $0^\circ\text{C}$  gives  $R$ . The reaction of  $R$  with  $\text{CH}_3\text{COCl}$  in the presence of anhydrous  $\text{AlCl}_3$  in  $\text{CH}_2\text{Cl}_2$  followed by treatment with  $\text{H}_2\text{O}$  produces compound  $S$ . [Et in compound  $P$  is ethyl group]



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21. The product *S* is (2017 Adv.)



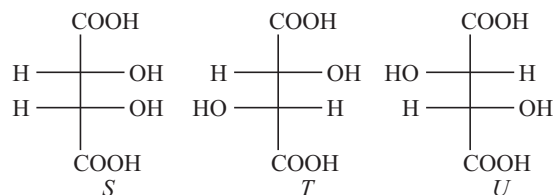
22. The reactions, *Q* to *R* and *R* to *S*, are

- Aromatic sulfonation and Friedel-Crafts acylation
- Friedel-Crafts alkylation and Friedel-Crafts acylation
- Friedel-Crafts alkylation, dehydration and Friedel-Crafts acylation
- Dehydration and Friedel-Crafts acylation

### Passage 2

*P* and *Q* are isomers of dicarboxylic acid  $C_4H_4O_4$ . Both decolorize  $Br_2/H_2O$ . On heating, *P* forms the cyclic anhydride.

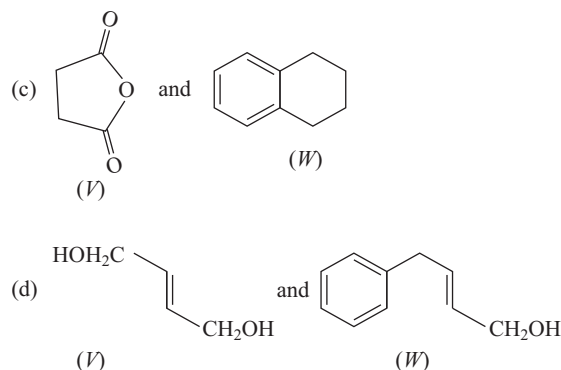
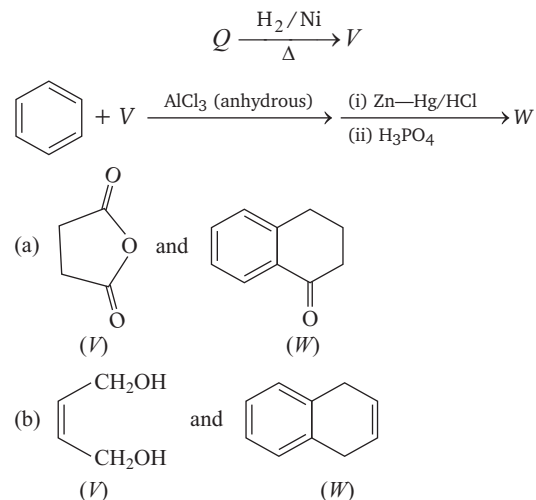
Upon treatment with dilute alkaline  $KMnO_4$ , *P* as well as *Q* could produce one or more than one form *S*, *T* and *U*. (2013 Adv.)



23. Compounds formed from *P* and *Q* are, respectively

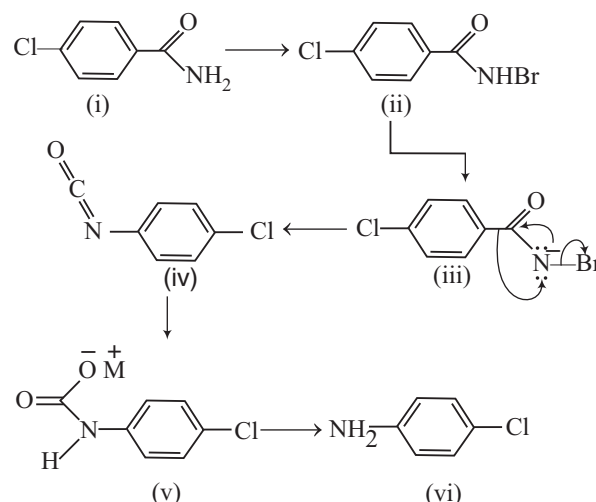
- Optically active *S* and optically active pair (*T*, *U*)
- Optically inactive *S* and optically inactive pair (*T*, *U*)
- Optically active pair (*T*, *U*) and optically active *S*
- Optically inactive pair (*T*, *U*) and optically inactive *S*

24. In the following reaction sequences *V* and *W* are respectively



### Passage 3

$RCONH_2$  is converted into  $RNH_2$  by means of Hofmann's bromamide degradation.



In this reaction,  $RCONHBr$  is formed from which this reaction has derived its name. Electron donating group at phenyl activates the reaction. Hofmann's degradation reaction is an intramolecular reaction. (2006,  $3 \times 4M = 12M$ )

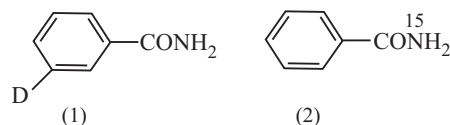
25. How can the conversion of (i) to (ii) be brought about?

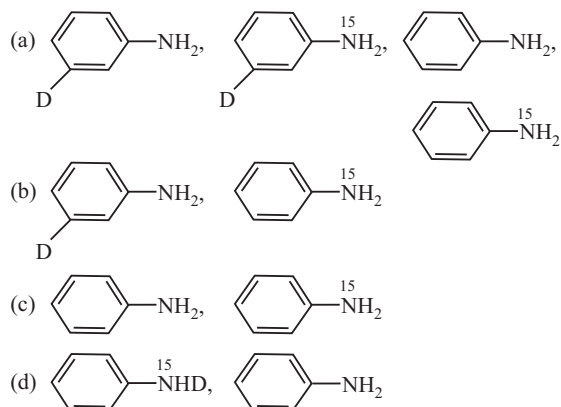
- KBr
- KBr +  $CH_3ONa$
- KBr + KOH
- $Br_2 + KOH$

26. Which is the rate determining step in Hofmann's bromamide degradation?

- Formation of (i)
- Formation of (ii)
- Formation of (iii)
- Formation of (iv)

27. What are the constituent amines formed when the mixture of (1) and (2) undergoes Hofmann's bromamide degradation?



**Fill in the Blank**

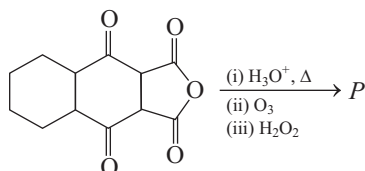
28. Formic acid when heated with conc.  $\text{H}_2\text{SO}_4$  produces ..... (1983, 1M)

**True/False**

29. The boiling point of propanoic acid is less than that of *n*-butyl alcohol, an alcohol of comparable molecular weight. (1991, 1M)
30. Hydrolysis of an ester in the presence of a dilute acid is known as saponification. (1983, 1M)

**Integer Type Question**

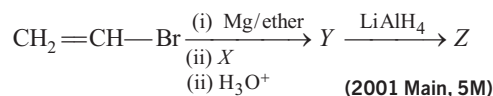
31. The total number of carboxylic acid groups in the product *P* is (2013 Adv.)

**Subjective Questions**

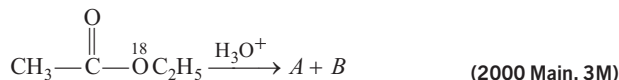
32. Identify *A* to *D*. (2004, M)

33. Compound *A* of molecular formula  $\text{C}_9\text{H}_7\text{O}_2\text{Cl}$  exists in keto form and predominantly in enolic form *B*. On oxidation with  $\text{KMnO}_4$ , *A* gives *m*-chlorobenzoic acid. Identify *A* and *B*. (2003 Main, 2M)
34. ( $\pm$ ) 2-phenylpropanoic acid on treatment with (+) 2-butanol gives (*A*) and (*B*). Deduce their structures and also establish stereochemical relation between them. (2003)
35. Identify *X* and *Y* in the following synthetic scheme and write their structures. Explain the formation of labelled

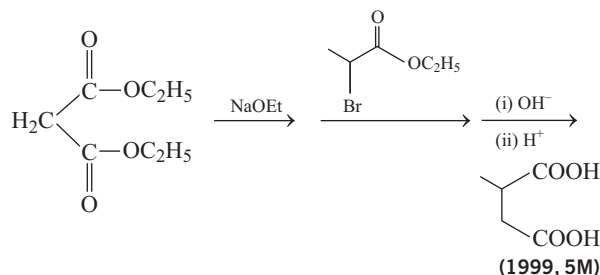
formaldehyde ( $\text{H}_2\text{C}^*\text{O}$ ) as one of the products when compound (*Z*) is treated with  $\text{HBr}$  and subsequently ozonolysed. Mark the  $\text{C}^*$  carbon in the entire scheme.



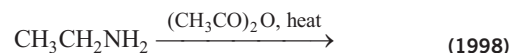
36. Write the structures of the products *A* and *B*.



37. Explain briefly the formation of the products giving the structures of the intermediates



38. Write the structures of the products :

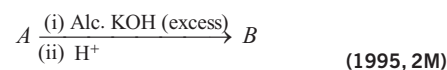


39. An ester *A* ( $\text{C}_4\text{H}_8\text{O}_2$ ), on treatment with excess methyl magnesium chloride followed by acidification, gives an alcohol *B* as the sole organic product. Alcohol *B*, on oxidation with  $\text{NaOCl}$  followed by acidification, gives acetic acid. Deduce the structures of *A* and *B*. Show the reactions involved. (1998)
40. Complete the following, giving the structures of the principal organic products



41. A hydrocarbon *A* of the formula  $\text{C}_8\text{H}_{10}$ , on ozonolysis gives compound *B* ( $\text{C}_4\text{H}_6\text{O}_2$ ) only. The compound *B* can also be obtained from the alkyl bromide *C* ( $\text{C}_3\text{H}_5\text{Br}$ ) upon treatment with magnesium in dry ether, followed by carbon dioxide and acidification. Identify *A*, *B* and *C* and also give equations for the reactions. (1996, 3M)

42. Complete the following sequence of reactions with appropriate structures



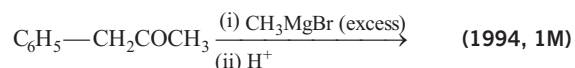


## 378 Carboxylic Acids and Their Derivatives

43. Which of the following carboxylic acids undergoes decarboxylation easily? Explain briefly.

- (i)  $\text{C}_6\text{H}_5\text{COCH}_2\text{COOH}$   
 (ii)  $\text{C}_6\text{H}_5\text{COCO}_2\text{H}$   
 (iii)  $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{COOH}$   
 (iv)  $\text{C}_6\text{H}_5\text{CH}(\text{NH}_2)\text{COOH}$  (1995, 2M)

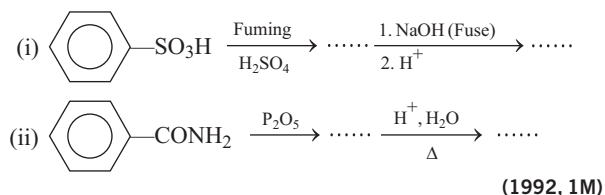
44. Predict the major product in the following reaction :



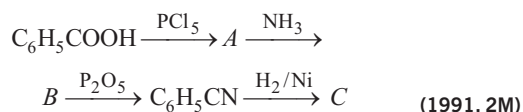
45. In the following reactions, identify the compounds *A*, *B*, *C* and *D*.

- (i)  $\text{PCl}_5 + \text{SO}_2 \longrightarrow \text{A} + \text{B}$   
 (ii)  $\text{A} + \text{CH}_3\text{COOH} \longrightarrow \text{C} + \text{SO}_2 + \text{HCl}$   
 (iii)  $2\text{C} + (\text{CH}_3)_2\text{Cd} \longrightarrow 2\text{D} + \text{CdCl}_2$  (1994, 1M  $\times 4 = 4\text{M}$ )

46. Complete the following sequence of the reactions with appropriate structures

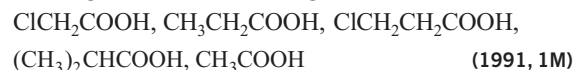


47. In the following identify the compounds/reaction conditions represented by the alphabets *A*, *B*, and *C* :



48. Arrange the following as stated:

“Increasing order of acidic strength.”



49. How will you bring about the following conversion?

“Ethanoic acid to a mixture of methanoic acid and diphenyl ketone.” (1990, 2M)

50. Give reasons for :

“Carbon-oxygen bond lengths in formic acid are 1.23 Å

and 1.36 Å and both the carbon-oxygen bonds in sodium formate have the same value, i.e. 1.27 Å.” (1988, 2M)

51. Write balanced equations for the following reaction :

“Acetamide is reacted with bromine in the presence of potassium hydroxide.” (1987, 1M)

52. A liquid *X*, having a molecular formula  $\text{C}_6\text{H}_{12}\text{O}_2$  is hydrolysed with water in the presence of an acid to give a carboxylic acid *Y* and an alcohol *Z*. Oxidation of *Z* with chromic acid gives *Y*. What are the structures of *X*, *Y* and *Z*? (1986, 3M)

53. An ester *A* ( $\text{C}_4\text{H}_8\text{O}_2$ ) on treatment with excess of methyl magnesium chloride followed by acidification, gives an alcohol *B* as the sole organic product. Alcohol *B*, on oxidation with  $\text{NaOCl}$  followed by acidification, gives acetic acid. Deduce structures of *A* and *B*. Show the reactions involved. (1998)

54. Complete the following with appropriate structures :



55. Arrange the following in order of their increasing ease of hydrolysis :

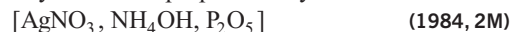


56. Give reasons in one or two sentences for the following :

“Formic acid is a stronger acid than acetic acid.” (1985, 1M)

57. Write down the reactions involved in the preparation of the following using the reagents indicated against in parenthesis.

“Propionic anhydride from propionaldehyde”



58. Give reasons for the following in one or two sentences.

“Acetic acid can be halogenated in the presence of  $\text{P}$  and  $\text{Cl}_2$ , but formic acid cannot be halogenated in the same way.” Why? (1983, 1M)

59. State with balanced equation, what happens when, “Acetic anhydride reacts with phenol in presence of a base.” (1982, 1M)

60. Write the structural formula of main organic product formed when ethyl acetate is treated with double the molar quantity of methyl magnesium bromide and the reaction mixture is poured into water. (1981, 1/2 M)

61. Write the chemical equation to show what happens when, “Ethyl acetate is treated with sodium ethoxide in ethanol and the reaction mixture is acidified”. (1981, 2M)

## Answers

### Topic 1

1. (b)      2. (c)      3. (d)      4. (d)  
 5. (b)      6. (d)      7. (c)      8. (d)  
 9. (d)      10. (c)      11. (d)      12. (a)  
 13. (d)

### Topic 2

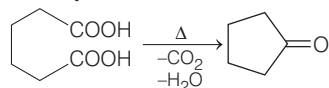
1. (d)      2. (d)      3. (a)      4. (b)

5. (b)      6. (c)      7. (a)      8. (a)  
 9. (b)      10. (c)      11. (b)      12. (a)  
 13. (c)      14. (b)      15. (b)      16. (a,c,d)  
 17. (b,d)      18. (a,c)      19. (d)      20. (c)  
 21. (a)      22. (c)      23. (b)      24. (a)  
 25. (d)      26. (d)      27. (b)  
 28.  $\text{H}_2\text{O}$  and  $\text{CO}$  gas      29. False      30. False  
 31. (2)

# Hints & Solutions

## Topic 1 Carboxylic Acids

1. Heating of  $(\text{CH}_2)_4$   $\begin{matrix} \text{COOH} \\ \diagup \\ \text{COOH} \end{matrix}$  (adipic acid) with a dehydrating agent, decarboxylates ( $-\text{CO}_2$ ) to give a ketone (cyclopentanone), not an anhydride.

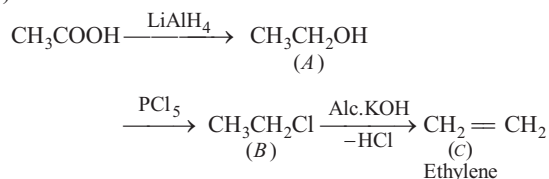


### Codes

P  $\rightarrow$  1, Q  $\rightarrow$  3, R  $\rightarrow$  4, S  $\rightarrow$  2

Thus, (a) is the correct choice.

2. This problem is based on successive reduction, chlorination and elimination reaction. To solve such problem, use the function of the given reagents.
- $\text{LiAlH}_4$  causes reduction
  - $\text{PCl}_5$  causes chlorination
  - Alc. KOH causes elimination reaction

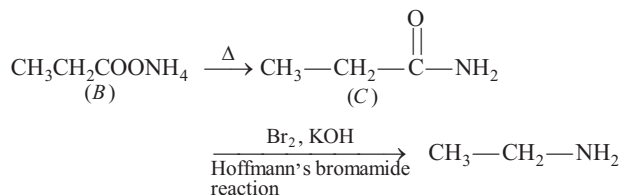
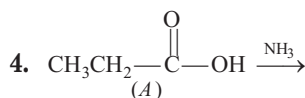


3. **PLAN**  $\text{NaHCO}_3 \rightleftharpoons \text{Na}^+ + \text{HCO}_3^-$

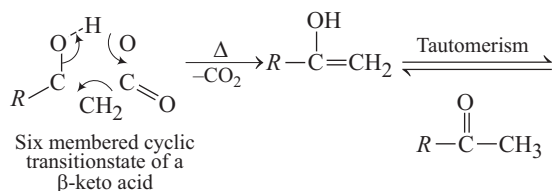
$\text{HCO}_3^-$  is decomposed by acid releasing  $\text{CO}_2$



If acid is stronger than  $\text{HCO}_3^-$  then  $\text{CO}_2$  is released. Phenol is less acidic and thus does not liberate  $\text{CO}_2$  with  $\text{NaHCO}_3$ .



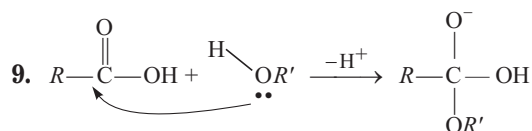
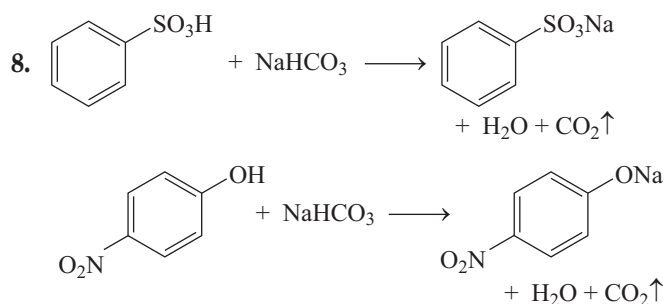
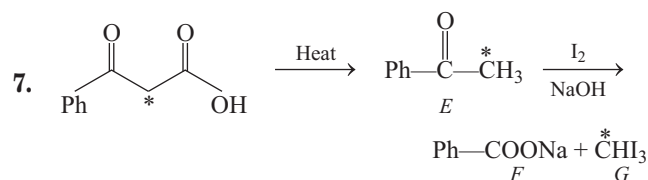
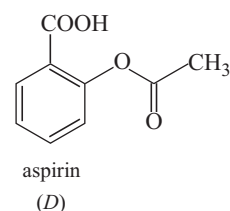
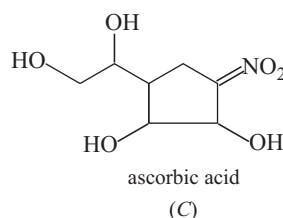
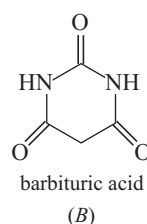
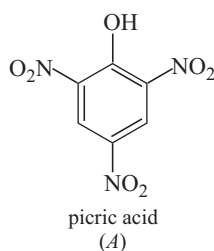
5. It is a  $\beta$ -keto acid which undergo decarboxylation in very mild condition, i.e. on simple heating. This occur through a six member cyclic transition state as



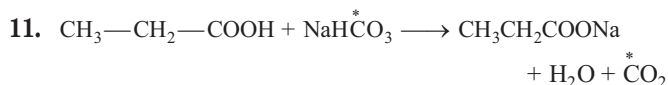
### NOTE

- Ordinary carboxylic acid require soda-lime catalyst for decarboxylation.
- Final step of decarboxylation in the above shown mechanism involve tautomerism, therefore, for decarboxylation of  $\beta$ -keto acid by above mechanism, the acid must contain an  $\alpha$ -H].

6. Structures of the various compounds are



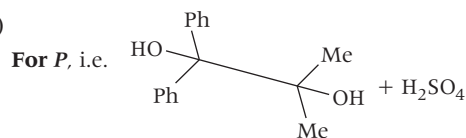
Reaction occur at planar  $sp^2$  carbon giving racemic mixture of product.



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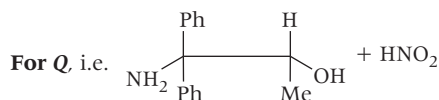
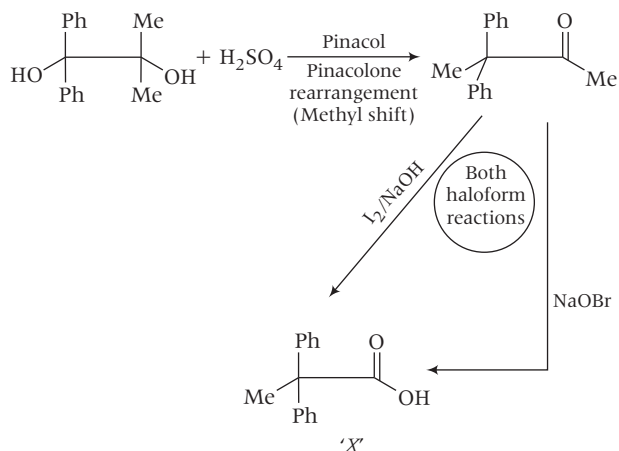
12. Ethanol is the weakest acid among these, hence it is most basic.

13. (d)



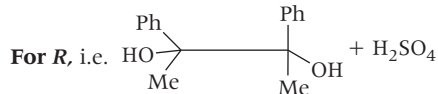
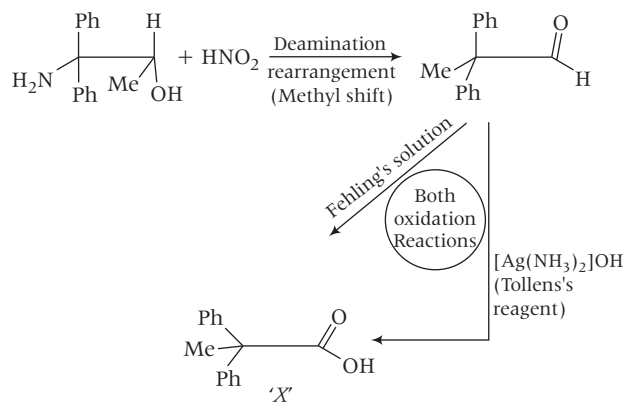
The correct match is 1 i.e.,  $\text{I}_2$ , NaOH and 5 i.e., NaOBr

The reactions proceed as



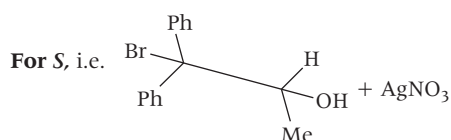
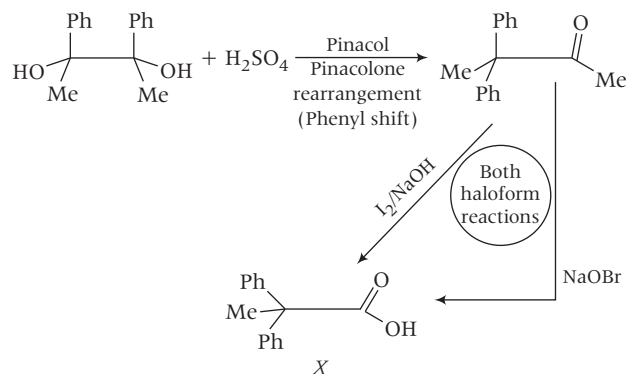
The correct match is 2 i.e.,  $[\text{Ag}(\text{NH}_3)_2]\text{OH}$  and 3 i.e., Fehling's solution.

The reactions proceed as



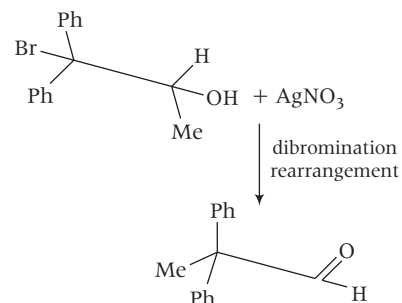
The correct match is 1, 5 again.

The reaction proceed as

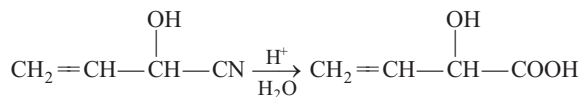
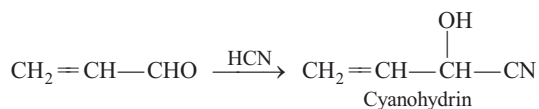
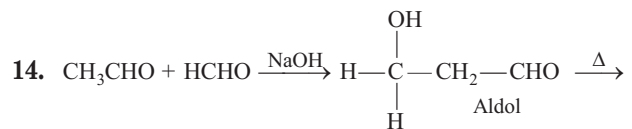


The correct match is 2, 3.

The reaction proceed as



Rest procedure is same as seen for Q above i.e., via oxidation.

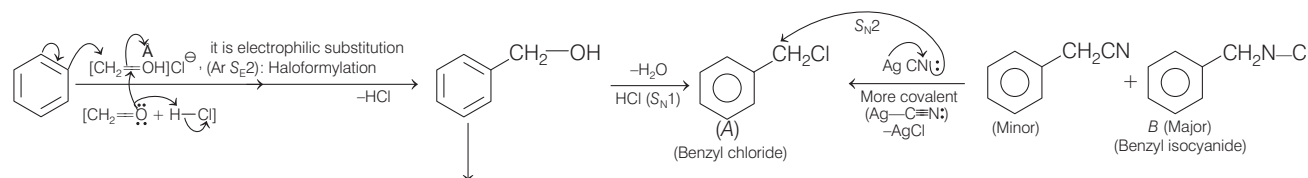


$$\text{Cl}^- > \text{O}^- - \overset{\text{O}}{\parallel} \text{C} - \text{CH}_3 > \bar{\text{O}} - \text{CH}_3 > \text{NH}_2$$

Good leaving group  Poor leaving group

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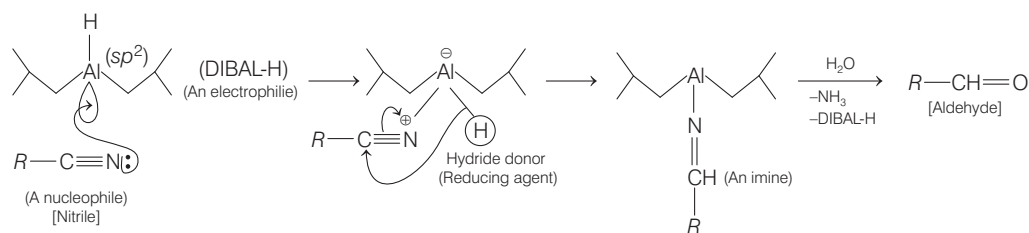
6. The mechanism of the given reaction is as follows:



Thus, both benzyl cyanide and benzyl isocyanide are the products of reaction but benzyl isocyanide being the major product gives the correct option as (c).

7. **Key Idea** DIBAL-H is diisobutyl aluminium hydride,  $[(CH_3)_2CHCH_2]_2AlH$ . It is a selective reducing agent. It reduces carboxylic acids, carboxylic acid derivatives and nitriles into aldehydes. It is an electrophilic reducing agent.

The mechanism of the reaction is as follows:



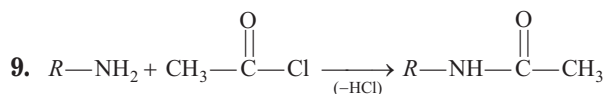
So,  $R-\overset{\overset{O}{\parallel}}{C}H$  is the correct answer.

8. **PLAN** This problem can be solved by using the stability of radical obtained after fragmentation of peroxyester.

Allylic radicals are more stable than alkyl radicals, so when there is a possibility of formation of allyl radical, it will undergo fragmentation through formation of allyl radical. i.e. fragmentation produces stable radical.

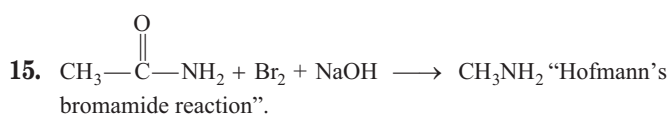
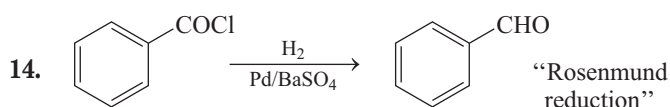
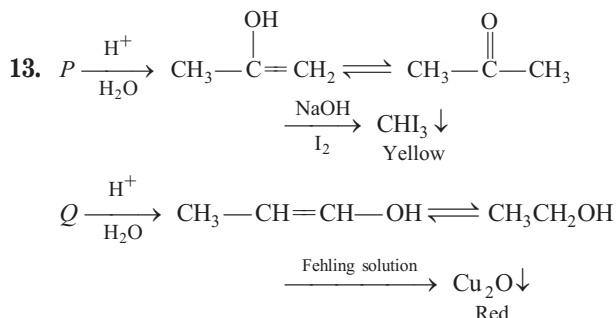
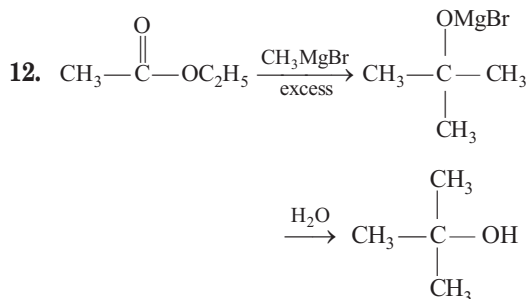
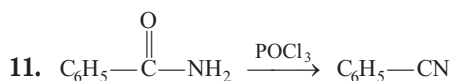
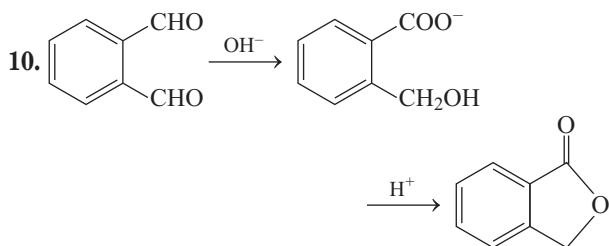
On the basis of stability of radical, fragmentation can be done as

| Column I | Column II                                                   | Explanation                                                                                                                                    |
|----------|-------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------|
| P. 1.    | $C_6H_5H_2C-\overset{O}{\parallel}-O-O-CH_3$                | $C_6H_5-\dot{C}H_2 + CO_2 + \dot{CH}_3O$                                                                                                       |
| Q. 3.    | $C_6H_5H_2C-\overset{O}{\parallel}-O-O-C(CH_3)_2CH_2C_6H_5$ | $C_6H_5-\dot{C}H_2 + CO_2 + Ph-CH_2-\overset{O^\bullet}{\underset{CH_3}{\mid}}{C}-CH_3 \rightarrow Ph-\dot{C}H_2 + CH_3-CO-CH_3$               |
| R. 4.    | $C_6H_5-\overset{O}{\parallel}-O-O-C(CH_3)_2C_6H_5$         | $C_6H_5-\dot{C}O_2 + CH_3-\overset{O^\bullet}{\underset{C_6H_5}{\mid}}{C}-CH_3 \xrightarrow{-CO_2} Ph\dot{C} + CH_3-CO-Ph + \dot{CH}_3 + CO_2$ |
| S. 2.    | $C_6H_5-\overset{O}{\parallel}-O-O-CH_3$                    | $C_6H_5-\dot{C}O_2 + \dot{CH}_3O \rightarrow C_6H_5\dot{C} + CO_2$                                                                             |

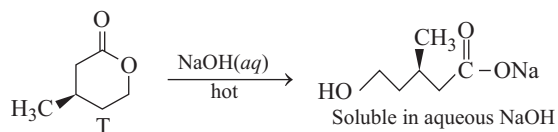


Since, each  $-COCH_3$  group displace one H atom in the reaction of one mole of  $CH_3-C(=O)Cl$  with one  $-NH_2$  group, the molecular mass increases with 42 unit.

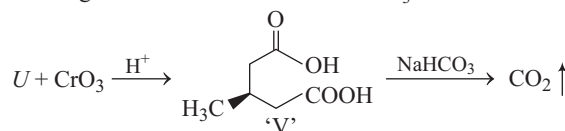
Since the mass increases by  $(390 - 180) = 210$ , hence the number of  $-NH_2$  group is  $\frac{210}{42} = 5$ .



16. (a) *T* undergoes an ester hydrolysis in hot aqueous alkali as

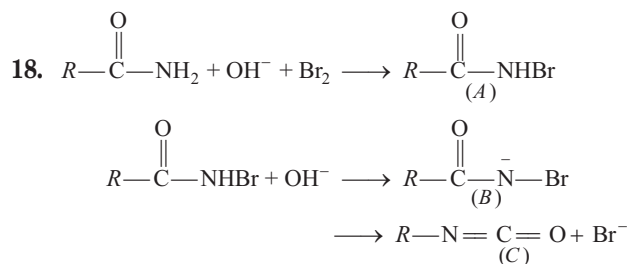


- (b)  $LiAlH_4$  reduces ester to alcohol as  
 “U” No chiral carbon optically inactive.  
 (c) *U* on treatment with excess of acetic anhydride forms a diester as  
 (d) *U* on treatment with  $CrO_3/H^+$  undergo oxidation to diacid which gives effervescence with  $NaHCO_3$ .

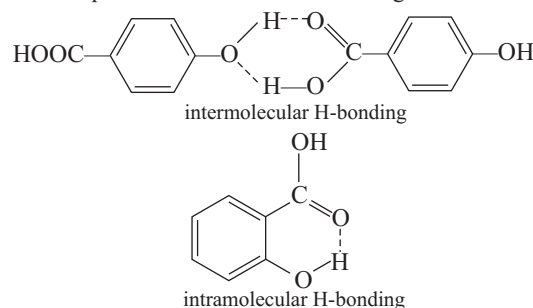


17. For separation by differential extraction one of the component must form salt with the given base so that the salt will be extracted in aqueous layer leaving other component in organic layer.

- (a) Both phenol and benzoic acid forms salt with NaOH, hence this mixture can't be separated.  
 (b) Benzoic acid forms salt with NaOH while benzyl alcohol does not, hence the mixture can be separated using NaOH. Also benzoic acid forms salt with  $NaHCO_3$  but benzyl alcohol does not, hence  $NaHCO_3$  can be used for separation.  
 (c) Neither benzyl alcohol nor phenol forms salt with  $NaHCO_3$ , mixture cannot be separated using  $NaHCO_3$ .  
 (d)  $C_6H_5CH_2COOH$  forms salt with NaOH,  $C_6H_5CH_2OH$  does not, hence mixture can be separated using NaOH.  $C_6H_5CH_2COOH$  forms salt with  $NaHCO_3$ ,  $C_6H_5CH_2OH$  does not, hence mixture can be separated using  $NaHCO_3$ .



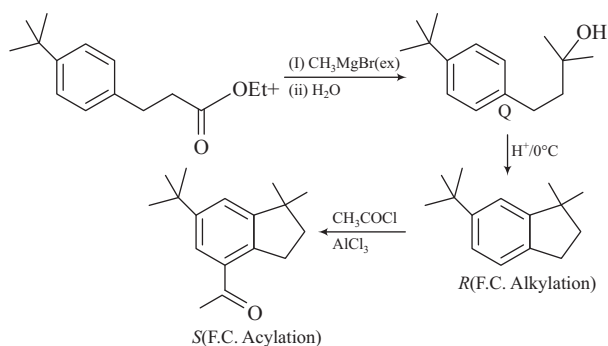
19. *p*-hydroxy benzoic acid has higher boiling point than *o*-hydroxy benzoic acid because former prefers intermolecular H-bonding while the latter prefer intramolecular H-bonding.



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20. Compounds with  $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-$  or  $\text{CH}_3-\text{CH}(\text{OH})-$  group gives haloform reaction but this reaction is given only by aldehydes, ketones and alcohols, so acetic acid does not give haloform reaction. However acetic acid has three  $\alpha$ -H, therefore, statement I is true but statement II is false.

### Passage-1



**22. (a)**

**22. (c)**

- 23. PLAN** Ikenes decolourise  $\text{Br}_2$  water
- isomer  $\xrightarrow{\text{dil. KMnO}_4}$  isomers by addition
- isomer  $\xrightarrow{\text{dil. KMnO}_4}$   $d(+)$  and  $l(-)$  isomers by

Formation of anhydride from dicarboxylic acid indicates trans-isomer.

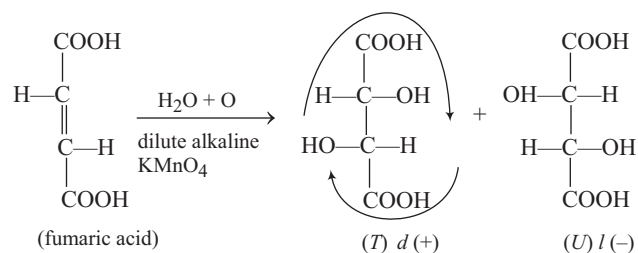
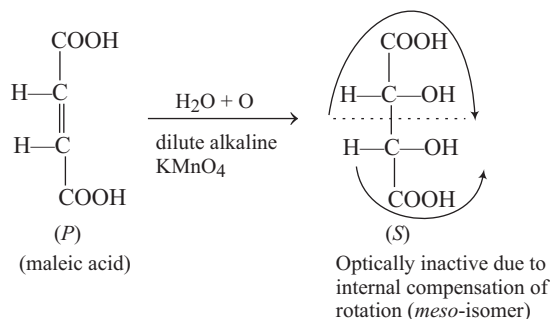
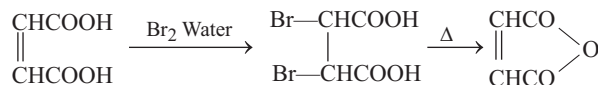
$P$  and  $Q$  are isomers of dicarboxylic acids.

$$P, Q \xrightarrow{\text{Br}_2 \text{ water}} \text{decolourised}$$

*P* and *Q* have (C=C) bond

$$P \xrightarrow{\Delta} \text{anhydride}$$

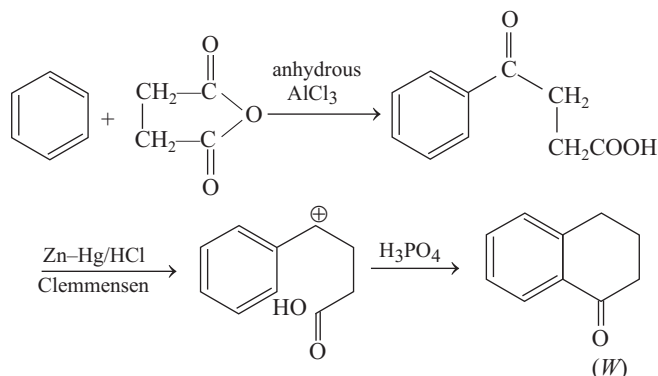
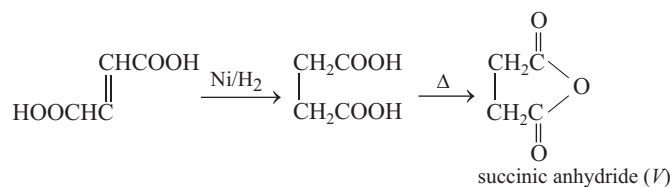
Thus,  $P$  is *cis*-isomer.





*T* and *U* (in 1 : 1 molar ratio) form optically inactive (racemic mixture) due to external compensation.

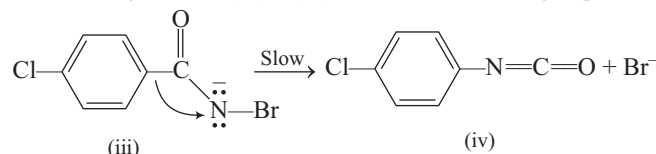
- 24. PLAN** Ni / H<sub>2</sub> reduces (C=C) bond.

Benzene undergoes Friedel-Crafts reaction Zn-Hg/HCl reduces carbonyl group (Clemmensen reduction)



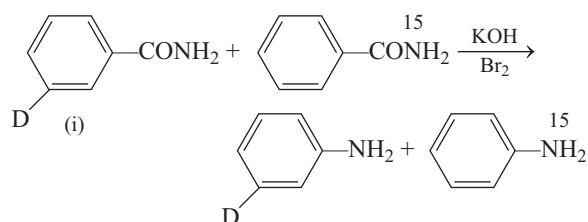
25.   $\text{Cl}-\text{C}_6\text{H}_4-\text{C}(=\text{O})\text{NH}_2 + \text{KOH} + \text{Br}_2 \longrightarrow$   
(i)   
an intermediate (ii)

- 26.** Rearrangement of (iii) to (iv) is the rate determining step :



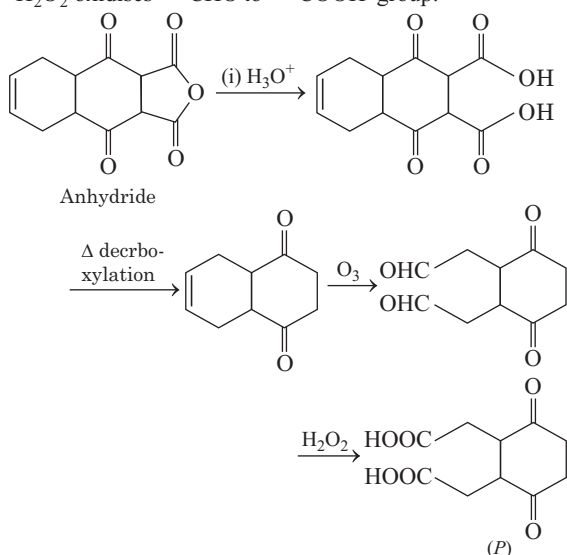
- 27.** The rate determining step of Hofmann's bromamide reaction is unimolecular rearrangement of bromamide anion (iii) and no cross-products are formed when mixture of amides are taken.



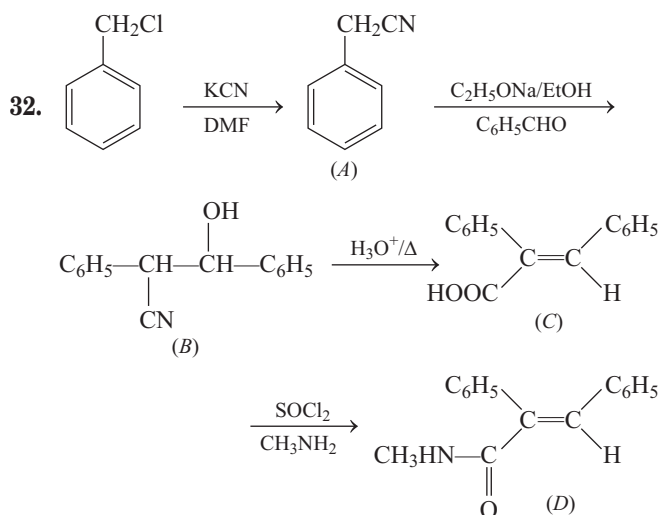


28.  $\text{HCOOH} + \text{H}_2\text{SO}_4 \xrightarrow[\text{conc.}]{\Delta} \text{H}_2\text{O} + \text{CO} \uparrow$
29. Propanoic acid has higher boiling point than *n*-butanol because of more exhaustive H-bonding in former case.
30. Saponification is hydrolysis of ester in presence of dilute base rather in presence of dilute acid.
31. **PLAN** reactant is cyclic anhydride and changes to dicarboxylic acid on hydrolysis.

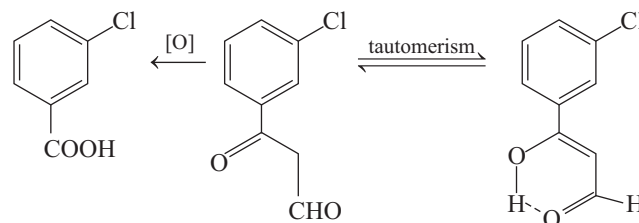
Also there is decarboxylation on heating if there is keto group *w.r.t*  $-\text{COOH}$  group. Ozonolysis cleaves  $(\text{C}=\text{C})$  bond and  $\text{H}_2\text{O}_2$  oxidises  $-\text{CHO}$  to  $-\text{COOH}$  group.



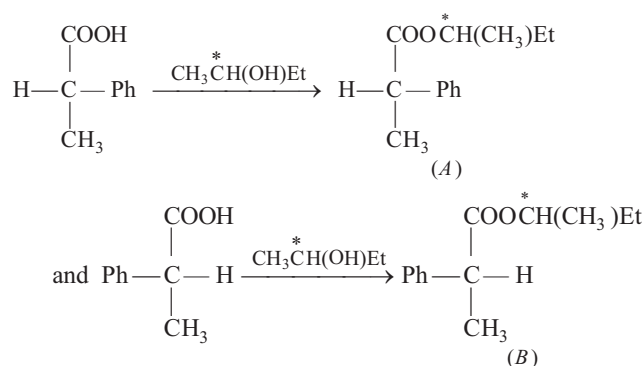
Thus, number of  $-\text{COOH}$  groups in *P* = 2.



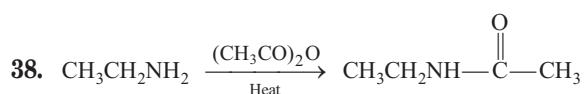
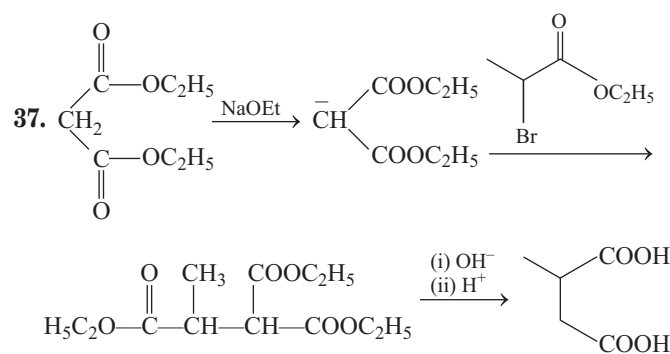
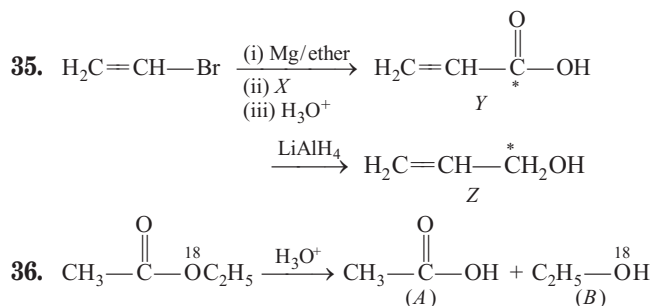
33. Compound *A* of molecular formula  $\text{C}_9\text{H}_7\text{O}_2\text{Cl}$  exist in keto and predominantly in enolic form *B*. Hence, *A* must be a carbonyl compound which contain  $\alpha$ -H. Enolic form of *B* predominates because of presence of intramolecular H-bonding.



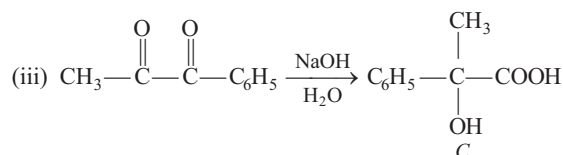
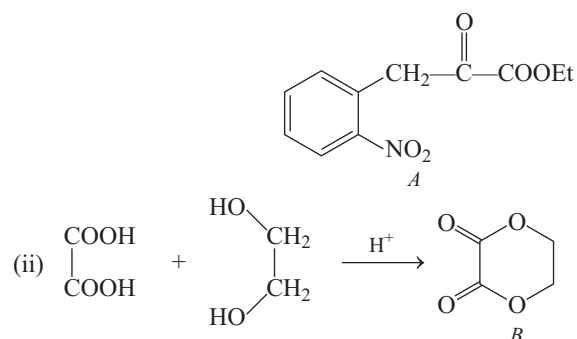
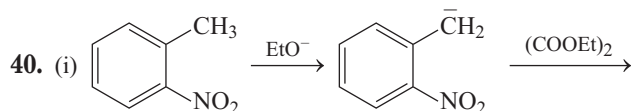
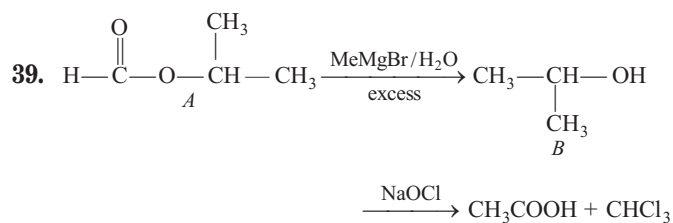
34. The two stereoisomers of 2-phenyl propanoic acid in the racemic mixture are :



Here *A* and *B* are diastereomers.

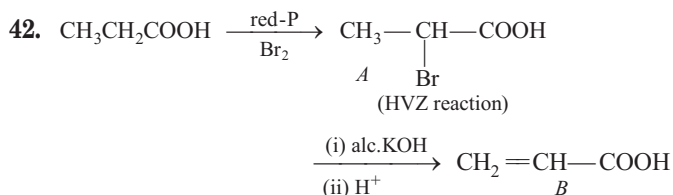
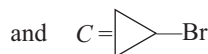
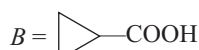
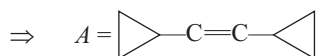


## 386 Carboxylic Acids and Their Derivatives

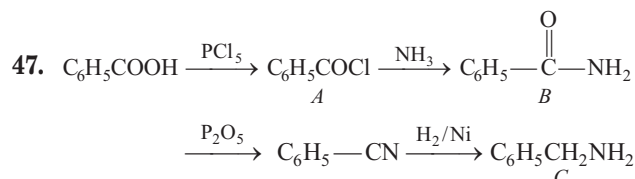
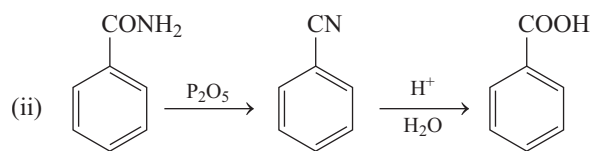
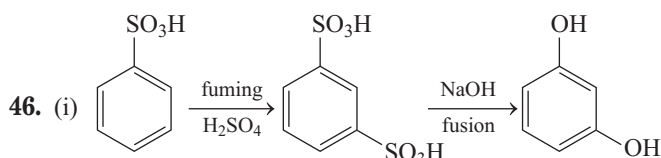
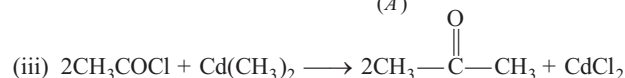
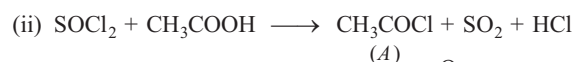
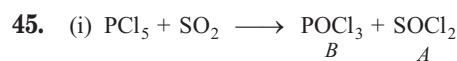
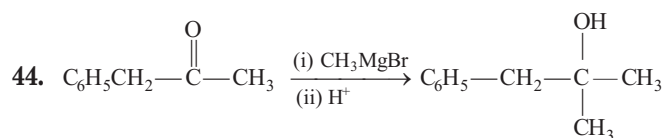
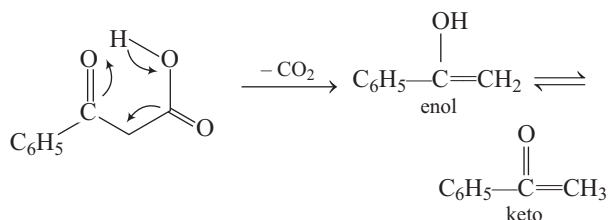


41. B is  $\text{C}_3\text{H}_5\text{COOH}$  and A is  $\text{C}_3\text{H}_5-\text{C}\equiv\text{C}-\text{C}_3\text{H}_5$

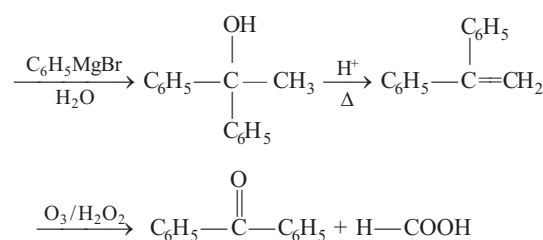
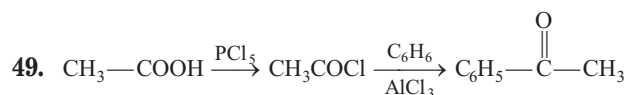
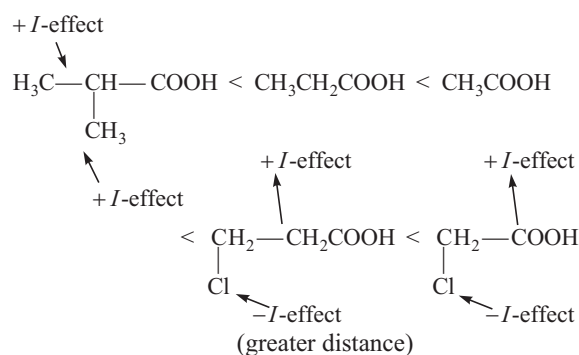
Also A on ozonolysis gives B indicates that there is no olefinic bond in  $\text{C}_3\text{H}_5$ -unit of A and it is cyclopropyl group.



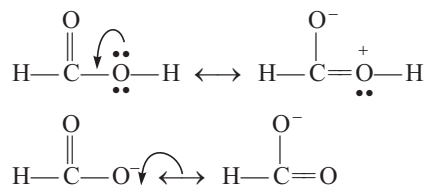
43. A  $\beta$ -keto acid undergo very fast decarboxylation



48. Electron withdrawing inductive effect increases acid strength while electron donating inductive effect decreases acid strength.



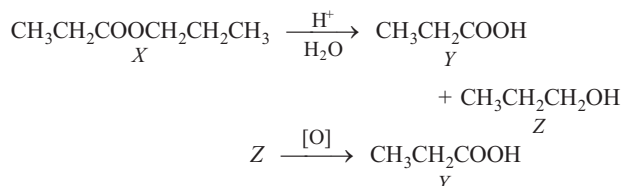
50. Both formic acid and sodium formate exhibit the phenomenon of resonance as :



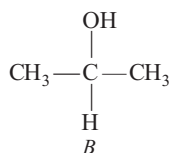
In formic acid, the extent of delocalisation is less compared to sodium formate because of charge separation in the former case. Due to this reason, the bond length between carbon and  $sp^3$  oxygen in formic acid is slightly greater than the same between carbon and  $sp^2$  oxygen. In formate ion, there is no separation of charge and both the resonance structures are equivalent giving equal bond length of both carbon oxygen bonds.

51.  $\text{CH}_3\text{CONH}_2 + \text{Br}_2 \xrightarrow{\text{NaOH}} \text{CH}_3\text{NH}_2 + \text{Na}_2\text{CO}_3$   
Hoffman bromamide reaction

52.  $X$  is an ester and both its acid and alcohol fragments have same number of carbons. Hence,  $X$  is :



53.  $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\underset{\text{A}}{\underset{\text{CH}_3}{\text{CH}}}-\text{CH}_3 \xrightarrow[\text{excess}]{\text{MeMgCl}} \xrightarrow{\text{H}^+/\text{H}_2\text{O}}$



54.  $(\text{CH}_3\text{CO})_2\text{O} \xrightarrow{\text{C}_2\text{H}_5\text{OH}} \text{CH}_3\text{COOH} + \text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{OC}_2\text{H}_5$

55. Among acid derivatives, the reactivity towards nucleophilic acyl substitution is in the order of :

Amide < Ester < Anhydride < Acid chloride

Hydrolysis is an example of nucleophilic acyl substitution, hence the reactivity towards hydrolysis is :



56.  $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH} < \text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$   
+I-effect does not affect acidity.  
decreases acid-strength

57.  $\text{CH}_3\text{CH}_2\text{CHO} + \text{AgNO}_3 \xrightarrow{\text{NH}_4\text{OH}} \text{CH}_3\text{CH}_2\text{COOH}$   
 $\xrightarrow[\Delta]{\text{P}_2\text{O}_5} (\text{CH}_3\text{CH}_2\text{CO})_2\text{O}$

58.  $\text{CH}_3-\text{COOH} + \text{Cl}_2 \xrightarrow{\text{Red-P}} \underset{\text{Cl}}{\text{CH}_2}-\text{COOH}$  (HVZ reaction)

For this reaction to occur, presence of a  $\alpha$ -H is essential requirement. Formic acid does not have any  $\alpha$ -H, fails in HVZ reaction.

59.  $\text{C}_6\text{H}_5\text{OH} + (\text{CH}_3\text{CO})_2\text{O} \xrightarrow{\text{OH}^-} \text{C}_6\text{H}_5\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$

60.  $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{OC}_2\text{H}_5 + 2\text{CH}_3\text{MgBr} \longrightarrow \text{CH}_3-\overset{\text{OMgBr}}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_3$   
 $\xrightarrow{\text{H}_2\text{O}} \text{CH}_3-\overset{\text{OH}}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_3$

61.  $\text{CH}_3\text{COOC}_2\text{H}_5 \xrightarrow{\text{C}_2\text{H}_5\text{O}^-} \text{CH}_2\text{COOC}_2\text{H}_5$   
 $\xrightarrow{\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{OC}_2\text{H}_5} \text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{COOC}_2\text{H}_5$   
Claisen condensation  
 $\xrightarrow[\text{H}_2\text{O}]{\text{H}^+} \text{C}_2\text{H}_5\text{OH} + \text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2\text{COOH}$

Download Chapter Test  
<http://tinyurl.com/y2y69czp>

or

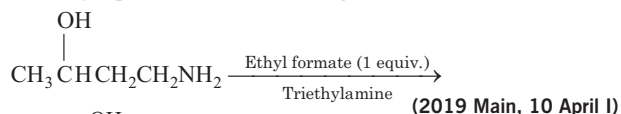


# 27

## Aliphatic Compounds Containing Nitrogen

### Objective Questions I (Only one correct option)

1. The major product of the following reaction is



- (a)  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{NHCHO}$  (b)  $\text{CH}_3\text{CH}=\text{CH}-\text{CH}_2\text{NH}_2$   
 (c)  $\text{CH}_3-\text{CH}(\text{OH})-\text{CH}=\text{CH}_2$  (d)  $\text{CH}_3\text{CH}(\text{O}-\text{CH}=\text{CH}_2)\text{CH}_2\text{CH}_2\text{NH}_2$

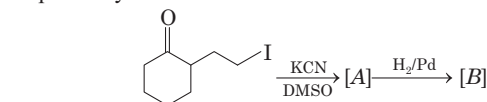
2. Ethylamine ( $\text{C}_2\text{H}_5\text{NH}_2$ ) can be obtained from *N*-ethylphthalimide on treatment with (2019 Main, 10 April I)

- (a)  $\text{NaBH}_4$  (b)  $\text{NH}_2\text{NH}_2$  (c)  $\text{H}_2\text{O}$  (d)  $\text{CaH}_2$

3. Hinsberg's reagent is (2019 Main, 9 April II)

- (a)  $\text{SOCl}_2$  (b)  $\text{C}_6\text{H}_5\text{COCl}$  (c)  $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$  (d)  $(\text{COCl})_2$

4. The major products *A* and *B* for the following reactions are, respectively (2019 Main, 9 April II)



- (a)  $\text{Cyclohexanone} \xrightarrow{\text{KCN}} \text{Cyclohexanone}-\text{CH}_2\text{CH}_2\text{CN}$  ;  $\text{Cyclohexanone}-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$   
 (b)  $\text{Cyclohexanone}-\text{CH}_2\text{CH}_2\text{CN}$  ;  $\text{Cyclohexanone}-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$   
 (c)  $\text{Cyclohexanone} \xrightarrow{\text{KCN}} \text{Cyclohexanone}-\text{CH}_2\text{CH}_2\text{CN}$  ;  $\text{Cyclohexanone}-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$   
 (d)  $\text{Cyclohexanone}-\text{CH}_2\text{CH}_2\text{CN}$  ;  $\text{Cyclohexanone}-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$

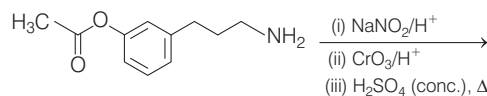
5. Which of the following amines can be prepared by Gabriel phthalimide reaction? (2019 Main, 8 April I)

- (a) *n*-butylamine  
 (b) triethylamine  
 (c) *t*-butylamine  
 (d) *neo*-pentylamine

6. In the following compounds, the decreasing order of basic strength will be (2019 Main, 8 April I)

- (a)  $\text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3 > (\text{C}_2\text{H}_5)_2\text{NH}$   
 (b)  $(\text{C}_2\text{H}_5)_2\text{NH} > \text{NH}_3 > \text{C}_2\text{H}_5\text{NH}_2$   
 (c)  $(\text{C}_2\text{H}_5)_2\text{NH} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3$   
 (d)  $\text{NH}_3 > \text{C}_2\text{H}_5\text{NH}_2 > (\text{C}_2\text{H}_5)_2\text{NH}$

7. The major product of the following reaction is (2019 Main, 12 Jan II)

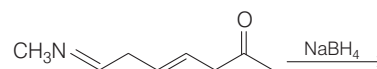


- (a)  $\text{CH}_3-\text{C}(=\text{O})-\text{O}-\text{C}_6\text{H}_4-\text{Cyclopentenone}$  (b)  $\text{HO}-\text{C}_6\text{H}_4-\text{Cyclopentenone}$   
 (c)  $\text{HO}-\text{C}_6\text{H}_4-\text{Cyclopentenone}$  (d)  $\text{CH}_3-\text{C}(=\text{O})-\text{O}-\text{C}_6\text{H}_4-\text{Cyclopentenone}$

8. A compound '*X*' on treatment with  $\text{Br}_2/\text{NaOH}$ , provided  $\text{C}_3\text{H}_9\text{N}$ , which gives positive carbylamine test. Compound '*X*' is (2019 Main, 11 Jan II)

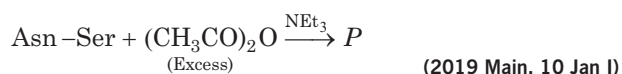
- (a)  $\text{CH}_3\text{COCH}_2\text{NHCH}_3$   
 (b)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CONH}_2$   
 (c)  $\text{CH}_3\text{CON}(\text{CH}_3)_2$   
 (d)  $\text{CH}_3\text{CH}_2\text{COCH}_2\text{NH}_2$

9. The major product of the following reaction is (2019 Main, 10 Jan II)



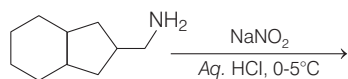
- (a)
- (b)
- (c)
- (d)

**10.** The correct structure of product 'P' in the following reaction is



- (a)
- (b)
- (c)
- (d)

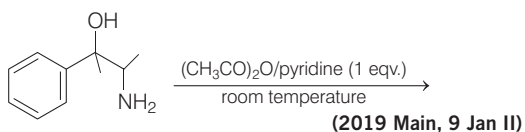
**11.** The major product formed in the reaction given below will be



(2019 Main, 10 Jan I)

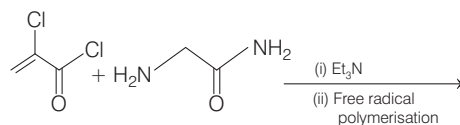
- (a)
- (b)
- (c)
- (d)

**12.** The major product obtained in the following reaction is



- (a)
- (b)
- (c)
- (d)

**13.** Major product of the following reaction is



(2019 Main, 9 Jan I)

- (a)
- (b)
- (c)
- (d)

**14.** The increasing order of basicity of the following compounds is

- I.
- II.
- III.
- IV.

(2018 Main)

- (a) (I) < (II) < (III) < (IV)  
 (b) (II) < (I) < (III) < (IV)  
 (c) (II) < (I) < (IV) < (III)  
 (d) (IV) < (II) < (I) < (III)

**15.** The order of basicity among the following compounds is

(2017 Adv.)

- (I)
- (II)
- (III)
- (IV)

- (a) II > I > IV > III  
 (b) I > IV > III > I  
 (c) IV > I > II > I  
 (d) IV > I > II > III

**16.** In the Hofmann-bromamide degradation reaction, the number of moles of NaOH and Br<sub>2</sub> used per mole of amine produced are

(2016 Main)

- (a) four moles of NaOH and two moles of Br<sub>2</sub>  
 (b) two moles of NaOH and two moles of Br<sub>2</sub>  
 (c) four moles of NaOH and one mole of Br<sub>2</sub>  
 (d) one mole of NaOH and one mole of Br<sub>2</sub>

## 390 Aliphatic Compounds Containing Nitrogen

17. Considering the basic strength of amines in aqueous solution, which one has the smallest  $pK_b$  value? (2014 Main)

(a)  $(\text{CH}_3)_2\text{NH}$  (b)  $\text{CH}_3\text{NH}_2$   
(c)  $(\text{CH}_3)_3\text{N}$  (d)  $\text{C}_6\text{H}_5\text{NH}_2$

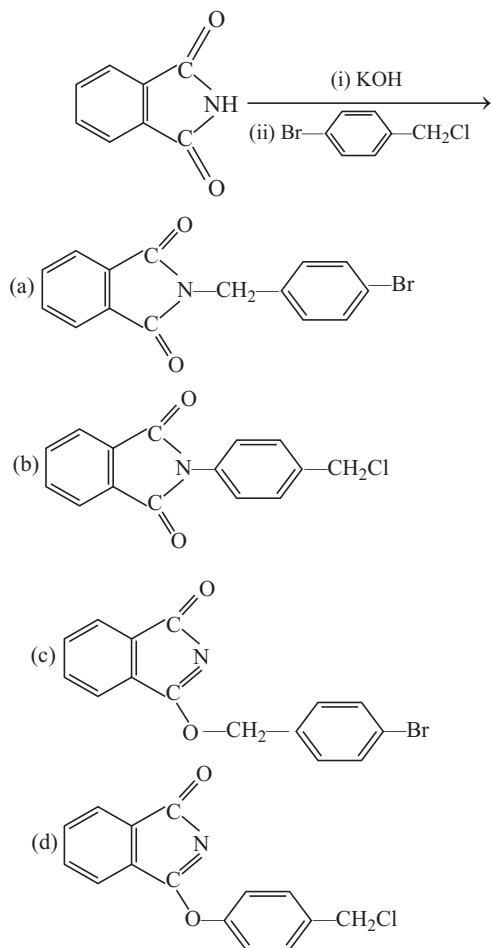
18. On heating an aliphatic primary amine with chloroform and ethanolic potassium hydroxide, the organic compound formed is

(a) an alkanol (b) an alkanediol (2014 Main)  
(c) an alkyl cyanide (d) an alkyl isocyanide

19. The gas leaked from a storage tank of the Union Carbide plant in Bhopal gas tragedy was (2013 Main)

(a) methyl isocyanate  
(b) methylamine  
(c) ammonia  
(d) phosgene

20. The major product of the following reaction is (2011)



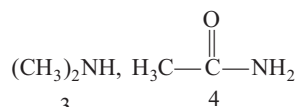
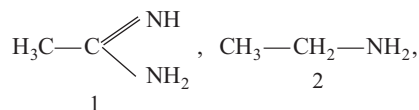
21.  $\text{CH}_3\text{NH}_2 + \text{CHCl}_3 + \text{KOH} \rightarrow$  Nitrogen containing compound +  $\text{KCl} + \text{H}_2\text{O}$ . Nitrogen containing compound is (2006)

(a)  $\text{CH}_3\text{CN}$  (b)  $\text{CH}_3\text{NHCH}_3$   
(c)  $\text{CH}_3-\text{N}^+\equiv\text{C}^-$  (d)  $\text{CH}_3-\text{N}^+\equiv\text{C}^-$

22. Benzamide on treatment with  $\text{POCl}_3$  gives (2004)

(a) aniline (b) benzonitrile  
(c) chlorobenzene (d) benzyl amine

23. The correct order of basicities of the following compounds is



(2001, 1M)

(a)  $2 > 1 > 3 > 4$  (b)  $1 > 3 > 2 > 4$  (c)  $3 > 1 > 2 > 4$  (d)  $1 > 2 > 3 > 4$

24. A positive carbylamine test is given by (1999, 2M)

(a) N, N-dimethylaniline (b) 2, 4-dimethylaniline  
(c) N-methyl-o-methylaniline (d) p-methylbenzylamine

25. p-chloroaniline and anilinium hydrochloride can be distinguished by (1998, 2M)

(a) Sandmeyer reaction (b)  $\text{NaHCO}_3$   
(c)  $\text{AgNO}_3$  (d) Carbylamine test

26. Carbylamine test is performed in alc. KOH by heating a mixture of (1984, 1M)

(a) chloroform and silver powder  
(b) trihalogenated methane and a primary amine  
(c) an alkyl halide and a primary amine  
(d) an alkyl cyanide and a primary amine

27. Acetamide is treated separately with the following reagents. Which of these would give methylamine? (1983, 1M)

(a)  $\text{PCl}_5$  (b) Sodalime  
(c)  $\text{NaOH} + \text{Br}_2$  (d) Hot, conc.  $\text{H}_2\text{SO}_4$

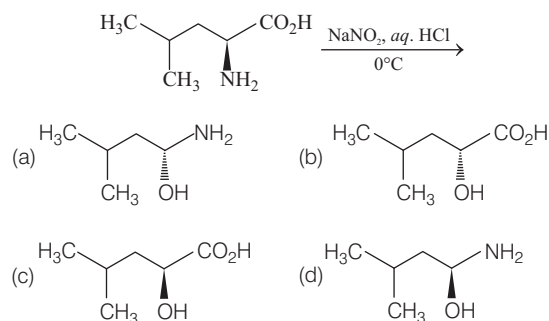
28. The compound which on reaction with aqueous nitrous acid at low temperature produces an oily nitrosamine, is

(a) methylamine (b) ethylamine (1981, 1M)  
(c) diethylamine (d) triethylamine

### Objective Question II

(Only one more than one correct option)

29. The major product of the reaction is (2015, Adv.)



30. A positive carbylamine test is given by (1999, 2M)

(a) N, N-dimethyl aniline (b) 2, 4-dimethyl aniline  
(c) N-methyl-o-methyl aniline (d) p-methyl benzyl amine

### Fill in the Blanks

31.  $(\text{CH}_3\text{OH}_2^+)$  is ..... acidic than  $(\text{CH}_3\text{NH}_3^+)$ . (1997 C, 1M)

## Match the Columns

32. Match each of the compounds in Column I with its characteristic reaction(s) in Column II. (2016, Adv.)

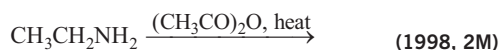
| Column I                                                      | Column II                                                                     |
|---------------------------------------------------------------|-------------------------------------------------------------------------------|
| (A) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$              | (p) Reduction with $\text{Pd} - \text{C}/\text{H}_2$                          |
| (B) $\text{CH}_3\text{CH}_2\text{OCOCH}_3$                    | (q) Reduction with $\text{SnCl}_2/\text{HCl}$                                 |
| (C) $\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}$             | (r) Development of foul smell on treatment with chloroform and alcoholic KOH. |
| (D) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ | (s) Reduction with diisobutylaluminium hydride (DIBAL-H)                      |
|                                                               | (t) Alkaline hydrolysis                                                       |

## Subjective Questions

33.  $\text{C}_5\text{H}_{13}\text{N} \xrightarrow[\text{-N}_2]{\text{NaNO}_2, \text{HCl}} \text{Y}(\text{tertiary alcohol} + \text{other products})$   
 optically active  $X$   
 Find  $X$  and  $Y$ . Is  $Y$  optically active? Write the intermediate steps (2005, 4M)

34. Give reasons for the following in one or two sentences.  
 Dimethylamine is a stronger base than trimethylamine. (1998, 2M)

35. Following reaction gives two products. Write the structures of the products.



36. Give the structure of  $A$ . ' $A$  ( $\text{C}_3\text{H}_9\text{N}$ ) reacts with benzenesulphonyl chloride to give a solid, insoluble in alkali'. (1993, 1M)

37. A basic volatile nitrogen compound gave a foul smelling gas when treated with chloroform and alcoholic KOH. A 0.295 g sample of the substance dissolved in aq. HCl and treated with  $\text{NaNO}_2$  solution at  $0^\circ\text{C}$ , liberated a colourless, odourless gas whose volume corresponds to 112 mL at STP.

