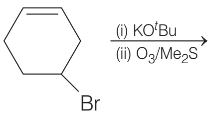
25

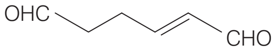
Aldehydes and Ketones

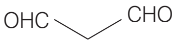
Objective Questions I (Only one correct option)

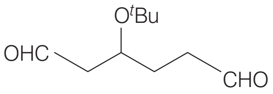
1. The major product(s) obtained in the following reaction is/are **(2019 Main, 12 April I)**



(a) 

(b) 

(c) 

(d) 

2. In the following reaction,

Carbonyl compound + MeOH $\overset{HCl}{\rightleftharpoons}$ acetal

Rate of the reaction is the highest for: **(2019 Main, 9 April II)**

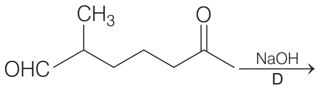
(a) Acetone as substrate and methanol in excess

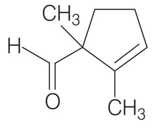
(b) Propanal as substrate and methanol in stoichiometric amount

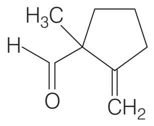
(c) Acetone as substrate and methanol in stoichiometric amount

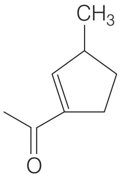
(d) Propanal as substrate and methanol in excess

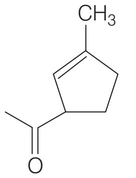
3. The major product obtained in the following reaction is **(2019 Main, 8 April II)**



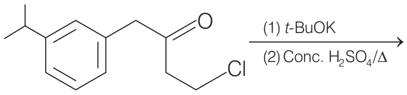
(a) 

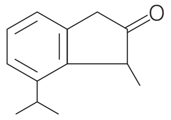
(b) 

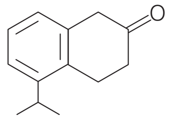
(c) 

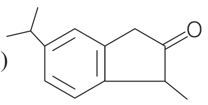
(d) 

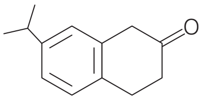
4. The major product of the following reaction is **(2019 Main, 8 April II)**



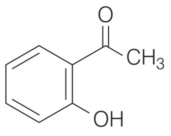
(a) 

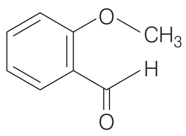
(b) 

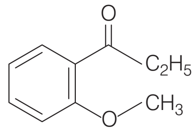
(c) 

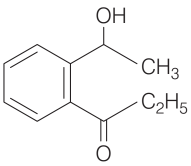
(d) 

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)**

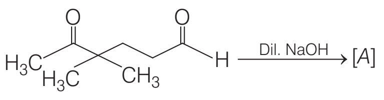
(a) 

(b) 

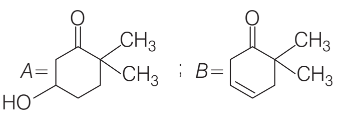
(c) 

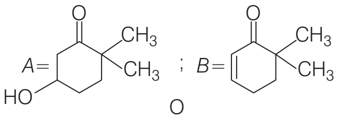
(d) 

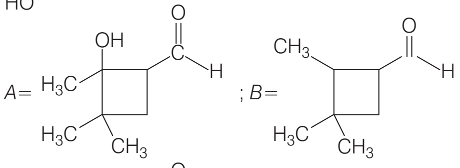
6. In the following reactions, products *A* and *B* are **(2019 Main, 12 Jan I)**

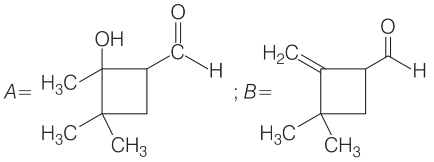


[*A*] $\xrightarrow[\Delta]{H_3O^+}$ [*B*]

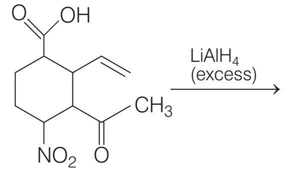
(a) 

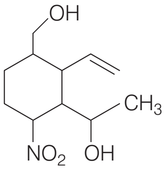
(b) 

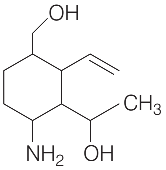
(c) 

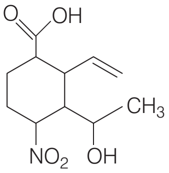
(d) 

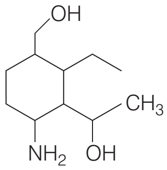
7. The major product obtained in the following reaction is **(2019 Main, 11 Jan II)**



(a) 

(b) 

(c) 

(d) 

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

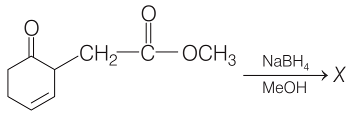
	Item 'I' (Compound)		**Item 'II'** (Reagent)
(A)	Lysine	(P)	1-naphthol
(B)	Furfural	(Q)	Ninhydrin
(C)	Benzyl alcohol	(R)	$KMnO_4$
(D)	Styrene	(S)	Ceric ammonium nitrate

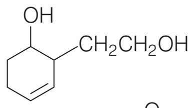
(2019 Main, 10 Jan II)

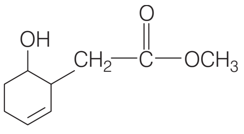
Codes

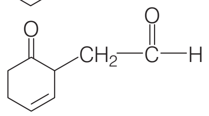
	A	B	C	D
(a)	Q	R	S	P
(b)	R	P	Q	S
(c)	Q	P	S	R
(d)	Q	P	R	S

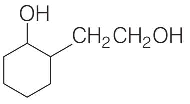
9. The major product '*X*' formed in the following reaction is **(2019 Main, 10 Jan I)**



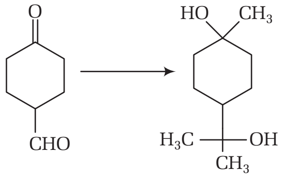
(a) 

(b) 

(c) 

(d) 

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



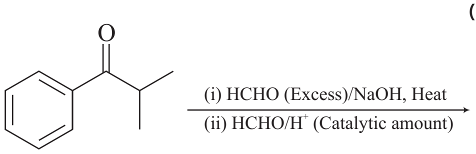
(a) $[Ag(NH_3)_2]^+ OH^-, H^+ / CH_3OH, CH_3MgBr$

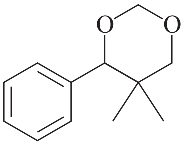
(b) $CH_3MgBr, H^+ / CH_3OH, [Ag(NH_3)_2]^+ OH^-$

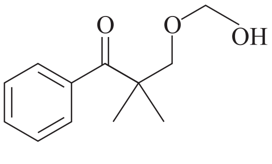
(c) $CH_3MgBr, [Ag(NH_3)_2]^+ OH^-, H^+ / CH_3OH$

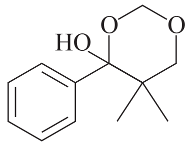
(d) $[Ag(NH_3)_2]^+ OH^-, CH_3MgBr, H^+ / CH_3OH$

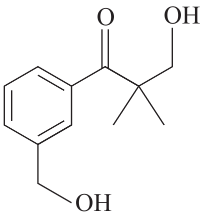
11. The major product of the following reaction sequence is **(2016 Adv.)**



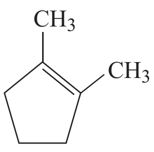
(a) 

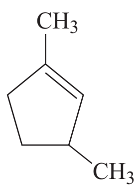
(b) 

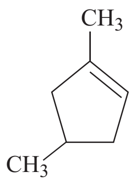
(c) 

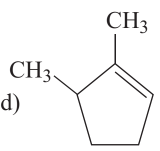
(d) 

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

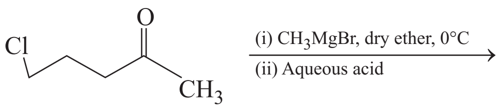
(a) 

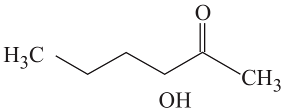
(b) 

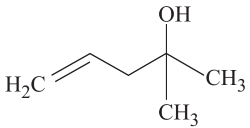
(c) 

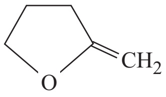
(d) 

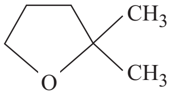
13. The major product in the following reaction is **(2014 Adv.)**



(a) 

(b) 

(c) 

(d) 

14. The most suitable reagent for the conversion of $R-CH_2-OH \rightarrow R-CHO$ is **(2014 Main)**

(a) $KMnO_4$

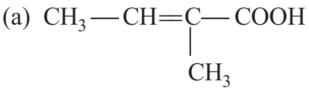
(b) $K_2Cr_2O_7$

(c) CrO_3

(d) PCC (pyridinium chlorochromate)

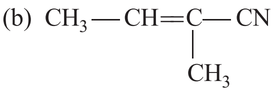
15. The major product H in the given reaction sequence is

$$CH_3-CH_2-CO-CH_3 \xrightarrow{CN^{\ominus}} G \xrightarrow{95\%\ H_2SO_4} H$$

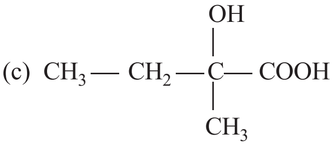
(a) 

$CH_3-CH=\underset{\substack{|\\ CH_3}}{C}-COOH$

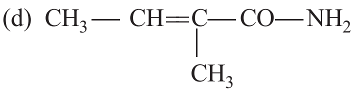
(2012)

(b) 

$CH_3-CH=\underset{\substack{|\\ CH_3}}{C}-CN$

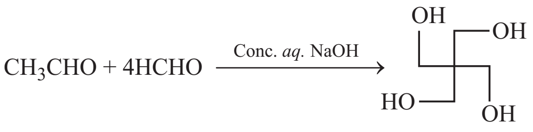
(c) 

$CH_3-CH_2-\overset{\substack{OH\\ |}}{\underset{\substack{|\\ CH_3}}{C}}-COOH$

(d) 

$CH_3-CH=\underset{\substack{|\\ CH_3}}{C}-CO-NH_2$

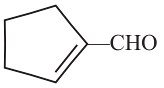
16. The number of aldol reaction(s) that occurs in the given transformation is **(2012)**

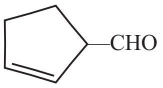


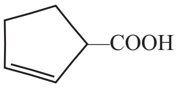
(a) 1 (b) 2

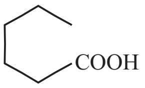
(c) 3 (d) 4

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 NH_2OH 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

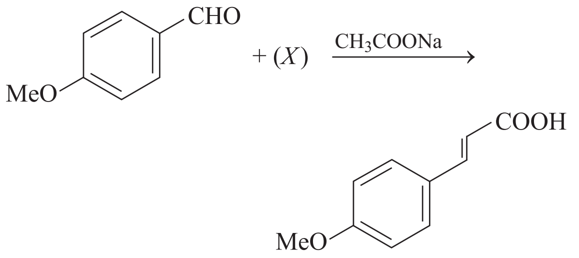
19. Butan-2-one can be converted to propanoic acid by which of the following ? **(2006)**

(a) NaOH, NaI/H^+

(b) Fehling's solution

(c) NaOH, I_2/H^+

(d) Tollen's reagent

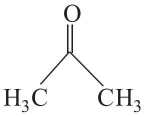
20. 

What is *X*?

