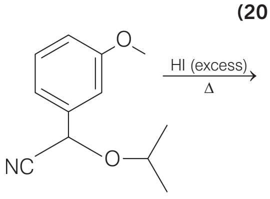
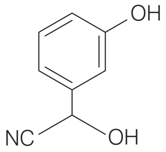
24

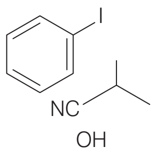
Alcohols and Ethers

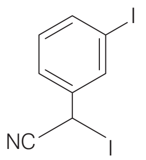
Objective Questions I (Only one correct option)

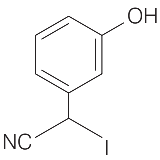
1. The major product of the following reaction is **(2019 Main, 10 April I)**



(a) 

(b) 

(c) 

(d) 

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

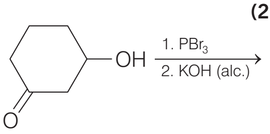
3. The major product of the following reaction is

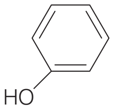
$CH_3CH = CHCO_2CH_3 \xrightarrow{LiAlH_4}$ **(2019 Main, 9 April I)**

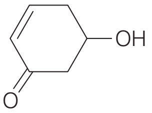
(a) $CH_3CH = CHCH_2OH$ (b) $CH_3CH_2CH_2CH_2OH$

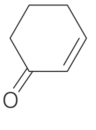
(c) $CH_3CH_2CH_2CO_2CH_3$ (d) $CH_3CH_2CH_2CHO$

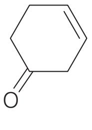
4. The major product of the following reaction is **(2019 Main, 9 April I)**



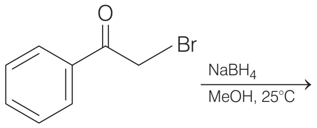
(a) 

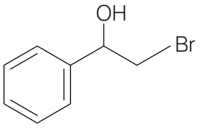
(b) 

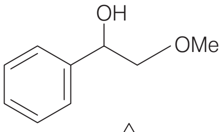
(c) 

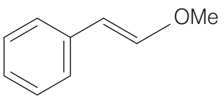
(d) 

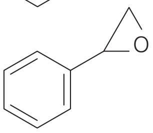
5. The major product of the following reaction is **(2019 Main, 8 April I)**



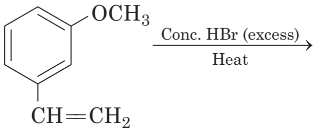
(a) 

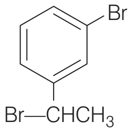
(b) 

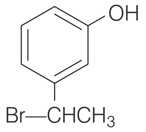
(c) 

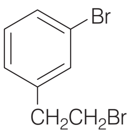
(d) 

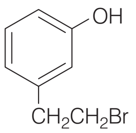
6. The major product of the following reaction is **(2019 Main, 8 April I)**

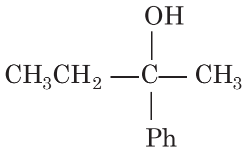


(a) 

(b) 

(c) 

(d) 

7.  cannot be prepared by **(2019 Main, 12 Jan I)**

$$CH_3CH_2-\overset{\displaystyle OH}{\underset{\displaystyle Ph}{\overset{|}{\underset{|}{C}}}}-CH_3$$

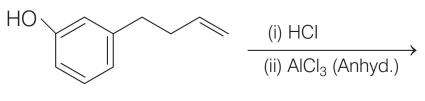
(a) $CH_3CH_2COCH_3 + PhMgX$

(b) $PhCOCH_3 + CH_3CH_2MgX$

(c) $PhCOCH_2CH_3 + CH_3MgX$

(d) $HCHO + PhCH(CH_3)\,CH_2MgX$

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



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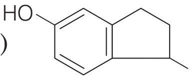

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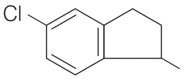

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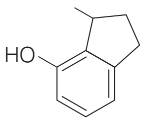

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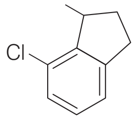
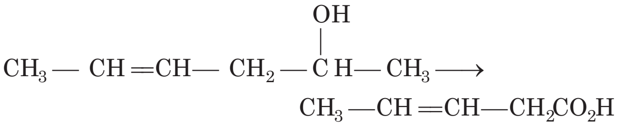


9. Which is the most suitable reagent for the following transformation? **(2019 Main, 10 Jan II)**

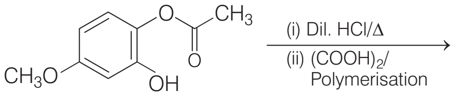


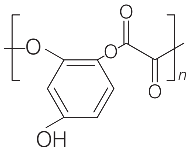
$$\mathrm{CH_3-CH=CH-CH_2-\overset{OH}{\overset{|}{C}}H-CH_3} \longrightarrow \mathrm{CH_3-CH=CH-CH_2CO_2H}$$

(a) Tollen's reagent (b) $I_2/NaOH$

(c) Alkaline $KMnO_4$ (d) CrO_2Cl_2/CS_2

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



(a)


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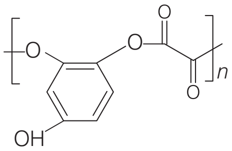

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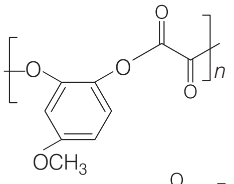

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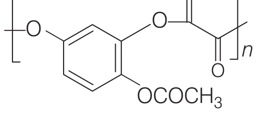
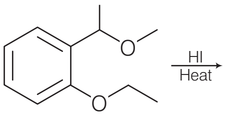
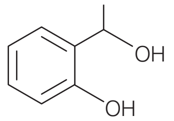


11. The major product formed in the following reaction is



(2018 Main)

(a)


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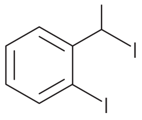

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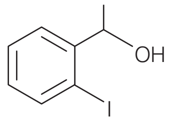

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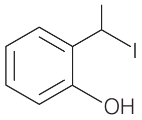
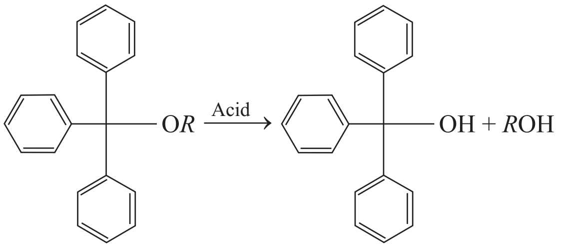


12. The acidic hydrolysis of ether (X) shown below is fastest when **(2014 Adv.)**



[X]

(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?

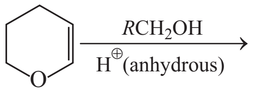
(a) Secondary alcohol by S_N1 **(2013 Main)**

(b) Tertiary alcohol by S_N1

(c) Secondary alcohol by S_N2

(d) Tertiary alcohol by S_N2

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) I < II < III < IV (b) I < II < IV < III

(c) IV < I < II < III (d) IV < II < I < III

16. The best method to prepare cyclohexene from cyclohexanol is by using **(2005, 1M)**

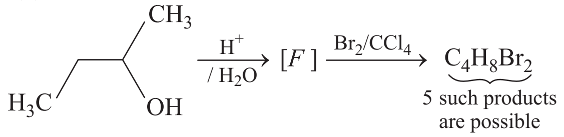
(a) conc. HCl + $ZnCl_2$ (b) conc. H_3PO_4

(c) HBr (d) conc. HCl

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

18.