After evolution of the gas was complete, the aqueous solution was distilled to give an organic liquid which did not contain nitrogen and which on warming with alkali and iodine gave a yellow precipitate. Identify the original substance assuming that it contains one N-atom per molecule. (1993, 4M)

38. Arrange the following in increasing order of basic strength: methylamine, dimethylamine, aniline, N-methylaniline. (1988, 1M)

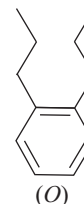
39. Give a chemical test and the reagent used to distinguish between the following: "Ethylamine and diethylamine". (1988, 1M)

40. For nitromethane molecule, write structures  
 (i) showing significant resonance stabilisation  
 (ii) indicating tautomerism (1986, 1M + 1M = 2M)

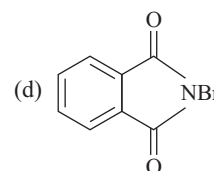
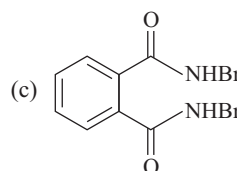
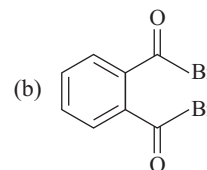
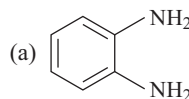
41. State the equation for the preparation of following compounds:  $n$ -propyl amine from ethyl chloride. (1982,  $2 \times 1\text{M} = 2\text{M}$ )

## Passage Based Questions

Treatment of compound  $O$  with  $\text{KMnO}_4/\text{H}^+$  gave  $P$ , which on heating with ammonia gave  $Q$ . The compound  $Q$  on treatment with  $\text{Br}_2/\text{NaOH}$  produced  $R$ . On strong heating,  $Q$  gave  $S$ , which on further treatment with ethyl 2-bromopropanoate in the presence of KOH followed by acidification, gave a compound  $T$ . (2016 Adv.)



42. The compound  $R$  is



43. The compound  $T$  is

- (a) glycine  
 (c) valine

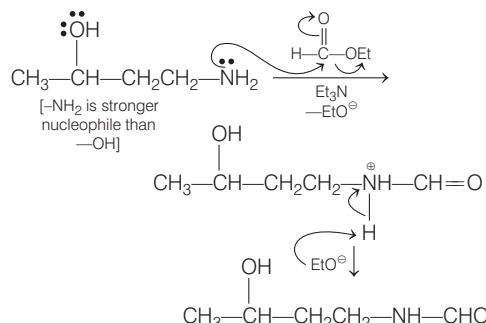
- (b) alanine  
 (d) serine

## Answers

- |         |         |         |         |         |           |            |         |
|---------|---------|---------|---------|---------|-----------|------------|---------|
| 1. (a)  | 2. (b)  | 3. (c)  | 4. (c)  | 5. (a)  | 6. (c)    | 7. (c)     | 8. (b)  |
| 9. (c)  | 10. (a) | 11. (*) | 12. (b) | 13. (d) | 14. (c)   | 15. (d)    | 16. (c) |
| 17. (a) | 18. (d) | 19. (a) | 20. (a) | 21. (d) | 22. (b)   | 23. (b)    | 24. (d) |
| 25. (c) | 26. (b) | 27. (c) | 28. (c) | 29. (c) | 30. (b,d) | 31. (more) |         |
32.  $A \rightarrow p, q, s, t$ ;  $B \rightarrow p, s, t$ ;  $C \rightarrow p$ ;  $D \rightarrow r$       42. (a)      43. (b)

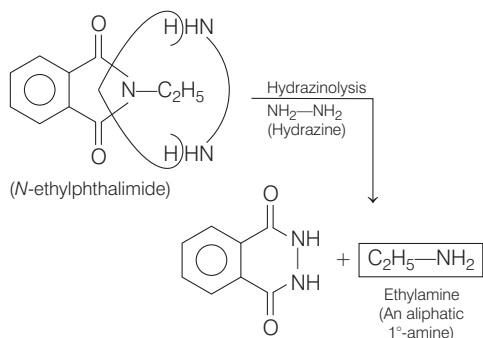
# Hints & Solutions

1. The mechanism of the given reaction is as follows:



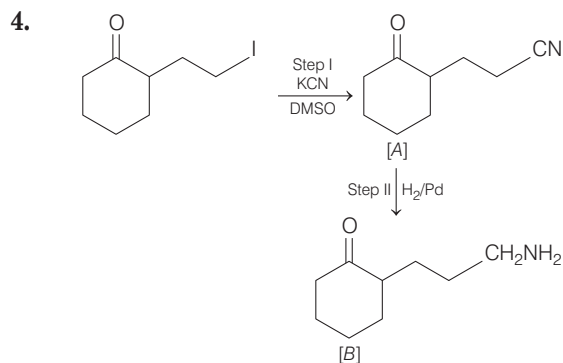
The basic mechanism of the reaction is acyl S<sub>N</sub>2 because the nucleophile, CH<sub>3</sub>(OH)CH<sub>2</sub>CH<sub>2</sub> NH<sub>2</sub> attacks the sp<sup>2</sup> carbon of the ester (H — CO<sub>2</sub>Et) and gets substituted.

2. The reaction for the production of ethylamine from *N*-ethylphthalimide can take place as follows:



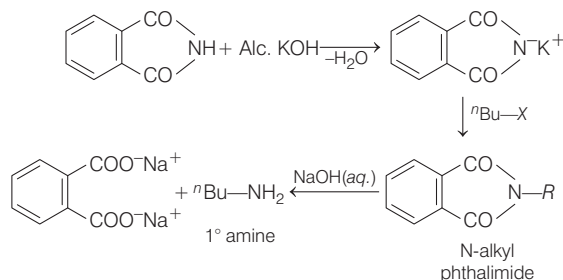
This reaction is the second step of Gabriel phthalimide synthesis for the preparation of aliphatic 1°-amines and amino acid. In this step concentrated alkali can also be used in place of hydrazine.

3. Hinsberg's reagent is C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>Cl (benzene sulphonyl chloride). This reagent is used to distinguish between primary, secondary and tertiary amines.



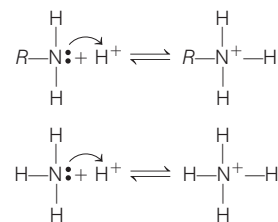
**Step I** involves the nucleophilic substitution reaction in which I (Iodine) is substituted by —CN group. **In step II**, H<sub>2</sub>/Pd reagent is used for reduction process. Here, —CN group reduces itself to —CH<sub>2</sub>NH<sub>2</sub>.

5. *n*-butylamine (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>) can be prepared by Gabriel phthalimide reaction. This method produces only primary amines without the traces of secondary or tertiary amines. In this method, phthalimide is treated with ethanolic KOH, it forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis forms corresponding primary amines.



Triethylamine, *t*-butylamine and *neo*-pentylamine cannot be prepared by Gabriel phthalimide reaction.

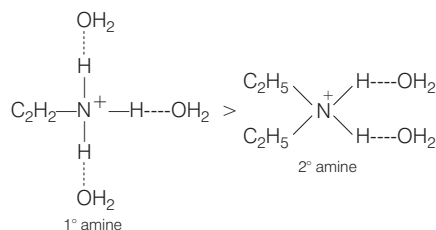
6. Basic strength can be compared by the reaction of an alkanamine and ammonia with proton.



Basicity of an amine in aqueous solution depends upon the solubility of ammonium cation formed by accepting proton from water. The stability of ammonium cation depends upon the following factors.

- (a) +I effect (b) Steric effect  
(c) Solvation effect

In first case, on increasing the size of alkyl group +I effect increases and the positive charge of ammonium cation gets dispersed more easily. Therefore, order of basicity is 2° amine > 1° amine > ammonia. In second case, substituted ammonium cation is also stabilised by solvation with water molecules. Greater the size of ion, lesser will be the solvation and less stabilised is the ion.



Considering both steric and solvation effect, it can be concluded that greater the number of H-atoms on the N-atom, greater will be the H-bonding and hence more stable is the ammonium

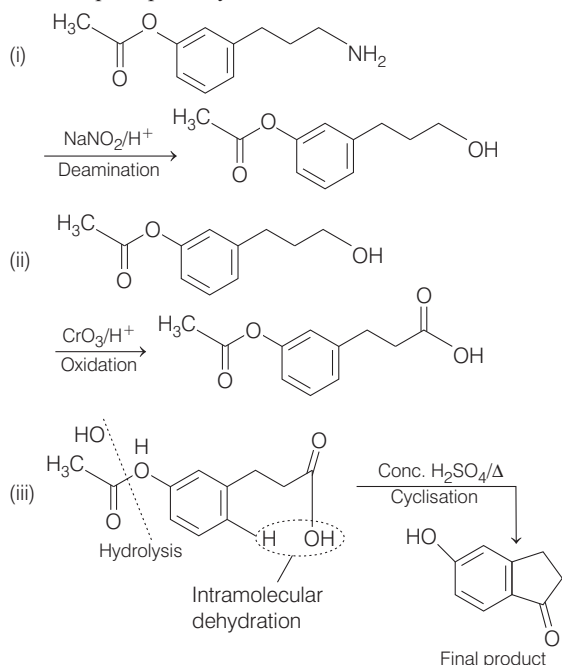


cation. But in case of  $\text{—C}_2\text{H}_5$  group, +I effect predominates over H-bonding. Therefore, order is  $2^\circ$  amine  $>$   $1^\circ$  amine  $>$  ammonia i.e.  $(\text{C}_2\text{H}_5)_2\text{NH} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3$ .

**7. Key Idea** The reaction involves:

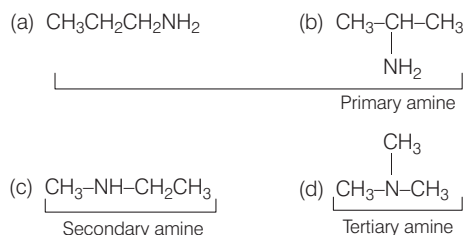
- A. Deamination in step (i)
- B. Oxidation in step (ii)
- C. Hydrolysis in step (iii)

The complete pathway of reactions is as follows:

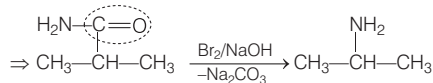
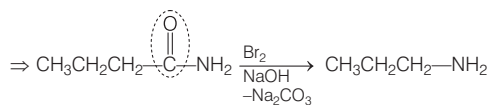


Thus, option (c) is the correct answer.

**8.** The molecular formula,  $\text{C}_3\text{H}_9\text{N}$  refers to four structural isomers of amines



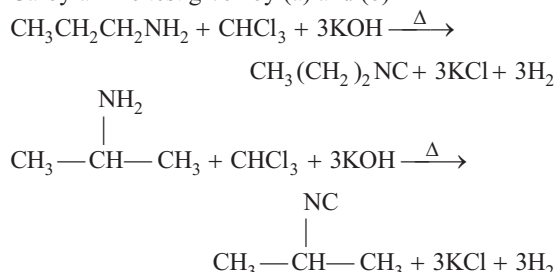
Here, only *a* and *b* (primary amines) can be prepared from their respective amides by Hoffmann bromamide ( $\text{Br}_2/\text{NaOH}$ ) method and can give positive carbylamine test.



So, 'X' can be  $\text{CH}_3\text{CH}_2\text{CH}_2\text{—CONH}_2$  (a)

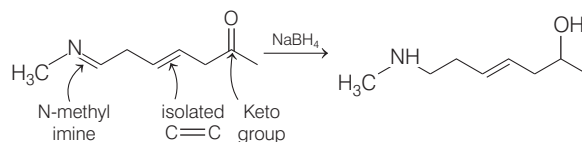
or  $\text{CH}_3\text{CH}(\text{CONH}_2)\text{CH}_3$  (b).

Carbylamine test given by (a) and (b)



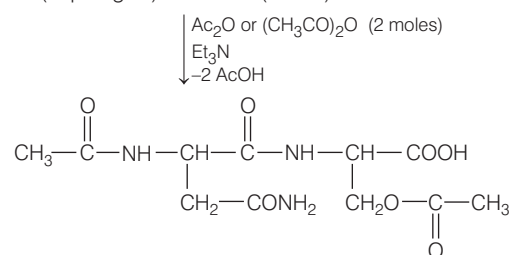
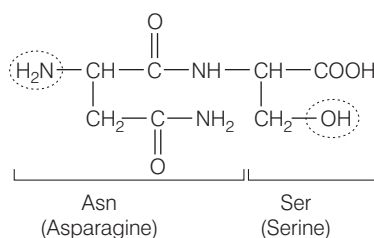
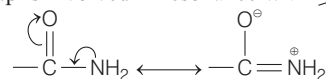
As (b) is not among the given options So, it is ruled out and compound (X) is  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CONH}_2$ .

**9.**  $\text{NaBH}_4$  is a selective reducing agent. It can reduce  $>\text{C}=\text{O}$  group into alcohol, N-methyl imine group,  $\text{Me—N}=\text{CH—}$  into  $2^\circ$ -amine but cannot reduce an isolated  $\text{C}=\text{C}$ .



**10** Acetylation by  $\text{Ac}_2\text{O}/\text{Et}_3\text{N}$  is possible with  $\text{—NH}_2$  ( $1^\circ$ -amine) and  $\text{—OH}$  (alcohol) groups only, but not with ' $\text{—NH}_2$ ' part of

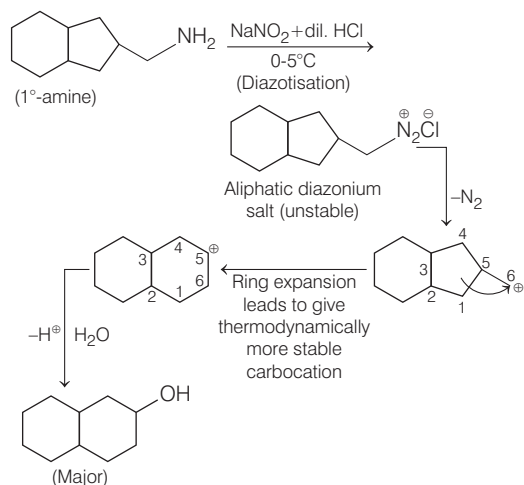
$\text{—C(=O)—NH}_2$  (amide) groups, because the *lp* of nitrogen in amide group is involved in resonance with  $>\text{C}=\text{O}$  part.



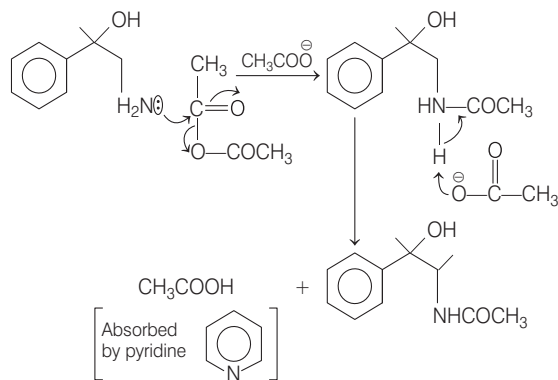
**11.** No option is the correct answer.

Amines in presence of  $\text{NaNO}_2 + \text{dil. HCl}$  undergoes diazotisation. The diazotised product readily loses nitrogen gas with the formation of carbocation. The resulting carbocation rearranges itself to give the expanded ring.

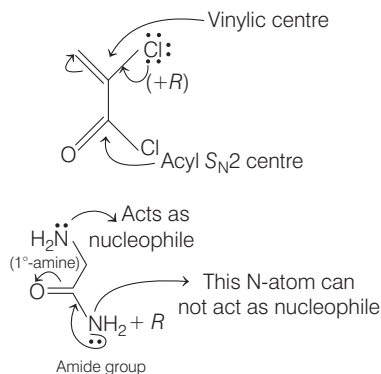
## 394 Aliphatic Compounds Containing Nitrogen



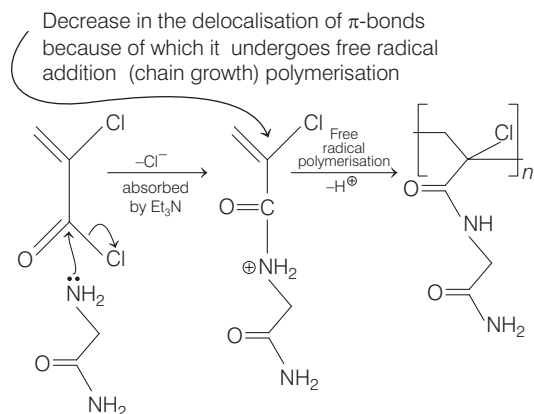
12. Rate of acetylation :  $\text{—NH}_2 > \text{—OH}$  because N-bases are stronger than O-bases. Size of N-atom is larger than O-atom and at the same time, N atom is less electronegative than O-atom. So, N-atom of the  $\text{—NH}_2$  group can donate its lone pair of electrons (Lewis basicity) more easily than that of O atom of the  $\text{—OH}$  group.



13. The analysis of both the substrates :



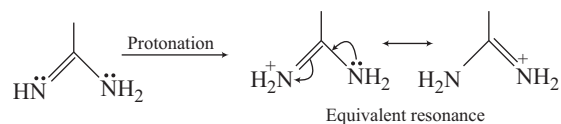
So, the reaction can take place as follows:



14. **Key Idea** Among the given compounds the basic nature depends upon their tendency to donate electron pair.

Among the given compounds in  $\text{CH}_2=\text{CHNH}_2$ , Nitrogen is  $sp^2$ -hybridised. This marginally increases the electronegativity of nitrogen which in turn decreases the electron donation tendency of nitrogen. Thus making compound least basic.

Among the rest  $\text{CH}_2=\text{CHNH}_2$  is totally different from others as in this compound lone pair of one nitrogen are in conjugation with  $\pi$  bond i.e. As a result of this conjugation the cation formed after protonation becomes resonance stabilised



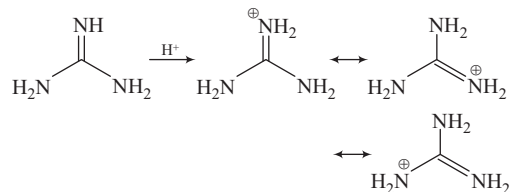
This equivalent resonance in cation makes  $\text{CH}_3\text{CH}_2\text{NH}_3^+$  most basic among all.

Categorisation is very simple between rest two as  $\text{CH}_3\text{CH}_2\text{NH}_2$  (primary amine) is less basic than  $\text{CH}_3\text{CH}_2\text{N}(\text{CH}_3)_2$  (secondary amine)

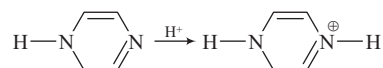
Hence, the correct order is

(II) < (I) < (IV) < (III) i.e. option (c) is correct.

15. IV is most basic as conjugate acid is stabilised by resonance of two  $\text{—NH}_2$ .

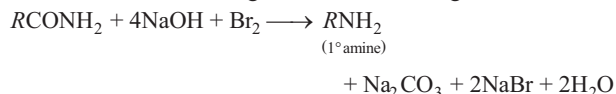


III is least basic as



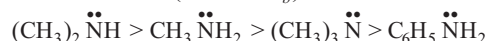
Destabilised by  $-I$ -effect of  $sp^2$ -carbons.

- 16.** Hofmann-bromamide degradation reaction is given as:



Hence, four moles of NaOH and one mole of  $\text{Br}_2$  are used.

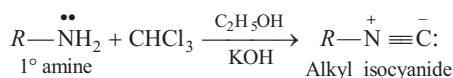
17. This problem can be solved by using the concept of effect of steric hindrance, hydration and H-bonding in basic strength of amines. Order of basic strength of aliphatic amine in aqueous solution is as follows (order of  $K_b$ )



As we know,  $\text{p}K_b = -\log K_b$

So,  $(\text{CH}_3)_2\ddot{\text{N}}\text{H}$  will have smallest  $\text{p}K_b$  value. In case of phenyl amine, N is attached to  $sp^2$ -hybridised carbon, hence it has highest  $\text{p}K_b$  and least basic strength.

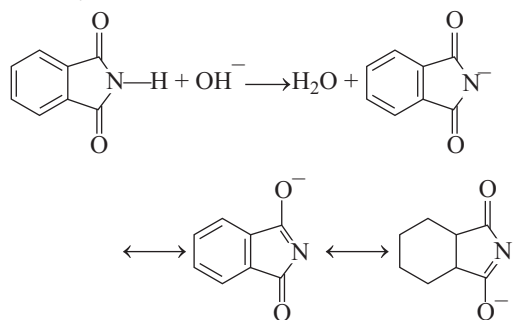
- 18.** This reaction is an example of carbylamine test which includes conversion of amine to isocyanide.



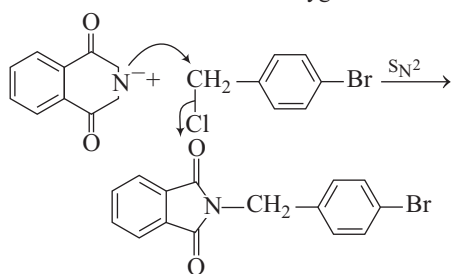
**NOTE** The mechanism of this reaction included rearrangement of nitrene in which migration of alkyl group from carbon to nitrogen takes place.

- 19.** Methyl isocyanate  $\text{CH}_3\text{—N}=\text{C}=\text{O}$  (MIC) gas was leaked from the storage tank of the union carbide plant in Bhopal gas tragedy.

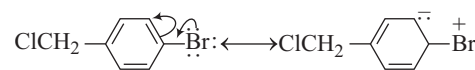
20. It is the first step of Gabriel's phthalimide synthesis. The hydrogen bonded to nitrogen is sufficiently acidic due to two  $\alpha$ -carbonyls.



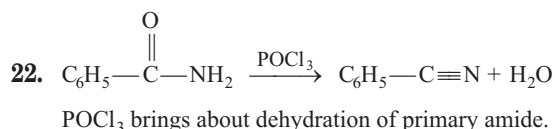
The conjugate base formed above act as nucleophile in the subsequent step of reaction. As shown above, the nucleophile exist in three resonating form, one may think of oxygen being the donor atom in the nucleophilic attack. However, nitrogen act as donor as it is better donor than oxygen.



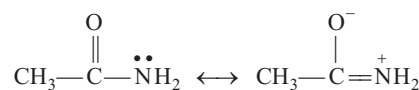
Bromine is not substituted in the above reaction as it is in resonance with benzene ring giving partial double bond character to C—Br bond, hence difficult to break.



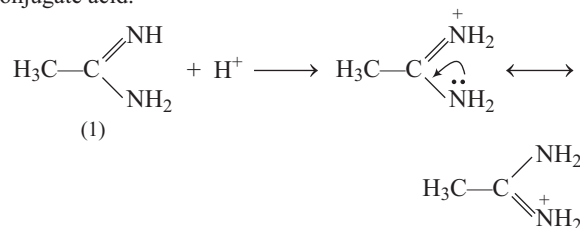
- 21.**  $\text{CH}_3\text{NH}_2 + \text{CHCl}_3 + \text{KOH} \longrightarrow \text{CH}_3-\overset{+}{\text{N}}\equiv\overset{-}{\text{C}} + \text{KCl} + \text{H}_2\text{O}$   
isocyanide



- 23.** 4, (acetamide) is least basic because lone pair of nitrogen is involved in delocalisation.

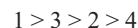


'1' is most basic due to formation of resonance stabilised conjugate acid.



3 (secondary amine) is stronger base than 2 (primary amine).

Hence, overall order of basic strength is :



24.  $\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{CH}_2\text{NH}_2 + \text{CHCl}_3 \xrightarrow{\text{KOH}}$
- p*-methyl benzylamine  
(a primary amine)
- $\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{CH}_2-\text{NC}$   
(isocyanide)

Carbylamine test is not given by secondary or tertiary amine.

25.  $\text{C}_6\text{H}_5\text{NH}_3^+\text{Cl}^- + \text{AgNO}_3 \longrightarrow \text{C}_6\text{H}_5\text{NH}_3^+\text{NO}_3^- + \text{AgCl}(s) \downarrow$   
 anilinium  
 hydrochloride

No such precipitate of  $\text{AgCl}(s)$  would be formed with *p*-chloroaniline.

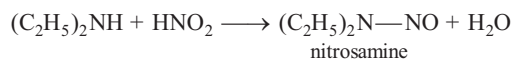
- 26.**  $R-NH_2 + CHCl_3 \xrightarrow{KOH} R-NC$  'Carbylamine test'  
isocyanide  
(foul smell)

The above test is characteristic of primary amine and used to distinguish primary amine from other amines.

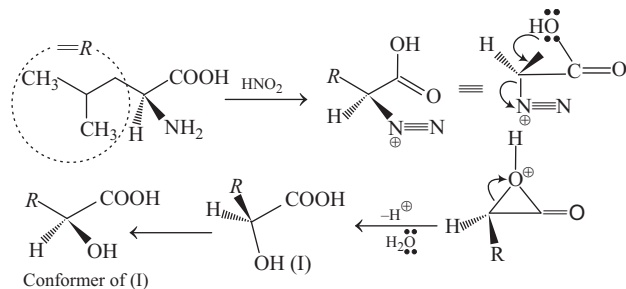
27. 
$$\text{CH}_3\text{—}\overset{\text{O}}{\parallel}\text{C—NH}_2 + \text{Br}_2 \xrightarrow{\text{NaOH}} \text{CH}_3\text{NH}_2$$
  
acetamide methylamine  
(Hofmann's bromamide reaction)

## 396 Aliphatic Compounds Containing Nitrogen

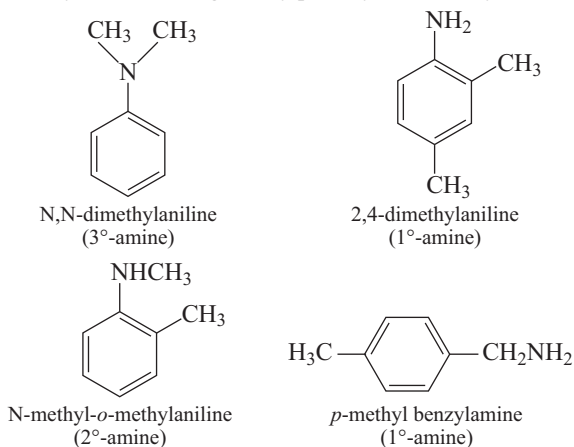
28. A secondary amine, on treatment with aqueous nitrous acid at low temperature produces oily nitrosamine.



29. Reaction proceeds *via* diazonium salt with neighbouring group participation.

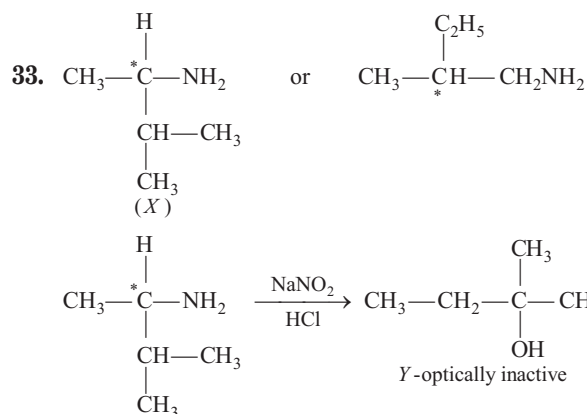


30. Carbylamine test is given by primary amines only.



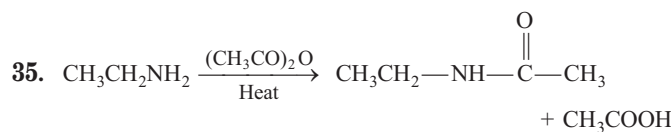
31. More :  $CH_3NH_2$  is stronger base than  $CH_3OH$ .

| Column I                         | Column II                                                                                                                                                      |
|----------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------|
| (A) $CH_3CH_2CH_2CN$ :           | Gives amine with Pd-C/ $H_2$<br>Gives aldehyde with $SnCl_2/HCl$ Gives amide with diisobutyl- aluminium hydride. Gives carboxylic acid on alkaline hydrolysis. |
| (B) $CH_3CH_2OCOCH_3$ :<br>ester | Reduced to alcohol with Pd -C/ $H_2$ Reduced with diisobutylaluminium hydride into aldehyde. Undergo alkaline hydrolysis.                                      |
| (C) $CH_3CH=CHCH_2OH$<br>:       | Reduced to butanol when treated with Pd-C/ $H_2$ .                                                                                                             |
| (D) $CH_3CH_2CH_2CH_2NH_2$       | A primary amine, gives carbylamine test.                                                                                                                       |

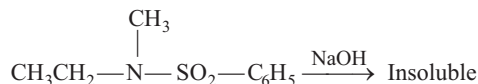


Above reaction proceeds *via* carbocation intermediate, hence rearrangement takes place.

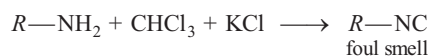
34. Conjugate acid of dimethylamine is more stable than conjugate base of triethyl amine due to exhaustive H-bonding with water.



36. A must be a secondary amine :



37. Starting compound is a primary amine.



$$\text{Moles of } N_2 = \frac{112}{22500} = 5 \times 10^{-3}$$

$\therefore$  One mole of  $N_2$  is obtained from 1.0 mole of  $R-NH_2$ , mole of  $R-NH_2 = 5 \times 10^{-3}$

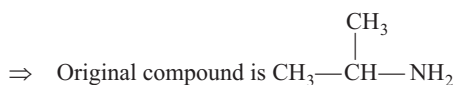
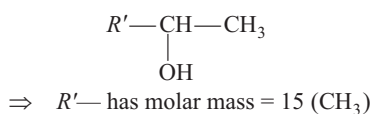
$$\Rightarrow 5 \times 10^{-3} \text{ mol } R-NH_2 \text{ weigh} = 0.295 \text{ g}$$

$$1 \text{ mole of } R-NH_2 \text{ will weigh} = \frac{0.295}{5 \times 10^{-3}} = 59 \text{ g}$$

In  $R-NH_2$ ,  $-NH_2$  has molar mass = 16

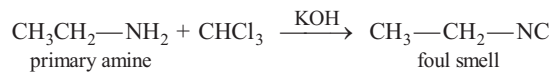
$$\Rightarrow R- \text{ has molar mass} = 43$$

Also, the alcohol  $R-OH$  gives iodoform test; it must has the following skeleton :

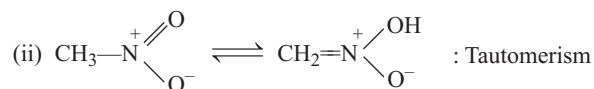
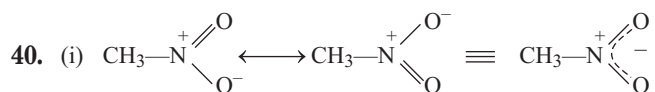
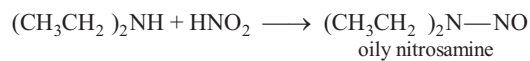


38. Aniline > N-methylaniline < methylamine < dimethylamine.

39. Carbylamine test given only by primary amine.

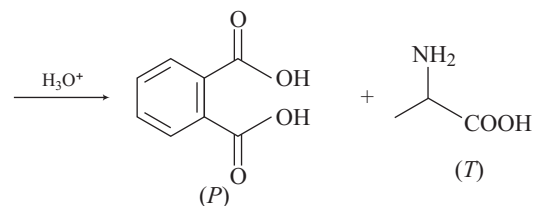
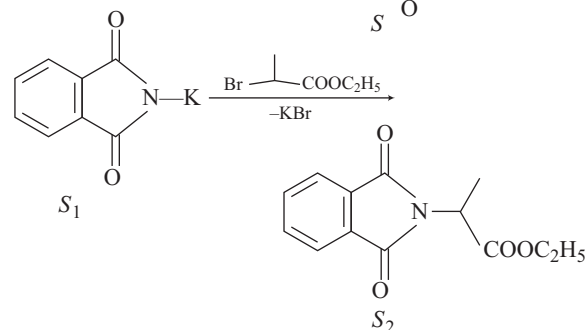
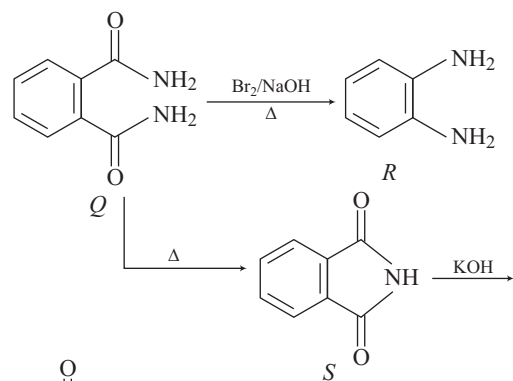
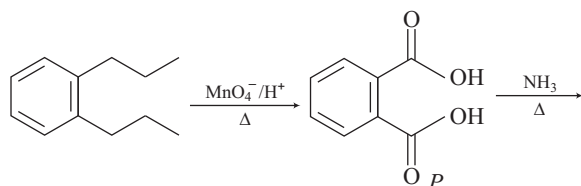


Nitrosamine test is given only by secondary amine.



42. (a)

43. Explanation



**Download Chapter Test**

<http://tinyurl.com/y6nlww9e>

or

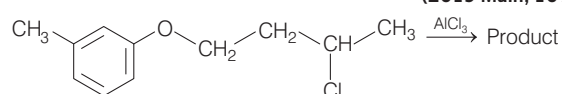


# 28

## Benzene and Alkyl Benzene

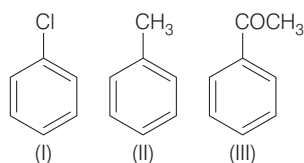
### Objective Questions I (Only one correct option)

1. The major product obtained in the given reaction is  
(2019 Main, 10 April II)

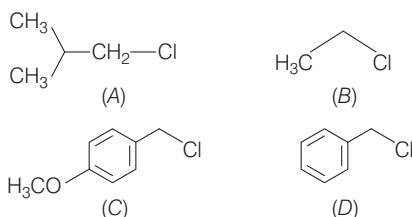


- (a) CC1=CC=C(C=C1)OCC(C)C  
 (b) CC1=CC=C(C=C1)OCC(C)C  
 (c) CC1=CC=C(C=C1)OCC(C)C  
 (d) CC1=CC=C(C=C1)OCC(C)C

2. The increasing order of the reactivity of the following compounds towards electrophilic aromatic substitution reaction is  
(2019 Main, 10 April I)

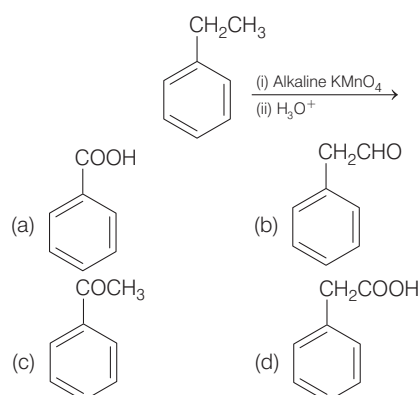


- (a) III < I < II    (b) II < I < III  
 (c) III < II < I    (d) I < III < II
3. Increasing order of reactivity of the following compounds for  $S_N1$  substitution is  
(2019 Main, 9 April II)

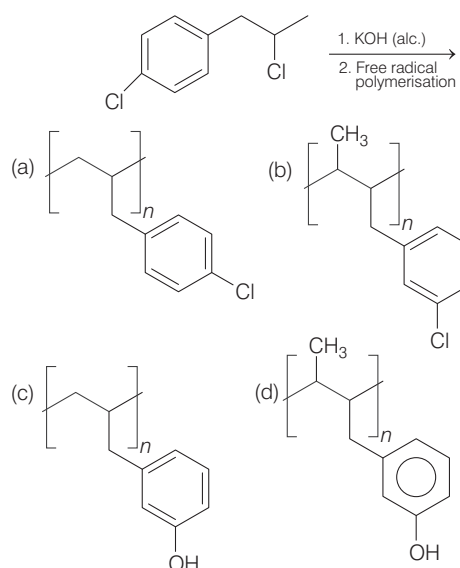


- (a) (A) < (B) < (D) < (C)  
 (b) (B) < (C) < (D) < (A)  
 (c) (B) < (A) < (D) < (C)  
 (d) (B) < (C) < (A) < (D)

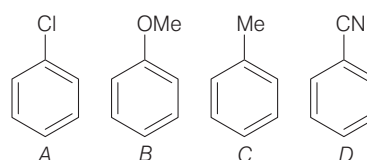
4. The major product of the following reaction is  
(2019 Main, 9 April I)



5. The major product of the following reaction is  
(2019 Main, 9 April I)



6. The increasing order of reactivity of the following compounds towards aromatic electrophilic substitution reaction is  
(2019 Main, 9 April I)

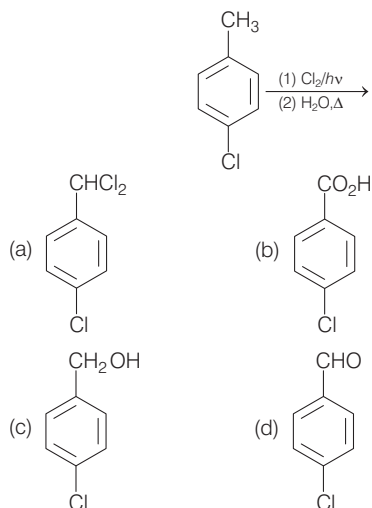


- (a)  $A < B < C < D$  (b)  $B < C < A < D$   
 (c)  $D < A < C < B$  (d)  $D < B < A < C$

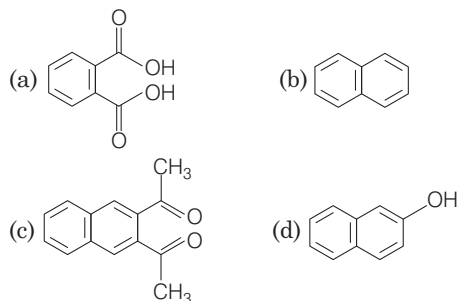
7. Polysubstitution is a major drawback in (2019 Main, 8 April II)

- (a) Friedel-Craft's alkylation  
 (b) Reimer-Tiemann reaction  
 (c) Friedel-Craft's acylation  
 (d) Acetylation of aniline

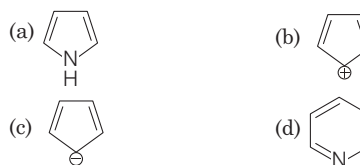
8. The major product of the following reaction is (2019 Main, 8 April II)



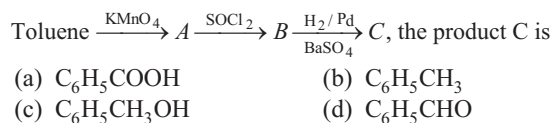
9. Among the following four aromatic compounds, which one will have the lowest melting point? (2019 Main, 12 Jan I)



10. Which of the following compounds is not aromatic? (2019 Main, 9 Jan II)



11. In the following sequence of reactions (2015 Main)



12. Match the four starting materials given in Column I with the corresponding reaction schemes provided in Column II and select the correct answer using the code given below the lists.

| Column I |  | Column II |                                                                                                                                                                                                                                                                             |
|----------|--|-----------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| A.       |  | p.        | <b>Scheme I</b><br>(i) $\text{KMnO}_4, \text{HO}^-$ , heat (ii) $\text{H}^+$ , $\text{H}_2\text{O}$<br>(iii) $\text{SOCl}_2$ (iv) $\text{NH}_3$<br>? $\longrightarrow \text{C}_7\text{H}_6\text{N}_2\text{O}_3$                                                             |
| B.       |  | q.        | <b>Scheme II</b><br>(i) $\text{Sn}/\text{HCl}$ (ii) $\text{CH}_3\text{COCl}$ (iii) Conc. $\text{H}_2\text{SO}_4$<br>(iv) $\text{HNO}_3$ (v) Dil. $\text{H}_2\text{SO}_4$ , heat (vi) $\text{HO}^-$<br>? $\longrightarrow \text{C}_6\text{H}_6\text{N}_2\text{O}_2$          |
| C.       |  | r.        | <b>Scheme III</b><br>(i) Red hot iron, 873 K (ii) fuming $\text{HNO}_3$ , $\text{H}_2\text{SO}_4$ , heat<br>(iii) $\text{H}_2\text{S}$ , $\text{NH}_3$ (iv) $\text{NaNO}_2$ , $\text{H}_2\text{SO}_4$ (v) hydrolysis<br>? $\longrightarrow \text{C}_6\text{H}_5\text{NO}_3$ |
| D.       |  | s.        | <b>Scheme IV</b><br>(i) Conc. $\text{H}_2\text{SO}_4$ , $60^\circ\text{C}$<br>(ii) Conc. $\text{HNO}_3$ , conc. $\text{H}_2\text{SO}_4$ (iii) Dil. $\text{H}_2\text{SO}_4$ , heat<br>? $\longrightarrow \text{C}_6\text{H}_5\text{NO}_4$                                    |

#### Codes

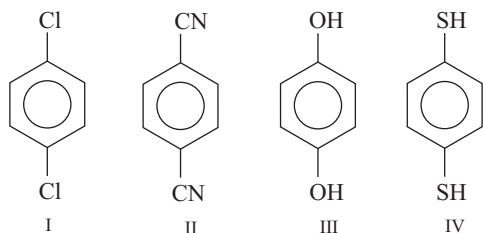
- A B C D  
 (a) p s q r  
 (c) r s q p

- A B C D  
 (b) r p s q  
 (d) s p r q

(2014 Adv.)

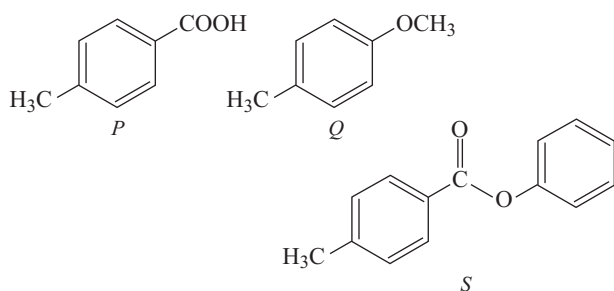
## 400 Benzene and Alkyl Benzene

13. For which of the following molecule significant  $\mu \neq 0$ ?

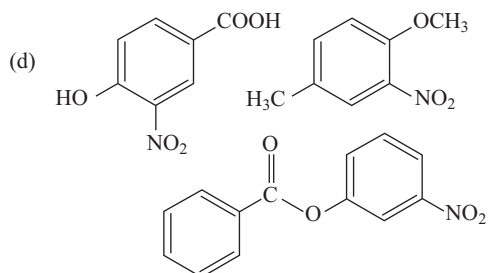
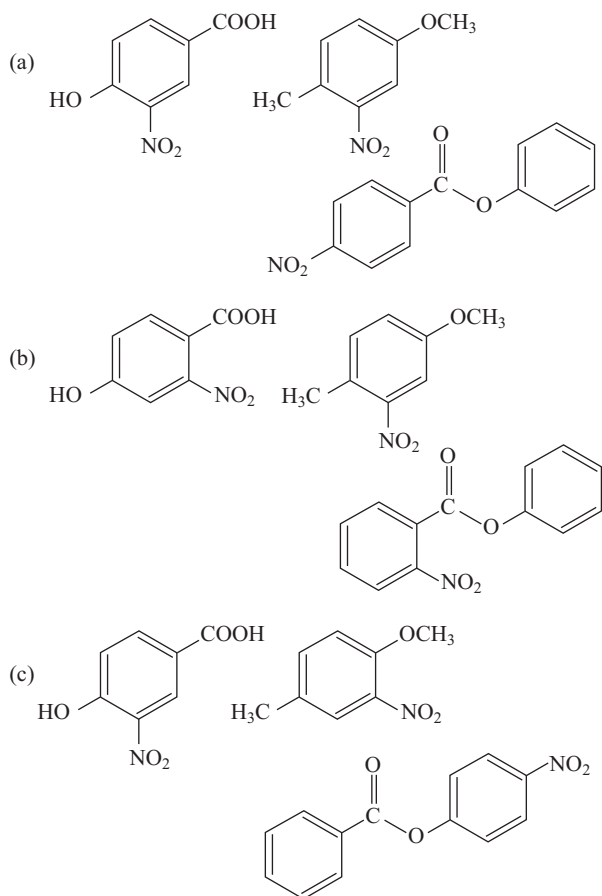


- (a) Only I                      (b) I and II                      (2014 Main)  
(c) Only III                      (d) III and IV

14. The compounds *P*, *Q* and *S*



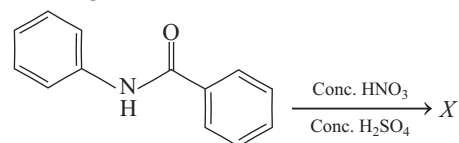
were separately subjected to nitration using  $\text{HNO}_3 / \text{H}_2\text{SO}_4$  mixture. The major product formed in each case respectively, is (2010)



15. In the reaction, the products are, (2010)

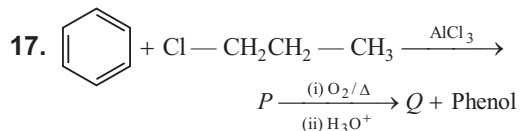
- (a) and  $\text{H}_2$     (b) and  $\text{CH}_3\text{Br}$   
(c) and  $\text{CH}_3\text{OH}$     (d) and  $\text{CH}_3\text{Br}$

16. In the following reaction,



The product *X* is (2007, 3M)

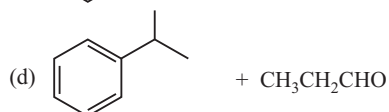
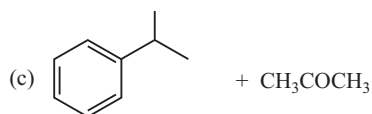
- (a)
- (b)
- (c)
- (d)



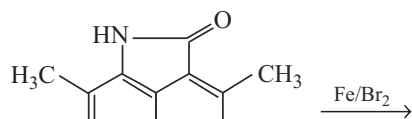
*P* and *Q* are respectively (2006, 5M)

- (a) +  $\text{CH}_3\text{CH}_2\text{CHO}$   
(b) +  $\text{CH}_3\text{COCH}_3$

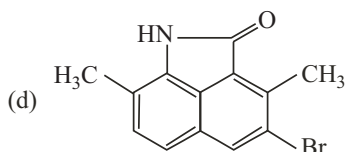
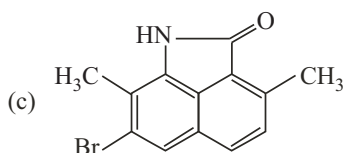
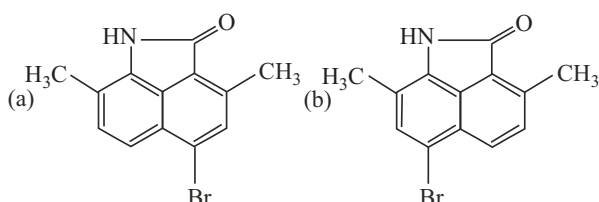




18.



product on monobromination of this compound is (2004, 1M)



19. Identify the correct order of reactivity in electrophilic substitution reactions of the following compounds Benzene (1), Toluene (2), Chlorobenzene (3) and Nitrobenzene (4) (2002)

- (a)  $1 > 2 > 3 > 4$  (b)  $4 > 3 > 2 > 1$   
(c)  $2 > 1 > 3 > 4$  (d)  $2 > 3 > 1 > 4$

20. A solution of (+) -2-chloro-2-phenylethane in toluene racemises slowly in the presence of small amount of  $\text{SbCl}_5$ , due to the formation of (1999, 2M)

- (a) carbanion (b) carbene  
(c) free-radical (d) carbocation

21. Benzyl chloride ( $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ ) can be prepared from toluene by chlorination with (1998, 2M)

- (a)  $\text{SO}_2\text{Cl}_2$  (b)  $\text{SOCl}_2$  (c)  $\text{Cl}_2$  (d)  $\text{NaOCl}$

22. Chlorination of toluene in the presence of light and heat followed by treatment with aqueous  $\text{NaOH}$  gives (1990, 1M)

- (a) *o*-cresol (b) *p*-cresol  
(c) 2, 4-dihydroxy toluene (d) benzoic acid

23. The reaction of toluene with chlorine in the presence of ferric chloride ( $\text{FeCl}_3$ ) gives predominantly (1986, 1M)

- (a) benzoyl chloride (b) *m*-chlorotoluene  
(c) benzyl chloride (d) *o*- and *p*-chlorotoluene

24. The compound that is most reactive towards electrophilic substitution is (1985, 1M)

- (a) toluene (b) benzene  
(c) benzoic acid (d) nitrobenzene

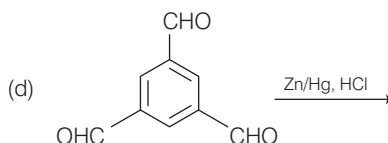
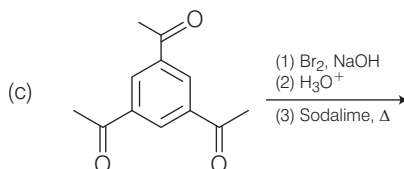
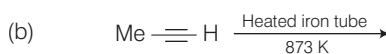
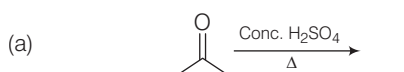
25. Among the following, the compound that can be most readily sulphonated is (1982)

- (a) benzene (b) nitrobenzene  
(c) toluene (d) chlorobenzene

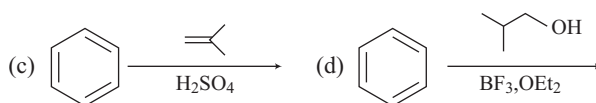
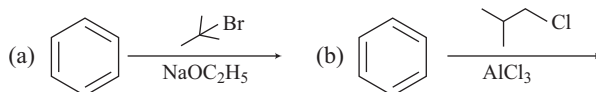
## Objective Questions II

(One or more than one correct option)

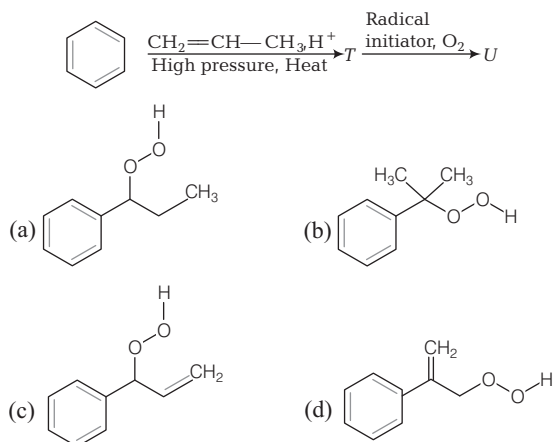
26. The reaction(s) leading to the formation of 1,3,5-trimethylbenzene is (are) (2018 Adv.)



27. Among the following reactions(s), which gives(give) *tert*-butyl benzene as the major product? (2016 Adv.)

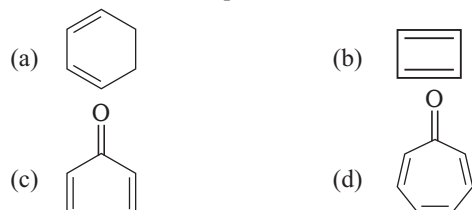


28. The major product *U* in the following reaction is (2015 Adv.)



## 402 Benzene and Alkyl Benzene

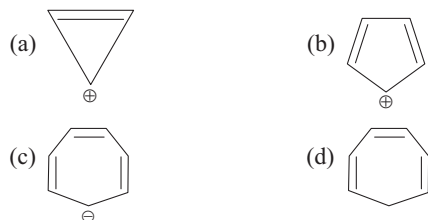
29. Which of the following molecules, in pure form, is/are unstable at room temperature? (2012)



30. An aromatic molecule will (1999, 3M)

- (a) have  $4n$   $\pi$ -electrons  
 (b) have  $(4n + 2)\pi$ -electrons  
 (c) be planar  
 (d) be cyclic

31. Which compound(s) out of the following is/are not aromatic? (2019 Main, 11 Jan I)



32. Toluene, when treated with  $\text{Br}_2/\text{Fe}$ , gives *p*-bromotoluene as the major product because the  $\text{CH}_3$  group (1999, 3M)

- (a) is *para*-directing  
 (b) is *meta*-directing  
 (c) activates the ring by hyperconjugation  
 (d) deactivates the ring

33. A new carbon-carbon bond formation is possible in (1998)

- (a) Cannizzaro's reaction (b) Friedel-Craft's alkylation  
 (c) Clemmensen reduction (d) Reimer-Tiemann reaction

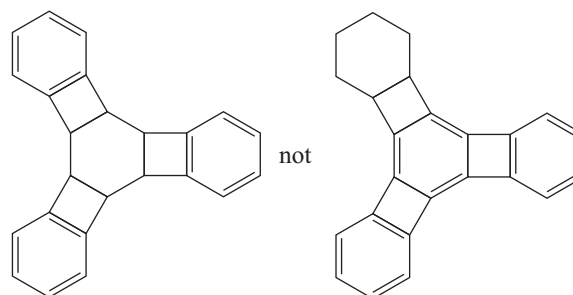
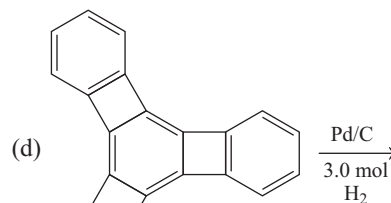
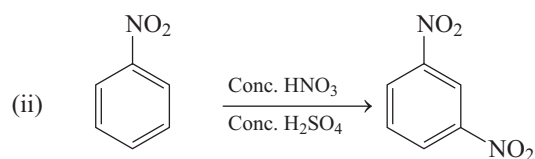
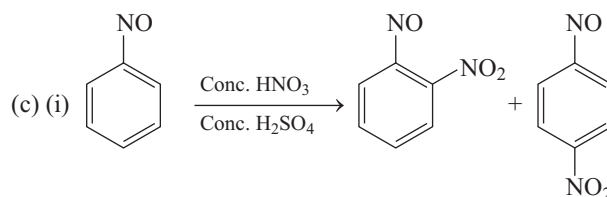
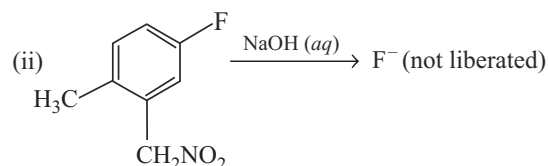
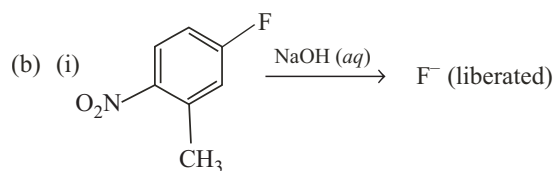
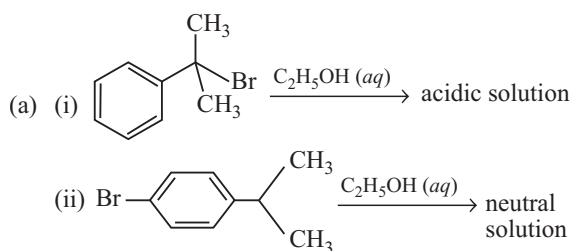
### True or False

34. An electron donating substituent in benzene orients the incoming electrophilic group to the *meta*-position. (1987, 1M)

35. In benzene, carbon uses all the three *p*-orbitals for hybridisation. (1987, 1M)

### Subjective Questions

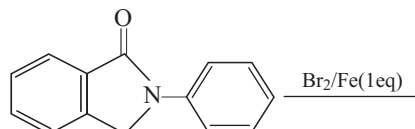
36. Explain the followings :



(2005)

37. 7-bromo-1, 3, 5-cycloheptatriene exists as ionic species in aqueous solution while 5-bromo-1,3-cyclopentadiene doesn't ionise even in presence of  $\text{Ag}^+(aq)$ . Explain. (2004)

38. What would be the major product in the following reaction? (2000, Main, 1M)



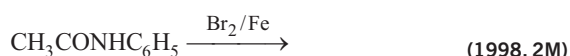
39. Give reasons for the following :

- tert*-butylbenzene does not give benzoic acid on treatment with acidic  $\text{KMnO}_4$ .
- Normally, benzene gives electrophilic substitution reaction rather than electrophilic addition reaction although it has double bond. (2000)

40. Show the steps to carry out the following transformations.

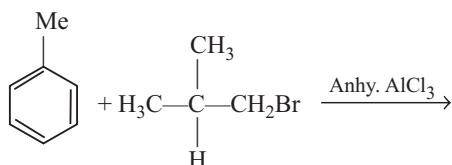
- Ethylbenzene  $\rightarrow$  benzene
- Ethylbenzene  $\rightarrow$  2-phenylpropionic acid

41. Write the structures of the products.



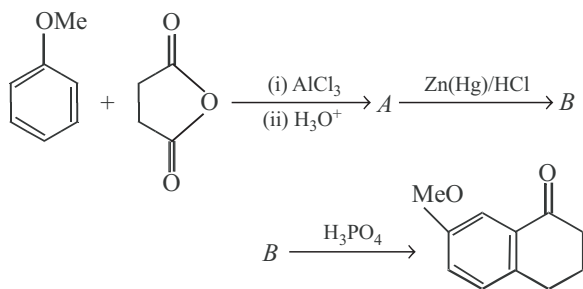
42. Give reasons for the following in one or two sentences  
“Nitrobenzene does not undergo Friedel-Craft’s alkylation.” (1998, 2M)

43. Complete the following, giving the structures of the principal organic products. (1997)

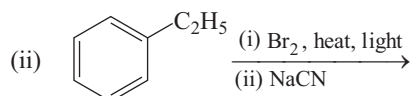
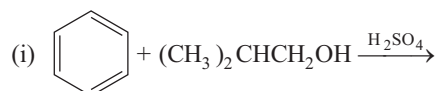


44. Toluene reacts with bromine in the presence of the light to give benzyl bromide, while in presence of  $\text{FeBr}_3$  it gives *p*-bromotoluene. Give explanation for the above observation. (1996)

45. Predict the structures of the intermediates/products in the following reaction sequences (1996)

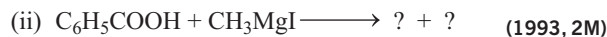
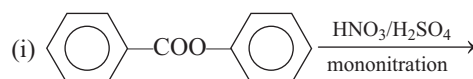


46. Predict the major product in the following reactions (1994)

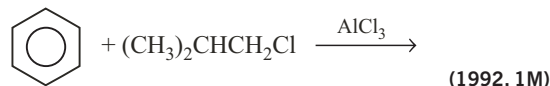


47. Give reason for the following ‘In acylium ion the structure  $\text{R}-\text{C}\equiv\text{O}^+$  is more stable than  $\text{R}-\text{C}^+=\text{O}$ ’ (1994, 1M)

48. Identify the major product in the following reactions :



49. Write the structure of the major organic product expected from the following reaction



50. Give reasons in two or three sentences only for the following:  
Phenyl group is known to exert negative inductive effect, but each phenyl ring in biphenyl ( $\text{C}_6\text{H}_5-\text{C}_6\text{H}_5$ ) is more reactive than benzene towards electrophilic substitution. (1992, 1M)

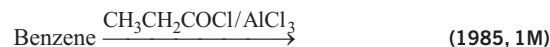
51. Arrange the following in increasing order of reactivity towards sulphonation with fuming sulphuric acid.  
Benzene, toluene, methoxy benzene, chlorobenzene. (1988, 1M)

52. Answer the following with suitable equation wherever necessary

(i) How can you prepare benzene from lime ?

(ii) How will you convert toluene to *m*-nitrobenzoic acid ? (1987, 2M)

53. Write down the main product of the following reaction



54. How many sigma and pi-bonds are present in a benzene molecule ? (1985, 1M)

55. Write down the reaction involved in the preparation of following using the reagents indicated against in parenthesis.  
“Ethyl benzene from benzene.”

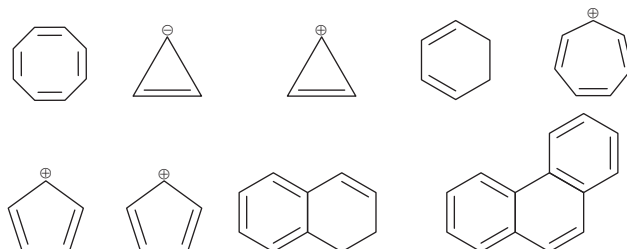


56. Show with balanced equation what happens when the ‘*p*-xylene is reacted with concentrated sulphuric acid and the resultant product is fused with  $\text{KOH}$ ’. (1984, 1M)

57. Give reasons for the following in one or two sentences :  
‘Although benzene is highly unsaturated, normally it does not undergo addition reaction.’ (1983, 1M)

## Integer Type Questions

58. Among the following, the number of aromatic compound(s) is



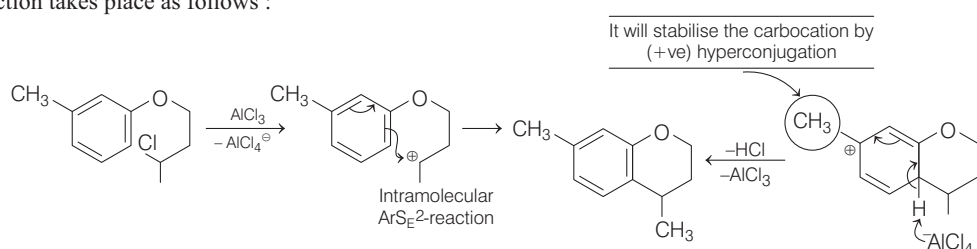
## 404 Benzene and Alkyl Benzene

### Answers

- |         |         |         |         |           |             |             |               |
|---------|---------|---------|---------|-----------|-------------|-------------|---------------|
| 1. (c)  | 2. (a)  | 3. (c)  | 4. (a)  | 21. (a)   | 22. (d)     | 23. (d)     | 24. (a)       |
| 5. (a)  | 6. (c)  | 7. (a)  | 8. (d)  | 25. (c)   | 26. (a,b,d) | 27. (b,c,d) | 28. (b)       |
| 9. (b)  | 10. (b) | 11. (d) | 12. (c) | 29. (b,c) | 30. (b,c,d) | 31. (b,c,d) | 32. (a,c)     |
| 13. (d) | 14. (c) | 15. (d) | 16. (b) | 33. (b,d) | 34. False   | 35. False   | 54. (12σ, 3π) |
| 17. (c) | 18. (b) | 19. (c) | 20. (d) | 58. (5)   |             |             |               |

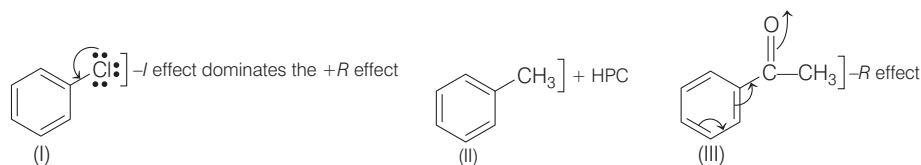
### Hints & Solutions

1. The given reaction takes place as follows :

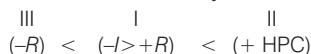


2. **Key Idea** In electrophilic aromatic substitution ( $\text{Ar S}_\text{E}2$ ) reaction, the aromatic (benzene nucleus here) compound (substrate) acts as a nucleophile which gets attacked by an electrophile in the rate determining step (rds).

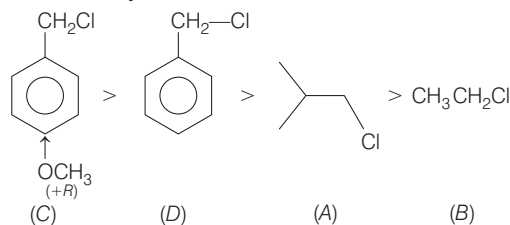
Higher electron density on the nucleophile, i.e. benzene nucleus will fasten the rate of the reaction. Electron-donating groups (EDG) will increase electron density in benzene nucleus by any or both of their  $+R/+M$  and hyperconjugative (HPC) effects. Now, let us consider the given substrate.



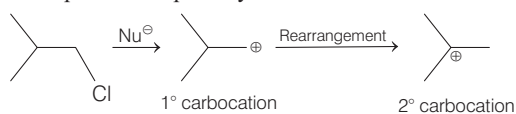
As  $-R$  effect is more powerful than  $-I$  effect, the order of their reactivity, towards an electrophile will be



3. Reactivity of substitution nucleophilic unimolecular ( $\text{S}_\text{N}1$ ) reaction depends on the formation of carbocation. Greater the stability of carbocation, greater will be its ease of formation of alkyl halide and faster will be the rate of reaction. So, the correct order of ( $\text{S}_\text{N}1$ ) reactivity is

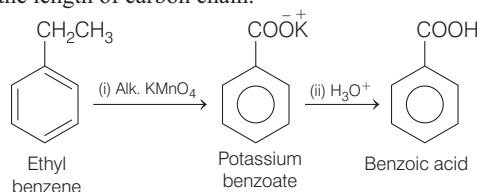


In compound C, the carbocation formed is stabilised by activating group ( $-\text{OCH}_3$ ). Compound D forms benzyl carbocation ( $\text{C}_6\text{H}_5-\text{CH}_2^+$ ) that is stabilised by resonance. Compound A produces a primary carbocation that further rearranges itself to secondary carbocation.

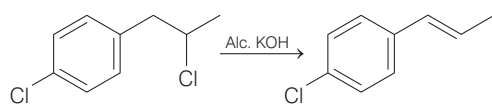


Compound B produces primary carbocation which is least stable among all the given options.

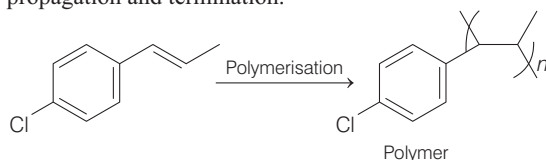
4. The major product of the given reaction is benzoic acid ( $\text{C}_6\text{H}_5\text{COOH}$ ). On vigorous oxidation of alkyl benzene with acidic or alkaline  $\text{KMnO}_4$ , aromatic acids are obtained. During oxidation of alkyl benzene, the aromatic nucleus remains intact and the entire chain is oxidised to  $-\text{COOH}$  group irrespective of the length of carbon chain.



5. In presence of alc. KOH, the given halide undergoes elimination reaction



The alkene produced undergoes polymerisation *via* free radical mechanism. This process involve three steps, i.e. initiation, propagation and termination.