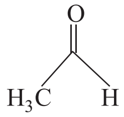
(a) CH_3COOH (b) $BrCH_2COOH$

(c) $(CH_3CO)_2O$ (d) HOC—COOH

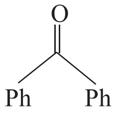
21. The order of reactivity of phenyl magnesium bromide with the following compounds is **(2004, 1M)**



(I)



(II)



(III)

(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)**

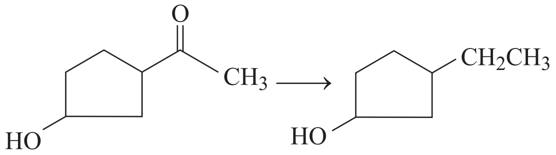
(a) benzyl alcohol and sodium formate

(b) sodium benzoate and methyl alcohol

(c) sodium benzoate and sodium formate

(d) benzyl alcohol and methyl alcohol

23. The appropriate reagent for the following transformation:

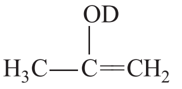


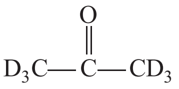
(a) Zn (Hg), HCl (b) NH_2NH_2, OH^-
(c) H_2/Ni (d) $NaBH_4$

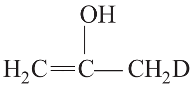
24. Which of the following has the most acidic hydrogen? **(2000, 1M)**

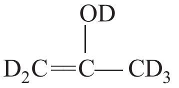
(a) 3-hexanone (b) 2, 4-hexanedione
(c) 2, 5-hexanedione (d) 2, 3-hexanedione

25. The enol form of acetone, after treatment with D_2O, gives **(1999, 2M)**

(a)  $H_3C-\overset{OD}{\overset{|}{C}}=CH_2$

(b)  $D_3C-\overset{O}{\overset{\|}{C}}-CD_3$

(c)  $H_2C=\overset{OH}{\overset{|}{C}}-CH_2D$

(d)  $D_2C=\overset{OD}{\overset{|}{C}}-CD_3$

26. Which of the following will react with water? **(1998, 2M)**

(a) $CHCl_3$ (b) Cl_3CCHO
(c) CCl_4 (d) $ClCH_2CH_2Cl$

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) Cu_2O (d) Cu + Cu_2O + CuO

31. A compound that gives a positive iodoform test is **(1982, 1M)**

(a) 1-pentanol (b) 3-pentanone
(c) 2- pentanone (d) pentanal

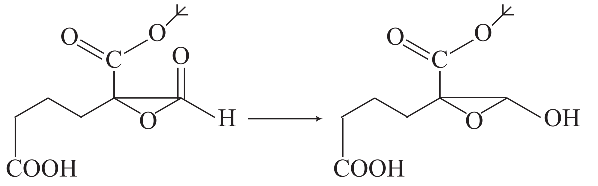
32. The reagent with which both acetaldehyde and acetone react easily is **(1981, 1M)**

(a) Tollen's reagent (b) Schiff's reagent
(c) Grignard's reagent (d) Fehling's reagent

Objective Questions II

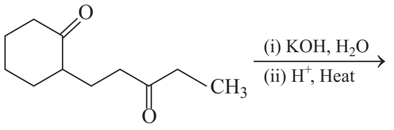
(One or more than one correct option)

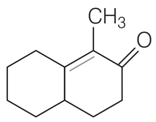
33. Reagent(s) which can be used to bring about the following transformation is (are) **(2016 Adv.)**

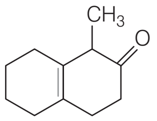


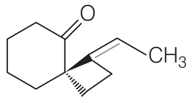
(a) $LiAlH_4$ in $(C_2H_5)_2O$ (b) BH_3 in THF
(c) $NaBH_4$ in C_2H_5OH (d) Raney Ni/H_2 in THF

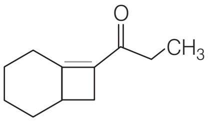
34. The major product of the following reaction is **(2015 Adv.)**



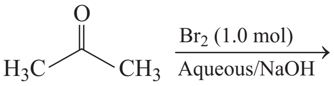
(a) 

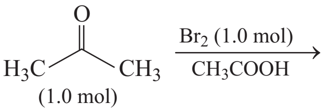
(b) 

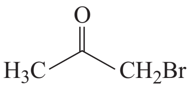
(c) 

(d) 

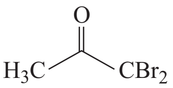
35. After completion of the reactions (I and II), the organic compound (s) in the reaction mixtures is/are **(2013)**

Reaction I 

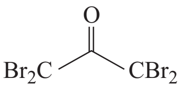
Reaction II 



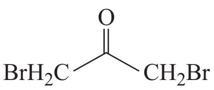
P



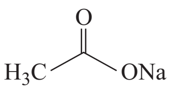
Q



R



S

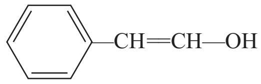


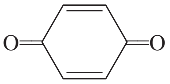
T

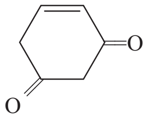
$CHBr_3$
U

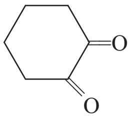
(a) reaction I : *P* and reaction II : *P*
(b) reaction I : *U*, acetone and reaction II : *Q*, acetone
(c) reaction I : *T*, *U*, acetone and reaction II : *P*
(d) reaction I : *R*, acetone and reaction II : *S*, acetone

36. Tautomerism is exhibited by **(1998)**

(a) 

(b) 

(c) 

(d) 

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)**

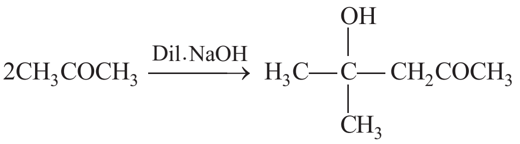
(a) Acetaldehyde
(b) Propanaldehyde
(c) Benzaldehyde
(d) Trideutero acetaldehyde

39. Among the following compounds, which will react with acetone to give a product containing $>C=N-$?

(a) $C_6H_5NH_2$ (b) $(CH_3)_3N$ **(1998, 2M)**
(c) $C_6H_5NHC_6H_5$ (d) $C_6H_5NHNH_2$

40. Which of the following is an example of aldol condensation?

(a) $2CH_3CHO \xrightarrow{\text{Dil.NaOH}} CH_3CH(OH)CH_2CHO$ **(1989, 1M)**

(b) 

$$2CH_3COCH_3 \xrightarrow{\text{Dil.NaOH}} H_3C-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2COCH_3$$

(c) $2HCHO \xrightarrow{\text{Dil.NaOH}} CH_3OH + HCOONa$

(d) $C_6H_5CHO + HCHO \xrightarrow{\text{Dil.NaOH}} C_6H_5CH_2OH + HCOONa$

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

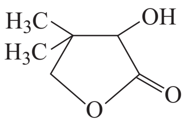
43. Base catalysed aldol condensation occurs with **(1984, 1M)**

(a) propionaldehyde
(b) benzaldehyde
(c) 2-methyl propionaldehyde
(d) 2, 2-dimethyl propionaldehyde

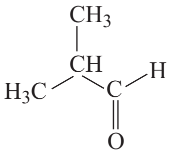
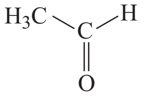
Passage Based Questions

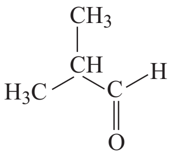
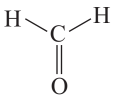
Passage 1

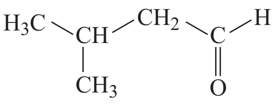
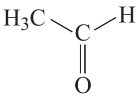
Two aliphatic aldehydes *P* and *Q* react in the presence of aqueous K_2CO_3 to give compound *R*, which upon treatment with HCN provides compound *S*. On acidification and heating, *S* gives the product shown below : **(2010)**

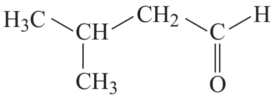
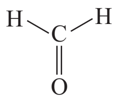


44. The compounds *P* and *Q* respectively are

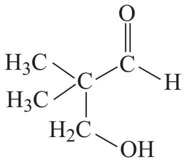
(a)  and 

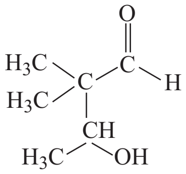
(b)  and 

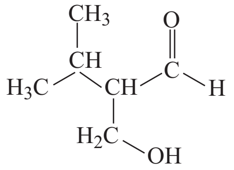
(c)  and 

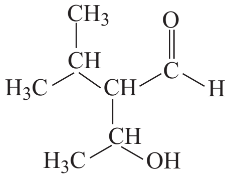
(d)  and 

45. The compound *R* is

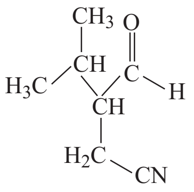
(a) 

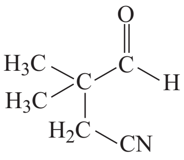
(b) 

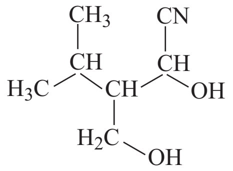
(c) 

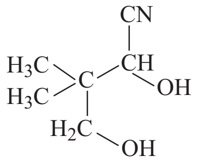
(d) 

46. The compound *S* is

(a) 

(b) 

(c) 

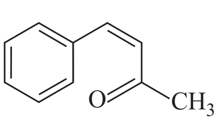
(d) 

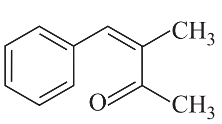
Passage 2

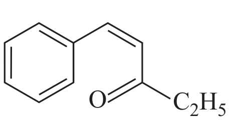
A carbonyl compound *P*, which gives positive iodoform test, undergoes reaction with MeMgBr followed by dehydration to give an olefin *Q*. Ozonolysis of *Q* leads to a dicarbonyl compound *R*, which undergoes intramolecular aldol reaction to give predominantly *S*. **(2009)**

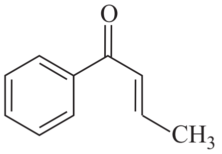
$$P \xrightarrow[\substack{2.\ H^+,\ H_2O \\ 3.\ H_2SO_4\ /\ \text{heat}}]{1.\ \text{MeMgBr}} Q \xrightarrow{O_3/Zn\text{-}H_2O} R \xrightarrow[\text{heat}]{OH^-} S$$

47. The structure of the carbonyl compound *P*, is

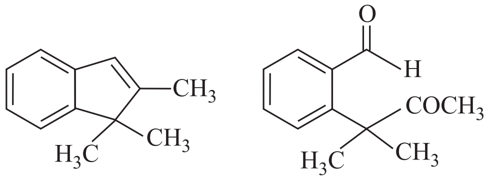
(a) 

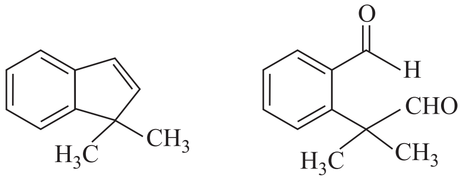
(b) 

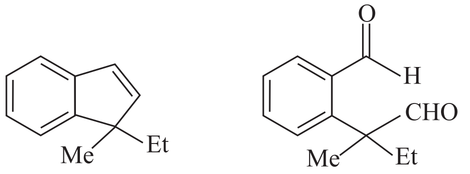
(c) 

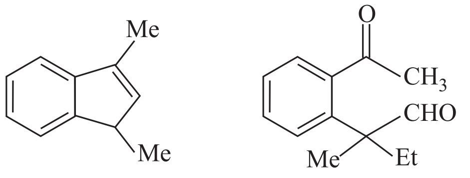
(d) 

48. The structures of the products *Q* and *R*, respectively, are

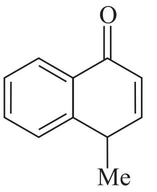
(a) 

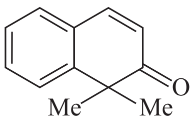
(b) 

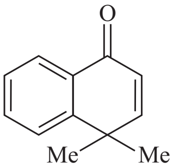
(c) 

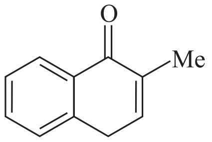
(d) 

49. The structure of the product *S*, is

(a) 

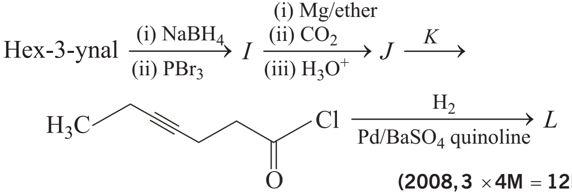
(b) 

(c) 

(d) 

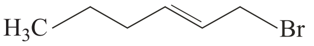
Passage 3

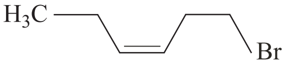
In the following sequence, product *I*, *J* and *L* are formed. *K* represents a reagent.