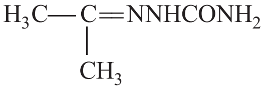
How many structures of *F* is possible? **(2003, 1M)**

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

19. Compound '*A*' (molecular formula C_3H_8O) is treated with acidified potassium dichromate to form a product '*B*' (molecular formula C_3H_6O) '*B*' forms a shining silver mirror on warming with ammoniacal silver nitrate. '*B*' when treated with an aqueous solution of $H_2NCONHNH_2$ and sodium acetate gives a product '*C*'. Identify the structure of '*C*'. **(2002, 3M)**

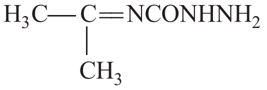
(a) $CH_3CH_2CH{=}NNHCONH_2$

(b)



$H_3C{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}NNHCONH_2$

(c)



$H_3C{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}NCONHNH_2$

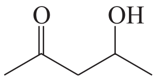
(d) $CH_3CH_2OH + NCONHNH_2$

20. 1-propanol and 2-propanol can be best distinguished by **(2001, 1M)**

(a) oxidation with alkaline $KMnO_4$ followed by reaction with Fehling solution
(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 H_2SO_4 followed by reaction with Fehling solution

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

(a)



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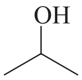

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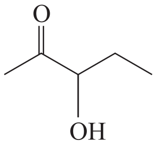

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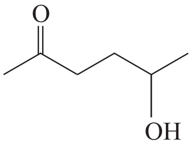


22. The products of combustion of an aliphatic thiol (*R*SH) at 298 K are **(1992)**

(a) $CO_2(g), H_2O(g)$ and $SO_2(g)$
(b) $CO_2(g), H_2O(l)$, and $SO_2(g)$
(c) $CO_2(l), H_2O(l)$ and $SO_2(g)$
(d) $CO_2(g), H_2O(l)$ and $SO_2(l)$

23. In CH_3CH_2OH, the bond that undergoes heterolytic cleavage most readily is **(1988, 1M)**

(a) C—C (b) C—O
(c) C—H (d) O—H

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

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

25. 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 $ZnO\text{-}Cr_2O_3$
(b) by reacting methane with steam at 900°C with nickel catalyst
(c) by reducing formaldehyde with $LiAlH_4$
(d) by reacting formaldehyde with aqueous sodium hydroxide solution

27. Diethyl ether on heating with conc. HI gives two moles of **(1983, 1M)**

(a) ethanol (b) iodoform
(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. H_2SO_4. The product formed is **(1980, 1M)**

(a) $CH_3COOC_2H_5$ (b) C_2H_2
(c) C_2H_4 (d) C_2H_6

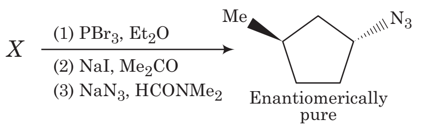
30. Which of the following is soluble in water? **(1980, 1M)**

(a) CS_2 (b) C_2H_5OH
(c) CCl_4 (d) $CHCl_3$

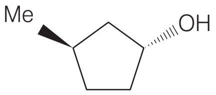
Objective Questions II

(One or more than one correct option)

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



(a)



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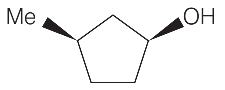

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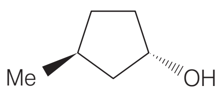

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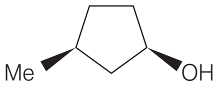


32. The correct statement(s) about the following reaction sequence is (are)

$$\text{Cumene } (C_9H_{12}) \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } O_2} P \xrightarrow{CHCl_3/NaOH}$$

$$Q(\text{major}) + R(\text{minor}),\ Q \xrightarrow[PhCH_2Br]{NaOH} S$$

(2016 Adv.)

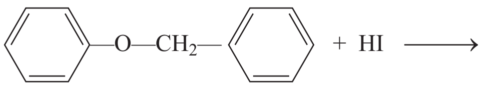
(a) R is steam volatile

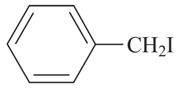
(b) Q gives dark violet colouration with 1% aqueous $FeCl_3$ solution

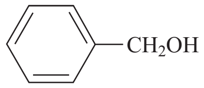
(c) S gives yellow precipitate with 2, 4-dinitrophenylhydrazine

(d) S gives dark violet colouration with 1% aqueous $FeCl_3$ solution

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



(a)


(b)


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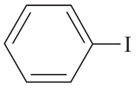

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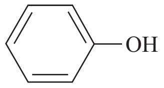


34. The products of reaction of alcoholic silver nitrate with ethyl bromide are **(1991, 1M)**

(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.

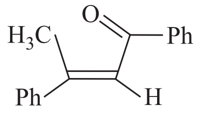
35. **Statement I** Solubility of *n*-alcohol in water decreases with increase in molecular weight.

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.

$M =$


(2008, 3 ×4M = 12M)

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

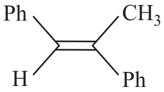
(a) $PhCOCH_3$, $PhCH_2COCH_3$ and $PhCH_2COO^-K^+$

(b) $PhCHO$, $PhCH_2CHO$ and $PhCOO^-K^+$

(c) $PhCOCH_3$, $PhCH_2CHO$ and $CH_3COO^-K^+$

(d) $PhCHO$, $PhCOCH_3$ and $PhCOO^-K^+$

37. The structure of compound I is

(a)


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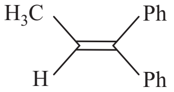

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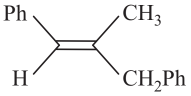

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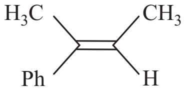
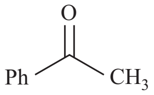
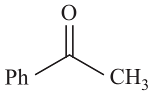


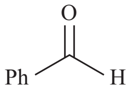
38. Compound H is formed by the reaction of

(a)


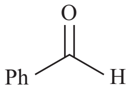
; PhMgBr

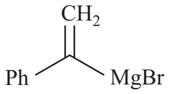
(b)


; $PhCH_2MgBr$

(c)


; $PhCH_2MgBr$

(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)**

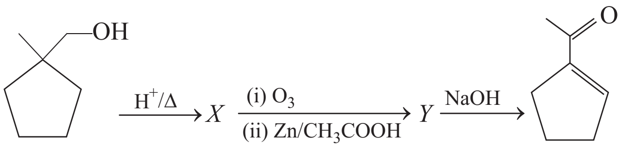
True or False

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

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

45.



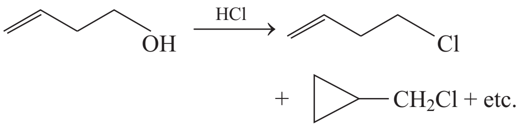
Identify X and Y. **(2005, 2M)**

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)**

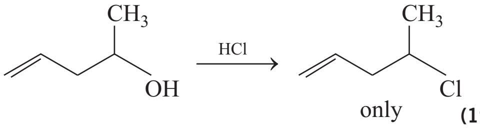
47. Cyclobutylbromide on treatment with magnesium in dry ether forms an organometallic compound (A). The organometallic reacts with ethanal to give an alcohol (B) after mild acidification. Prolonged treatment of alcohol (B) with an equivalent amount of HBr gives 1-bromo-1-methylcyclopentane (C). Write 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.