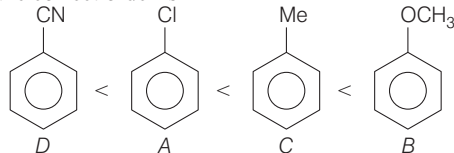


6. Aromatic electrophilic substitution reactions are fast in those compounds in which the attacking site possess high electron density. Electron withdrawing groups (EWGs) reduces the electron density in the benzene ring due to its strong  $-I$  effect and makes further substitution difficult. Hence, called as deactivating groups. While electron releasing groups (ERGs) increases the electron density in the benzene due to resonance. Therefore, activates the benzene ring for the attack by an electrophile. Hence, called as activating groups.

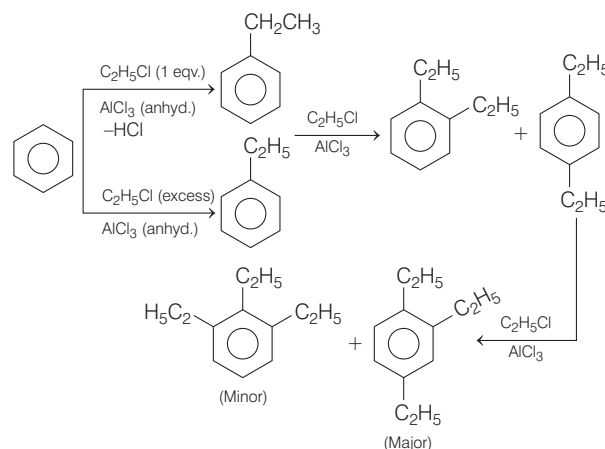
In given options, Activating groups are  $-\text{CH}_3 < -\ddot{\text{O}}\text{CH}_3$   
 (+I, +R)      Strong +R effect

Deactivating groups are  $\text{—CN} > \text{—Cl}$   
 Strong  $-I$  effect ( $-I > -R$ )

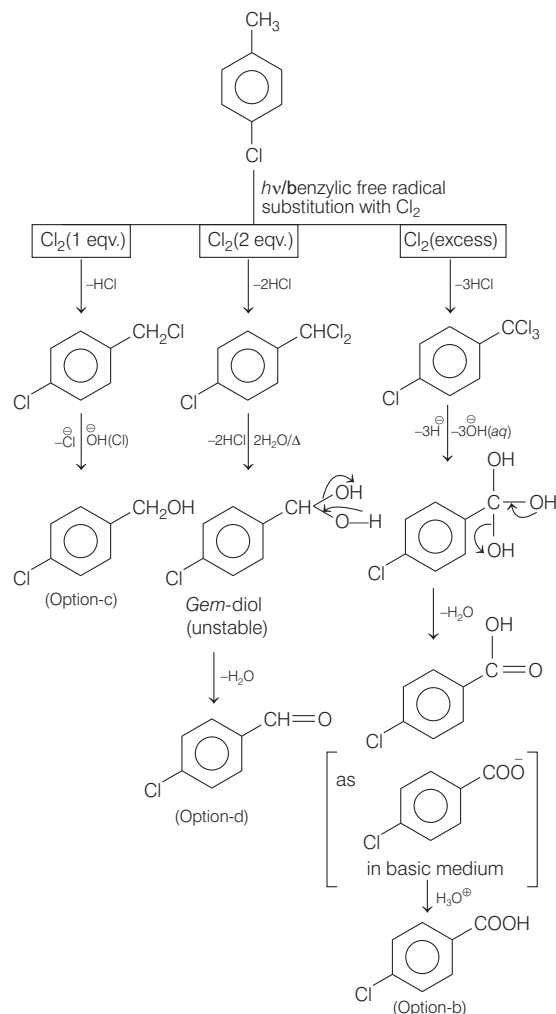
So, the correct order is



7. Through aromatic electrophilic substitution mechanism ( $\text{ArS}_{\text{E}2}$ ) when mono-alkylation (Friedel-Craft's reaction) is performed, we get mono-alkylated benzene. As, the alkyl group is ring activating (towards  $\text{ArS}_{\text{E}2}$ ) in nature, again *o*- and *p*-substituted alkyl benzene will be obtained and so on. e.g.



- 8.



So, considering the second reaction condition,  $\text{Cl}^-$ ,  $\text{H}_2\text{O}$ ,  $\Delta$  in the statement of the question, the correct answer is option (d).

## 406 Benzene and Alkyl Benzene

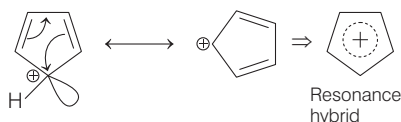
9. Melting point of a compound depends on size and force of attraction between the molecules. Compound (c) has largest size and also possess weak intermolecular association due to dipole - dipole interactions.

Compound (a) is a dicarboxylic acid and possess high melting point due to intermolecular hydrogen bonding.

As a result, it exist as associated molecule. Compound (d) is an alcohol and possess intermolecular H-bonding. No interactions are present in hydrocarbon (naphthalene) compound (b).

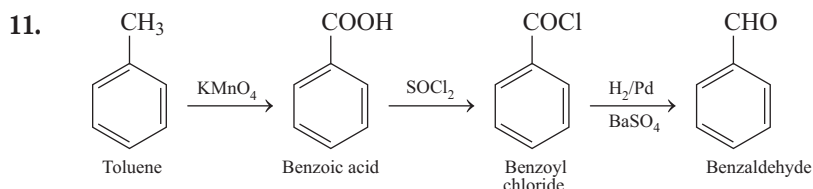
Hence, melting point is lowest for naphthalene ( $\approx 80^\circ\text{C}$ ), i.e. compound (b).

10. Aromaticity of a compound can be decided by Huckel's rule. In cyclopentadienyl cation (b), resonance takes place as follows:



Hence,  is anti-aromatic does not follow

Huckel's rule as it has conjugated  $4\pi$ -electron ( $4n\pi$ ,  $n = 1$ ) system. Rest of the species are aromatic as each of them belongs to  $6\pi$ -electron [ $(4n + 2)\pi$ ,  $n = 1$ ] system.



12. **PLAN** This problem can be solved by using the various concepts synthesis of benzene, electrophilic substitution reaction and directive influence of various substituents, including oxidation and reduction.

$\Rightarrow$   $-\text{OH}$  and  $-\text{NH}_2$  are *o/p*-directing groups.

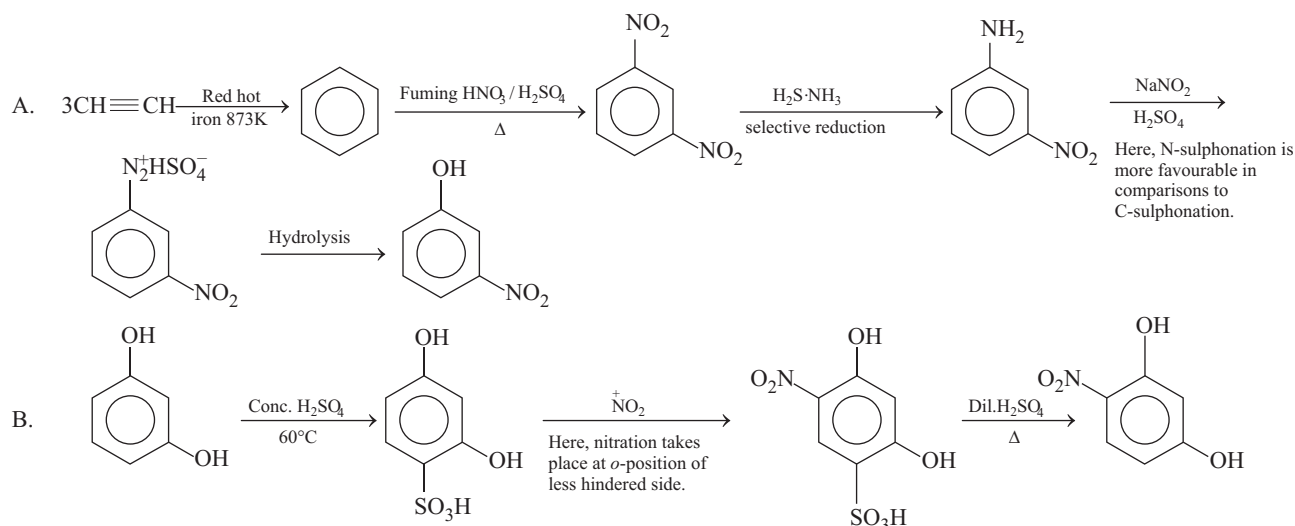
$\Rightarrow$  N-acetylation is more favourable than C-acylation.

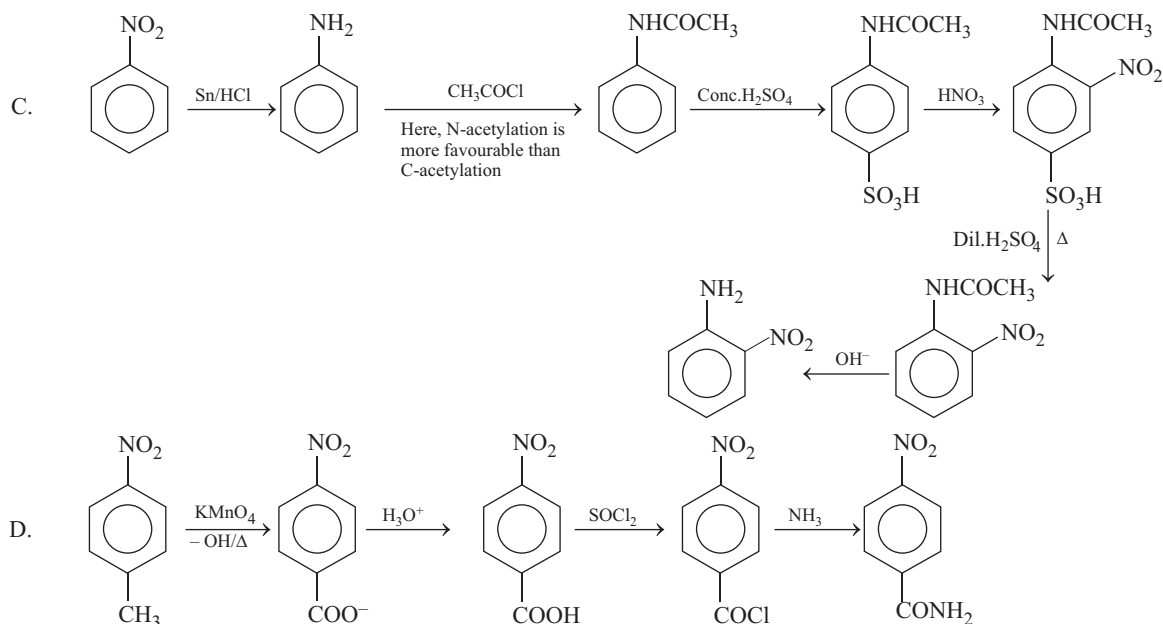
$\Rightarrow$  N-sulphonation is more favourable than C-sulphonation.

$\Rightarrow$   $\text{NO}_2$  is a meta-directing group.

$\Rightarrow$   $\text{H}_2\text{S} \cdot \text{NH}_3$  reduces only one  $\text{NO}_2$  group selectively in the presence of two  $\text{NO}_2$  groups.

Using above concepts the correct sequence of reaction can be written as

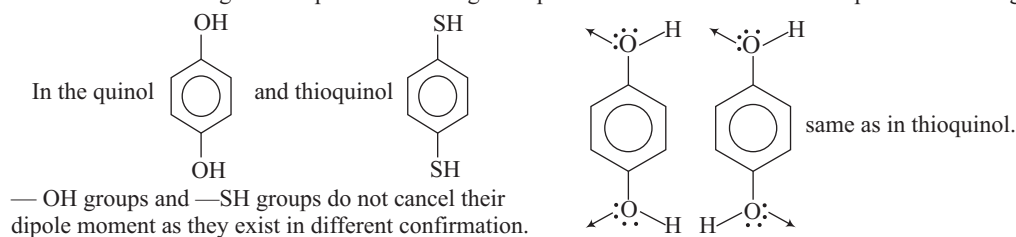




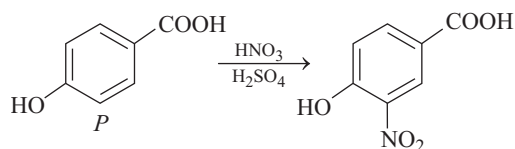
Above reaction proceeds through oxidation, chlorination and amide formation sequentially.

$\therefore A \rightarrow r, B \rightarrow s, C \rightarrow q, D \rightarrow p$  Hence, the correct choice is (c).

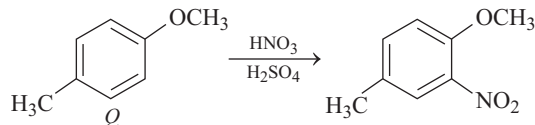
13. Draw the structure of organic compounds indicating net dipole moment which includes lone pair and bond angle also.



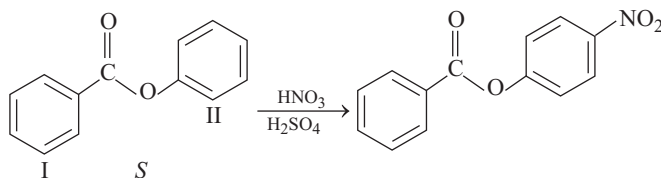
14.



—OH is activating while —COOH is deactivating group in  $S_E Ar$  reaction. Therefore, electrophile attack to *ortho* of the activating —OH group.

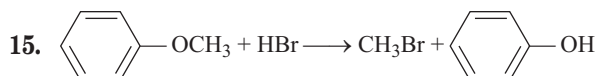


Both —OCH<sub>3</sub> and —CH<sub>3</sub> are activating *ortho/para* directing groups but —OCH<sub>3</sub> is stronger activator, electrophile attack to *ortho* of —OCH<sub>3</sub>.



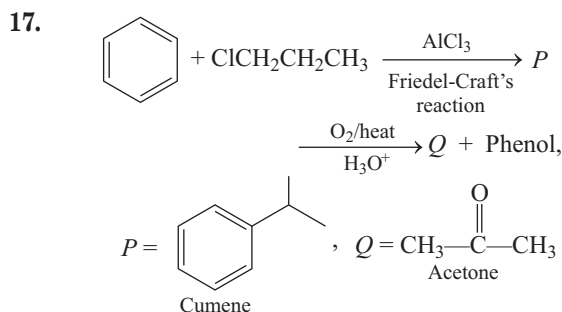
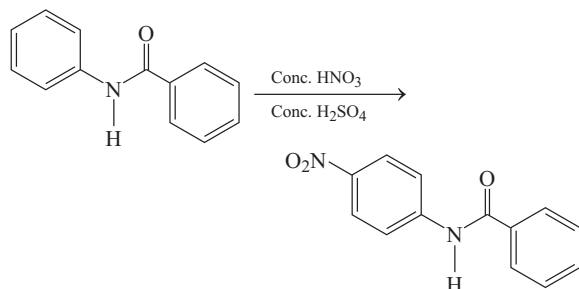
Ring II is activated while ring I is deactivated in  $S_E Ar$  reaction. Therefore, electrophile attack at *para* to ring-II, the less hindered position.

## 408 Benzene and Alkyl Benzene

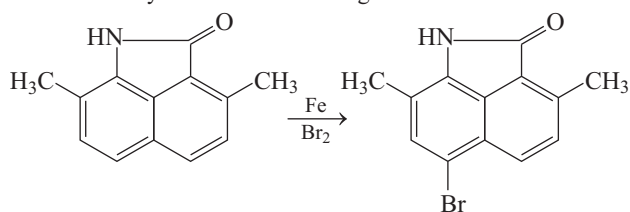


—OH of phenol is not further substituted by bromide due to resonance with the ring.

16. Ring attached to nitrogen is activated while ring attached to C=O is deactivated. Also, electrophilic substitution occurs predominantly at *para* position of the activated ring due to immense steric hindrance at *ortho* position.



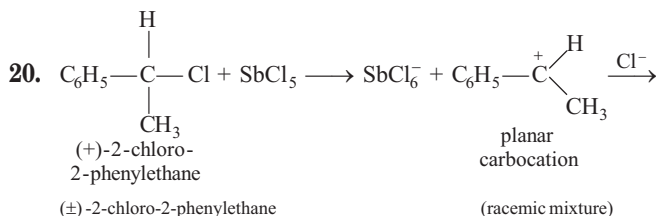
18. Ring attached to nitrogen is activated by electron donating resonance effect while ring attached to carbonyl group is deactivated by electron withdrawing resonance effect :



19. Both chloro and nitro groups are deactivating in electrophilic aromatic substitution reaction. Also nitro group is stronger deactivating group. Methyl group is activator in electrophilic aromatic substitution.

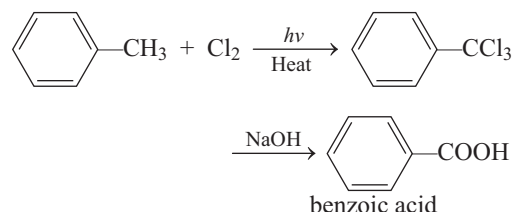
Hence, overall order of reactivity is :

nitrobenzene < chlorobenzene < benzene < toluene

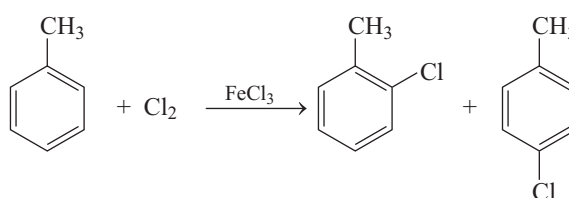


21. SO<sub>2</sub>Cl<sub>2</sub> brings about free-radical chlorination at —CH<sub>3</sub> group.

22. Free radical chlorination occurs at —CH<sub>3</sub>.



23. The methyl group in toluene is *ortho/para* directing activating group :

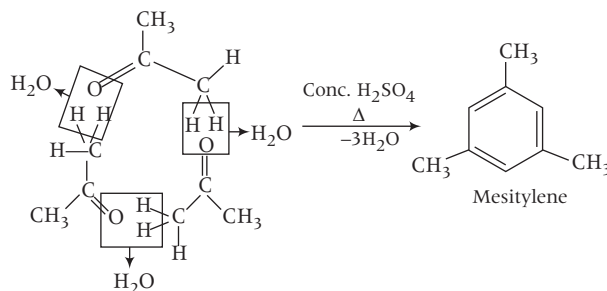


24. Toluene is most reactive among these. Nitro and carboxylic groups are deactivating in aromatic electrophilic substitution reaction.

25. Toluene is most readily sulphonated among these because methyl group is electron donating (+I effect), activates benzene ring for electrophilic aromatic substitution.

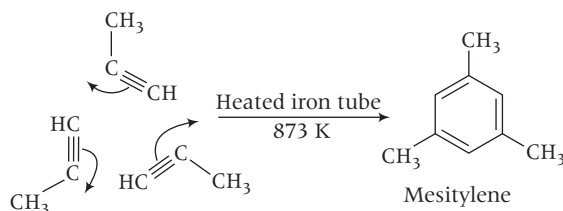
26. Reaction shown in option (a) is aldol condensation in the presence of conc. H<sub>2</sub>SO<sub>4</sub> at high temperature.

In summarised way the formation of mesitylene through this can be visualised as



Reaction given in option (b) is simple polymerisation (trimerisation) reaction of alkyne i.e.,

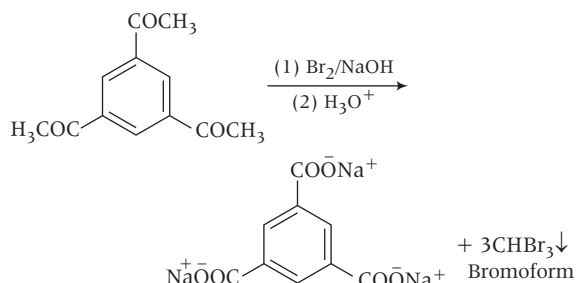
Me—C≡CH or CH<sub>3</sub>—C≡CH when passed through heated iron tube at 873K then mesitylene is formed as



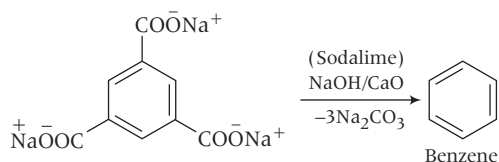
This reaction is also called aromatisation.



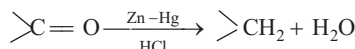
(1) and (2) reactions of option (c) combined to give haloform reaction while (3) reaction given in this option is decarboxylation reaction i.e.,



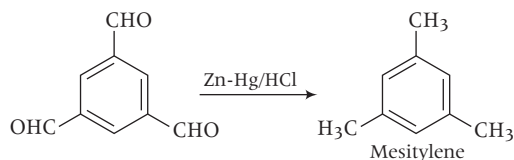
The above product of haloform reaction on decarboxylation gives benzene as



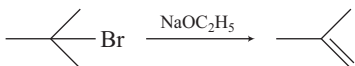
The reaction given in option (d) is Clemmensen reduction i.e.,



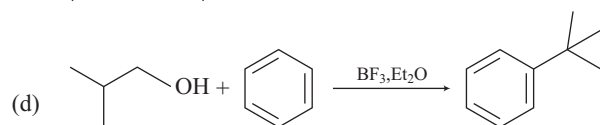
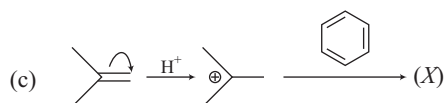
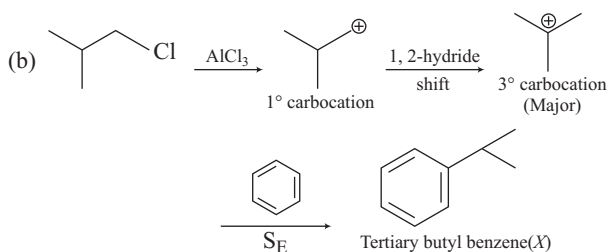
Hence, the final product of this reaction is also mesitylene which can be seen as



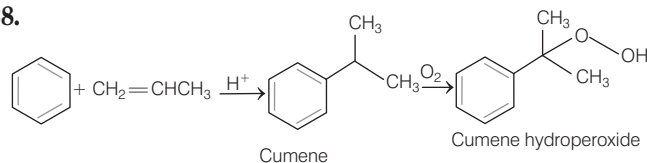
27. (a)



$\text{C}_2\text{H}_5\text{O}^-$  (a strong nucleophile) causes  $\text{E1}$  reaction to form isobutene as the major product.



28.

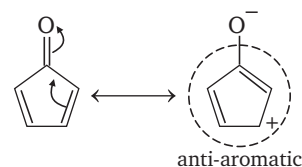


Cumene hydroperoxide formed above is an intermediate in the synthesis of phenol.

29. According to Huckel rule, the compounds which have  $4n$  ( $n = 0, 1, 2, 3, \dots$ ) delocalised  $\pi$ -electrons in a close-loop are anti-aromatic and characteristically unstable. Compound *B* satisfy the criteria of anti-aromaticity as :

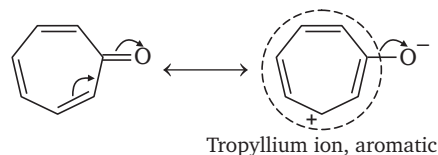


Compound *C* is anti-aromatic in its resonance form :



Compound *A* has  $4\pi$ -electrons which are also delocalised but do not constitute close loop, hence non-aromatic.

Compound *D* is aromatic, characteristically stable.



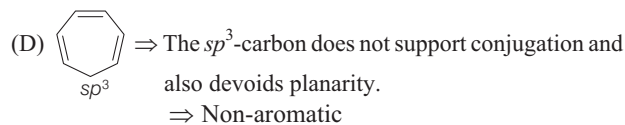
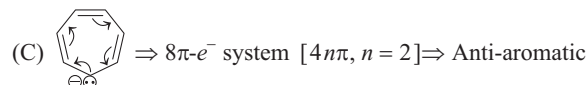
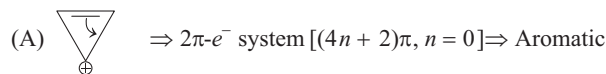
Order of stability Aromatic > Non-aromatic > Anti-aromatic

30. Aromatic molecule must.

- (b) have  $(4n + 2)\pi$  electrons. (c) be planar.  
(d) be cyclic.

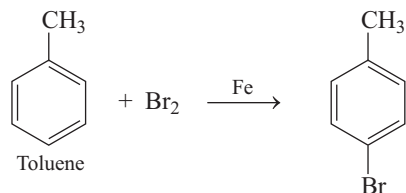
31. A compound is considered to be aromatic, if it follows three rules:

- (a) Must be cyclic and planar.  
(b) Must have conjugated system in it.  
(c) It must follow Huckel rule which states that number of  $\pi$ -electrons =  $(4n + 2)$



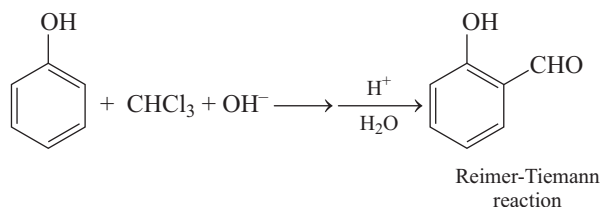
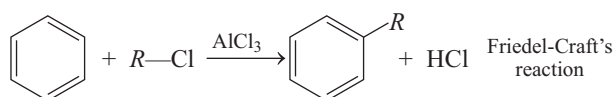
## 410 Benzene and Alkyl Benzene

32.



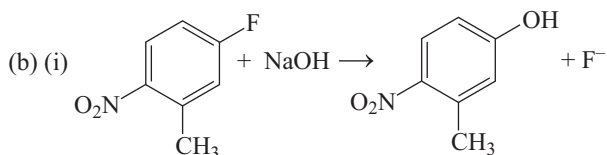
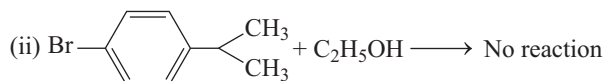
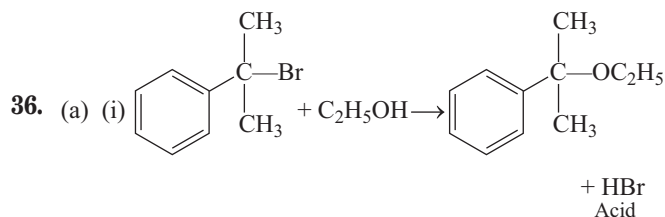
—CH<sub>3</sub> in toluene is *para* directing group. It activates the ring by both inductive and hyperconjugation effect.

33. In both Friedel-Craft's reaction and Reimer-Tiemann reaction, new carbon-carbon bond is formed :

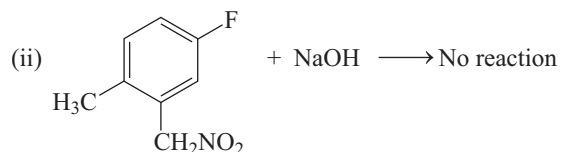


34. An electron donating substituent in benzene orient *ortho/para* substitution.

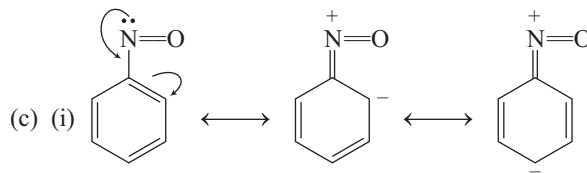
35. In benzene, carbons are  $sp^2$ -hybridised only, hence only two *p*-orbitals are involved in hybridisation.



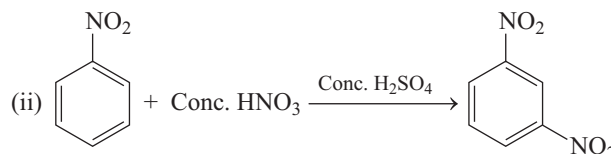
Nitro group from *para* position activate aromatic nucleophilic substitution.



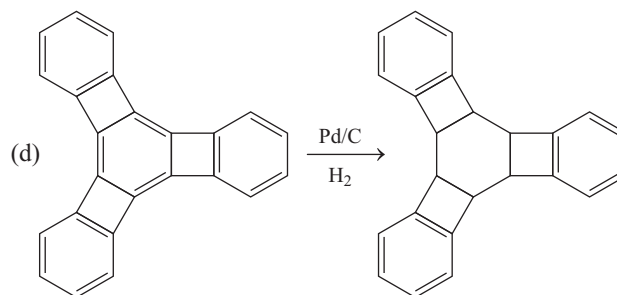
—NO<sub>2</sub> is not in resonance with benzene ring, does not activate the aromatic nucleophilic substitution reaction, hence fluoride is not formed.



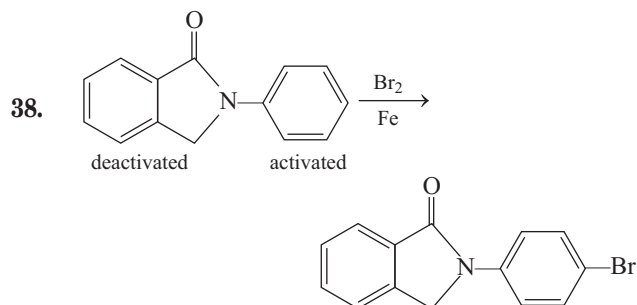
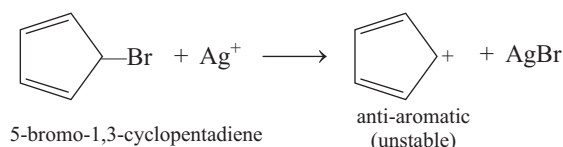
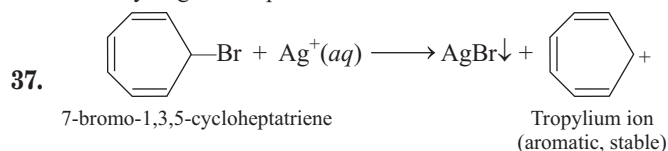
Hence, —NO is *ortho/para* directing although deactivating group. Therefore, *ortho/para* nitro derivatives are formed on treatment with mixed acid.



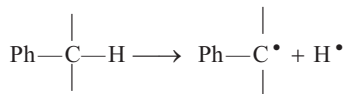
Nitro group is *meta* directing as well as strongly deactivating.



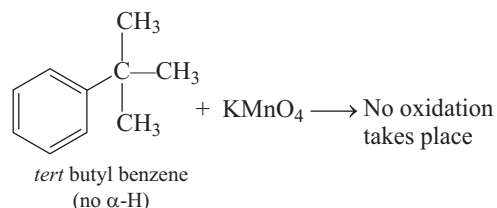
In the above hydrogenation reaction, the anti-aromatic character of three cyclobutadiene rings are relieved that provide stability to the hydrogenation product.



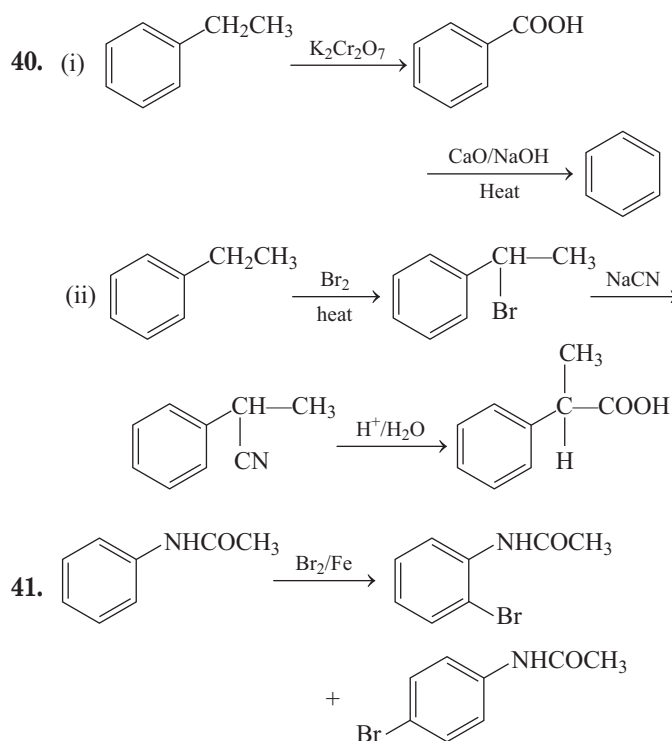
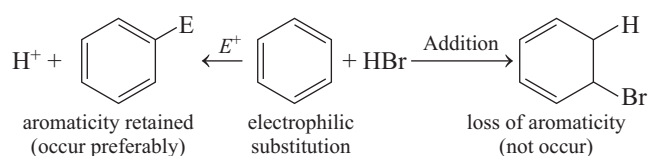
39. (i) Oxidation of side-chain alkyl group of benzene occur through free radical mechanism and it initiates at  $\alpha$ -C as.



In tertiary butyl benzene, there is no  $\alpha$ -H, required to initiate free radical oxidation reaction, hence not oxidised with  $\text{KMnO}_4$ .

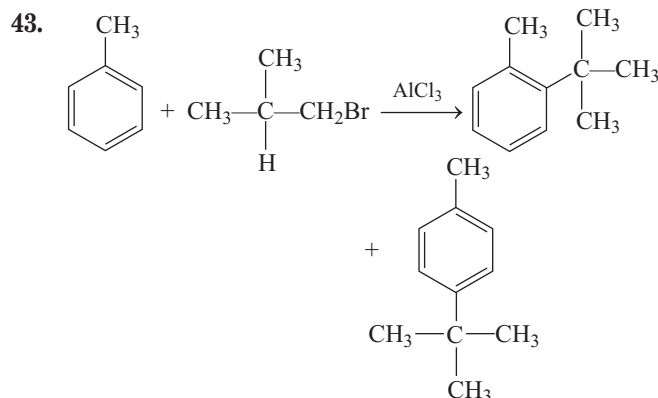


- (ii) Pi-electrons of double bonds are involved in aromatic delocalisation (aromaticity), hence electrophilic addition do not occur as it would destroy aromatic stability. However, electrophilic substitution do not destroy aromaticity.

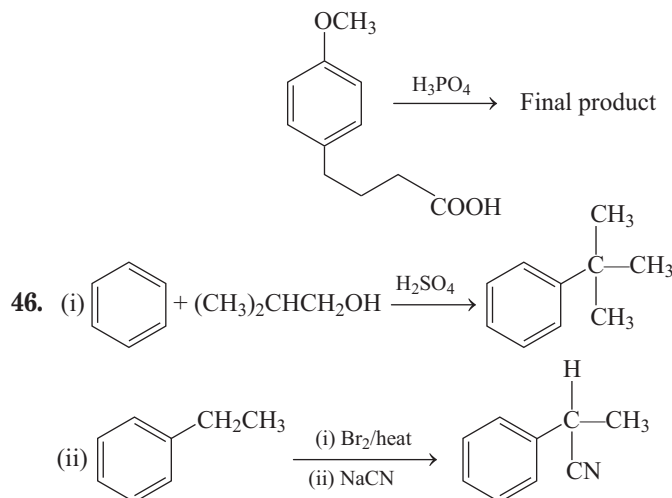
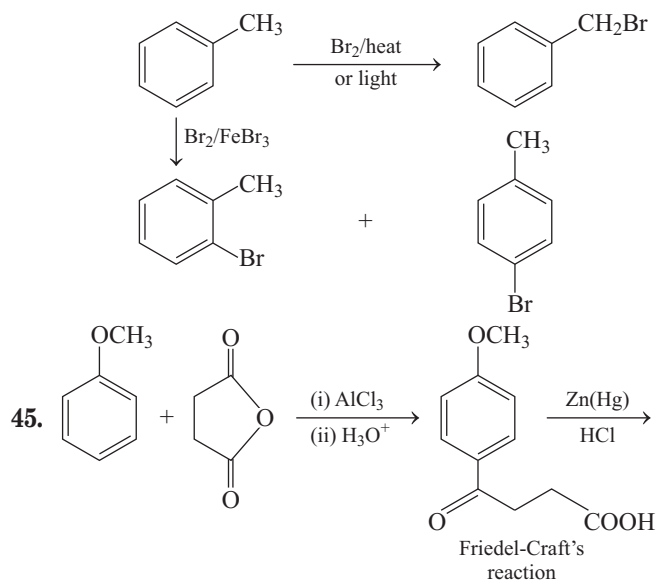


$\text{NHCOCH}_3$  is *ortho/para* directing although deactivating group. Therefore, *Ortho/para* bromoderivatives are formed on treatment.

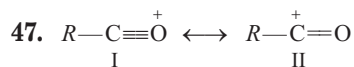
42. Nitro group is a very strong deactivating group, the very slow Friedel-Craft's reaction does not take place in presence of nitro group.



44. In presence of light, free radical reaction takes place at  $-\text{CH}_3$  group while in presence of  $\text{FeBr}_3$ , electrophilic substitution occurs in the ring.



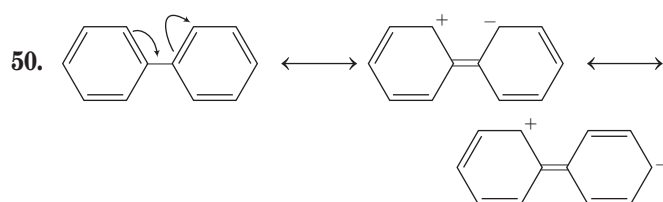
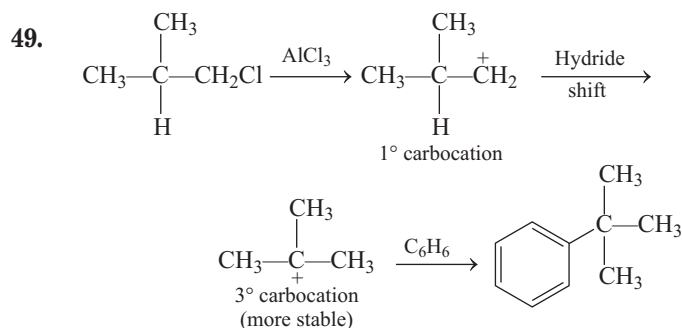
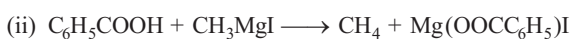
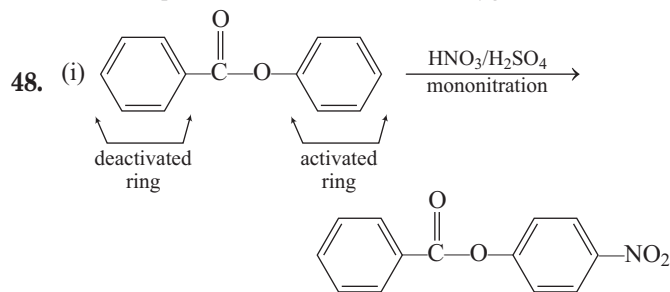
## 412 Benzene and Alkyl Benzene



I is more stable resonance structure of acylium ion than II on the following grounds.

It has more covalent bonds.

It has complete octet of both carbon and oxygen.



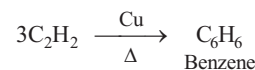
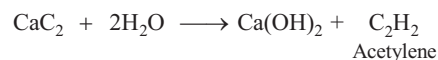
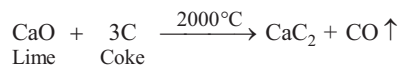
The above resonance activate an aromatic ring for electrophilic substitution reaction.

51. Both  $-\text{CH}_3$  and  $-\text{OCH}_3$  are activating groups but chloro is deactivating group in electrophilic aromatic substitution reaction.

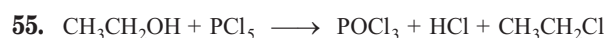
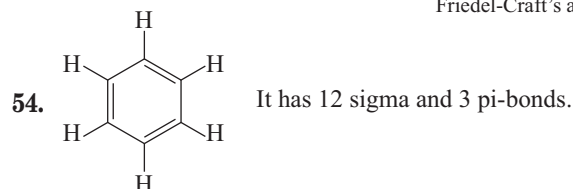
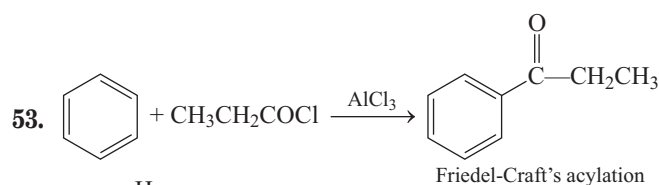
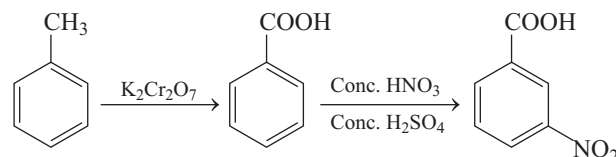
Also  $-\text{OCH}_3$  activate more than  $-\text{CH}_3$  due to resonance effect by the former group. Therefore, the overall order of reactivity is:

Chlorobenzene < benzene < toluene < methoxy benzene

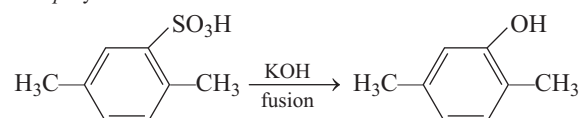
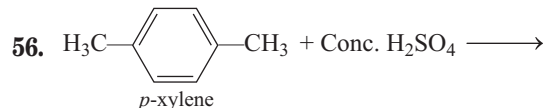
52. (i) Lime is heated with coke at high temperature and then, hydrolysed to form acetylene. This acetylene on passing red hot tube polymerises to form benzene :



(ii)  $-\text{CH}_3$  in toluene is *ortho/para* directing group, first oxidised to  $-\text{COOH}$  in order to make it *meta* directing and then nitrated.

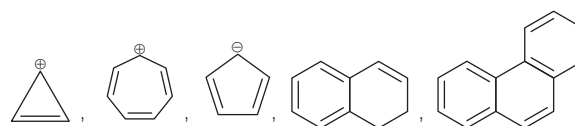


Friedel-Craft's reaction



57. Pi-bonds of benzene are involved in aromaticity, not open for electrophilic addition reaction. Rather, it undergo electrophilic substitution reaction.

58. The aromatic systems are



**Download Chapter Test**  
<http://tinyurl.com/y23lzk9x>

or

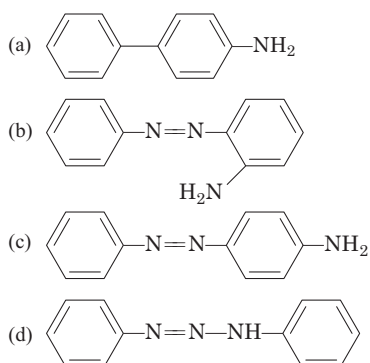


# 29

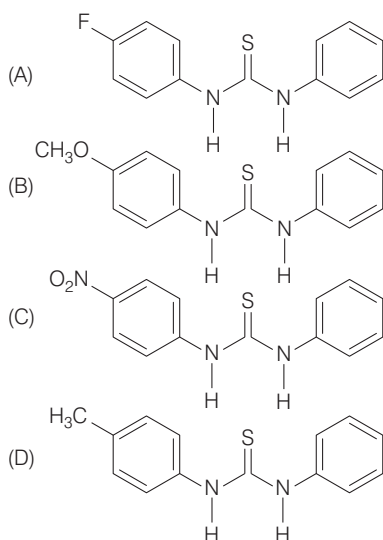
## Aromatic Compounds Containing Nitrogen

### Objective Questions I (Only one correct option)

1. Benzene diazonium chloride on reaction with aniline in the presence of dilute hydrochloric acid gives (2019 Main, 12 April II)



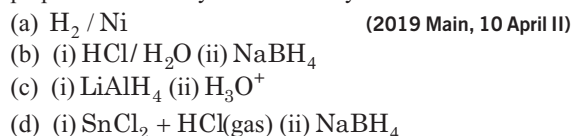
2. The increasing order of the  $pK_b$  of the following compound is



(2019 Main, 12 April I)

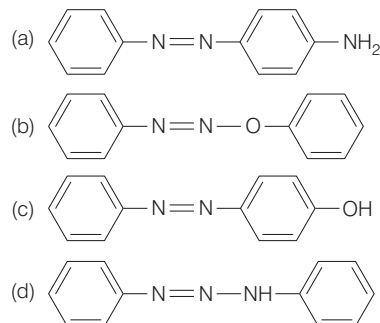
- (a) (A) < (C) < (D) < (B)  
 (b) (C) < (A) < (D) < (B)  
 (c) (B) < (D) < (A) < (C)  
 (d) (B) < (D) < (C) < (A)

3. Which of the following is not a correct method of the preparation of benzylamine from cyanobenzene?

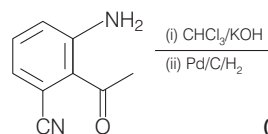


4. Aniline dissolved in dil.  $HCl$  is reacted with sodium nitrite at  $0^\circ C$ . This solution was added dropwise to a solution containing equimolar mixture of aniline and phenol in dil.  $HCl$ . The structure of the major product is

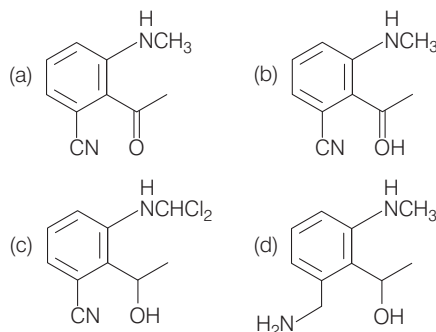
(2019 Main, 9 April I)



5. The major product obtained in the following reaction is

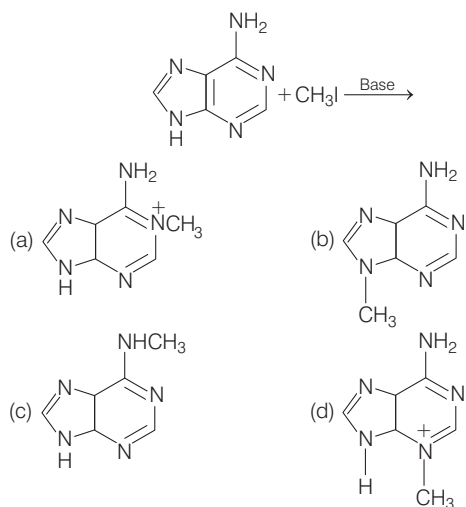


(2019 Main, 8 April II)

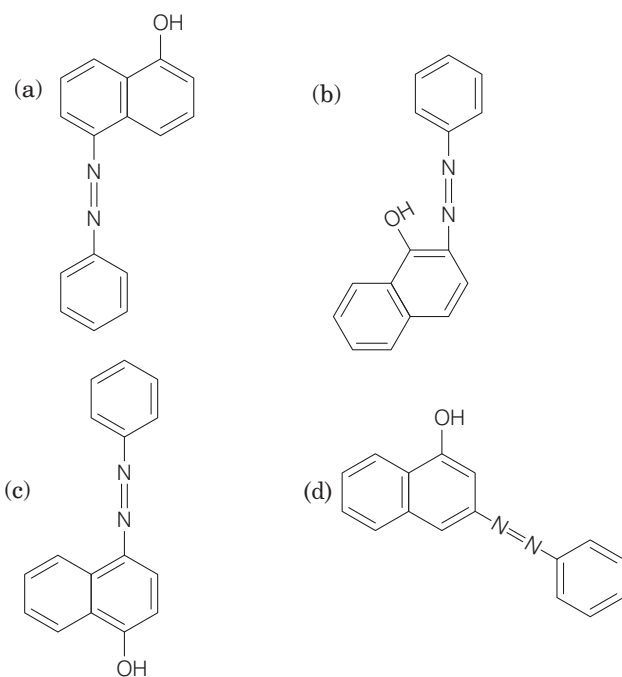


## 414 Aromatic Compounds Containing Nitrogen

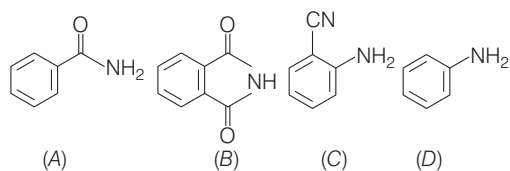
6. The major product in the following reaction is  
(2019 Main, 8 April II)



7. Coupling of benzene diazonium chloride with 1-naphthol in alkaline medium will give  
(2019 Main, 8 April I)

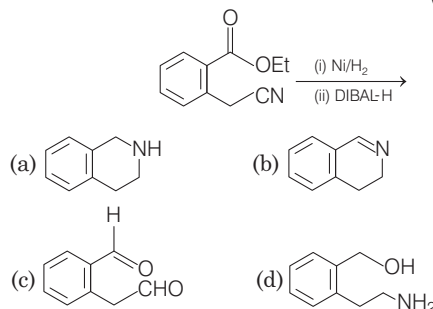


8. The increasing order of reactivity of the following compounds towards reaction with alkyl halides directly is  
(2019 Main, 12 Jan I)

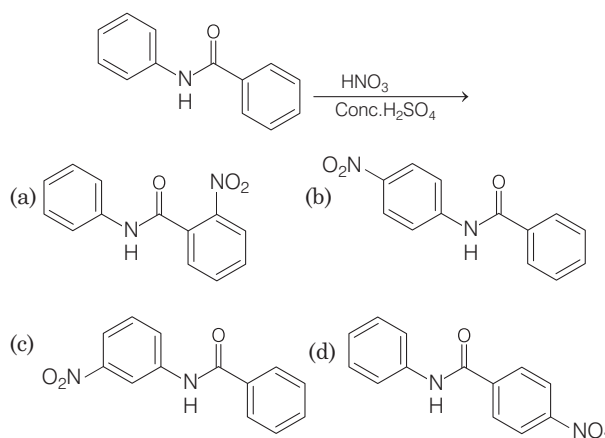


- Options:
- (a)  $(A) < (C) < (D) < (B)$
  - (b)  $(B) < (A) < (C) < (D)$
  - (c)  $(B) < (A) < (D) < (C)$
  - (d)  $(A) < (B) < (C) < (D)$

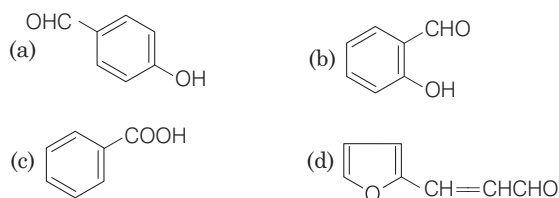
9. The major product of the following reaction is  
(2019 Main, 11 Jan I)



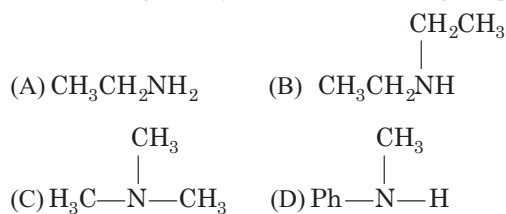
10. What will be the major product in the following mononitration reaction?  
(2019 Main, 10 Jan II)



11. An aromatic compound 'A' having molecular formula  $\text{C}_7\text{H}_6\text{O}_2$  on treating with aqueous ammonia and heating forms compound 'B'. The compound 'B' on reaction with molecular bromine and potassium hydroxide provides compound 'C' having molecular formula  $\text{C}_6\text{H}_7\text{N}$ . The structure of 'A' is  
(2019 Main, 10 Jan II)



12. The increasing basicity order of the following compounds is



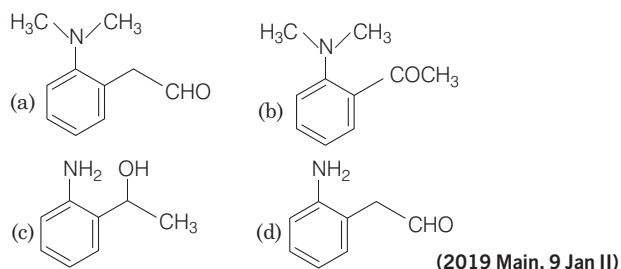
- Options:
- (a)  $(D) < (C) < (B) < (A)$
  - (b)  $(A) < (B) < (C) < (D)$
  - (c)  $(A) < (B) < (D) < (C)$
  - (d)  $(D) < (C) < (A) < (B)$

(2019 Main, 9 Jan II)

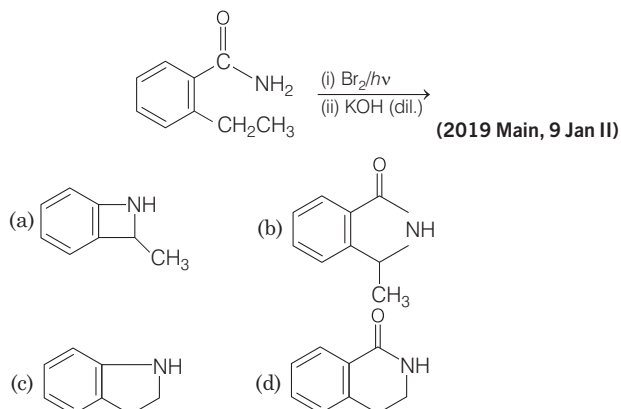
13. The tests performed on compound *X* and their inferences are :

| Test               | Inference            |
|--------------------|----------------------|
| (a) 2, 4- DNP test | Coloured precipitate |
| (b) Iodoform test  | Yellow precipitate   |
| (c) Azo-dye test   | No dye formation     |

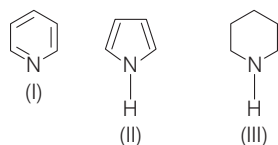
Compound '*X*' is



14. The major product of the following reaction is



15. Arrange the following amines in the decreasing order of basicity: (2019 Main, 9 Jan I)

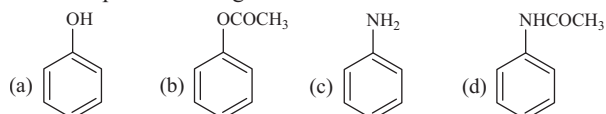


- (a) I > II > III (b) III > II > I (c) I > III > II (d) III > I > II

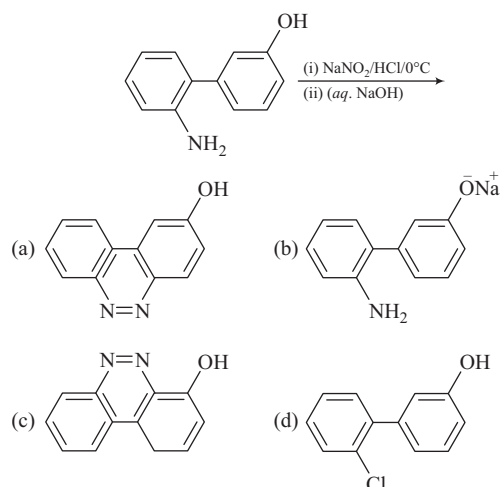
16. The correct decreasing order for acid strength is (2019 Main, 9 Jan I)

- (a)  $\text{FCH}_2\text{COOH} > \text{NCCH}_2\text{COOH} > \text{NO}_2\text{CH}_2\text{COOH} > \text{ClCH}_2\text{COOH}$   
 (b)  $\text{CNCH}_2\text{COOH} > \text{O}_2\text{NCH}_2\text{COOH} > \text{FCH}_2\text{COOH} > \text{ClCH}_2\text{COOH}$   
 (c)  $\text{NO}_2\text{CH}_2\text{COOH} > \text{NCCH}_2\text{COOH} > \text{FCH}_2\text{COOH} > \text{ClCH}_2\text{COOH}$   
 (d)  $\text{NO}_2\text{CH}_2\text{COOH} > \text{FCH}_2\text{COOH} > \text{CNCH}_2\text{COOH} > \text{ClCH}_2\text{COOH}$

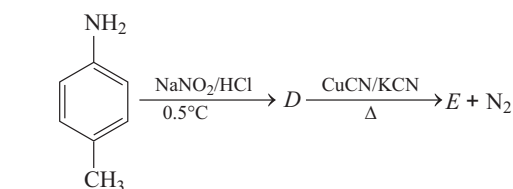
17. Which of the following compounds will give significant amount of *meta*-product during mononitration reaction? (2017 Main)



18. The major product of the following reaction is (2017 Adv.)

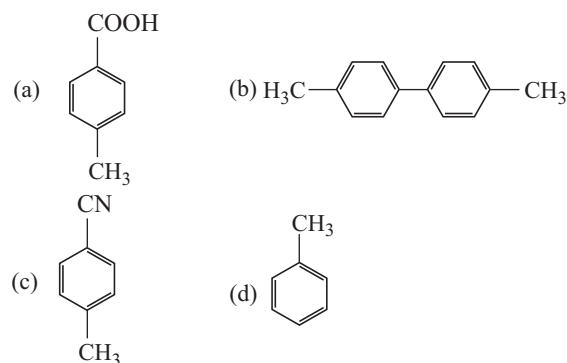


19. In the reaction,

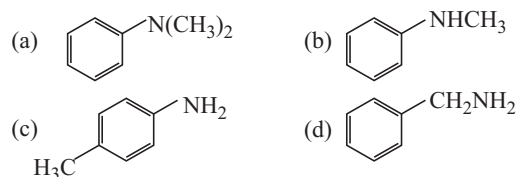


The product *E* is

(2015 Main)



20. Amongst the compounds given, the one that would form a brilliant coloured dye on treatment with  $\text{NaNO}_2$  in dil.  $\text{HCl}$  followed by addition to an alkaline solution of  $\beta$ -naphthol is

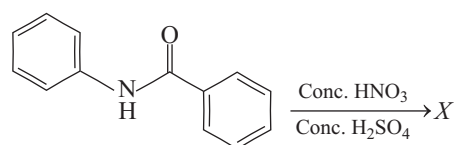


(2011)

21. The species having pyramidal shape is (2010)

- (a)  $\text{SO}_3$  (b)  $\text{BrF}_3$  (c)  $\text{SiO}_3^{2-}$  (d)  $\text{OSF}_2$

22. In the following reaction,

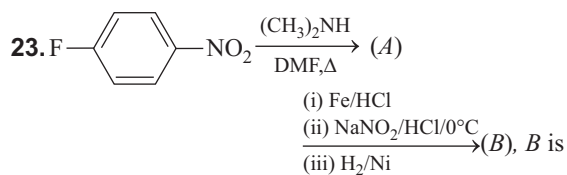


## 416 Aromatic Compounds Containing Nitrogen

The structure of the major product *X* is

(2007, 3M)

- (a)
- (b)
- (c)
- (d)



(2003, 1 M)

- (a)
- (b)
- (c)
- (d)

24. The most unlikely representation of resonance structures of *p*-nitrophenoxide ion is

(1999, 2M)

- (a)
- (b)
- (c)
- (d)

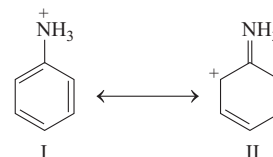
25. Benzene diazonium chloride on reaction with phenol in weakly basic medium gives

(1998, 2M)

- (a) diphenyl ether (b) *p*-hydroxy azobenzene  
(c) chlorobenzene (d) benzene

26. Examine the following two structures of anilinium ion and choose the correct statement from the ones given below :

(1993, 1M)



- (a) II is not an acceptable canonical structure because carbonium ions are less stable than ammonium ions  
(b) II is not an acceptable canonical structure because it is non-aromatic  
(c) II is not an acceptable canonical structure because the nitrogen has 10 valence electrons  
(d) II is an acceptable canonical structure

27. Chlorobenzene can be prepared by reacting aniline with

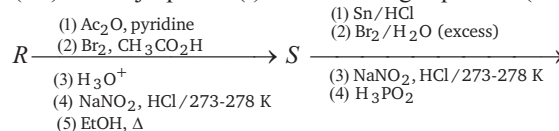
(1984, 1M)

- (a) hydrochloric acid  
(b) cuprous chloride  
(c) chlorine in the presence of anhydrous  $\text{AlCl}_3$   
(d) nitrous acid followed by heating with cuprous chloride

### Objective Questions II

(One or more than one correct option)

28. Aniline reacts with mixed acid (conc.  $\text{HNO}_3$  and conc.  $\text{H}_2\text{SO}_4$ ) at 288 K to give P (51%), Q (47%) and R (2%). The major product(s) of the following sequence is (are)



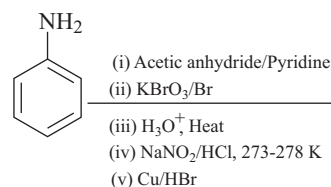
Major product(s)

(2018 Adv.)

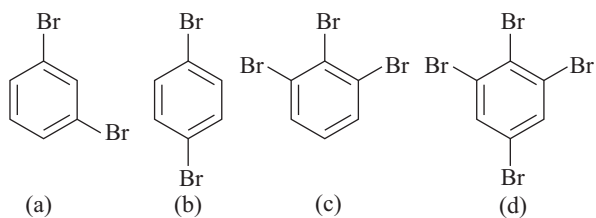
- (a)
- (b)
- (c)
- (d)

29. The product(s) of the following reaction sequence is (are)

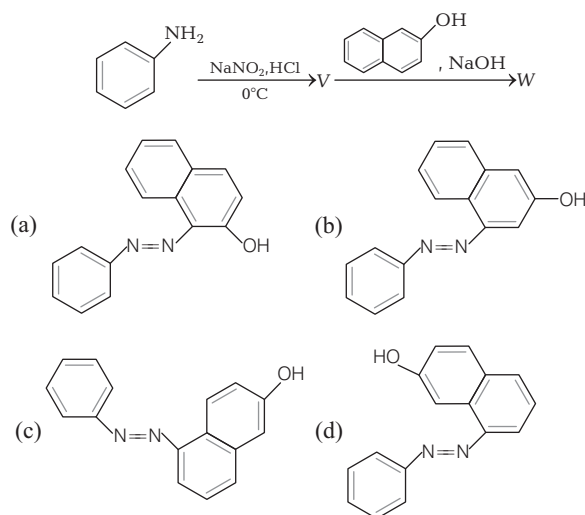
(2017, Adv.)



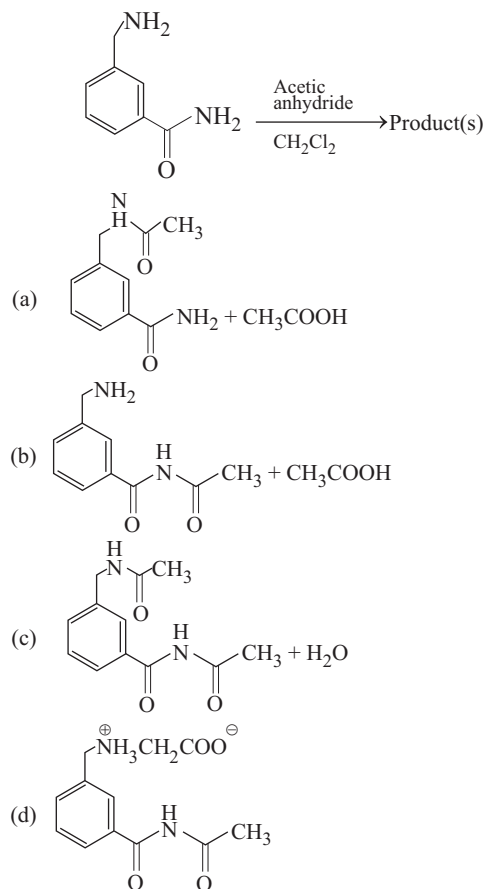




30. In the following reactions, the major product *W* is (2015 Adv.)



31. In the reaction shown below, the major product(s) formed is/are (2014 Adv.)



32. *p*-chloroaniline and anilinium hydrochloride can be distinguished by (1998, 2M)

- (a) Sandmeyer reaction (b)  $\text{NaHCO}_3$   
(c)  $\text{AgNO}_3$  (d) Carbylamine test

33. When nitrobenzene is treated with  $\text{Br}_2$  in the presence of  $\text{FeBr}_3$ , the major product formed is *m*-bromonitrobenzene. Statements which are related to obtain the *m*-isomer, are (1992, 1M)

- (a) the electron density on *meta* carbon is more than that on *ortho* and *para* positions  
(b) the intermediate carbonium ion formed after initial attack of  $\text{Br}^+$  at the *meta* position is less destabilised  
(c) loss of aromaticity when  $\text{Br}^+$  attacks at the *ortho* and *para* positions and not at *meta* position  
(d) easier loss of  $\text{H}^+$  to regain aromaticity from *meta* position than from *ortho* and *para* positions

### Assertion and Reason

Read the following questions and answer as per the direction given below :

- (a) Statement I is correct; Statement II is correct; Statement II is the correct explanation of Statement I.  
(b) Statement I is correct; Statement II is correct; Statement II is not the correct explanation of Statement I.  
(c) Statement I is correct; Statement II is incorrect.  
(d) Statement I is incorrect; Statement II is correct.

34. **Statement I** Aniline on reaction with  $\text{NaNO}_2/\text{HCl}$  at  $0^\circ\text{C}$  followed by coupling with  $\beta$ -naphthol gives a dark blue coloured precipitate.

**Statement II** The colour of the compound formed in the reaction of aniline with  $\text{NaNO}_2/\text{HCl}$  at  $0^\circ\text{C}$  followed by coupling with  $\beta$ -naphthol is due to the extended conjugation

(2008, 3M)

35. **Statement I** In strongly acidic solution, aniline becomes more reactive towards electrophilic reagents.

**Statement II** The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on nitrogen is no longer available for resonance.

(2001, 1M)

### Match the Column

36. Match the compounds in Column I with their characteristic test(s)/reaction(s) given in Column II. (2008, 6M)

| Column I                                          | Column II                                                                                 |
|---------------------------------------------------|-------------------------------------------------------------------------------------------|
| (A) $\text{H}_2\text{N}-\text{NH}_3^+\text{Cl}^-$ | (p) Sodium fusion extract of the compound gives Prussian blue colour with $\text{FeSO}_4$ |
| (B)                                               | (q) Gives positive $\text{FeCl}_3$ test                                                   |

## 418 Aromatic Compounds Containing Nitrogen

| Column I | Column II                                                                |
|----------|--------------------------------------------------------------------------|
| (C)      | (r) Gives white precipitate with AgNO <sub>3</sub>                       |
| (D)      | (s) Reacts with aldehydes to form the corresponding hydrazone derivative |

### Fill in the Blanks

37. The high melting point and insolubility in organic solvents of sulphanilic acid are due to its..... structure. (1994, 1M)
38. In an acidic medium, ..... behaves as the strongest base. (nitrobenzene, aniline, phenol) (1981, 1M)

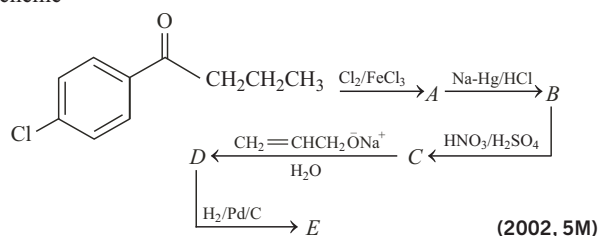
### Subjective Questions

39. Convert to in not more than four steps. Also mention the reaction conditions and temperature. (2004, 4M)

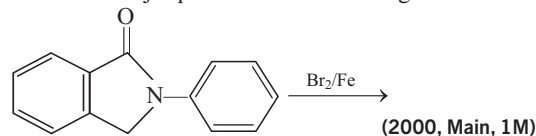
40. Which of the following is more acidic and why?
- I II

41. Convert (in not more than 3 steps) :

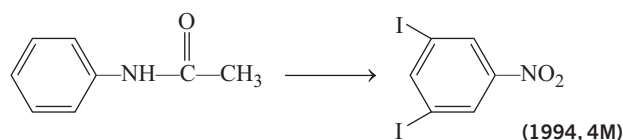
42. There is a solution of *p*-hydroxybenzoic acid and *p*-amino benzoic acid. Discuss one method by which we can separate them and also write down the confirmatory test of the functional group present. (2003, 4M)
43. Write structures of the products A, B, C, D and E in the following scheme



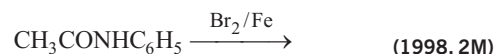
44. What would be the major product in the following reaction?



45. How would you bring about the following conversion (in 3 steps)?  
Aniline  $\longrightarrow$  Benzylamine (2000, 3M)
46. Complete the following reactions with appropriate reagents

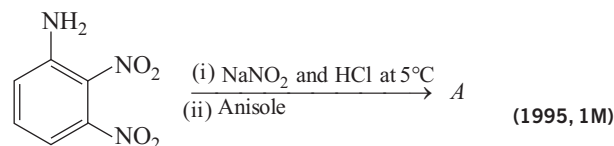


47. Following reaction gives two products. Write the structures of the products.

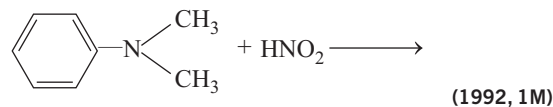


48. Write the structure of foul smelling compound obtained when aniline is treated with chloroform in the presence of KOH. (1996, 1M)

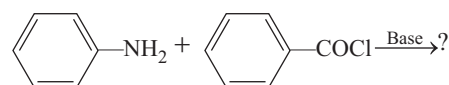
49. Complete the following with appropriate structure:



50. How will you bring about the following conversions?  
“Benzamide from nitrobenzene” (1994, 2M)
51. How will you bring about the following conversions?  
“4-nitrobenzaldehyde from benzene” (1994, 2M)
52. Outline a synthesis of *p*-bromonitrobenzene from benzene in two steps. (1993, 2M)
53. Write the structure of the major organic product expected from the following reaction.



