CHAPTER 20

Aldehydes, Ketones and Carboxylic Acids

Section-A JEE Advanced/ IIT-JEE

A Fill in the Blanks

1. Formic acid when heated with conc. H_2SO_4 produces .... *(1983 - 1 Mark)*
2. Fehling's solution 'A' consists of an aqueous solution of copper sulphate, while Fehling's solution 'B' consists of an alkaline solution of .... *(1990 - 1 Mark)*
3. The structure of the intermediate product, formed by the oxidation of toluene with CrO_3 and acetic anhydride, whose hydrolysis gives benzaldehyde is .... *(1992 - 1 Mark)*
4. The structure of the enol form of $CH_3–CO–CH_2–CO–CH_3$ with intramolecular hydrogen bonding is .... *(1993 - 1 Mark)*

B True / False

1. Benzaldehyde undergoes aldol condensation in an alkaline medium. *(1982 - 1 Mark)*
2. Hydrolysis of an ester in presence of a dilute acid is known as saponification. *(1983 - 1 Mark)*
3. The yield of ketone when a secondary alcohol is oxidized is more than the yield of aldehyde when a primary alcohol is oxidized. *(1983 - 1 Mark)*
4. The reaction of methyl magnesium iodide with acetone followed by hydrolysis gives secondary butanol. *(1987 - 1 Mark)*
5. The boiling point of propionic acid is less than that of *n*-butyl alcohol, an alcohol of comparable molecular weight. *(1991 - 1 Mark)*

C MCQs with One Correct Answer

1. The reagent with which both acetaldehyde and acetone react easily is *(1981 - 1 Mark)*
   (a) Fehling's reagent
   (b) Grignard reagent
   (c) Schiff's reagent
   (d) Tollen's reagent
2. When acetaldehyde is heated with Fehling's solution it gives a precipitate of *(1983 - 1 Mark)*
   (a) Cu
   (b) CuO
   (c) Cu_2O
   (d) $Cu + Cu_2O + CuO$
3. The Cannizzaro reaction is not given by *(1983 - 1 Mark)*
   (a) trimethylacetaldehye
   (b) acetaldehyde
   (c) benzaldehyde
   (d) formaldehyde
4. The compound that will not give iodoform on treatment with alkali and iodine is : *(1985 - 1 Mark)*
   (a) acetone
   (b) ethanol
   (c) diethyl ketone
   (d) isopropyl alcohol
5. Polarisation of electrons in acrolein may be written as *(1988 - 1 Mark)*
   (a) $\overset{\delta^-}{C}H_2=CH-\overset{\delta^+}{C}H=O$
   (b) $\overset{\delta^-}{C}H_2=CH-CH=\overset{\delta^+}{O}$
   (c) $\overset{\delta^-}{C}H_2=\overset{\delta^+}{C}H-CH=O$
   (d) $\overset{\delta^+}{C}H_2=CH-CH=\overset{\delta^-}{O}$
6. The enolic form of acetone contains *(1990 - 1 Mark)*
   (a) 9 sigma bonds, 1 pi-bond and 2 lone pairs
   (b) 8 sigma bonds, 2 pi-bonds and 2 lone pairs
   (c) 10 sigma bonds, 1 pi-bond and 1 lone pair
   (d) 9 sigma bonds, 2 pi-bonds and 1 lone pair
7. *m*-Chlorobenzaldehyde on reaction with conc. KOH at room temperature gives *(1991 - 1 Mark)*
   (a) potassium *m*-chlorobenzoate and *m*-hydroxybenzaldehyde
   (b) *m*-hydroxybenzaldehyde and *m*-chlorobenzyl alcohol
   (c) *m*-chlorobenzyl alcohol and *m*-hydroxybenzyl alcohol
   (d) potassium *m*-chlorobenzoate and *m*-chlorobenzyl alcohol.
8. Hydrogenation of benzoyl chloride in the presence of Pd on $BaSO_4$ gives *(1992 - 1 Mark)*
   (a) Benzyl alcohol
   (b) Benzaldehyde
   (c) Benzoic acid
   (d) Phenol
9. The organic product formed in the reaction *(1995S)*

   $$C_6H_5COOH \xrightarrow[\text{II } H_3O^+]{\text{I } LiAlH_4}$$

   (a) $C_6H_5CH_2OH$
   (b) C_6H_5COOH & CH_4
   (c) $C_6H_5CH_3$ & CH_3OH
   (d) $C_6H_5CH_3$ & CH_4
10. The reaction products of $C_6H_5OCH_3 + HI \xrightarrow{\Delta}$ is : *(1995S)*
   (a) $C_6H_5OH + CH_3I$
   (b) $C_6H_5I + CH_3OH$
   (c) $C_6H_5CH_3 + HOI$
   (d) $C_6H_6 + CH_3OH$

11. In the Cannizzaro reaction given below, *(1996 - 1 Mark)*

$$2PhCHO \xrightarrow{^{-}OH} PhCH_2OH + PhCO_2^- ,$$

the slowest step is

(a) the attack of ^{-}OH at the carbonyl group,

(b) the transfer of hydride to the carbonyl group,

(c) the abstraction of proton from the carboxylic acid,

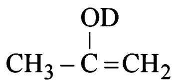
(d) the deprotonation of $PhCH_2OH$.

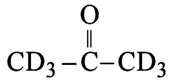
12. When propionic acid is treated with aqueous sodium bicarbonate, CO_2 is liberated. The 'C' of CO_2 comes from *(1999 - 2 Marks)*

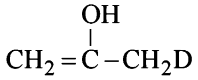
(a) methyl group (b) carboxylic acid group

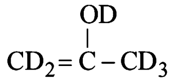
(c) methylene group (d) bicarbonate

13. The enol form of acetone, after treatment with D_2O, gives. *(1999 - 2 Marks)*

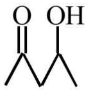
(a)

$CH_3-\overset{\overset{\large OD}{|}}{C}=CH_2$

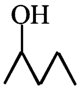
(b)

$CD_3-\overset{\overset{\large O}{\|}}{C}-CD_3$

(c)

$CH_2=\overset{\overset{\large OH}{|}}{C}-CH_2D$

(d)

$CD_2=\overset{\overset{\large OD}{|}}{C}-CD_3$

14. Which one of the following will most readily be dehydrated in acidic condition ? *(2000S)*

(a)


(b)


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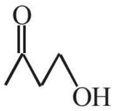
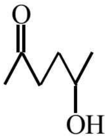


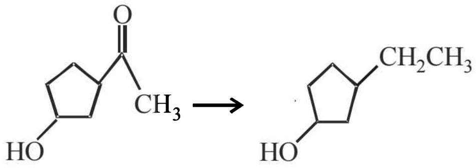
(d)


15. Benzoyl chloride is prepared from benzoic acid by *(2000S)*

(a) Cl_2, hv (b) SO_2Cl_2

(c) $SOCl_2$ (d) Cl_2, H_2O

16. The appropriate reagent for the following transformation is *(2000S)*



(a) Zn(Hg), HCl (b) NH_2NH_2, OH^-

(c) H_2/Ni (d) $NaBH_4$

17. A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives *(2001S)*

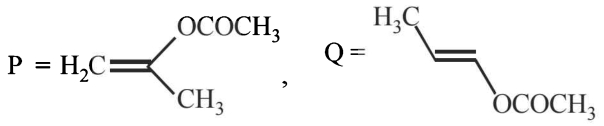
(a) benzyl alcohol and sodium formate

(b) sodium benzoate and methyl alcohol

(c) sodium benzoate and sodium formate

(d) benzyl alcohol and methyl alcohol

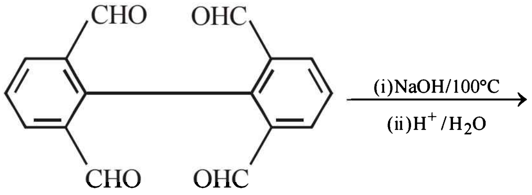
18. The product of acid hydrolysis of P and Q can be distinguished by *(2003S)*



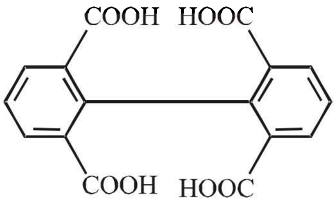
(a) Lucas Reagent (b) 2,4–DNP

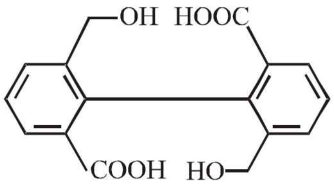
(c) Fehling's Solution (d) $NaHSO_3$

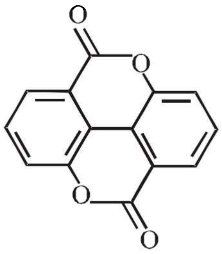
19.

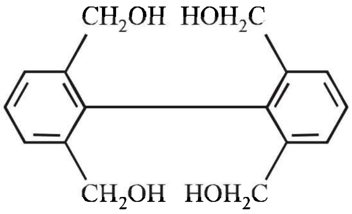


Major product is : *(2003S)*

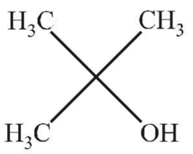
(a)


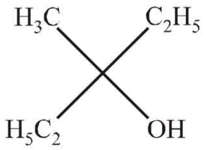
(b)


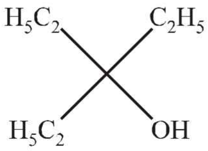
(c)


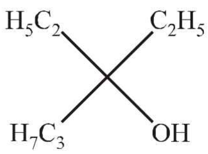
(d)


20. Ethyl ester $\xrightarrow[\text{excess}]{CH_3MgBr}$ P. The product P will be *(2003S)*

(a)


(b)


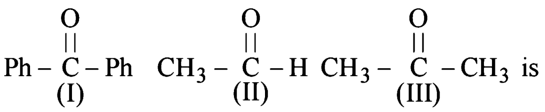
(c)


(d)


21. An enantiomerically pure acid is treated with a racemic mixture of an alcohol having one chiral carbon. The ester formed will be *(2003S)*

(a) Optically active mixture (b) Pure enantiomer
(c) Meso compound (d) Racemic mixture

22. The correct order of reactivity of PhMgBr with *(2004S)*



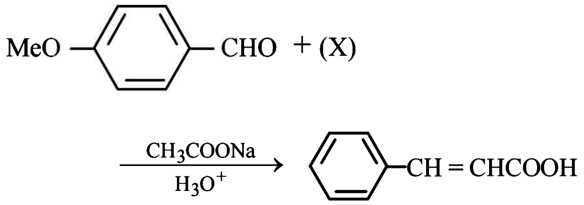
$\underset{(I)}{Ph-\overset{O}{\overset{||}{C}}-Ph}\quad \underset{(II)}{CH_3-\overset{O}{\overset{||}{C}}-H}\quad \underset{(III)}{CH_3-\overset{O}{\overset{||}{C}}-CH_3}$ is

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

23. How will you convert butan–2–one to propanoic acid? *(2005S)*

(a) Tollen's reagent (b) Fehling's solution
(c) $NaOH/I_2/H^+$ (d) $NaOH/NaI/H^+$

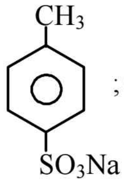
24.