(i)



(ii)



(1999, 3M)

49. Write the structures of the products :

$$(CH_3)_2CH—OCH_3 \xrightarrow[\text{heat}]{\text{HI (excess)}}$$

(1998, 2M)

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 :

$$\text{Ethanol} \xrightarrow{I_2/NaOH}$$

(1985, 1M)

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)**

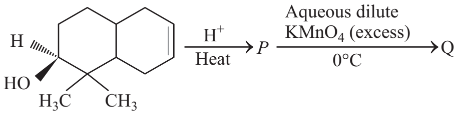
62. State the conditions under which the following preparations are carried out. Give necessary equations which need not be balanced.
(i) Ethanol from acetylene
(ii) Lead tetraethyl from sodium-lead alloy
(iii) Methyl chloride from aluminium carbide **(1983, 3M)**

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°C, possessing a rather pleasant odour, on heating with concentrated sulphuric acid gives a gaseous product '*B*' with the empirical formula, CH_2. '*B*' decolourises bromine water as well as alkaline permanganate solution and takes up one mole of 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.)**

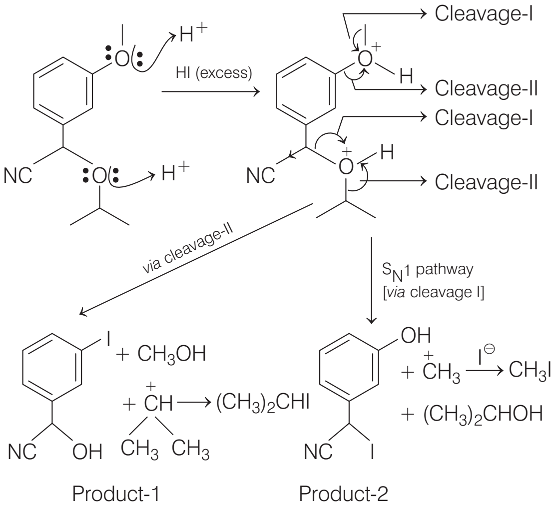


Answers

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 & Solutions

1. The given reaction takes place as follows:



Product-2 is formed because

(i) Cleavage-I will give more stable aryl carbocation.

(ii) Cleavage- I will give intermediate which is in conjugation with ring.

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

$$\underset{\substack{\text{Water gas}\\ \text{or}\\ \textit{syn}\text{ gas}}}{[CO+H_2]}+H_2 \xrightarrow[\text{300 atm, 300° C}]{ZnO+Cr_2O_3} \underset{\text{Methanol}}{CH_3OH}$$

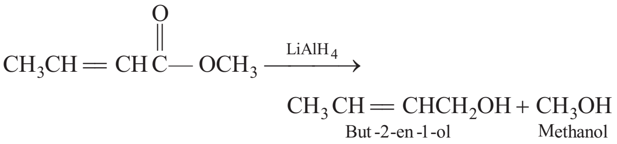
It is an industrial process used for the production of methanol where volume ratio of the reactant gases is maintained as:

syn gas : $H_2 = 2:1$ and ZnO-Cr_2O_3 act as catalysts

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

3. **Key Idea** $LiAlH_4$ reagent is used for the reduction of $-CHO$, $-\overset{\overset{\displaystyle O}{\|}}{C}OCH_3$. It does not reduce double bonds.

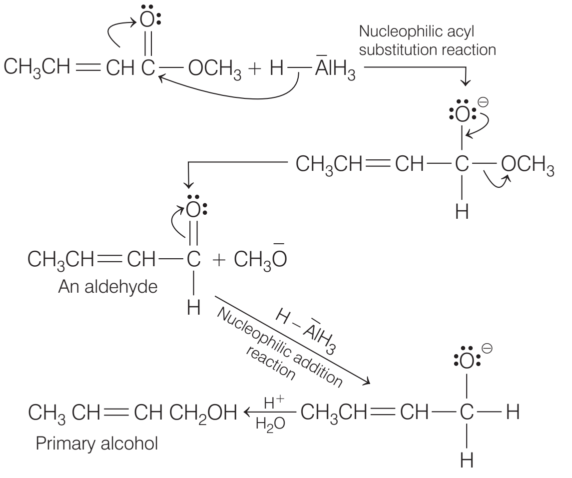
The reaction of an ester with $LiAlH_4$ produces two alcohols, one corresponding to the acyl portion of the ester and one corresponding to the alkyl portion.



$$CH_3CH=CH\overset{\overset{\displaystyle O}{\|}}{C}-OCH_3 \xrightarrow{LiAlH_4} \underset{\text{But-2-en-1-ol}}{CH_3CH=CHCH_2OH}+\underset{\text{Methanol}}{CH_3OH}$$

Thus, the major product of the given reactant $CH_3CH=CH\overset{\overset{\displaystyle O}{\|}}{C}OCH_3$ in presence of $LiAlH_4$ is $CH_3CH=CH\,CH_2OH$ and CH_3OH. The reaction proceeds through following mechanism.

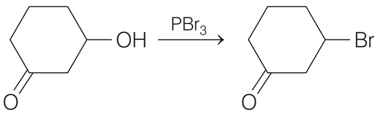
Mechanism



4. **Key Idea** PBr_3 reagent is used for the substitution of —Br group while alc. KOH reagent is used to carry out elimination reaction.

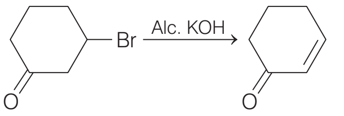
The given reaction proceed in following manner:

Step I In presence of PBr_3, alcohols undergo substitution reactions to give halides. Reagent PBr_3 is usually generated *insitu* by the reaction of red phosphorus with bromine.



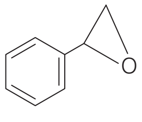
3-bromohexanone

Step II 3-bromohexanone in presence of alc. KOH undergoes elimination reaction and gives cyclohex-2-en-1-one.

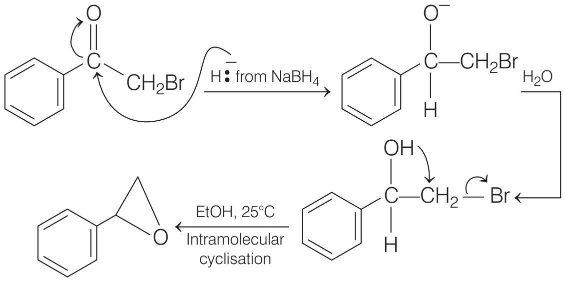


Cyclohex-2-en-1-one

5. Major product obtained in the given reaction is

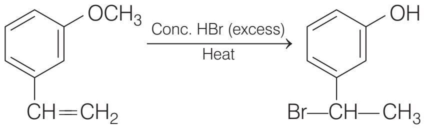


$NaBH_4$ in the reaction is used for the reduction by addition of a hydride ion and a proton. Carbon-oxygen double bonds are easily reduced by sodium borohydride. The actual reducing agent in these reductions is hydride ion (H^-). Hydride ion adds to the carbonyl carbon and the alkoxide ion that is formed is subsequently protonated by water. In other words, the carbonyl group is reduced by adding an H^- followed by an H^+. The mechanism of the given reaction is as follows :



6. **Key Idea** Ethers are least reactive functional groups. The cleavage of C — O bond in ethers take place under drastic conditions with excess of HX.