54. How will you bring about the following conversion?  
“4-nitro aniline to 1, 2, 3-tribromobenzene.” (1990, 2M)
55. Complete the following with appropriate structures: (1986, 1M)



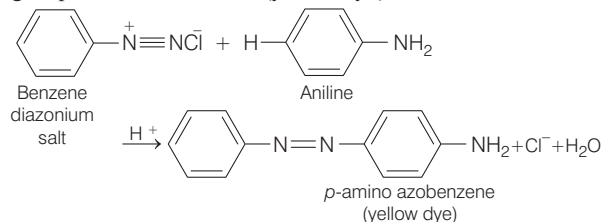
56. How would you convert aniline into chlorobenzene? (1985, 1M)
57. State the conditions under which the following preparation is carried out. “Aniline from benzene” (1983, 1M)
58. State the equation for the preparation of following compound.  
Chlorobenzene from aniline (in 2 steps). (1982, 1M)

## Answers

- |         |         |         |         |                                               |             |         |           |
|---------|---------|---------|---------|-----------------------------------------------|-------------|---------|-----------|
| 1. (c)  | 2. (c)  | 3. (b)  | 4. (a)  | 25. (b)                                       | 26. (c)     | 27. (d) | 28. (d)   |
| 5. (d)  | 6. (*)  | 7. (c)  | 8. (b)  | 29. (b)                                       | 30. (a)     | 31. (a) | 32. (c,d) |
| 9. (b)  | 10. (b) | 11. (c) | 12. (d) | 33. (a,b)                                     | 34. (d)     | 35. (d) |           |
| 13. (b) | 14. (a) | 15. (d) | 16. (c) | 36. A → r, s   B → p, q   C → p, q, r   D → p |             |         |           |
| 17. (c) | 18. (a) | 19. (c) | 20. (c) | 37. zwitter ionic                             | 38. Aniline |         |           |
| 21. (d) | 22. (b) | 23. (a) | 24. (c) |                                               |             |         |           |

## Hints & Solutions

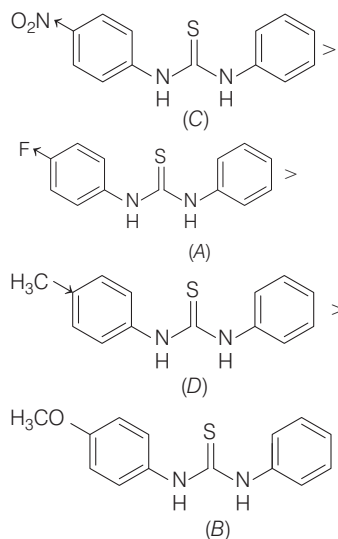
1. Benzene diazonium chloride on reaction with aniline in the presence of dilute hydrochloric acid undergoes coupling reaction and produces *p*-amino azobenzene. In this reaction, benzene diazonium chloride reacts with aniline in which aniline molecule at its *para*-position is coupled with diazonium salt to give *p*-amino azobenzene (yellow dye).



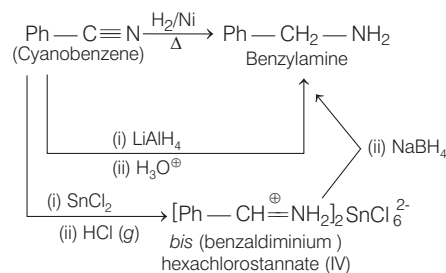
2. **Key Idea**  $\text{p}K_b$  value is defined as the minus logarithm of  $K_b$  smaller the value of  $\text{p}K_b$  stronger is the base and *vice-versa*.

In the given options, +R effect is shown by  $-\text{CH}_3$  and  $-\text{OCH}_3$  group ( $-\text{OCH}_3 > -\text{CH}_3$ ). These group increases the electron density at *o* and *p*-positions. Groups such as  $-\text{F}$  and  $-\text{NO}_2$  shows -R-effect ( $-\text{NO}_2 > -\text{F}$ ). These group decreases the electron density at *o* and *p*-positions.

Increase in electron density at *p*-position makes the unshared electron pair of 'N' more available and decrease in electron density at *p*-position makes the unshared electron pair of 'N' less available. Compound containing  $-\text{OCH}_3$  group act as strongest base and hence possess lowest value of  $\text{p}K_b$ . So, the correct increasing order of  $\text{p}K_b$  in the given compound is

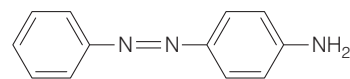


3. The preparation of benzylamine from cyanobenzene using given reagents are as follows :



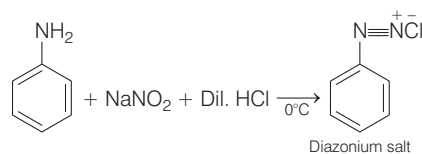
Thus, option (b) is incorrect.

4. Major product of the reaction is

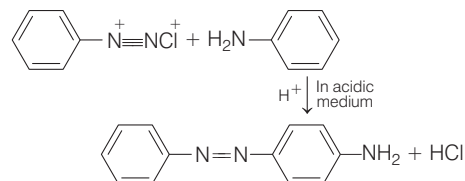


It is obtained by coupling reaction.

Reaction of aniline with dil. HCl and sodium nitrite at  $0^\circ\text{C}$  is shown below :

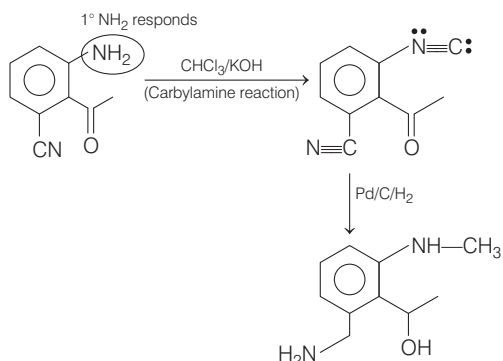


Diazonium salt formed when added to equimolar mixture of aniline and phenol in dil. HCl then aniline couples with diazonium salt. Reaction is as follows :



For an effective coupling, the solution must be so alkaline that the concentration of diazonium ion is too low. It must not be so acidic that the concentration of free amine or phenoxide ion is too low. That is why amines couple fastest in mild acidic solution and phenols couple fastest in mild alkaline solution.

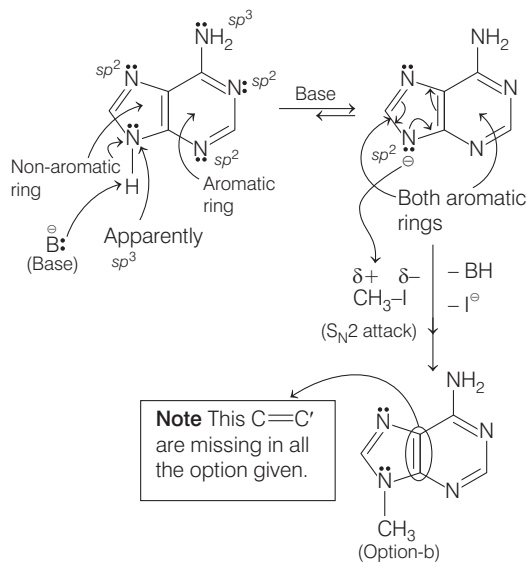
5.



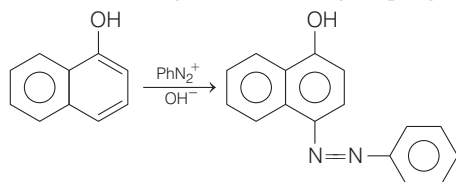
In step (i), 1° amine is converted into isocyanide, when reacts with  $\text{CHCl}_3$  / KOH. This reaction is known as carbylamine reaction. This reaction is used to detect primary amine in a compound.

In step (ii), isocyanide is reduced to secondary amine and cyanide is reduced to primary amine, and carbonyl group to alcoholic group when treated with Pd/C/H<sub>2</sub>.

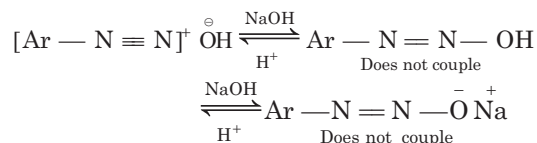
6. N is more electronegative than 'C'. So, H of  $\overset{\delta-}{\text{N}}-\overset{\delta+}{\text{H}}$  bond is more acidic than that of C—H bond in the ring.  
Again,  $sp^2$ -N is more electronegative ( $s\% = 33.3$ ) than  $sp^3$ -N ( $s\% = 25$ ) of the  $-\text{NH}_2$  group.



7. Coupling of benzene diazonium chloride with 1-naphthol in alkaline medium will give the following coupling reaction.

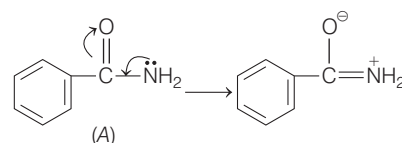


In the presence of  $\text{OH}^-$  ion,  $\text{ArN}_2^+$  exists in equilibrium with an unionised compound ( $\text{Ar}-\text{N}=\text{N}-\text{OH}$ ) and salts  $[\text{ArN}=\text{N}^+]-\text{OH}^-$  derived from it, which do not couple.



Following conditions are very useful for coupling reaction to take place.

- (a) The solution must be so alkaline that the concentration of diazonium ion is too low.
  - (b) It must not be so acidic that the concentration of free phenoxide ion is too low.
- 8.** The reaction of alkyl halide with amine or amides is a nucleophilic substitution reaction. More nucleophilic nitrogen is more reactive with alkyl halide. Compound (A) is benzamide and lone pair of 'N' of it, is not available in this compound.

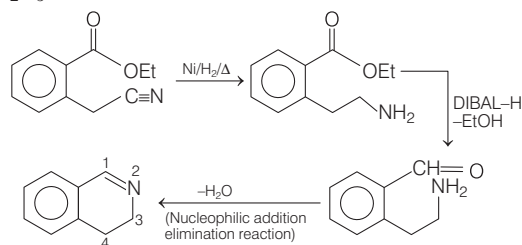


In compound (D), lone pair of 'N' are available but in compound (C), the lone pair of 'N' are not readily available due to the presence of electron withdrawing group ( $\text{—CN}$ ) attach to benzene ring.

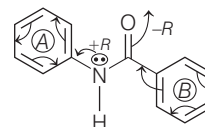
In compound (*B*), i.e. phthalimide, 'N' is not nucleophilic due to the presence of two polar groups attached to it that pulls lone pair towards them. Hence, the correct order is:

$$(B) < (A) < (C) < (D).$$

9.  $\text{Ni}/\text{H}_2$  can reduce  $-\text{C}\equiv\text{N}$  into  $-\text{CH}_2-\text{NH}_2$  ( $1^\circ$ -amine) but cannot reduce an ester group ( $-\text{CO}_2\text{Et}$ ) whereas DIBAL-H, di-isobutylaluminium hydride,  $[(\text{CH}_3)_2\text{CH}]_2\text{AlH}$  reduces the ester group ( $-\text{CO}_2\text{Et}$ ) into  $-\text{CHO}$  (an aldehyde) and  $\text{C}_9\text{H}_5\text{OH}$ .

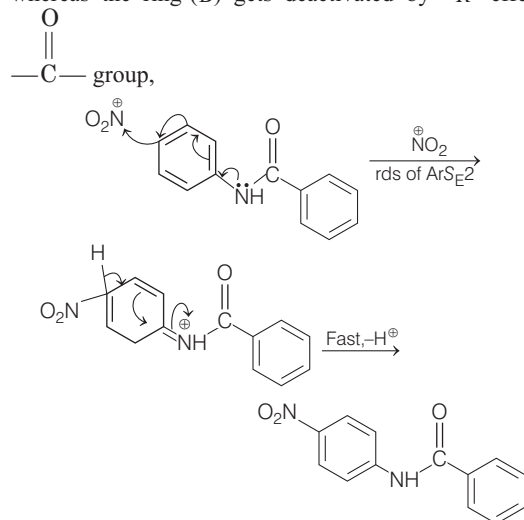


10. Here, in mononitration the electrophile produced from mixed acid ( $\text{HNO}_3 + \text{conc. H}_2\text{SO}_4$ ) is  $\text{NO}_2^+$ .

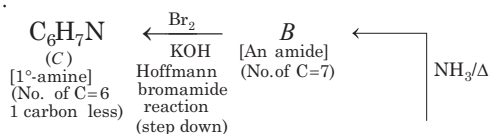


Ring-(A) is activated, i.e. becomes more nucleophilic by the +R effect of the  $\text{—}\ddot{\text{N}}\text{H—}$  group and it becomes *o*/*p*-directing towards the electrophile,  $\text{NO}_2^+$  in the  $\text{ArS}_E2$  reaction. For mononitration,  $\text{NO}_2^+$  will preferably come at *p*-position,

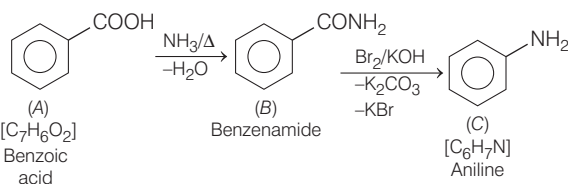
whereas the ring-(B) gets deactivated by  $-R$ -effect of the



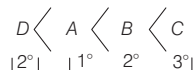
11. Using retro-synthesis, to get the required compounds, A, B and C.



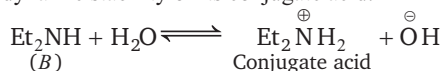
So, the reactions can be shown as:



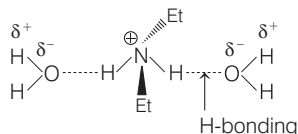
12. If we consider Lewis basicity (basicity in aprotic solvents or in vapour phase), the order of basicity will be.



But, this order does not match with the options given. So, it has been asked on basicity of the amines in aqueous solution. When no phase is given, then basicity of amine is considered in aqueous solution as they are liquids. In aqueous solution, basicity of 2°-amines (aliphatic) is maximum because, of the thermodynamic stability of its conjugate acid.



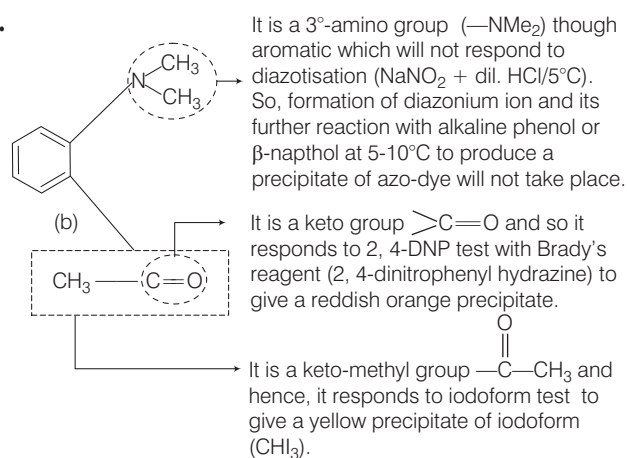
$\text{Et}_2\text{NH}_2^+$  is a sterically symmetric tetrahedral ion as it contains equal number (two) of bulkier Et-group and small size H-atoms. Here, two H-atoms give additional stability through hydrogen bonding with  $\text{H}_2\text{O}$  (solvent) molecules.



Aromatic amines (D) are always weaker bases than aliphatic amines, because of the conjugation of  $lp$  of electrons of N (+R-effect) with the benzene ring.

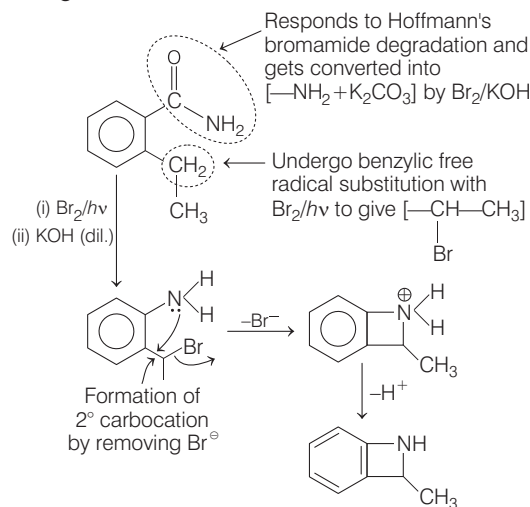
So, the correct order is (D) < (C) < (A) < (B).

13.



Compound (c) is an alcohol and does not give positive 2, 4-DNP test. Hence, eliminated (a) and (d) does not have  $\text{—CH}_3\text{CO}$  group and does not give iodoform test. Hence, eliminated.

14. In the given reaction,

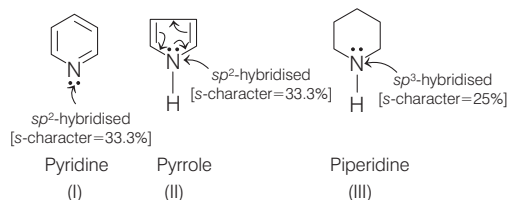


15. Key Idea

Basicity  $\propto$  Ease of donation of lone pair of electrons

$$\propto \frac{1}{\% \text{ of } s\text{-character of } N} \propto \frac{1}{\text{Electronegativity of } N}$$

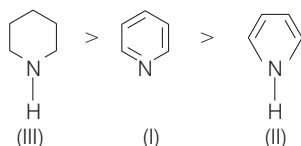
The % of  $s$ -character in the given amines are as follows:



Therefore, piperidine (III) having minimum

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% s-character is most basic. Among the rest, pyridine (I) and pyrrole (II) the lone pair of electrons of N in pyrrole (II) is involved in delocalisation and follows  $(4n + 2)\pi$  aromatic ( $n = 1$ ) system. So, the N-atom of pyrrole (II) will show least basicity. Thus, the order of basicity is as follows:

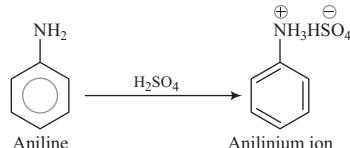


16. All the given compounds are  $\alpha$ -monosubstituted acetic acid derivatives and the  $\alpha$ -substitutions have been made by strong- $I$  groups/atoms. More powerful the  $-I$  group, stronger will be the acid.

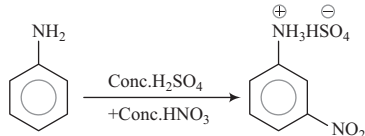
$-I$  power of different groups is as follows :  
 $-\text{NO}_2 > -\text{CN} > -\text{F} > -\text{Cl}$

Thus, the correct decreasing order for acid strength is:  
 $\text{NO}_2\text{CH}_2\text{COOH} > \text{NCCH}_2\text{COOH} > \text{FCH}_2\text{COOH}$   
 $> \text{ClCH}_2\text{COOH}$ .

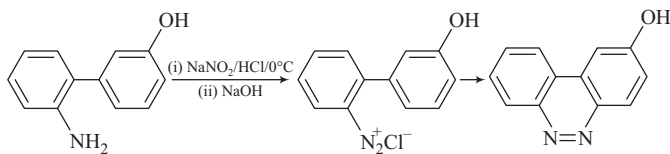
17. Aniline in presence of nitrating mixture (conc.  $\text{HNO}_3$  + conc.  $\text{H}_2\text{SO}_4$ ) gives significance amount ( $\approx 47\%$ ) of meta-product because in presence of  $\text{H}_2\text{SO}_4$  its protonation takes place and anilinium ion is formed.



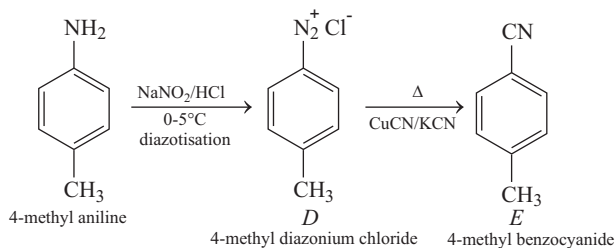
Here, anilinium ion is strongly deactivating group and *meta*-directing in nature. So, it gives *meta*-nitration product.



18. Diazo coupling occur at *para*-position of phenol.

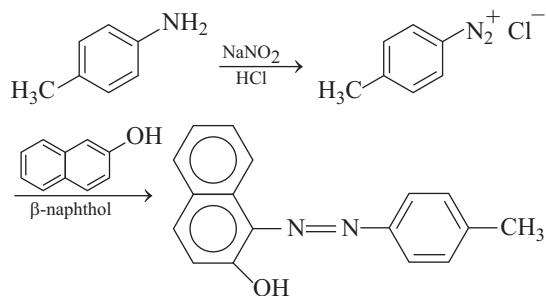


19.

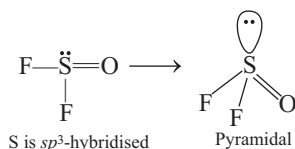


20. As we know, benzenediazonium salt forms brilliant coloured dye with  $\beta$ -naphthol, the compound under consideration must be *p*-toluidine (c) as it is a primary aromatic amine. Primary

aromatic amine, on treatment with  $\text{NaNO}_2$  in dil.  $\text{HCl}$  forms the corresponding diazonium chloride salt.

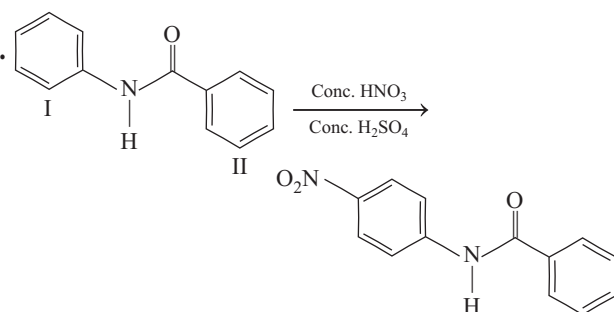


21.



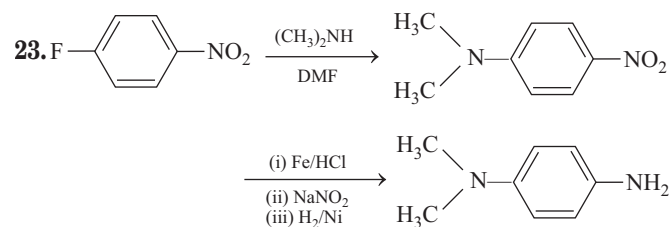
$\text{SO}_3$  is planar (S is  $sp^2$ -hybridised),  $\text{BrF}_3$  is T-shaped and  $\text{SiO}_3^{2-}$  is planar (Si is  $sp^2$ -hybridised).

22.

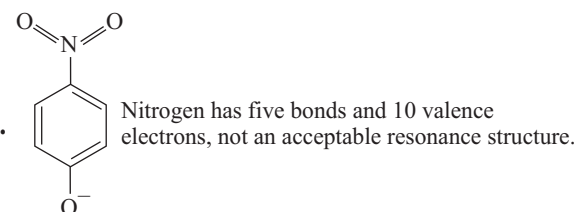


Ring-I is activated while ring-II is deactivated towards electrophilic aromatic substitution reaction.

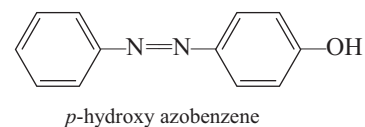
23.



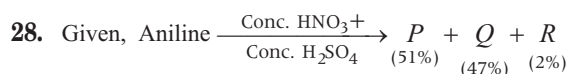
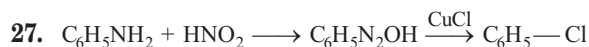
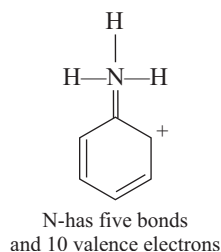
24.



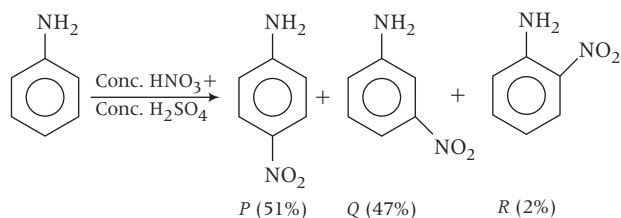
25.  $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^- + \text{C}_6\text{H}_5\text{OH} \longrightarrow$



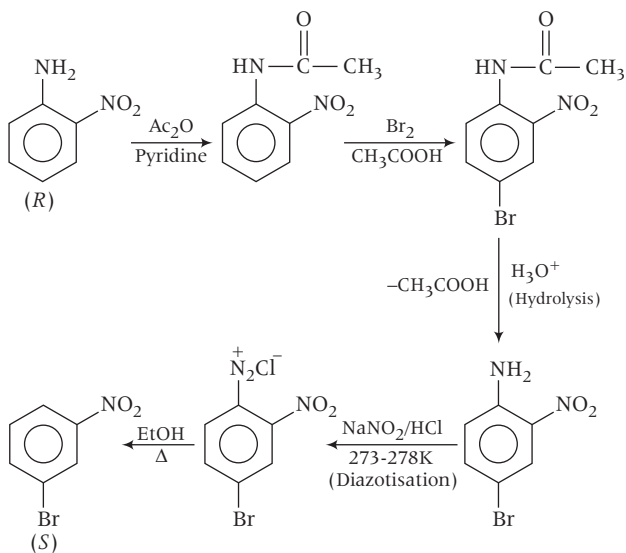
26. In structure II, nitrogen is associated with five bonds and 10 valence electrons, hence not acceptable.



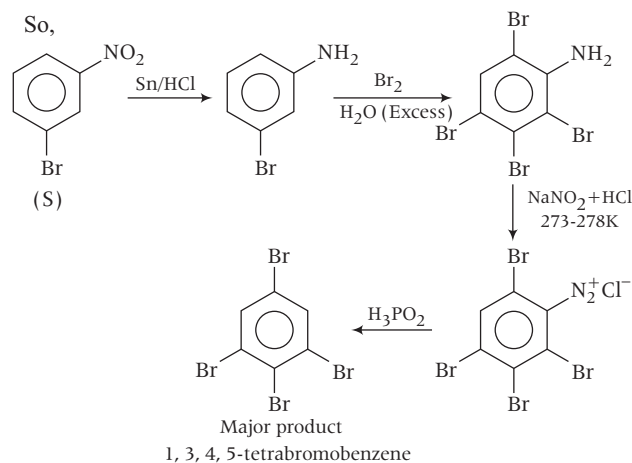
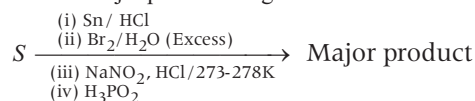
Then  $P$ ,  $Q$  and  $R$  will be



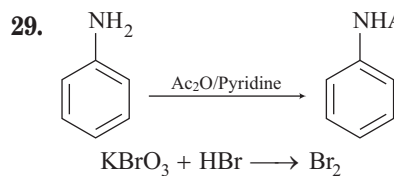
Its given  $R \xrightarrow[\text{(v) EtOH, } \Delta]{\text{(i) Ac}_2\text{O, Pyridine; (ii) Br}_2, \text{CH}_3\text{COOH; (iii) H}_3\text{O}^+; \text{(iv) NaNO}_2, \text{HCl/273-278 K}}$   $S$



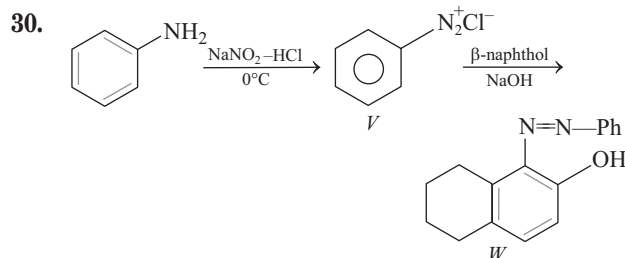
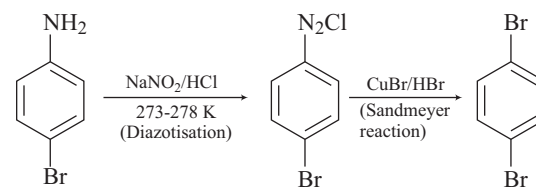
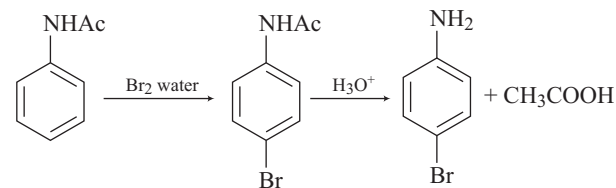
Now from  $S$  to major products its given.



Hence, only (d) is the correct answer.



Ac is  $\text{CH}_3\text{CO}$  (acetyl), it protects  $\text{—NH}_2$  group from being oxidised.

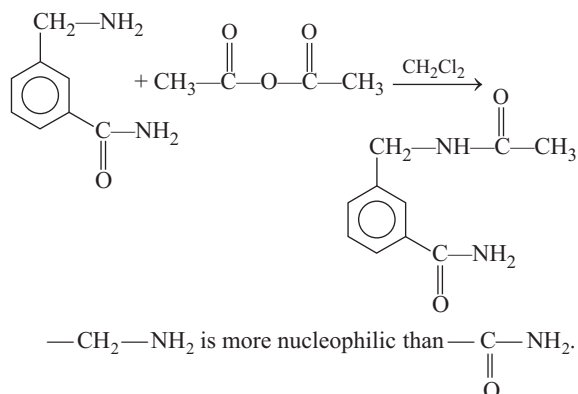


31. **PLAN** This problem includes concept of acetylation reaction and regioselectivity of chemical reaction.

Regioselectivity means which group will react selectively in the presence of two or more than two functional groups. Here, among two functional group  $\text{—NH}_2$  and  $\text{—CONH}_2$ ,  $\text{NH}_2$  is more nucleophilic, hence  $\text{NH}_2$  group will undergo reaction faster than  $\text{CONH}_2$ .



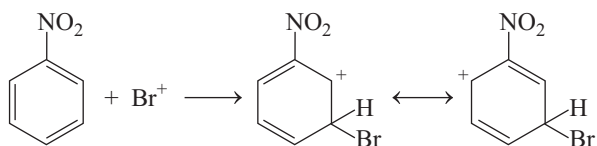
## 424 Aromatic Compounds Containing Nitrogen



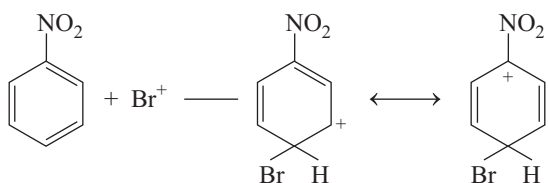
Hence, correct choice is (a).

32.  $(\text{C}_6\text{H}_5\text{NH}_3\text{Cl}^+) + \text{AgNO}_3 \longrightarrow \text{AgCl} \downarrow$   
 anilinium hydrochloride precipitate  
 No such precipitate is formed with *p*-chloroaniline.  
 Also, carbylamine test will not be given by anilinium hydrochloride but *p*-chloroaniline give this test.

33. Nitro group withdraws electrons more from *ortho*/*para* position than from *meta* position. Also the  $\sigma$ -complex formed from *meta* attack is less destabilised than from *ortho*/*para* positions.



Nitro group not destabilising the positive charge by resonance.

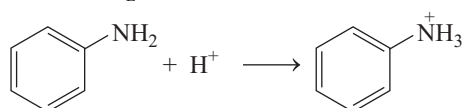


Nitro group destabilises the positive charge directly by resonance, less stable  $\sigma$ -complex.

Similar phenomenon is observed with *ortho* attack.

34.  $\text{C}_6\text{H}_5\text{NH}_2 + \text{NaNO}_2 / \text{HCl} \xrightarrow{0^\circ\text{C}} \text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$   
 $\xrightarrow{\beta\text{-naphthol}} \text{coloured dye}$

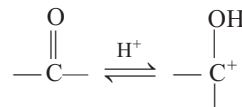
35. In strongly acidic medium, aniline is fully protonated, becomes deactivated for  $\text{S}_\text{E}\text{Ar}$  reaction.



Lone pair on nitrogen is not available for resonance. Positive charge makes the group strongly electron withdrawing.

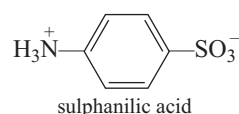
36. Sodium fusion extract gives Prussian blue colouration, nitrogen and carbon both present in the compound. Phenolic group and salt of carboxylic acid gives  $\text{FeCl}_3$  test.

Chloride salt gives white precipitate of  $\text{AgCl}$  on treatment with  $\text{AgNO}_3$ . Hydrazone formation occurs effectively at  $\text{pH} = 4.5$ . The reaction proceeds in that condition only when  $\text{H}^+$  concentration is just sufficient to activate the following enolisation.

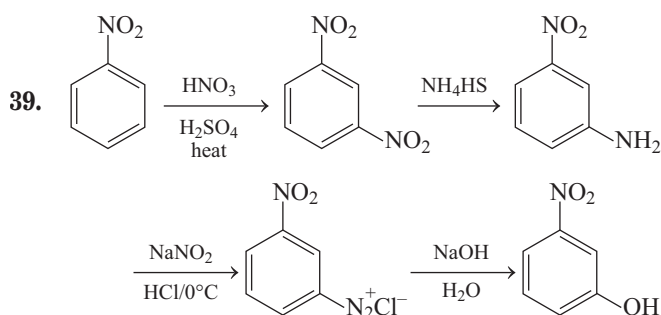


As  $\text{H}^+$  concentration rises sufficiently, a large number of molecules of hydrazine gets converted into hydrazinium ion which is not nucleophilic and reaction becomes impossible. Further low concentration of  $\text{H}^+$  (in the case of 2,4-dinitrophenyl hydrazinium bromide) is not effective to proceed elimination.

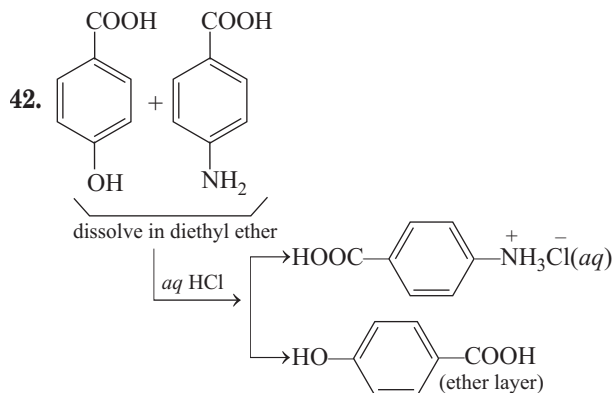
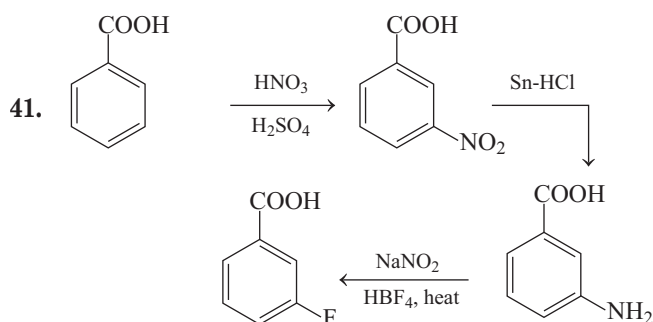
37. Zwitter ionic



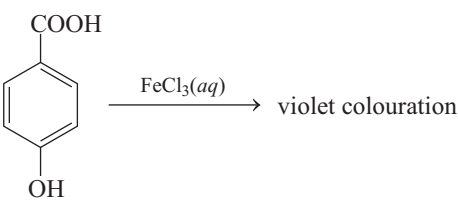
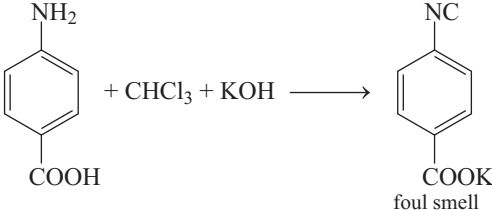
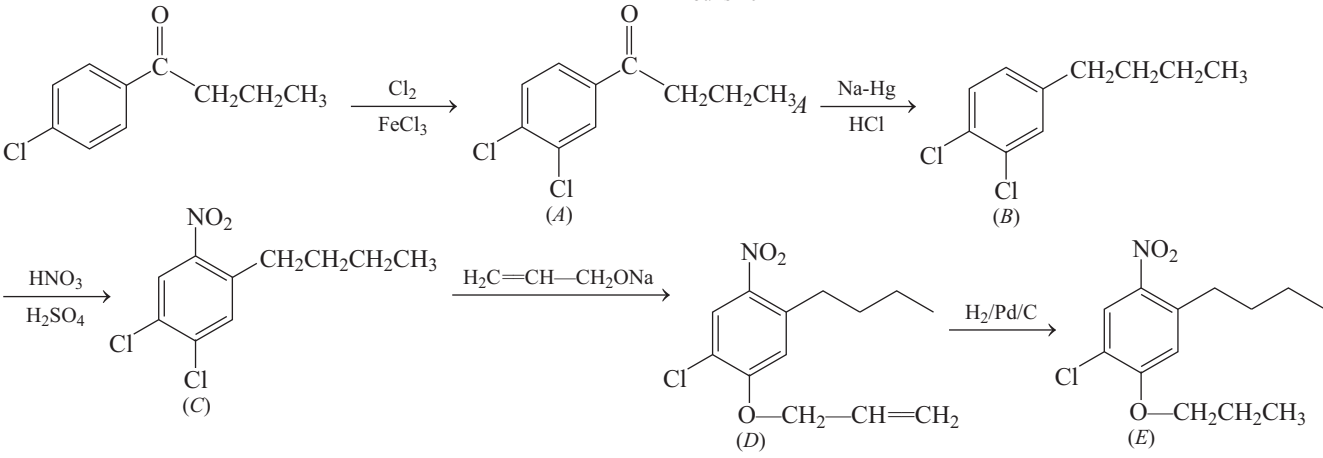
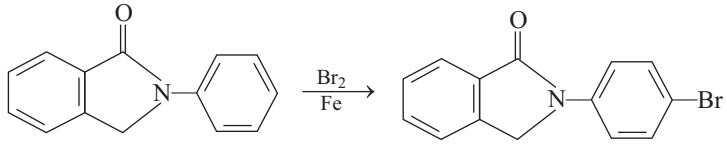
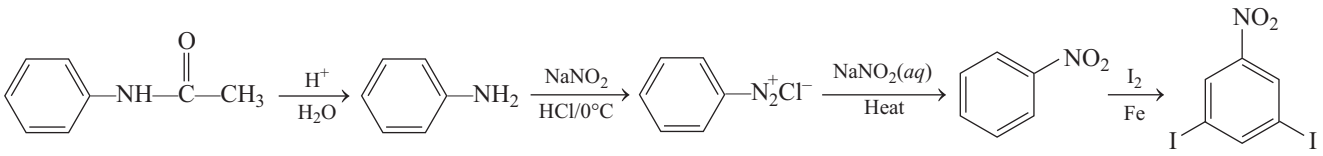
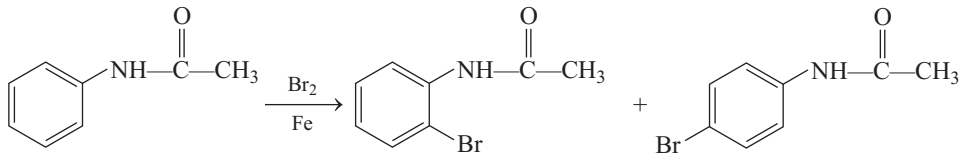
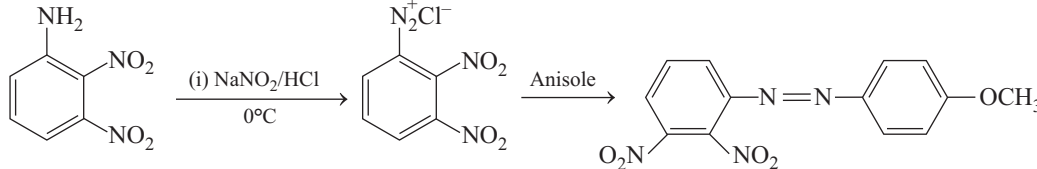
38. Aniline It is a stronger base than either phenol or nitrobenzene.



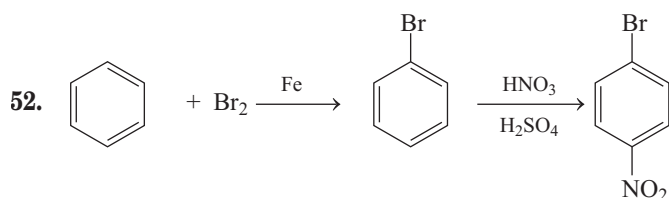
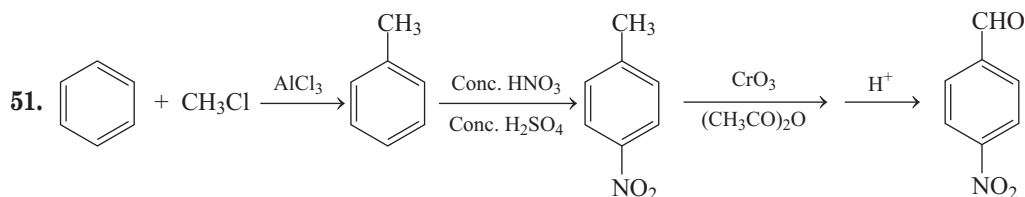
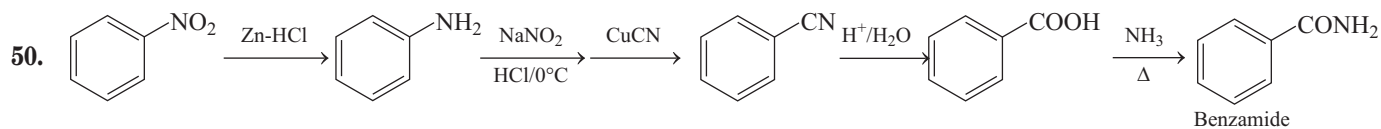
40. It is more acidic due to  $-I$  effect of F.



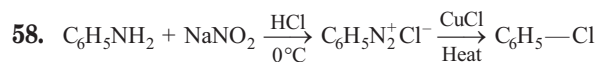
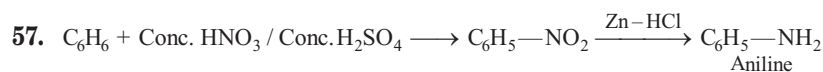
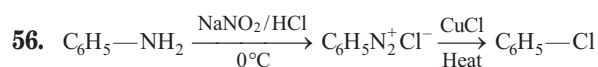
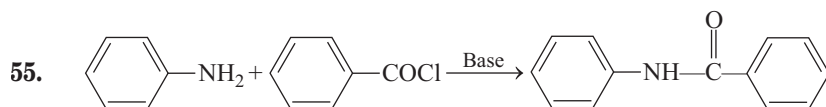
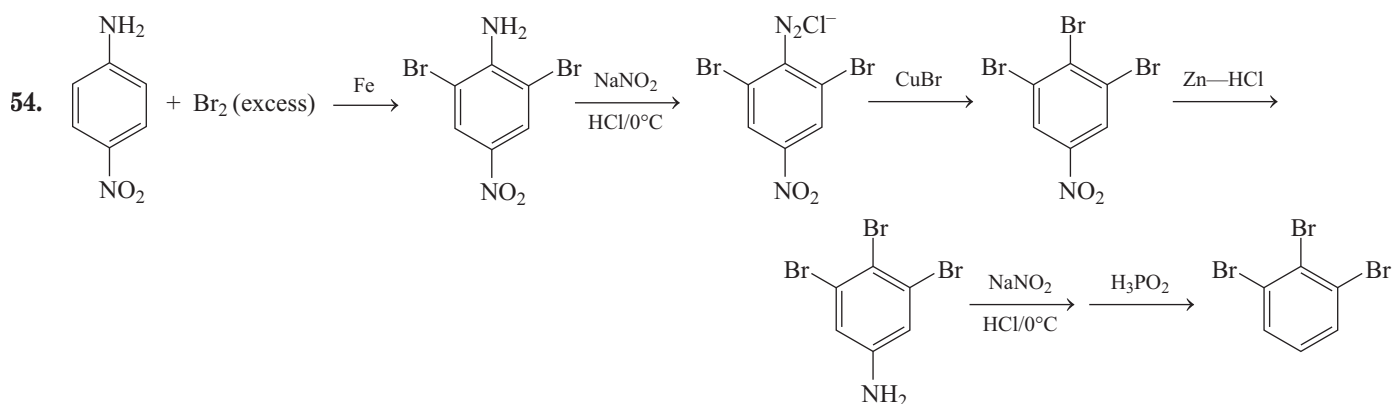


- 
- 
- 43.**

- 44.**

- 45.**  $\text{C}_6\text{H}_5\text{NH}_2 \xrightarrow[\text{HCl}/0^\circ\text{C}]{\text{NaNO}_2} \text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^- \xrightarrow{\text{CuCN}} \text{C}_6\text{H}_5\text{CN} \xrightarrow{\text{LiAlH}_4} \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$
- 46.**

- 47.**

- 48.**  $\text{C}_6\text{H}_5\text{NH}_2 + \text{CHCl}_3 + \text{KOH} \longrightarrow \text{C}_6\text{H}_5\text{NC}$   
 Isocyanide  
 (foul smell)
- 49.**


## 426 Aromatic Compounds Containing Nitrogen



53. No reaction. Tertiary amine does not react with nitrous acid.



**Download Chapter Test**  
<http://tinyurl.com/y437rg2e>

or

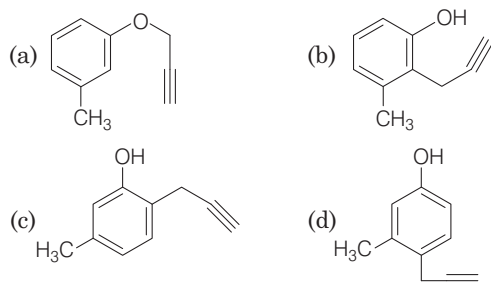


# 30

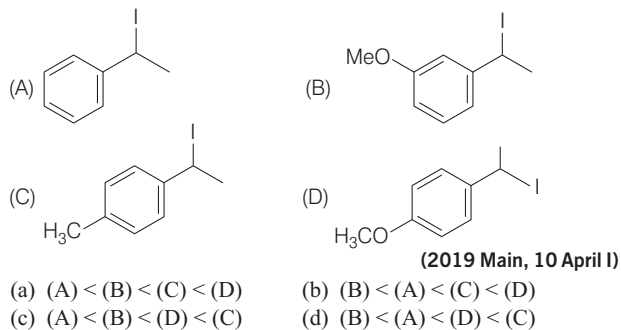
## Aryl Halides and Phenols

### Objective Questions I (Only one correct option)

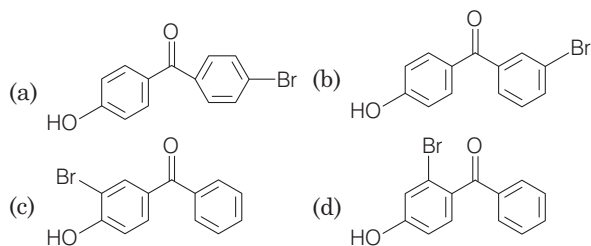
1. What will be the major product when *m*-cresol is reacted with propargyl bromide ( $\text{HC}\equiv\text{C}-\text{CH}_2\text{Br}$ ) in presence of  $\text{K}_2\text{CO}_3$  in acetone? (2019 Main, 12 April II)



2. Increasing rate of  $\text{S}_{\text{N}}1$  reaction in the following compounds is

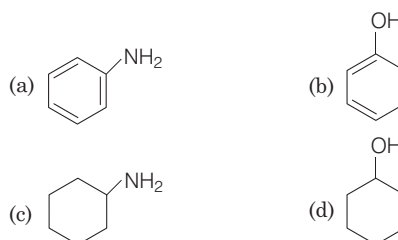


3. *p*-hydroxybenzophenone upon reaction with bromine in carbon tetrachloride gives (2019 Main, 9 April II)

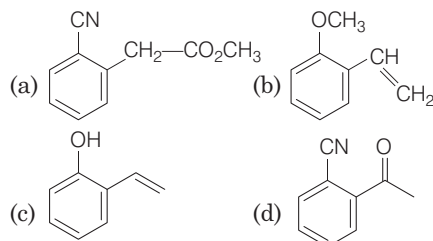


4. The organic compound that gives following qualitative analysis is (2019 Main, 9 April I)

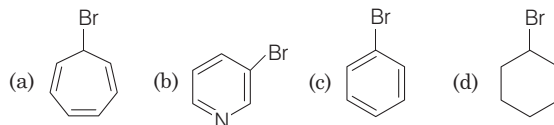
| Test                       | Inference       |
|----------------------------|-----------------|
| (i) Dil. HCl               | Insoluble       |
| (ii) NaOH solution         | Soluble         |
| (iii) $\text{Br}_2$ /water | Decolourisation |



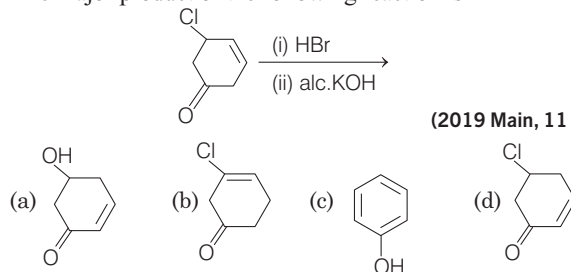
5. Which of the following compounds reacts with ethyl magnesium bromide and also decolourises bromine water solution (2019 Main, 11 Jan II)



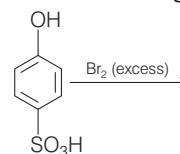
6. Which of the following compounds will produce a precipitate with  $\text{AgNO}_3$ ? (2019 Main, 11 Jan I)



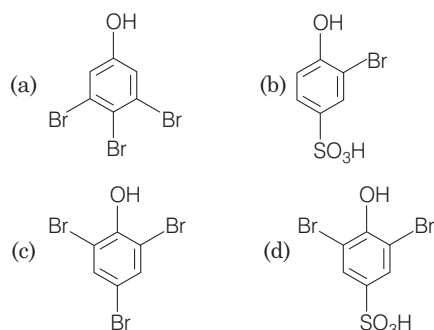
7. The major product of the following reaction is (2019 Main, 11 Jan I)



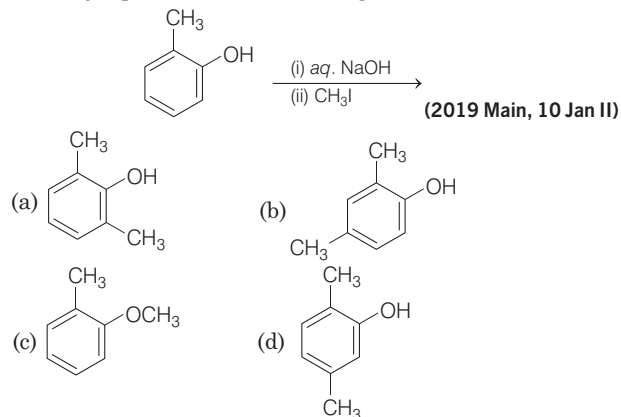
8. The major product of the following reaction is (2019 Main, 11 Jan I)



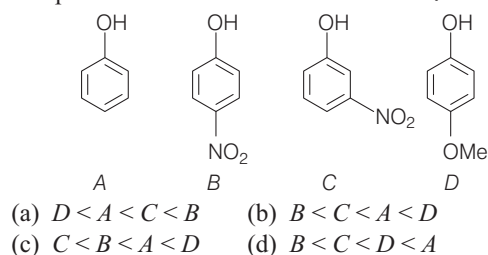
## 428 Aryl Halides and Phenols



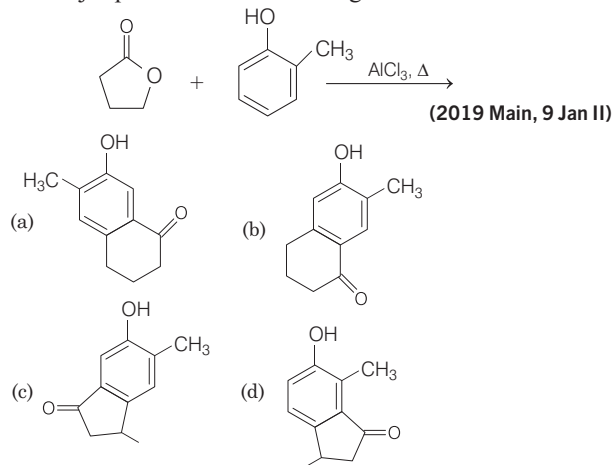
9. The major product of the following reaction is



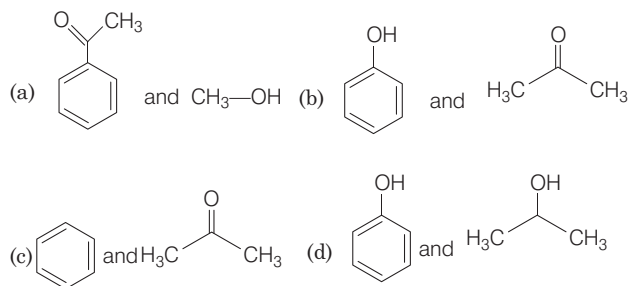
10. The increasing order of the  $pK_a$  values of the following compounds is (2019 Main, 10 Jan I)



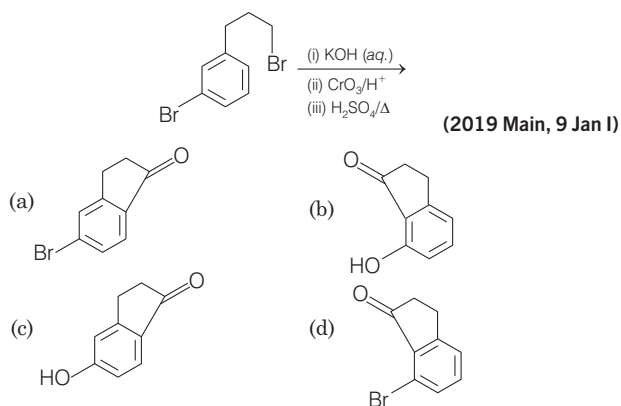
11. The major product of the following reaction is



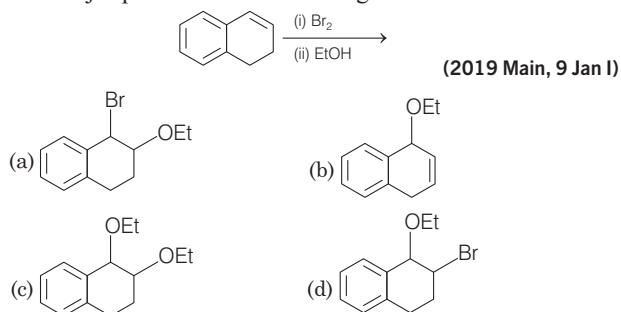
12. The products formed in the reaction of cumene with  $O_2$  followed by treatment with dil. HCl are (2019 Main, 9 Jan II)



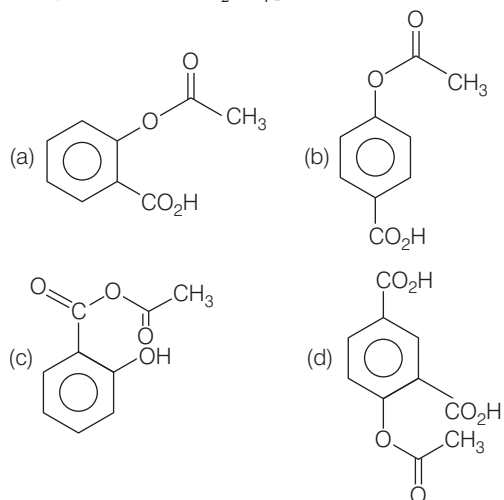
13. The major product of the following reaction is



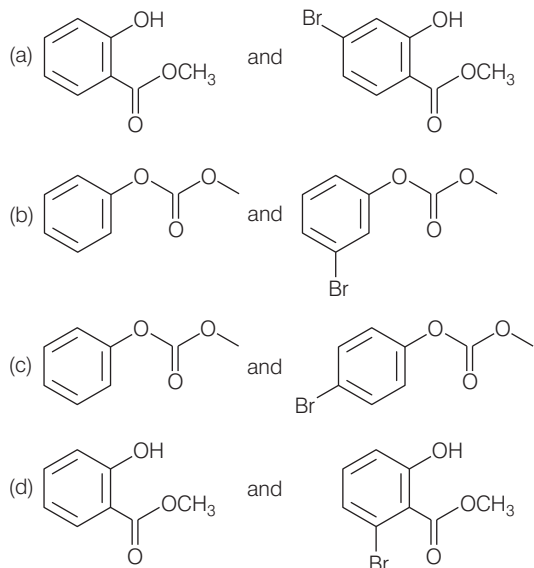
14. The major product of the following reaction is



15. Phenol on treatment with  $CO_2$  in the presence of NaOH followed by acidification produces compound X as the major product. X on treatment with  $(CH_3CO)_2O$  in the presence of catalytic amount of  $H_2SO_4$  produces: (2018 Main)



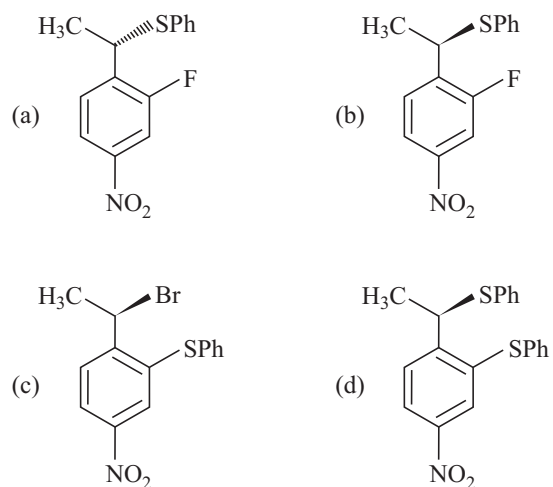
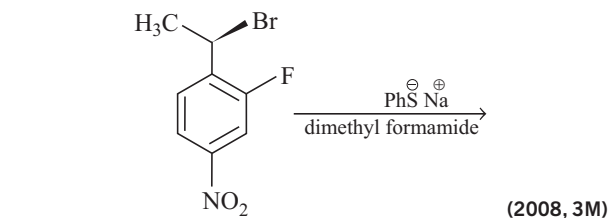
16. Phenol reacts with methyl chloroformate in the presence of NaOH to form product A. A reacts with Br<sub>2</sub> to form product B. A and B are respectively (2018 Main)



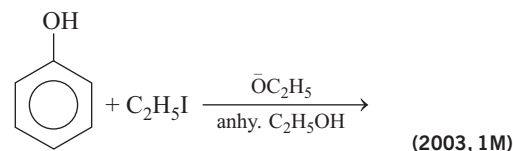
17. For the identification of β-naphthol using dye test, it is necessary to use (2014 Adv.)

- (a) dichloromethane solution of β-naphthol  
(b) acidic solution of β-naphthol  
(c) neutral solution of β-naphthol  
(d) alkaline solution of β-naphthol

18. The major product of the following reaction is



- 19.



- (a) C<sub>6</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>5</sub> (b) C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>5</sub>  
(c) C<sub>6</sub>H<sub>5</sub>OC<sub>6</sub>H<sub>5</sub> (d) C<sub>6</sub>H<sub>5</sub>I

20. In the reaction of *p*-chlorotoluene with KNH<sub>2</sub> in liq. NH<sub>3</sub>, the major product is (1997, 1M)

- (a) *o*-toluidine (b) *m*-toluidine  
(c) *p*-toluidine (d) *p*-chloroaniline

21. Phenol reacts with bromine in carbon disulphide at low temperature to give (1988, 1M)

- (a) *m*-bromophenol (b) *o*- and *p*-bromophenol  
(c) *p*-bromophenol (d) 2, 4, 6-tribromophenol

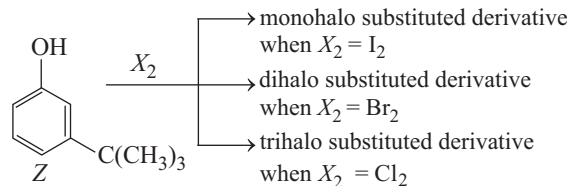
22. When phenol is treated with excess of bromine water, it gives (1984, 1M)

- (a) *m*-bromophenol (b) *o*- and *p*-bromophenol  
(c) 2, 4-dibromophenol (d) 2, 4, 6-tribromophenol

## Objective Questions II

(One or more than one correct option)

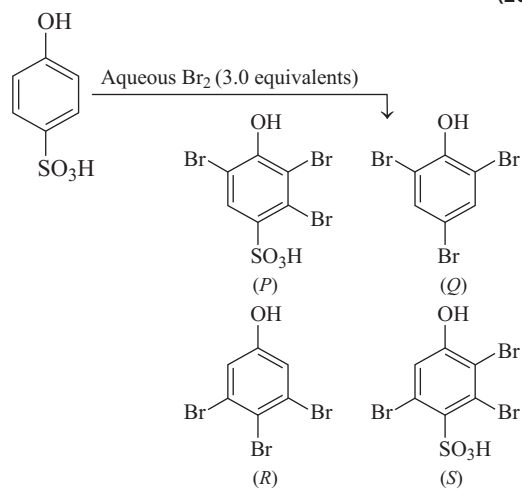
23. The reactivity of compound Z with different halogens under appropriate conditions is given below



The observed pattern of electrophilic substitution can be explain by

- (a) the steric effect on the halogen  
(b) the steric effect of the *tert*-butyl group  
(c) the electronic effect of the phenolic group  
(d) the electronic effect of the *tert*-butyl group

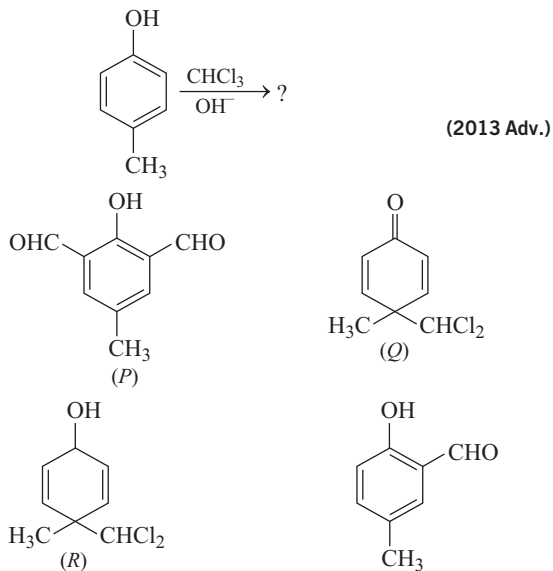
24. The major product(s) of the following reaction is/are (2013 Adv.)



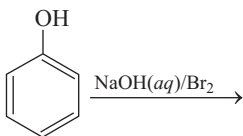
- (a) P (b) Q (c) R (d) S

## 430 Aryl Halides and Phenols

25. In the following reaction, the product (s) formed is/are

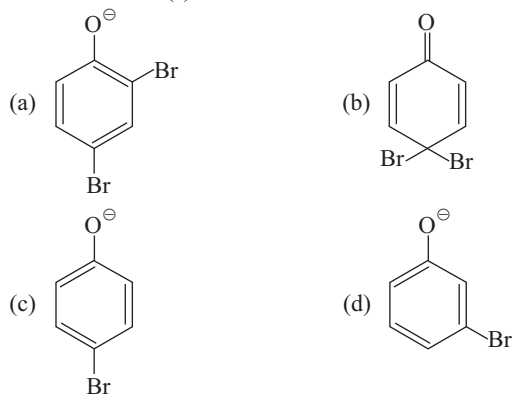


26. In the reaction,



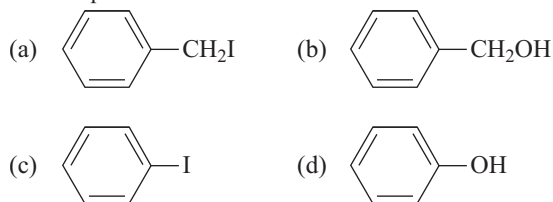
the intermediate(s) is/are

(2010)



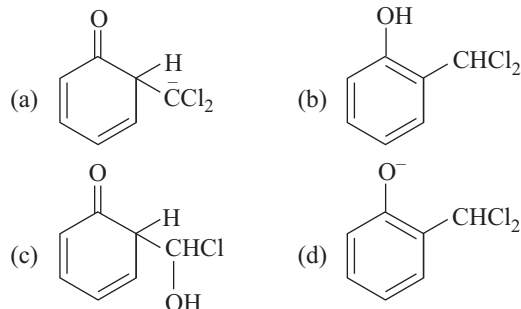
27. The ether , when treated with HI produces

(1999, 3M)



28. When phenol is reacted with  $\text{CHCl}_3$  and  $\text{NaOH}$  followed by acidification, salicylaldehyde is formed. Which of the following species are involved in the above mentioned reaction as intermediates ?

(1995, 2M)



29. Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halide due to

(1990, 1M)

- (a) the formation of less stable carbonium ion  
 (b) resonance stabilisation  
 (c) longer carbon halogen bond  
 (d)  $sp^2$ -hybridised carbon bonded to halogen

### Assertion and Reason

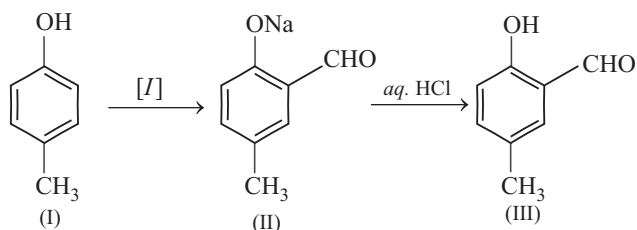
Read the following questions and answer as per the direction given below :

- (a) Statement I is correct; Statement II is correct Statement II is the correct explanation of Statement I  
 (b) Statement I is correct; Statement II is correct Statement II is not the correct explanation of Statement I  
 (c) Statement I is correct; Statement II is incorrect  
 (d) Statement I is incorrect; Statement II is correct
30. **Statement I** Bromobenzene, upon reaction with  $\text{Br}_2/\text{Fe}$  gives 1,4-dibromobenzene as the major product.  
**Statement II** In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in directing the incoming electrophile. (2008, 3M)
31. **Statement I** Phenol is more reactive than benzene towards electrophilic substitution reaction.  
**Statement II** In the case of phenol, the intermediate carbocation is more resonance stabilised. (2000, M)
32. **Statement I** Benzonitrile is prepared by the reaction of chlorobenzene with potassium cyanide.  
**Statement II** Cyanide ( $\text{CN}^-$ ) is a strong nucleophile. (1998, 2M)
33. **Statement I** Aryl halides undergo nucleophilic substitution with ease.  
**Statement II** The carbon halogen bond in aryl halides has partial double bond character. (1991, 2M)

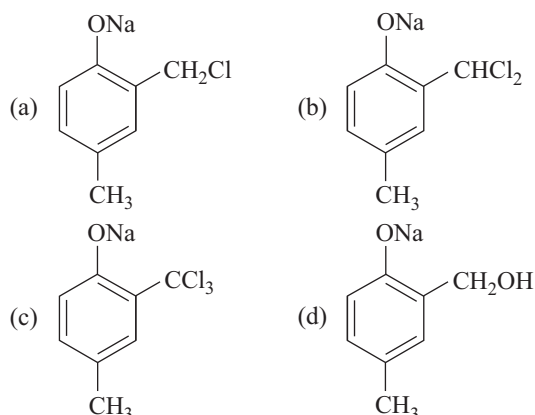
## Passage Based Problems

### Passage 1

Reimer-Tiemann reaction introduces an aldehyde group, on to the aromatic ring of phenol, *ortho* to the hydroxyl group. This reaction involves electrophilic aromatic substitution. This is a general method for the synthesis of substituted salicylaldehydes as depicted below.



34. The structure of the intermediate *I* is



35. The electrophile in this reaction is

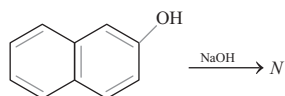
- (a)  $\cdot\text{CHCl}$     (b)  $^+\text{CHCl}_2$     (c)  $\cdot\text{CCl}_2$     (d)  $\cdot\text{CCl}_3$

36. Which one of the following reagents is used in the above reaction?

- (a) aq NaOH +  $\text{CH}_3\text{Cl}$       (b) aq NaOH +  $\text{CH}_2\text{Cl}_2$   
 (c) aq NaOH +  $\text{CHCl}_3$       (d) aq NaOH +  $\text{CCl}_4$

## Integer Type Questions

37. The number of resonance structures for *N* is (2015, Adv.)



## Fill in the Blanks

38. Amongst the three isomers of nitrophenol, the one that is least soluble in water is ..... (1992, 1M)

39. Phenol is acidic due to resonance stabilisation of its conjugate base, namely ..... (1990, 1M)

40. Formation of phenol from chlorobenzene is an example of ..... aromatic substitution. (1989, 1M)

41. The acidity of phenol is due to the ..... of its anion. (1984, 1M)

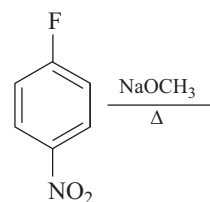
## Subjective Questions

42. Carry out the following conversions.

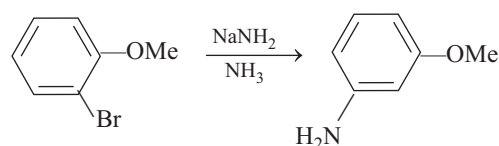
- (i) Phenol to aspirin  
 (ii) Benzoic acid to *meta*-fluorobenzoic acid in not more than three steps. (2003)

43. How would you synthesise 4-methoxyphenol from bromobenzene in not more than five steps? State clearly the reagents used in each step and show the structures of the intermediate compounds in your synthetic scheme. (2001, 5M)

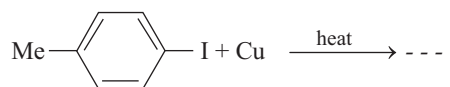
44. What would be the major product in the following reaction?