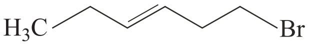


(2008, 3 × 4M = 12M)

50. The structure of the product *I* is

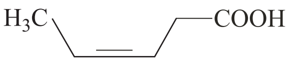
(a) 

(b) 

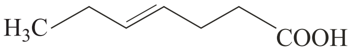
(c) 

(d) 

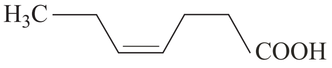
51. The structures of compounds *J* and *K*, respectively, are

(a) 

and $SOCl_2$

(b) 

and SO_2Cl_2

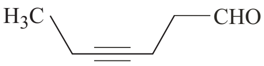
(c) 

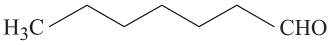
and $SOCl_2$

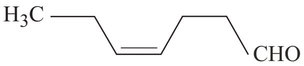
(d) 

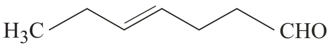
and CH_3SO_2Cl

52. The structure of product *L* is

(a) 

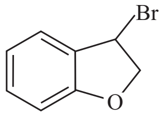
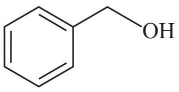
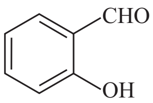
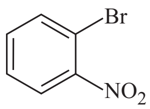
(b) 

(c) 

(d) 

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)**

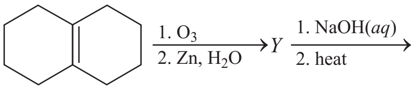
57. Benzaldehyde undergoes aldol condensation in an alkaline medium. **(1982 , 1M)**

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



(2010)

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)

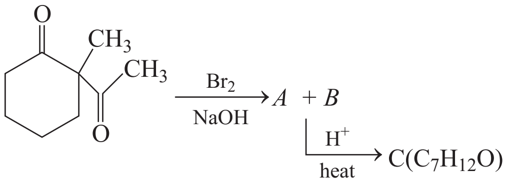
$(F) + (G) \xrightarrow{\text{Conc. NaOH}}$ HCOONa + A primary alcohol

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)**

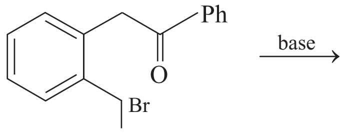
63. Identify *A, B* and *C*, and give their structures.



(2000)

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 ?



(2000, 1M)

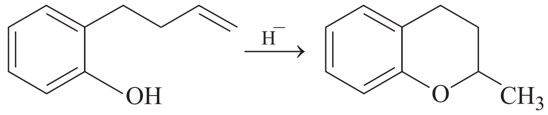
66. (a) Compound *A* (C_8H_8O) on treatment with NH_2OH. HCl given *B* and *C*. *B* and *C* rearrange to give *D* and *E*, respectively, on treatment with acid. *B*, *C*, *D* and *E* are all isomers of molecular formula (C_8H_9NO). When *D* is boiled with alcoholic KOH, an oil *F* (C_6H_7N) separates 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.

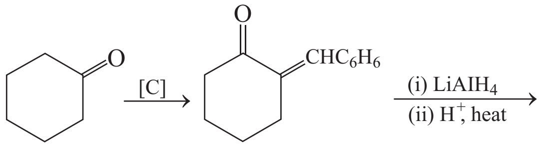
1-butyne $\longrightarrow$ 2-pentanone **(1999, 3M)**

67. Write the intermediate steps for each of the following reactions

(i) $C_6H_5CH(OH)C\equiv CH \xrightarrow{H_3O^+} C_6H_5CH=CHCHO$

(ii) 

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

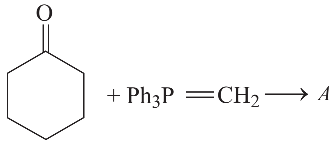


(1998)

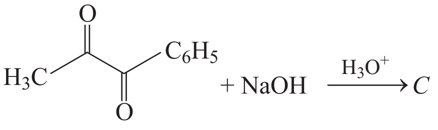
69. An aldehyde *A* ($C_{11}H_8O$), which does not undergo self aldol condensation, gives benzaldehyde and two moles of *B* on ozonolysis. Compound *B*, on oxidation with silver ion gives oxalic acid. Identify the compounds *A* and *B*. **(1998, 2M)**

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,

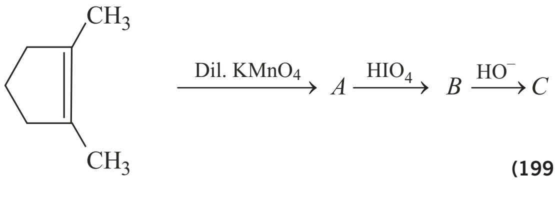
(i) 

(ii) $ClCH_2CH_2CH_2COPh + KOH + MeOH \longrightarrow B$

(iii) 

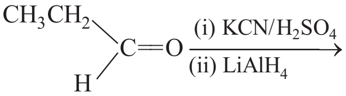
(1997, 2M)

72. Suggest appropriate structures for the missing compounds. (the number of carbon atoms remains the same throughout the reaction)



(1996, 3M)

73 Complete the following reaction with appropriate structure :



$$\begin{matrix} CH_3CH_2 \\ H \end{matrix}\!\!>C{=}O \xrightarrow[\text{(ii) LiAlH}_4]{\text{(i) KCN/H}_2\text{SO}_4}$$

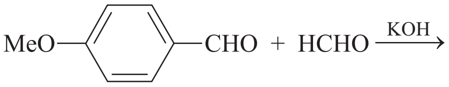
(1996, 1M)

74. Complete the following reaction with appropriate structure.

$$C_6H_5CHO + CH_3COOC_2H_5 \xrightarrow[C_2H_5OH\text{ heat}]{NaOC_2H_5\text{ in absolute}} A$$

(1995, 1M)

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.

CH_3COCH_2CHO, CH_3COCH_3, CH_3CHO, $CH_3COCH_2COCH_3$ **(1992, 1M)**

77. Give reason in one or two sentences :

"Iodoform is obtained by the reaction of acetone with hypoiodite but not with iodide". **(1991)**

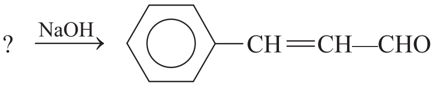
78. A ketone *A*, which undergoes haloform reaction, gives compound *B* on reduction. *B* on heating with sulphuric acid gives compound *C*, which forms mono-ozonide *D*. *D* on hydrolysis in the presence of zinc dust gives only acetaldehyde. Identify *A*, *B* and *C*. Write down the reactions involved. **(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



(1986, 1M)

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:

"Hydrazones of aldehydes and ketones are not prepared in highly acidic medium". **(1986, 1M)**

83. Write down product of the following reaction

$$\text{Propanal} \xrightarrow[\text{heat}]{NaOH}$$

(1985, 1M)

84. Arrange the following in order of their increasing reactivity towards HCN :

CH_3CHO, CH_3COCH_3, $HCHO$, $C_2H_5COCH_3$ **(1985, 1M)**

85. Write down the reactions involved in the preparation of the following using the reagents indicated against in parenthesis:

"Acetoxime from acetaldehyde."

[$K_2Cr_2O_7$ / H^+, $Ca(OH)_2$ and NH_2OH, HCl] **(1984, 2M)**

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)**

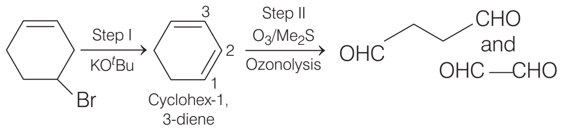
89. Write the structural formula of the main organic product formed when methanal reacts with ammonia. **(1981, 1/2M)**

Answers

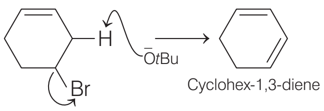
1. (a)
2. (d)
3. (c)
4. (d)
5. (d)
6. (b)
7. (b)
8. (c)
9. (b)
10. (a)
11. (a)
12. (b)
13. (d)
14. (d)
15. (a)
16. (c)
17. (a)
18. (b)
19. (c)
20. (c)
21. (c)
22. (a)
23. (b)
24. (b)
25. (b)
26. (b)
27. (c)
28. (c)
29. (b)
30. (c)
31. (c)
32. (c)
33. (c)
34. (a)
35. (c)
36. (a,c,d)
37. (b,d)
38. (a,b,d)
39. (a,d)
40. (a,b)
41. (a,b,d)
42. (a,b)
43. (a,c)
44. (b)
45. (a)
46. (d)
47. (b)
48. (a)
49. (b)
50. (d)
51. (a)
52. (c)
53. A → p, q, t B → p, s, t C → r, s D → p.
54. A → p, q, s B → q, r C → q, r, s D → q, r.
55. Sodium potassium tartarate
56. False
57. False
58. (5)
59. (1)

Hints & Solutions

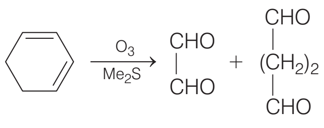
1.



In step-1 dehydrohalogenation reaction takes place. Here, hydrogen is eliminated from β-carbon and the halogen is lost from α-carbon atom. As a result diene is formed.



Cyclohex -1, 3-diene on ozonolysis gives butane-1, 4- dial and ethane- 1, 2- dial.

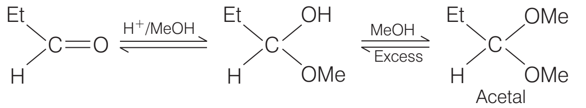


2. **Key Idea** Aldehydes are more reactive than ketones in nucleophilic addition reactions.

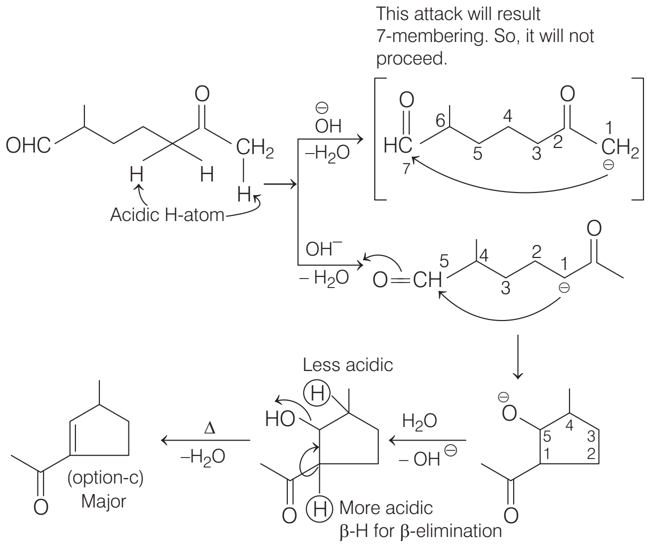
For the reaction,

Carbonyl compound + MeOH $\overset{HCl}{\rightleftharpoons}$ Acetal

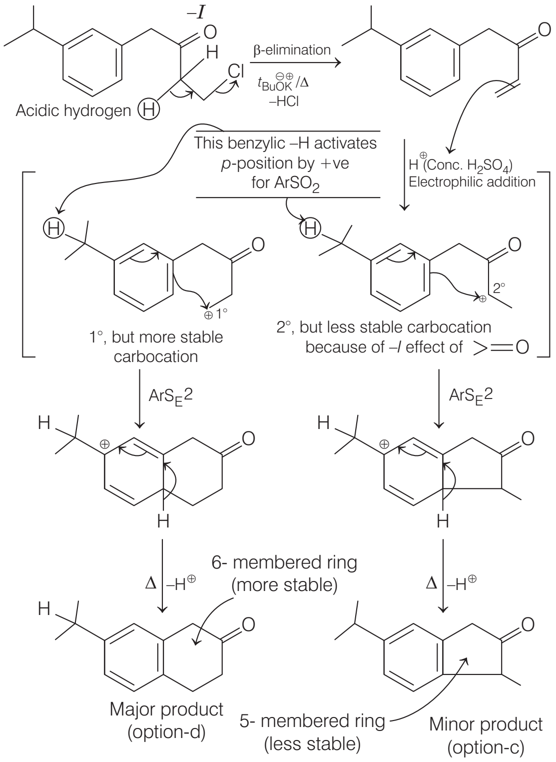
Rate of reaction is the highest for propanal as substrate and methanol in excess. Propanal is an aldehyde and more reactive than ketones. When MeOH is taken in excess then reaction moves in the forward direction that results in the formation of acetal. Reaction involved is as follows :



3. It is an intramolecular aldol condensation reaction.

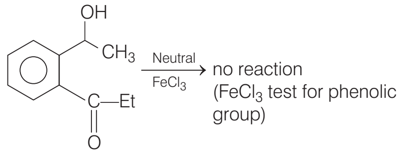


4.