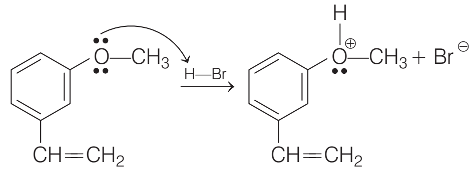
The major product obtained in the reaction is as follows :



As conc. HBr is in excess. So, reaction will take place at both the substituents.

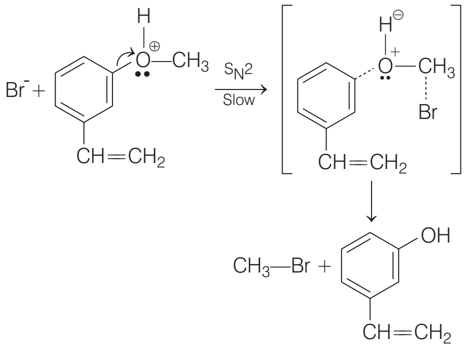
Mechanism

Step 1 Protonation of ether to form oxonium ion.

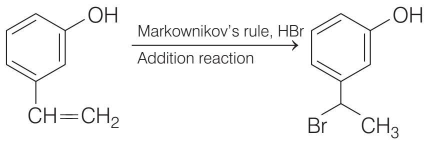


Oxonium ion

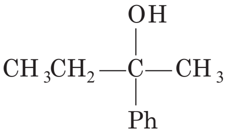
Step 2 Attack of nucleophile at the protonated ether.



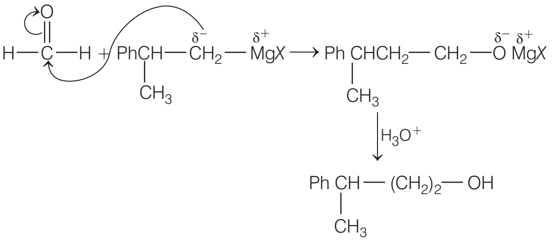
Step 3 As HBr is in excess, so, reaction will also take place at alkene.



7.

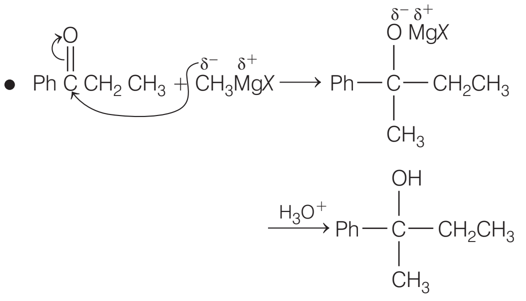


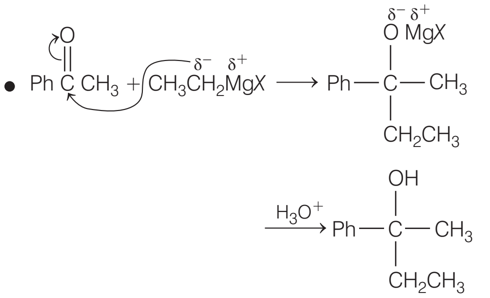
$CH_3CH_2—\overset{\overset{OH}{|}}{\underset{\underset{Ph}{|}}{C}}—CH_3$ cannot be prepared by HCHO and $PhCH(CH_3)CH_2MgX$. This can be easily illustrated by following reaction.

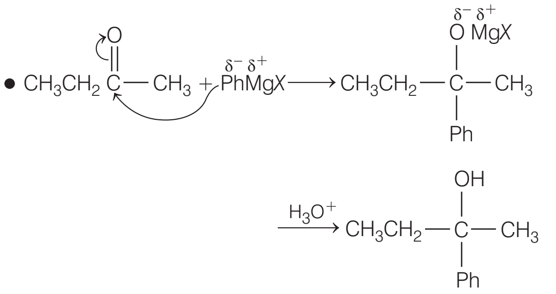


The obtained product is not the required substance. While option (a), (b) and (c) can readily prepare the required substance.

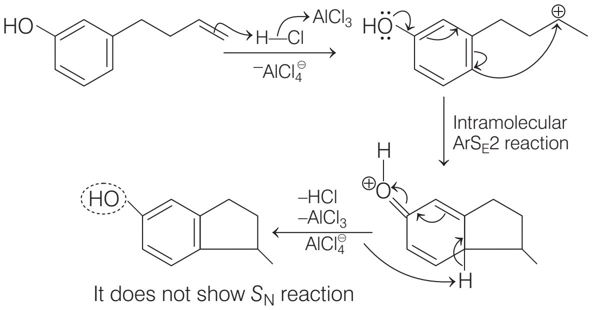
The reactions are as follows :

- 

- 

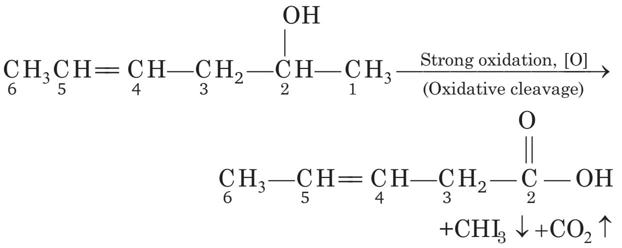
- 

8. In the given reaction, $AlCl_3$ helps in the generation of electrophile that further undergoes ArS_E2 reaction to give the required product.



It does not show S_N reaction with HCl because of double bond nature of the O—C bond, (due to +*R*-effect of the —OH group.)

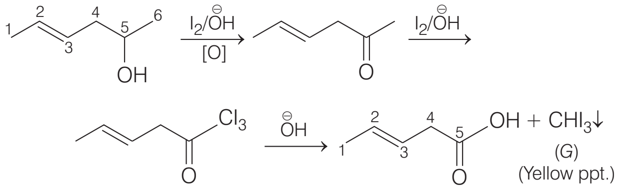
9. The most suitable reagent to carry out given transformation is I_2/NaOH



$$\underset{6}{\text{CH}_3}\underset{5}{\text{CH}}=\underset{4}{\text{CH}}-\underset{3}{\text{CH}_2}-\underset{2}{\overset{\overset{\text{OH}}{|}}{\text{CH}}}-\underset{1}{\text{CH}_3}\xrightarrow[\text{(Oxidative cleavage)}]{\text{Strong oxidation, [O]}}$$

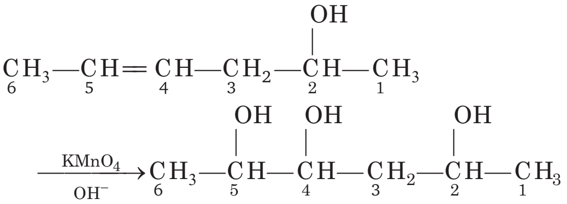
$$\underset{6}{\text{CH}_3}-\underset{5}{\text{CH}}=\underset{4}{\text{CH}}-\underset{3}{\text{CH}_2}-\underset{2}{\overset{\overset{\text{O}}{\|}}{\text{C}}}-\text{OH}$$
$$+\text{CHI}_3\downarrow+\text{CO}_2\uparrow$$

Here, the haloform reaction will give following reaction:



(i) Tollen's reagent ($AgNO_3$ + NH_4OH) is a mild oxidising agent. It does not react with $\underset{\text{OH}}{\underset{|}{-\text{CH}}}-\text{CH}_3$ group (2°-alcohol).