45. Explain briefly the formation of the products giving the structures of the intermediates.



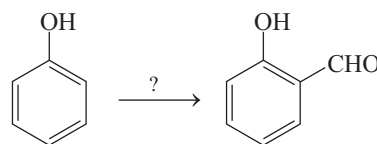
46. Complete the following, giving the structures of the principal organic products



47. How will you prepare *m*-bromiodobenzene from benzene (in not more than 5-7 steps)? (1996, 2M)

48. Explain the following in one or two sentences only :  
 "Phenol is an acid, but it does not react with sodium bicarbonate." (1987, 1M)

49. Complete the following with appropriate structures :



(1986, 1M)

50. A compound of molecular formula  $\text{C}_7\text{H}_8\text{O}$  is insoluble in water and dilute sodium bicarbonate but dissolve in dilute NaOH solution and gives a characteristic colour with  $\text{FeCl}_3$ . On treatment with bromine water, it readily gives a precipitate of  $\text{C}_7\text{H}_5\text{OBr}_3$ . Write down the structure of the compound. (1985, 2M)

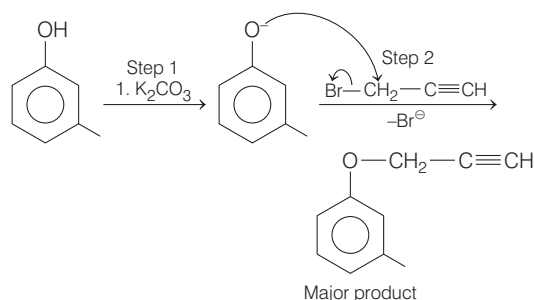
51. Give reason in one or two sentences for the following :  
 "*o*-nitrophenol is steam volatile whereas *p*-nitrophenol is not." (1985, 1M)

## Answers

- |         |         |             |         |                                                      |                               |            |           |
|---------|---------|-------------|---------|------------------------------------------------------|-------------------------------|------------|-----------|
| 1. (a)  | 2. (b)  | 3. (c)      | 4. (b)  | 25. (b,d)                                            | 26. (b,c)                     | 27. (a, d) | 28. (a,d) |
| 5. (c)  | 6. (a)  | 7. (c)      | 8. (c)  | 29. (b,d)                                            | 30. (c)                       | 31. (a)    | 32. (d)   |
| 9. (c)  | 10. (b) | 11. (c)     | 12. (b) | 33. (d)                                              | 34. (b)                       | 35. (c)    | 36. (c)   |
| 13. (a) | 14. (d) | 15. (a)     | 16. (c) | 37. (9)                                              | 38. <i>ortho</i> -nitrophenol |            |           |
| 17. (d) | 18. (a) | 19. (a)     | 20. (b) | 39. phenoxide ion 40. nucleophilic 41. phenoxide ion |                               |            |           |
| 21. (c) | 22. (d) | 23. (a,b,c) | 24. (b) |                                                      |                               |            |           |

## Hints & Solutions

1. The major product when *m*-cresol reacts with propargyl bromide ( $\text{HC}\equiv\text{C}-\text{CH}_2\text{Br}$ ) in presence of  $\text{K}_2\text{CO}_3$  in acetone is given in the following reaction:

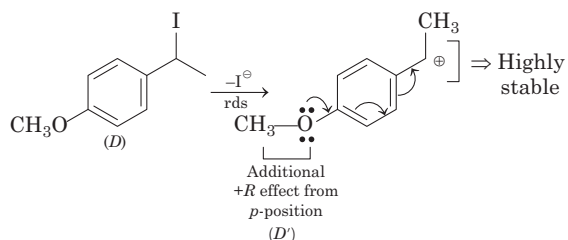
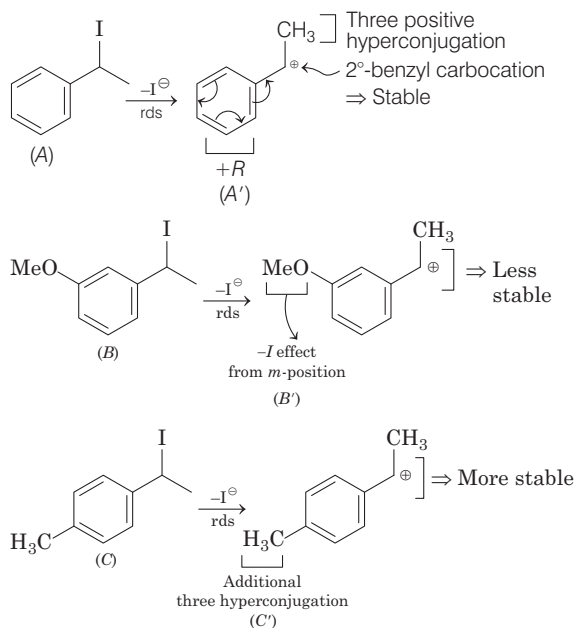


In **step 1**  $\text{K}_2\text{CO}_3$  act as a base and abstract H-atom from  $-\text{OH}$  group. This leads to the formation of substituted phenoxide ion (highly stable).

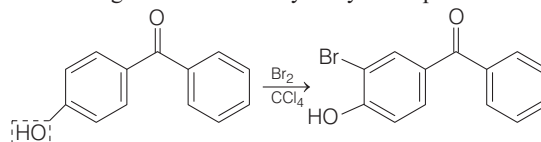
In **step 2** substituted phenoxide ion on reaction with  $\text{Br}-\text{CH}_2-\text{C}\equiv\text{CH}$  gives the required product.

2. More stable the carbocation intermediate, higher will be the rate of  $\text{S}_{\text{N}}1$  reaction.

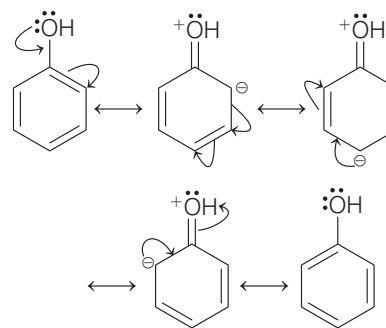
The reaction involving carbocation intermediate formation for the given compounds are as follows:



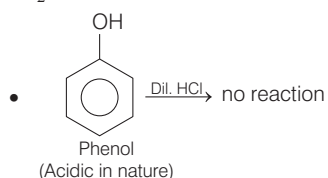
3. *p*-hydroxy benzophenone upon reaction with bromine in carbon tetrachloride gives 3-bromo-4-hydroxy benzophenone.



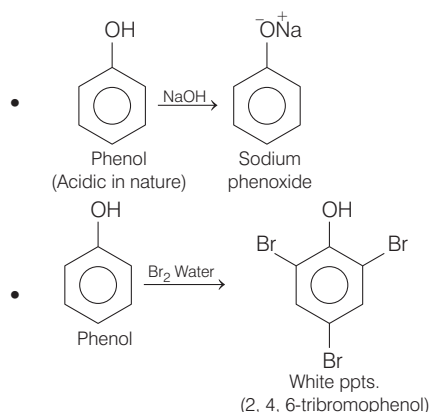
$-\text{OH}$  group attached on the benzene ring direct the incoming group at *ortho* and *para*-positions due to increase in electron density at *o* and *p*-positions.  $-\text{OH}$  group also exhibit  $-\text{I}$  group that reduces the electron density to some extent at *o* and *p*-positions. But overall electron density increases at these positions of the ring due to resonance. Hence, attack of  $-\text{Br}$  occur at *ortho* position. Resonating structures are as follows:



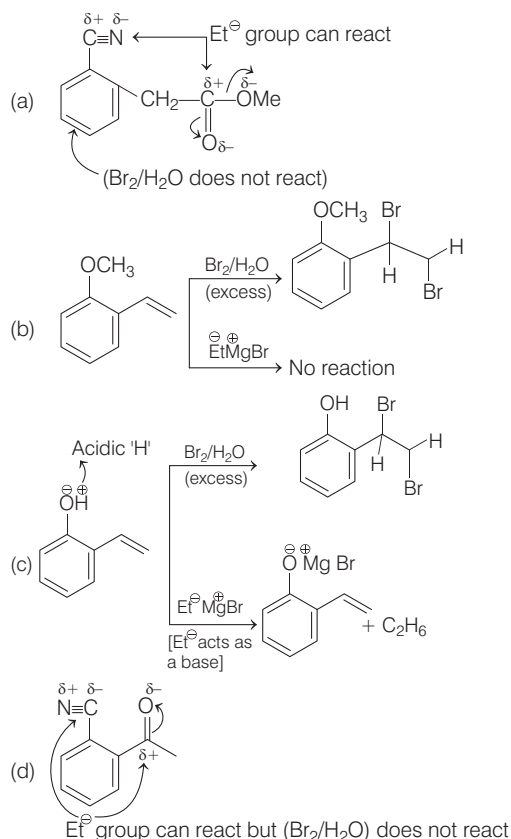
4. Phenol ( $\text{ArOH}$ ) is insoluble in dil.  $\text{HCl}$  and readily soluble in  $\text{NaOH}$  solution. It reacts with  $\text{Br}_2/\text{water}$  to give 2, 4, 6-tribromophenol. It readily decolourises the yellow colour of  $\text{Br}_2$  water. Reactions involved are as follows :



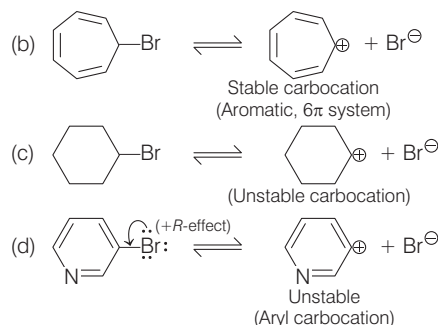
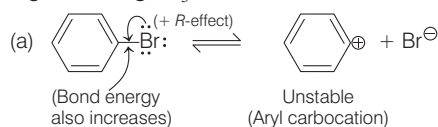




5. Ethyl magnesium bromide is a Grignard reagent (GR), it constitutes  $\text{C}_2\text{H}_5^- [\text{C}_2\text{H}_5^+ \text{MgBr}]$  in ether/aprotic medium which can act as nucleophile as well as strong base. Bromine water ( $\text{Br}_2/\text{H}_2\text{O}$ , red) gets decolourised with phenol derivatives (option, c), anisole derivatives (option, b) etc., as  $\text{>C=C<}$  is present outside the ring (aliphatic, not aromatic).

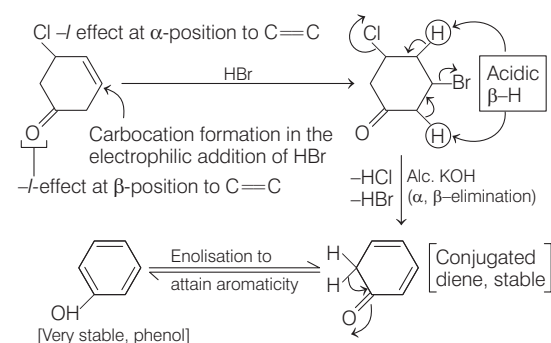


6. Only ionic halides ( $\text{X}^-$ ) give precipitate of  $\text{AgX}$  with  $\text{AgNO}_3$  solution. So, an organic bromide able to produce  $\text{R}^+$  (stable carbocation) and  $\text{Br}^-$  in aqueous solution will give precipitate of  $\text{AgBr}$  with  $\text{AgNO}_3$ .

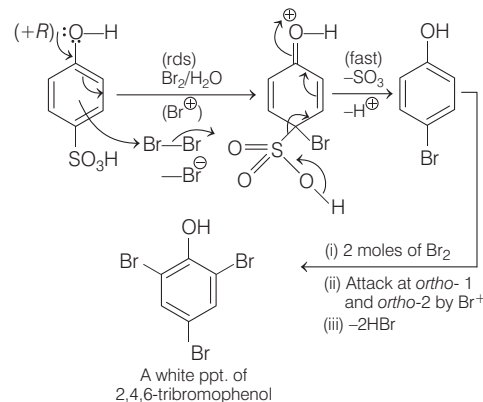


So, only produces a precipitate of  $\text{AgBr}$  with  $\text{AgNO}_3$  solution.

7. In presence of  $\text{HBr}$ , reactant containing  $\text{>C=C<}$  undergoes electrophilic addition reaction and give substituted alkyl halide. On further reaction with alc.  $\text{KOH}$ ,  $\alpha, \beta$ -elimination takes place that give corresponding diene. The diene undergoes enolisation to give stable product (phenol).

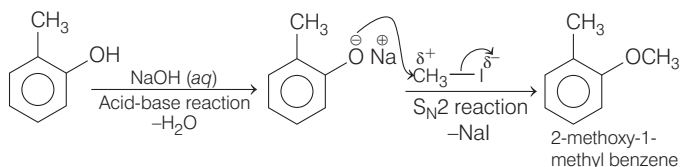


8. In , ipso-substitution takes place with the carbon bearing  $\text{—SO}_3\text{H}$  group. After the attack of the electrophilic  $\text{Br}^+$  in the rate determining step (rds) of the  $\text{ArS}_{\text{E}2}$  pathway desulphonation ( $\text{—SO}_3$ ) takes place with a faster rate.



9. Substituted phenols react with  $\text{aq. NaOH}$  to form sodium phenoxides which on reaction with  $\text{CH}_3\text{I}$  undergoes  $\text{S}_{\text{N}}2$  reaction to give 2-methoxy-1-methyl benzene.

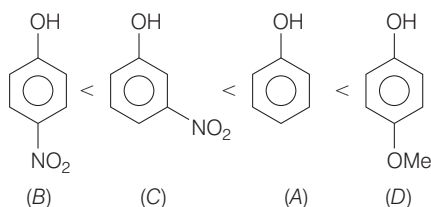
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10. Acidic strength is inversely proportional to  $pK_a$  value. The acidity of phenols is due to greater resonance stabilisation of phenoxide ion relative to phenol. Therefore, any substituent which stabilises the phenoxide ion more by dispersal of negative charge will tend to increase the acidity of phenol. Electron withdrawing groups ( $-\text{NO}_2$ ) increases the acidic strength of phenol whereas electron donating group ( $-\text{OCH}_3$ ) decreases the acidic strength of phenol. In case of  $-\text{NO}_2$  group attached to phenol, the dispersal of negative charge is more pronounced at *o*- and *p*-position than at *m*-position.

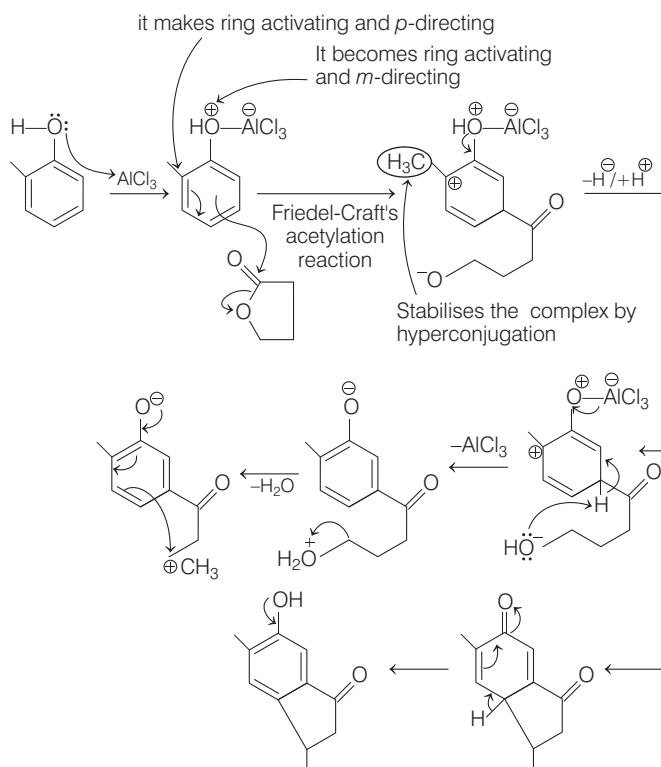
Thus, order of acidic strength of nitrophenol is:

*p*-nitrophenol > *o*-nitrophenol and the correct order of the  $pK_a$  values of give option is



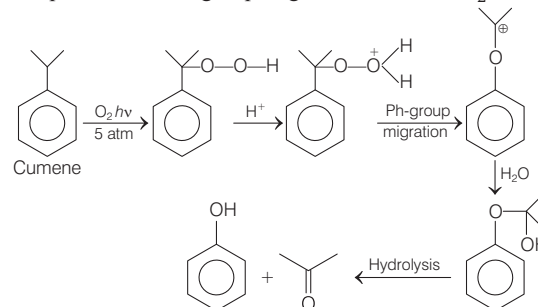
11. It is an aromatic electrophilic substitution reaction ( $\text{ArS}_{\text{E}2}$ ).

The reaction follows  $\text{ArS}_{\text{E}2}$  (Aromatic electrophilic substitution pathway) as shown below :



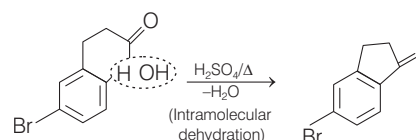
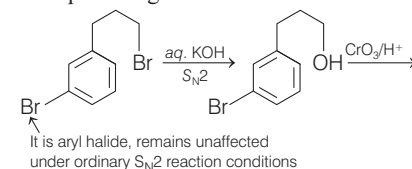
12. The given process is cumene process (Hock process) to synthesise phenol and acetone industrially.

In Hock process,  $\text{Ph}-\text{C}(\text{CH}_3)_2$  group migrate and release  $\text{H}_2\text{O}$ .

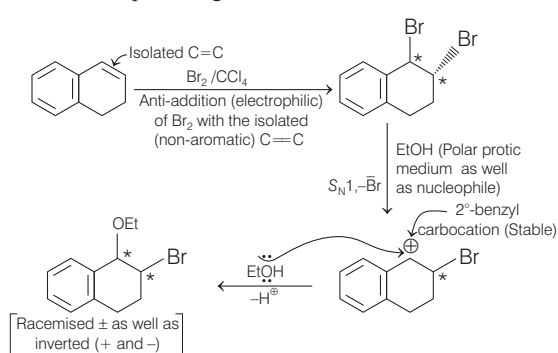


13. **Key Idea** The reaction involves hydrolysis or nucleophilic substitution in first step followed by oxidation and dehydration in last step. The most important fact is that, the Br group attached directly to aromatic ring will not undergo substitution in step 1.

The road map of the given reaction is as follows:

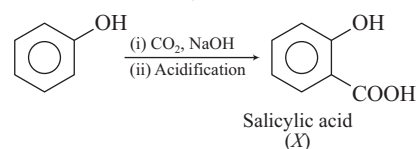


14. The road map of the given reaction is :

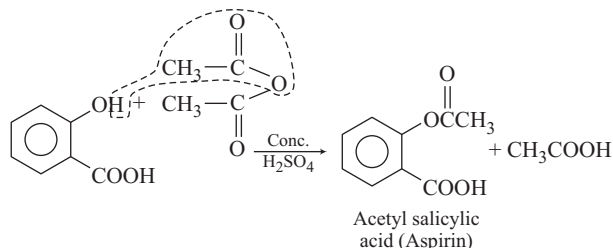


15. c1ccccc1O +  $\text{CO}_2$  +  $\text{NaOH}$   $\xrightarrow{\text{Followed by acidification}}$   $\text{X}$  ( $(\text{CH}_3\text{CO})_2\text{O}$ , conc.  $\text{H}_2\text{SO}_4$  (Catalytic amount))

The very first reaction in the above road map looks like Kolbe's reaction which results to salicylic acid as

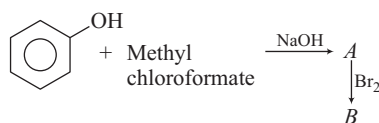


The salicylic acid with acetic anhydride  $[(\text{CH}_3\text{CO})_2\text{O}]$  in the presence of catalytic amount of conc.  $\text{H}_2\text{SO}_4$  undergoes acylation to produce aspirin as



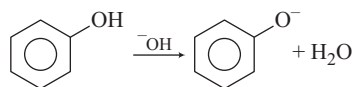
Aspirin is a non-narcotic analgesic (Pain killer).

16. Given,

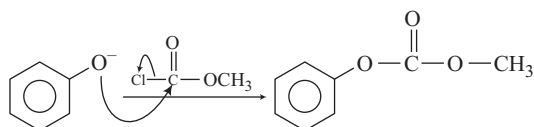


In the above road map, first reaction appears as acid base reaction followed by  $\text{S}_{\text{N}}\text{AE}$  (Nucleophilic substitution through Addition and Elimination). Both the steps are shown below

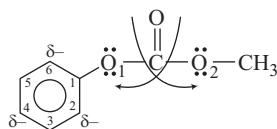
(i) **Acid base reaction**



(ii)  **$\text{S}_{\text{N}}\text{AE}$**

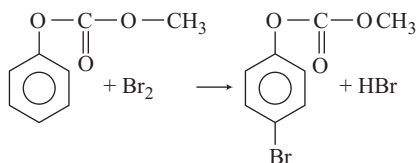


In the product of  $\text{S}_{\text{N}}\text{AE}$  the attached group is *ortho* and *para*-directing due to following cross conjugation



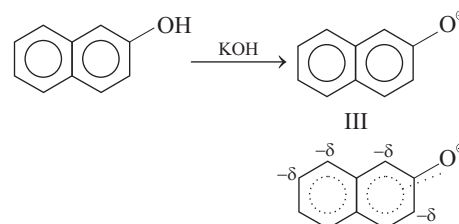
Cross conjugation due to which lone pair of oxygen 1 will be easily available to ring resulting to higher electron density at 2, 4, 6 position with respect to group. However from the stability point of view *ortho* positions are not preferred by substituents as group  $-\text{O}-\text{C}(=\text{O})-\text{O}-\text{CH}_3$  is bulky.

Hence, on further bromination of  $\text{S}_{\text{N}}\text{AE}$  product *para* bromo derivative will be the preferred product i.e.

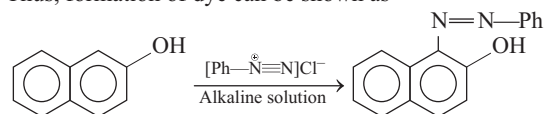


17. **PLAN** This problem can be solved by using the concept of synthesis of dye using electrophilic aromatic substitution reaction.

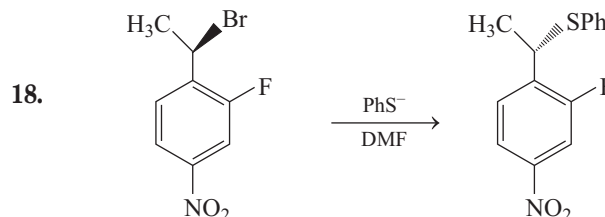
In basic (alkaline) solution naphthol exists as naphthoxide ion which is a strong *o*, *p*-directing group.



Thus, formation of dye can be shown as

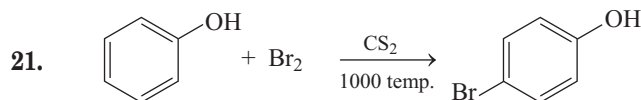
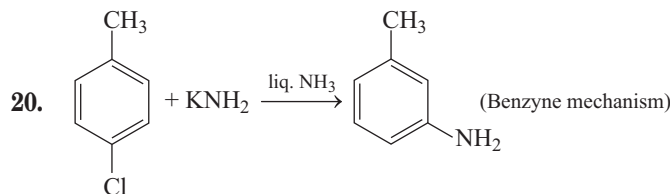
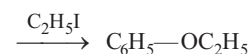


Thus, (d) is the correct choice.

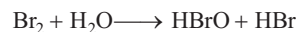
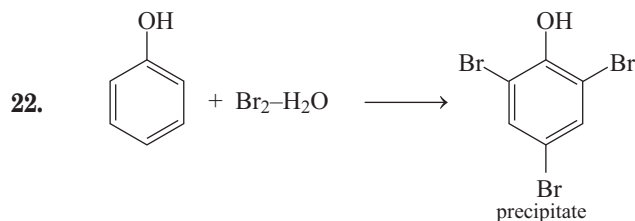


$\text{S}_{\text{N}}2$  reaction bring about inversion of configuration.

19.  $\text{C}_6\text{H}_5\text{OH} + \text{C}_2\text{H}_5\text{O}^- \longrightarrow \text{C}_6\text{H}_5\text{O}^-$



In carbon disulphide, no phenoxide ion exist, therefore only monobromination takes place.



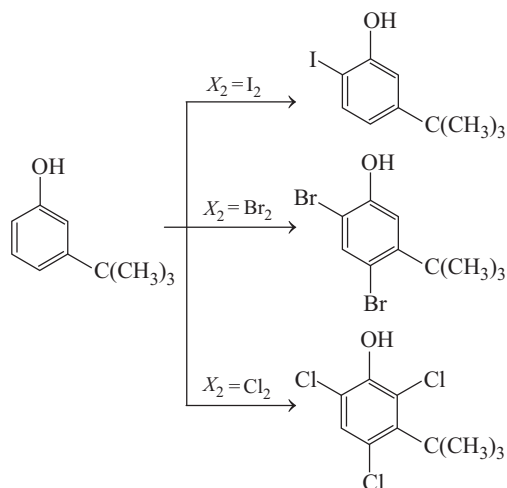
It is a reversible reaction, but equilibrium is significantly shifted to left, also indicated as  $\text{Br}_2(\text{aq})$ .

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**23. PLAN** This problem includes concept of effect of steric and electronic effect on reactivity of organic compounds.

Steric effect of halogens are as follows  $\text{Cl}_2 < \text{Br}_2 < \text{I}_2$

Electronic effect of phenolic group directs the approaching electrophile towards *ortho* and *para* positions. Tertiary butyl group has large size so it causes steric effect around aromatic nucleus. On the basis of above factors the products of the given reactions are as follows:



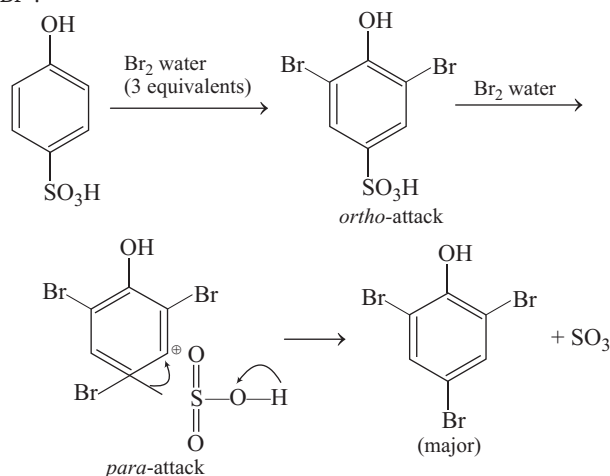
Hence, orientation in electrophilic substitution reaction is decided by

- (a) The steric effect of the halogen
- (b) The steric effect of the *tert*-butyl group
- (c) The electronic effect of the phenolic group

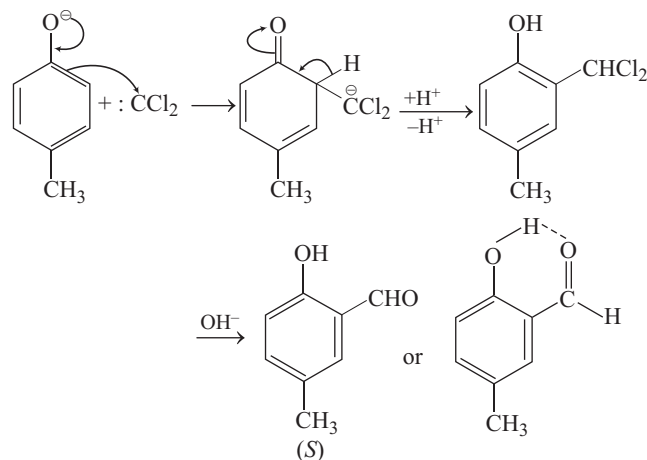
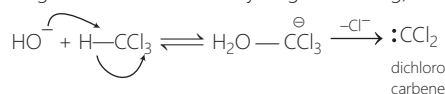
So, (a), (b) and (c) are correct choices.

**24. PLAN** —OH group is activating group and is *o*- and *p*-directing.

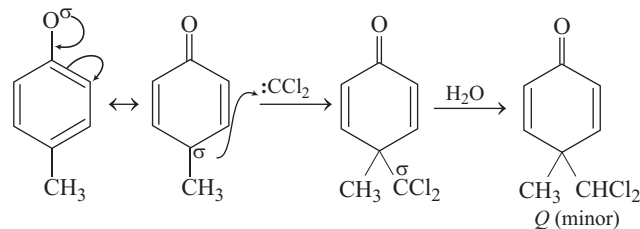
Also, —SO<sub>3</sub>H is a better leaving group and is knocked out by  $\text{Br}^-$ .



**25. PLAN** Phenolic compounds in alkaline solution react with chloroform ( $\text{CHCl}_3$ ) at a temperature lower than that of  $\text{CHCl}_3$  to form *ortho*-isomer as the major product (due to greater stability resulting from intramolecular hydrogen bonding).

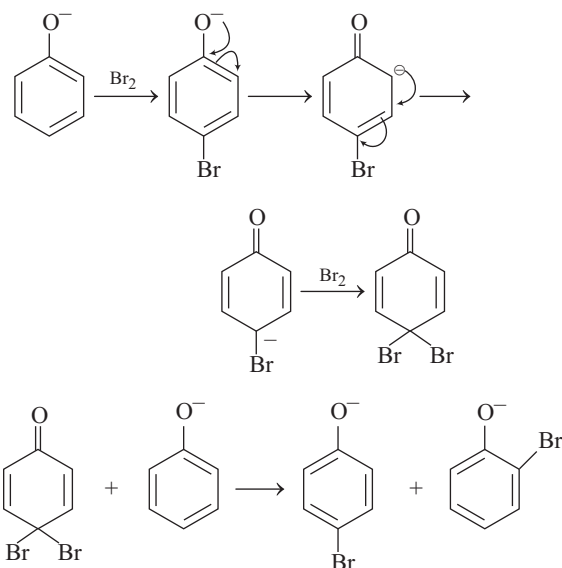


Major as stable due to intramolecular H-bonding.

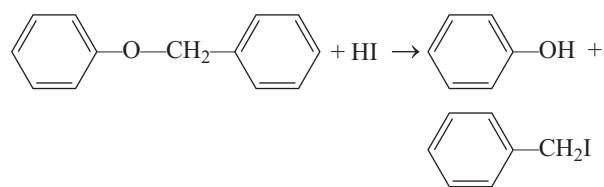


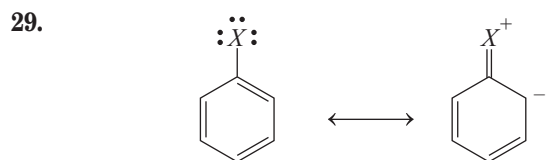
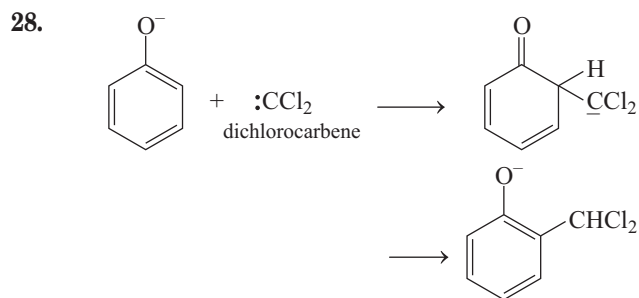
Thus, (b) and (d) are correct.

**26.** —OH in phenol is *ortho/para* directing group.



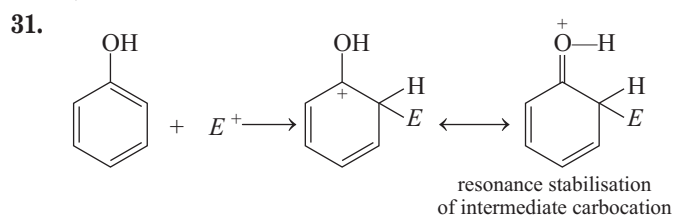
**27.**





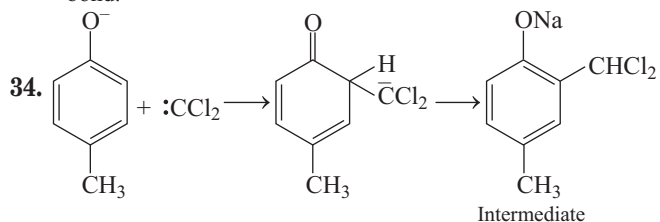
Above resonance makes  $X^-$  a poor leaving group. Also, the carbon bearing  $X$  is  $sp^2$ -hybridised.

30. Bromo group is deactivating due to dominance of inductive effect over resonance effect. However, orientation is determined by mesomeric effect of  $-Br$ .



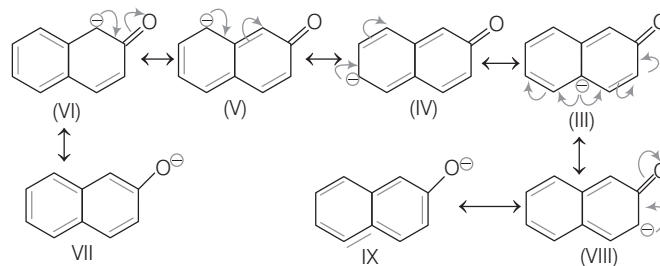
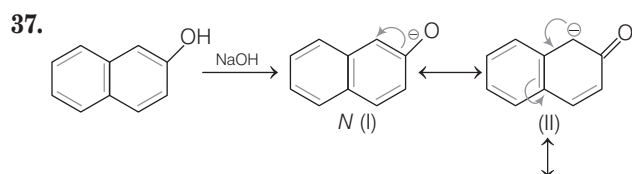
32. Statement I is incorrect, aryl halides do not undergo nucleophilic substitution reaction with ease. Cyanide ion ( $CN^-$ ) is a strong nucleophile.

33. Statement I is incorrect, aryl halides do not usually undergo nucleophilic substitution with ease. Statement II is correct, resonance introduces partial double bond character to  $C-X$  bond.



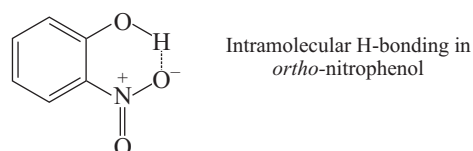
35. Dichlorocarbene is the electrophile as shown above.

36.  $CHCl_3 + NaOH \longrightarrow :CCl_2$  (Dichlorocarbene) electrophile



All the above shown nine resonance structures are different.

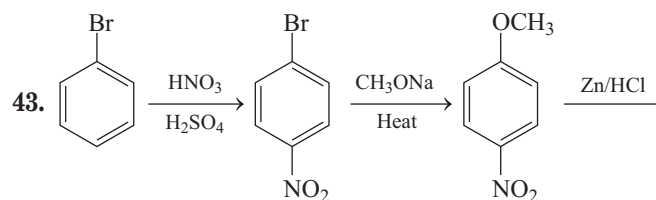
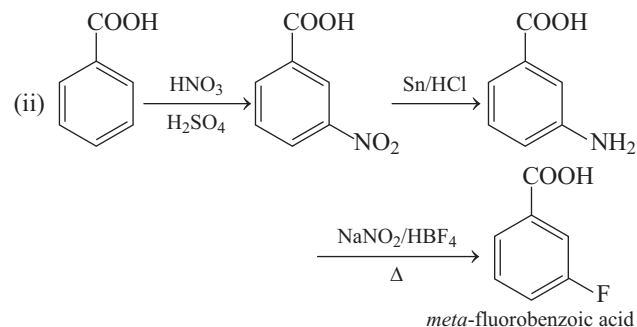
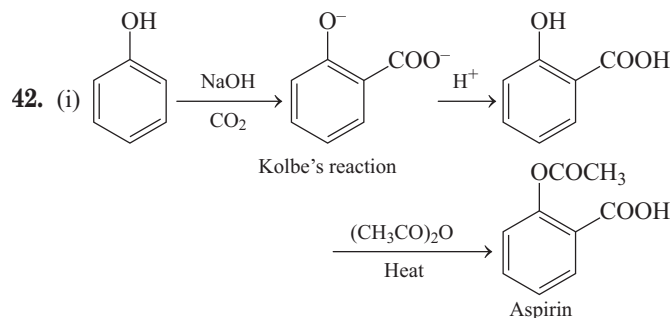
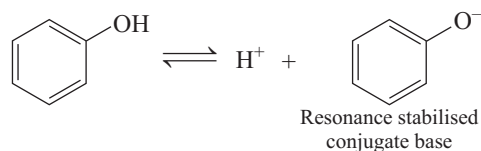
38. *Ortho*-nitrophenol : Due to intramolecular H-bonding.



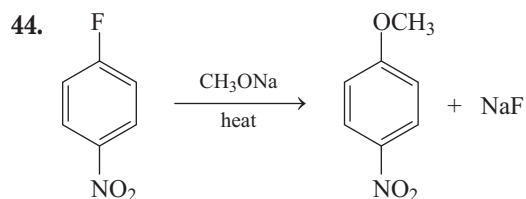
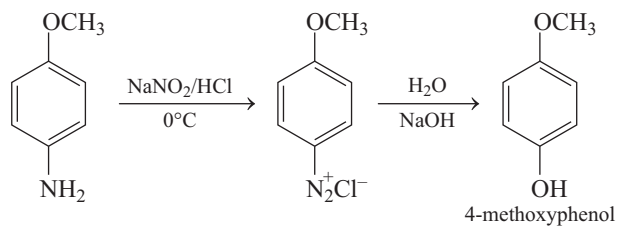
39. Phenoxide ion

40. Nucleophilic

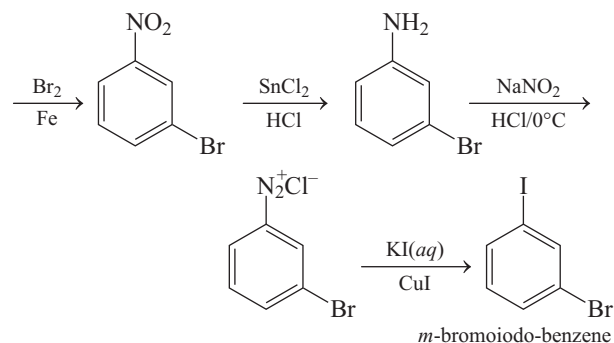
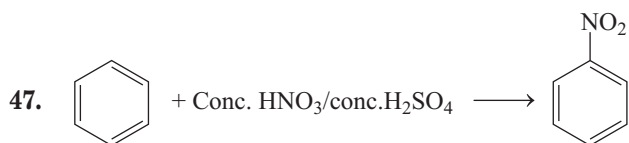
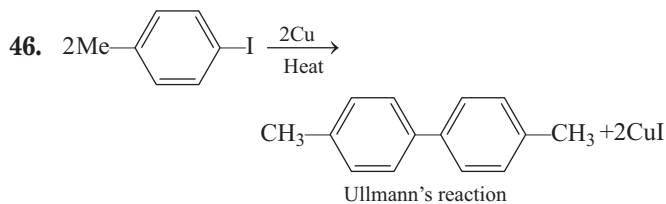
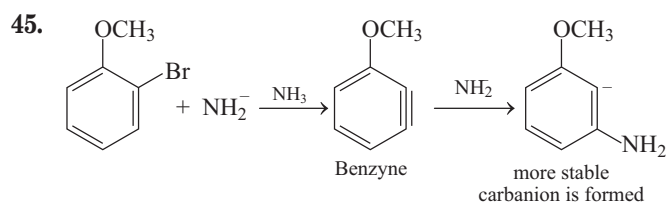
41. Phenoxide ion :



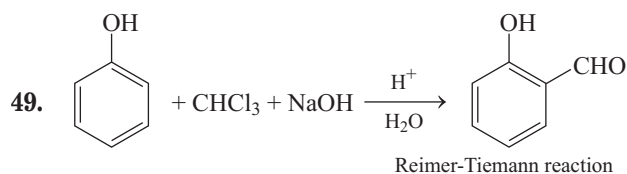
## 438 Aryl Halides and Phenols



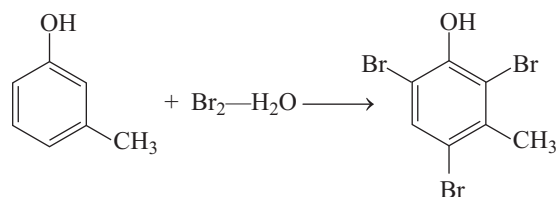
Nucleophilic aromatic substitution occurs which is assisted by electron withdrawing  $\text{—NO}_2$  group from *para* position.



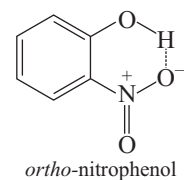
48. Phenol is weaker acid than carbonic acid.



50. The compound must contain a hydroxy group on the ring with all three *ortho/para* positions vacant :



51. Intramolecular H-bonding in *ortho*-nitrophenol lowers its boiling point. No such intramolecular H-bonding is possible with *p*-nitrophenol and rather it is associated together by intermolecular H-bonding which increases the boiling point.



Download Chapter Test  
<http://tinyurl.com/y2xlovfc>

or

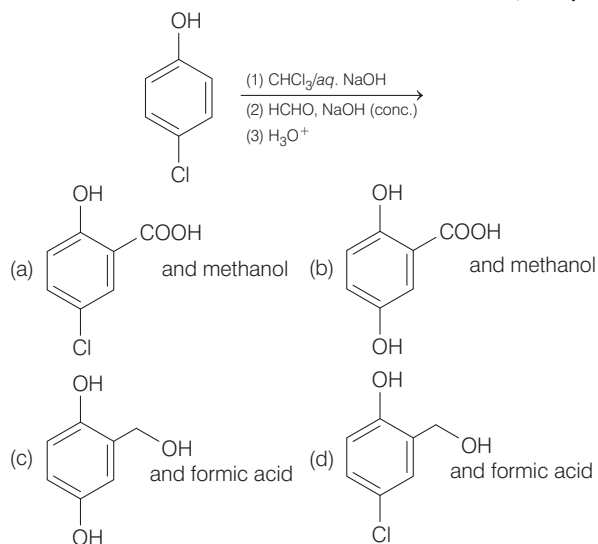


# 31

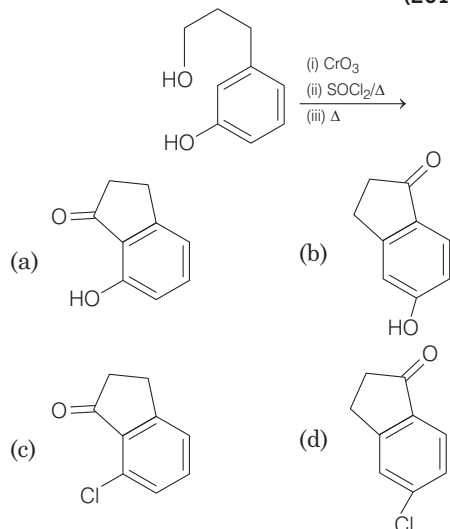
## Aromatic Aldehydes, Ketones and Acids

### Objective Questions I (Only one correct option)

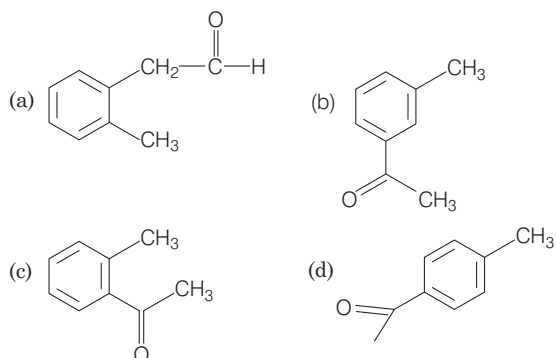
1. The major products of the following reaction are  
(2019 Main, 12 April I)



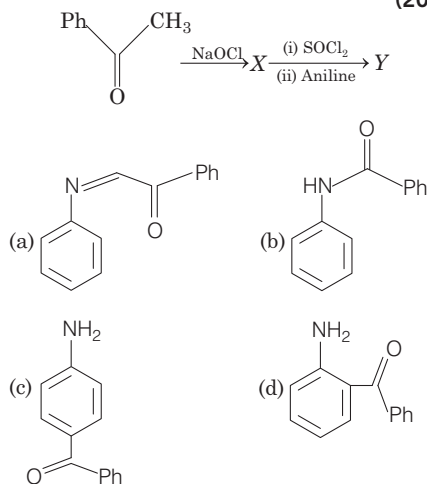
2. The major product of the following reaction is  
(2019 Main, 12 April I)



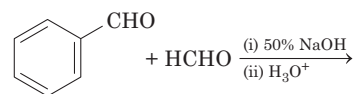
3. Compound  $A$  ( $\text{C}_9\text{H}_{10}\text{O}$ ) shows positive iodoform test. Oxidation of  $A$  with  $\text{KMnO}_4/\text{KOH}$  gives acid  $B$  ( $\text{C}_8\text{H}_6\text{O}_4$ ). Anhydride of  $B$  is used for the preparation of phenolphthalein. Compound  $A$  is (2019 Main, 10 April II)



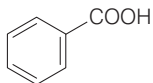
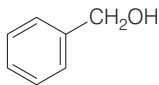
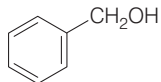
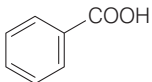
4. The major product  $Y$  in the following reaction is  
(2019 Main, 10 April II)



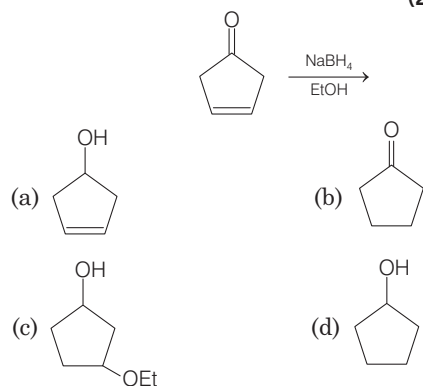
5. Major products of the following reaction are  
(2019 Main, 10 April I)



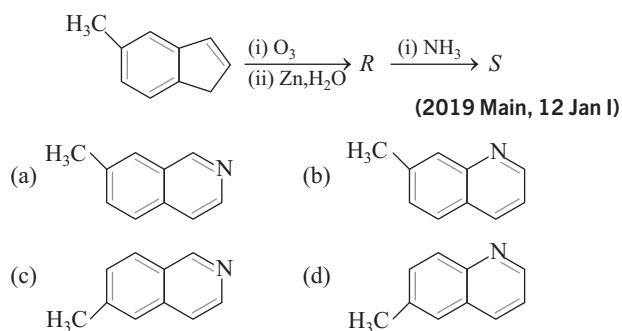
## 440 Aromatic Aldehydes, Ketones and Acids

- (a)  $\text{CH}_3\text{OH}$  and  $\text{HCO}_2\text{H}$   
 (b)  $\text{CH}_3\text{OH}$  and   
 (c)  $\text{HCOOH}$  and   
 (d)  and 

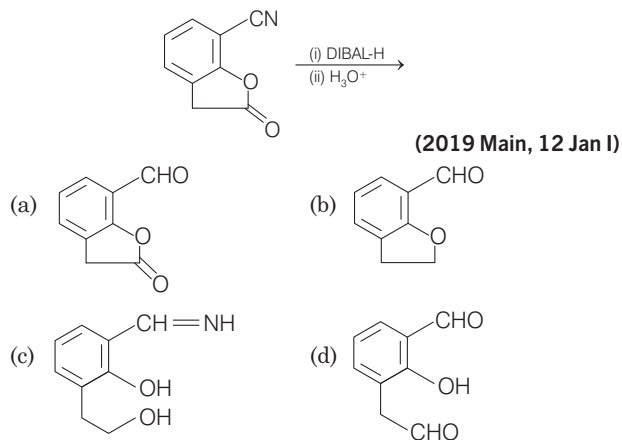
6. The major product of the following reaction is  
 (2019 Main, 12 Jan II)



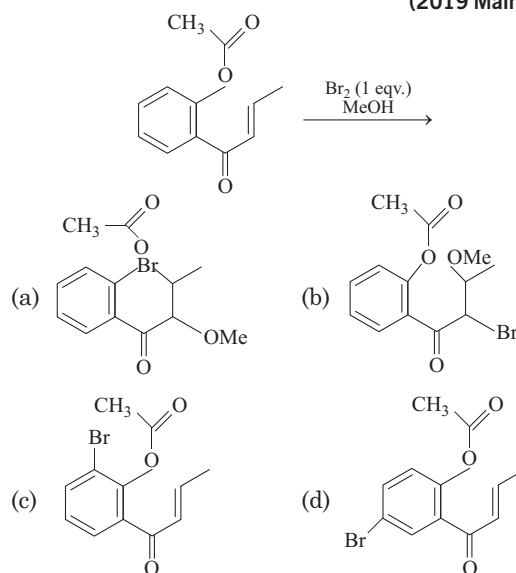
7. In the following reactions, the product *S* is



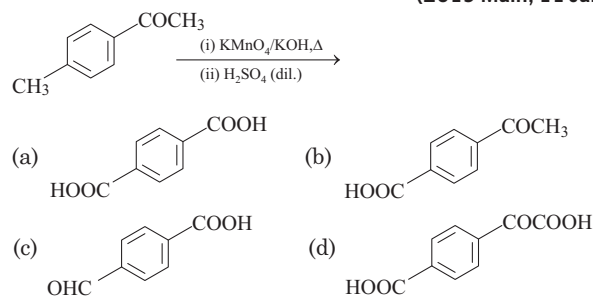
8. The major product of the following reaction is



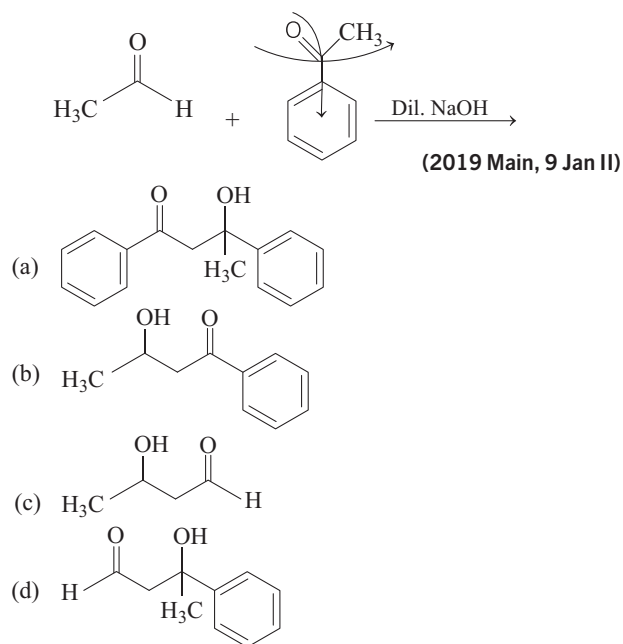
9. The major product obtained in the following conversion is  
 (2019 Main, 11 Jan II)



10. The major product of the following reaction is  
 (2019 Main, 11 Jan I)

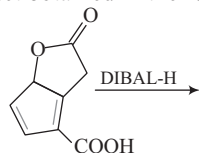


11. The major product formed in the following reaction is





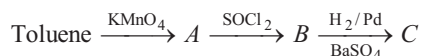
12. The major product obtained in the following reaction is



(2017 Main)

- (a) (b)   
 (c) (d)

13. In the following sequence of reaction,

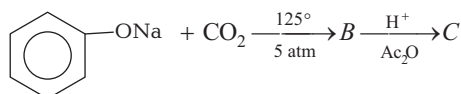


(2015 Main)

The product *C* is

- (a)  $\text{C}_6\text{H}_5\text{COOH}$  (b)  $\text{C}_6\text{H}_5\text{CH}_3$   
 (c)  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$  (d)  $\text{C}_6\text{H}_5\text{CHO}$

14. Sodium phenoxide when heated with  $\text{CO}_2$  under pressure at  $125^\circ\text{C}$  yields a product which on acetylation produces *C*.

The major product *C* would be

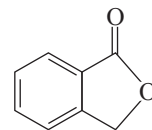
(2014 Main)

- (a) (b)   
 (c) (d)

15. Compound (*A*),  $\text{C}_8\text{H}_9\text{Br}$  gives a white precipitate when warmed with alcoholic  $\text{AgNO}_3$ . Oxidation of (*A*) gives an acid (*B*),  $\text{C}_8\text{H}_6\text{O}_4$ . (*B*) easily forms anhydride on heating. Identify the compound (*A*). (2013 Main)

- (a) (b)   
 (c) (d)

16. Which of the following reactants on reaction with conc.  $\text{NaOH}$  followed by acidification gives following lactone as the main product? (2006, 5M)



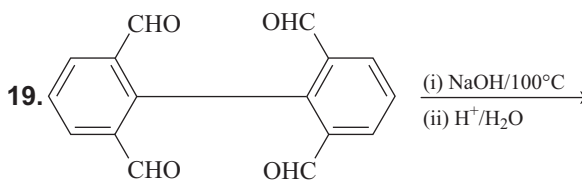
- (a) (b)   
 (c) (d)

17. 4-methyl benzene sulphonic acid reacts with sodium acetate to give (2005, 1M)

- (a) ;  $\text{CH}_3\text{CO}_2\text{H}$  (b) ;  $\text{SO}_3$   
 (c) ;  $\text{SO}_3$  (d) ;  $\text{NaOH}$

18.  $\text{Ph}-\text{C}\equiv\text{C}-\text{CH}_3 \xrightarrow{\text{Hg}^{2+}/\text{H}^+} A$ , *A* is (2003, 1M)

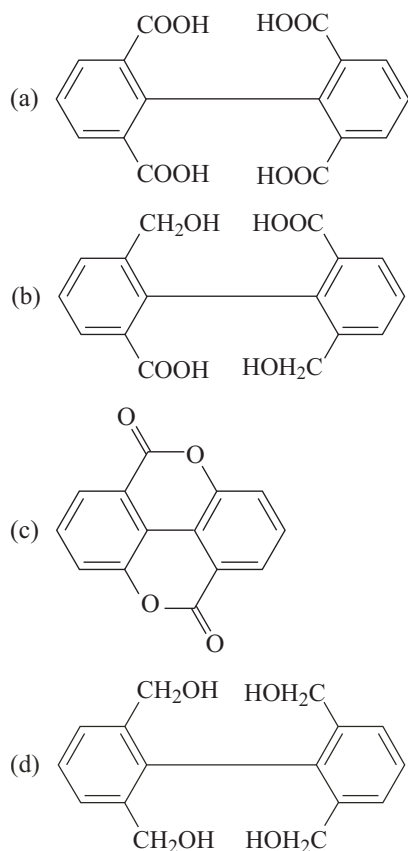
- (a) (b)   
 (c) (d)



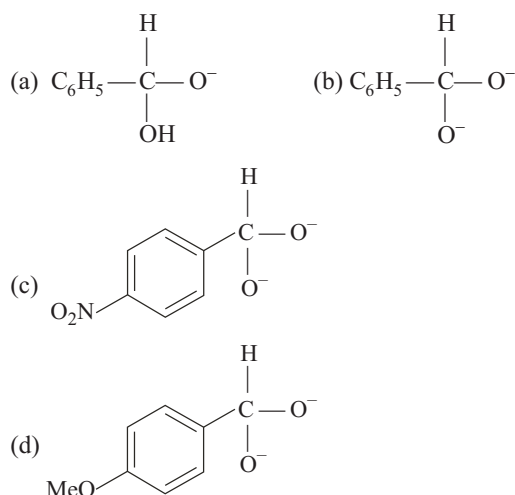
Major product

(2003, 1M)

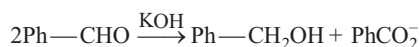
## 442 Aromatic Aldehydes, Ketones and Acids



20. In Cannizzaro's reaction, the intermediate which is the best hydride donor is (1997)



21. In the Cannizzaro's reaction given below :



The slowest step is (1996, 1M)

- (a) the attack of  $\text{OH}^-$  at the carbonyl group  
 (b) the transfer of hydride to the carbonyl group  
 (c) the abstraction of proton from the carboxylic acid  
 (d) the deprotonation of  $\text{Ph}-\text{CH}_2\text{OH}$

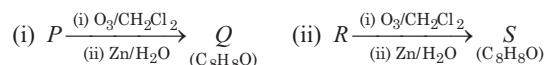
22. *m*-chlorobenzaldehyde on reaction with conc. KOH at room temperature gives (1991, 1M)

- (a) potassium *m*-chlorobenzoate and *m*-chlorobenzyl alcohol  
 (b) *m*-hydroxy benzaldehyde and *m*-chlorobenzyl alcohol  
 (c) *m*-chlorobenzyl alcohol and *m*-hydroxy benzyl alcohol  
 (d) potassium *m*-chlorobenzoate and *m*-hydroxy benzaldehyde

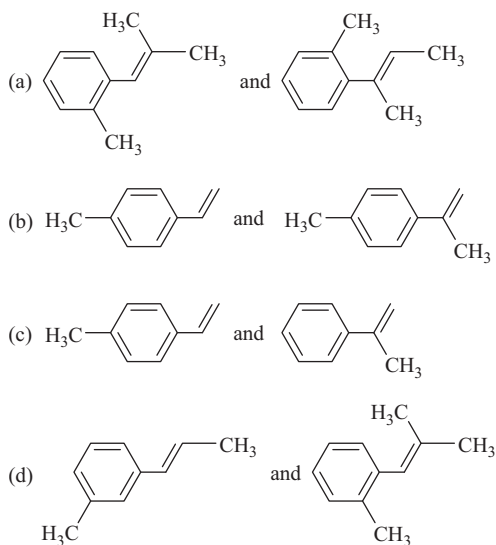
### Objective Questions II

(One or more than one correct option)

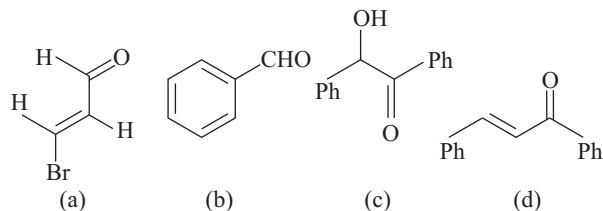
23. Compound *P* and *R* upon ozonolysis produce *Q* and *S*, respectively. The molecular formula of *Q* and *S* is  $\text{C}_8\text{H}_8\text{O}$ . *Q* undergoes Cannizzaro reaction but not haloform reaction, whereas *S* undergoes haloform reaction but not Cannizzaro reaction. (2017 Adv.)



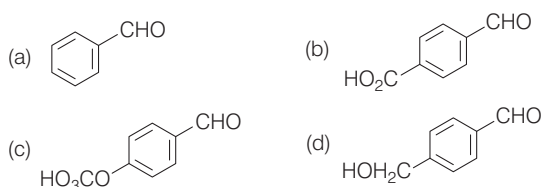
The option(s) with suitable combination of *P* and *R*, respectively, is(are)



24. Positive Tollen's test is observed for



25. The aldehydes which will not form Grignard product with one equivalent Grignard reagents are (2019 Main 12 Jan II)

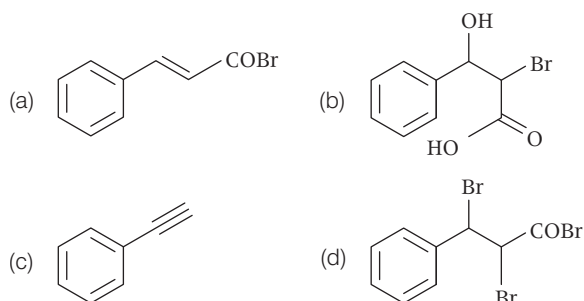


## Passage Based Questions

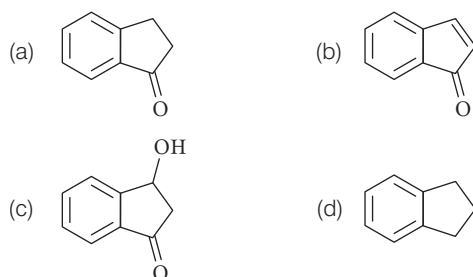
## Paragraph X

Treatment of benzene with CO / HCl in the presence of anhydrous  $\text{AlCl}_3$  /  $\text{CuCl}$  followed by reaction with  $\text{Ac}_2\text{O}$  /  $\text{NaOAc}$  gives compound  $X$  as the major product. Compound  $X$  upon reaction with  $\text{Br}_2$  /  $\text{Na}_2\text{CO}_3$  followed by heating at 473 K with moist KOH furnishes  $Y$  as the major product. Reaction of  $X$  with  $\text{H}_2$  /  $\text{Pd} - \text{C}$ , followed by  $\text{H}_3\text{PO}_4$  treatment gives  $Z$  as the major product.

26. The compound  $Y$  is (2018 Adv.)

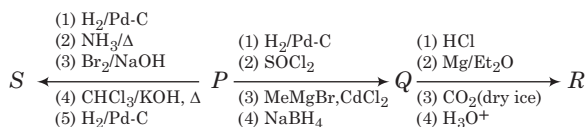


27. The compound  $Z$  is

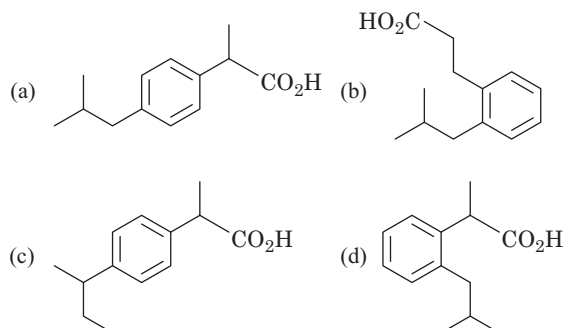


## Paragraph A

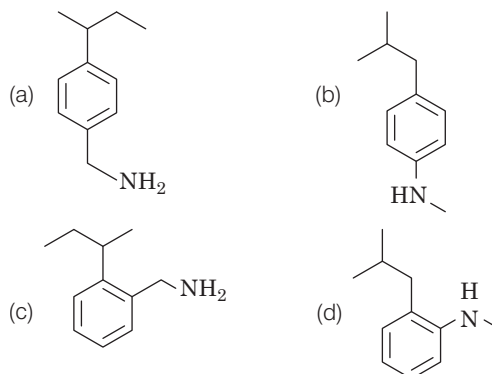
An organic acid  $P$  ( $\text{C}_{11}\text{H}_{12}\text{O}_2$ ) can easily be oxidised to a dibasic acid which reacts with ethylene glycol to produce a polymer dacron. Upon ozonolysis,  $P$  gives an aliphatic ketone as one of the products.  $P$  undergoes the following reaction sequences to furnish  $R$  via  $Q$ . The compound  $P$  also undergoes another set of reactions to produce  $S$ . (2018 Adv.)



28. The Compound  $R$  is

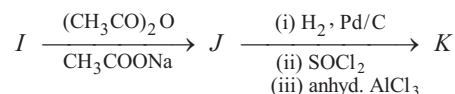


29. The compound  $S$  is



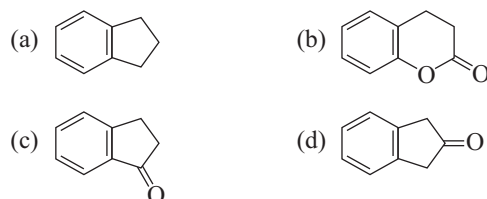
## Passage

In the following reactions sequence, the compound  $J$  is an intermediate.

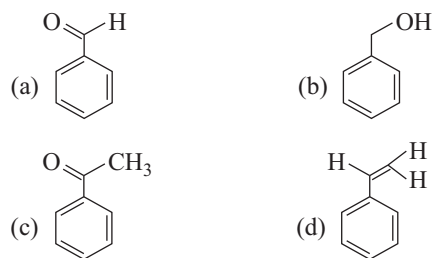


$J$  ( $\text{C}_9\text{H}_8\text{O}_2$ ) gives effervescence on treatment with  $\text{NaHCO}_3$  and positive Baeyer's test. (2012)

30. The compound  $K$ , is



31. The compound  $I$ , is



## Fill in the Blanks

32. The structure of the intermediate product formed by the oxidation of toluene with  $\text{CrO}_3$  and acetic anhydride, whose hydrolysis gives benzaldehyde is ..... (1992, 2M)

## True/False

33. Benzaldehyde undergoes aldol condensation in an alkaline medium. (1982, 1M)

## 444 Aromatic Aldehydes, Ketones and Acids

### Subjective Questions

- 34.** Five isomeric *para*-disubstituted aromatic compounds *A* to *E* with molecular formula  $C_8H_8O_2$  were given for identification.

Based on the following observations, give structures of the compounds : **(2002, Main, 5M)**

- Both *A* and *B* form a silver mirror with Tollen's reagent; also, *B* gives a positive test with  $FeCl_3$  solution.
- C* gives positive iodoform test.
- D* is readily extracted in aqueous  $NaHCO_3$  solution.
- E* on acid hydrolysis gives 1, 4-dihydroxy benzene.

- 35.** An organic compound *A*,  $C_8H_4O_3$ , in dry benzene in the presence of anhydrous  $AlCl_3$  gives compound *B*. The compound *B* on treatment with  $PCl_5$ , followed by reaction with  $H_2/Pd/(BaSO_4)$  gives compound *C*, which on reaction with hydrazine gives a cyclised compound *D* ( $C_{14}H_{10}N_2$ ). Identify *A*, *B*, *C* and *D*. Explain the formation of *D* from *C*. **(2000, 5M)**

- 36.** Explain, why *o*-hydroxy benzaldehyde is a liquid at room temperature while *p*-hydroxy benzaldehyde is a high melting solid? **(1999, 2M)**

### Matching Type Questions

Answer Q. 22, Q. 23 and Q. 24 by appropriately matching the information given in the three columns of the following table.

Column 1, 2 and 3 contain starting materials, reaction conditions, and type of reactions, respectively. **(2017 Adv.)**

|       | Column 1     |       | Column 2               |     | Column 3      |
|-------|--------------|-------|------------------------|-----|---------------|
| (I)   | Toluene      | (i)   | $NaOH/Br_2$            | (P) | Condensation  |
| (II)  | Acetophenone | (ii)  | $Br_2/h\nu$            | (Q) | Carboxylation |
| (III) | Benzaldehyde | (iii) | $(CH_3CO)_2O/CH_3COOK$ | (R) | Substitution  |
| (IV)  | Phenol       | (iv)  | $NaOH/CO_2$            | (S) | Haloform      |

- 37.** The only **CORRECT** combination in which the reaction proceeds through radical mechanism is

- (IV) (i) (Q)
- (III) (ii) (P)
- (II) (iii) (R)
- (I) (ii) (R)

- 38.** For the synthesis of benzoic acid, the only **CORRECT** combination is

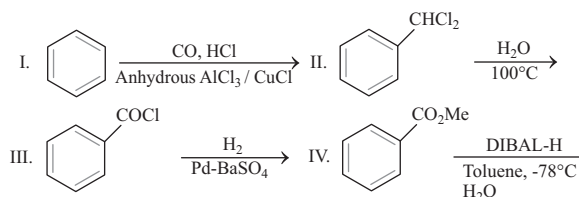
- (II) (i) (S)
- (I) (iv) (Q)
- (IV) (ii) (P)
- (III) (iv) (R)

- 30.** The only **CORRECT** combination that gives two different carboxylic acids is

- (IV) (iii) (Q)
- (II) (iv) (R)
- (I) (i) (S)
- (III) (iii) (P)

### Integer Type Questions

- 40.** Among the following the number of reaction(s) that produce(s) benzaldehyde is **(2015 Adv.)**

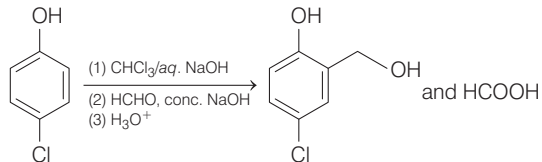


## Answers

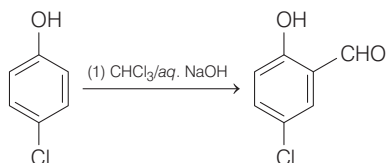
- |         |         |         |         |                        |         |           |             |
|---------|---------|---------|---------|------------------------|---------|-----------|-------------|
| 1. (d)  | 2. (b)  | 3. (c)  | 4. (b)  | 21. (b)                | 22. (a) | 23. (b,c) | 24. (a,b,c) |
| 5. (c)  | 6. (a)  | 7. (a)  | 8. (d)  | 25. (b,d)              | 26. (c) | 27. (a)   | 28. (a)     |
| 9. (b)  | 10. (a) | 11. (c) | 12. (a) | 29. (b)                | 30. (c) | 31. (a)   |             |
| 13. (d) | 14. (a) | 15. (d) | 16. (c) | 32. $C_6H_5-CH(OAc)_2$ |         | 33. False | 37. (a)     |
| 17. (a) | 18. (a) | 19. (b) | 20. (d) | 38. (d)                | 39. (b) | 40. (4)   |             |

# Hints & Solutions

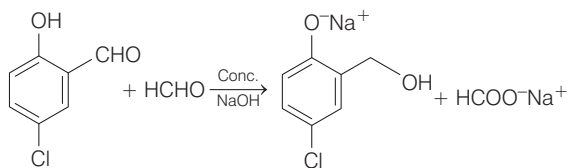
1. The major products of the given reaction are as follows:



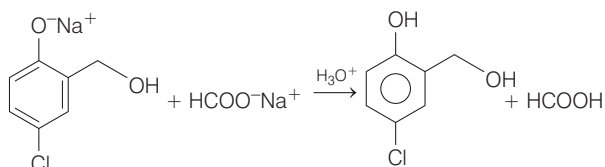
In step-I, substituted phenol undergoes Reimer-Tiemann reaction in presence of  $\text{CHCl}_3$  / aq. NaOH



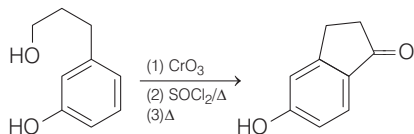
The aldehyde obtained in above equation does not possess  $\alpha$ -hydrogen. In presence of formaldehyde and conc. NaOH it undergoes Cannizzaro reaction. In this reaction, one molecule of aldehyde is reduced to alcohol while another molecule is oxidised to salt of carboxylic acid.