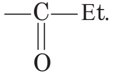


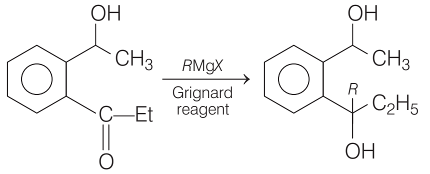
5. According to the given conditions, compound (d) neither reacts with neutral ferric chloride solution nor with Fehling solution. It however reacts with Grignard reagent and gives positive iodoform test.

- As the compound does not contain any phenolic —OH group. Hence, it gives negative neutral $FeCl_3$ test.

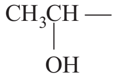


- Compound gives reaction with RMgX as it contains

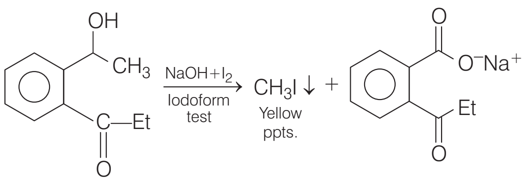

$-\underset{\underset{O}{\|}}{C}-Et.$



Compound with

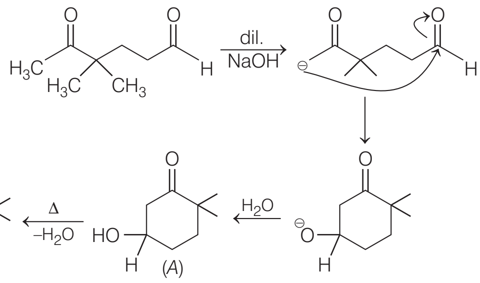

$CH_3\underset{\underset{OH}{|}}{C}H-$

group undergoes iodoform test in presence of NaOH and I_2.

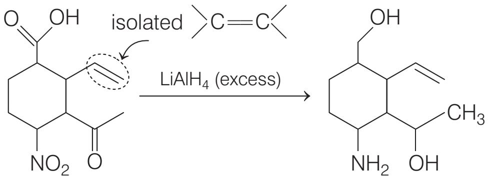


6. The reactant in presence of dil·NaOH undergoes intramolecular aldol condensation reaction.

As a result of this, β-hydroxyketone (A) is obtained which on hydrolysis followed by heating produces α, β-unsaturated ketone (B)



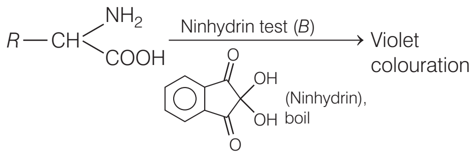
7. $LiAlH_4$ acts as a nucleophilic reducing agent that can reduce —COOH to $—CH_2OH$, $-\underset{|}{C}=O$ into $-\underset{|}{C}H-OH$ and $—NO_2$ into $—NH_2$, but it cannot reduce isolated $>C=C<$



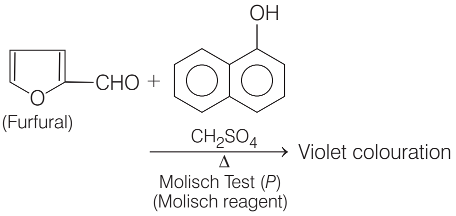
Compound (b)

8. (A) → Q; B → (P) ; C → (S), D → (R)

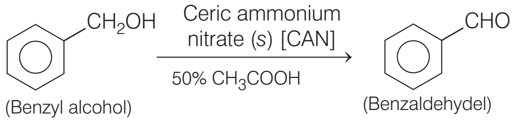
(A) Lysine (R=$-(CH_2)_4-NH_2$)



(B)

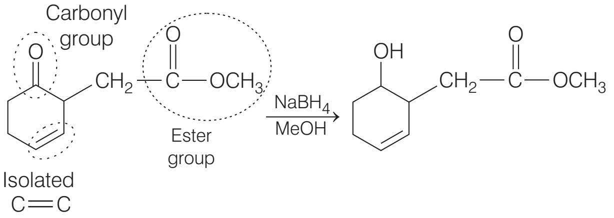


(C)

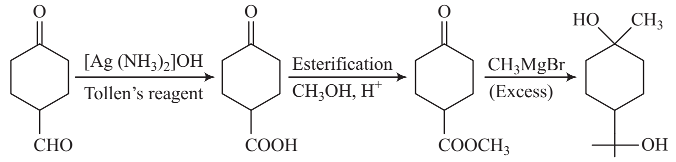


(D)

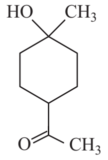
9. NaBH$_4$ is a selective reducing agent. It reduces carbonyl $\left(>C=O\right)$ group into an alcohol but cannot reduce an isolated C$=$C and an ester group too.



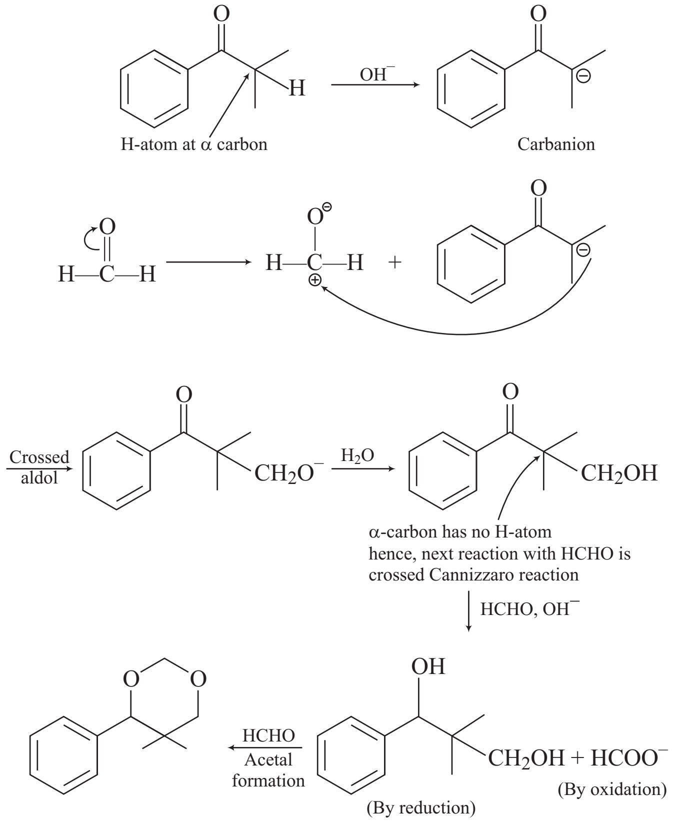
10.



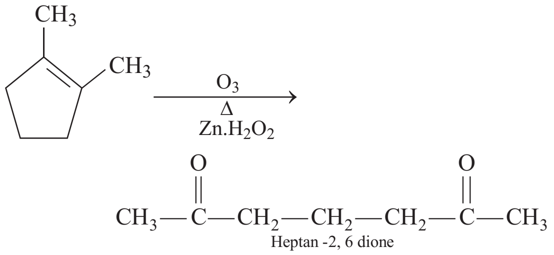
Before final product is formed, intermediate is



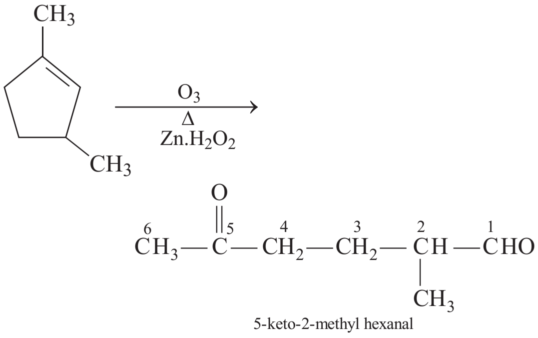
11.



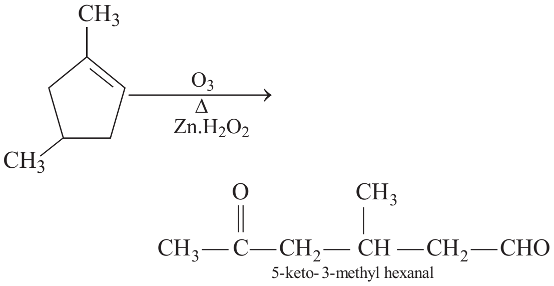
12. (a)



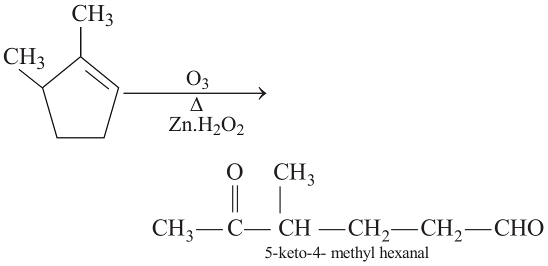
(b)



(c)

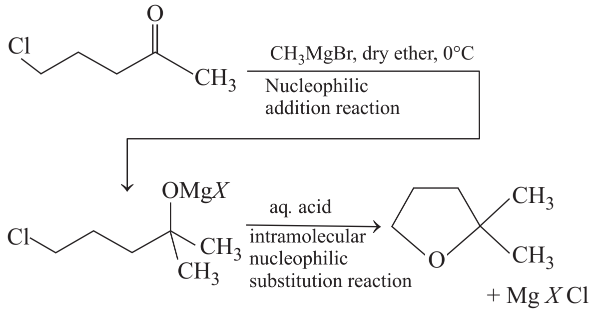


(d)



13. **PLAN** This problem includes concept of nucleophilic addition reaction to carbonyl compound (ketone here) and intramolecular nucleophilic substitution reaction.

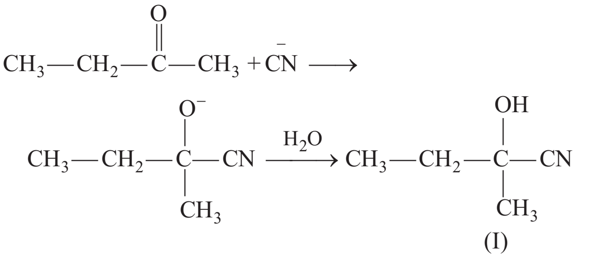
Complete reaction sequence is as shown below:



14. $R—CH_2OH \xrightarrow{PCC} R—CH{=}O$

Pyridinium chlorochromate is the mild oxidising agent which causes conversion of alcohol to aldehyde stage. While others causes conversion of alcohol to acid.

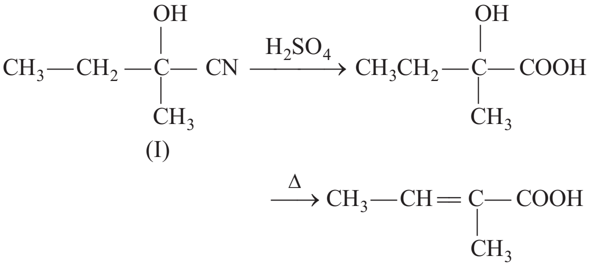
15. The first step is cyanohydrin reaction



$$CH_3—CH_2—\overset{O}{\overset{\|}{C}}—CH_3 + \overset{-}{C}N \longrightarrow CH_3—CH_2—\underset{CH_3}{\overset{O^-}{C}}—CN \xrightarrow{H_2O} CH_3—CH_2—\underset{CH_3}{\overset{OH}{C}}—CN$$

(I)

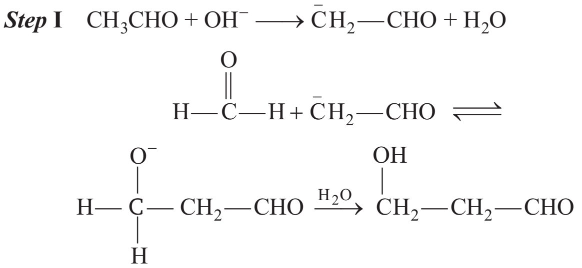
In the second step the — CN of intermediate (I) is first hydrolysed and then dehydrated on heating in the presence of conc. H_2SO_4.



$$\underset{(I)}{CH_3—CH_2—\underset{CH_3}{\overset{OH}{C}}—CN} \xrightarrow{H_2SO_4} CH_3CH_2—\underset{CH_3}{\overset{OH}{C}}—COOH \xrightarrow{\Delta} CH_3—CH{=}\underset{CH_3}{C}—COOH$$