(ii) Alkaline $KMnO_4$ cannot perform the oxidative cleavage, rather it will hydroxylate the C═C.

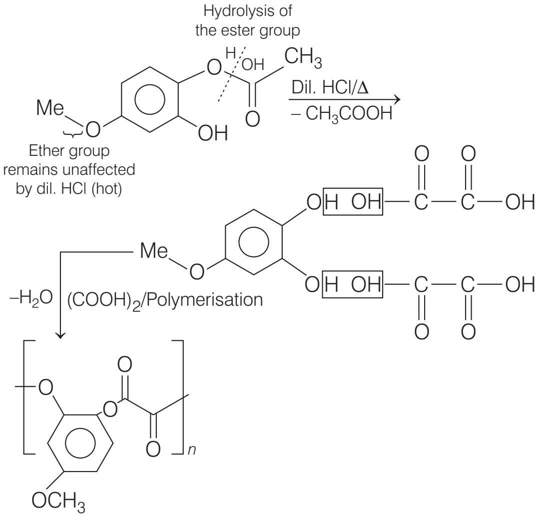


$$\underset{6}{\text{CH}_3}-\underset{5}{\text{CH}}=\underset{4}{\text{CH}}-\underset{3}{\text{CH}_2}-\underset{2}{\overset{\overset{\text{OH}}{|}}{\text{CH}}}-\underset{1}{\text{CH}_3}$$

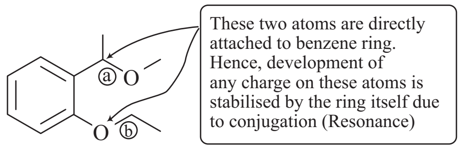
$$\xrightarrow[\text{OH}^-]{\text{KMnO}_4}\underset{6}{\text{CH}_3}-\underset{5}{\overset{\overset{\text{OH}}{|}}{\text{CH}}}-\underset{4}{\overset{\overset{\text{OH}}{|}}{\text{CH}}}-\underset{3}{\text{CH}_2}-\underset{2}{\overset{\overset{\text{OH}}{|}}{\text{CH}}}-\underset{1}{\text{CH}_3}$$

(iv) CrO_2Cl_2/CS_2 will not react here.

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



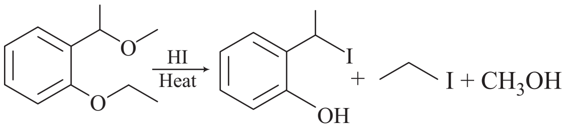
11. **Key idea** The reaction given is a nucleophilic substitution reaction in which cleavage at C—O bond is visible. The product formation can be visualised with the help of following analysis.



These two atoms are directly attached to benzene ring. Hence, development of any charge on these atoms is stabilised by the ring itself due to conjugation (Resonance)

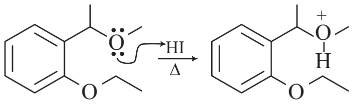
If any one properly visualise the fact written with figure above, than a conclusion can be made that C—O bonds marked (a) and (b) in the figure will undergo heterolysis during the reaction.

The reaction can be represented as



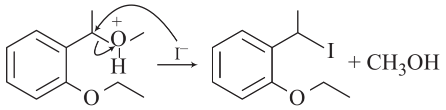
Mechanism

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

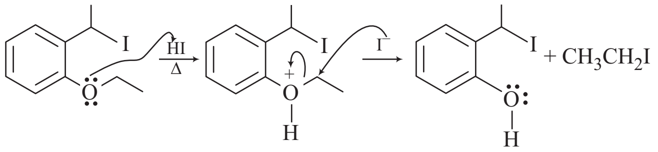


Oxonium ion

***Step* II** This oxonium ion undergoes lysis and addition of I^- to form two products as



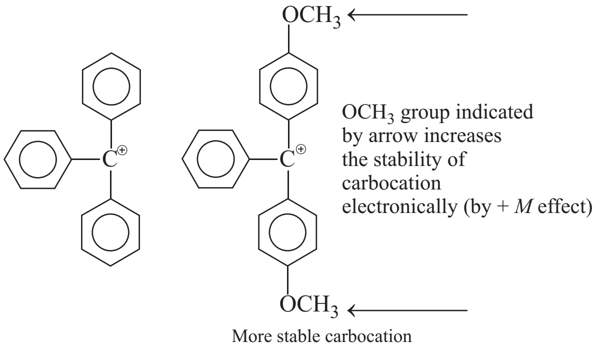
***Step* III** Similar pathway is followed at the other oxygen atom, which can be visualised as



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 S_N1 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.



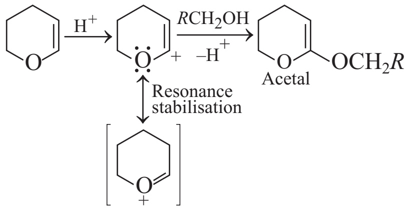
OCH_3 group indicated by arrow increases the stability of carbocation electronically (by + *M* effect)

More stable carbocation

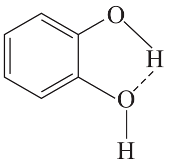
Hence, (c) is the correct choice.

13. The reaction of alcohol with Lucas reagent is mostly an S_N1 reaction and the rate of reaction is directly proportional to the stability of carbocation formed in the reaction. Since 3° R—OH forms 3° carbocation (most stable), hence it will react fastest.

14.

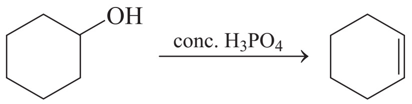


15. All dihydroxy benzene will have higher boiling points than monohydroxy benzene. Also, among dihydroxy benzenes, 1, 2,-di-hydroxy benzene has lowest boiling point due to intramolecular H-bonding.



(intramolecular H-bonding in 1,2-dihydroxy benzene)

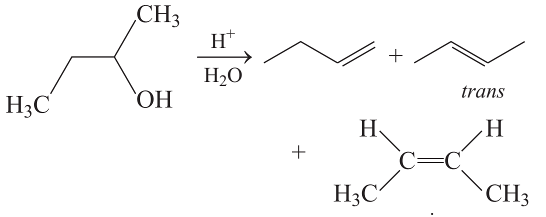
16.



Concentrated H_3PO_4 solution does not involve any substitution product while with others, substitution products are also formed.

17. $C_6H_5MgBr + (CH_3)_3COH \longrightarrow C_6H_6 + Mg[(CH_3)_3CO]Br$

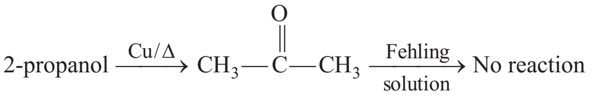
18.



19. *A* is an alcohol and its oxidation product gives Tollen's test, i.e. *B* must be an aldehyde (CH_3CH_2CHO).

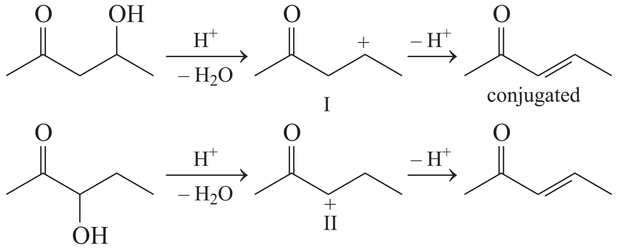
$$CH_3CH_2CHO + \underset{\text{semicarbazide}}{H_2NHN—CO—NH_2} \longrightarrow CH_3CH_2—CH{=}N—NH—CONH_2$$

20. 1-propanol $\xrightarrow{Cu/\Delta} CH_3—CH_2—CHO \xrightarrow[\text{solution}]{\text{Fehling}} \underset{\text{red}}{Cu_2O\downarrow}$



2-propanol $\xrightarrow{Cu/\Delta} CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—CH_3 \xrightarrow[\text{solution}]{\text{Fehling}}$ No reaction

21.