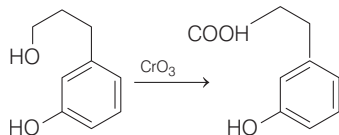
Upon hydrolysis, following reaction takes place



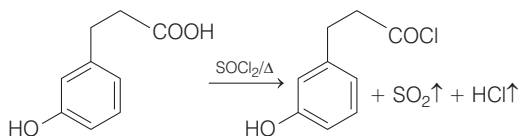
2. The major product formed in the reaction is as follows :



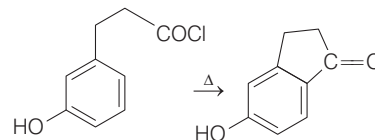
Primary alcohol readily oxidised to corresponding carboxylic acid with oxidising agent, chromium trioxide ( $\text{CrO}_3$ ) in acidic medium.



$-\text{OH}$  group of carboxylic acid get substituted by  $-\text{Cl}$  in presence of  $\text{SOCl}_2$  (Thionyl chloride).



Further, heating of product leads to intramolecular cyclisation.

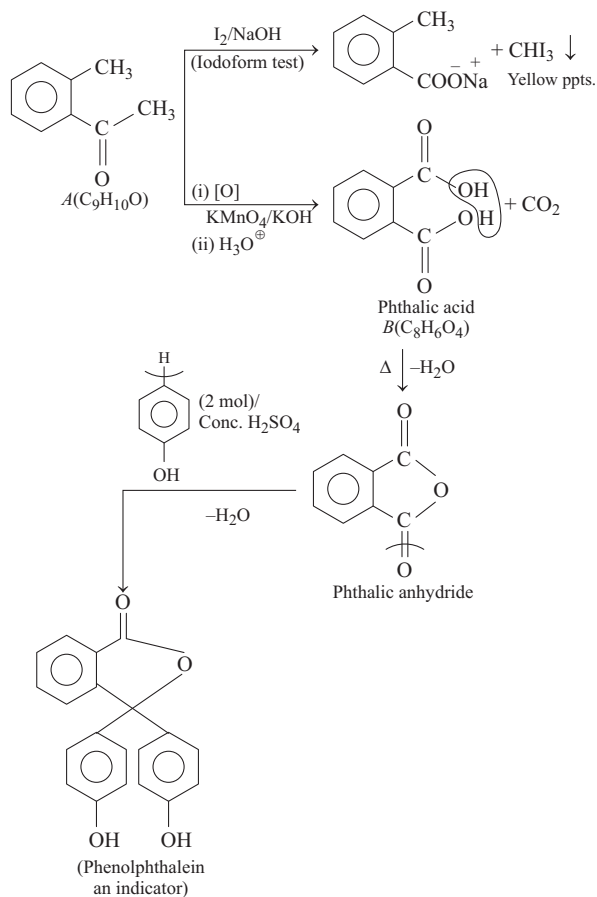


3. (i)  $\text{C}_9\text{H}_{10}\text{O}$  shows positive iodoform test thus,  $-\text{C}(=\text{O})\text{CH}_3$  group is present.

(ii)  $\text{C}_9\text{H}_{10}\text{O}$  on strong oxidation ( $\text{KMnO}_4/\text{KOH}$ ), gives acid ( $\text{C}_8\text{H}_6\text{O}_4$ ), indicating it can be a dicarboxylic acid. So, 'A' contains  $-\text{COCH}_3$  and one  $-\text{CH}_3$  group which get oxidised into  $-\text{COOH}$  and  $-\text{COOH}$  respectively.

(iii) In the preparation of phenolphthalein from phenol, phthalic anhydride is used. So, 'B' can be phthalic acid (benzene-1,2-dicarboxylic acid) which readily forms anhydride.

Thus, the reaction sequence is as follows :

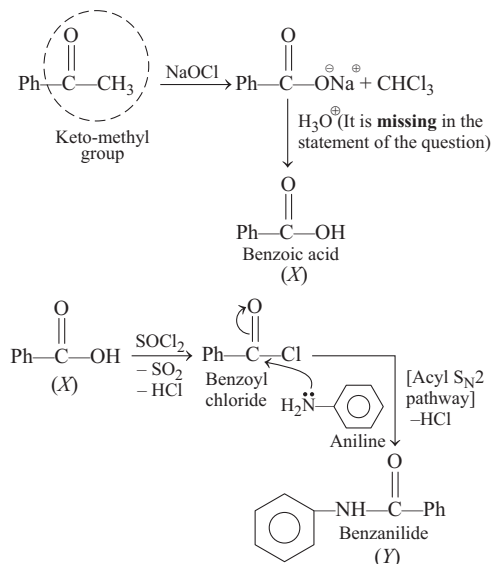


4.  $\text{NaOCl}$  (sodium hypochlorite) is the reagent of haloform (chloroform formation) reaction.

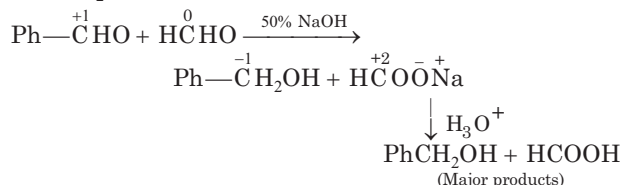


## 446 Aromatic Aldehydes, Ketones and Acids

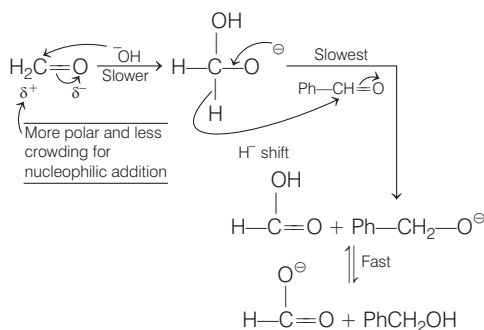
The given reaction takes place as follows :



5. The given reaction is a crossed Cannizzaro reaction which is a redox reaction too. Oxidation number of carbon atom of the  $\text{—CHO}$  groups of  $\text{Ph—CHO}$  and  $\text{H—CHO}$  are +1 and zero respectively. So,  $\text{HCHO}$  is the stronger reducing agent than  $\text{PhCHO}$ . As a result,  $\text{HCHO}$  is oxidised to  $\text{HCOONa}$  (by donation of hydride,  $\text{H}^-$ ) and  $\text{PhCHO}$  ( $\text{H}^-$  acceptor) is reduced to  $\text{PhCH}_2\text{OH}$ .



The reaction proceed *via* following mechanism.



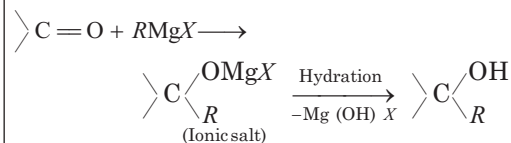
6. Reducing agents like  $\text{LiAlH}_4$ ,  $\text{NaBH}_4$ , i.e. complex hydrides usually does not affect olefinic or  $\pi$ -bonds. Thus, if  $\text{NaBH}_4$  is

applied to a compound like then its  $\text{>C=O}$  bond will be

reduced only and we get as the final product.

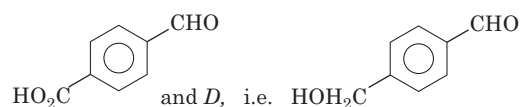
Thus, option (a) is correct answer.

7. **Key Idea** Grignard reagent usually attacks on  $\text{>C=O}$  group as :

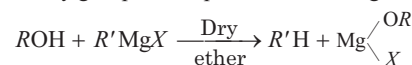


The question is related to above reaction only with the condition that the consumption of  $\text{RMgX}$  will be more than 1 equivalent in some of the given cases.

Among the given compounds B, i.e.



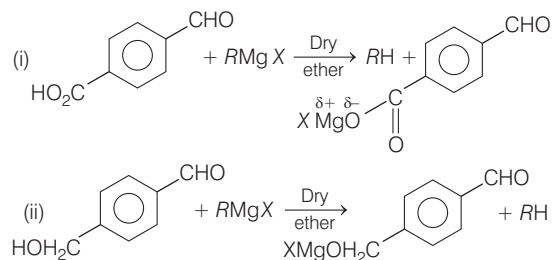
contain additional groups which can give active hydrogens. Grignard reagents produce alkanes whenever come in contact with any group or compound which can give active hydrogen as:



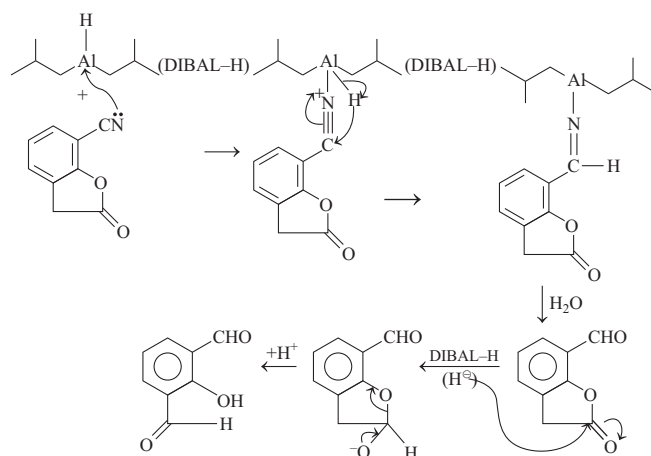
These reactions are equivalent to acid-base reactions. So, in both of these compounds more than one equivalent will be required to form Grignard products. Remember these compounds will give 2 type of products as:

- from the  $\text{>C=O}$  group
- from the group which release active hydrogen

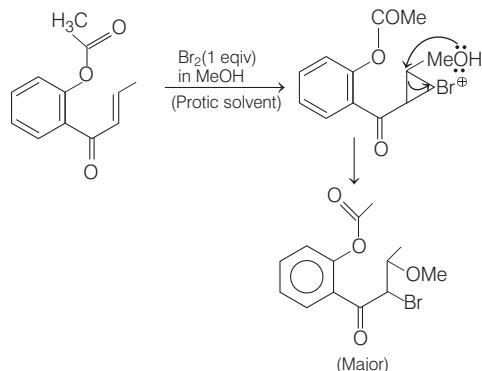
The additional reactions involved are:



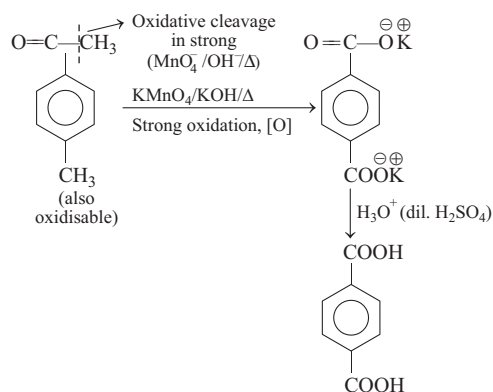
8. DIBAL-H (Diisobutylaluminium hydride) is a reducing agent with formula  $[\lambda\text{-Bu}_2\text{AlH}]$ . At ordinary temperatures, nitriles give imines which are readily converted in aldehydes by hydrolysis whereas lactones are reduced directly to aldehydes.



9. In presence of  $\text{Br}_2/\text{EtOH}$ , the reactant containing double bond undergoes electrophilic addition reaction *via* the formation of bromonium ion. On further attack of  $\text{—}\ddot{\text{O}}\text{Me}$  on bromonium ion gives the addition product.



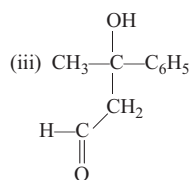
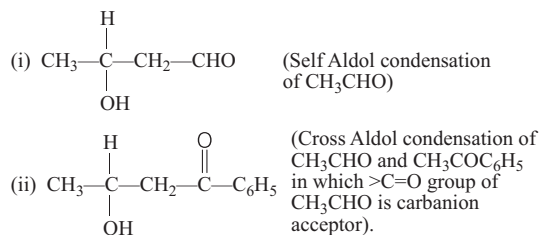
10. In presence of alkaline  $\text{KMnO}_4$ , vigorous oxidation of alkyl or acyl benzene takes place. During oxidation, aromatic nucleus remains intact but the entire chain is oxidised to  $\text{—COOH}$  group irrespective of the length of carbon chain.



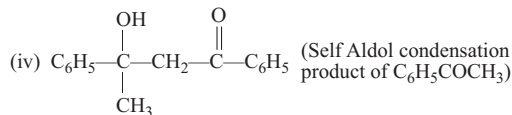
11. In aldol condensation, generally aldehydes react at a faster rate than ketones towards base. In the given case  $\text{CH}_3\text{CHO}$  will lose

$\alpha$ -hydrogen faster than  $\text{Ph—C(=O)—CH}_3$  due to one more reason, i.e. conjugation between benzene ring and  $\text{>C=O}$  group. Along with sterically less hindered nucleophile of  $\text{CH}_3\text{CHO}$  will also add to the major product formation.

Following four products are possible in the reaction:

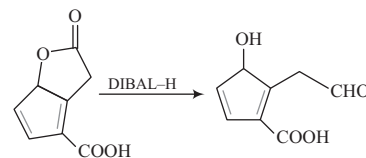


(Cross Aldol condensation of  $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{COC}_6\text{H}_5$  in which  $\text{>C=O}$  group of  $\text{C}_6\text{H}_5\text{COCH}_3$  is carbanion acceptor).

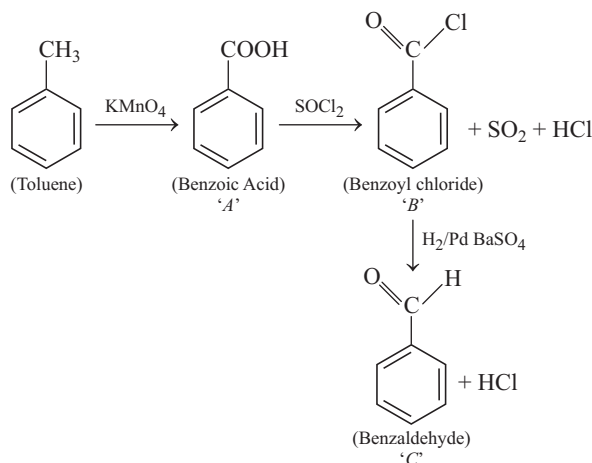


$\text{O}^-$  of base will prefer to attack on  $\text{—CH}_3$  group of  $\text{CH}_3\text{CHO}$  for the formation of carbanion and as among the  $\text{>C=O}$  groups available, the  $\text{>C=O}$  group of  $\text{CH}_3\text{CHO}$  is the best carbanion acceptor. Hence, self condensation product of  $\text{CH}_3\text{CHO}$  will be the major product.

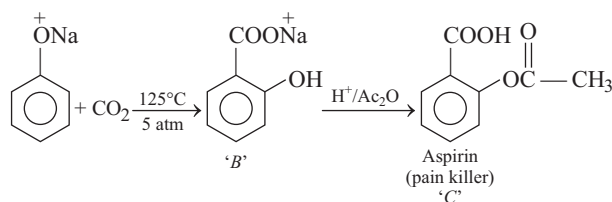
12. DIBAL-H (Di-isobutyl aluminium hydride) is a reducing agent with formula. This is generally used for the preparation of aldehydes. Using DIBAL  $\text{—H}$ , Lactones are reduced directly to aldehydes.



13. Toluene undergoes oxidation with  $\text{KMnO}_4$ , forms benzoic acid. In this conversion, alkyl part of toluene converts into carboxylic group. Further, benzoic acid reacts with thionyl chloride ( $\text{SOCl}_2$ ) to give benzoyl chloride which upon reduction with  $\text{H}_2/\text{Pd}$  or  $\text{BaSO}_4$  forms benzaldehyde (Rosenmund reduction) The conversion look like,



14. It is a Kolbe Schmidt reaction.

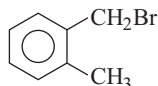


The second step of the reaction is an example of acetylation reaction.

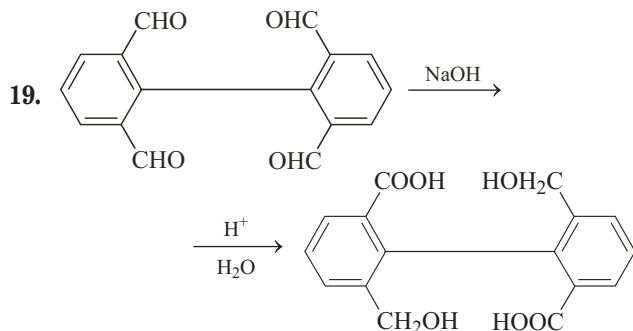
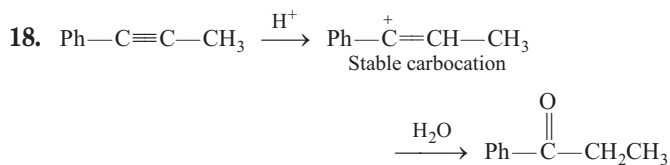
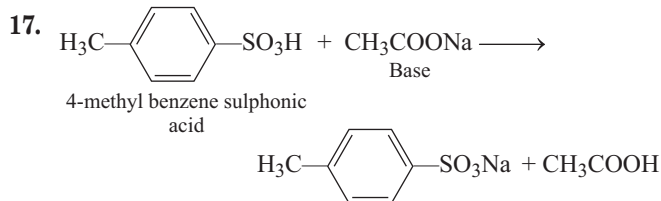
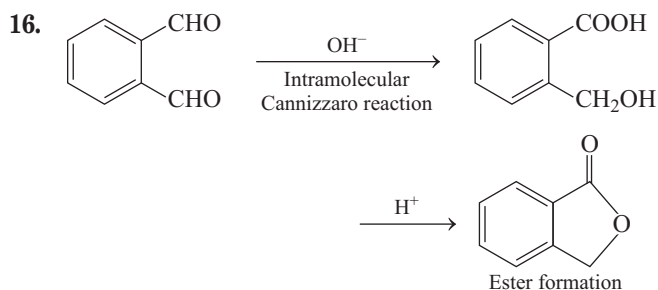
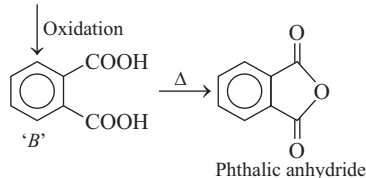
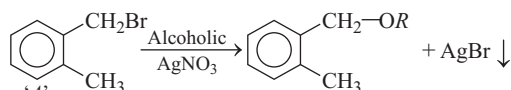


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15. Compound *A* gives a precipitate with alcoholic  $\text{AgNO}_3$ , so it must contain Br in side chain. On oxidation, it gives  $\text{C}_8\text{H}_6\text{O}_4$ , which shows the presence of two alkyl chains attached directly with the benzene nucleus. Since, compound *B* gives anhydride on heating, the two alkyl substituent must occupy adjacent (1, 2) position. Thus, *A* must be

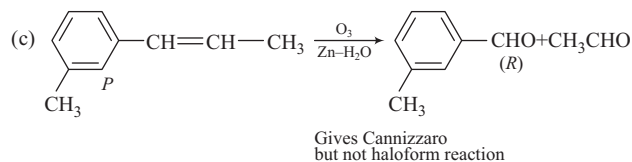
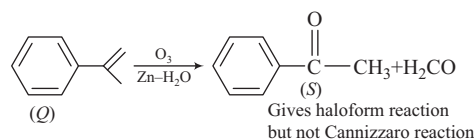
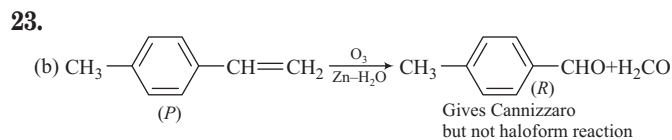
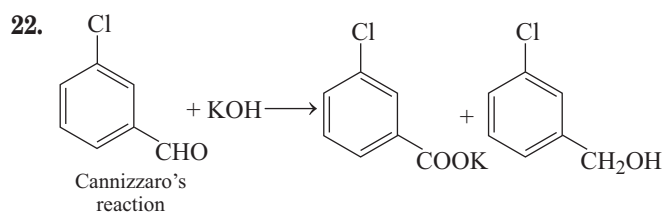
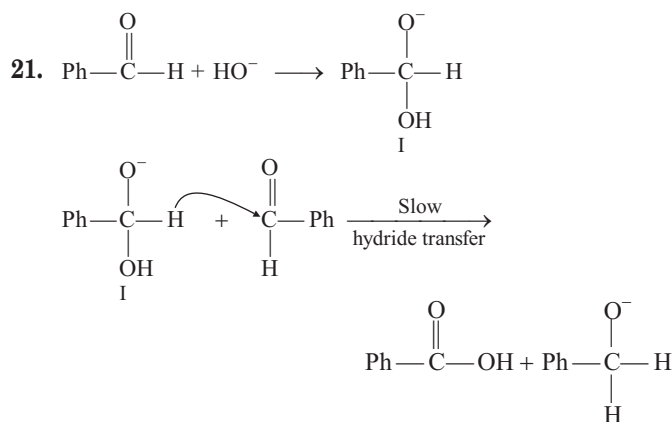
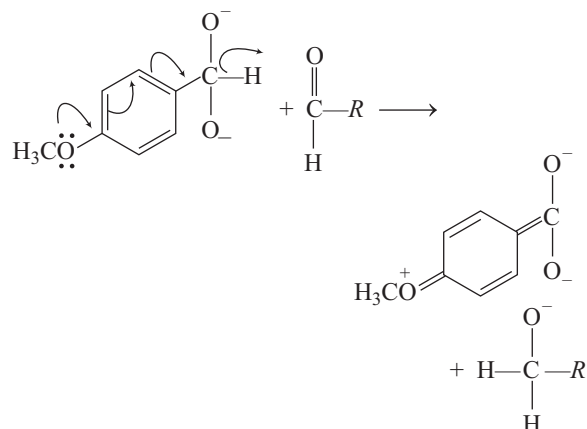


and the reactions are as follows :

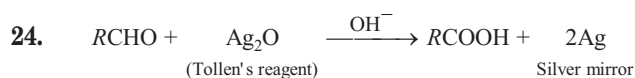


The above reaction is an example of intramolecular Cannizzaro reaction.

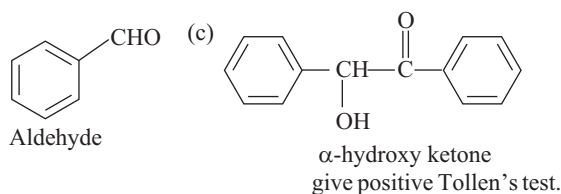
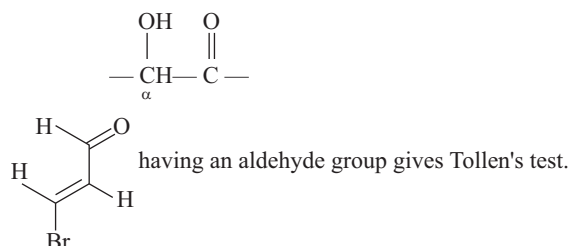
20. Dioxoanion is better hydride donor. Electron donating group at *ortho/para* position further promote  $\text{H}^-$  transfer.



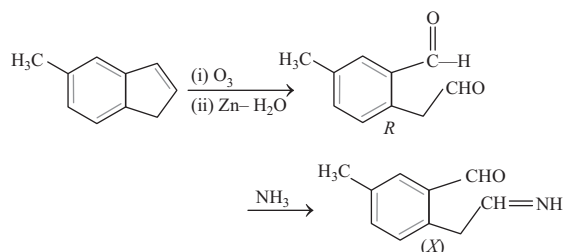




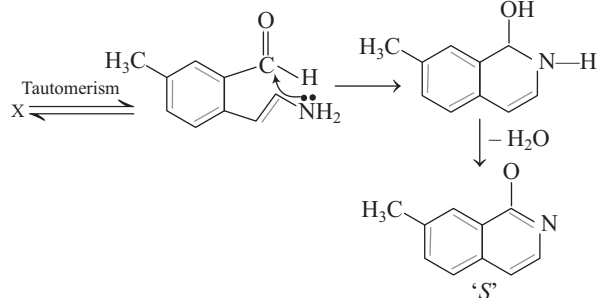
Tollen's test is given by all aldehydes and all reducing sugars as glucose, fructose and  $\alpha$ -hydroxy ketones.



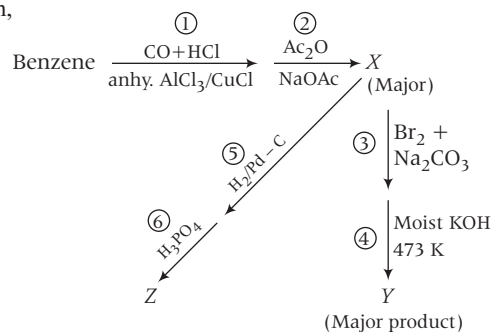
25.



In the above reaction,  $NH_3$  prefer to attack at aliphatic aldehyde group than an less reactive aromatic aldehyde group.

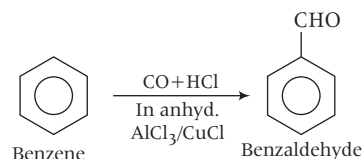


26. Given,

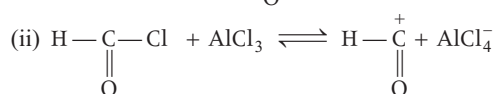
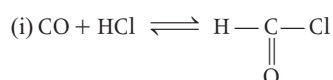


For this question we require only reaction 1 to 4 written above. Let us explore them one by one.

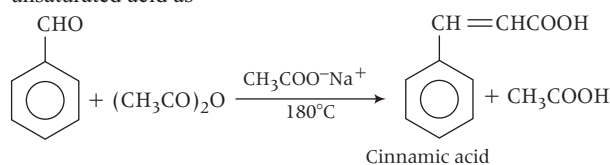
**Reaction 1** It is called formylation or Gatterman Koch reaction. A  $-CHO$  group is introduced to benzene ring through this reaction as



The attacking electrophile is  $H-C^+=O$  which is generated as

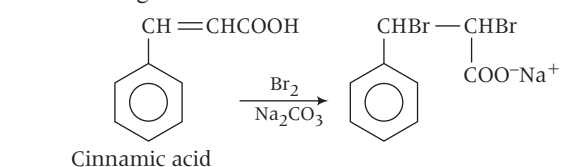


**Reaction 2** It is Perkin condensation which results in  $\alpha, \beta$  unsaturated acid as

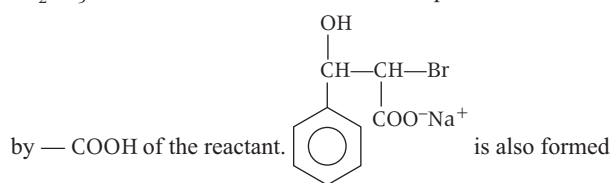


**Note** Besides  $CH_3COO^-Na^+$ , quinoline, pyridine,  $Na_2CO_3$ , triethylamine can also be used as bases in this reaction.

**Reaction 3** It is simple addition of bromine to unsaturated acid formed through reaction 2.

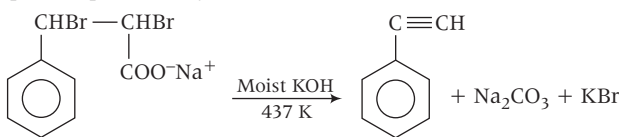


$Na_2CO_3$  works as a base in the reaction to trap  $H^+$  to be released



in the reaction as the minor product.

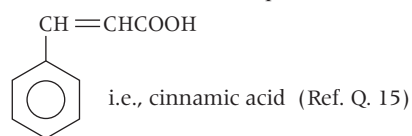
**Reaction 4** It is decarboxylation and dehydrohalogenation of product produced by reaction 3 as



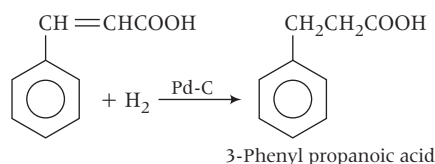
Hence, Y is i.e., (c) is the correct answer.

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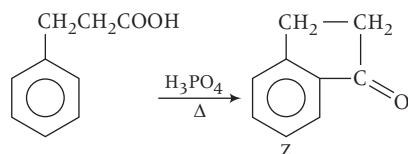
**27. Reaction 5** The Perkin condensation product *X* is



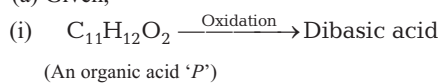
This compound on hydrogenation with  $H_2$  in the presence of Pd activated with charcoal (Pd-C) gives



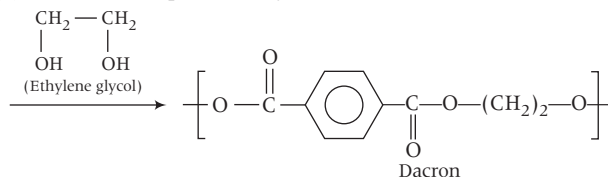
**Reaction 6** The product of reaction 5 on heating with  $H_3PO_4$  dehydrates to give



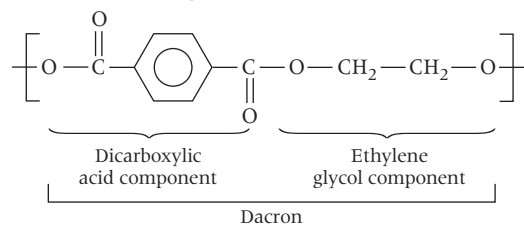
**28. (a)** Given,



(ii) Dibasic acid produced by oxidation of *P*



This indicates presence of benzene ring in *P*; as concluded from the structure of dacron given below.

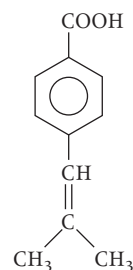


Attachment of  $-COO$  group in dacron also confirm the *para* position of branch with respect to  $-COOH$  group in *P*.

(iii)  $P \xrightarrow{\text{Ozonolysis}}$  Aliphatic ketone + other oxidised products.

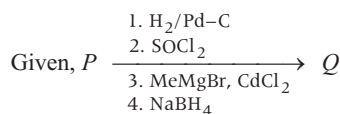
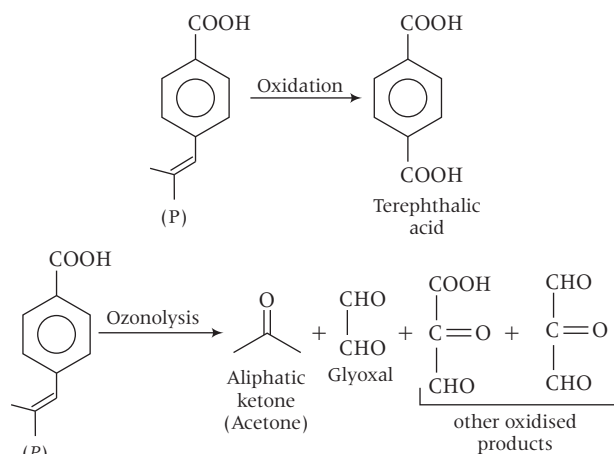
This reaction confirms the presence of multiple bonded branch i.e., alkenyl group in *P*.

Thus *P* can be

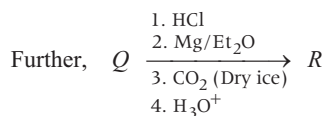
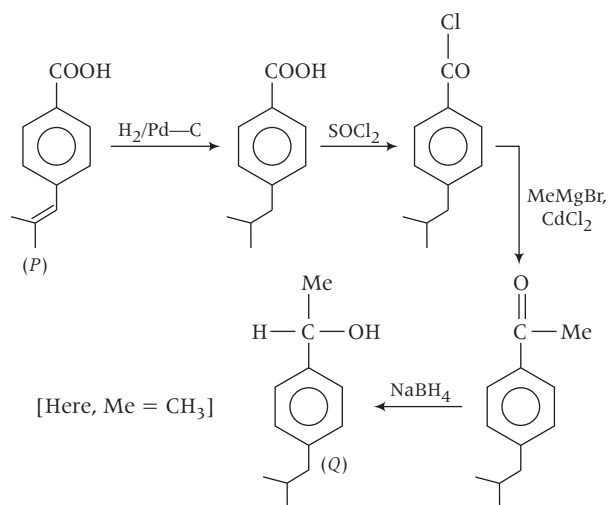


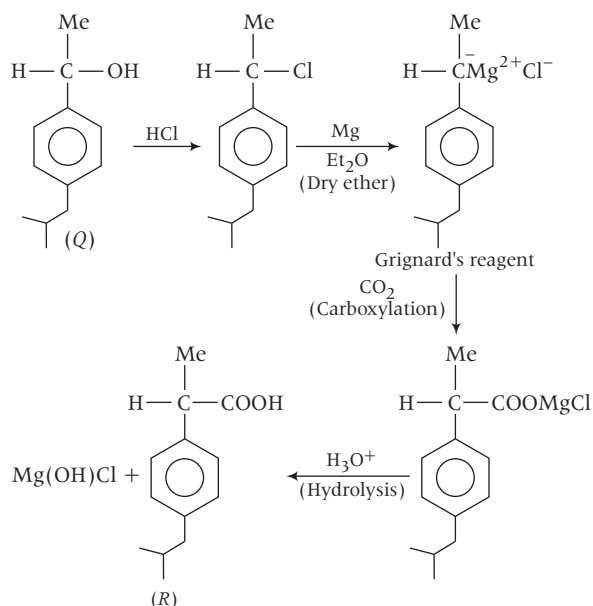
IUPAC name : 4-(2-methyl) prop-1-enyl benzoic acid

Now look for the reactions

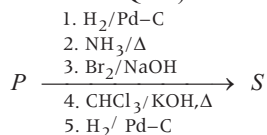


So,

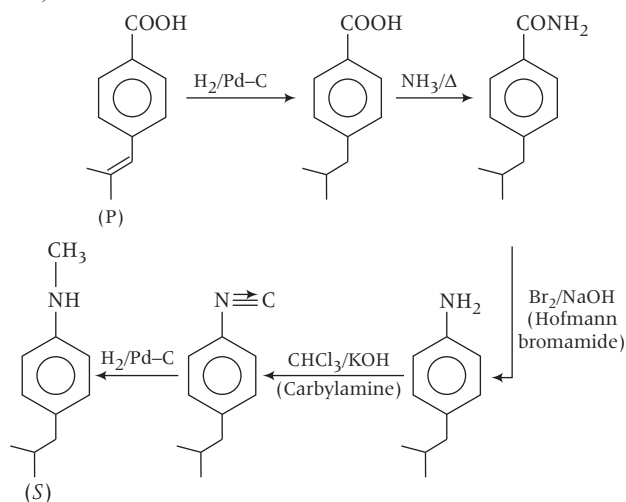




29. Given (In connection with Q. 17)

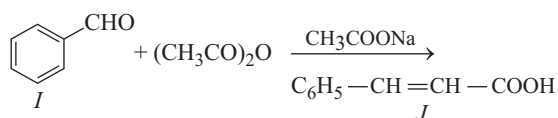


So,



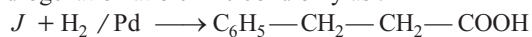
### Passage

Sol for (Q. Nos. 30 to 31) The first step of reaction is Perkin's condensation.

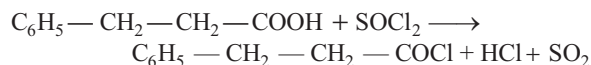


J being a carboxylic acid gives effervescence with NaHCO<sub>3</sub>. Also, J has olefinic bond, it will decolourise Baeyer's reagent.

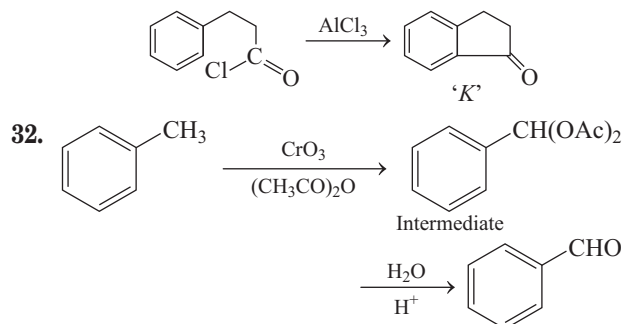
In the second step, J on treatment with H<sub>2</sub> / Pd / C undergo hydrogenation at olefinic bond only as :



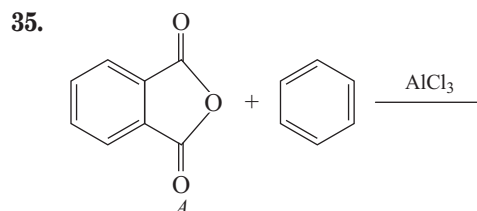
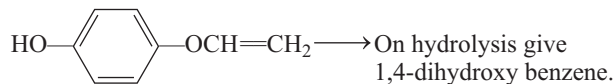
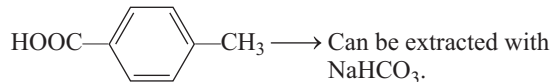
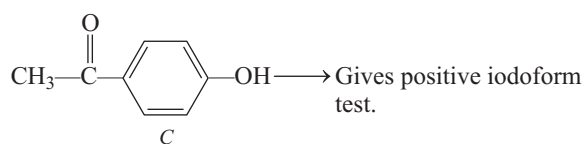
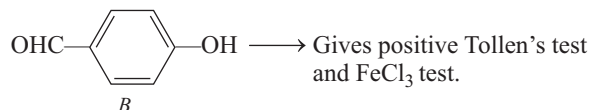
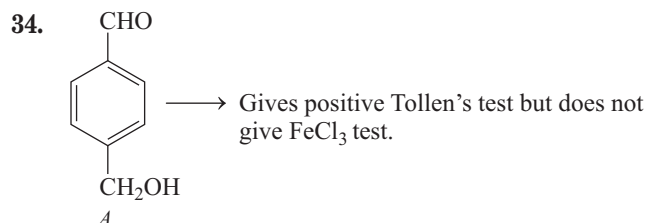
The hydrogenated acid, on treatment with SOCl<sub>2</sub> gives acid chloride.



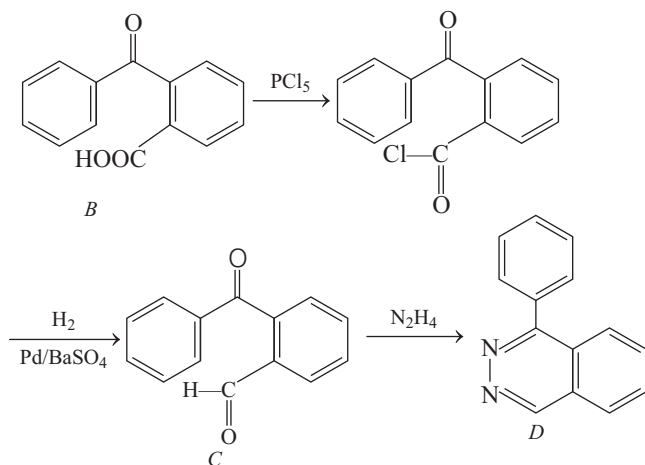
In the final step, acid chloride formed above undergo intramolecular Friedel-Craft acylation as:



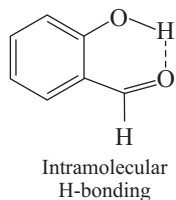
33. For aldol condensation, presence of at least one α-H is essential, which is not available to benzaldehyde.



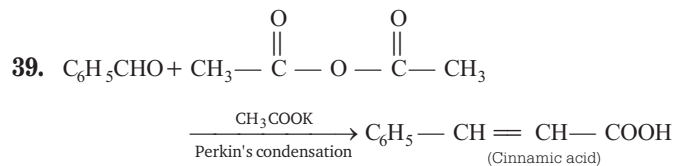
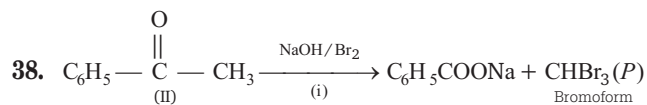
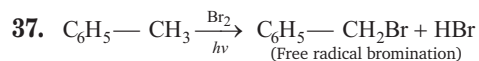
## 452 Aromatic Aldehydes, Ketones and Acids



36. Intramolecular H-bonding in *ortho* hydroxy benzaldehyde is responsible for decrease in melting and boiling points.



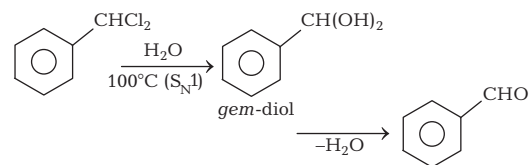
*p*-hydroxy benzaldehyde molecules are associated by intermolecular H-bonding, has higher melting and boiling points.



Cinnamic acid shows *cis-trans* isomerism.

40. I. Gattermann-Koch reaction.

II.



III. Rosenmund's reduction.

IV. Acid chloride, anhydride and ester undergo controlled reduction with di-iso-butylaluminium hydride (DIBAL-H) at  $-78^\circ\text{C}$  to give aldehydes.

**Download Chapter Test**  
<http://tinyurl.com/y4tw8a24>

or



# 32

## Biomolecules and Chemistry in Everyday Life

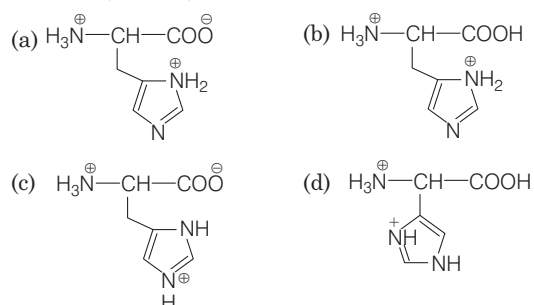
### Topic 1 Biomolecules

#### Objective Questions I (Only one correct option)

- Which of the given statements is incorrect about glycogen?  
(2019 Main, 12 April II)
  - It is straight chain polymer similar to amylose
  - Only  $\alpha$ -linkages are present in the molecule
  - It is present in animal cells
  - It is present in some yeast and fungi
- Which of the following statement is not true about RNA?  
(2019 Main, 12 April I)
  - It controls the synthesis of protein
  - It has always double stranded  $\alpha$ -helix structure
  - It usually does not replicate
  - It is present in the nucleus of the cell
- Number of stereo-centers present in linear and cyclic structures of glucose are respectively (2019 Main, 10 April II)
  - 4 and 5
  - 4 and 4
  - 5 and 4
  - 5 and 5
- Amylopectin is composed of (2019 Main, 10 April I)
  - $\beta$ -D-glucose,  $C_1$ - $C_4$  and  $C_2$ - $C_6$  linkages
  - $\alpha$ -D-glucose,  $C_1$ - $C_4$  and  $C_2$ - $C_6$  linkages
  - $\beta$ -D-glucose,  $C_1$ - $C_4$  and  $C_1$ - $C_6$  linkages
  - $\alpha$ -D-glucose,  $C_1$ - $C_4$  and  $C_1$ - $C_6$  linkages
- The peptide that gives positive ceric ammonium nitrate and carbylamine tests is (2019 Main, 09 April II)
  - Lys-Asp
  - Ser-Lys
  - Gln-Asp
  - Asp-Gln
- Which of the following statement is not true about sucrose?  
(2019 Main, 09 April I)
  - It is also named as invert sugar.
  - The glycosidic linkage is present between  $C_1$  of  $\alpha$ -glucose and  $C_1$  of  $\beta$ -fructose
  - It is a non-reducing sugar
  - On hydrolysis, it produces glucose and fructose
- Fructose and glucose can be distinguished by  
(2019 Main, 08 April II)
  - Fehling's test
  - Barfoed's test
  - Benedict's test
  - Seliwanoff's test

- Maltose on treatment with dilute HCl gives  
(2019 Main, 08 April I)
  - D-glucose and D-fructose
  - D-fructose
  - D-galactose
  - D-glucose

- The correct structure of histidine in a strongly acidic solution (pH = 2) is  
(2019 Main, 12 Jan II)



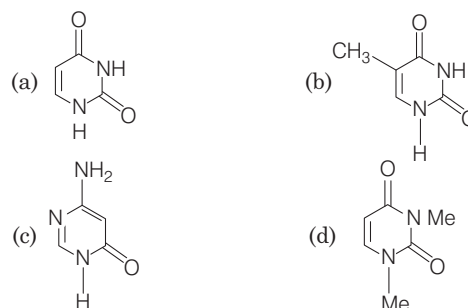
- The correct match between Item I and Item II is

| Item I                | Item II |
|-----------------------|---------|
| A. Ester test         | P. Tyr  |
| B. Carbylamine test   | Q. Asp  |
| C. Phthalein dye test | R. Ser  |
|                       | S. Lys  |

(2019 Main, 11 Jan II)

- (a)  $A \rightarrow Q; B \rightarrow S; C \rightarrow R$  (b)  $A \rightarrow R; B \rightarrow Q; C \rightarrow P$   
 (c)  $A \rightarrow R; B \rightarrow S; C \rightarrow Q$  (d)  $A \rightarrow Q; B \rightarrow S; C \rightarrow P$

- Among the following compounds, which one is found in RNA?  
(2019 Main, 11 Jan I)

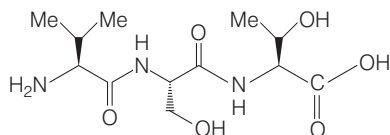


## 454 Biomolecules and Chemistry in Everyday Life

12. Which of the following tests cannot be used for identifying amino acids ? (2019 Main, 10 Jan II)

(a) Barfoed test (b) Ninhydrin test  
(c) Xanthoproteic test (d) Biuret test

13. The correct sequence of amino acids present in the tripeptide given below is (2019 Main, 9 Jan II)



(a) Thr - Ser - Leu (b) Leu - Ser - Thr  
(c) Val - Ser - Thr (d) Thr - Ser - Val

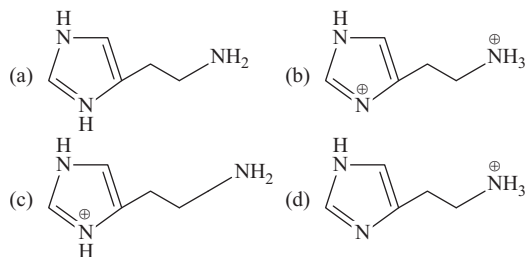
14. The increasing order of  $pK_a$  of the following amino acids in aqueous solution is Gly, Asp, Lys, Arg (2019 Main, 9 Jan I)

(a) Asp < Gly < Arg < Lys (b) Arg < Lys < Gly < Asp  
(c) Gly < Asp < Arg < Lys (d) Asp < Gly < Lys < Arg

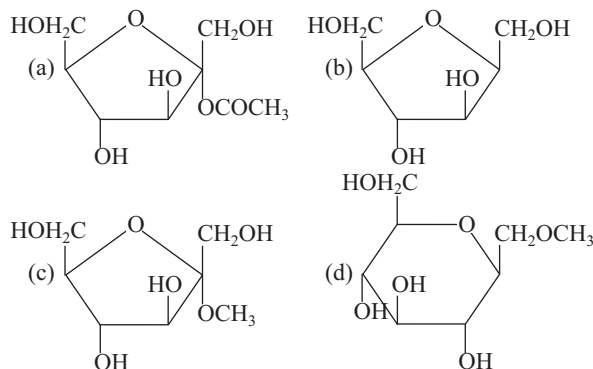
15. Glucose on prolonged heating with HI gives (2018 Main)

(a) *n*-hexane (b) 1-hexene  
(c) Hexanoic acid (d) 6-iodohexanal

16. The predominant form of histamine present in human blood is ( $pK_a$ , Histidine = 6.0) (2018 Main)



17. Which of the following compounds will behave as a reducing sugar in an aqueous KOH solution? (2017 Main)



18. Thiol group is present in (2016 Main)
- (a) cystine (b) cysteine  
(c) methionine (d) cytosine

19. Which of the vitamins given below is water soluble? (2015 Main)
- (a) Vitamin C (b) Vitamin D  
(c) Vitamin E (d) Vitamin K

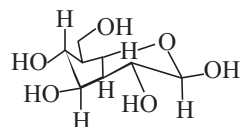
20. Which one of the following bases is not present in DNA? (2014 Main)

(a) Quinoline (b) Adenine  
(c) Cytosine (d) Thymine

21. Synthesis of each molecule of glucose in photosynthesis involves (2013 Main)

(a) 18 molecules of ATP (b) 10 molecules of ATP  
(c) 8 molecules of ATP (d) 6 molecules of ATP

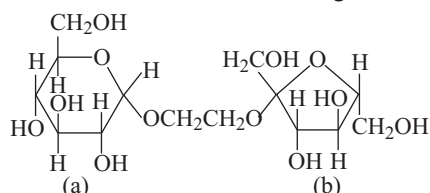
22. The following carbohydrate is



(2011)

(a) a ketohexose (b) an aldohexose  
(c) an  $\alpha$ -furanose (d) an  $\alpha$ -pyranose

23. The correct statement about the following disaccharide is



(2010)

(a) Ring (a) is pyranose with  $\alpha$ -glycosidic link  
(b) Ring (a) is furanose with  $\alpha$ -glycosidic link  
(c) Ring (b) is furanose with  $\alpha$ -glycosidic link  
(d) Ring (b) is pyranose with  $\beta$ -glycosidic link

24. Two forms of D-glucopyranose, are called (2005, 1M)

(a) enantiomers (b) anomers  
(c) epimers (d) diastereomers

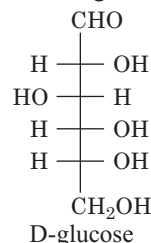
25. Which of the following pairs give positive Tollen's test ? (2004, 1M)

(a) Glucose, sucrose (b) Glucose, fructose  
(c) Hexanal, acetophenone (d) Fructose, sucrose

## Objective Question II

(One or more than one correct option)

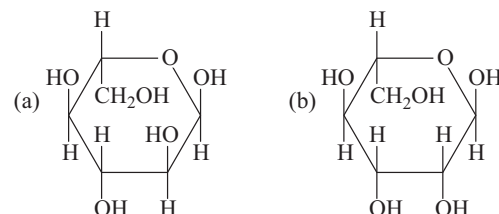
26. The Fischer presentation of D-glucose is given below.

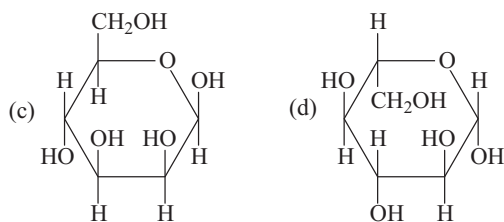


D-glucose

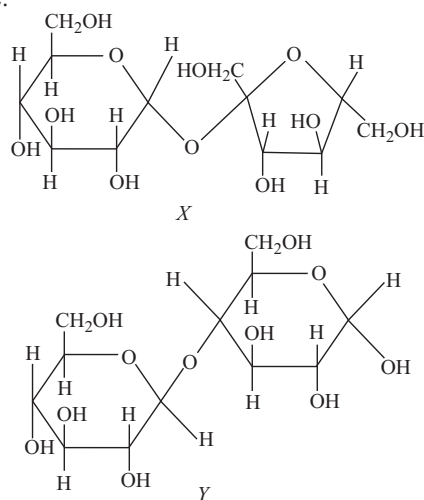
The correct structure(s) of  $\beta$ -L-glucopyranose is (are)

(2018 Adv.)





27. For 'invert sugar', the correct statement(s) is (are)  
 (Given: specific rotations of (+) - sucrose, (+) - maltose, L-(−)-glucose and L-(+)-fructose in aqueous solution are +66°, +140°, −52° and 92°, respectively) **(2016 Adv.)**
- (a) Invert sugar is prepared by acid catalysed hydrolysis of maltose  
 (b) Invert sugar is an equimolar mixture of D-(+) -glucose and D-(−)- fructose  
 (c) Specific rotation of invert sugar is −20°  
 (d) On reaction with Br<sub>2</sub> water, invert sugar forms saccharic acid as one of the products
28. The correct statement(s) about the following sugars *X* and *Y* is/are: **(2009)**



- (a) *X* is a reducing sugar and *Y* is a non-reducing sugar  
 (b) *X* is a non-reducing sugar and *Y* is a reducing sugar  
 (c) The glucosidic linkages in *X* and *Y* are  $\alpha$  and  $\beta$ , respectively  
 (d) The glucosidic linkages in *X* and *Y* are  $\beta$  and  $\alpha$ , respectively

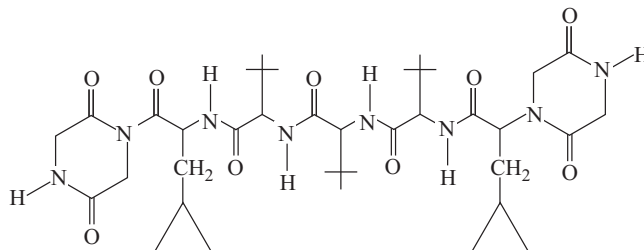
### Assertion and Reason

Read the following questions and answer as per the direction given below :

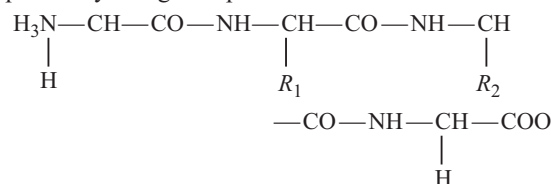
- (a) Statement I is correct; Statement II is correct; Statement II is a correct explanation of Statement I.  
 (b) Statement I is correct; Statement II is correct; Statement II is not the correct explanation of Statement I.  
 (c) Statement I is correct; Statement II is incorrect.  
 (d) Statement I is incorrect; Statement II is correct.
29. **Statement I** Glucose gives a reddish-brown precipitate with Fehling's solution.  
**Statement II** Reaction of glucose with Fehling's solution gives CuO and gluconic acid. **(2007, 3M)**

### Integer Answer Type Questions

30. The total number of distinct naturally occurring amino acids obtained by complete acidic hydrolysis of the peptide shown below is **(2014 Adv.)**

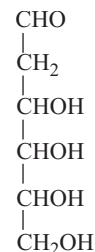


31. A tetrapeptide has —COOH group on alanine. This produces glycine (Gly), valine (Val), phenyl alanine (Phe) and alanine (Ala), on complete hydrolysis. For this tetrapeptide, the number of possible sequences (primary structures) with —NH<sub>2</sub> group attached to a chiral centre is **(2013 Adv.)**
32. The substituents *R*<sub>1</sub> and *R*<sub>2</sub> for nine peptides are listed in the table given below. How many of these peptides are positively charged at pH = 7.0 ? **(2012)**



| Peptide | <i>R</i> <sub>1</sub>                           | <i>R</i> <sub>2</sub>                           |
|---------|-------------------------------------------------|-------------------------------------------------|
| I       | H                                               | H                                               |
| II      | H                                               | CH <sub>3</sub>                                 |
| III     | CH <sub>2</sub> COOH                            | H                                               |
| IV      | CH <sub>2</sub> CONH <sub>2</sub>               | (CH <sub>2</sub> ) <sub>4</sub> NH <sub>2</sub> |
| V       | CH <sub>2</sub> CONH <sub>2</sub>               | CH <sub>2</sub> CONH <sub>2</sub>               |
| VI      | (CH <sub>2</sub> ) <sub>4</sub> NH <sub>2</sub> | (CH <sub>2</sub> ) <sub>4</sub> NH <sub>2</sub> |
| VII     | CH <sub>2</sub> COOH                            | CH <sub>2</sub> CONH <sub>2</sub>               |
| VIII    | CH <sub>2</sub> OH                              | (CH <sub>2</sub> ) <sub>4</sub> NH <sub>2</sub> |
| IX      | (CH <sub>2</sub> ) <sub>4</sub> NH <sub>2</sub> | CH <sub>3</sub>                                 |

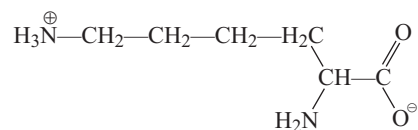
33. When the following aldohexose exists in its D-configuration, the total number of stereoisomers in its pyranose form, is **(2012)**



34. A decapeptide (Molecular weight 796) on complete hydrolysis gives glycine (Molecular weight 75), alanine and phenylalanine. Glycine contributes 47.0% to the total weight of the hydrolysed products. The number of glycine units present in the decapeptide is **(2011)**

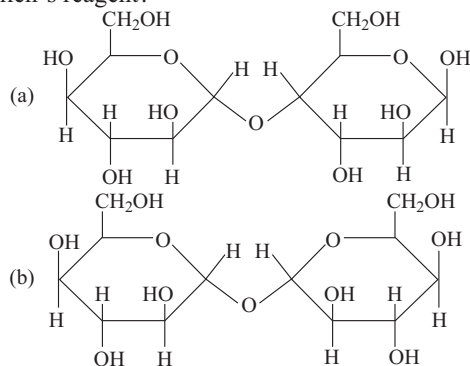
## 456 Biomolecules and Chemistry in Everyday Life

35. The total number of basic groups in the following form of lysine is (2010)

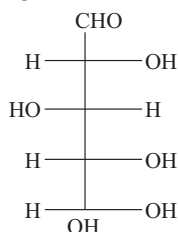


### Subjective Questions

36. Which of the following disaccharide will not reduce Tollen's reagent? (2005, 2M)

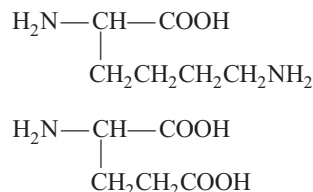


37. The structure of D-glucose is as follows :

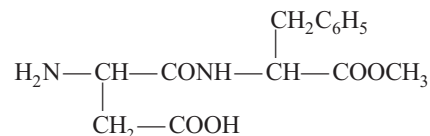


- (i) Draw the structure of L-glucose.  
(ii) Give the reaction of L-glucose with Tollen's reagent. (2004, 2M)

38. Following two amino acids lysine and glutamine form dipeptide linkage. What are two possible dipeptides? (2003, 2M)



39. Aspartame, an artificial sweetener, is a peptide and has the following structure



- (i) Identify the four functional groups.  
(ii) Write the Zwitter ionic structure.  
(iii) Write the structures of the amino acids obtained from the hydrolysis of aspartame.  
(iv) Which of the two amino acids is more hydrophobic? (2001, 5M)
40. Give the structures of the products in the following reaction
- $$\text{Sucrose} \xrightarrow{\text{H}^+} \text{A} + \text{B} \quad (2000, 2\text{M})$$
41. Write the structure of alanine at pH = 2 and pH = 10. (2000, 2M)

## Topic 2 Chemistry in Everyday Life

### Objective Questions I (Only one correct option)

1. Which of the following is a thermosetting polymer? (2019 Main, 12 April I)
- (a) Bakelite (b) Buna-N  
(c) Nylon-6 (d) PVC
2. The correct match between **Item-I** and **Item-II** is

| Item-I                    | Item-II                                           |
|---------------------------|---------------------------------------------------|
| A. High density polythene | I. Peroxide catalyst                              |
| B. Polyacrylonitrile      | II. Condensation at high temperature and pressure |
| C. Novolac                | III. Ziegler-Natta catalyst                       |
| D. Nylon-6                | IV. Acid or base catalyst                         |

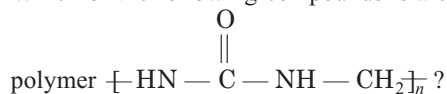
(2019 Main, 10 April II)

#### Codes

- A B C D A B C D  
(a) III I IV II (b) IV II I III  
(c) II IV I III (d) III I II IV

3. Which of the following is a condensation polymer? (2019 Main, 10 April I)
- (a) Nylon-6, 6 (b) Neoprene  
(c) Teflon (d) Buna - S
4. Noradrenaline is a/an (2019 Main, 9 April II)
- (a) antidepressant (b) antihistamine  
(c) neurotransmitter (d) antacid

5. Which of the following compounds is a constituent of the

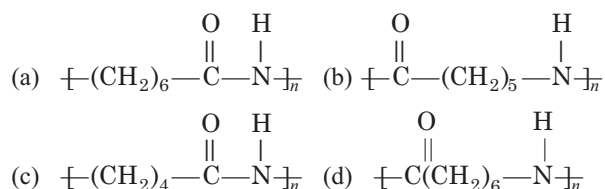


(2019 Main, 9 April II)

- (a) N-methyl urea  
(b) Methylamine  
(c) Ammonia  
(d) Formaldehyde

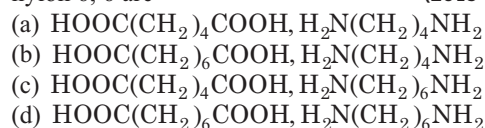


6. The structure of nylon-6 is



(2019 Main, 8 April II)

7. The two monomers for the synthesis of nylon 6, 6 are (2019 Main, 12 Jan II)

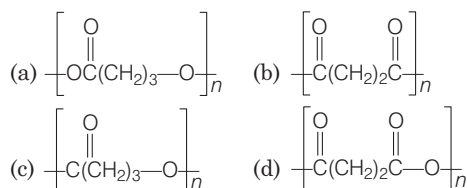


8. Poly- $\beta$ -hydroxybutyrate-Co- $\beta$ -hydroxyvalerate (PHBV) is a copolymer of .....

(2019 Main, 12 Jan I)

- (a) 3-hydroxybutanoic acid and 2-hydroxypentanoic acid  
 (b) 2-hydroxybutanoic acid and 3-hydroxypentanoic acid  
 (c) 3-hydroxybutanoic acid and 4-hydroxypentanoic acid  
 (d) 3-hydroxybutanoic acid and 3-hydroxypentanoic acid

9. The homopolymer formed from 4-hydroxybutanoic acid is



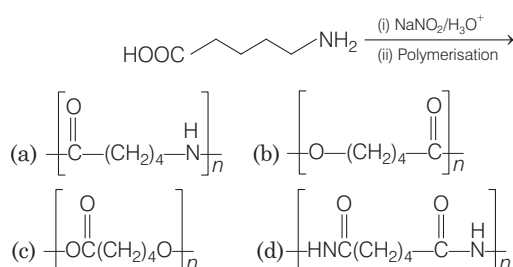
(2019 Main, 11 Jan II)

10. The correct match between Item I and Item II is

| Item I                   | Item II                                                             |
|--------------------------|---------------------------------------------------------------------|
| A. Allosteric effect     | P. Molecule binding to the active site of enzyme.                   |
| B. Competitive inhibitor | Q. Molecule crucial for communication in the body.                  |
| C. Receptor              | R. Molecule binding to a site other than the active site of enzyme. |
| D. Poison                | S. Molecule binding to the enzyme covalently.                       |

- (a)  $A \rightarrow P; B \rightarrow R; C \rightarrow S; D \rightarrow Q$   
 (b)  $A \rightarrow P, B \rightarrow R; C \rightarrow Q; D \rightarrow S$   
 (c)  $A \rightarrow R; B \rightarrow P; C \rightarrow S; D \rightarrow Q$   
 (d)  $A \rightarrow R; B \rightarrow P; C \rightarrow Q; D \rightarrow S$  (2019 Main, 11 Jan II)

11. The polymer obtained from the following reaction is: (2019 Main, 11 Jan I)



12. The correct match between item (I) and item (II) is

| Item - I          | Item - II         |
|-------------------|-------------------|
| (A) Norethindrone | (P) Antibiotic    |
| (B) Ofloxacin     | (Q) Antifertility |
| (C) Equanil       | (R) Hypertension  |
|                   | (S) Analgesics    |

(2019 Main, 11 Jan I)

- (a)  $(A) \rightarrow (Q); (B) \rightarrow (R); (C) \rightarrow (S)$   
 (b)  $(A) \rightarrow (Q); (B) \rightarrow (P); (C) \rightarrow (R)$   
 (c)  $(A) \rightarrow (R); (B) \rightarrow (P); (C) \rightarrow (S)$   
 (d)  $(A) \rightarrow (R); (B) \rightarrow (P); (C) \rightarrow (R)$

13. The correct match between Item - I and Item - II is

| Item I (Drug)     | Item II (Test)                    |
|-------------------|-----------------------------------|
| A. Chloroxylenol  | P. Carbylamine test               |
| B. Norethindrone  | Q. Sodium hydrogen carbonate test |
| C. Sulphapyridine | R. Ferric chloride test           |
| D. Penicillin     | S. Bayer's test                   |

(2019 Main, 9 Jan I)

- (a)  $A \rightarrow R; B \rightarrow P; C \rightarrow S; D \rightarrow Q$   
 (b)  $A \rightarrow R; B \rightarrow S; C \rightarrow P; D \rightarrow Q$   
 (c)  $A \rightarrow Q; B \rightarrow P; C \rightarrow S; D \rightarrow R$   
 (d)  $A \rightarrow Q; B \rightarrow S; C \rightarrow P; D \rightarrow R$

14. The formation of which of the following polymers involves hydrolysis reaction? (2017 Main)

- (a) Nylon-6  
 (b) Bakelite  
 (c) Nylon-6, 6  
 (d) Terylene

15. Which of the following statements about low density polythene is false? (2016 Main)

- (a) It is a poor conductor of electricity  
 (b) Its synthesis required dioxygen or a peroxide initiator as a catalyst  
 (c) It is used in the manufacture of buckets, dustbins etc.  
 (d) Its synthesis requires high pressure

16. Which of the following is an anionic detergent? (2016 Main)

- (a) Sodium lauryl sulphate  
 (b) Cetyltrimethyl ammonium bromide  
 (c) Glyceryl oleate  
 (d) Sodium stearate

17. On complete hydrogenation, natural rubber produces (2016 Adv.)

- (a) ethylene-propylene copolymer  
 (b) vulcanised rubber  
 (c) polypropylene  
 (d) polybutylene

18. Which polymer is used in the manufacture of paints and lacquers? (2015 Main)

- (a) Bakelite  
 (b) Glyptal  
 (c) Polypropene  
 (d) Polyvinyl chloride

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19. Match the polymers in Column I with their main uses in Column II and choose the correct answer:

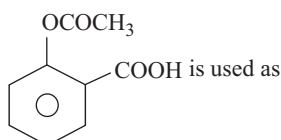
| Column I               | Column II              |
|------------------------|------------------------|
| (A) Polystyrene        | 1. Paints and lacquers |
| (B) Glyptal            | 2. Raincoats           |
| (C) Polyvinyl chloride | 3. Manufacture of toys |
| (D) Bakelite           | 4. Computer discs      |

### Codes

| A     | B | C | D |
|-------|---|---|---|
| (a) 2 | 1 | 3 | 4 |
| (c) 2 | 4 | 3 | 1 |

| A     | B | C | D |
|-------|---|---|---|
| (b) 3 | 1 | 2 | 4 |
| (d) 3 | 4 | 2 | 1 |

20.