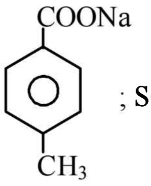
The compound (X) is *(2005S)*

(a) CH_3COOH (b) $BrCH_2-COOH$
(c) $(CH_3CO)_2O$ (d) $CHO-COOH$

25. 4–Methylbenzenesulphonic acid reacts with sodium acetate to give *(2005S)*

(a) 

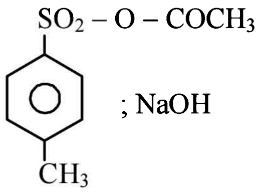
; CH_3COOH

(b) 

; SO_3

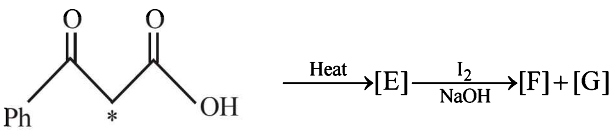
(c) 

; SO_3

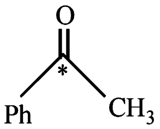
(d) 

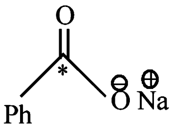
; NaOH

26. In the following reaction sequence, the correct structures of E, F and G are

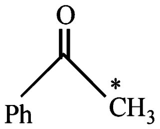


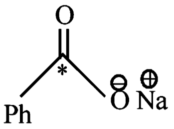
[* implies ^{13}C labelled carbon) *(2008)*

(a) E= 

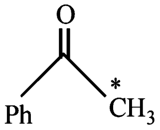
F = 

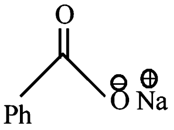
G = CHI_3

(b) E= 

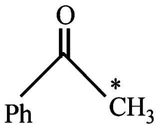
F = 

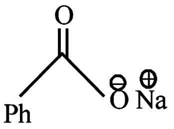
G = CHI_3

(c) E= 

F = 

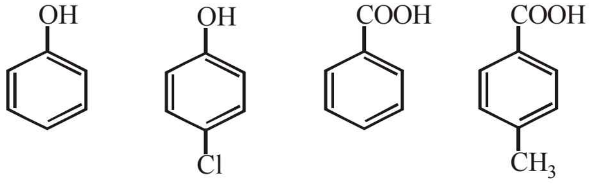
G = $\overset{*}{C}HI_3$

(d) E= 

F = 

G = $\overset{*}{C}H_3I$

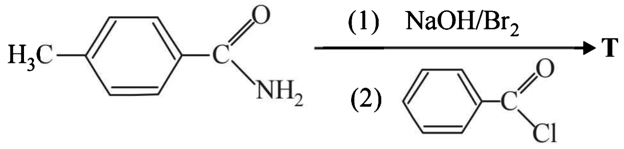
27. The correct acidity order of the following is *(2009S)*



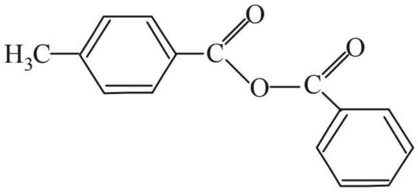
(I) (II) (III) (IV)

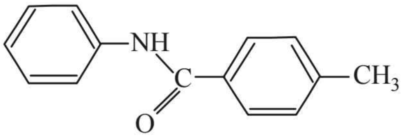
(a) (III) > (IV) > (II) > (I) (b) (IV) > (III) > (I) > (II)
(c) (III) > (II) > (I) > (IV) (d) (II) > (III) > (IV) > (I)

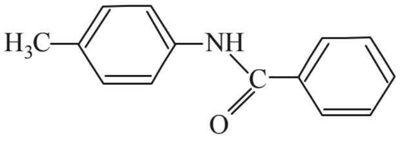
28. In the reaction

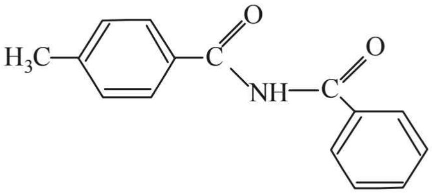


the structure of the product **T** is : *(2010)*

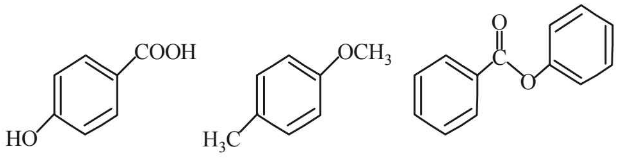
(a) 

(b) 

(c) 

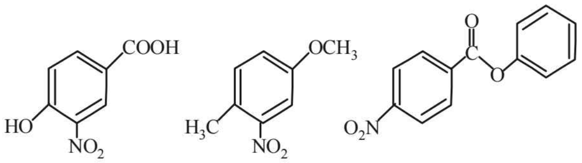
(d) 

29. The compounds P, Q and S



P Q S

were separately subjected to nitration using HNO_3/H_2SO_4 mixture. The major product formed in each case respectively, is : *(2010)*

(a)


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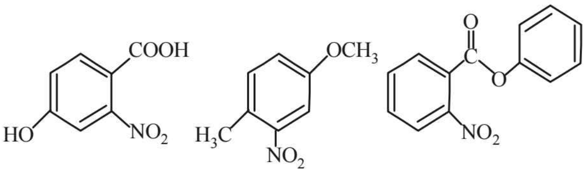
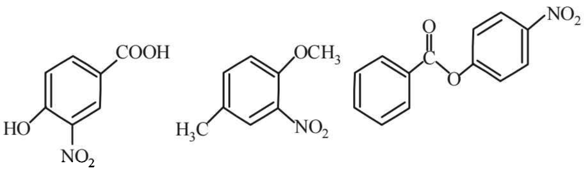


(c)


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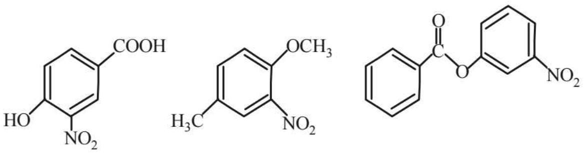
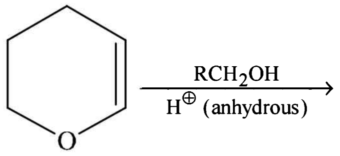


30. The major product of the following reaction is *(2011)*



(a) a hemiacetal (b) an acetal

(c) an ether (d) an ester

31. The carboxyl functional group (–COOH) is present in *(2012)*

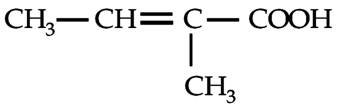
(a) picric acid (b) barbituric acid

(c) ascorbic acid (d) aspirin

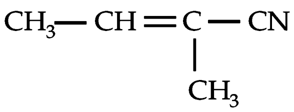
32. The major product **H** of the given reaction sequence is

$$CH_3-CH_2-CO-CH_3 \xrightarrow{\overset{\ominus}{C}N} G \xrightarrow[\text{Heat}]{95\%\ H_2SO_4} H$$

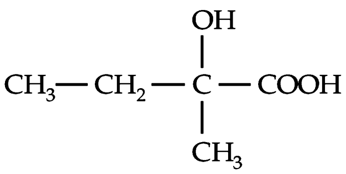
(2012 - II)

(a)


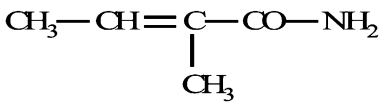
$CH_3-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-COOH$

(b)


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

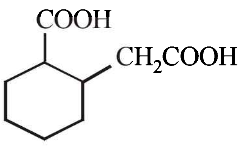
(c)


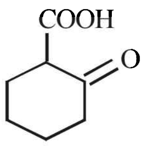
$CH_3-CH_2-\overset{\displaystyle OH}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-COOH$

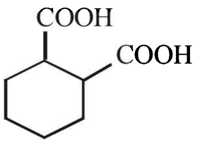
(d)


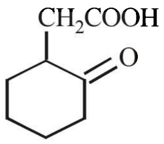
$CH_3-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-CO-NH_2$

33. The compound that undergoes decarboxylation most readily under mild condition is *(2012)*

(a)


(b)


(c)


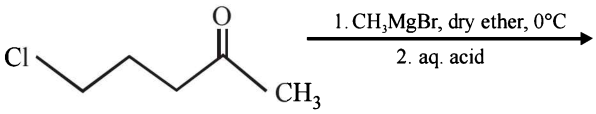
(d)


34. The compound that does **NOT** liberate CO_2, on treatment with aqueous sodium bicarbonate solution, is *(JEE Adv. 2013)*

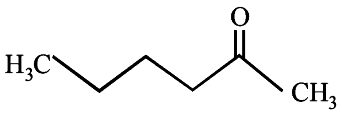
(a) Benzoic acid (b) Benzenesulphonic acid

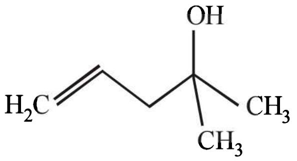
(c) Salicylic acid (d) Carbolic acid (Phenol)

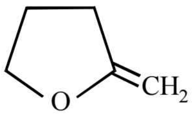
35. The major product in the following reaction is

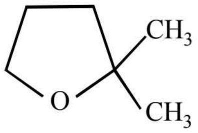


(JEE Adv. 2014)

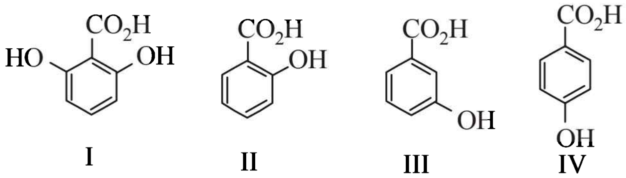
(a)


(b)


(c)


(d)


36. The correct order of acidity for the following compounds is

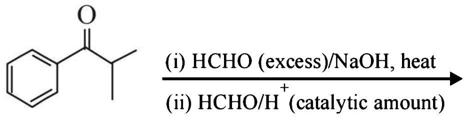


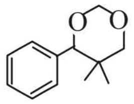
I II III IV

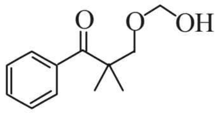
(JEE Adv. 2016)

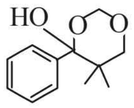
(a) I > II > III > IV (b) III> I > II > IV
(c) III > IV > II > I (d) I > III > IV > II

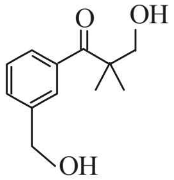
37. The major product of the following reaction sequence is *(JEE Adv. 2016)*



(a)


(b)


(c)


(d)


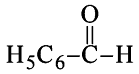
D MCQs with One or More Than One Correct

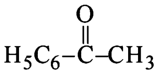
1. Base catalysed aldol condensation occurs with : *(1984 - 1 Mark)*
(a) propionaldehyde
(b) benzaldehyde
(c) 2-methylpropionaldehyde
(d) 2, 2-dimethylpropionaldehyde

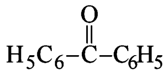
2. Which of the following compounds will give a yellow precipitate with iodine and alkali? *(1984 - 1 Mark)*
(a) 2-Hydroxypropane (b) acetophenone
(c) methyl acetate (d) acetamide

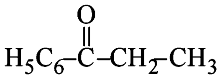
3. Which of the following compounds will react with ethanolic KCN? *(1984 - 1 Mark)*
(a) ethyl chloride (b) acetyl chloride
(c) chlorobenzene (d) benzaldehyde

4. Keto-enol tautomerism is observed in *(1988 - 1 Mark)*

(a)

$H_5C_6-\overset{O}{\overset{\|}{C}}-H$

(b)

$H_5C_6-\overset{O}{\overset{\|}{C}}-CH_3$

(c)

$H_5C_6-\overset{O}{\overset{\|}{C}}-C_6H_5$

(d)

$H_5C_6-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$

5. Which of the following are examples of aldol condensation? *(1989 - 1 Mark)*

(a) $2CH_3CHO \xrightarrow{\text{dil. NaOH}} CH_3CHOHCH_2CHO$

(b) $2CH_3COCH_3 \xrightarrow{\text{dil. NaOH}} CH_3COH(CH_3)CH_2COCH_3$

(c) $2HCHO \xrightarrow{\text{dil. NaOH}} CH_3OH$

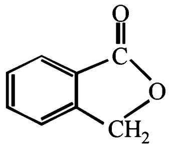
(d) $C_6H_5CHO + HCHO \xrightarrow{\text{dil. NaOH}} C_6H_5CH_2OH$

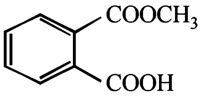
6. A new carbon-carbon bond formation is possible in
(a) Cannizzaro reaction *(1998 - 2 Marks)*
(b) Friedel–Craft alkylation
(c) Clemmensen reduction
(d) Reimer–Tiemann reaction

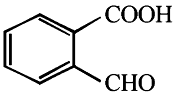
7. Which of the following will react with water? *(1998 - 2 Marks)*
(a) $CHCl_3$ (b) Cl_3CCHO
(c) CCl_4 (d) $ClCH_2CH_2Cl$

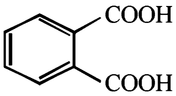
8. Which of the following will undergo aldol condensation? *(1998 - 2 Marks)*
(a) acetaldehyde (b) propanaldehyde
(c) benzaldehyde (d) trideuteroacetaldehyde

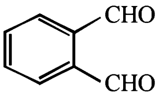
9. Which of the following reactants on reaction with conc. NaOH followed by acidification gives following lactone as the product? *(2006 - 5M, –1)*



(a)


(b)


(c)


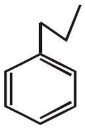
(d)


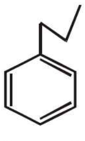
10.