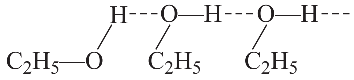


Although both reactions are giving the same product, carbocation I is more stable than II.

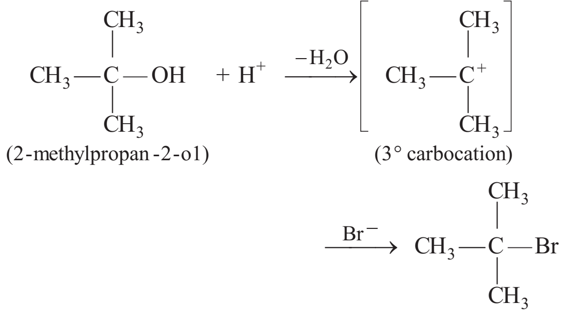
22. Thiol, (RSH), on combustion produces CO_2 (g), SO_2 (g) and $H_2O(l)$. At 298 K, H_2O will be in liquid phase.

23. OH ⟶ $O^- + H^+$ (has maximum electronegativity difference)

24. Ethanol is capable in forming intermolecular H-bonds :



25. Reaction proceeds *via* carbocation intermediates :



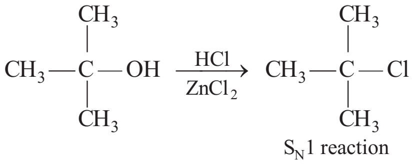
$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH + H^+ \xrightarrow{-H_2O} \left[CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C^+}}}}\right] \xrightarrow{Br^-} CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-Br$$

(2-methylpropan-2-o1) (3° carbocation)

26. $CO + H_2 \xrightarrow[\text{heat}]{ZnO\text{-}Cr_2O_3} CH_3OH$

27. $CH_3-CH_2-O-CH_2-CH_3 + HI \longrightarrow 2C_2H_5I$

28. 2-methyl propan-2-ol is a tertiary alcohol, will react fastest with Lucas reagent :



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH \xrightarrow[ZnCl_2]{HCl} CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-Cl$$

S_N1 reaction

29. On heating with concentrated H_2SO_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., S_N2 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

$$ROH \xrightarrow[\text{In diethyl ether }(Et_2O)]{PBr_3} RBr$$

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

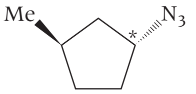
$$RX + NaI \xrightarrow{\text{In acetone}(Me_2CO)} RI + NaX$$

where X = Cl or Br

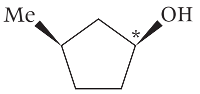
Reaction 3 in its generalised format seen as

$$RI + NaN_3 \xrightarrow{HCONMe_2} RN_3 + NaI$$

Now if the given product is

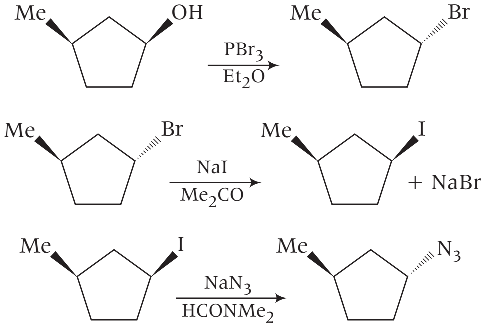


and which is too enantiomerically pure i.e. 100% either dextrorotatory or leavorotatory form, then the 'X' must be

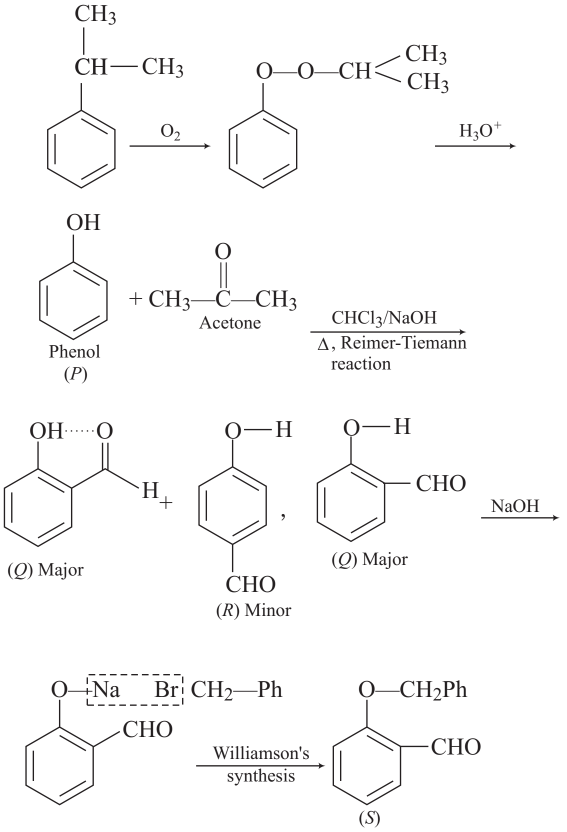


Note The configuration at carbon * atom in 'X' becomes inverted due to S_N2 mechanism which is visible in the product as well.

Thus, the probable reactions will be



32.



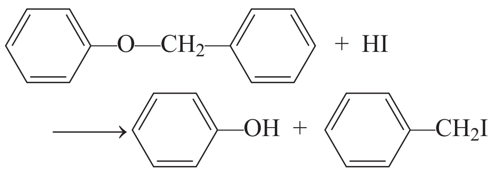
(a) R is not steam volatile, but Q is steam volatile thus, incorrect.

(b) Q has enolic group thus, gives violet colour with 1% aqueous $FeCl_3$ solution thus, correct.

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

(d) *S* does not give colour with $FeCl_3$ thus, incorrect.

33.



Phenol does not react further with HI.

34. $CH_3CH_2Br + \underset{\text{ambident nucleophile}}{O{=}\ddot{N}{-}O^-} \longrightarrow \underset{\text{nitroethane}}{CH_3CH_2NO_2} + \underset{\text{ethyl nitrite}}{CH_3CH_2ONO}$

35. *R*—OH ← Hydrophilic

Hydrophobic

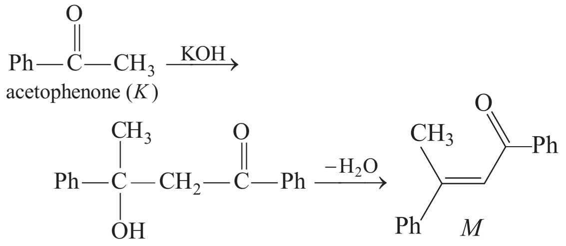
Increasing molecular weight increases hydrocarbon (*R*) proportion that lowers the solubility in water.