16. The given reaction is an example of repeated aldol condensation followed by Cannizzaro reaction.

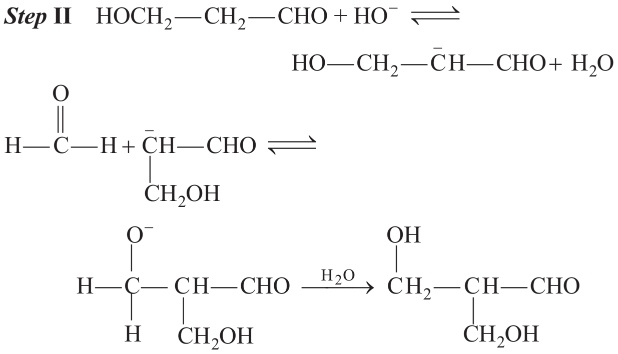
***Step* I**



$$CH_3CHO + OH^- \longrightarrow \overset{-}{C}H_2—CHO + H_2O$$

$$H—\overset{O}{\overset{\|}{C}}—H + \overset{-}{C}H_2—CHO \rightleftharpoons H—\underset{H}{\overset{O^-}{C}}—CH_2—CHO \xrightarrow{H_2O} \overset{OH}{C}H_2—CH_2—CHO$$

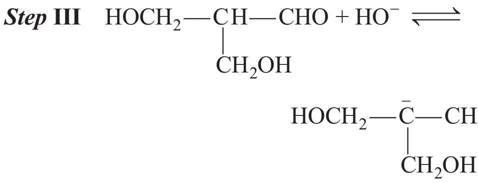
***Step* II**



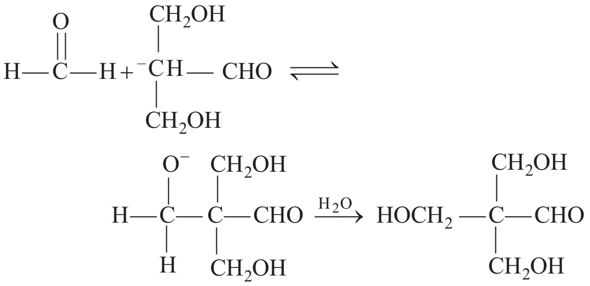
$$HOCH_2—CH_2—CHO + HO^- \rightleftharpoons HO—CH_2—\overset{-}{C}H—CHO + H_2O$$

$$H—\overset{O}{\overset{\|}{C}}—H + \underset{CH_2OH}{\overset{-}{C}H}—CHO \rightleftharpoons H—\underset{H}{\overset{O^-}{C}}—\underset{CH_2OH}{CH}—CHO \xrightarrow{H_2O} \overset{OH}{C}H_2—\underset{CH_2OH}{CH}—CHO$$

***Step* III**

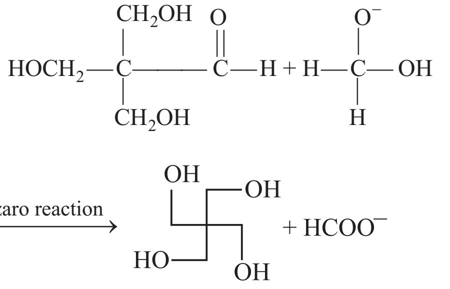


$$HOCH_2—\underset{CH_2OH}{CH}—CHO + HO^- \rightleftharpoons HOCH_2—\underset{CH_2OH}{\overset{-}{C}}—CHO + H_2O$$



$$H—\overset{O}{\overset{\|}{C}}—H + \underset{CH_2OH}{\overset{CH_2OH}{^{-}CH}}— CHO \rightleftharpoons H—\underset{H}{\overset{O^-}{C}}—\underset{CH_2OH}{\overset{CH_2OH}{C}}—CHO \xrightarrow{H_2O} HOCH_2—\underset{CH_2OH}{\overset{CH_2OH}{C}}—CHO$$

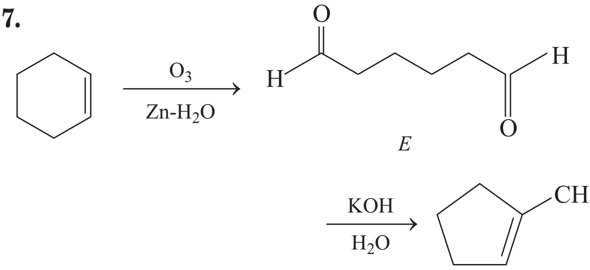
***Step* IV**



$$HOCH_2—\underset{CH_2OH}{\overset{CH_2OH}{C}}—\overset{O}{\overset{\|}{C}}—H + H—\underset{H}{\overset{O^-}{C}}—OH \xrightarrow{\text{Cannizzaro reaction}} C(CH_2OH)_4 + HCOO^-$$

In the last step, formaldehyde is oxidised and the other aldehyde is reduced giving the desired products.

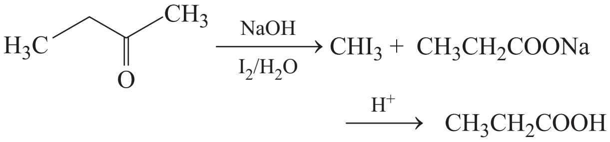
17.



Intramolecular aldol condensation reaction

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.

19.

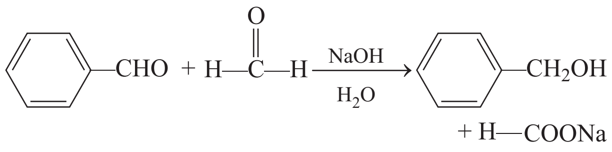


20. *X* is $(CH_3CO)_2O$ and it is an example of Perkin's reaction.

21. The reactivity of carbonyl compound towards nucleophilic addition of Grignard's reagent depends on extent of steric hindrance at α-carbon. Greater the steric hindrance smaller the reactivity. Hence, reactivity order is

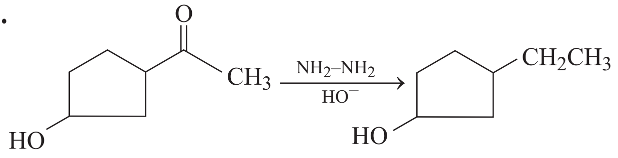
$$\underset{II}{CH_3CHO} > \underset{I}{CH_3—CO—CH_3} > \underset{III}{Ph—CO—Ph}$$

22.



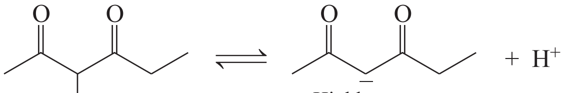
This is an example of cross Cannizzaro reaction in which formaldehyde is always oxidised.

23.



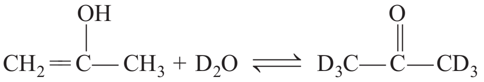
(Wolff-Kishner reduction)

24.



Highly resonance stabilised

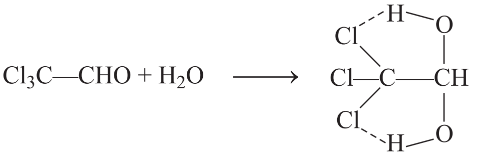
25.



$$CH_2{=}\overset{\overset{OH}{|}}{C}—CH_3 + D_2O \rightleftharpoons D_3C—\overset{\overset{O}{\|}}{C}—CD_3$$

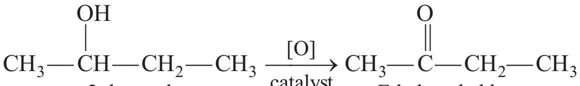
All α-H will be replaced by deuterium.

26.



Highly stable hydrate

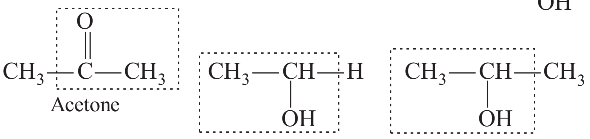
27.



$$CH_3—\overset{\overset{OH}{|}}{C}H—CH_2—CH_3 \xrightarrow[\text{catalyst}]{[O]} CH_3—\overset{\overset{O}{\|}}{C}—CH_2—CH_3$$

2-butanol Ethyl methyl ketone

28. Compounds that contain either $CH_3—CO$ or $CH_3—\underset{\underset{OH}{|}}{CH}—$ group gives iodoform test :



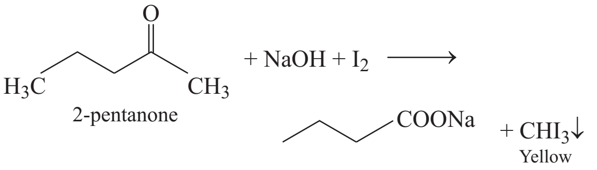
Acetone Ethanol Isopropyl alcohol

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 α-H undergo Cannizzaro reaction. When treated with aqueous base CH_3CHO does not undergo Cannizzaro reaction because it has α-H and in the presence of aqueous base it undergoes aldol condensation.

30. $CH_3—CHO$ + Fehling's solution $\longrightarrow \underset{\text{Red}}{Cu_2O\downarrow}$

31. For iodoform test, $CH_3—\overset{\overset{O}{\|}}{C}—$ group is required

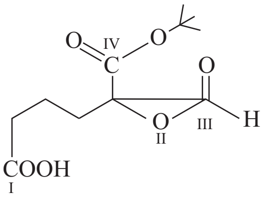


2-pentanone

32. Grignard's reagent reacts with both aldehydes and ketones while other three reagents reacts only with aldehydes, not with ketones.

33. Only — CHO group is to be reduced to $—CH_2OH$.

It can be done using $NaBH_4$ in C_2H_5OH.



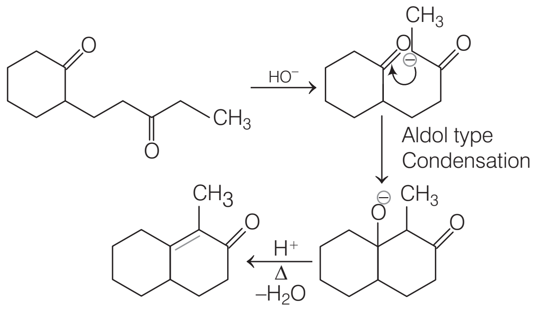
(a) $LiAlH_4 / (C_2H_5)_2O$ reduces I, II and III into $—CH_2OH$, and IV into diol.

(b) BH_3 / THF show same properties as (a).

(c) $NaBH_4 / C_2H_5OH$ reduces III into $—CH_2OH$.

(d) Raney nickel, same as (a) and (b), thus (c) is correct reagent.

34.



α, β-unsaturated ketone

35. **Plan** When acetone reacts with Br_2 in basic medium, bromoform is formed.

Reaction I

$$\underset{\substack{1\text{ mol}\\ \frac{1}{3}\text{mol}}}{CH_3COCH_3} + \underset{\substack{3\text{ mol}\\ 1\text{ mol}}}{3Br_2} + 4NaOH$$

$$\longrightarrow \underset{(T)}{CH_3COONa} + \underset{(U)}{CHBr_3} + 3NaBr + 3H_2O$$

When CH_3COCH_3 and Br_2 are in equimolar quantity, all the Br_2 (limiting reactant) is converted into desired products and 2/3 mole of CH_3COCH_3 remains unreacted, being in excess.

When acetone reacts with Br_2 in acidic medium, there is monobromination of acetone.

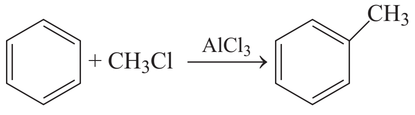
Reactions II

$$\underset{1\text{ mol}}{CH_3COCH_3} + \underset{1\text{ mol}}{Br_2} \xrightarrow{CH_3COOH} \underset{(P)}{CH_3COCH_2Br} + HBr$$

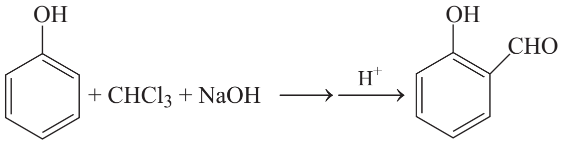
CH_3COCH_3 and Br_2 react in 1 : 1 mole ratio and (*P*) is formed. In reaction I, (*U*) and (*T*) are formed and acetone (reactant) remains unreacted. In reaction II, (*P*) is formed.