- (a) Insecticide (b) Antihistamine  
(c) Analgesic (d) Antacid

21. Which of the following is not an antacid? (2015 Main)

- (a) Aluminium hydroxide (b) Cimetidine  
(c) Phenelzine (d) Ranitidine

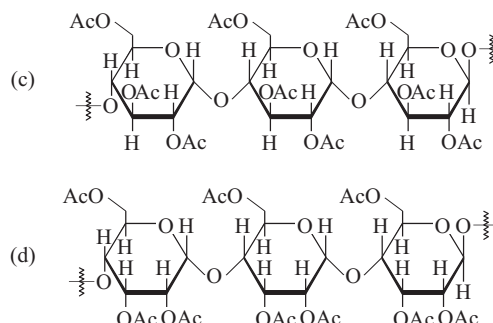
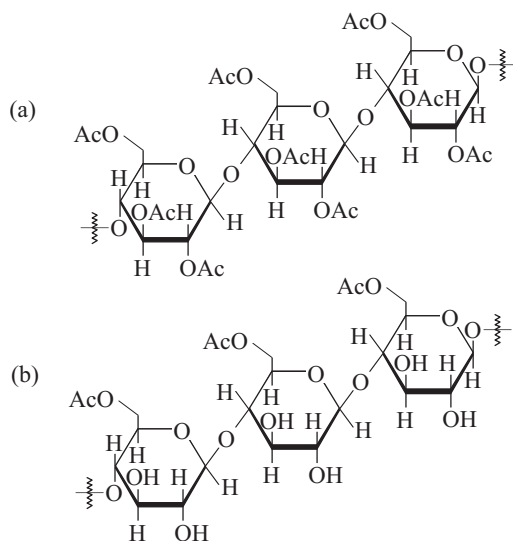
22. Which one is classified as a condensation polymer? (2014 Main)

- (a) Dacron (b) Neoprene  
(c) Teflon (d) Acrylonitrile

23. Among cellulose, poly (vinyl chloride), nylon and natural rubber, the polymer in which the intermolecular force of attraction is weakest is (2009)

- (a) nylon  
(b) poly (vinyl chloride)  
(c) cellulose  
(d) natural rubber

24. Cellulose upon acetylation with excess acetic anhydride/ $\text{H}_2\text{SO}_4$  (catalytic) gives cellulose triacetate whose structure is (2008, 3M)



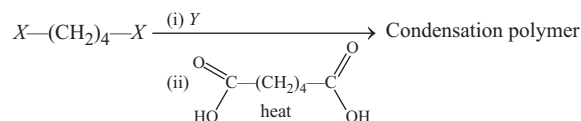
### Objective Question II

(One or more than one correct option)

25. Under hydrolysis conditions, the compounds used for preparation of linear polymer and for chain termination, respectively are (2012)

- (a)  $\text{CH}_3\text{SiCl}_3$  and  $\text{Si}(\text{CH}_3)_4$  (b)  $(\text{CH}_3)_2\text{SiCl}_2$  and  $(\text{CH}_3)_3\text{SiCl}$   
(c)  $(\text{CH}_3)_3\text{SiCl}_2$  and  $\text{CH}_3\text{SiCl}_3$  (d)  $\text{SiCl}_4$  and  $(\text{CH}_3)_3\text{SiCl}$

26. The correct functional group  $X$  and the reagent/reaction conditions  $Y$  in the following schemes are (2011)



- (a)  $X = \text{COOCH}_3$ ,  $Y = \text{H}_2/\text{Ni}/\text{heat}$   
(b)  $X = \text{CONH}_2$ ,  $Y = \text{H}_2/\text{Ni}/\text{heat}$   
(c)  $X = \text{CONH}_2$ ,  $Y = \text{Br}_2/\text{NaOH}$   
(d)  $X = \text{CN}$ ,  $Y = \text{H}_2/\text{Ni}/\text{heat}$

### Match the Columns

27. Match the chemical substances in Column I with type of polymers/type of bond in Column II. (2007, 6M)

| Column I     | Column II            |
|--------------|----------------------|
| A. Cellulose | p. Natural polymer   |
| B. Nylon-66  | q. Synthetic polymer |
| C. Protein   | r. Amide linkage     |
| D. Sucrose   | s. Glycoside linkage |

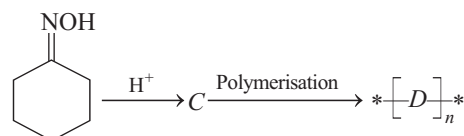
### Subjective Questions

28. Monomer  $A$  of a polymer on ozonolysis yields two moles of  $\text{HCHO}$  and one mole of  $\text{CH}_3\text{COCHO}$ . (2005)

- (a) Deduce the structure of  $A$ .  
(b) Write the structure of 'all *cis*' - form of polymer of compound  $A$ .

29. Name the heterogeneous catalyst used in the polymerisation of ethylene. (2003)

30. Give the structures of the products in the following reaction. (2000, 2M)



# Answers

## Topic 1

- |         |         |           |           |
|---------|---------|-----------|-----------|
| 1. (a)  | 2. (b)  | 3. (a)    | 4. (d)    |
| 5. (b)  | 6. (b)  | 7. (d)    | 8. (d)    |
| 9. (a)  | 10. (d) | 11. (a)   | 12. (a)   |
| 13. (c) | 14. (d) | 15. (a)   | 16. (d)   |
| 17. (a) | 18. (b) | 19. (a)   | 20. (a)   |
| 21. (a) | 22. (b) | 23. (a)   | 24. (b)   |
| 25. (b) | 26. (d) | 27. (b,c) | 28. (b,c) |
| 29. (c) | 30. (1) | 31. (4)   | 32. (4)   |
| 33. (8) | 34. (6) | 35. (2)   |           |

## Topic 2

- |                                         |                  |         |         |
|-----------------------------------------|------------------|---------|---------|
| 1. (a)                                  | 2. (a)           | 3. (a)  | 4. (c)  |
| 5. (d)                                  | 6. (b)           | 7. (c)  | 8. (d)  |
| 9. (c)                                  | 10. (d)          | 11. (b) | 12. (b) |
| 13. (b)                                 | 14. (a)          | 15. (c) | 16. (a) |
| 17. (a)                                 | 18. (b)          | 19. (b) | 20. (c) |
| 21. (c)                                 | 22. (a)          | 23. (d) | 24. (a) |
| 25. (b)                                 | 26. (a, b, c, d) |         |         |
| 27. A → p, s; B → q, r; C → p, r; D → s |                  |         |         |

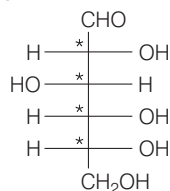
# Hints & Solutions

## Topic 1 Biomolecules

- Statement (a) is incorrect. Glycogen is not a straight chain polymer similar to amylose. It is highly branched structure similar to amylopectin. It is known to be the storage material of animals. It is found in liver, muscles and brain. It breaks down to glucose by the action of enzymes when body needs a glucose. It is also found in yeast and fungi.
- RNA does not have double stranded  $\alpha$ -helix structure. Helixes present in RNA are single-stranded but sometimes they fold back on themselves to form a double helix structure. RNA usually does not replicate.  
It is present in the nucleus of the cell. It controls the synthesis of protein. RNA molecules are of three types, i.e. messenger's RNA (*m*-RNA), ribosomal RNA (*r*-RNA), transfer RNA (*t*-RNA).

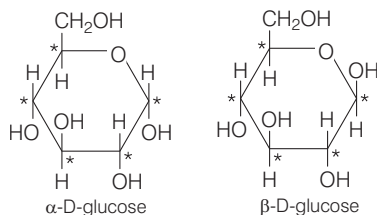
- Key Idea** Chiral centre is also called stereo-centre or stereogenic center.

Linear structure of glucose is as follows :



**Fischer formula** Number of stereo-centre ( $\text{C}^*$ ) = 4.

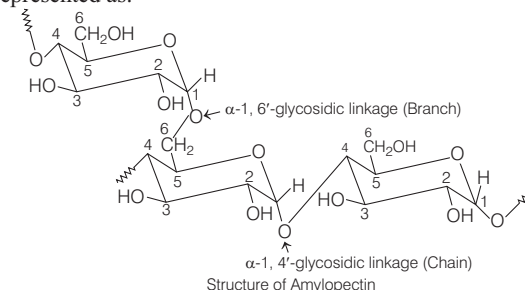
Cyclic structure of glucose are as follows :



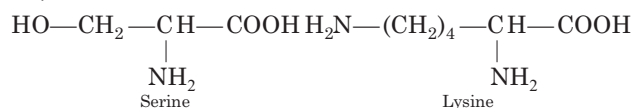
**Haworth formula** Number of stereo-centre ( $\text{C}^*$ ) in each anomer = 5.

- Amylopectin is the water-soluble component of starch. It is a branched-chain polymer of  $\alpha$ -D-glucose. The main chain consists of an  $\alpha$ -1, 4'- glycosidic linkages between  $\alpha$ -D-

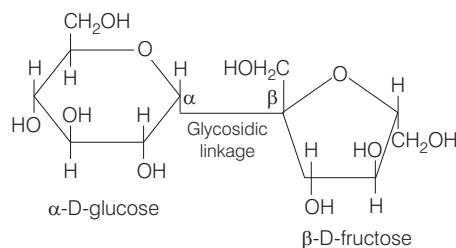
$\alpha$ -D-glucose units and the branches are connected to the main chain by  $\alpha$ -1,6'- glycosidic linkages. Its structure can be represented as:



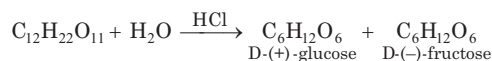
- The peptide that gives positive ceric ammonium nitrate and carbylamine tests is ser - lys. The structures of serine and lysine are,



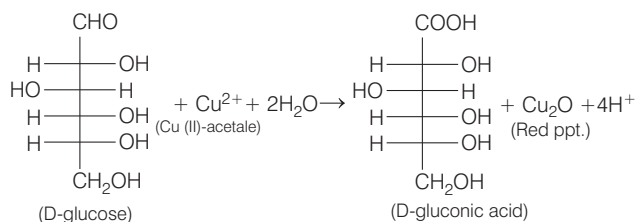
- Statement-(b) is not true for sucrose. It is linked through a glycosidic linkage between C-1 of  $\alpha$ -glucose and C-2 of  $\beta$ -fructose. Since, the reducing groups of glucose and fructose are involved in glycosidic bond formation, sucrose is a non-reducing sugar.



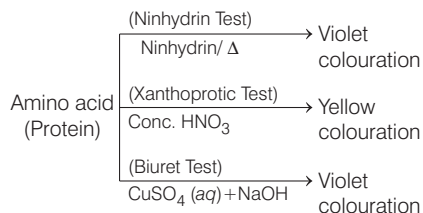
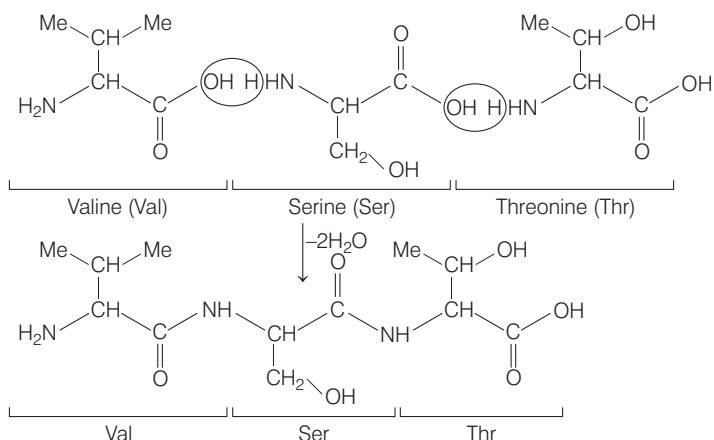
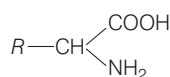
On hydrolysis with acids or enzyme, sucrose gives equimolar mixture of D-(+)-glucose and D-(-)-fructose.



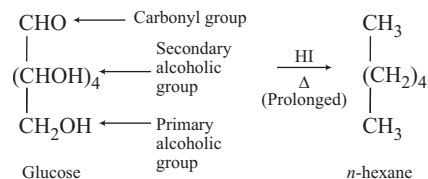
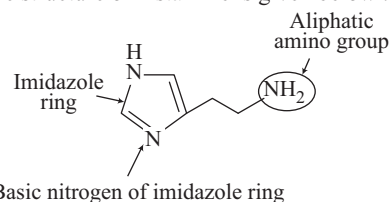
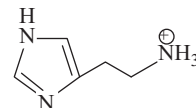
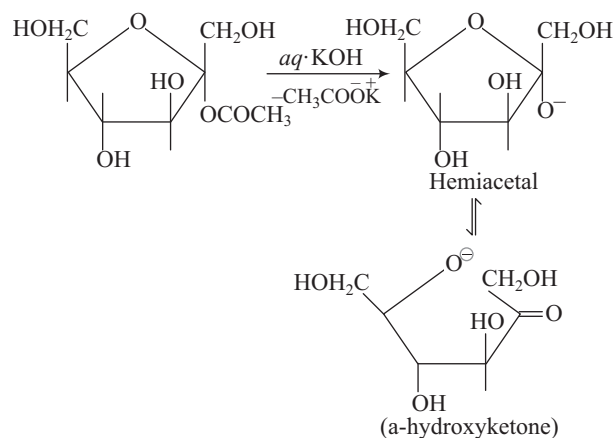




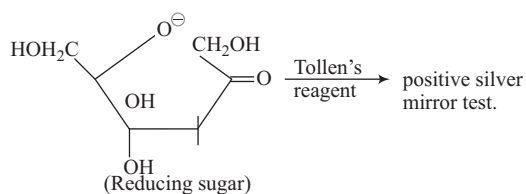
(ii)


**13.** Formation of the tripeptide (Val-Ser-Thr) can be shown as:

**14** Amino acid molecules can be represented as,

 Nature of the 'R' group will determine the basicity (hence,  $\text{pK}_a$ ) of an amino acid.

| 'R' in the amino group                                                                                                                       | Nature of R | Nature of the amino acids                             |
|----------------------------------------------------------------------------------------------------------------------------------------------|-------------|-------------------------------------------------------|
| 1. $\text{---}(\text{CH}_2)_3\text{---NH---C} \begin{array}{l} \nearrow \text{NH}_2 \\ \searrow \text{NH}_2 \end{array}$<br>(Arginine : Arg) | Basic       | More basic (due to the presence of acetamidine group) |
| 2. $\text{---CH}_2\text{---C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{O}^- \end{array}$<br>(Aspartic acid: Asp)                 | Acidic      | Acidic                                                |
| 3. $\text{---H}$ (Glycine) : Gly                                                                                                             | Neutral     | Neutral                                               |
| 4. $\text{---}(\text{CH}_2)_4\text{---NH}_3^+$<br>(Lysine : Lys)                                                                             | Basic       | Basic                                                 |

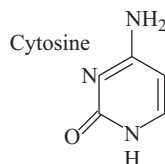
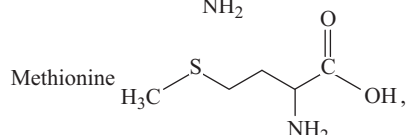
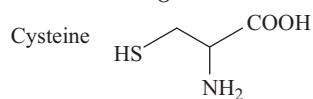
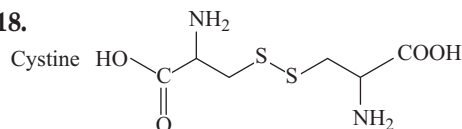
**15.** HI is a strong reducing agent. It reduces both primary and secondary alcoholic groups of glucose along with the carbonyl group to produce *n*-hexane as

**16.** Our blood is slightly basic in nature with pH range from 7.35-7.4. The structure of histamine is given below :

 It is produced by decarboxylation of histidine having following structure. It is clearly visible from the above structure that histamine has two basic centres namely aliphatic amino group and basic nitrogen of imidazole ring. The aliphatic amino group has  $\text{pK}_a$  around 9.4. In blood with pH around 7.4 the aliphatic amino group of histamine become protonated to give a single charged cation as shown below

**17.** Sugars that have an aldehyde, a ketone, a hemiacetal or a hemiketal group is able to reduce an oxidising agent. These sugars are classified as reducing sugars.


Hemiacetal can be easily reduced by oxidising agent such as Tollen's reagent.



## 462 Biomolecules and Chemistry in Everyday Life

18.

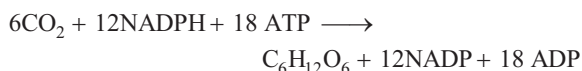


Thiol group (SH) is present in cysteine.

19. Vitamin B and C are water soluble while vitamin A, D, E and K are fat soluble or water insoluble.

20. Quinoline is an alkaloid, it is not present in DNA. DNA has four nitrogen bases in adenine, guanine, cytosine and thymine.

21. 18 ATPs are involved in the formation of 1 glucose molecule as shown in the reaction below :



22. Here, the —OH of hemiacetal group is equatorial therefore, it is a  $\beta$ -pyranose of an aldohexose.

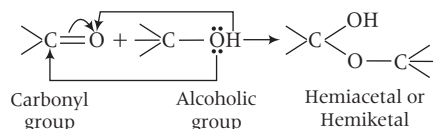
23. The six-membered cyclic ether is known as pyranose while the five membered cyclic ether is known as furanose. Hence, ring (a) is a pyranose and it has ether linkage at  $\alpha$ -position that is known as  $\alpha$ -glycosidic linkage in carbohydrate chemistry.

24. " $\alpha$ " and " $\beta$ " cyclic hemiacetals of D-glucose having difference in configuration at C-1 only are called anomers.

25. Both glucose and fructose are reducing sugars, reduces Tollen's reagent to metallic silver.

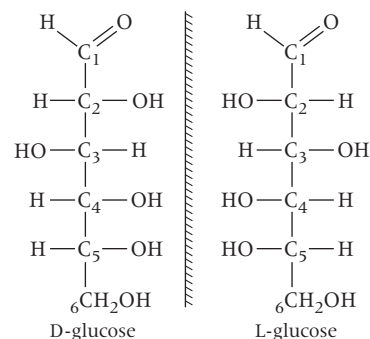
26. (d) A pyranose ring is a 6 membered ring having 5 carbon atoms and one oxygen atom. In glucose, it is formed by the reaction between  $>\text{C}=\text{O}$  group at position 1 and —OH group at 5th carbon atom. In general reaction between  $>\text{C}=\text{O}$  group

and  $\text{>C}-\text{OH}$  looks like

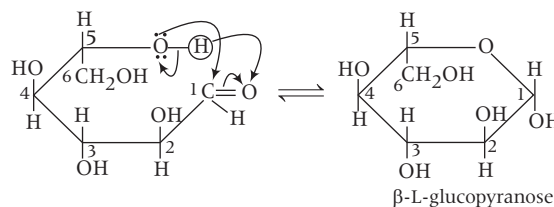


The product formed is called **hemiacetal**

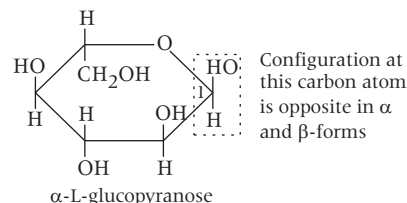
(if  $>\text{C}=\text{O}$  group belongs to an aldehyde) or **hemiketal** (if  $>\text{C}=\text{O}$  group belongs to a ketone). L-glucose has the mirror image configuration of D-glucose i.e.,



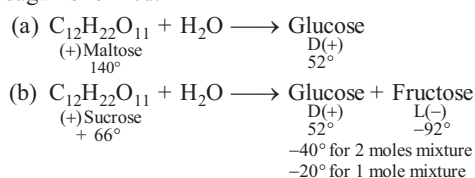
So,  $\beta$ -L glucopyranose is formed as



The  $\alpha$ -L-glucopyranose has configurational change at  $\text{C}_1$  only and looks like



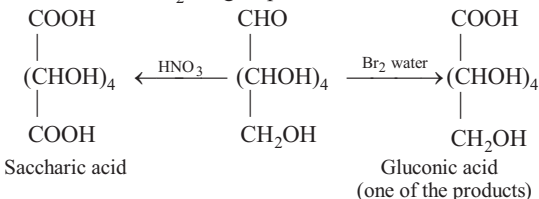
27. If there is inversion of specific rotation from (+) to (−), then invert sugar is formed.



There is formation of invert sugar. Thus, correct.

(c) Specific rotation of invert sugar is  $-20^\circ$  per mole. Thus, correct.

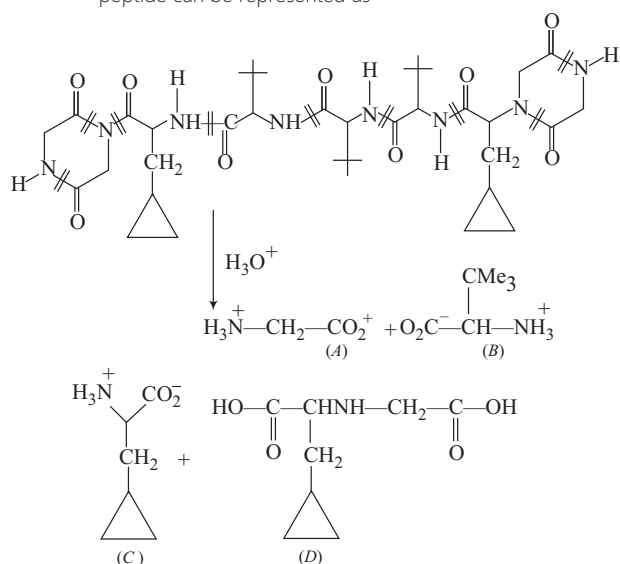
(d)  $\text{Br}_2$  water is a weak oxidising agent. It oxidises —CHO to —COOH. — $\text{CH}_2\text{OH}$  group is not affected.



$\text{HNO}_3$  (a strong oxidising agent) oxidises invert sugar to saccharic acid. Thus, incorrect.

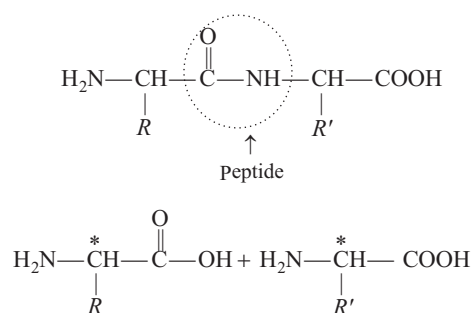


28.  $X$  is acetal, has no free hemiacetal, hence a non-reducing sugar while  $Y$  has a free hemiacetal group, it is reducing sugar. Also, glucosidic linkage of  $X$  is ' $\alpha$ ' while that of  $Y$  is  $\beta$ -linkage.
29. **Statement I is correct** Presence of  $\text{—CHO}$  group in glucose is tested by Fehling's solution test where a reddish-brown precipitate of  $\text{Cu}_2\text{O}$  is formed.  
Hence, Statement II is incorrect.
30. **PLAN** This problem can be solved by performing hydrolysis of peptide and deciding the nature of product.  
Chemical reaction and product formed after hydrolysis of given peptide can be represented as



(A) is glycine which is only naturally occurring amino acid. While (B), (C) and (D) are not the naturally occurring amino acids. Hence, correct integer is (1).

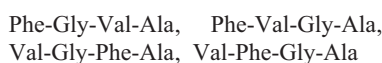
31. **PLAN** A peptide linkage is hydrolysed to two free amino acids.



$\text{C}^*$  is chiral carbon tetrapeptide has four amino acids joined by three peptide linkage.

$\text{—COOH}$  group is on alanine part, thus it is at fixed C-terminal position in each combination.

Glycine is optically inactive thus it cannot be on the N-terminal side. Thus, possible combinations are



Thus, in all **four combinations are possible**.

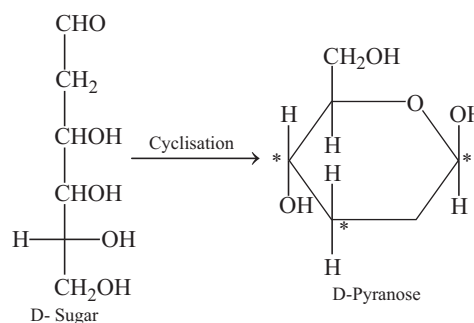
32. The amino acid remain completely in Zwitter ionic form at its isoelectric point. Amino acids with additional acidic group have their isoelectric pH less than 7.0 and increasing pH above isoelectric point makes them anionic.

On the other hand, amino acids with additional basic group have their isoelectric pH greater than 7.0 and decreasing pH below isoelectric point (by adding acid solution) makes them cationic. The given peptide with followings  $R_1$  and  $R_2$  are basic, will remain protonated (cationic) at  $\text{pH} = 7.0$ .

| Peptide | $R_1$                        | $R_2$                        |
|---------|------------------------------|------------------------------|
| IV      | $\text{CH}_2\text{CONH}_2$   | $(\text{CH}_2)_4\text{NH}_4$ |
| VI      | $(\text{CH}_2)_4\text{NH}_2$ | $(\text{CH}_2)_4\text{NH}_4$ |
| VIII    | $\text{CH}_2\text{OH}$       | $(\text{CH}_2)_4\text{NH}_4$ |
| IX      | $(\text{CH}_2)_4\text{NH}_2$ | $\text{CH}_3$                |

Thus, 4 is the correct integer.

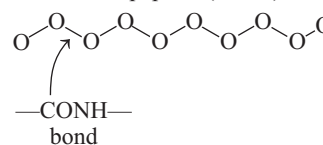
33. The D-form of given sugar is



Configurations at the three chiral carbons (starred) can be changed maintaining D-configuration. Hence, the total number of stereoisomers of D-pyranose  $= 2^3 = 8$

Thus, the correct integer is 8.

34. A decapeptide has nine peptide (amide) linkage as



Therefore, on hydrolysis, it will absorb nine water molecules.

Hence, total mass of hydrolysis product  $= 796 + 18 \times 9 = 958$

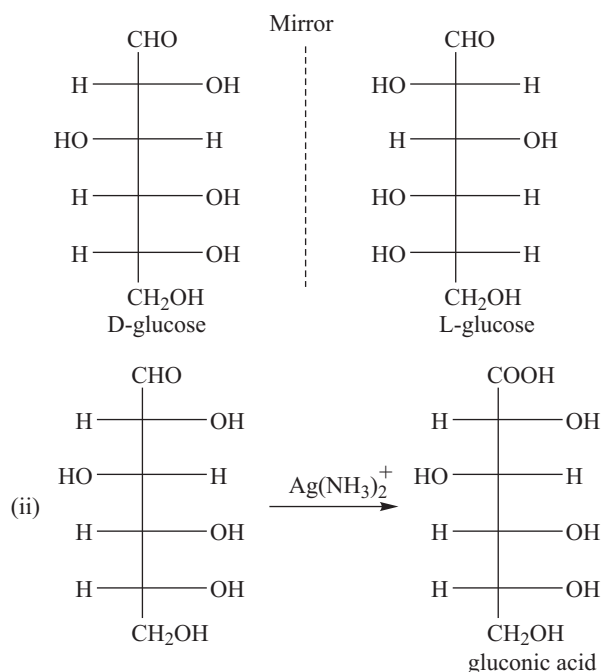
$$\Rightarrow \text{mass of glycine in hydrolysis product} = \frac{958 \times 47}{100} = 450$$

$$\Rightarrow \text{number of glycine molecule in one molecule of decapeptide} = \frac{450}{75} = 6$$

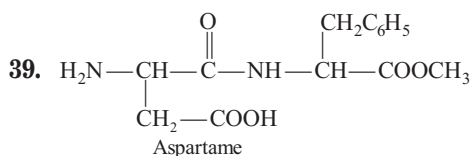
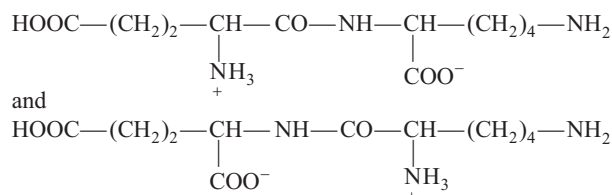
35.  $\text{—OO}^-$  and  $\text{—NH}_2$  are two basic groups in lysine.

36. In structure (a), one ring has a free hemiacetal group, will hydrolyse into open chain in aqueous solution and therefore will reduce Tollen's reagent. Structure (b) has only acetal groups, will not hydrolyse in aqueous solution into open chain, will not reduce Tollen's reagent

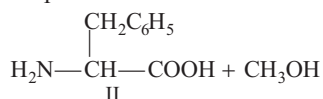
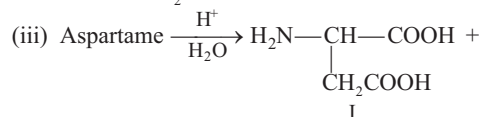
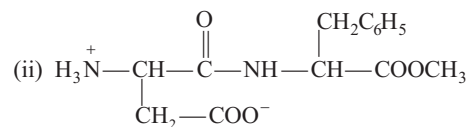
37. (i) D-glucose and L-glucose are enantiomers, hence



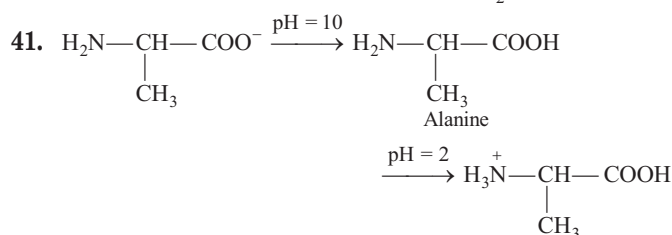
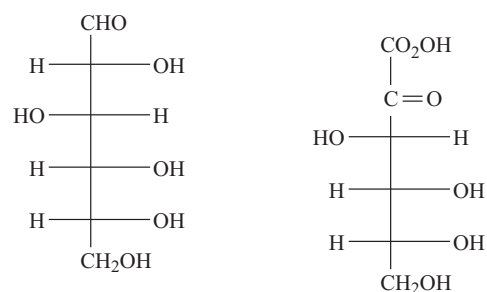
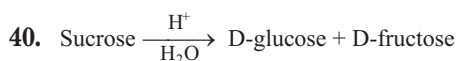
38. The dipeptides are



- (i) Aspartame has amine, acid, amide and ester groups.

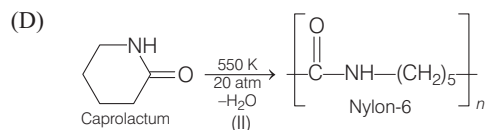
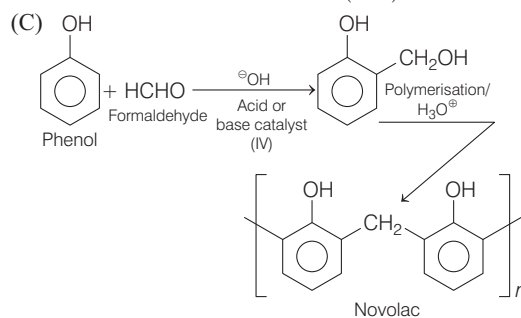
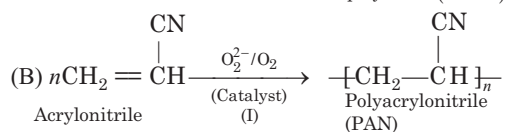
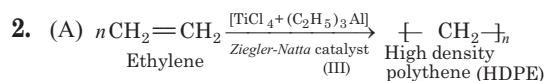


- (iv) II is more hydrophobic due to the presence of phenyl group.



## Topic 2 Chemistry in Everyday Life

1. Bakelite is a thermosetting polymer. These polymers are cross-linked or heavily branched molecules which on heating undergo extensive cross linking in moulds and become infusible. Once they get set, they cannot be reshaped and reused.

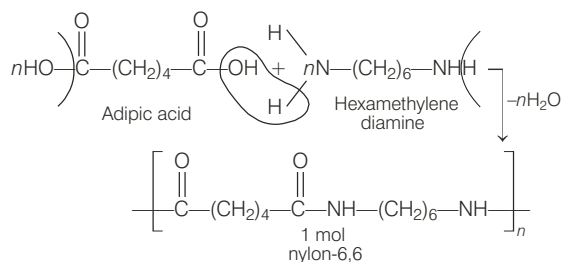


Thus, the correct match is as follows :

(A) → (III), (B) → (I), (C) → (IV), (D) → (II)

3. Nylon-6, 6 (an amide) is a condensation copolymer because it is obtained by condensation between adipic acid and hexamethylenediamine.

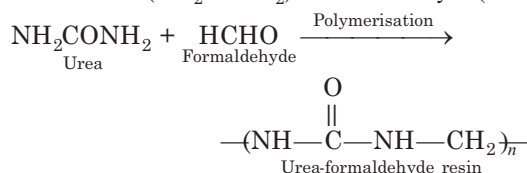




Neoprene, teflon and buna-S are addition polymers.

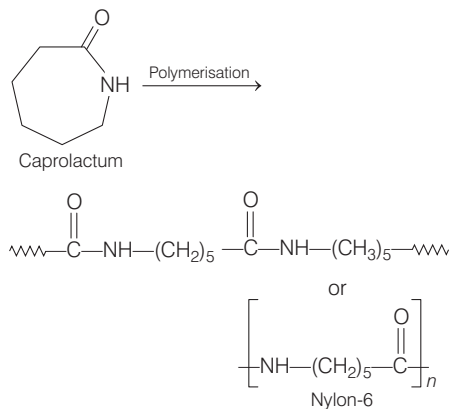
4. Noradrenaline is one of the example of neurotransmitters. It plays a major role in mood changes. If the level of noradrenaline is low for some reason, then signal-sending activity becomes low and the person suffers from depression.

5. Monomer of  $-\left[\text{NH}-\overset{\text{O}}{\parallel}\text{C}-\text{NH}-\text{CH}_2\right]_n-$  is formaldehyde. The polymer is also known as urea-formaldehyde resin. It is made from urea ( $\text{NH}_2\text{CONH}_2$ ) and formaldehyde ( $\text{HCHO}$ ).



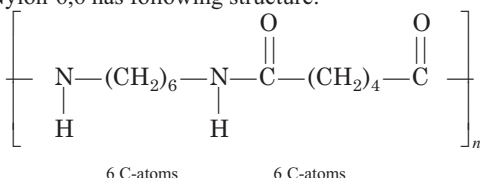
It is used for making unbreakable cups and laminated sheets.

6.



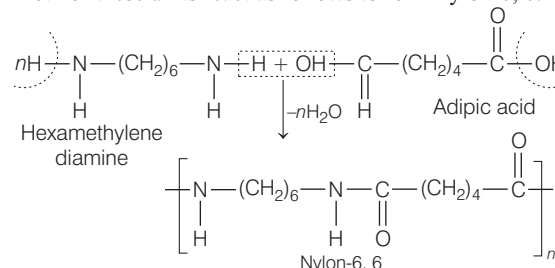
Nylon-6 is prepared by ring opening polymerisation of caprolactam. It is heated about 533 K in an inert atmospheric nitrogen about 4-5 hrs. Nylon-6 fibres are tough, possessing high tensile strength, as well as elasticity and lustre. They are wrinkle proof and highly resistant to abrasion and chemicals such as acids and alkalis.

7. Nylon-6,6 has following structure:

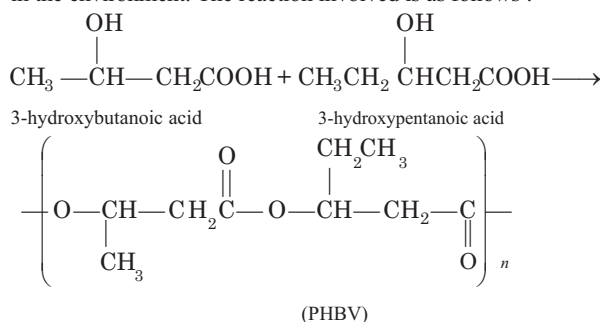


As it is a condensation polymer hence, each of its monomeric unit must contain 6 carbon atoms in them. Hence, a combination

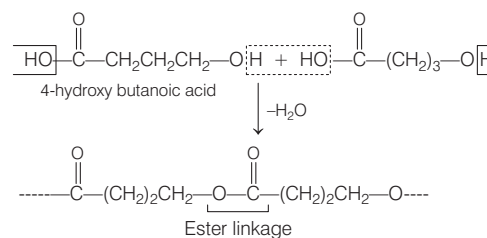
of adipic acid and hexamethylene diamine is the correct answer. Both of these units react as follows to form nylon-6, 6.



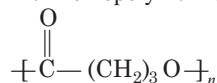
8. Poly-β-hydroxy butyrate Co-β-hydroxyvalerate (PHBV) is a copolymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid. It is used in speciality packaging, orthopaedic devices and in controlled release of drugs. PHBV undergoes bacterial degradation in the environment. The reaction involved is as follows :



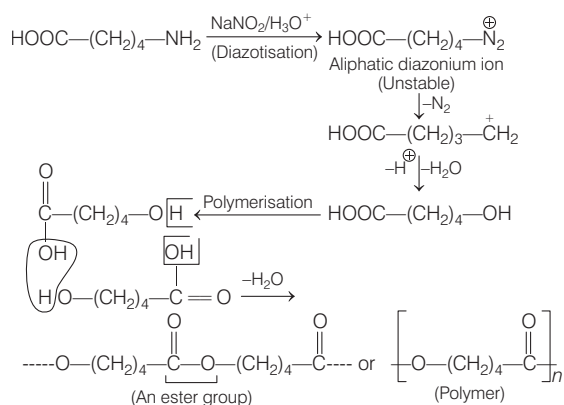
9. On polymerisation, 4-hydroxy butanoic acid will produce a condensation homopolymer by loss of  $\text{H}_2\text{O}$  molecules.



The homopolymer obtained can also be represented as



10. (A) Molecule binding to a site other than the active site of enzyme is called allosteric effect.  
 (B) Molecule binding to the active site of enzyme is called competitive inhibitor.  
 (C) Molecule crucial for communication in the body is called receptor.  
 (D) Molecule binding to the enzyme covalently is called poison.  
 Thus, the correct match is : A → R, B → P, C → Q, D → S
11. Given amino acid on reaction with  $\text{NaNO}_2/\text{H}_3\text{O}^+$  gives diazotisation reaction which further evolves  $-\text{N}_2$  gas along with formation of carbocation. On further reaction with water, it form  $\text{HOOC}-(\text{CH}_2)-\text{OH}$  that undergoes polymerisation to give polymer.



12. The correct match is:

A → (Q) B → (P) C → (R)

(A) **Norethindrone** It is an antifertility drug (Q) containing synthetic progesterone derivative. [Other similar drug, is ethinylestradiol (novestrol)].

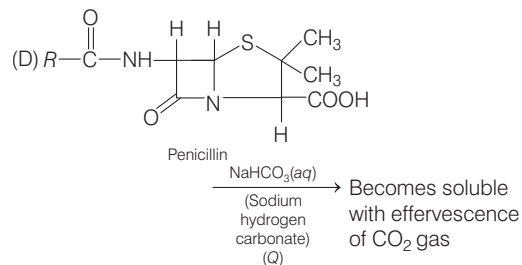
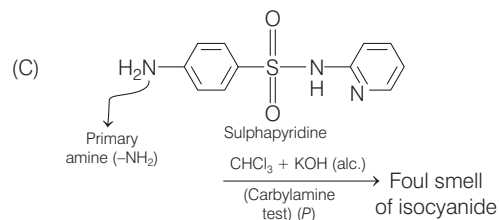
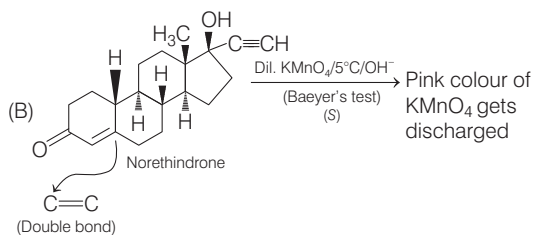
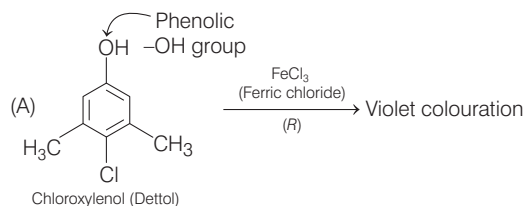
(B) **Ofloxacin** It is an antibiotic (P),

i.e. produced wholly or partly by chemical synthesis with low concentration of microorganism. [Some other similar drugs : Penicillin, chloramphenicol, salvarsan etc.]

(C) **Equanil (meprobamate)** It is a mild tranquilizer for relieving hypertension. It relieves anxiety, stress, excitement by inducing a sense of well being.

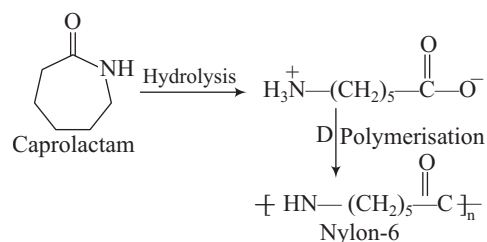
(Other similar drug is chlordiazepoxide.)

13



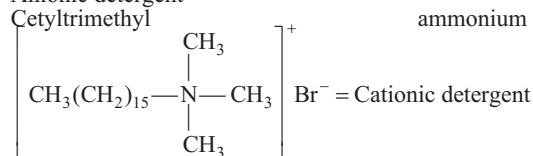
Thus, the correct match is: A → R; B → S; C → P; D → Q

14. Nylon-6 or perlon is prepared by polymerisation of amino caproic acid at high temperature. Caprolactam is first hydrolysed with water to form amino acid which on heating undergoes polymerisation to give nylon-6.



15. High density polythene is used in the manufacture of buckets, dustbins etc.

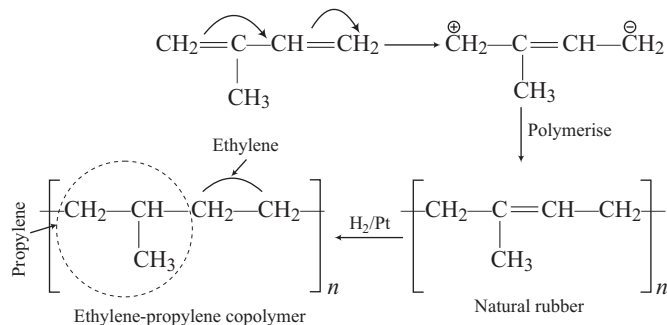
16. Sodium lauryl sulphate  $[(\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OSO}_3^-\text{Na}^+)]$  = Anionic detergent



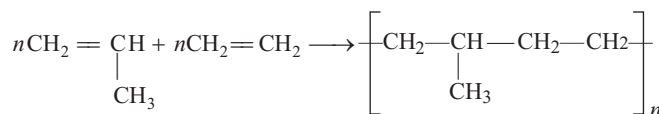
Glyceryl oleate  $[(\text{C}_{17}\text{H}_{32}\text{COO})_3\text{C}_3\text{H}_5]$  = Non-ionic detergent

Sodium stearate  $[\text{C}_{17}\text{H}_{35}\text{COO}^-\text{Na}^+]$  = Anionic soap

17. Natural rubber is formed by polymerisation of isoprene.



This co-polymer is formed from propylene and ethylene.



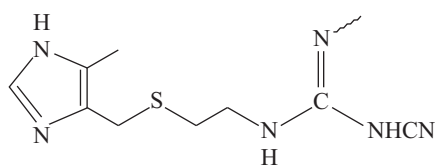
18. (a) Bakelite is used for making gears, protective coating and electrical fittings.  
 (b) Glyptal is used in the manufacture of paints and lacquers.  
 (c) PP is used in the manufacture of textile, packaging materials etc.  
 (d) Polyvinyl chloride (PVC) is used in the manufacture of rain coats, hand bags, leather clothes etc.

19. (a) Polystyrene- manufacturing toys (b) Glyptal- Paints and lacquers  
 (c) Polyvinyl chloride (PVC)- Raincoats (d) Bakelite- computer discs

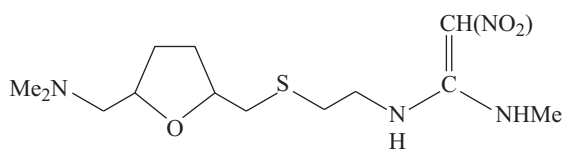
Thus, the correct match is A  $\rightarrow$  (1), B  $\rightarrow$  (1), C  $\rightarrow$  (2), D  $\rightarrow$  (4)

20. The given structure is of aspirin which is used as analgesic.

21. Aluminium hydroxide  $\text{Al}(\text{OH})_3$ , cimetidine and ranitidine are antacids while phenelzine is not.

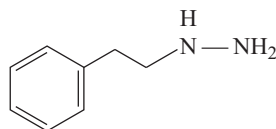


Cimetidine



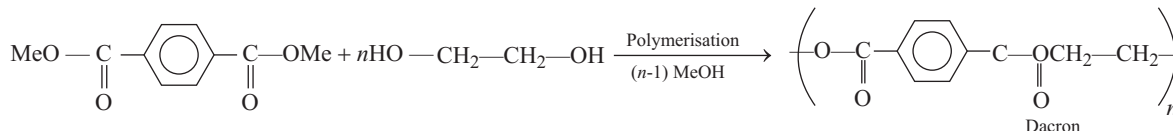
Ranitidine

Phenelzine is a tranquilizer, not an antacid.



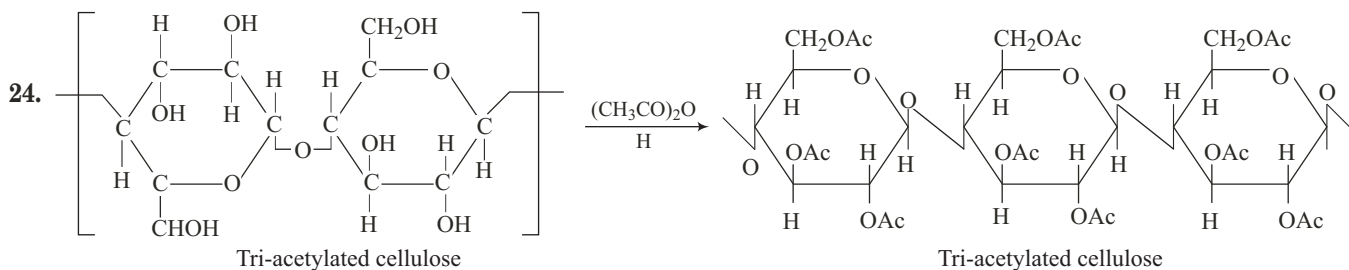
Phenelzine is used as antidepressant drug.

22. Dacron is a condensation polymer of ethylene glycol and methyl terephthalate. Formation of dacron can be shown as



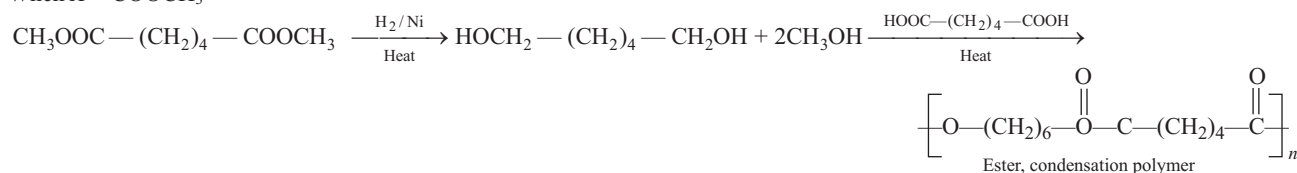
Here, elimination of  $\text{MeOH}$  occurs as a by product. So, this reaction is known as condensation polymerisation.

23. Cellulose and nylons have H-bonding type of intermolecular attraction while poly (vinyl chloride) is polar. Natural rubber is hydrocarbon and has the weakest intermolecular force of attraction, i.e. van der Waals' force of attraction.



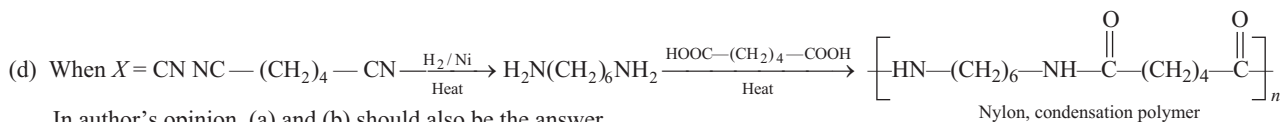
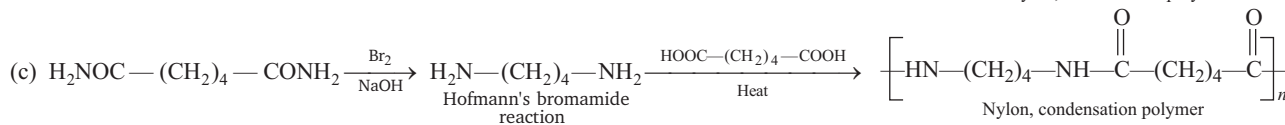
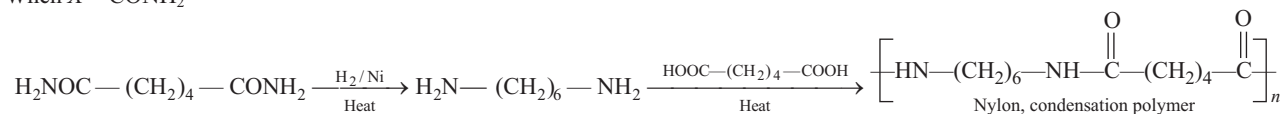
25.  $(\text{CH}_3)_2\text{SiCl}_2 + \text{H}_2\text{O} \rightarrow \text{HO}-\text{Si}(\text{CH}_3)_2-\text{OH} \xrightarrow{\text{Polymerisations}} \text{HO}-\text{Si}(\text{CH}_3)_2-\text{O}-\left[ \text{Si}(\text{CH}_3)_2-\text{O} \right]_n-\text{Si}(\text{CH}_3)_2-\text{OH} \xrightarrow{(\text{CH}_3)_3\text{XSiCl}} \text{CH}_3-\text{Si}(\text{CH}_3)_2-\text{O}-\left[ \text{Si}(\text{CH}_3)_2-\text{O} \right]_n-\text{Si}(\text{CH}_3)_2-\text{CH}_3$
- Linear chain polymer
- Chain terminated linear chain silicone

26. (a) When  $X = \text{COOCH}_3$

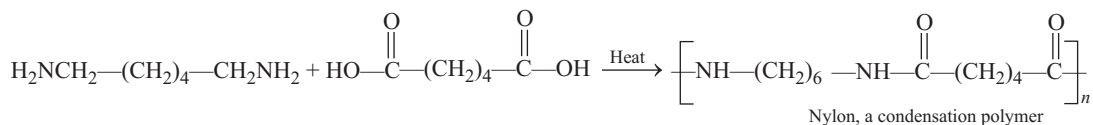
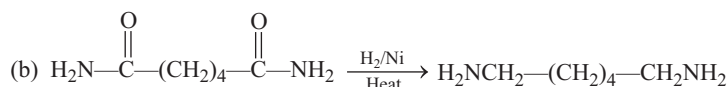
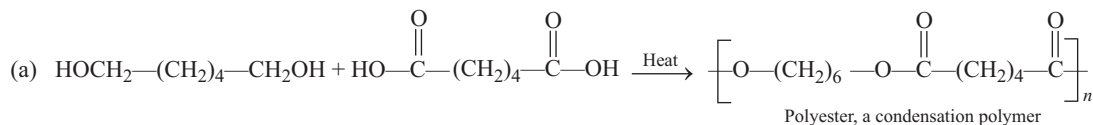


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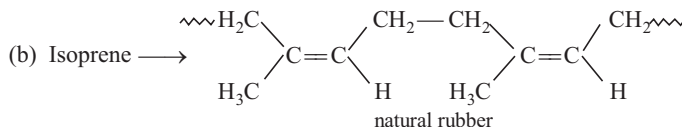
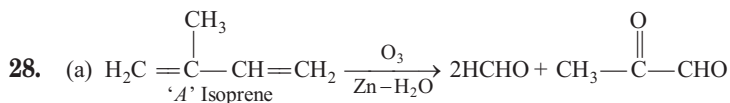
(b) When  $X = \text{CONH}_2$



In author's opinion (a) and (b) should also be the answer.

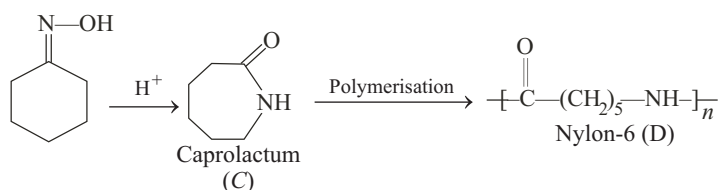


27. (A) Cellulose—a natural polymer of  $\alpha$ -D-glucose, linked by glycoside linkage.  
 (B) Nylon-6, 6—a synthetic polymer of adipic acid and 1,6-diaminohexane. The diacid is linked with diamine through amide linkage.  
 (C) Protein—a natural polymer of  $\alpha$ -amino acids where individual amino acid units are linked by amide linkage.  
 (D) Sucrose—has glycoside linkage, a disaccharide.



29. Zeigler-Natta catalyst, which is a mixture of triethylaluminium ' $(\text{C}_2\text{H}_5)_3\text{Al}$ ' and  $\text{TiCl}_4$ , is used as heterogeneous catalyst in polymerisation of ethylene.

30.



**Download Chapter Test**

<http://tinyurl.com/y45zhmup>

or



# 33

## Environmental Chemistry

### Objective Questions I (Only one correct option)

- The primary pollutant that leads to photochemical smog is  
(2019 Main, 12 April II)  
(a) acrolein (b) nitrogen oxides  
(c) ozone (d) sulphur dioxide
- The correct set of species responsible for the photochemical smog is  
(2019 Main, 12 April I)  
(a)  $\text{N}_2$ ,  $\text{NO}_2$  and hydrocarbons  
(b)  $\text{CO}_2$ ,  $\text{NO}_2$ ,  $\text{SO}_2$  and hydrocarbons  
(c)  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{O}_3$  and hydrocarbons  
(d)  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{O}_3$  and hydrocarbons
- Air pollution that occurs in sunlight is (2019 Main, 10 April II)  
(a) acid rain (b) oxidising smog  
(c) fog (d) reducing smog
- The regions of the atmosphere, where clouds form and where we live, respectively, are (2019 Main, 10 April I)  
(a) stratosphere and stratosphere  
(b) troposphere and troposphere  
(c) troposphere and stratosphere  
(d) stratosphere and troposphere
- The layer of atmosphere between 10 km to 50 km above the sea level is called as (2019 Main, 9 April II)  
(a) stratosphere (b) mesosphere  
(c) thermosphere (d) troposphere
- Excessive release of  $\text{CO}_2$  into the atmosphere results in  
(2019 Main, 9 April I)  
(a) formation of smog (b) depletion of ozone  
(c) polar vortex (d) global warming
- The maximum prescribed concentration of copper in drinking water is (2019 Main, 8 April II)  
(a) 5 ppm (b) 0.5 ppm  
(c) 0.05 ppm (d) 3 ppm
- Assertion (A)** Ozone is destroyed by CFCs in the upper stratosphere.  
**Reason (R)** Ozone holes increase the amount of UV radiation reaching the earth. (2019 Main, 8 April I)  
(a) Assertion and Reason are incorrect.  
(b) Assertion and Reason are both correct and the Reason is the correct explanation for the Assertion.  
(c) Assertion and Reason are correct, but the Reason is not the explanation for the Assertion.  
(d) Assertion is false, but the Reason is correct.
- Which is wrong with respect to our responsibility as a human being to protect our environment? (2019 Main, 8 April I)  
(a) Restricting the use of vehicles  
(b) Avoiding the use of floodlighted facilities  
(c) Setting up compost tin in gardens  
(d) Using plastic bags
- The upper stratosphere consisting of the ozone layer protects us from the sun's radiation that falls in the wavelength region of (2019 Main, 12 Jan II)  
(a) 600 - 750 nm (b) 400 - 550 nm  
(c) 0.8 - 1.5 nm (d) 200 - 315 nm
- The compound that is not a common component of photochemical smog is (2019 Main, 12 Jan II)  
(a)  $\text{CF}_2\text{Cl}_2$  (b)  $\text{H}_3\text{C}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{OONO}_2$   
(c)  $\text{CH}_2 = \text{CHCHO}$  (d)  $\text{O}_3$
- Water samples with BOD values of 4 ppm and 18 ppm, respectively, are (2019 Main, 12 Jan I)  
(a) clean and clean  
(b) highly polluted and clean  
(c) highly polluted and highly polluted  
(d) clean and highly polluted
- The molecule that has minimum/no role in the formation of photochemical smog, is (2019 Main, 12 Jan I)  
(a)  $\text{N}_2$  (b)  $\text{CH}_2 = \text{O}$   
(c)  $\text{NO}$  (d)  $\text{O}_3$
- Taj Mahal is being slowly disfigured and discoloured. This is primarily due to (2019 Main, 11 Jan II)  
(a) water pollution (b) soil pollution  
(c) global warming (d) acid rain
- The higher concentration of which gas in air can cause stiffness of flower buds? (2019 Main, 11 Jan II)  
(a)  $\text{SO}_2$  (b)  $\text{CO}$   
(c)  $\text{CO}_2$  (d)  $\text{NO}_2$
- Peroxyacetyl nitrate (PAN), an eye irritant is produced by (2019 Main, 11 Jan I)  
(a) organic waste  
(b) acid rain  
(c) classical smog  
(d) photochemical smog

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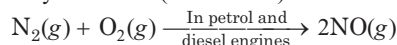
17. The concentration of dissolved oxygen (DO) in cold water can go upto (2019 Main, 11 Jan I)  
 (a) 14 ppm (b) 10 ppm  
 (c) 8 ppm (d) 16 ppm
18. The reaction that is not involved in the ozone layer depletion mechanism in the stratosphere is (2019 Main, 10 Jan II)  
 (a)  $\text{CH}_4 + 2\text{O}_3 \longrightarrow 3\text{CH}_2 = \text{O} + 3\text{H}_2\text{O}$   
 (b)  $\text{Cl}\dot{\text{O}}(\text{g}) + \text{O}(\text{g}) \longrightarrow \dot{\text{Cl}}(\text{g}) + \text{O}_2(\text{g})$   
 (c)  $\text{HOCl}(\text{g}) \xrightarrow{h\nu} \dot{\text{O}}\text{H}(\text{g}) + \dot{\text{Cl}}(\text{g})$   
 (d)  $\text{CF}_2\text{Cl}_2(\text{g}) \xrightarrow{h\nu} \dot{\text{C}}\text{F}_2\text{Cl}(\text{g}) + \dot{\text{C}}\text{F}_2\text{Cl}(\text{g})$
19. Water filled in two glasses *A* and *B* have BOD values of 10 and 20, respectively. The correct statement regarding them, is (2019 Main, 10 Jan I)  
 (a) *A* is more polluted than *B* (b) *A* is suitable for drinking, whereas *B* is not  
 (c) Both *A* and *B* are suitable for drinking  
 (d) *B* is more polluted than *A*
20. The pH of rain water, is approximately (2019 Main, 9 Jan II)  
 (a) 7.5 (b) 6.5  
 (c) 5.6 (d) 7.0
21. The condition for methemoglobinemia by drinking water is (2019 Main, 9 Jan II)  
 (a) > 50 ppm nitrate (b) > 50 ppm chloride  
 (c) > 50 ppm lead (d) > 100 ppm sulphate
22. A water sample has ppm level concentration of the following metals: Fe = 0.2; Mn = 5.0; Cu = 3.0; Zn = 5.0. The metal that makes the water sample unsuitable for drinking is (2019 Main, 9 Jan I)  
 (a) Cu (b) Fe  
 (c) Mn (d) Zn

## Answers

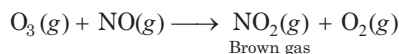
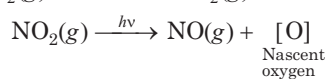
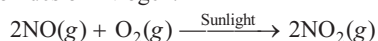
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|--------|---------|---------|---------|---------|---------|---------|---------|
| 1. (b) | 2. (c)  | 3. (b)  | 4. (b)  | 13. (a) | 14. (d) | 15. (a) | 16. (d) |
| 5. (a) | 6. (d)  | 7. (d)  | 8. (c)  | 17. (b) | 18. (a) | 19. (d) | 20. (c) |
| 9. (d) | 10. (d) | 11. (a) | 12. (d) | 21. (a) | 22. (c) |         |         |

## Hints & Solutions

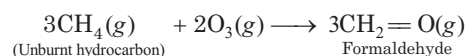
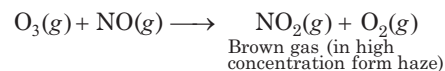
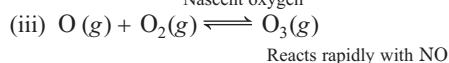
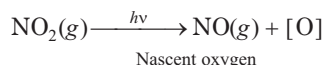
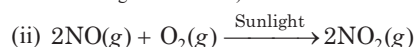
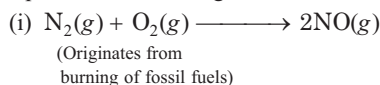
1. The primary pollutant that leads to photochemical smog is nitrogen oxides. Burning of fossil fuels such as petrol and diesel in automobiles, reaction between nitrogen and oxygen and other such reactions result in a variety of pollutants, two main of which are hydrocarbons (unburnt fuel) and nitric oxide (NO).



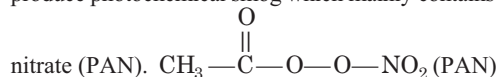
When the concentration of these pollutants is sufficiently high, a chain reaction initiate because of the interaction of sunlight with oxides of nitrogen.



2. The correct set of species responsible for the photochemical smog is NO, NO<sub>2</sub>, O<sub>3</sub> and hydrocarbons. Photochemical smog appears in warm, dry and sunny climate which are obtained by the action of sunlight on unsaturated hydrocarbons and nitrogen oxides. Following reactions are involved during the formation of photochemical smog.



3. In sunlight oxidising smog or photochemical smog or Los-Angeles smog is formed. This smog is brown in colour. It occurs in warm, dry and sunny climate. In presence of sunlight, NO<sub>x</sub> (N-oxides), O<sub>2</sub> and unburnt hydrocarbons of air combine to produce photochemical smog which mainly contains peroxyacetyl



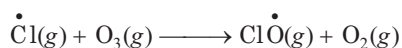
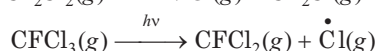
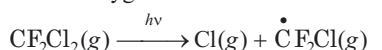
4. The lowest region of atmosphere is troposphere which extends upto the height of 10 km (approx) from sea level. We live in the tropospheric region. It contains air, water vapour and dust which can form clouds with the help of strong air movement. Above the troposphere, stratospheric region extends upto 50 km from sea level. It contains mainly N<sub>2</sub>, O<sub>2</sub>, O<sub>3</sub> and little water vapour. O<sub>3</sub> in the stratosphere absorbs 99.5% of the sun's harmful UV radiations and thus protects the lives on the earth.
5. The atmosphere between the heights 10 to 50 km above the sea level is stratosphere. Atmosphere is not of the same thickness at heights.
6. The effect of release of CO<sub>2</sub> gas into atmosphere is global warming.

7. According to W.H.O. and US environmental protection agency guidelines, maximum allowable concentration of metals in drinking water are as follows :

| Metal | Maximum concentration<br>(ppm or mg dm <sup>-3</sup> ) |
|-------|--------------------------------------------------------|
| Cd    | 0.005                                                  |
| Mn    | 0.05 (option-c)                                        |
| Al    | 0.2                                                    |
| Fe    | 0.2                                                    |
| Cu    | 3.0 (option-d)                                         |
| Zn    | 5.0 (option-a)                                         |

8. Ozone is destroyed by CFCs in the upper stratosphere.

These compounds ultimately reach the stratosphere where they get broken down by powerful UV radiations and release chlorine free radical. The chlorine free radicals react with ozone and cause its depletion by converting it into chlorine monoxide radical and molecular oxygen.



Ozone holes increase the amount of UV radiation reaching the earth. These radiations can cause skin cancer, sunburns, ageing of skin.

9. Using plastic bags is wrong with respect to responsibility as a human being to protect our environment. Plastic bags are non-biodegradable in nature. It remains in the environment as such and does not degraded by bacteria. If it is not disposed properly then it may lead serious threat to the environment. The activities that can be used to protect our environment are as follows:

- Restricting the use of vehicles.
- Avoiding the use of flood lighted facilities.
- Setting up compost tin in gardens.

10. Sun emits UV-radiations, which according to following EM categorisation have the wavelength range from 1 nm to 400 nm.

| Type             | Wavelength range            |
|------------------|-----------------------------|
| Radio wave       | > 0.1 m                     |
| Microwave        | 0.1 m to 1 mm               |
| Infrared wave    | 1 mm to 700 nm              |
| Visible rays     | 700 nm to 400 nm            |
| Ultraviolet rays | 400 nm to 1 nm              |
| X-rays           | 1 nm to 10 <sup>-3</sup> nm |
| Gamma rays       | < 10 <sup>-3</sup> nm       |

Thus, option (d) with 200-315 nm range is the correct option.

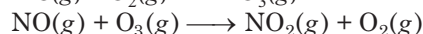
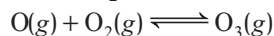
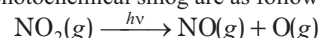
11. Freons or CFCs or chlorofluoro carbons, i.e.  $\text{CF}_2\text{Cl}_2$  is not the common component of photochemical smog. This smog is produced as the result of tropospheric pollution while freons are the components of stratospheric pollution. These are infact considered as the major cause of ozone layer depletion.

12. The amount of oxygen required by bacteria to break down the organic matter present in a certain value of a sample of water is called biochemical oxygen demand (BOD). The amount of BOD in the water is a measure of the amount of organic material in the water, in terms of how much oxygen will be required to break it down biologically. Clean water would have BOD value of less than 5ppm whereas highly polluted water would have BOD value of 17 ppm or more.

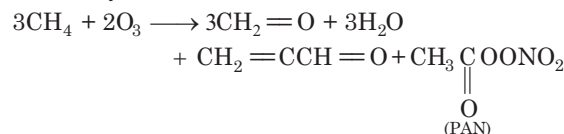
BOD value of clean water = 4 ppm

BOD value of highly polluted water = 18 ppm

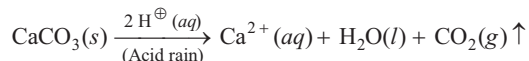
13.  $\text{N}_2$  molecule has minimum role in the formation of photochemical smog. While  $\text{CH}_2 = \text{O}$ ,  $\text{O}_3$  and  $\text{NO}$  has major role. When fossil fuels are burnt, a variety of pollutants are emitted. Two of them are hydrocarbons (unburnt) and  $\text{NO}$ . When these pollutants build upto high levels, a chain reaction occurs from their interaction with sunlight. The reactions involved in the formation of photochemical smog are as follows:



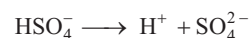
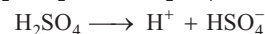
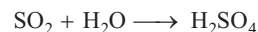
$\text{O}_3$  reacts with unburnt hydrocarbons to produce chemicals such as formaldehyde, acrolein and PAN.



14. Acid rain (pH = 3.5 – 5.6) constitutes strong acids like  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_3$  which slowly react with marble ( $\text{CaCO}_3$ ) of Taj Mahal and make it disfigured and discoloured. Here,  $\text{CaCO}_3$  (marble) gets dissolved in acids.



15. Organic pigments (colourents) present in flower buds retain their colour in the oxidised form of the pigment as their nature is itself oxidising in nature. When they comes in contact with moist  $\text{SO}_2$  (acid rain) of higher concentration, they get decoloured and stiff.



Due to the release of  $\text{H}^+$  ion (acid), the flower get decoloured and stiff.

As a result, flower eventually falls off from plants.

16. Molecular formula of peroxyacetyl nitrate (PAN) is

$\text{CH}_3 - \overset{\text{O}}{\underset{||}{\text{C}}} - \text{O} - \text{O} - \text{NO}_2$ . It is a secondary pollutant. It is present in photochemical smog (oxidising or Los Angeles smog). PAN is a powerful lachrymator or tear producer and it also causes breathing troubles.

17. Dissolved oxygen (DO) is the oxygen dissolved in water either from atmosphere or by photosynthesis. The lower the concentration of DO in a water sample, the more polluted is the water sample.

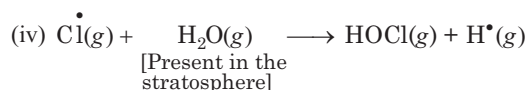
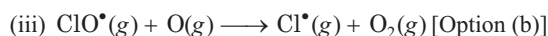
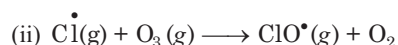
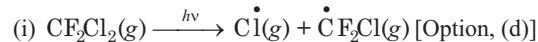


## 472 Environmental Chemistry

The concentration range of dissolved oxygen (DO) in cold water reaches upto 10 ppm, but that in normal water (at room temperature) is within 5 ppm.

18.  $\text{CH}_4$  is not present in the stratosphere and also it cannot diffuse or escape into the stratosphere like freon-12 ( $\text{CF}_2\text{Cl}_2$ ) from the atmosphere.

In the stratosphere, ozone layer depletion take place mainly by chlorofluorocarbons (CFCs) like  $\text{CF}_2\text{Cl}_2$  and the mechanism of ozone layer depletion can be shown as:



$\Rightarrow$  One  $\text{Cl}^\bullet$  can destroy or deplete  $10^5$   $\text{O}_3$  molecules.

As (i) reaction is involved in the formation of photochemical smog, not in ozone layer depletion. So option (a) is correct.

19. BOD is defined as the amount of oxygen required by bacteria to break down the organic matter present in a certain volume of a

sample of water. Clean water or drinking water has a BOD value  $< 5$  ppm.

So, water filled with A, BOD = 10 ppm is polluted and water filled with B, BOD = 20 ppm, is also polluted. But, B is more polluted than A.

20. In clean air, rain water picks up some acidic oxides like  $\text{CO}_2$  and  $\text{SO}_2$  (obtained from volcanic eruptions). These substance make the rain slightly acidic ( $\text{pH} = 5.6 - 6$ ).

21. According to EEC (European Environment Commission), excess of  $\text{NO}_3^-$  ( $> 50$  ppm) in drinking water may lead to methemoglobinemia ('Blue baby syndrome'). It also may cause stomach-cancer.

22. For drinking water, the maximum recommended levels of some metals, set by European Environment Commission (EEC) is

| Metal | Max. concentration in ppm |
|-------|---------------------------|
| Zn    | 5                         |
| Mn    | 0.05                      |
| Fe    | 0.2                       |
| Cu    | 3                         |

As the concentration of Mn in the given water sample is more than the recommended concentration. Thus, it makes water unsuitable for drinking.



# JEE ADVANCED

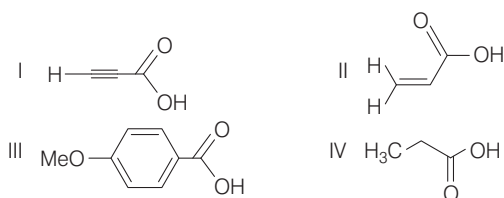
## Solved Paper 2019

### Paper 1

#### Section 1 (Maximum Marks : 12)

- This section contains **FOUR (04)** questions.
- Each question has **FOUR** options. **ONLY ONE** of these four options is the correct answer.
- For each question, choose the option corresponding to the correct answer.
- Answer to each question will be evaluated according to the following marking scheme:  
*Full Marks* : +3 If **ONLY** the correct options is chosen.  
*Zero Marks* : 0 If none of the options is chosen. (i.e. the question is unanswered)  
*Negative Marks* : -1 In all other cases.