Passage 1

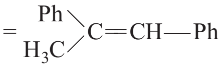
Compound *J* must be benzaldehyde because it on treatment with KOH undergoing Cannizzaro's reaction producing benzyl alcohol and pot-benzoate (*L*).

$$\underset{J}{C_6H_5{-}CHO} \xrightarrow{KOH} \underset{\text{benzyl alcohol}}{C_6H_5{-}CH_2OH} + C_6H_5COOK(L)$$

Also *M* is aldol condensation product formed from acetophenone

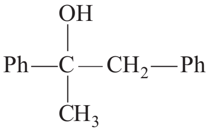


⇒ *I* =



$$\begin{matrix}Ph\\H_3C\end{matrix}\!\!>C{=}CH{-}Ph$$

and *H* =

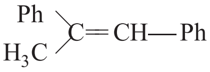


$$Ph{-}\overset{\displaystyle OH}{\underset{\displaystyle CH_3}{C}}{-}CH_2{-}Ph$$

3°-alcohol

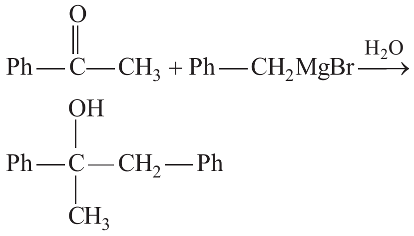
36. $J = C_6H_5CHO,\ K = Ph{-}\overset{O}{\overset{\|}{C}}{-}CH_3,\ L = PhCO\bar{O}K^+$

37. *I* =



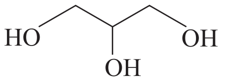
$$\begin{matrix}Ph\\H_3C\end{matrix}\!\!>C{=}CH{-}Ph$$

38.



$$Ph{-}\overset{O}{\overset{\|}{C}}{-}CH_3 + Ph{-}CH_2MgBr \xrightarrow{H_2O} \underset{H}{Ph{-}\overset{\displaystyle OH}{\underset{\displaystyle CH_3}{C}}{-}CH_2{-}Ph}$$

39. Secondary :



C–2(OH) is secondary

40. Peroxides : $H_2O_2 + Fe^{2+} \longrightarrow H_2O + Fe^{3+}$

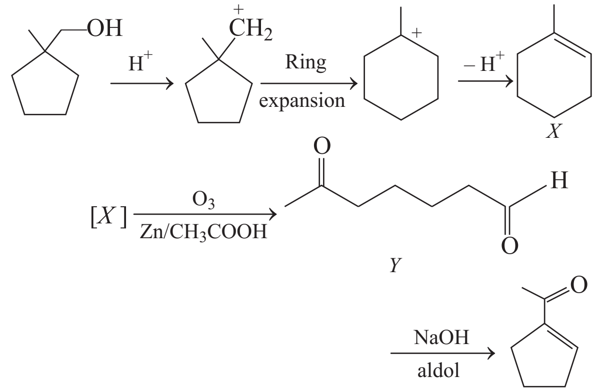
41. *Vicinal*, same

42. $C_2H_5OH \xrightarrow[\Delta]{Cu} CH_3CHO \xrightarrow[H_2O]{NaOH} \underset{\text{aldol}}{CH_3{-}\overset{\displaystyle OH}{\overset{|}{C}H}{-}CH_2{-}CHO}$

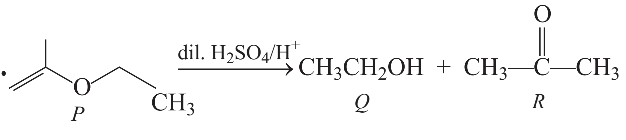
43. Ethanol is weaker acid than water, not neutralised with NaOH.

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

45.

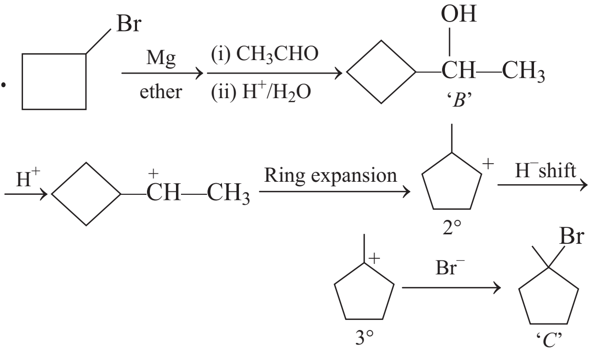


46.

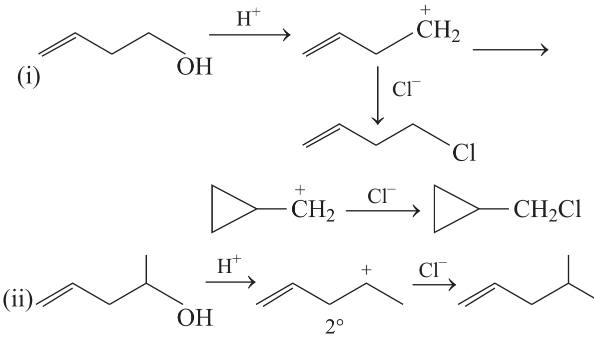


$\xrightarrow{I_2/NaOH}$ Both gives positive iodoform test.

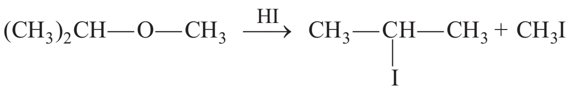
47.



48.

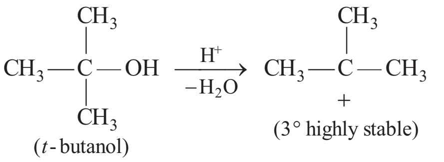


49.



$$(CH_3)_2CH-O-CH_3 \xrightarrow{HI} CH_3-\underset{I}{\underset{|}{CH}}-CH_3 + CH_3I$$

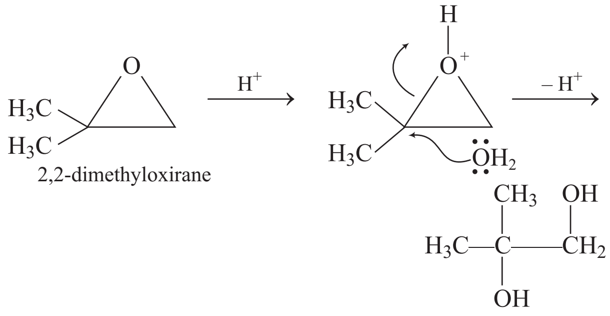
50. Acid catalysed dehydration proceeds *via* carbocation intermediate. Also, greater the stability of reactive intermediate, faster the reaction :



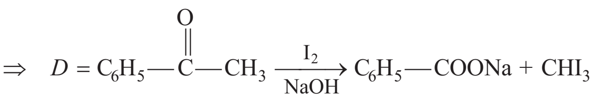
$$\underset{(t\text{-butanol})}{CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OH} \xrightarrow[-H_2O]{H^+} \underset{(3°\text{ highly stable})}{CH_3-\overset{CH_3}{\overset{|}{\underset{+}{C}}}-CH_3}$$

n-butanol forms less stable (1°) carbocation.

51.