36. All those carbonyl compounds containing α-H to sp^2 carbon show keto-enol tautomerism.

37. In both Friedel-Craft's reaction and Reimer-Tiemann reaction new carbon-carbon bond is formed.



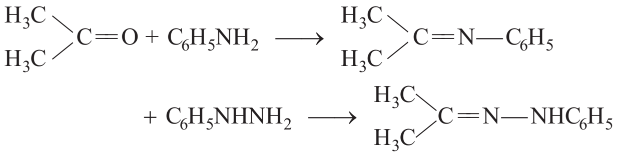
Friedel-Crafts' alkylation



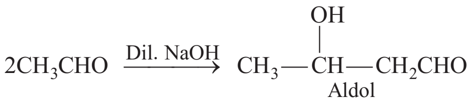
Reimer-Tiemann' reaction

38. All carbonyl compounds containing α-H or α-D undergo aldol condensation. In given example, benzaldehyde does not contain α-H to —CHO, hence does not undergo aldol condensation.

39.

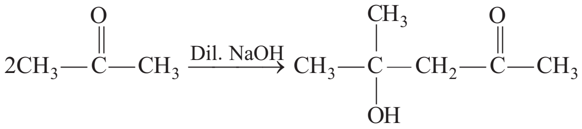


40.



$$2CH_3CHO \xrightarrow{\text{Dil. NaOH}} CH_3-\overset{\overset{OH}{|}}{C}H-CH_2CHO$$

Aldol



$$2CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{\text{Dil. NaOH}} CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$$

Aldol

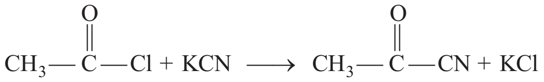
$$2HCHO \xrightarrow{\text{Dil. NaOH}} CH_3OH + HCOONa$$

Cannizzaro reaction

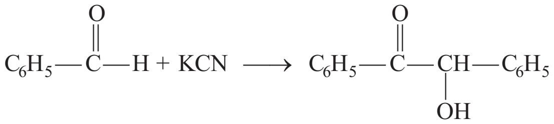
$$C_6H_5CHO + HCHO \xrightarrow{\text{Dil. NaOH}} C_6H_5CH_2OH + HCOONa$$

Cannizzaro reaction

41. $CH_3CH_2Cl + KCN \xrightarrow{S_N2} CH_3CH_2CN + KCl$



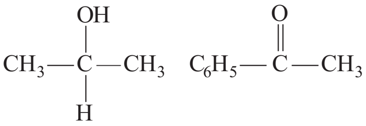
$$CH_3-\overset{\overset{O}{\|}}{C}-Cl + KCN \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-CN + KCl$$



$$C_6H_5-\overset{\overset{O}{\|}}{C}-H + KCN \longrightarrow C_6H_5-\overset{\overset{O}{\|}}{C}-\underset{\underset{OH}{|}}{C}H-C_6H_5$$

Benzoin

42. Aldehyde, ketones containing $CH_3-\overset{\overset{O}{\|}}{C}-$ group gives iodoform test. Also alcohol containing $CH_3-\underset{\underset{OH}{|}}{C}H-$ group gives iodoform test.

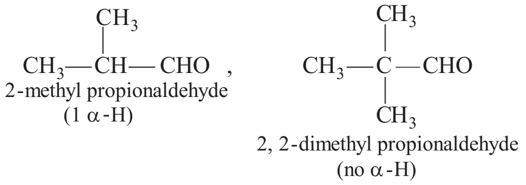


$$CH_3-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3 \quad C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3$$

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 α-H to carbonyl group.

CH_3-CH_2-CHO,
Propionaldehyde
(2 α-H)



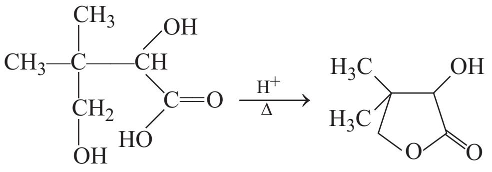
$$CH_3-\overset{\overset{CH_3}{|}}{C}H-CHO, \qquad CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CHO$$

2-methyl propionaldehyde
(1 α-H)

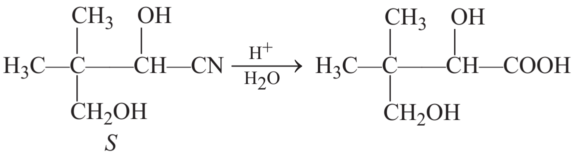
2, 2-dimethyl propionaldehyde
(no α-H)

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 :



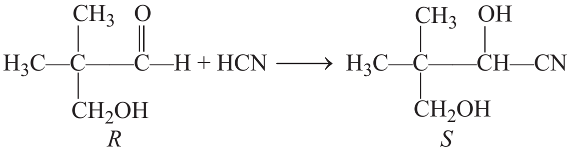
Acid above is obtained by acid hydrolysis of cyanohydrin *S* as



$$H_3C-\underset{\underset{CH_2OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\overset{OH}{|}}{C}H-CN \xrightarrow[H_2O]{H^+} H_3C-\underset{\underset{CH_2OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\overset{OH}{|}}{C}H-COOH$$

S

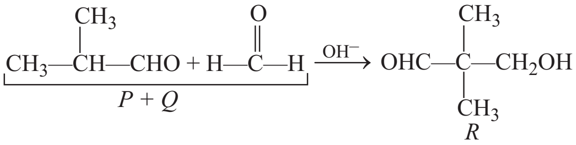
S is obtained by nucleophile addition of HCN on *R*, hence *R* is



$$H_3C-\underset{\underset{CH_2OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\overset{O}{\|}}{C}-H + HCN \longrightarrow H_3C-\underset{\underset{CH_2OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\overset{OH}{|}}{C}H-CN$$

R *S*

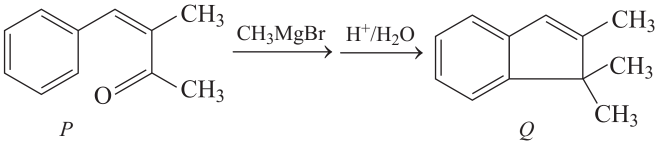
R is obtained by treatment of *P* and *Q* with aqueous K_2CO_3 through aldol condensation reaction as



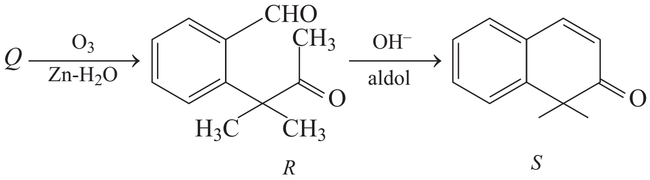
$$\underbrace{CH_3-\overset{\overset{CH_3}{|}}{C}H-CHO + H-\overset{\overset{O}{\|}}{C}-H}_{P+Q} \xrightarrow{OH^-} OHC-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2OH$$

R

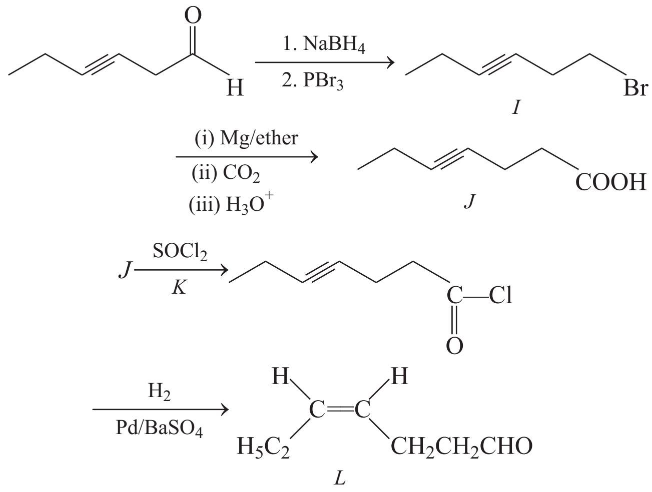
Passage 2 (For Q. Nos. 47-49)



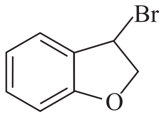
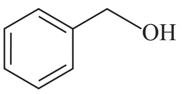
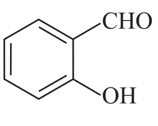
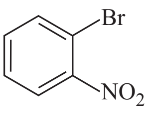
(gives positive iodoform test)



Passage 3 (For Q. Nos. 50-52)



53.

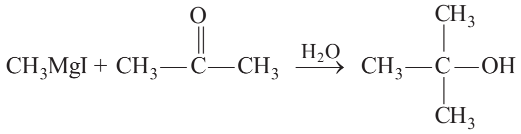
	Column I	Column II
A.		Undergo nucleophilic substitution of Br$^-$. Undergo elimination of HBr. Does not undergo nucleophilic addition. Does not esterify with acetic anhydride, can be dehydrogenated.
B.		Undergo nucleophilic substitution with SOCl$_2$, PCl$_5$ etc. Does not undergo elimination. Does not undergo nucleophilic addition. Undergo esterification with acetic anhydride. Undergo dehydrogenation to give C$_6$H$_5$CHO.
C.		Does not undergo nucleophilic substitution, there is no leaving group. Does not undergo elimination. Undergo nucleophilic addition at carbonyl carbon of —CHO. Undergo esterification with acetic anhydride. Does not undergo dehydrogenation.
D.		Undergo aromatic nucleophilic substitution (S$_N$Ar) Does not undergo elimination, nucleophilic addition, esterification or dehydrogenation.

54.

	Column I	Column II
A.	C$_6$H$_5$CHO	Gives phenyl hydrazone with 2, 4-dinitrophenyl hydrazine. Gives precipitate with AgNO$_3$, Tollen's test forms cyanohydrin.
B.	CH$_3$—C≡CH	Gives precipitate (CH$_3$—C≡CAg) with AgNO$_3$. A nucleophile, undergo electrophilic attack.
C.	CN$^-$	Forms AgCN with AgNO$_3$. A nucleophile is involved in cyanohydrin formation.
D.	I$^-$	Gives AgI precipitate with AgNO$_3$ and it is a nucleophile.

55. Sodium potassium tartarate

56.



$$CH_3MgI + CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{H_2O} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH$$

Tertiary alcohol

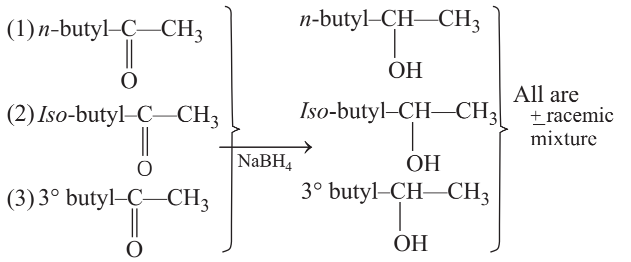
57. Benzaldehyde, lacking α-H does not undergo aldol condensation, rather it undergoes Cannizzaro reaction.

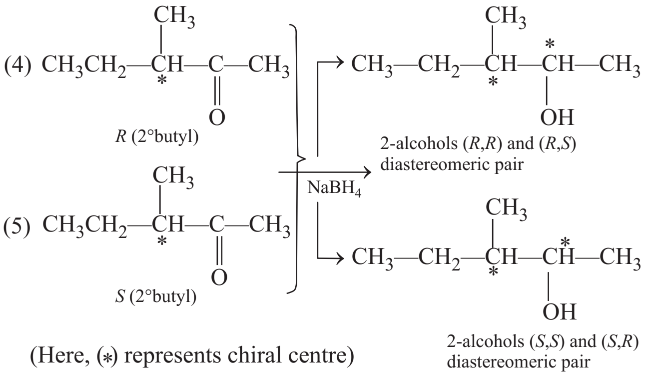
58. Molecular weight of the ketone is 100

So, molecular formula = C$_6$ H$_{12}$O

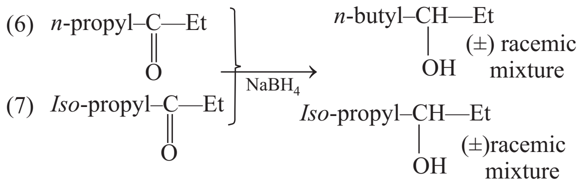
Degree of unsaturation = $(6+1)-\frac{12}{2}=1$

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.