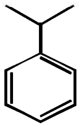
$+ Cl-CH_2CH_2CH_3$

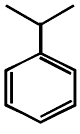
$\xrightarrow{AlCl_3} P \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } O_2/\Delta} Q + \text{Phenol}$

The major products P and Q are *(2006 - 5M, –1)*

(a)

and CH_3CH_2CHO

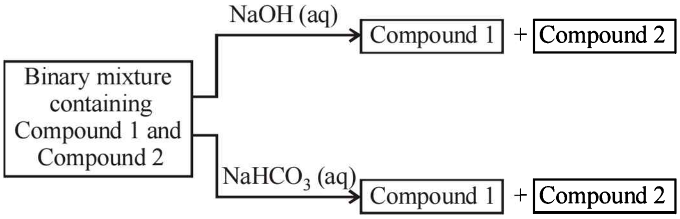
(b)

and CH_3COCH_3

(c)

and CH_3COCH_3

(d)

and CH_3CH_2CHO

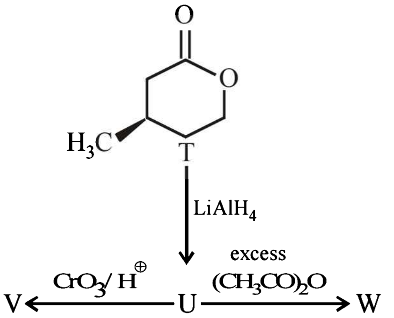
11. The smallest ketone and its next homologue are reacted with NH_2OH to form oxime *(2006 - 5M, –1)*
(a) Two different oximes are formed
(b) Three different oximes are formed
(c) Two oximes formed are optically active
(d) All oximes formed are optically active

12. Identify the binary mixture(s) that can be separated into individual compounds, by differential extraction as shown in the given scheme. *(2012)*



(a) C_6H_5OH and C_6H_5COOH
(b) C_6H_5COOH and $C_6H_5CH_2OH$
(c) $C_6H_5CH_2OH$ and C_6H_5OH
(d) $C_6H_5CH_2OH$ and $C_6H_5CH_2COOH$

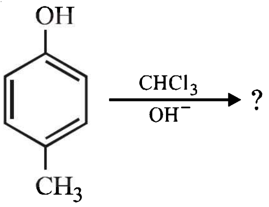
13. With reference to the scheme given below, which of the given statement(s) about T, U, V and W is (are) correct ?

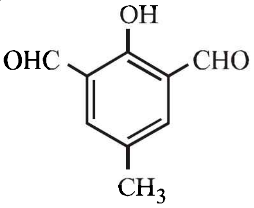


(2012)

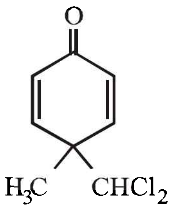
(a) T is soluble in hot aqueous NaOH
(b) U is optically active
(c) Molecular formula of W is $C_{10}H_{18}O_4$
(d) V gives effervescence on treatment with aqueous $NaHCO_3$.

14. In the following reaction, the product(s) formed is(are) *(JEE Adv. 2013)*

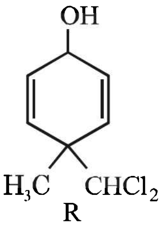




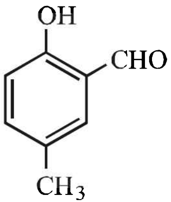
P



Q



R

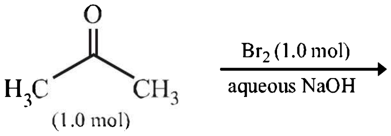


S

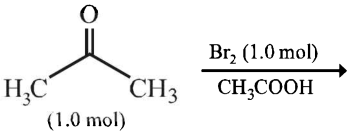
(a) P (major)
(b) Q (minor)
(c) R (minor)
(d) S (major)

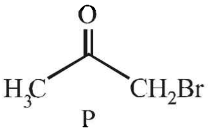
15. After completion of the reactions (I and II), the organic compound(s) in the reaction mixtures is(are) *(JEE Adv. 2013)*

Reaction I :

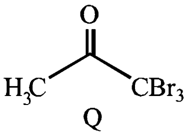


Reaction II :

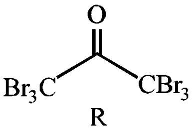




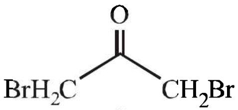
P



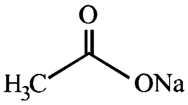
Q



R



S



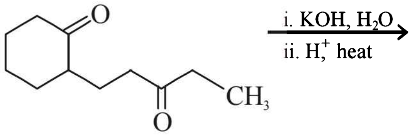
T

$CHBr_3$

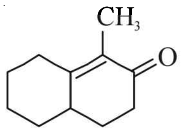
U

(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

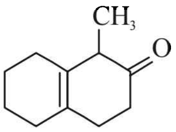
16. The major product of the following reaction is *(JEE Adv. 2015)*



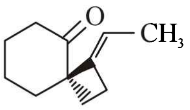
(a)



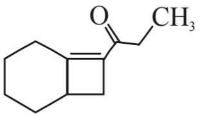
(b)



(c)

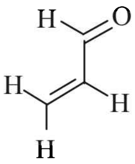


(d)

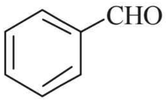


17. Positive Tollen's test is observed for *(JEE Adv. 2016)*

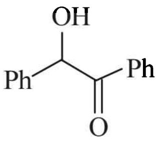
(a)



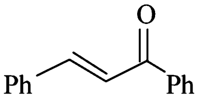
(b)



(c)



(d)



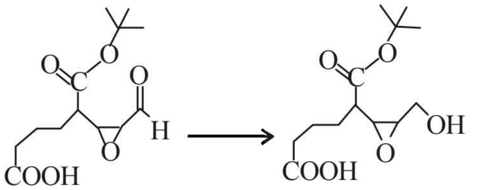
18. The correct statement(s) about the following reaction sequence is(are) *(JEE Adv. 2016)*

$$\text{Cumene}(C_9H_{12})\xrightarrow[\text{(ii)}H_3O^+]{\text{(i)}O_2}\mathbf{P}\xrightarrow{CHCl_3/NaOH}\mathbf{Q}\,(\text{major})+\mathbf{R}\,(\text{minor})$$

$$\mathbf{Q}\xrightarrow[PhCH_2Br]{NaOH}\mathbf{S}$$

(a) **R** is steam Volatile
(b) **Q** gives dark violet coloration with 1% aqueous $FeCl_3$ solution
(c) **S** gives yellow precipitate with 2, 4–dinitrophenylhydrazine
(d) **S** gives dark violet coloration with 1% aqueous $FeCl_3$ solution

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



(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

E Subjective Problems

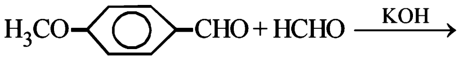
1. Write the structural formula of the main organic product formed when :

(i) methanal reacts with ammonia *(1981 - ½ Mark)*

(ii) ethyl acetate is treated with double the molar quantity of ethyl magnesium bromide and the reaction mixture poured into water. *(1981 - ½ Mark)*

(iii) benzene $\xrightarrow{CH_3CH_2COCl/AlCl_3}$ *(1985 - 1 Mark)*

(iv) propanal $\xrightarrow[\text{heat}]{NaOH}$ *(1985 - 1 Mark)*

(v)  *(1992 - 1 Mark)*

(vi) $C_6H_5COOH + CH_3MgI \rightarrow ? + ?$ *(1993 - 2 Marks)*

(vii) $C_6H_5CH_2CO_2CH_3 \xrightarrow[\text{(ii) }H^+]{\text{(i)}CH_3MgBr(\text{excess})}$ *(1994 - 1 Mark)*

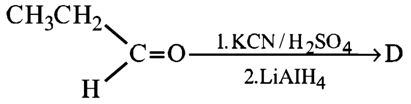
(viii) $CH_3-CH_2-COOH \xrightarrow[\text{bromine}]{\text{P and}} \overset{\mathbf{A}}{-----} \xrightarrow[2.H^+]{1.\text{alcoholic KOH (excess)}} \overset{\mathbf{B}}{-----}$ *(1995 - 2 Marks)*

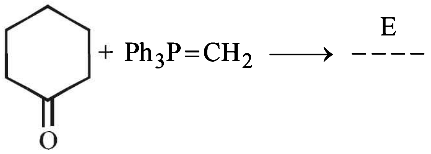
(ix) $C_6H_5-CHO + CH_3-COOC_2H_5 \xrightarrow[C_2H_5OH\text{ and heat}]{NaOC_2H_5\text{ in absolute}} \overset{\mathbf{D}}{------}$ *(1995 - 1 Mark)*

(x) $o-HOOC-C_6H_4-CH_2-C_6H_5 \xrightarrow{SOCl_2} \overset{\mathbf{G}}{------} \xrightarrow[AlCl_3]{\text{anhydrous}} \overset{\mathbf{H}}{------}$

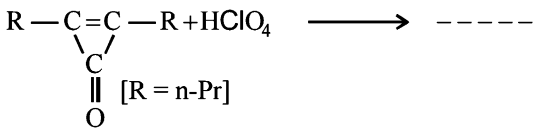
$\mathbf{H} \xrightarrow[HCl]{Zn-Hg} \overset{\mathbf{I}}{------}.$ *(1995 - 2 Marks)*

(xi) Complete the following reaction with appropriate structure. *(1996 - 1 Mark)*



(xii)  *(1997 - 1 Mark)*

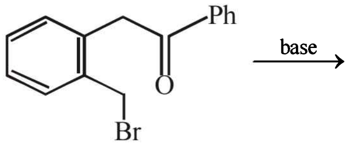
(xiii) $(COOH)_2 + (CH_2OH)_2 + \text{Conc.}H_2SO_4 \longrightarrow \overset{\mathbf{F}}{----}$ *(1997 - 1 Mark)*

(xiv)  *(1997 - 1 Mark)*

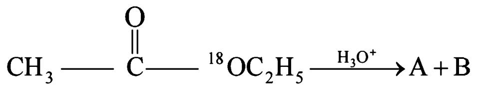
(xv) $ClCH_2CH_2CH_2COPh + KOH + MeOH \longrightarrow -----$ *(1997 - 1 Mark)*

(xvi) $H_3CCOCOC_6H_5 + NaOH/H_3O^{\oplus} \longrightarrow ----$ *(1997 - 1 Mark)*

(xvii) $(CH_3)_2CHOCH_3 \xrightarrow{HI(\text{excess}),\text{ heat}}$ 2 Products. *(1998 - 2 Marks)*

(xviii)  $\xrightarrow{\text{base}}$ *(2000 - 1 Mark)*

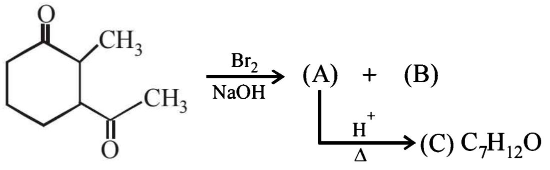
(xix) Write the structures of the products A and B.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-{}^{18}OC_2H_5\xrightarrow{H_3O^+}A+B$$

(2000 - 2 Marks)

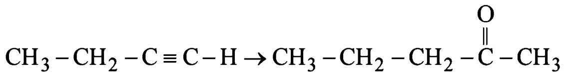
(xx) Identify A, B, C and give their structures.