1. The correct order of acid strength of the following carboxylic acids is



- (a) III > II > I > IV  
 (b) I > II > III > IV  
 (c) II > I > IV > III  
 (d) I > III > II > IV

2. The green colour produced in the borax bead test of a chromium (III) salt is due to

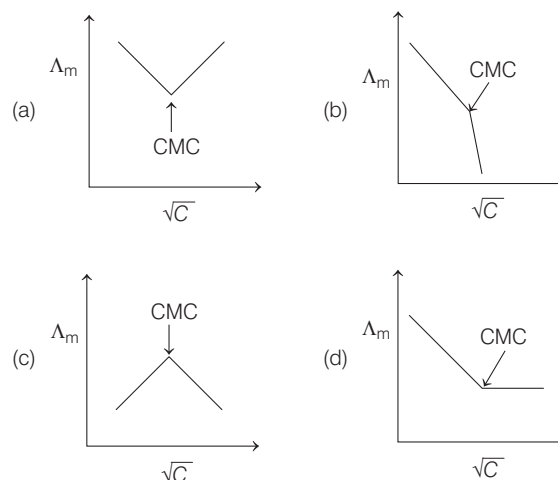
- (a)  $\text{Cr}_2\text{O}_3$  (b) CrB  
 (c)  $\text{Cr}(\text{BO}_2)_3$  (d)  $\text{Cr}_2(\text{B}_4\text{O}_7)_3$

3. Calamine, malachite, magnetite and cryolite, respectively, are

- (a)  $\text{ZnCO}_3$ ,  $\text{CuCO}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Na}_3\text{AlF}_6$   
 (b)  $\text{ZnSO}_4$ ,  $\text{CuCO}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{AlF}_3$   
 (c)  $\text{ZnSO}_4$ ,  $\text{Cu}(\text{OH})_2$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{Na}_3\text{AlF}_6$   
 (d)  $\text{ZnCO}_3$ ,  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{Na}_3\text{AlF}_6$

4. Molar conductivity ( $\Lambda_m$ ) of aqueous solution of sodium stearate, which behaves as a strong electrolyte, is recorded at varying concentrations ( $C$ ) of sodium stearate. Which one of the following plots provides the correct representation of micelle formation in the solution?

(critical micelle concentration (CMC) is marked with an arrow in the figures)



## 2 JEE Advanced Solved Paper 2019

### Section 2 (Maximum Marks : 32)

- This section contains **EIGHT (08)** questions.
- Each question has **FOUR** options. **ONE OR MORE THAN ONE** of these four option(s) is (are) correct option(s).
- For each question, choose the option(s) corresponding to (all) the correct answer(s).
- Answer to each question will be evaluated according to the following marking scheme:
 

*Full Marks* : +4 If only (all) the correct option(s) is (are) chosen.  
*Partial Marks* : +3 If all the four options are correct but ONLY three options are chosen.  
*Partial Marks* : +2 If three or more options are correct but ONLY two options are chosen, both of which are correct and both of which are correct.  
*Partial Marks* : +1 If two or more options are correct but ONLY one option is chosen and it is a correct option;  
*Zero Marks* : 0 If none of the option is chosen (i.e., the question is unanswered);  
*Negative Marks* : -1 In all other cases.
- For example, in a question, if (A), (B) and (D) are the ONLY three options corresponding to correct answers, then
 

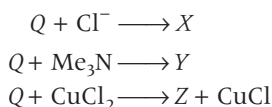
|                                                   |                                              |
|---------------------------------------------------|----------------------------------------------|
| choosing ONLY (A), (B) and (D) will get + 4 marks | choosing ONLY (A) and (B) will get + 2 marks |
| choosing ONLY (A) and (D) will get + 2 marks      | choosing ONLY (B) and (D) will get + 2 marks |
| choosing ONLY (A) will get + 1 marks              | choosing ONLY (B) will get + 1 marks         |
| choosing ONLY (D) will get + 1 marks              |                                              |

 choosing no option (i.e., the question is unanswered) will get 0 marks; and choosing any other combination of options will get - 1 mark.

5. Choose the reaction(s) from the following options, for which the standard enthalpy of reaction is equal to the standard enthalpy of formation.

- (a)  $2\text{C}(g) + 3\text{H}_2(g) \longrightarrow \text{C}_2\text{H}_6(g)$   
 (b)  $2\text{H}_2(g) + \text{O}_2(g) \longrightarrow 2\text{H}_2\text{O}(l)$   
 (c)  $\frac{3}{2}\text{O}_2(g) \longrightarrow \text{O}_3(g)$   
 (d)  $\frac{1}{8}\text{S}_8(s) + \text{O}_2(g) \longrightarrow \text{SO}_2(g)$

6. A tin chloride  $Q$  undergoes the following reactions (not balanced)

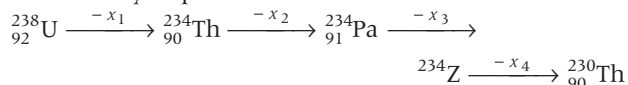


$X$  is a monoanion having pyramidal geometry. Both  $Y$  and  $Z$  are neutral compounds.

Choose the correct option(s).

- (a) There is a coordinate bond in  $Y$   
 (b) The central atom in  $Z$  has one lone pair of electrons  
 (c) The oxidation state of the central atom in  $Z$  is + 2  
 (d) The central atom in  $X$  is  $sp^3$  hybridised

7. In the decay sequence.



$x_1, x_2, x_3$  and  $x_4$  are particles/radiation emitted by the respective isotopes. The correct option(s) is(are)

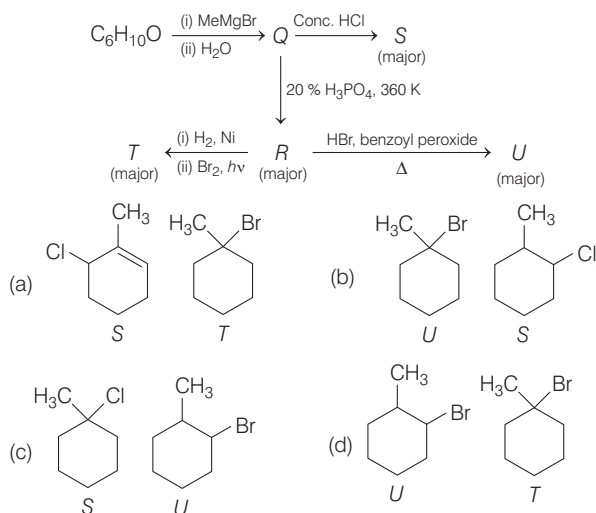
- (a)  $Z$  is an isotope of uranium  
 (b)  $x_2$  is  $\beta^-$

- (c)  $x_1$  will deflect towards negatively charged plate  
 (d)  $x_3$  is  $\gamma$ -ray

8. Which of the following statement(s) is(are) correct regarding the root mean square speed ( $U_{\text{rms}}$ ) and average translational kinetic energy ( $E_{\text{av}}$ ) of a molecule in a gas at equilibrium?

- (a)  $U_{\text{rms}}$  is inversely proportional to the square root of its molecular mass  
 (b)  $U_{\text{rms}}$  is doubled when its temperature is increased four times  
 (c)  $E_{\text{av}}$  is doubled when its temperature is increased four times  
 (d)  $E_{\text{av}}$  at a given temperature does not depend on its molecular mass

9. Choose the correct option(s) for the following set of reactions.



10. Which of the following statement(s) is(are) true?

- (a) The two six-membered cyclic hemiacetal forms of D-(+)-glucose are called anomers
- (b) Oxidation of glucose with bromine water gives glutamic acid
- (c) Monosaccharides cannot be hydrolysed to given polyhydroxy aldehydes and ketones
- (d) Hydrolysis of sucrose gives dextrorotatory glucose and laevorotatory fructose

11. Fusion of  $\text{MnO}_2$  with  $\text{KOH}$  in presence of  $\text{O}_2$  produces a salt  $W$ . Alkaline solution of  $W$  upon electrolytic oxidation yields another salt  $X$ . The manganese containing ions present in  $W$  and  $X$ , respectively, are  $Y$  and  $Z$ . Correct statement(s) is (are)

- (a) Both  $Y$  and  $Z$  are coloured and have tetrahedral shape
- (b)  $Y$  is diamagnetic in nature while  $Z$  is paramagnetic
- (c) In both  $Y$  and  $Z$ ,  $\pi$ -bonding occurs between  $p$ -orbitals of oxygen and  $d$ -orbitals of manganese
- (d) In aqueous acidic solution,  $Y$  undergoes disproportionation reaction to give  $Z$  and  $\text{MnO}_2$

12. Each of the following options contains a set of four molecules. Identify the option(s) where all four molecules possess permanent dipole moment at room temperature.

- (a)  $\text{SO}_2$ ,  $\text{C}_6\text{H}_5\text{Cl}$ ,  $\text{H}_2\text{Se}$ ,  $\text{BrF}_5$
- (b)  $\text{BeCl}_2$ ,  $\text{CO}_2$ ,  $\text{BCl}_3$ ,  $\text{CHCl}_3$
- (c)  $\text{NO}_2$ ,  $\text{NH}_3$ ,  $\text{POCl}_3$ ,  $\text{CH}_3\text{Cl}$
- (d)  $\text{BF}_3$ ,  $\text{O}_3$ ,  $\text{SF}_6$ ,  $\text{XeF}_6$

### Section 3 (Maximum Marks : 18)

- This section contains **SIX (06)** questions. The answer to each question is a **NUMERICAL VALUE**.
- Four each question, enter the correct numerical value of the answer using the mouse and the on-screen virtual numeric keypad in the place designated to enter the answer. If the numerical value has more than two decimal places, truncate/round-off the value to TWO decimal places.
- Answer to each question will be evaluated according to the following marking scheme:  
Full Marks : + 3 If ONLY the correct numerical value is entered.  
Zero Marks : 0 In all other cases.

13. Among  $\text{B}_2\text{H}_6$ ,  $\text{B}_3\text{N}_3\text{H}_6$ ,  $\text{N}_2\text{O}$ ,  $\text{N}_2\text{O}_4$ ,  $\text{H}_2\text{S}_2\text{O}_3$  and  $\text{H}_2\text{S}_2\text{O}_8$ , the total number of molecules containing covalent bond between two atoms of the same kind is .....

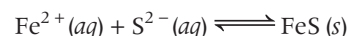
14. On dissolving 0.5 g of a non-volatile non-ionic solute to 39 g of benzene, its vapour pressure decreases from 650 mmHg to 640 mmHg. The depression of freezing point of benzene (in K) upon addition of the solute is ..... (Given data : Molar mass and the molal freezing point depression constant of benzene are  $78 \text{ g mol}^{-1}$  and  $5.12 \text{ K kg mol}^{-1}$ , respectively).

15. Consider the kinetic data given in the following table for the reaction  $A + B + C \longrightarrow \text{Product}$

| Experiment No. | [A] ( $\text{mol dm}^{-3}$ ) | [B] ( $\text{mol dm}^{-3}$ ) | [C] ( $\text{mol dm}^{-3}$ ) | Rate of reaction ( $\text{mol dm}^{-3}\text{s}^{-1}$ ) |
|----------------|------------------------------|------------------------------|------------------------------|--------------------------------------------------------|
| 1              | 0.2                          | 0.1                          | 0.1                          | $6.0 \times 10^{-5}$                                   |
| 2              | 0.2                          | 0.2                          | 0.1                          | $6.0 \times 10^{-5}$                                   |
| 3              | 0.2                          | 0.1                          | 0.2                          | $12 \times 10^{-4}$                                    |
| 4              | 0.3                          | 0.1                          | 0.1                          | $9.0 \times 10^{-5}$                                   |

The rate of the reaction for  $[A] = 0.15 \text{ mol dm}^{-3}$ ,  $[B] = 0.25 \text{ mol dm}^{-3}$  and  $[C] = 0.15 \text{ mol dm}^{-3}$  is found to be  $Y \times 10^{-5} \text{ mol dm}^{-3}\text{s}^{-1}$ . The value of  $Y$  is .....

16. For the following reaction, the equilibrium constant  $K_c$  at 298 K is  $1.6 \times 10^{17}$ .

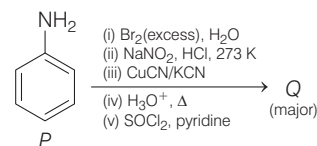


When equal volumes of  $0.06 \text{ M Fe}^{2+}(\text{aq})$  and  $0.2 \text{ M S}^{2-}(\text{aq})$  solutions are mixed, the equilibrium concentration of  $\text{Fe}^{2+}(\text{aq})$  is found by  $Y \times 10^{-17} \text{ M}$ . The value of  $Y$  is .....

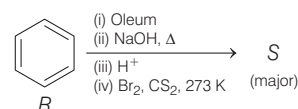
17. At 143 K, the reaction of  $\text{XeF}_4$  with  $\text{O}_2\text{F}_2$  produces a xenon compound  $Y$ . The total number of lone pair(s) of electrons present on the whole molecule of  $Y$  is .....

18. Schemes 1 and 2 describe the conversion of  $P$  to  $Q$  and  $R$  to  $S$ , respectively. Scheme 3 describes the synthesis of  $T$  from  $Q$  and  $S$ . The total number of Br atoms in a molecule of  $T$  is .....

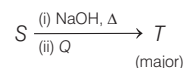
#### Scheme 1



#### Scheme 2



#### Scheme 3



# Paper 2

## Section 1 (Maximum Marks : 32)

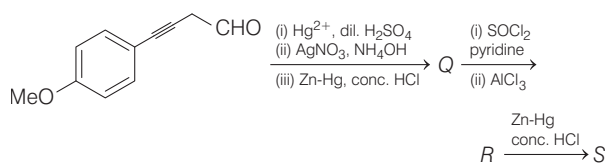
- This section contains **EIGHT (08)** questions.
- Each question has **FOUR** options for correct answer(s). **ONE OR MORE THAN ONE** of these four option(s) is (are) correct option(s).
- For each question, choose the correct option(s) to answer the question.
- Answer to each question will be evaluated according to the following marking scheme:
 

*Full Marks* : +4 If only (all) the correct option(s) is (are) chosen.  
*Partial Marks* : +3 If all the four options are correct but ONLY three options are chosen.  
*Partial Marks* : +2 If three or more options are correct but ONLY two options are chosen, both of which are correct options.  
*Partial Marks* : +1 If two or more options are correct but ONLY one option is chosen and it is a correct option.  
*Zero Marks* : 0 If none of the options is chosen (i.e. the question is unanswered).  
*Negative Marks* : -2 In all other cases.
- For example:** in a question, if (A), (B) and (D) are the ONLY three options corresponding to correct answer, then
 

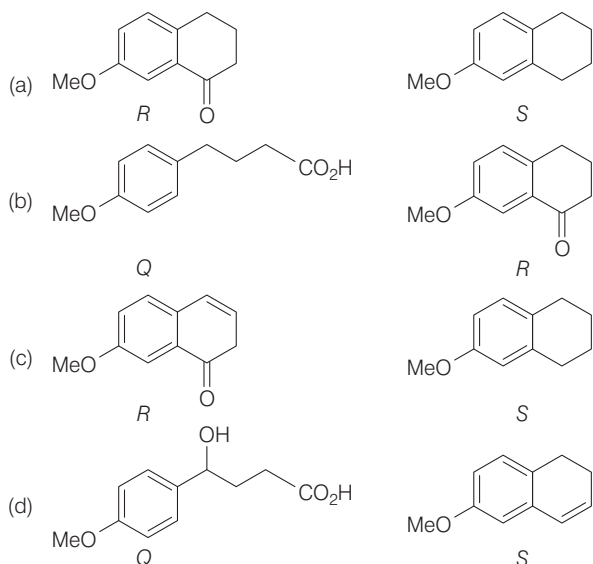
|                                                   |                                              |
|---------------------------------------------------|----------------------------------------------|
| choosing ONLY (A), (B) and (D) will get +4 marks; | choosing ONLY (A) and (B) will get +2 marks; |
| choosing ONLY (A) and (D) will get +2 marks;      | choosing ONLY (B) and (D) will get +2 marks; |
| choosing ONLY (A) will get +1 mark;               | choosing ONLY (B) will get +1 mark;          |
| choosing ONLY (D) will get +1 mark;               |                                              |

 choosing no option (i.e. the question is unanswered) will get 0 marks; and  
 choosing any other combination of options will -1 mark.

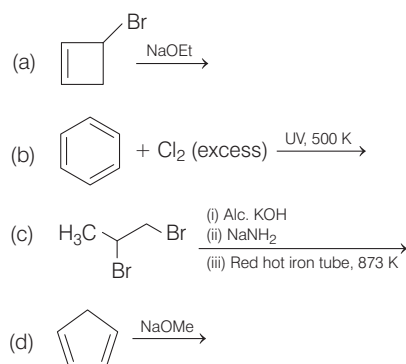
1. Choose the correct option(s) for the following reaction sequence



Consider Q, R and S as major products.

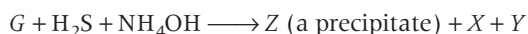
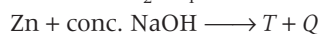


2. Choose the correct option(s) that give(s) an aromatic compound as the major product.



3. The ground state energy of hydrogen atom is -13.6 eV. Consider an electronic state  $\Psi$  of  $\text{He}^+$  whose energy, azimuthal quantum number and magnetic quantum number are -3.4 eV, 2 and 0, respectively. Which of the following statement(s) is(are) true for the state  $\Psi$ ?
- (a) It is a 4d state  
 (b) The nuclear charge experienced by the electron in this state is less than  $2e$ , where  $e$  is the magnitude of the electronic charge  
 (c) It has 2 angular nodes  
 (d) It has 3 radial nodes

4. Consider the following reactions (unbalanced).



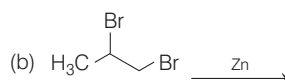
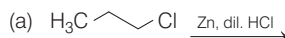
Choose the correct option(s).

- (a) The oxidation state of Zn in T is +1  
 (b) R is a V-shaped molecule  
 (c) Bond order of Q is 1 in its ground state  
 (d) Z is dirty white in colour
5. With reference to *aqua-regia*, choose the correct option(s).  
 (a) *Aqua-regia* is prepared by mixing conc. HCl and conc. HNO<sub>3</sub> in 3 : 1 (v / v) ratio  
 (b) The yellow colour of *aqua-regia* is due to the presence of NOCl and Cl<sub>2</sub>  
 (c) Reaction of gold with *aqua-regia* produces an anion having Au in +3 oxidation state  
 (d) Reaction of gold with *aqua regia* produces NO<sub>2</sub> in the absence of air
6. Choose the correct option(s) from the following.  
 (a) Teflon is prepared by heating tetrafluoroethene in presence of a persulphate catalyst at high pressure

- (b) Natural rubber is polyisoprene containing *trans* alkene units  
 (c) Cellulose has only  $\alpha$ -D-glucose units that are joined by glycosidic linkages  
 (d) Nylon-6 has amide linkages

7. The cyanide process of gold extraction involves leaching out gold from its ore with CN<sup>-</sup> in the presence of Q in water to form R. Subsequently, R is treated with T to obtain Au and Z. Choose the correct option(s).  
 (a) Q is O<sub>2</sub> (b) Z is [Zn(CN)<sub>4</sub>]<sup>2-</sup>  
 (c) T is Zn (d) R is [Au(CN)<sub>4</sub>]<sup>-</sup>

8. Which of the following reactions produce(s) propane as a major product?



## Section 2 (Maximum Marks : 18)

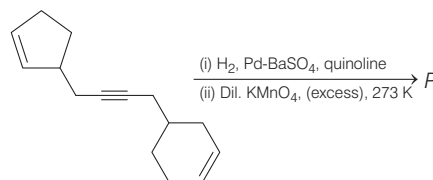
- This section contains **SIX (06)** questions. The answer to each question is a **NUMERICAL VALUE**.
- For each question, enter the correct numerical value of the answer using the mouse and the on-screen virtual numeric keypad in the place designated to enter the answer. If the numerical value has more than two decimal places, **truncate/round-off** the value to **TWO** decimal places.
- Answer to each question will be evaluated according to the following marking scheme:  
 Full Marks : +3 If ONLY the correct numerical value is entered as answer.  
 Zero Marks : 0 In all other cases.

9. The decomposition reaction

$2\text{N}_2\text{O}_5(\text{g}) \xrightarrow{\Delta} 2\text{N}_2\text{O}_4(\text{g}) + \text{O}_2(\text{g})$  is started in a closed cylinder under isothermal isochoric condition at an initial pressure of 1 atm. After  $Y \times 10^3$  s, the pressure inside the cylinder is found to be 1.45 atm. If the rate constant of the reaction is  $5 \times 10^{-4} \text{ s}^{-1}$ , assuming ideal gas behaviour, the value of Y is .....

10. The mole fraction of urea in an aqueous urea solution containing 900 g of water is 0.05. If the density of the solution is  $1.2 \text{ g cm}^{-3}$ , then molarity of urea solution is ..... (Given data : Molar masses of urea and water are  $60 \text{ g mol}^{-1}$  and  $18 \text{ g mol}^{-1}$ , respectively)

11. Total number of hydroxyl groups present in a molecule of the major product P is .....



12. Total number of *cis* N—Mn—Cl bond angles (that is Mn—N and Mn—Cl bonds in *cis* positions) present in a molecule of *cis* [Mn(en)<sub>2</sub>Cl<sub>2</sub>] complex is .....  
 (en = NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)
13. The amount of water produced (in g) in the oxidation of 1 mole of rhombic sulphur by conc. HNO<sub>3</sub> to a compound with the highest oxidation state of sulphur is ..... (Given data : Molar mass of water =  $18 \text{ g mol}^{-1}$ )
14. Total number of isomers considering both structural and stereoisomers of cyclic ethers with the molecular formula C<sub>4</sub>H<sub>8</sub>O is .....

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### Section 3 (Maximum Marks : 12)

- This section contains **TWO (02)** List-Match sets.
- Each List-Match set has **TWO (02)** Multiple Choice Questions.
- Each List-Match set has two lists : List-I and List-II
- List-I has **Four** entries (I), (II), (III) and (IV) and **List-II** has **Six** entries (P), (Q), (R), (S), (T) and (U).
- FOUR** options are given in each Multiple Choice Question based on **List-I** and **List-II** and **ONLY ONE** of these four options satisfies the condition asked in the Multiple Choice Questions.
- Answer to each question will be evaluated according to the following marking scheme :  
**Full Marks** : +3 If ONLY the option corresponding to the correct combination is chosen:  
**Zero Marks** : 0 If none of the options is chosen (i.e. the question is unanswered).  
**Negative Marks** : -1 In all other cases.

Answer the following by appropriately matching the lists based on the information given in the paragraph.

- 15.** Consider the Bohr's model of a one-electron atom where the electron moves around the nucleus. In the following List-I contains some quantities for the  $n$ th orbit of the atom and List-II contains options showing how they depend on  $n$ .

| List-I                                                    | List-II               |
|-----------------------------------------------------------|-----------------------|
| (I) Radius of the $n$ th orbit                            | (P) $\propto n^{-2}$  |
| (II) Angular momentum of the electron in the $n$ th orbit | (Q) $\propto n^{-1}$  |
| (III) Kinetic energy of the electron in the $n$ th orbit  | (R) $\propto n^0$     |
| (IV) Potential energy of the electron in the $n$ th orbit | (S) $\propto n^1$     |
|                                                           | (T) $\propto n^2$     |
|                                                           | (U) $\propto n^{1/2}$ |

Which of the following options has the correct combination considering List-I and List-II?

- (a) (III), (P)                      (b) (III), (S)  
 (c) (IV), (U)                    (d) (IV), (Q)

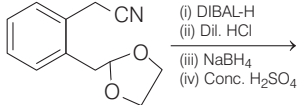
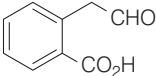
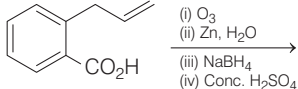
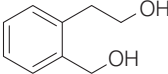
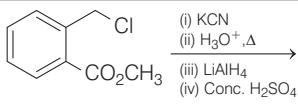
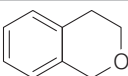
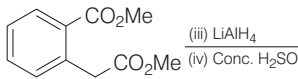
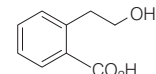
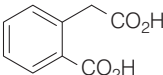
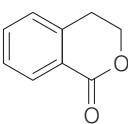
- 16.** Consider the Bohr's model of a one-electron atom where the electron moves around the nucleus. In the following List-I contains some quantities for the  $n$ th orbit of the atom and List-II contains options showing how they depend on  $n$ .

| List-I                                                    | List-II               |
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| (I) Radius of the $n$ th orbit                            | (P) $\propto n^{-2}$  |
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| (IV) Potential energy of the electron in the $n$ th orbit | (S) $\propto n^1$     |
|                                                           | (T) $\propto n^2$     |
|                                                           | (U) $\propto n^{1/2}$ |

Which of the following options has the correct combination considering List-I and List-II?

- (a) (II), (R)                      (b) (I), (P)  
 (c) (I), (T)                      (d) (II), (Q)

- 17.** List-I includes starting materials and reagents of selected chemical reactions. List-II gives structures of compounds that may be formed as intermediate products and/or final products from the reactions of List-I.

| List-I                                                                                      | List-II                                                                                   |
|---------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------|
| (I)    | (P)  |
| (II)   | (Q)  |
| (III)  | (R)  |
| (IV)   | (S)  |
|                                                                                             | (T)  |
|                                                                                             | (U)  |

Which of the following options has correct combination considering List-I and List-II?

- (a) (III), (S), (R)  
 (b) (IV), (Q), (R)  
 (c) (III), (T), (U)  
 (d) (IV), (Q), (U)

18. List-I includes starting materials and reagents of selected chemical reactions. List-II gives structures of compounds that may be formed as intermediate products and/or final products from the reactions of List-I.

| List-I | List-II |
|--------|---------|
| (I)    | (P)     |
| (II)   | (Q)     |
| (III)  | (R)     |

| List-I | List-II |
|--------|---------|
| (IV)   | (S)     |
|        | (T)     |
|        | (U)     |

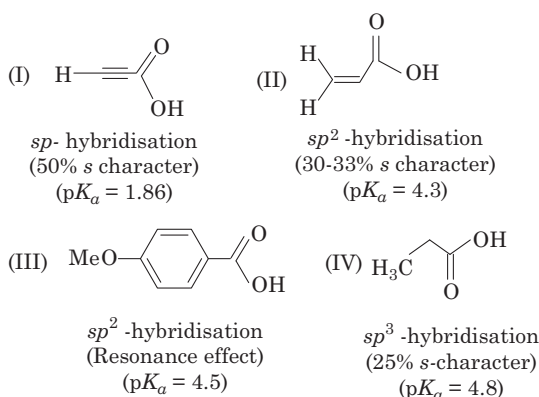
Which of the following options has correct combination considering List-I and List-II?

- (a) (II), (P), (S), (U)      (b) (I), (Q), (T), (U)  
(c) (II), (P), (S), (T)      (d) (I), (S), (Q), (R)

## Answer with Explanations

### Paper 1

1. (b) Acidic nature depends upon nature of electron withdrawing group and electronegativity. Electronegativity further depends on % *s* character. Higher the *s*-character, greater will be the electronegativity and hence tendency to loose H increases thus acidic character also increases.



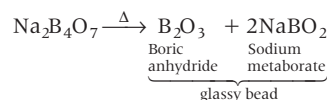
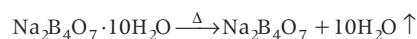
Hence, acidic order I > II > III > IV.

II is more acidic than III since electron donating group ( $-\text{OCH}_3$ ) is attached to benzene ring in III which decreases the acidic character.

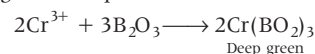
On the other hand,  $pK_a$  value also determined acidic nature, lower  $pK_a$  value gives maximum acidic character.

Hence, option (b) is correct.

2. (c) Borax bead test is performed only for coloured salt. Borax (sodium pyroborate),  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  on heating gets fused and lose water of crystallisation. It swells up into fluffy white porous mass which melts into a colourless liquid which later form a clear transparent glassy bead consisting of boric anhydride and sodium metaborate.



Boric anhydride is non-volatile. When it react with Cr(III) salt then deep green complex is formed.



Hence, option (c) is correct.

3. (d)  $\text{ZnCO}_3$ -Calamine (zinc ore)

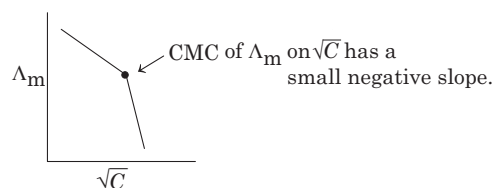
$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ -Malachite (copper ore)

$\text{Fe}_3\text{O}_4$ -Magnetite (iron ore)

$\text{Na}_3\text{AlF}_6$ -Cryolite (aluminium ore)

Thus, option (d) is correct.

4. (b) **Key Idea** The aqueous solution of ionic surfactant, i.e. sodium stearate ( $\text{C}_{17}\text{H}_{35}\text{COO}^-\text{Na}^+$ ) acts as a strong univalent type of electrolyte in the concentration range below the CMC and the linear function of dependence of  $\Lambda_m$  on  $\sqrt{C}$  has a small negative slope.



At normal or low concentration, sodium stearate  $[\text{CH}_3(\text{CH}_2)_{16}\text{COO}^-\text{Na}^+]$  behaves as strong electrolyte and for strong electrolyte, molar conductance ( $\Lambda_m$ ) decreases with increase in concentration.

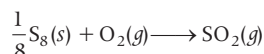
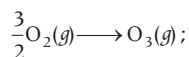


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Above particular concentration, sodium stearate forms aggregates known as micelles. The concentration is called as CMC. Since, number of ions decreases and hence  $\Lambda_m$  also decreases.

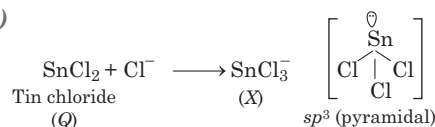
Hence, option (b) is correct.

5. (c, d) The standard enthalpy of formation is defined as standard enthalpy change for formation of 1 mole of a substance from its elements, present in their most stable state of aggregation.

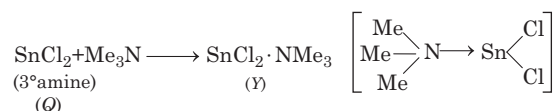


In the above two reactions standard enthalpy of reaction is equal to standard enthalpy of formation.

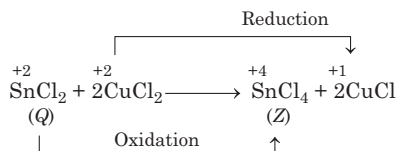
- 6.  $(a, d)$**



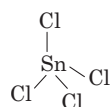
$\text{SnCl}_3^-$  has  $(3\sigma + 1lp)$  and exist in pyramidal structure.



Y complex has coordinate bond in between nitrogen and Sn metal.



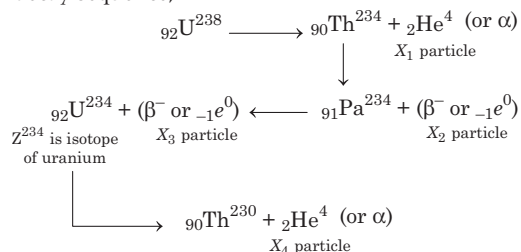
Z is oxidised product and oxidation state of Sn is +4 in Z compound. Structure of  $\text{SnCl}_4(\text{Z})$  is



Thus, options (a, d) are correct.

- 7. (a,b,c)** **Key Idea** The loss of one  $\alpha$ -particle will decrease the mass number by 4 and atomic number by 2. On the other hand, loss of  $\beta$ -particle will increase the atomic number by 1.

In decay sequence,



$X_1$  particle will deflect towards negatively charged plate due to presence of positive charge on  $\alpha$ - particles.

Hence, options (a, b, c) are correct.

- 8. (a, b, d)** The explanation of given statements are as follows:

(a)  $U_{\text{rms}}$  is inversely proportional to the square root of its molecular mass.

$$U_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

Hence, option (a) is correct.

(b) When temperature is increased four times then  $U_{\text{rms}}$  become doubled.

$$U_{\text{rms}} = \sqrt{\frac{3R}{M} \times 4T}$$

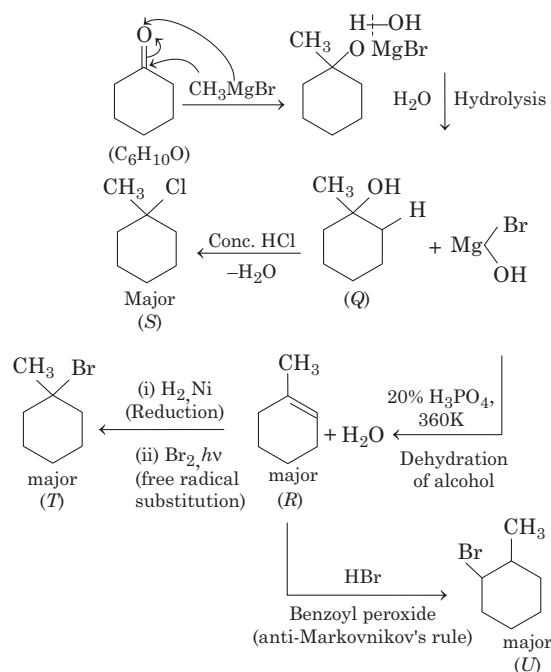
$$U_{\text{rms}} = 2 \times \sqrt{\frac{3RT}{M}}$$

Hence, option (b) is correct.

(c) and (d)  $E_{av}$  is directly proportional to temperature but does not depends on its molecular mass at a given temperature as  $E_{av} = \frac{3}{2}KT$ . If temperature raised four times than  $E_{av}$  becomes four time multiple.

Thus, option (c) is incorrect and option (d) is correct.

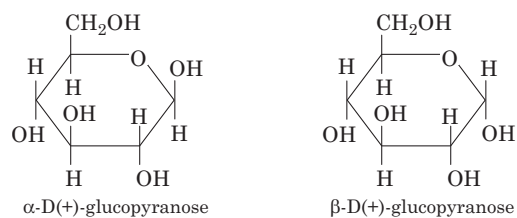
- 9. (c, d)** The given road map problem is



Hence, options (c, d) are correct.

- 10. (a, c, d)** The explanation of given statements are as follows:

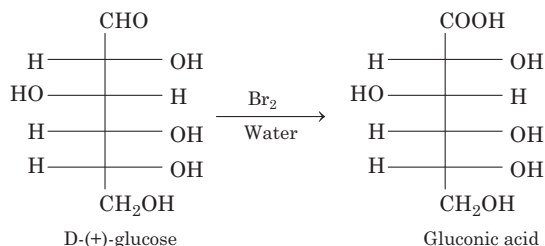
(a) Two six membered cyclic hemiacetal form of D-(+)- glucose are called anomers.



Both are anomers.

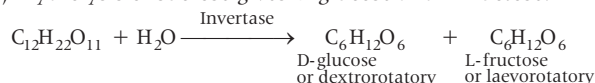


- (b) Oxidation of glucose in presence of  $\text{Br}_2$  water gives gluconic acid.

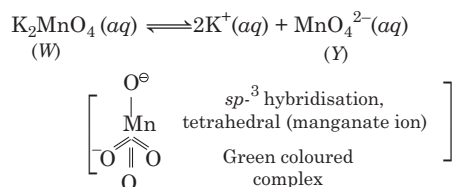
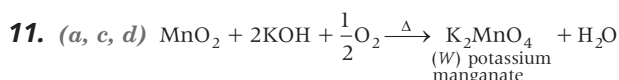


- (c) Monosaccharides can not be hydrolysed into polyhydroxy aldehydes and ketones.

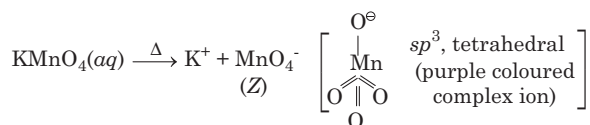
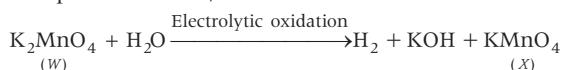
- (d) Hydrolysis of sucrose gives D-glucose and L-fructose.



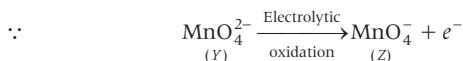
Hence, options (a, c, d) are correct.



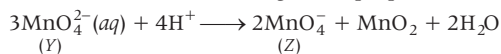
$\text{MnO}_4^{2-}$  ion has one unpaired electrons, therefore it gives  $d-d$  transition to form green colour. Y complex has paramagnetic nature due to presence of one unpaired electron. In aqueous solution,



$\text{MnO}_4^-$  ions gives charge transfer spectrum in which a fraction of electronic charge is transferred between the molecular entities.



In acidic medium, Y undergoes disproportionation reaction.



$\text{MnO}_4^{2-}$  and  $\text{MnO}_4^-$  both ions form  $\pi$ -bonding between

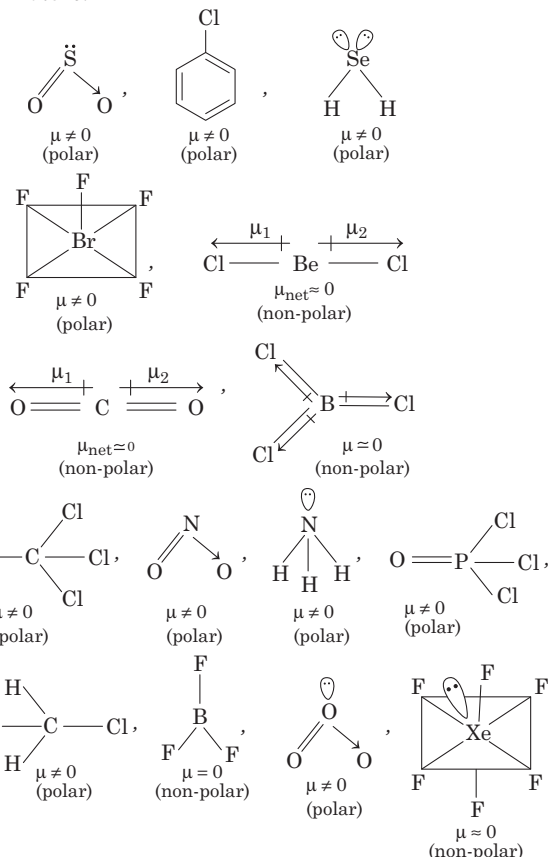
$p$ -orbitals of oxygen and  $d$ -orbitals of manganese.

Thus, options (a, c, d) are correct.

12. (a, c)

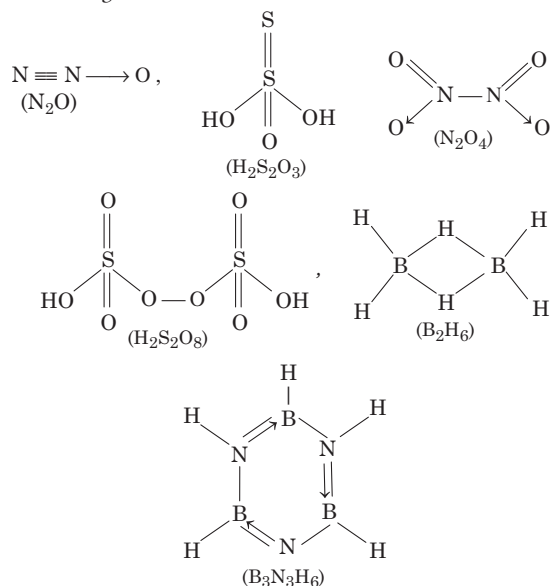
**Key Idea** Dipole moment of a bond depends on the difference in the electronegativities of bonded atoms. More is the difference in the electronegativities, greater will be the dipole moment. Also,  
 For symmetrical molecule,  $\mu = 0$   
 For unsymmetrical molecule,  $\mu \neq 0$

The molecules which gives permanent dipole moment are polar in nature.



Thus, options (a, c) are correct.

13. (4.00)  $\text{N}_2\text{O}$ ,  $\text{N}_2\text{O}_4$ ,  $\text{H}_2\text{S}_2\text{O}_3$  and  $\text{H}_2\text{S}_2\text{O}_8$  molecules are containing covalent bond between two atoms.



$\text{B}_2\text{H}_6$  and  $\text{B}_3\text{N}_3\text{H}_6$  have polar bond, but do not have same kind of atom.

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- 14. (1.02)** **Key Idea** First calculate, molar mass of solute using the formula,  $\frac{p^\circ - p_s}{p^\circ} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}}$  and then calculate  $\Delta T_f$  by applying the formula;  $\Delta T_f = K_f \times m$ .

When 0.5 g of non-volatile solute dissolve into 39 gm of benzene then relative lowering of vapour pressure occurs. Hence, vapour pressure decreases from 650 mmHg to 640 mmHg.

Given, vapour pressure of solvent ( $p^\circ$ ) = 650 mmHg

Vapour pressure of solution ( $p_s$ ) = 640 mmHg

Weight of non-volatile solute = 0.5 g

Weight of solvent (benzene) = 39 g

From relative lowering of vapour pressure,

$$\frac{p^\circ - p_s}{p^\circ} = x_{\text{solute}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}}$$

$$\frac{650 - 640}{650} = \frac{\frac{0.5}{\text{molar mass}}}{\frac{0.5}{\text{molar mass}} + \frac{39}{78}}$$

$$\frac{10}{650} = \frac{\frac{\text{molar mass}}{0.5}}{\frac{\text{molar mass}}{0.5} + 0.5}$$

$$0.5 + 0.5 \times \text{molar mass} = 65 \times 0.5$$

$$\therefore \text{Molar mass of solute} = 64 \text{ g}$$

From molal depression of freezing point,

$$\Delta T_f = K_f \times \text{molality}$$

$$= \frac{K_f \times w_{\text{solute}}}{(MW)_{\text{solute}} \times w_{\text{solvent}}}$$

$$\Delta T_f = 512 \times \frac{0.5 \times 1000}{64 \times 39} \Rightarrow \Delta T_f = 1.02 \text{ K}$$

- 15. (6.75)** Rate =  $k[A]^x[B]^y[C]^z$

$$\frac{(\text{Rate})_1}{(\text{Rate})_2} = \frac{[0.2]^x [0.1]^y [0.1]^z}{[0.2]^x [0.2]^y [0.1]^z} = \frac{6 \times 10^{-5}}{6 \times 10^{-5}}$$

$$\Rightarrow y = 0$$

$$\frac{(\text{Rate})_1}{(\text{Rate})_3} = \frac{[0.2]^x [0.1]^y [0.1]^z}{[0.2]^x [0.1]^y [0.2]^z} = \frac{6 \times 10^{-5}}{1.2 \times 10^{-4}}$$

$$\Rightarrow z = 1$$

$$\frac{(\text{Rate})_1}{(\text{Rate})_4} = \frac{[0.2]^x [0.1]^y [0.1]^z}{[0.3]^x [0.1]^y [0.1]^z} = \frac{6 \times 10^{-5}}{9 \times 10^{-5}}$$

$$\Rightarrow x = 1$$

$$\text{So, rate} = k[A]^1[C]^1$$

From exp-1st,

$$\text{Rate} = 6.0 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$$

$$6.0 \times 10^{-5} = k[0.2]^1[0.1]^1$$

$$k = 3 \times 10^{-3}$$

$$\text{Given, } [A] = 0.15 \text{ mol dm}^{-3}$$

$$[B] = 0.25 \text{ mol dm}^{-3}$$

$$[C] = 0.15 \text{ mol dm}^{-3}$$

$$\therefore \text{Rate} = (3 \times 10^{-3}) \times [0.15]^1 [0.25]^0 [0.15]^1 = 3 \times 10^{-3} \times 0.15 \times 0.15$$

$$\text{Rate} = 6.75 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$$

$$\text{Thus, } Y = 6.75$$

- 16. (8.9)** Given, equilibrium constant ( $K_c$ ) at 298 K =  $1.6 \times 10^{17}$

|                                          |                                                                                                |                   |   |
|------------------------------------------|------------------------------------------------------------------------------------------------|-------------------|---|
|                                          | $\text{Fe}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq}) \rightleftharpoons \text{FeS}(\text{s})$ |                   |   |
| At initial concentration (Before mixing) | 0.06 M                                                                                         | 0.2 M             | — |
| At initial concentration (After mixing)  | 0.03 M                                                                                         | 0.1 M             | — |
| At equilibrium                           | 0.03 - X                                                                                       | 0.1 - 0.03 = 0.07 | — |

[Here,  $K_c \gg 10^3$ , thus limiting reagent will be consumed almost completely,  $0.03 - X = 0 \therefore X = 0.03$ ]

From equilibrium constant,

$$K_c = \frac{[\text{FeS}]}{[\text{Fe}^{2+}][\text{S}^{2-}]}$$

$$K_c = \frac{1}{X \times 0.07} \quad [\text{For } \text{FeS}(\text{s}) = 1 \text{ mol L}^{-1} \text{ (Pure solid)}]$$

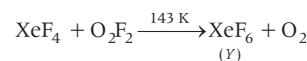
$$1.6 \times 10^{17} = \frac{1}{X \times 0.07}$$

$$X = \frac{1}{1.6 \times 10^{17} \times 0.07} = 8.9 \times 10^{-17}$$

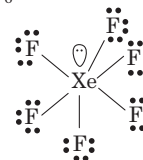
$$\text{Given, } X = Y \times 10^{-17} = 8.9 \times 10^{-17}$$

$$\therefore Y = 8.9$$

- 17. (19)**  $\text{XeF}_4$  reacts with  $\text{O}_2\text{F}_2$  to form  $\text{XeF}_6 \cdot \text{O}_2\text{F}_2$  is fluoronating reagent.



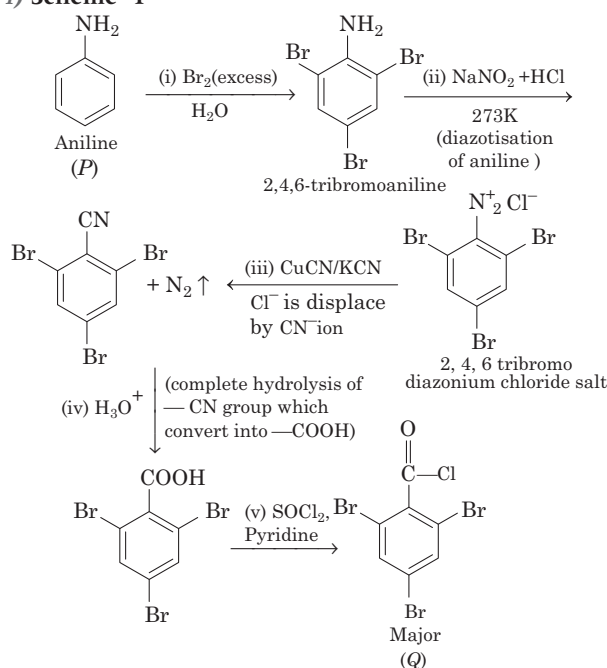
The structure of  $\text{XeF}_6$  is



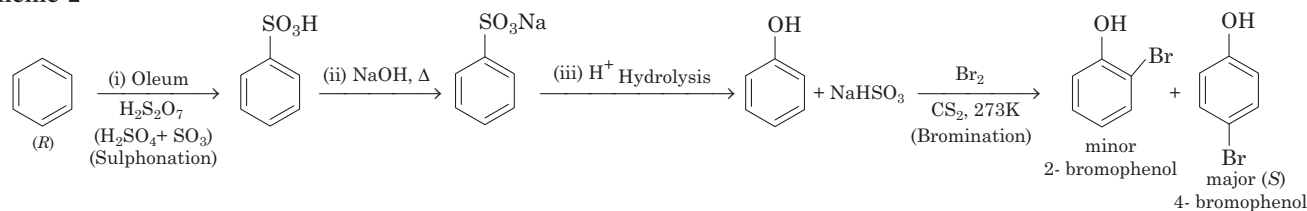
Y compound ( $\text{XeF}_6$ ) has 3 lone pair in each fluorine and one lone pair in xenon.

Hence, total number of lone pairs electrons is 19.

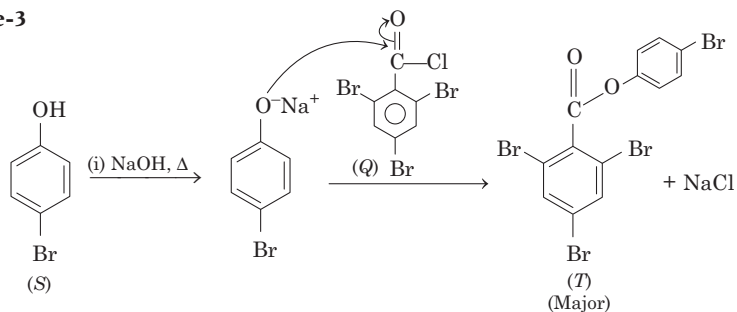
- 18. (4) Scheme -1**



Scheme-2

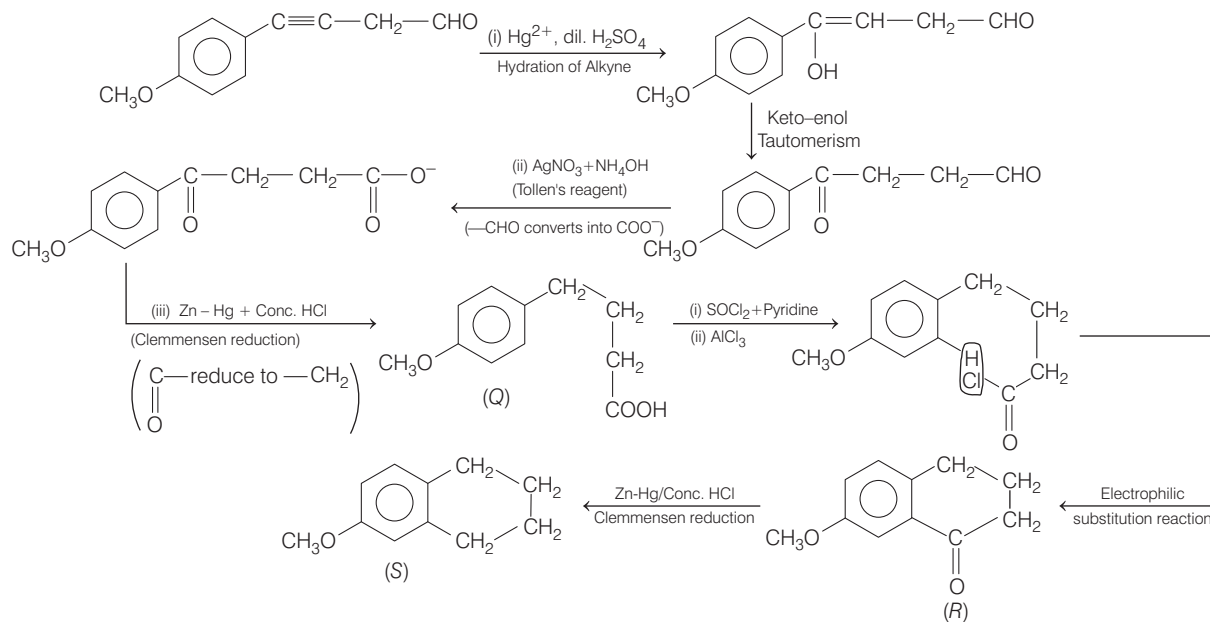
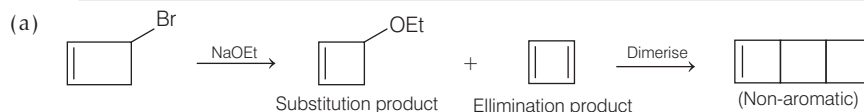
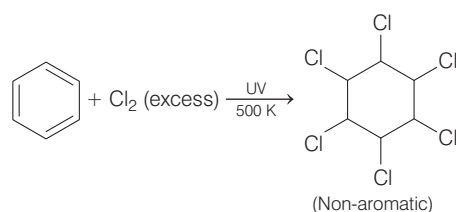


Scheme-3

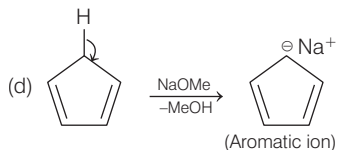
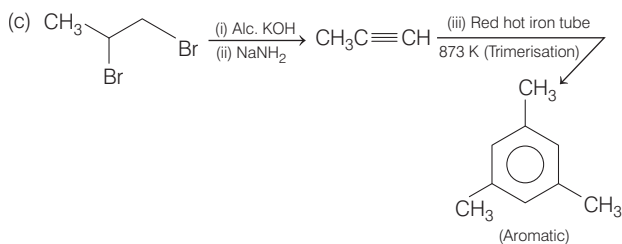


## Paper 2

1. (a, b)

2. (c, d) **Key Idea** An aromatic compound must be cyclic and planar. It must follow  $(4n + 2)e^-$  rule and have the conjugated system in it.(b) Benzene react with  $\text{Cl}_2$  (excess) in presence of UV light and 500 K of temperature to form benzene hexachloride (non-aromatic).

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Thus, (c) and (d) options are correct.

3. (a, c) Given, ground state energy of hydrogen atom =  $-13.6\text{ eV}$

$$\text{Energy of He}^+ = -34\text{ eV}, Z = 2$$

$$\text{Energy of He}^+, E = -\frac{13.6 \times Z^2}{n^2}\text{ eV}$$

$$-34\text{ eV} = -\frac{13.6 \times (2)^2}{n^2} \Rightarrow n = \sqrt{\frac{13.6 \times 4}{34}} \Rightarrow n = 4$$

Given, azimuthal quantum number ( $l$ ) =  $2(d\text{-subshell})$

Magnetic quantum number ( $m$ ) = 0

$\therefore$  Angular nodes ( $l$ ) = 2

Radial node =  $n - l - 1 = 4 - 2 - 1 = 1$

$$nl = 4d\text{ state}$$

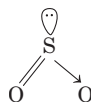
Hence, options (a), (c) are correct.

4. (b, c, d) When Zn react with hot conc.  $\text{H}_2\text{SO}_4$  then  $\text{SO}_2$  is released and  $\text{ZnSO}_4$  is obtained.



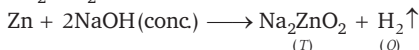
(Hot + Conc.) (G) (R) (X)

$\text{R}(\text{SO}_2)$  molecule is V-Shaped



Thus, option (b) is correct.

When Zn is react with conc. NaOH then  $\text{H}_2$  gas is evolved and  $\text{Na}_2\text{ZnO}_2$  is obtained.

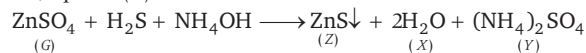


In ground state, H—H (Q) (bond order = 1)

Thus, option (c) is correct.

The oxidation state of Zn in  $\text{T}(\text{Na}_2\text{ZnO}_2)$  is +2

Thus, option (a) is incorrect.



$\text{ZnS}$  (Z) compound is dirty white coloured.

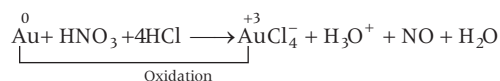
Thus, option (d) is correct.

5. (a, b, c) The explanation of given statements are as follows:

(a) *Aqua-regia* is prepared by mixing conc. HCl and conc.  $\text{HNO}_3$  in 3:1 (v/v) ratio and is used in oxidation of gold and platinum. Hence, option (a) is correct.

(b) Yellow colour of *aqua-regia* is due to its decomposition into NOCl (orange yellow) and  $\text{Cl}_2$  (greenish yellow). Hence, option (b) is correct.

(c) When gold reacts with *aqua-regia* then it produces  $\text{AuCl}_4^-$  anion complex in which Au has +3 oxidation state.



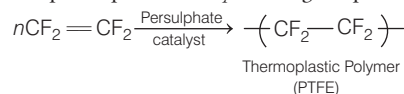
Hence, option (c) is correct.

(d) Reaction of gold with *aqua-regia* produces NO gas in absence of air.

Hence, option (d) is incorrect.

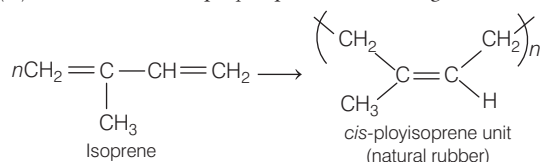
6. (a, d) The explanation of given statements are as follows:

(a) Teflon is prepared by heating tetrafluoroethene in presence of persulphate catalyst at higher pressure.



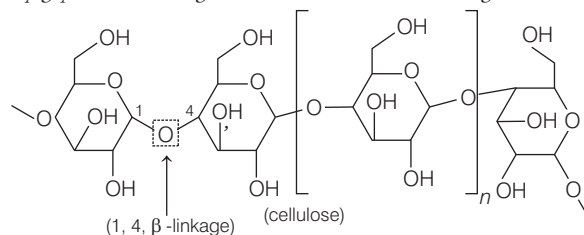
Thus, option (a) is correct.

(b) Natural rubber is polyisoprene containing *cis* alkene units.



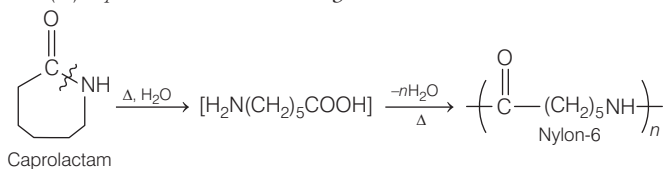
Thus, option (b) is incorrect.

(c) Cellulose has only  $\beta$ -D-glucose units that are joined together by glycosidic linkages as shown in the following structure:



Thus, option (c) is incorrect.

(d) Nylon-6 has amide linkages.

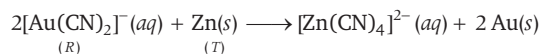
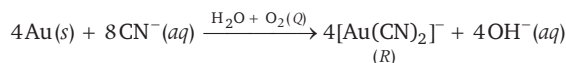


Thus, option (d) is correct.

7. (a, b, c) Cyanide process of gold extraction involves leaching out gold from its ore with  $\text{CN}^-$  in the presence of  $\text{O}_2$  (Q) in water to form  $[\text{Au}(\text{CN})_2]^-$  (R).

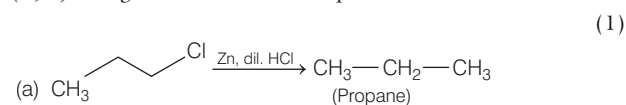
When  $[\text{Au}(\text{CN})_2]^-$  reacts with Zn (T), it forms  $[\text{Zn}(\text{CN})_4]^{2-}$  (Z) and Au.

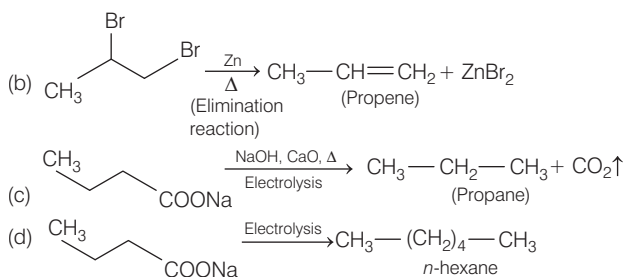
The corresponding reactions are as follows :



Hence, options (a, b, c) are correct.

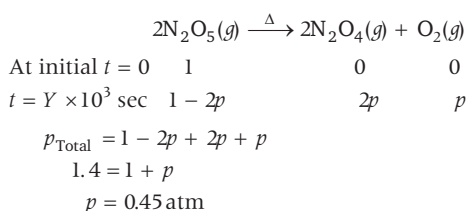
8. (a, c) The given reactions takes place as follows:





Thus, options (a, c) are correct.

9. (2.3) At constant  $V, T$



According to first order reaction,

$$k = \frac{2.303}{t} \log \frac{p_i}{p_i - 2p}$$

$$p_i = 1 \text{ atm (given)}$$

$$2p = 2 \times 0.45 = 0.9 \text{ atm}$$

On substituting the values in above equation,

$$2k \cdot t = 2.303 \log \frac{1}{1 - 0.9}$$

$$2 \times 5 \times 10^{-4} \times y \times 10^3 = 2.303 \log \frac{1}{0.1}$$

$$y = 2.303 = 2.3$$

**Note** Unit of rate constant ( $k$ ), i.e.  $\text{s}^{-1}$  represents that it is a first order reaction.

10. (2.98 mole)

**Key Idea** Molarity ( $M$ ) =  $\frac{\text{Number of moles of solute} \times 1000}{\text{Volume of solution (in mL)}}$

Also, volume =  $\frac{\text{Mass}}{\text{Density}}$

Given, mole fraction of urea ( $\chi_{\text{urea}}$ ) = 0.05

Mass of water = 900 g

Density =  $1.2 \text{ g/cm}^3$

$$\chi_{\text{urea}} = \frac{n_{\text{urea}}}{n_{\text{urea}} + 50} \quad [\because \text{Moles of water} = \frac{900}{18} = 50]$$

$$0.05 = \frac{n_{\text{urea}}}{n_{\text{urea}} + 50} \Rightarrow 19n_{\text{urea}} = 50$$

$$n_{\text{urea}} = 2.6315 \text{ moles}$$

$$w_{\text{urea}} = n_{\text{urea}} \times (M \cdot wt)_{\text{urea}} = (2.6315 \times 60) \text{ g}$$

$$V = \frac{2.6315 \times 60 + 900}{1.2} \quad [\because \text{Density} = \frac{\text{Mass of solution}}{\text{Volume of solution}}]$$

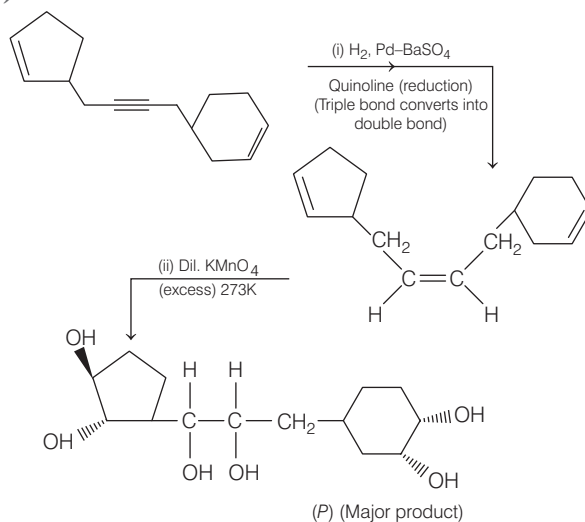
$$= 881.57 \text{ mL}$$

Now, molarity

$$= \frac{\text{Number of moles of solute} \times 1000}{\text{Volume of solution (mL)}}$$

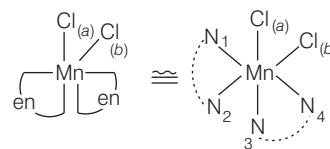
$$= \frac{2.6315 \times 1000}{881.57} = 2.98 \text{ M}$$

11. (6)

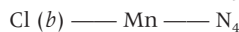
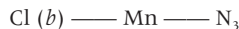
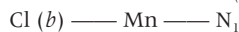


Compound (P) has total number of hydroxyl groups = 6

12. (6) The structure of  $\text{cis-}[\text{Mn}(\text{en})_2\text{Cl}_2]$  complex is



Bond angles (Mn—N and Mn—Cl bond in *cis* positions)



Number of *cis* Cl—Mn—N = 6

13. (288)

**Key Idea** Rhombic sulphur ( $\text{S}_8$ ) gets oxidised into sulphuric acid and water,  $\text{NO}_2$  gas is released on reaction with conc.  $\text{HNO}_3$ .

When rhombic sulphur ( $\text{S}_8$ ) is oxidised by conc.  $\text{HNO}_3$  then  $\text{H}_2\text{SO}_4$  is obtained and  $\text{NO}_2$  gas is released.

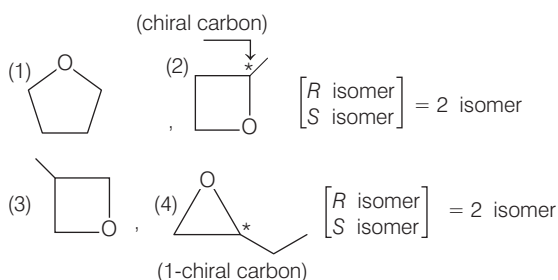


1 mole of rhombic sulphur produces = 16 moles of  $\text{H}_2\text{O}$

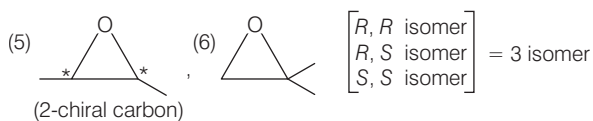
$\therefore$  Mass of water =  $16 \times 18$  (molar mass of  $\text{H}_2\text{O}$ )

$$= 288 \text{ g}$$

14. (10.0) The structure of cyclic ether with molecular formula,  $\text{C}_4\text{H}_8\text{O}$  are as follows:



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Total number of isomers of cyclic ether with molecular formula,  $C_4H_8O$  are 10.

15. (a) (III) Kinetic energy of the electron in  $n$ th orbit,

$$\text{K.E.} = +136 \times \frac{Z^2}{n^2}$$

or  $\text{K.E.} \propto \frac{1}{n^2}$  or  $\text{K.E.} \propto n^{-2}$

From list-II, correct match is (III P).

- (IV) Potential energy of the electron in the  $n$ th orbit,

$$\text{P.E.} = -2 \times 136 \times \frac{Z^2}{n^2}$$

$$\text{P.E.} \propto \frac{1}{n^2}$$

$$\text{P.E.} \propto n^{-2}$$

From List II, correct match is (IV P).

Hence, correct matching from list-I and list-II on the basis of given option is (III, P).

16. (c) (I) Radius of the  $n$ th orbit,

$$r = 0.529 \times \frac{n^2}{Z}$$

Here,  $r \propto n^2$

From list-II, correct match is (I, T)

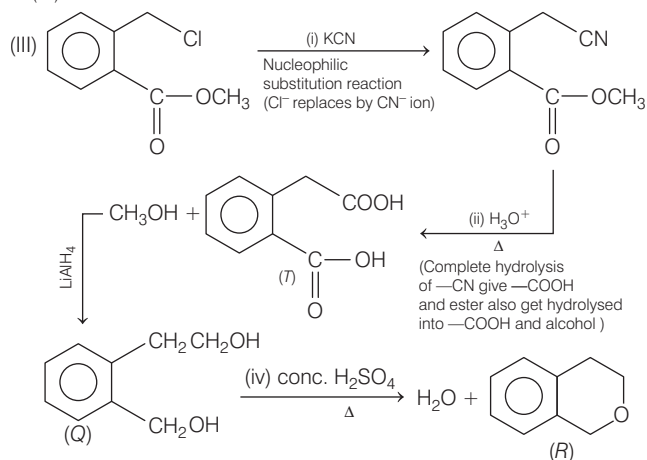
- (II) Angular momentum of the electron,

$$mvr = \frac{nh}{2\pi} \text{ or } mvr \propto n$$

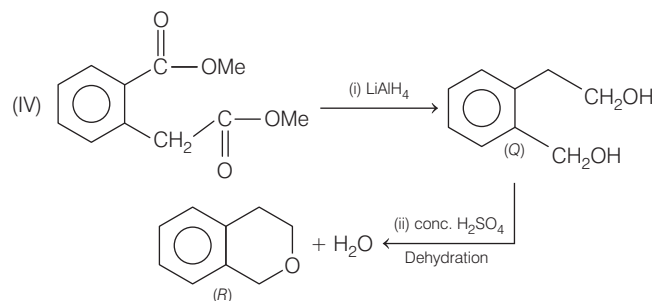
From list-II, correct match (II, S)

Hence, correct matching from list-I and list-II on the basis of given option is (I, T).

17. (b)



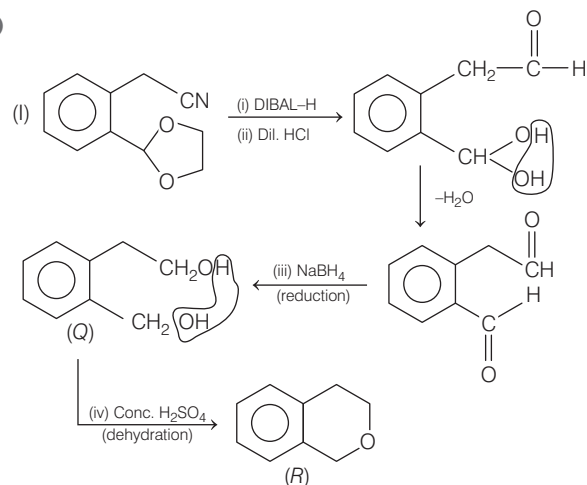
Hence, correct match of (III) are T, Q, R.



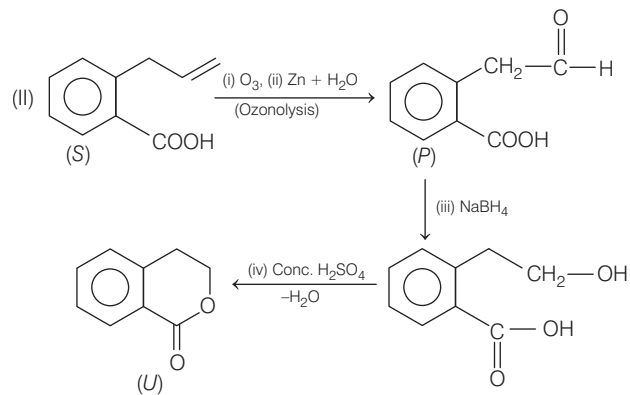
Hence, correct match of IV is Q, R.

Hence, correct matching from list-I and list II on the basis of given option is (IV), Q, R.

18. (a)



Hence, correct match of (I) are (Q, R)



Hence, correct match of II is (P, S, U).

Hence, correct matching from list-I and list-II on the basis of given option is (II), P, S, U.