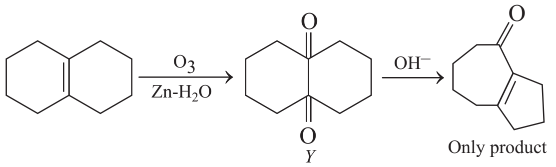


(Here, (*) represents chiral centre)

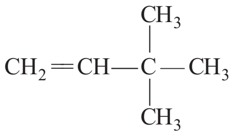


While in case of (4) and (5) they do not produce enantiomer due to the presence of stereogenic centre on ketone.

59.

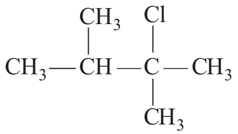


60.



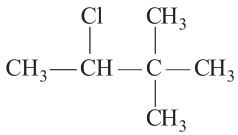
$CH_2{=}CH{-}C(CH_3)_2{-}CH_3$

A



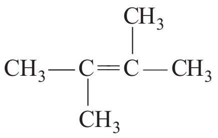
$CH_3{-}CH(CH_3){-}CCl(CH_3){-}CH_3$

B



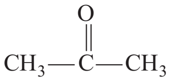
$CH_3{-}CHCl{-}C(CH_3)_2{-}CH_3$

C



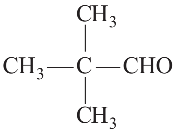
$CH_3{-}C(CH_3){=}C(CH_3){-}CH_3$

D



$CH_3{-}CO{-}CH_3$

E



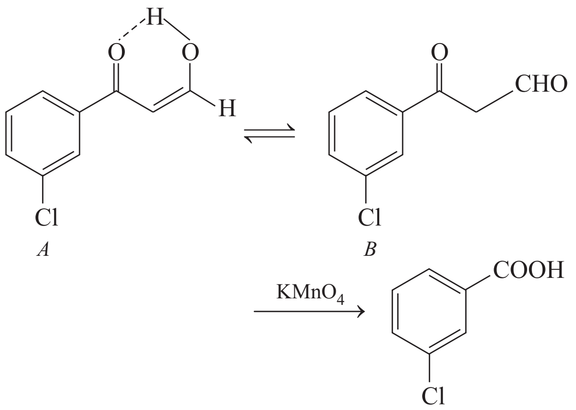
$CH_3{-}C(CH_3)_2{-}CHO$

F

HCHO

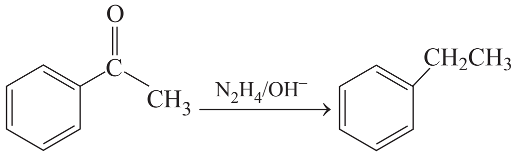
G

61.

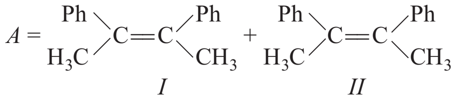


62. $B + NaOH / I_2 \longrightarrow C_6H_5COONa + CHI_3$

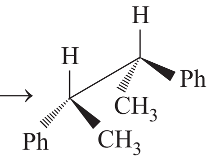
⇒ $B =$



$A =$

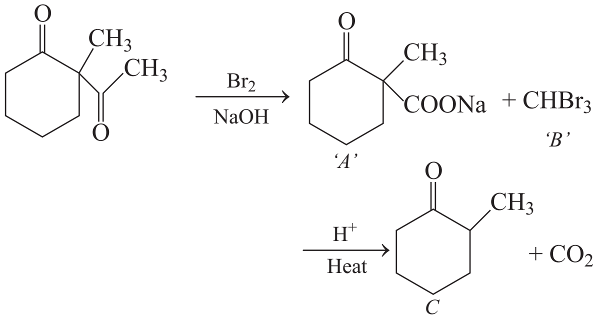


II + H_2/Pd ⟶

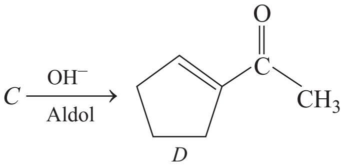


+ Enantiomer
= Racemic mixture

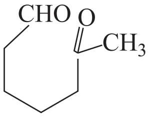
63.



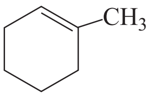
64.



⇒ $C =$

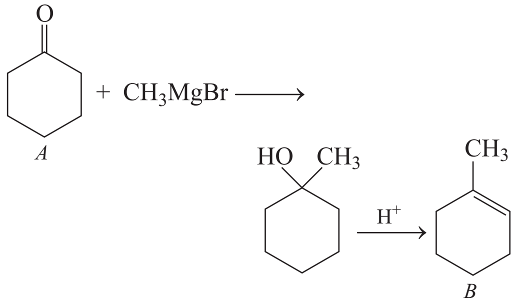


$B =$

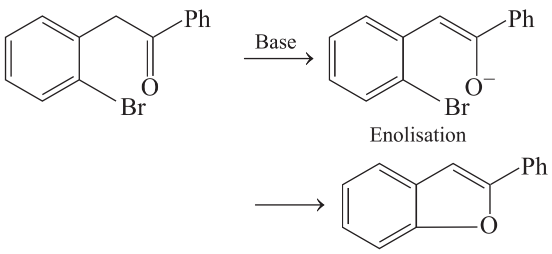


$A\ (C_6H_{10}O) \xrightarrow{MeMgBr} \xrightarrow{H^+} B$

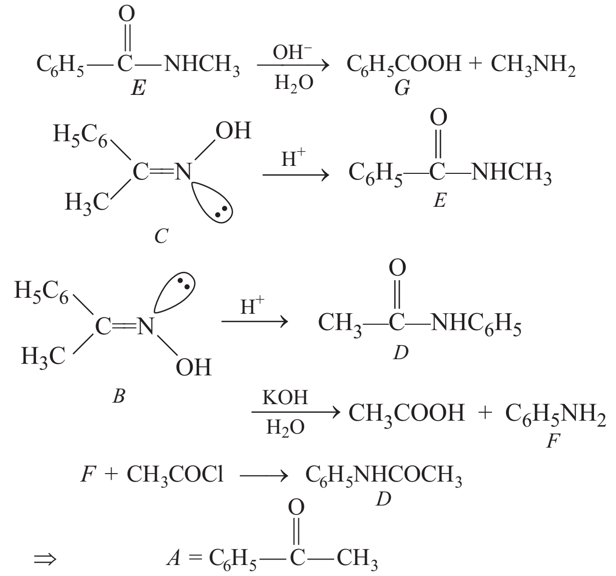
⇒



65.



66. (a) *G* is benzoic acid C_6H_5-COOH, *B* and *C* are two stereomeric oximes which undergo Beckmann's rearrangement on treatment with acid to give amides *D* and *E*.



$$\underset{E}{C_6H_5-\overset{\overset{O}{\|}}{C}-NHCH_3} \xrightarrow[H_2O]{OH^-} \underset{G}{C_6H_5COOH} + CH_3NH_2$$

$$\underset{C}{(H_5C_6)(H_3C)C{=}N{-}OH} \xrightarrow{H^+} \underset{E}{C_6H_5-\overset{\overset{O}{\|}}{C}-NHCH_3}$$

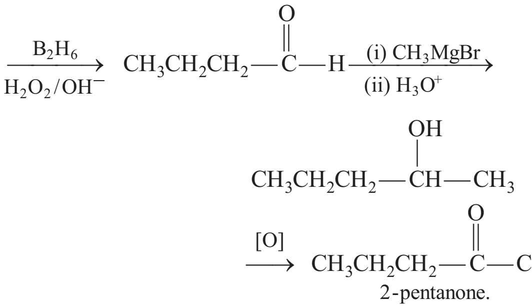
$$\underset{B}{(H_5C_6)(H_3C)C{=}N{-}OH} \xrightarrow{H^+} \underset{D}{CH_3-\overset{\overset{O}{\|}}{C}-NHC_6H_5}$$

$$\xrightarrow[H_2O]{KOH} CH_3COOH + \underset{F}{C_6H_5NH_2}$$

$$F + CH_3COCl \longrightarrow \underset{D}{C_6H_5NHCOCH_3}$$

$$\Rightarrow \quad A = C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3$$

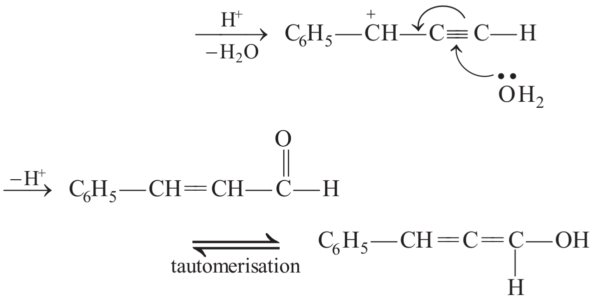
(b) $CH_3-CH_2-C\equiv CH$



$$\xrightarrow[H_2O_2/OH^-]{B_2H_6} CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-H \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CH_3MgBr} CH_3CH_2CH_2-\overset{\overset{OH}{|}}{CH}-CH_3$$

$$\xrightarrow{[O]} \underset{\text{2-pentanone.}}{CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-CH_3}$$

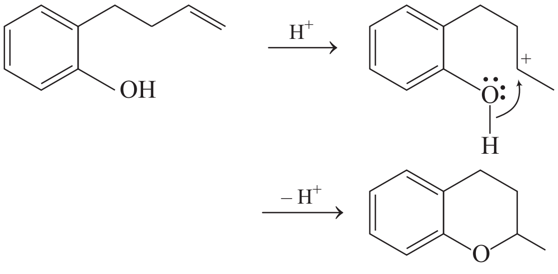
67. (i) $C_6H_5-\underset{\underset{OH}{|}}{CH}-C\equiv C-H$



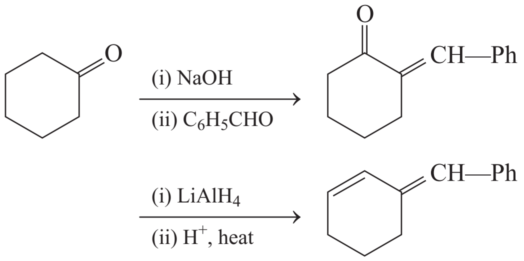
$$\xrightarrow[-H_2O]{H^+} C_6H_5-\overset{+}{C}H-C\equiv C-H \quad \ddot{O}H_2$$

$$\xrightarrow{-H^+} C_6H_5-CH{=}CH-\overset{\overset{O}{\|}}{C}-H \xrightleftharpoons{\text{tautomerisation}} C_6H_5-CH{=}C{=}\underset{\underset{H}{|}}{C}-OH$$

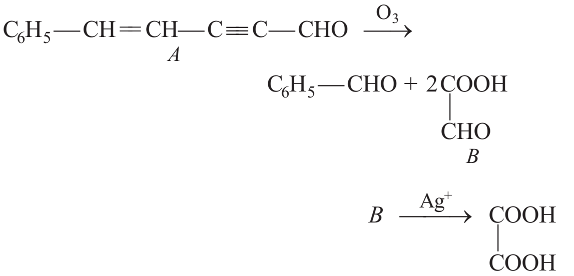
(ii)



68.



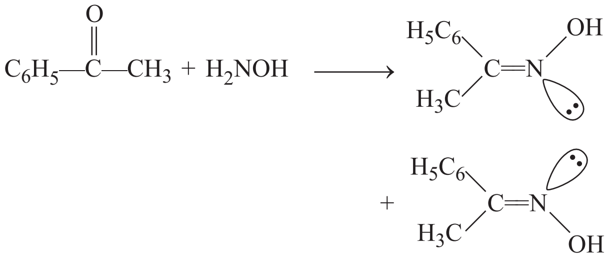
69. Aldehyde *A* does not has any α-H but undergo ozonolysis to give two moles of compound *B* and benzaldehyde. Compound *B* on oxidation gives oxalic acid, so *A* is



$$\underset{A}{C_6H_5-CH{=}CH-C\equiv C-CHO} \xrightarrow{O_3} C_6H_5-CHO + 2\underset{\underset{B}{CHO}}{\overset{COOH}{|}}$$

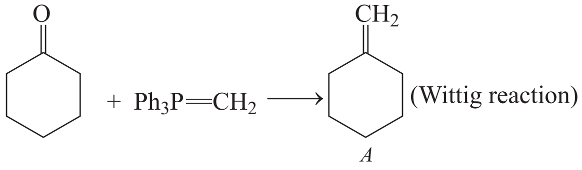
$$B \xrightarrow{Ag^+} \begin{matrix} COOH \\ | \\ COOH \end{matrix}$$

70.