(2000 - 3 Marks)

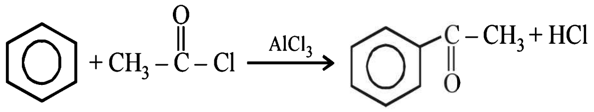
2. Write the chemical equation to show what happens when ethyl acetate is treated with sodium ethoxide in ethanol and the reaction mixture is acidified. ***(1981 - 2 Marks)***

3. Outline the reaction sequence for the conversion of
   - (i) methanal to ethanal (the number of steps should not be more than three). ***(1981 - 2 Marks)***
   - (ii) acetylene to acetone ***(1985 - 1 Mark)***
   - (iii) acetic acid to tertiary-butyl alcohol. ***(1989 - 1½ Marks)***
   - (iv) Ethanal to 2-hydroxy-3-butenoic acid. ***(1990 - 2 Marks)***
   - (v) Ethanoic acid to a mixture of methanoic acid and diphenyl ketone. ***(1990 - 2Marks)***
   - (vi) Carry out the following transformation in not more than three steps. ***(1999 - 3 Marks)***



$$CH_3-CH_2-C\equiv C-H \rightarrow CH_3-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

4. Outline the accepted mechanism of the following reaction. Show the various steps including the charged intermediates. ***(1981 - 3 Marks)***



5. An alkene (A) on ozonolysis yields acetone and an aldehyde. The aldehyde is easily oxidized to an acid (B). When B is treated with bromine in presence of phosphorus, it yields a compound (C) which on hydrolysis gives a hydroxy acid (D). This acid can also be obtained from acetone by reaction with hydrogen cyanide followed by hydrolysis. Identify the compounds A, B, C and D. ***(1982 - 2 Marks)***

6. Give reasons for the following :
   - (*i*) Acetic acid can be halogenated in the presence of red P and Cl_2 but formic acid cannot be halogenated in the same way. ***(1983 - 1 Mark)***
   - (*ii*) Formic acid is a stronger acid than acetic acid; ***(1985 - 1 Mark)***
   - (*iii*) 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 - 2 Marks)***
   - (*iv*) Hydrazones of aldehydes and ketones are not prepared in highly acidic medium. ***(1986 - 1 Mark)***
   - (*v*) Iodoform is obtained by the reaction of acetone with hypoiodite but not with iodide ion. ***(1991 - 1 Mark)***
   - (*vi*) In acylium ion, the structure $R-C\equiv O^+$ is more stable than $R-C^+=O$. ***(1994 - 1 Mark)***
   - (*vii*) Although phenoxide ion has more number of resonating structures than benzoate ion, benzoic acid is a stronger acid than phenol. Why? ***(1997 - 2 Marks)***
   - (*viii*) Explain why *o*-hydroxybenzaldehyde is a liquid at room temperature while p-hydroxybenzaldehyde is a high melting solid. ***(1999 - 2 Marks)***

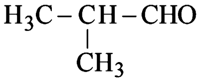
7. State the conditions under which the following preparation are carried out. Give the necessary equations which need not be balanced.
   - (*i*) Ethanol from acetylene ***(1983 - 1 Mark)***
   - (*ii*) Acetic acid from methyl iodide ***(1983 - 1 Mark)***

8. What happens when *p*-xylene is reacted with concentrated sulphuric acid and the resultant product is fused with KOH. ***(1984 - 2 Marks)***

9. Write down the reactions involved in the preparation of the following using the reagents indicated against it in parenthesis :
Propionic anhydride from propionaldehyde
[$AgNO_3/NH_4OH$, P_2O_5]. ***(1984 - 2 Marks)***

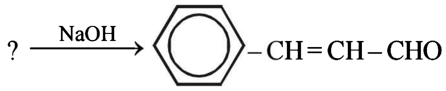
10. Give a chemical test/suggest a reagent to distinguish between acetaldehyde from acetone. ***(1987 - 1 Mark)***

11. Arrange the following in increasing ease of hydrolysis
$CH_3COOC_2H_5$, CH_3COCl, $(CH_3CO)_2O$, CH_3CONH_2. ***(1986 - 1 Mark)***

12. A white precipitate was formed slowly when silver nitrate was added to a compound (A) with molecular formula $C_6H_{13}Cl$. Compound (A) on treatment with hot alcoholic potassium hydroxide gave a mixture of two isomeric alkenes (B) and (C), having formula C_6H_{12}. The mixture of (B) and (C), on ozonolysis, furnished four compounds : ***(1986 - 4 Marks)***
   - (i) CH_3CHO;
   - (ii) C_2H_5CHO;
   - (iii) CH_3COCH_3 and
   - (iv)  $H_3C-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CHO$

What are the structures of (A), (B) and (C)?

13. A liquid (X), having a molecular formula $C_6H_{12}O_2$ is hydrolysed with water in the presence of an acid to give a carboxylic acid (Y) and an alcohol (Z). Oxidation of (Z) with chromic acid gives (Y). What are the structures of (X), (Y) and (Z)? ***(1986 - 3 Marks)***

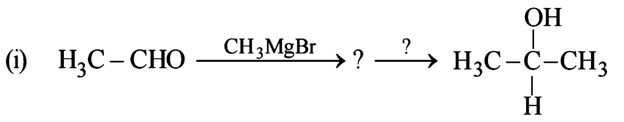
14. Complete the following with appropriate structures :
   - (*i*) $(CH_3CO)_2O \xrightarrow{C_2H_5OH} CH_3COOH + ?$ ***(1986 - 1 Mark)***
   - (*ii*) 

(1986 - 1 Mark)

15. An unknown compound of carbon, hydrogen and oxygen contains 69.77% carbon and 11.63% hydrogen and has a molecular weight of 86. It does not reduce Fehling solution, but forms a bisulphite addition compound and gives a positive iodoform test. What are the possible structures for the unknown compound? ***(1987 - 5 Marks)***

16. An organic compound (A) on treatment with acetic acid in the presence of sulphuric acid produces an ester (B), (A) on mild oxidation gives (C), (C) with 50% potassium hydroxide followed by acidification with dilute hydrochloric acid generates (A) and (D), (D) with phosphorus pentachloride followed by reaction with ammonia gives (E), (E) on dehydration produces hydrocyanic acid.
Identify the compounds A, B, C, D and E. ***(1987 - 5 Marks)***

17. Complete the following reactions :

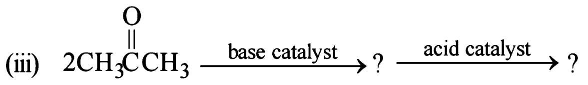


(i) $H_3C-CHO \xrightarrow{CH_3MgBr} ? \xrightarrow{?} H_3C-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$

(1988 - 1 Marks)

(ii) $CH_3COOH \xrightarrow{?} ClCH_2COOH \xrightarrow{\text{excess ammonia}} ?$

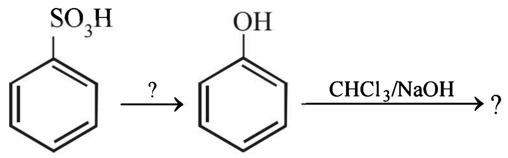
(1988 - 1 Marks)



(iii) $2CH_3\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow{\text{base catalyst}} ? \xrightarrow{\text{acid catalyst}} ?$

(1988 - 1 Marks)

(iv)



(1988 - 1 Marks)

18. A hydrocarbon A (molecular formula C_5H_{10}) yields 2-methylbutane on catalytic hydrogenation. A adds HBr (in accordance with Markownikoff's rule) to form a compound B which on reaction with silver hydroxide forms an alcohol C, $C_5H_{12}O$. Alcohol C on oxidation gives a ketone D. Deduce the structures of A, B, C and D and show the reactions involved. *(1988 - 5 Marks)*

19. A ketone 'A' which undergoes haloform reaction gives compound B on reduction. B on heating with sulphuric acid gives compound C, which forms monoozonide D, D on hydrolysis in presence of zinc dust gives only acetaldehyde. Identify A, B and C. Write down the reactions involved. *(1989 - 4 Marks)*

20. The sodium salt of a carboxylic acid, A, was produced by passing a gas, B, into an aqueous solution of caustic alkali at an elevated temperature and pressure. A, on heating in presence of sodium hydroxide followed by treatment with sulphuric acid gave a dibasic acid, C. A sample of 0.4 g of acid C, on combustion gave 0.08 g of water and 0.39 g of carbon dioxide. The silver salt of the acid C weighing 1.0 g on ignition yielded 0.71 g of silver as residue. Identify A, B and C. *(1990 - 5 Marks)*

21. Compound A ($C_6H_{12}O_2$) on reduction with $LiAlH_4$ yielded two compounds B and C. The compound B on oxidation gave D, which on treatment with aqueous alkali and subsequent heating furnished E. The latter on catalytic hydrogenation gave C. The compound D was oxidized further to give F which was found to be a monobasic acid (molecular weight = 60.0). Deduce the structures of A, B, C, D and E. *(1990 - 4 Marks)*

22. An organic compound containing C, H and O exists in two isomeric forms A and B. An amount of 0.108 g of one of the isomers gives on combustion 0.308 g of CO_2 and 0.072 g of H_2O. A is insoluble in NaOH and $NaHCO_3$ while B is soluble in NaOH. A reacts with conc. HI to give compounds C and D. C can be separated from D by ethanolic $AgNO_3$ solution and D is soluble in NaOH. B reacts readily with bromine water to give compound E of molecular formula, $C_7H_5OBr_3$. Identify, A, B, C, D and E with justification and give their structures. *(1991 - 6 Marks)*

23. (i) $C_6H_5COOH \xrightarrow{PCl_5} C$

$\xrightarrow{NH_3} D \xrightarrow{P_2O_5} C_6H_5CN \xrightarrow{H_2/Ni} E;$

Identify C, D and E. *(1991 - 2 Marks)*

(ii) $H_3C-CH=CH-CHO \xrightarrow{NaBH_4} F$

$\xrightarrow[ZnCl_2]{HCl} G \xrightarrow[H^+]{KCN} H;$

Identify F, G and H. *(1991 - 2 Marks)*

24. Compound 'X', containing chlorine on treatment with strong ammonia gives a solid 'Y' which is free from chlorine. 'Y' analysed as C = 49.31%, H = 9.59% and N = 19.18% and reacts with Br_2 and caustic soda to give a basic compound 'Z'. 'Z' reacts with HNO_2 to give ethanol. Suggest structures for 'X', 'Y' and 'Z'. *(1992 - 1 Mark)*

25. An organic compound 'A' on treatment with ethyl alcohol gives a carboxylic acid 'B' and compound 'C'. Hydrolysis of 'C' under acidic conditions gives 'B' and 'D'. Oxidation of 'D' with $KMnO_4$ also gives 'B'. 'B' on heating with $Ca(OH)_2$ gives 'E' (molecular formula, C_3H_6O). 'E' does not give Tollent's test and does not reduce Fehling's solution but forms a 2,4-dinitrophenylhydrazone. Identify 'A', 'B', 'C', 'D' and 'E'. *(1992 - 3 Marks)*

26. Arrange the following in increasing order of expected enol content *(1992 - 1 Mark)*

$CH_3COCH_2CHO, CH_3COCH_3, CH_3CHO, CH_3COCH_2COCH_3$

27. In the following reactions identify the compounds A, B, C and D. *(1994 - 1 × 4 = 4 Marks)*

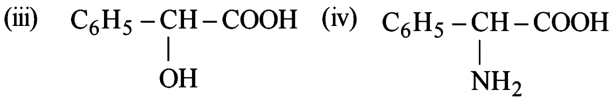
$$PCl_5 + SO_2 \longrightarrow A + B$$
$$A + CH_3COOH \longrightarrow C + SO_2 + HCl$$
$$2C + (CH_3)_2Cd \longrightarrow 2D + CdCl_2$$