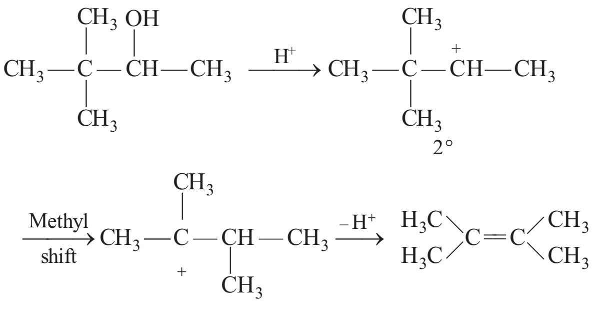


52. $E = C_6H_5COOH$ (benzoic acid)



$$\Rightarrow D = C_6H_5-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[NaOH]{I_2} C_6H_5-COONa + CHI_3$$

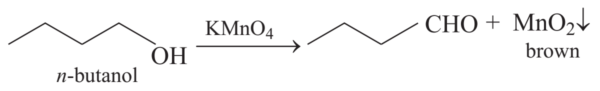
53.



$$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-\overset{OH}{\overset{|}{CH}}-CH_3 \xrightarrow{H^+} CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-\overset{+}{CH}-CH_3 \quad 2°$$

$$\xrightarrow[\text{shift}]{\text{Methyl}} CH_3-\overset{CH_3}{\overset{|}{\underset{+}{C}}}-\underset{CH_3}{\underset{|}{CH}}-CH_3 \xrightarrow{-H^+} \begin{matrix}H_3C\\H_3C\end{matrix}\!>C=C<\!\begin{matrix}CH_3\\CH_3\end{matrix}$$

54.



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

$C_5H_8O \xrightarrow[AgNO_3]{\text{Ammoniacal}}$ ppt, $X \xrightarrow[CH_3MgBr]{\text{Excess of}} CH_4$;

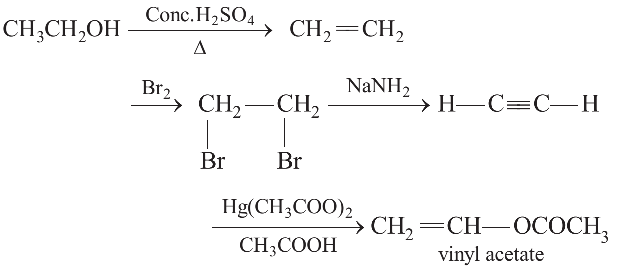
$X \xrightarrow[\text{HI excess}]{H_2/Pt} n$-pentane

Above information suggest that X has a terminal triple bond and it contain primary —OH group.

$$\Rightarrow \underset{X}{H-C\equiv C-CH_2-CH_2-CH_2OH} \xrightarrow{Ag(NH_3)_2^+}$$
$$Ag-C\equiv C-CH_2CH_2CH_2OH$$

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

57.



$$CH_3CH_2OH \xrightarrow[\Delta]{Conc.H_2SO_4} CH_2=CH_2$$
$$\xrightarrow{Br_2} \underset{Br}{\underset{|}{CH_2}}-\underset{Br}{\underset{|}{CH_2}} \xrightarrow{NaNH_2} H-C\equiv C-H$$
$$\xrightarrow[CH_3COOH]{Hg(CH_3COO)_2} \underset{\text{vinyl acetate}}{CH_2=CH-OCOCH_3}$$

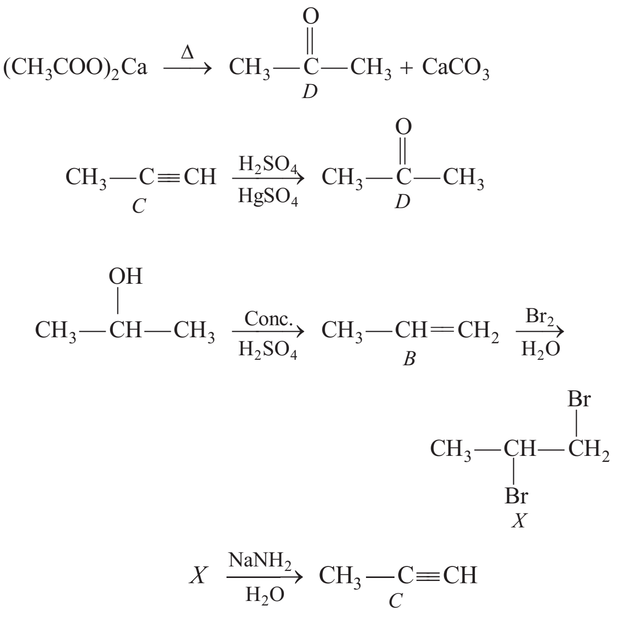
58. $C_2H_5OH \xrightarrow{I_2/NaOH} \underset{\text{iodoform}}{CHI_3} + HCOONa$

59. $CH_3-CH_2OH + I_2 + NaOH \longrightarrow \underset{\text{yellow}}{CHI_3\downarrow}$ (Iodoform test)

Iodoform test is not given by methanol.

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

61.



$$(CH_3COO)_2Ca \xrightarrow{\Delta} \underset{D}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3} + CaCO_3$$

$$\underset{C}{CH_3-C\equiv CH} \xrightarrow[HgSO_4]{H_2SO_4} \underset{D}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3}$$

$$CH_3-\overset{OH}{\overset{|}{CH}}-CH_3 \xrightarrow[H_2SO_4]{Conc.} \underset{B}{CH_3-CH=CH_2} \xrightarrow[H_2O]{Br_2}$$
$$\underset{X}{CH_3-\underset{Br}{\underset{|}{CH}}-\overset{Br}{\overset{|}{CH_2}}}$$

$$X \xrightarrow[H_2O]{NaNH_2} \underset{C}{CH_3-C\equiv CH}$$

62. (i) $H—C\equiv C—H \xrightarrow[H_2SO_4]{HgSO_4} CH_3—CHO \xrightarrow[H_2]{\text{Catalyst}} CH_3CH_2OH$

(ii) $4\,C_2H_5Br + \underset{\text{sodium-lead alloy}}{4\,(Na/Pb)} \xrightarrow{\text{Heat}} \underset{\text{tetraethyl lead}}{(C_2H_5)_4Pb}$

(iii) $Al_4C_3 \xrightarrow{H_2O} Al(OH)_3 + CH_4$

$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$

63. Compound X must be a symmetrical ether :

$\underset{X}{R—O—R} \xrightarrow{HI} \underset{Y}{2R—I} \xrightarrow{Na}$ No reaction, not an alcohol

$\xrightarrow[\text{reagent}]{\text{Schiffs'}}$ No reaction, not an aldehyde.

$$\begin{tikzcd} R—I \arrow[r, "H_2O"] & R—OH(Z) \arrow[r, "{[O]}"] \arrow[d, "I_2/P"] & \underset{EW = 60}{\text{Acid}} \\ & R—I & \end{tikzcd}$$

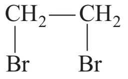
⇒ Acid is CH_3COOH and $Z = CH_3CH_2OH$

⇒ $X = C_2H_5—O—C_2H_5$, $Y = CH_3—CH_2—I$

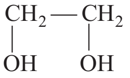
$\underset{X}{CH_3CH_2—O—CH_2CH_3} \xrightarrow{HI} \underset{Y}{2CH_3CH_2I}$

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

$C_2H_5OH + Conc.\,H_2SO_4 \longrightarrow CH_2{=}CH_2 \xrightarrow{H_2/Ni} CH_3—CH_3$



$CH_2{=}CH_2 + \underset{\text{(brown)}}{Br_2—H_2O} \longrightarrow \underset{\text{colourless}}{\underset{Br\quad\ Br}{CH_2—CH_2}}$



$CH_2{=}CH_2 + \underset{\text{purple}}{\text{alk. }KMnO_4} \longrightarrow \underset{\text{colourless}}{\underset{OH\quad OH}{CH_2—CH_2}}$

65.