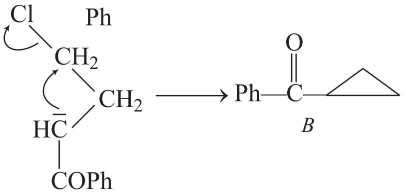


$$C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3 + H_2NOH \longrightarrow (H_5C_6)(H_3C)C{=}N{-}OH + (H_5C_6)(H_3C)C{=}N{-}OH$$

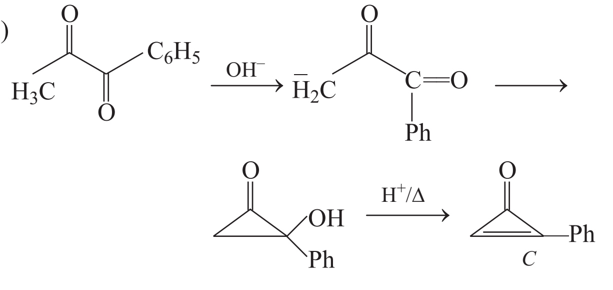
71. (i)



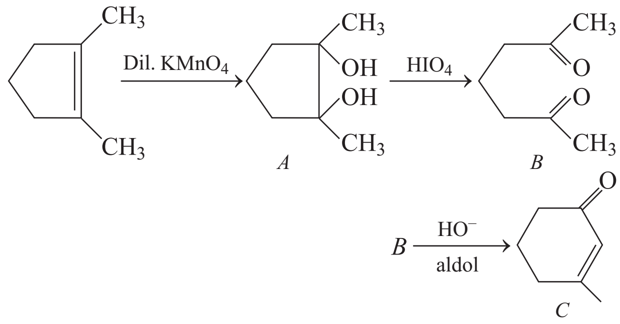
(ii) $Cl-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-Ph \xrightarrow{CH_3O^-}$



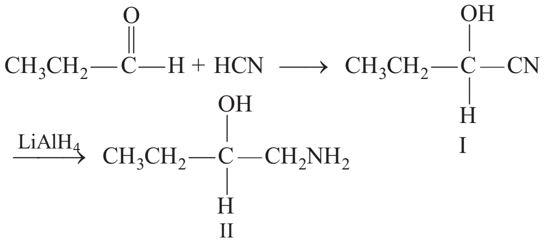
(iii)



72.



73. $KCN + H_2SO_4 \longrightarrow KHSO_4 + HCN$

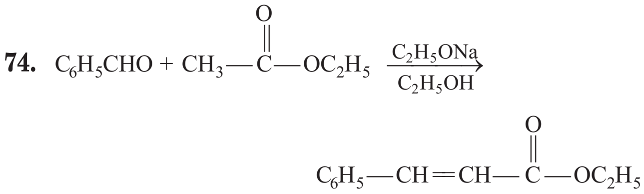


$$CH_3CH_2-\overset{\overset{O}{\|}}{C}-H + HCN \longrightarrow CH_3CH_2-\underset{\underset{\text{H}}{|}}{\overset{\overset{OH}{|}}{C}}-CN \quad \text{I}$$

$$\xrightarrow{LiAlH_4} CH_3CH_2-\underset{\underset{\text{H}}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2NH_2 \quad \text{II}$$

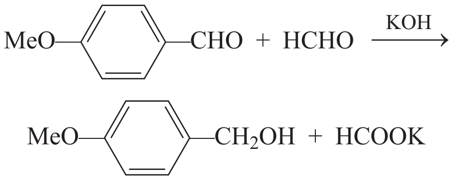
I is formed as racemic mixture.

74.



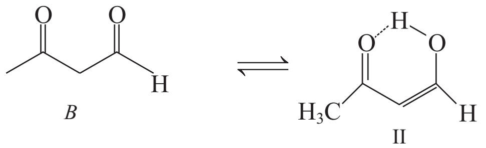
$$C_6H_5CHO + CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5 \xrightarrow[C_2H_5OH]{C_2H_5ONa} C_6H_5-CH{=}CH-\overset{\overset{O}{\|}}{C}-OC_2H_5$$

75.

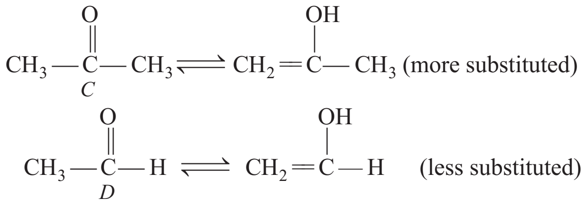


(Cannizzaro reaction)

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

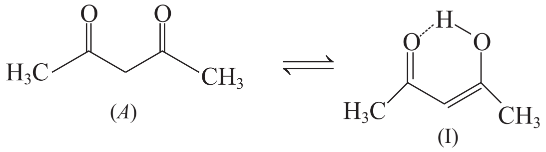


$$\underset{C}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} \rightleftharpoons CH_2{=}\overset{\overset{OH}{|}}{C}-CH_3 \text{ (more substituted)}$$

$$\underset{D}{CH_3-\overset{\overset{O}{\|}}{C}-H} \rightleftharpoons CH_2{=}\overset{\overset{OH}{|}}{C}-H \quad \text{(less substituted)}$$

Therefore, overall enol-content order is $D < C < B < A$

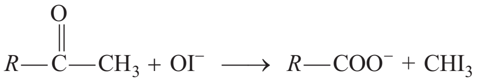
76. $CH_3-CO-CH_2-COCH_3$ has highest enol content due to resonance and formation of six membered ring through intramolecular H-bonding



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, CH_3COCH_2CHO forms next most stable enol

77. Iodoform reaction is an oxidation reaction in which hypoiodite OI^- acts as oxidising agent :



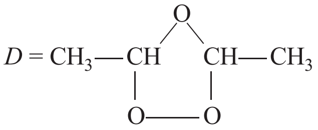
$$R-\overset{\overset{O}{\|}}{C}-CH_3 + OI^- \longrightarrow R-COO^- + CHI_3$$

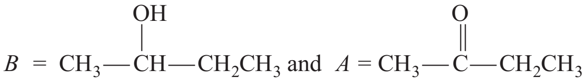
Iodide (I^-) is a reducing agent, does not give iodoform reaction.

78. $D \xrightarrow{O_3} \xrightarrow[H_2O]{Zn} CH_3CHO$ (only)

$C = CH_3-CH{=}CH-CH_3,$

$D =$

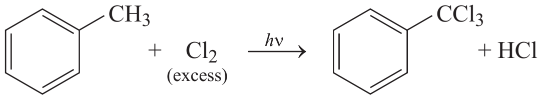




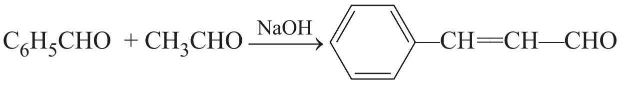
$$B = CH_3-\overset{\overset{OH}{|}}{C}H-CH_2CH_3 \text{ and } A = CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_3$$

79. (i) Tollen's reagent gives grey precipitate of Ag, acetone does not.

(ii)

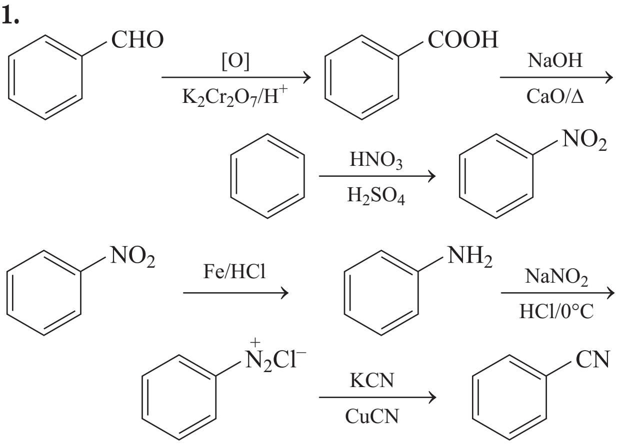


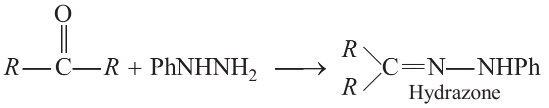
80.



Cross-aldol condensation

81.

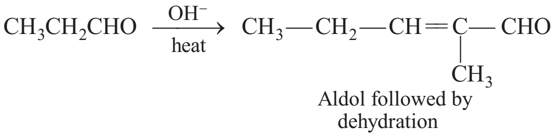


82. 

$$R-\overset{\overset{O}{\|}}{C}-R + PhNHNH_2 \longrightarrow \begin{matrix}R\\R\end{matrix}\!\!>C=N-NHPh$$

Hydrazone

In acidic medium, hydrazine reacts to form salt and hydrazone is hydrolysed back to aldehyde/ketone.

83. 

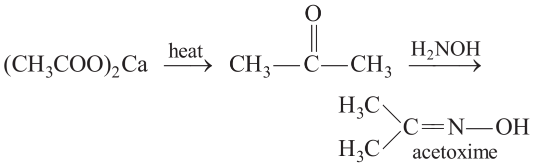
$$CH_3CH_2CHO \xrightarrow[\text{heat}]{OH^-} CH_3-CH_2-CH=\underset{\underset{CH_3}{|}}{C}-CHO$$

Aldol followed by dehydration

84. Steric hindrance at carbonyl carbon determine the reactivity towards nucleophilic addition reaction. Greater the steric hindrance, smaller the reactivity.

$C_2H_5COCH_3 < CH_3COCH_3 < CH_3CHO < HCHO$

85. $CH_3CHO \xrightarrow[K_2Cr_2O_7]{H^+} CH_3COOH \xrightarrow{Ca(OH)_2} (CH_3COO)_2Ca$



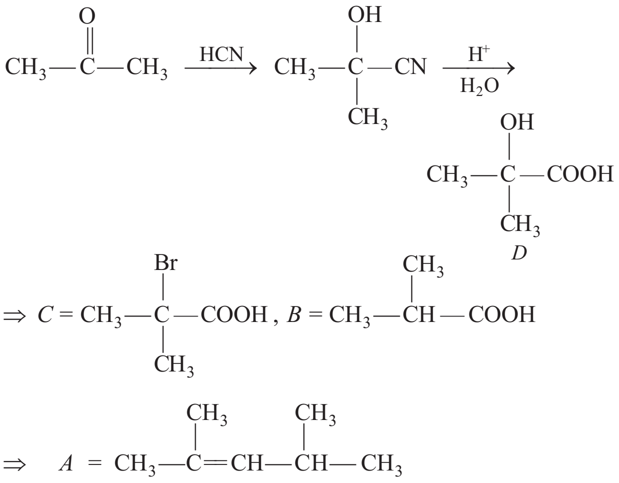
$$(CH_3COO)_2Ca \xrightarrow{\text{heat}} CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{H_2NOH} \begin{matrix}H_3C\\H_3C\end{matrix}\!\!>C=N-OH$$

acetoxime

86. $Cl_3C-CHO + NaOH(aq) \longrightarrow Cl_3C-CH_2OH$

Cannizzaro reaction

$+ Cl_3C-COONa$

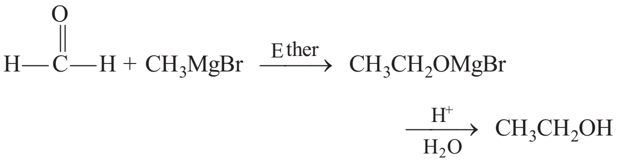
87. 

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{HCN} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CN \xrightarrow[H_2O]{H^+} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-COOH$$

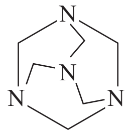
D

$$\Rightarrow C = CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{C}}-COOH,\ B = CH_3-\overset{\overset{CH_3}{|}}{CH}-COOH$$

$$\Rightarrow A = CH_3-\overset{\overset{CH_3}{|}}{C}=CH-\overset{\overset{CH_3}{|}}{CH}-CH_3$$

88. 

$$H-\overset{\overset{O}{\|}}{C}-H + CH_3MgBr \xrightarrow{\text{Ether}} CH_3CH_2OMgBr \xrightarrow[H_2O]{H^+} CH_3CH_2OH$$

89. $6CH_2O + 4NH_3 \longrightarrow$  "$(CH_2)_6N_4$"

Hexamine