28. When gas A is passed through dry KOH at low temperature, a deep red coloured compound B and a gas C are obtained. The gas A, on reaction with but-2-ene, followed by treatment with Zn/H_2O yields acetaldehyde. Identify A, B and C. *(1994 - 3 Marks)*

29. An organic compound A, C_8H_6, on treatment with dilute sulphuric acid containing mercuric sulphate gives a compound B, which can also be obtained from a reaction of benzene with an acid chloride in the presence of anhydrous aluminium chloride. The compound B, when treated with iodine in aqueous KOH, yields C and a yellow compound D. Identify A, B, C and D with justification. Show how B is formed from A. *(1994 - 3 Marks)*

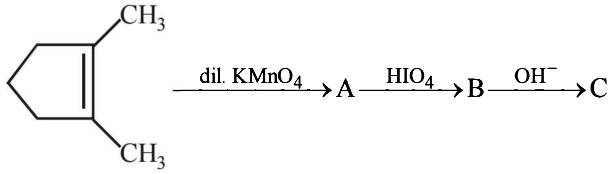
30. Which of the following carboxylic acids undergoes decarboxylation easily? Explain briefly. *(1995 - 2 Marks)*

(i) $C_6H_5-CO-CH_2-COOH$ (ii) $C_6H_5-CO-COOH$



(iii) $C_6H_5-\underset{\underset{OH}{|}}{CH}-COOH$ (iv) $C_6H_5-\underset{\underset{NH_2}{|}}{CH}-COOH$

31. Suggest appopriate structures for the missing compounds. (The number of carbon atoms remains the same throughout the reactions.) *(1996 - 3 Marks)*



32. An ester A ($C_4H_8O_2$), on treatment with excess methyl magnesium chloride followed by acidification, gives an alcohol B as the sole organic product. Alcohol B, on oxidation with NaOCl followed by acidification, gives acetic acid. Deduce the structures of A and B. Show the reactions involved. *(1998 - 6 Marks)*

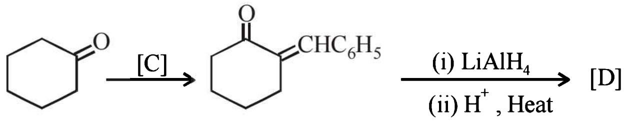
33. An aldehyde A ($C_{11}H_8O$), which does not undergo self aldol condensation, gives benzaldehyde and two moles of B on ozonolysis. Compound B, on oxidation with silver ion gives oxalic acid. Identify the compounds A and B. *(1998 - 2 Marks)*

34. Write the intermediate steps for the following reaction.

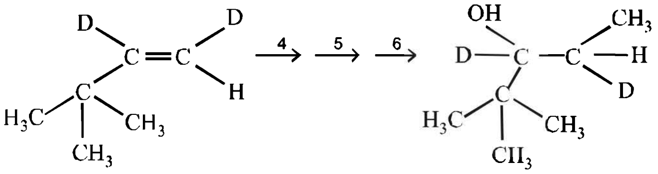
$$C_6H_5CH(OH)C\equiv CH \xrightarrow{H_3O^+} C_6H_5CH=CHCHO$$

(1998 - 2 Marks)

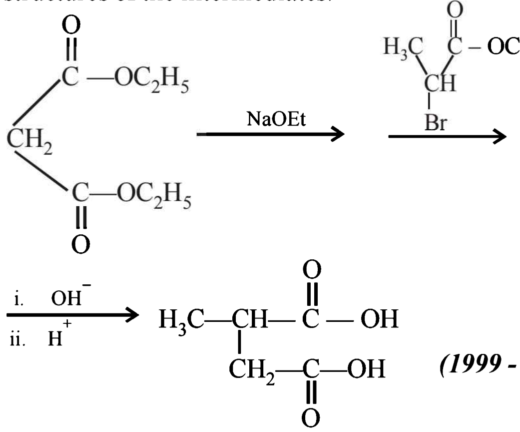
35. Complete the following reaction with appropriate structures of products/reagents : *(1998 - 2 + 2 Marks)*



36. Complete the following reaction with appropriate reagents : *(1999 - 3 Marks)*



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

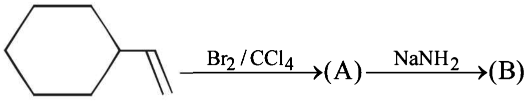


(1999 - 5 Marks)

38. 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-acetylcyclopentene **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 - 5 Marks)*

39. An organic compound **A,** $C_8H_4O_3$, in dry benzene in the presence of anhydrous $AlCl_3$ gives compound **B**. The compound **B** on treatment with PCl_5, followed by reaction with $H_2/Pd\,(BaSO_4)$ gives compound **C**, which on reaction with hydrazine gives a cyclic compound **D** ($C_{14}H_{10}N_2$). Identify **A, B, C** and **D**. Explain the formation of **D** from **C**. *(2000 - 5 Marks)*

40. Identify (A), (B), (C), (D) and (E) in the following schemes and write their structures : *(2001 - 5 Marks)*



$$\xrightarrow{HgSO_4/H_2SO_4} (C) \xrightarrow{NH_2NHCONH_2} (D)$$

$$[C] \xrightarrow{NaOD/D_2O(\text{excess})} (E)$$

41. Identify (X), (Y) and (Z) in the following synthetic scheme and write their structures.

$$Ba^*CO_3 + H_2SO_4 \longrightarrow (X)\text{ gas} \qquad [C^* \text{ denotes } C^{14}]$$

$$CH_2=CH-Br \xrightarrow[\text{(ii)X (iii) } H_3O^+]{\text{(i)Mg/ether}} (Y) \xrightarrow{LiAlH_4} (Z)$$

(2001 - 5 Marks)

Explain the formation of labelled formaldehyde (H_2C^*O) as one of the products when compound (Z) is treated with HBr and subsequently ozonolysed. Mark the C* carbon in the entire scheme.

42. Five isomeric para-disubstituted aromatic compounds A to E with molecular formula $C_8H_8O_2$ were given for identification. Based on the following observations, give structures of the compounds. *(2002 - 5 Marks)*

(i) Both **A** and **B** form a silver mirror with Tollen's reagent; also **B** gives a positive test with $FeCl_3$ solution.
(ii) **C** gives positive iodoform test.
(iii) **D** is readily extracted in aqueous $NaHCO_3$ solution.
(iv) **E** on acid hydrolysis gives 1,4-dihydroxybenzene.

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

$$CH_3CH_2C\equiv C-H \xrightarrow[\text{(ii) } CH_3CH_2Br]{\text{(i) } NaNH_2} X$$

$$\xrightarrow{H_2/Pd-BaSO_4} Y \xrightarrow{\text{alkaline } KMnO_4} Z$$

Is the compound Z optically active? Justify your answer. *(2002 - 5 Marks)*

44. A racemic mixture of (±) 2–phenylpropanoic acid on esterification with (+) 2–butanol gives two esters. Mention the stereochemistry of the two esters produced. *(2003 - 2 Marks)*

45. Compound A of molecular formula $C_9H_7O_2Cl$ exists in keto form and predominantly in enolic form 'B'. On oxidation with $KMnO_4$, 'A' gives *m*–chlorobenzoic acid. Identify 'A' and 'B'. *(2003 - 2 Marks)*

46. A monomer of a polymer on ozonolysis gives two moles of CH_2O and one mole of CH_3COCHO. Write the structure of monomer and write all – '*cis*' configuration of polymer chain. *(2005 - 2 Marks)*

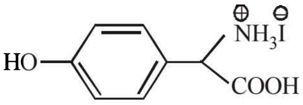
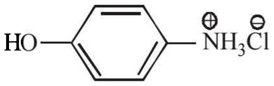
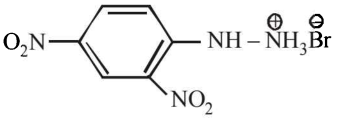
F Match the Following

DIRECTIONS (Q. No. 1) : *Each question contains statements given in two columns, which have to be matched. The statements in Column-I are labelled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and t. Any given statement in Column-I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example :*

If the correct matches are A-p, s and t; B-q and r; C-p and q; and D-s then the correct darkening of bubbles will look like the given.

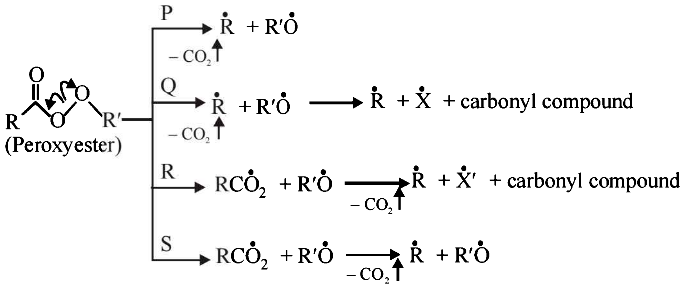
	p	q	r	s	t
A	●	○	○	●	●
B	○	●	●	○	○
C	●	●	○	○	○
D	○	○	○	●	○

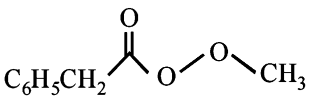
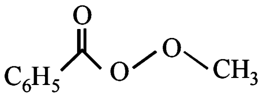
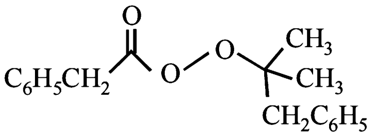
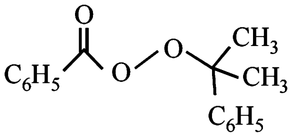
1. Match the entries in Column I with the correctly related quantum number(s) in Column II. Indicate your answer by darkening the appropriate bubbles of the 4 × 4 matrix given in the ORS *(2008)*

Column I	**Column II**
(A) $H_2N-\overset{\oplus}{N}H_3\overset{\ominus}{Cl}$	(p) sodium fusion extract of the compound gives Prussian blue colour with $FeSO_4$
(B) 	(q) gives positive $FeCl_3$ test
(C) 	(r) gives white precipitate with $AgNO_3$
(D) 	(s) reacts with aldehydes to form the corresponding hydrazone derivative

DIRECTIONS (Q. No. 2) : *Following question has matching lists. The codes for the list have choices (a), (b), (c) and (d) out of which ONLY ONE is correct.*

2. Different possible **thermal** decomposition pathways for peroxyesters are shown below. Match each pathway from **List-I** with an appropriate structure from **List-II** and select the correct answer using the code given below the lists. *(JEE Adv. 2014)*



List-I	**List-II**
P. Pathway P	1. 
Q. Pathway Q	2. 
R. Pathway R	3. 
S. Pathway S	4. 

Code :

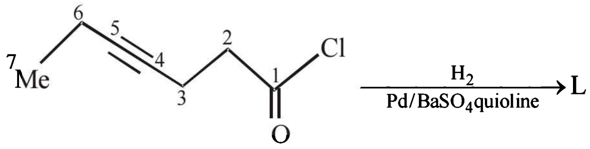
	P	Q	R	S
(a)	1	3	4	2
(b)	2	4	3	1
(c)	4	1	2	3
(d)	3	2	1	4

G Comprehension Based Questions

PASSAGE -1

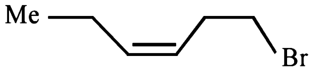
In the following reaction sequence, product I, J and L are formed. K represents a reagent. *(2008)*

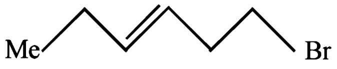
$$\text{Hex}-3-\text{ynal}\xrightarrow[2.PBr_3]{1.NaBH_4} I \xrightarrow[3.H_3O^+]{1.Mg/ether\ \ 2.CO_2} J \xrightarrow{K}$$

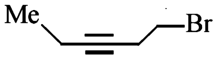


1. The structure of the product I is –

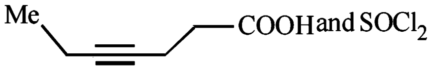
(a) 

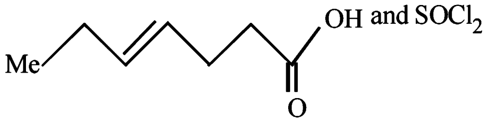
(b) 

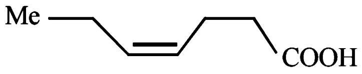
(c) 

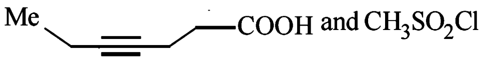
(d) 

2. The structures of compound J and K, respectively, are

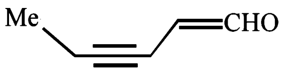
(a) 

(b) 

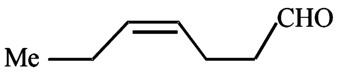
(c) 

(d) 

3. The structure of product L is

(a) 

(b) 

(c) 

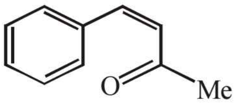
(d) 

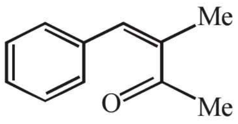
PASSAGE-2

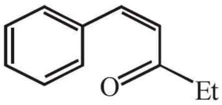
A carbonyl compound P, which gives positive iodoform test, undergoes reaction with MeMgBr followed by dehydration to give an olefin **Q**. Ozonolysis of **Q** leads to a dicarbonyl compound **R**, which undergoes intramolecular aldol reaction to give predominantly S. *(2009)*

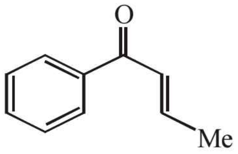
$$\mathbf{P}\xrightarrow[2.H^+,H_2O\ \ 3.H_2SO_4,\Delta]{1.\ MeMgBr}\mathbf{Q}\xrightarrow[2.\ Zn,H_2O]{1.\ O_3}\mathbf{R}\xrightarrow[2.\ \Delta]{1.\ OH^-}\mathbf{S}$$

4. The structure of the carbonyl compound **P** is

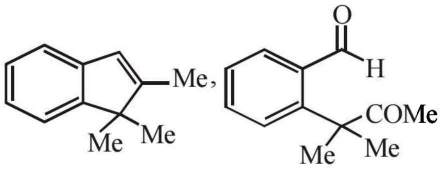
(a) 

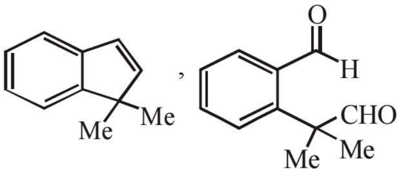
(b) 

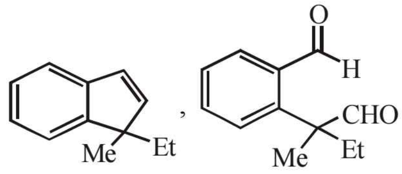
(c) 

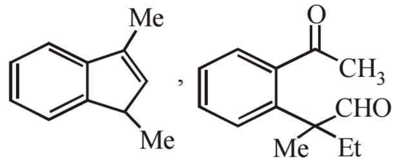
(d) 

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

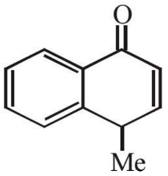
(a) 

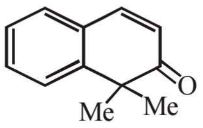
(b) 

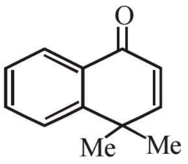
(c) 

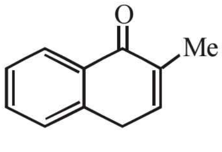
(d) 

6. The structure of the product **S** is

(a) 

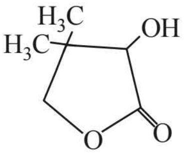
(b) 

(c) 

(d) 

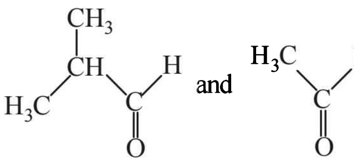
PASSAGE-3

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)*

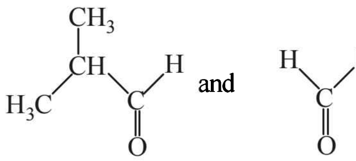


7. The compounds P and Q respectively are :

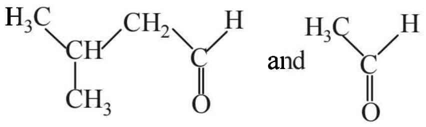
(a)



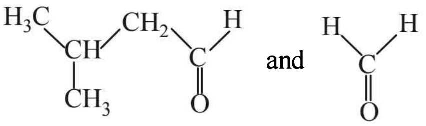
(b)



(c)

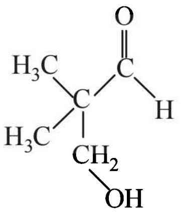


(d)

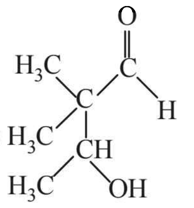


8. The compound R is :

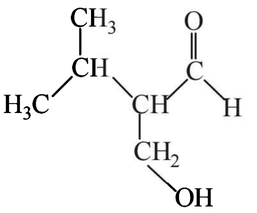
(a)



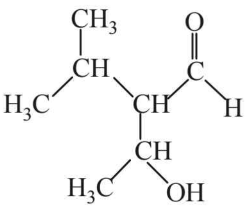
(b)



(c)

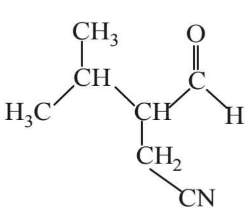


(d)

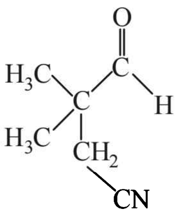


9. The compound S is :

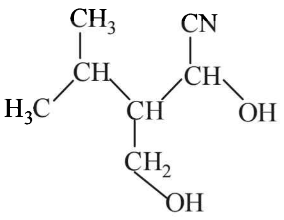
(a)



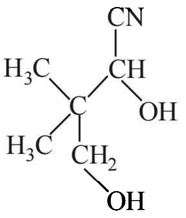
(b)



(c)



(d)



PASSAGE-4

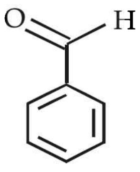
In the following reaction sequence, the compound J is an intermediate.

$$\text{I} \xrightarrow[\text{CH}_3\text{COONa}]{(\text{CH}_3\text{CO})_2\text{O}} \text{J} \xrightarrow[\substack{\text{(ii) SOCl}_2 \\ \text{(iii) anhyd. AlCl}_3}]{\text{(i) H}_2\text{, Pd/C}} \text{K}$$

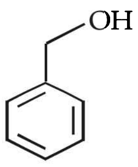
J ($C_9H_8O_2$) gives effervescence on treatment with $NaHCO_3$ and a positive Baeyer's test. *(2012)*

10. The compound **I** is

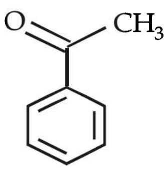
(A)



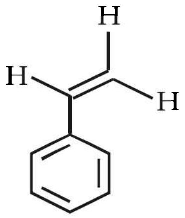
(B)



(C)

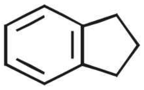


(D)

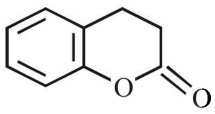


11. The compound **K** is

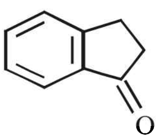
(a)



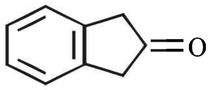
(c)



(b)

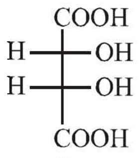


(d)

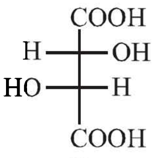


PASSAGE-5

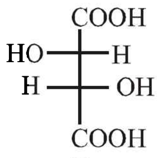
P and Q are isomers of dicarboxylic acid $C_4H_4O_4$. Both decolorize Br_2/H_2O. On heating, P forms the cyclic anhydride. Upon treatment with dilute alkaline $KMnO_4$, P as well as Q could produce one or more than one from S, T and U.



S



T



U

(JEE Adv. 2013)

12. Compounds formed from P and Q are, respectively

(a) Optically active S and optically active pair (T, U)

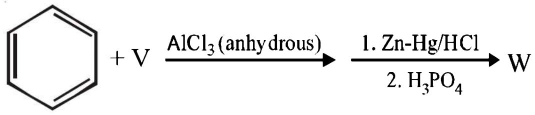
(b) Optically inactive S and optically inactive pair (T, U)

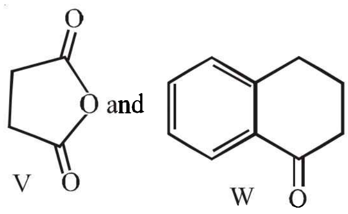
(c) Optically active pair (T, U) and optically active S

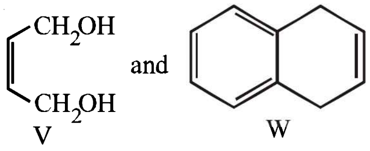
(d) Optically inactive pair (T, U)) and optically inactive S

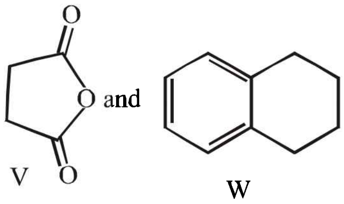
13. In the following reaction sequences V and W are respectively

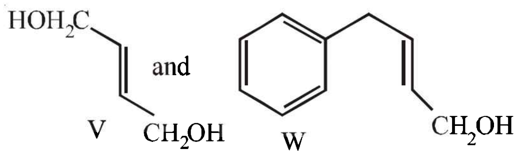
$$Q \xrightarrow[\Delta]{H_2/Ni} V$$



(a) 

(b) 

(c) 

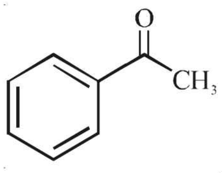
(d) 

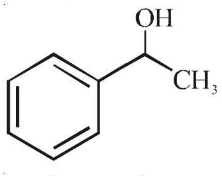
PASSAGE-6

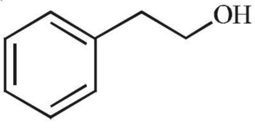
In the following reactions

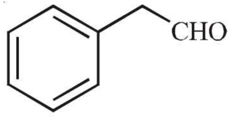
$$\begin{tikzcd}
C_8H_6 \arrow[r, "Pd-BaSO_4", "H_2"'] \arrow[d, "H_2O", "HgSO_4{,}H_2SO_4"'] & C_8H_8 \arrow[r, "(i)\ B_2H_6", "(ii) H_2O_2{,}\ NaOH{,}\ H_2O"'] & X \\
C_8H_8O \arrow[r, "(i)\ EtMgBr{,}\ H_2O", "(ii) H^+{,}\ heat"'] & Y &
\end{tikzcd}$$

14. Compound X is *(JEE Adv. 2015)*

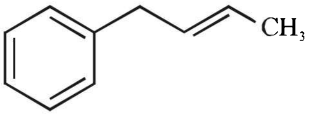
(a) 

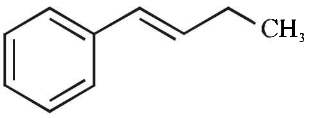
(b) 

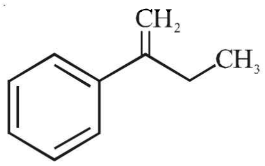
(c) 

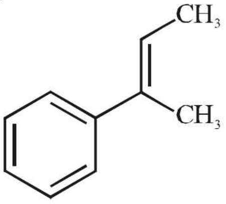
(d) 

15. The major compound Y is *(JEE Adv. 2015)*

(a) 

(b) 

(c) 

(d) 

H Assertion & Reason Type Questions

Each of this question contains STATEMENT-1 (Assertion/ Statement) and STATEMENT-2 (Reason/Explanation) and has 4 choices (a), (b), (c) and (d) out of which ONLY ONE is correct.

(a) Statement-1 is True, Statement-2 isTrue; Statement-2 is a correct explanation for Statement-1

(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1

(c) Statement-1 is True, Statement-2 is False

(d) Statement-1 is False, Statement-2 is True.

1. **Statement-1 :** Acetate ion is more basic than the methoxide ion.
Statement-2 : The acetate ion is resonance stabilized
(1994 - 2 Marks)

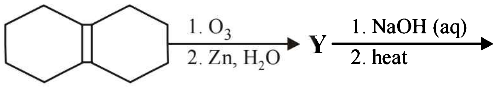
2. **Statement-1 :** Acetic acid does not undergo haloform reaction.
Statement-2 : Acetic acid has no alpha hydrogens.
(1998 - 2 Marks)

3. **Statement-1 :** Dimethyl sulphide is commonly used for the reduction of an ozonide of an alkene to get the carbonyl compounds.
Statement-2 : It reduces the ozonide giving water soluble dimethyl sulphoxide and excess of it evaporates. *(2001S)*

4. **Statement-1 :** *p*-Hydroxybenzoic acid has a lower boiling point than *o*-hydroxybenzoic acid.
Statement-2 : *o*-Hydroxybenzoic acid has intramolecular hydrogen bonding. *(2007)*

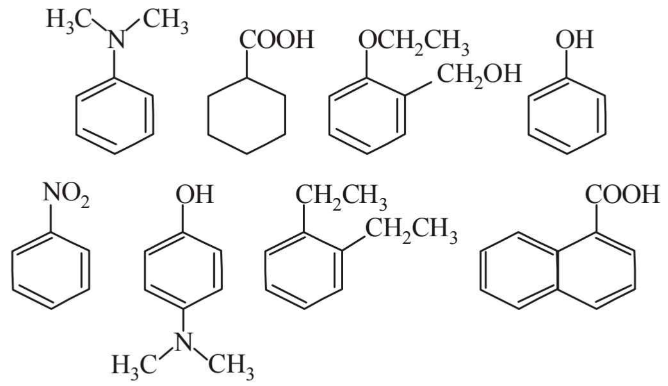
I Integer Value Correct Type

1. In the scheme given below, the total number of intramolecular aldol condensation products formed from 'Y' is



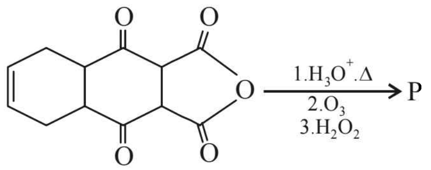
(2010)

2. Amongst the following, the total number of compounds soluble in aqueous NaOH is



(2010)

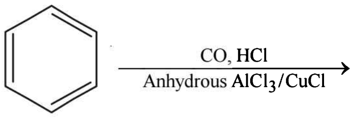
3. The total number of carboxylic acid groups in the product P is *(JEE Adv. 2013)*



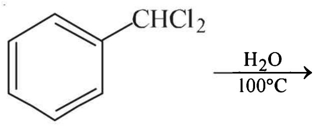
4. Consider all possible isomeric ketones, including stereoisomers of MW = 100. All these isomers are independently reacted with $NaBH_4$ (**NOTE:** stereoisomers are also reacted separately). The total number of ketones that give a racemic product(s) is/are *(JEE Adv. 2014)*

5. Among the following, the number of reaction(s) that produce(s) benzaldehyde is *(JEE Adv. 2015)*

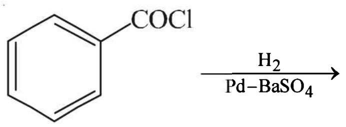
I.



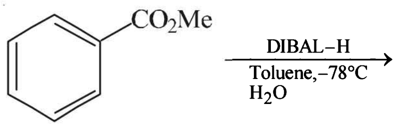
II.



III.



IV.



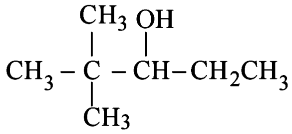
Section-B JEE Main / AIEEE

1. $CH_3CH_2COOH \xrightarrow[\text{red P}]{Cl_2} A \xrightarrow{\text{alc. KOH}} B.$ What is *B*?

(a) CH_3CH_2COCl (b) CH_3CH_2CHO **[2002]**
(c) $CH_2{=}CHCOOH$ (d) $ClCH_2CH_2COOH.$

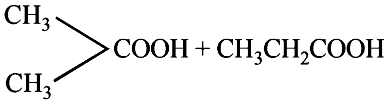
2. On vigorous oxidation by permanganate solution.
$(CH_3)_2C=CH-CH_2-CHO$ gives **[2002]**

(a)



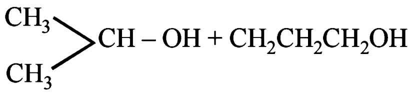
$CH_3-C(CH_3)_2-CH(OH)-CH_2CH_3$

(b)



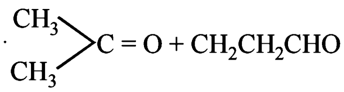
$(CH_3)_2COOH + CH_3CH_2COOH$

(c)



$(CH_3)_2CH-OH + CH_2CH_2CH_2OH$

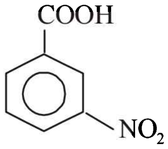
(d)



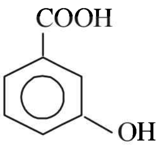
$(CH_3)_2C=O + CH_2CH_2CHO$

3. Picric acid is: **[2002]**

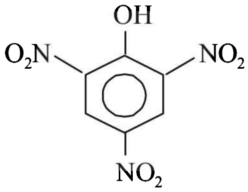
(a)



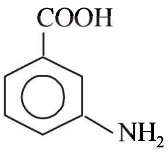
(b)



(c)



(d)



4. When $CH_2 = CH — COOH$ is reduced with $LiAlH_4$, the compound obtained will be **[2003]**

(a) $CH_2{=}CH—CH_2OH$ (b) $CH_3—CH_2—CH_2OH$
(c) $CH_3—CH_2—CHO$ (d) $CH_3—CH_2—COOH$

5. On mixing ethyl acetate with aqueous sodium chloride, the composition of the resultant solution is **[2004]**

(a) $CH_3COCl + C_2H_5OH + NaOH$
(b) $CH_3COONa + C_2H_5OH$
(c) $CH_3COOC_2H_5 + NaCl$
(d) $CH_3Cl + C_2H_5COONa$

6. Acetyl bromide reacts with excess of CH_3MgI followed by treatment with a saturated solution of NH_4Cl gives **[2004]**

(a) 2-methyl-2propanol (b) acetamide
(c) acetone (d) acetyl iodide

7. Which one of the following is reduced with zinc and hydrochloric acid to give the corresponding hydrocarbon?

(a) Acetamide (b) Acetic acid **[2004]**
(c) Ethyl acetate (d) Butan-2-one

8. Which one of the following undergoes reaction with 50% sodium hyroxide solution to give the corresponding alcohol and acid? **[2004]**

(a) Butanal (b) Benzaldehyde
(c) Phenol (d) Benzoic acid

9. Among the following acids which has the lowest pK_a value? **[2005]**

(a) CH_3CH_2COOH (b) $(CH_3)_2CH-COOH$

(c) $HCOOH$ (d) CH_3COOH

10. Reaction of cyclohexanone with dimethylamine in the presence of catalytic amount of an acid forms a compound if water during the reaction is continuously removed. The compound formed is generally known as **[2005]**

(a) an amine (b) an imine

(c) an anemine (d) a Schiff's base

11. The increasing order of the rate of HCN addition to compound A – D is **[2006]**

(A) HCHO (B) CH_3COCH_3

(C) $PhCOCH_3$ (D) PhCOPh

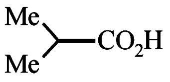
(a) D<C<B<A (b) C<D<B<A

(c) A<B<C<D (d) D<B<C<A

12. The correct order of increasing acid strenght of the compounds **[2006]**

(A) CH_3CO_2H (B) $MeOCH_2CO_2H$

(C) CF_3CO_2H (D)



is

(a) D<A<B<C (b) A<D<B<C

(c) B<D<A<C (d) D<A<C<B

13. A liquid was mixed with ethanol and a drop of concentrated H_2SO_4 was added. A compound with a fruity smell was formed. The liquid was : **[2009]**

(a) HCHO (b) CH_3COCH_3

(c) CH_3COOH (d) CH_3OH

14. Which of the following on heating with aqueous KOH, produces acetaldehyde? **[2009]**

(a) CH_3CH_2Cl (b) CH_2ClCH_2Cl

(c) CH_3CHCl_2 (d) CH_3COCl

15. In Cannizzaro reaction given below

$$2PhCHO \xrightarrow{:\overset{\ominus}{O}H} PhCH_2OH + PhC\ddot{O}_2^{\ominus}$$

the slowest step is : **[2009]**

(a) the transfer of hydride to the carbonyl group

(b) the abstraction of proton from the carboxylic group

(c) the deprotonation of Ph CH_2OH

(d) the attack of : $\overset{\ominus}{O}H$ at the carboxyl group

16. Which of the following reagents may be used to distinguish between phenol and benzoic acid? **[2011]**

(a) Aqueous NaOH (b) Tollen's reagent

(c) Molisch reagent (d) Neutral $FeCl_3$

17. Trichloroacetaldehyde was subjected to Cannizzaro's reaction by using NaOH. The mixture of the products contains sodium trichloroacetate and another compound. The other compound is : **[2011]**

(a) 2, 2, 2-Trichloroethanol

(b) Trichloromethanol

(c) 2, 2, 2-Trichloropropanol

(d) Chloroform

18. The strongest acid amongst the following compounds is :

(a) CH_3COOH **[2011]**

(b) HCOOH

(c) $CH_3CH_2CH(Cl)CO_2H$

(d) $ClCH_2CH_2CH_2COOH$

19. Sodium ethoxide has reacted with ethanoyl chloride. The compound that is produced in the above reaction is :

(a) Diethyl ether (b) 2-Butanone **[2011]**

(c) Ethyl chloride (d) Ethyl ethanoate

20. Silver Mirror test is given by which one of the following compounds? **[2011]**

(a) Acetaldehyde (b) Acetone

(c) Formaldehyde (d) Benzophenone

21. Iodoform can be prepared from all except : **[2012]**

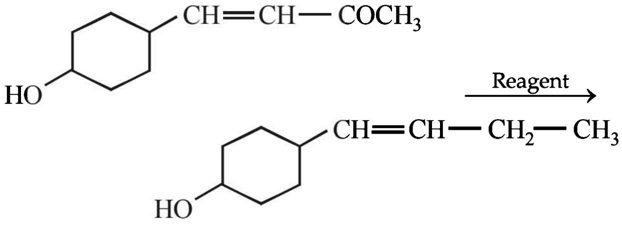
(a) Ethyl methyl ketone

(b) Isopropyl alcohol

(c) 3-Methyl 2-butanone

(d) Isobutyl alcohol

22. In the given transformation, which of the following is the most appropriate reagent ? **[2012]**



(a) $NH_2NH_2, \overset{\ominus}{O}H$ (b) Zn – Hg/ HCl

(c) Na, Liq NH_3 (d) $NaBH_4$

23. The most suitable reagent for the conversion of $R-CH_2-OH \rightarrow R-CHO$ is: **[JEE M 2014]**

(a) $KMnO_4$

(b) $K_2Cr_2O_7$

(c) CrO_3

(d) PCC (Pyridinium Chlorochromate)

24. In the reaction,

$$CH_3COOH \xrightarrow{LiAH_4} A \xrightarrow{PCl_5} B \xrightarrow{Alc.KOH} C,$$

the product C is: **[JEE M 2014]**

(a) Acetaldehyde (b) Acetylene

(c) Ethylene (d) Acetyl chloride

25. In the following sequence of reactions : **[JEE M 2015]**

$$\text{Toluene} \xrightarrow{KMnO_4} A \xrightarrow{SOCl_2} B \xrightarrow[BaSO_4]{H_2/Pd} C$$

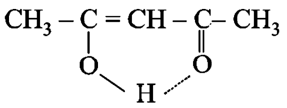
the product C is :

(a) $C_6H_5CH_2OH$ (b) C_6H_5CHO

(c) C_6H_5COOH (d) $C_6H_5CH_3$

20 Aldehydes, Ketones and Carboxylic Acids

Section-A : JEE Advanced/ IIT-JEE

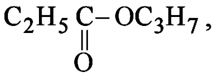
A	**1.**	CO	**2.**	sodium potassium tartarate	**3.**	$C_6H_5CH(OCOCH_3)_2$	**4.**	 $CH_3-\underset{\underset{O}{|}}{C}=CH-\underset{\underset{O}{\|}}{C}-CH_3$ (O–H···O)						
B	**1.**	F	**2.**	F	**3.**	T	**4.**	F	**5.**	F				
C	**1.**	(b)	**2.**	(c)	**3.**	(a, d)	**4.**	(c)	**5.**	(d)	**6.**	(a)	**7.**	(d)
	8.	(b)	**9.**	(a)	**10.**	(a)	**11.**	(b)	**12.**	(d)	**13.**	(b)	**14.**	(a)
	15.	(c)	**16.**	(b)	**17.**	(a)	**18.**	(c)	**19.**	(b)	**20.**	(a)	**21.**	(a)
	22.	(c)	**23.**	(c)	**24.**	(c)	**25.**	(a)	**26.**	(c)	**27.**	(a)	**28.**	(c)
	29.	(c)	**30.**	(b)	**31.**	(d)	**32.**	(a)	**33.**	(b)	**34.**	(d)	**35.**	(d)
	36.	(a)	**37.**	(a)										
D	**1.**	(a,c)	**2.**	(a, b)	**3.**	(a, b, d)	**4.**	(b, d)	**5.**	(a, b)	**6.**	(b, d)	**7.**	(b)
	8.	(a, b, d)	**9.**	(d)	**10.**	(c)	**11.**	(b)	**12.**	(b, d)	**13.**	(a, c, d)		
	14.	(b, d)	**15.**	(c)	**16.**	(a)	**17.**	(a, b, c)	**18.**	(b, c)	**19.**	(c, d)		

E **5.** $(CH_3)_2CHCH=C(CH_3)_2$, $(CH_3)_2CHCOOH$, $(CH_3)_2C(Br)COOH$, $(CH_3)_2C(OH)COOH$
A B C D

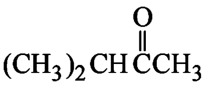
7. $CH_3.CH_2OH$, $CH_2=CH_2$, $CH\equiv CH$, $CH_3.CHO$
A B C D

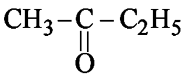
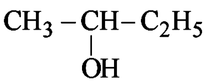
11. $CH_3CONH_2 < CH_3COOC_2H_5 < (CH_3CO)_2O < CH_3COCl$

12. $C_2H_5CH(Cl).CH(CH_3)_2$, $CH_3CH=CH.CH(CH_3)_2$, $C_2H_5CH=C(CH_3)_2$
A B C

13.  $C_2H_5\underset{\underset{O}{\|}}{C}-OC_3H_7$, C_2H_5COOH, n–C_3H_7OH **15.** $C_3H_7COCH_3$ or $(CH_3)_2CHCOCH_3$
(X) (Y) (Z)

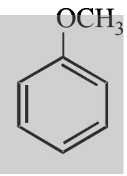
16. CH_3OH, CH_3COOCH_3, $HCHO$, $HCOOH$, $HCONH_2$
A B C D E

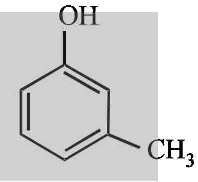
18. $(CH_3)_2CHCH=CH_2$, $(CH_3)_2CHCH(Br)CH_3$, $(CH_3)_2CHCH(OH)CH_3$,  $(CH_3)_2CH\overset{\overset{O}{\|}}{C}CH_3$
A B C D

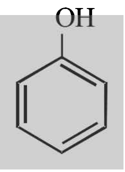
19.  $CH_3-\underset{\underset{O}{\|}}{C}-C_2H_5$,  $CH_3-\underset{\underset{OH}{|}}{CH}-C_2H_5$, $CH_3CH=CH.CH_3$
A B C

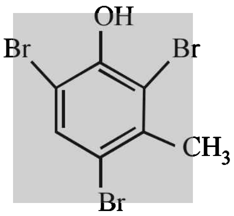
20. $HCOOH$, CO_2, $(COOH)_2$
A B C

21. $C_3H_7COOC_2H_5$, C_2H_5OH, C_4H_9OH, CH_3CHO

22. 

Anisole (A)
;


m-Cresol, (B)
; CH_3I ;
(C)


(D)
;


(E), $C_7H_5OBr_3$

24. $\underset{X}{C_2H_5COCl}, \underset{Y}{C_2H_5CONH_2}, \underset{Z}{C_2H_5NH_2}$ **25.** $\underset{A}{CH_3CO.O.COCH_3}, \underset{B}{CH_3COOH}, \underset{C}{CH_3COOC_2H_5}, \underset{D}{C_2H_5OH}, \underset{E}{CH_3COCH_3}$

26. $CH_3CHO < CH_3COCH_3 < CH_3COCH_2CHO < CH_3COCH_2COCH_3$

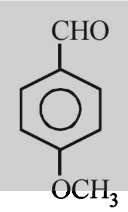
27. $\underset{A}{SOCl_2}, \underset{B}{POCl_3}, \underset{C}{CH_3COCl}, \underset{D}{CH_3COCH_3}$ **28.** $\underset{A}{O_3}, \underset{B}{KO_3}, \underset{C}{O_2}$

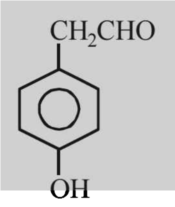
29. $\underset{A}{C_6H_5C \equiv CH}, \underset{B}{C_6H_5COCH_3}, \underset{C}{C_6H_5COOH}, \underset{D}{CHI_3}$ **30.** (i)

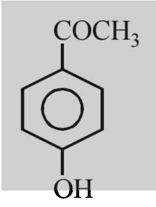
32. $\underset{A}{HCOOC_3H_7}, \underset{B}{(CH_3)_2CHOH}$

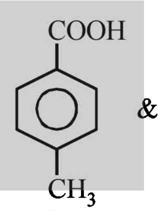
33. $\underset{A}{C_6H_5CH = CHCH = CCHO}, \underset{B}{CHO.COOH}$ **41.** $\underset{X}{\overset{*}{C}O_2}, \underset{Y}{CH_2 = CH\overset{*}{C}OOH}, \underset{Z}{CH_2 = CH\overset{*}{C}H_2OH}$

42.

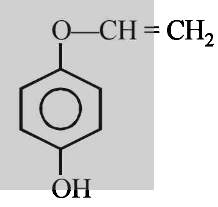

A


B

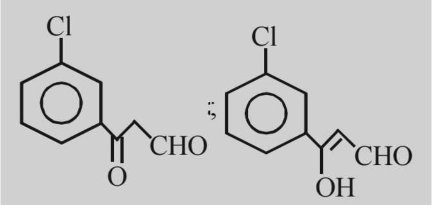

C


D

&


E

43.



46. $H_2C{=}C(CH_3).CH{=}CH_2$

F 1. **(A) - r, s; (B) - p, q; (C) - p, q, r; (D) - p, s** 2. (a)

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

H 1. (d) 2. (c) 3. (a) 4. (d)

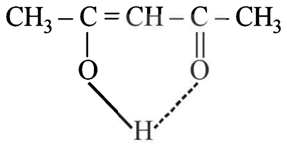
I 1. 1 2. 4 3. 2 4. 5 5. 4

Section-B : JEE Main/ AIEEE

1. (c) 2. (b) 3. (c) 4. (a) 5. (c) 6. (a) 7. (d)
8. (b) 9. (c) 10. (c) 11. (a) 12. (a) 13. (c) 14. (c)
15. (a) 16. (d) 17. (a) 18. (c) 19. (d) 20. (a, c) 21. (d)
22. (a) 23. (d) 24. (c) 25. (b)

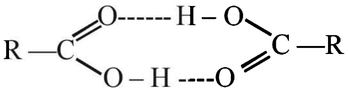
Section-A JEE Advanced/ IIT-JEE

A. Fill in the Blanks

1. **CO;** $HCOOH \xrightarrow[\text{heat}]{Conc.H_2SO_4} CO + H_2O$
2. **sodium potassium tartarate.**
3. **$C_6H_5CH(OCOCH_3)_2$ benzylidene acetate**
4. 
$CH_3-\underset{\underset{O}{|}}{C}=CH-\underset{\underset{O}{||}}{C}-CH_3$

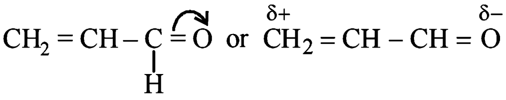
B. TRUE / FALSE

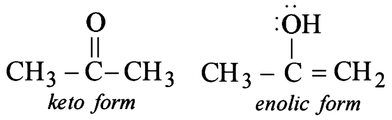
1. **False :** Benzaldehyde has no α-hydrogen atom hence it does not undergo aldol condensation but undergoes Cannizzaro reaction.
2. **False :** Saponification is alkaline hydrolysis of esters.
3. **True :** Aldehydes (from primary alchols) may further be oxidised easily to acids as compared to ketones (from secondary alcohols).
4. **False.** Grignard reagents react with ketones to form *ter*-alcohols; hence here *ter*-butanol will be formed.
5. **False :** H-bonding in propionic acid is stronger (carboxylic acids can form dimers) than that in butanol.



C. MCQs with ONE Correct Answer

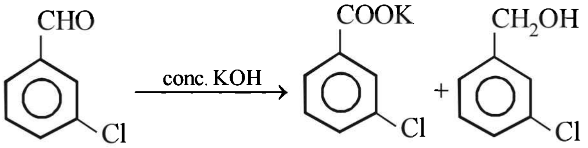
1. (b) Fehling solution, Schiff's reagent & Tollen's reagent react only with aldehydes but Grignard reagents react both with aldehydes and ketones.
2. (c) $\underset{\text{Fehling solution}}{CH_3CHO + 2Cu^{2+} + OH^-} \rightarrow CH_3COOH + \underset{\text{(red)}}{Cu_2O}\downarrow$
3. (b) **TIPS/Formulae :**
The compound containing α-H atom does not undergo Cannizzaro's reaction.
Acetaldehyde does not undergo Cannizzaro reaction since it has α-H atoms while formaldehyde, trimethylacetaldehyde and benzaldehyde undergo Cannizzaro reaction since they do not contain α-hydrogen atoms.
4. (c) **TIPS/Formulae :**
Iodoform test is given by compounds having $-COCH_3$ group.
In acetone $-COCH_3$ group is present. Further ethanol and isopropyl alcohol get oxidised to acetaldehyde and acetone respectively (both having $-COCH_3$ group) in presence of I_2 and they in turn give the test. Thus only diethyl ketone does not give this test.
5. (d) **NOTE :** –CHO produces –R effect i.e. it withdraws electrons from the double bond or from a conjugated system towards itself.


$CH_2=CH-\underset{\underset{H}{|}}{C}=O$ or $\overset{\delta+}{CH_2}=CH-CH=\overset{\delta-}{O}$

6. (a) 
$CH_3-\overset{\overset{O}{||}}{C}-CH_3$ $\quad CH_3-\overset{\overset{:\ddot{O}H}{|}}{C}=CH_2$
keto form *enolic form*

No. of σ bonds in enolic form : $3+1+1+1+1+2=9$
No. of π bonds in enolic form : 1
No. of lone pairs of electrons in enolic form = 2

7. (d) **NOTE :** *m*-Chlobenzaldehyde does not contains α-H atom. It is an example of Cannizzaro reaction



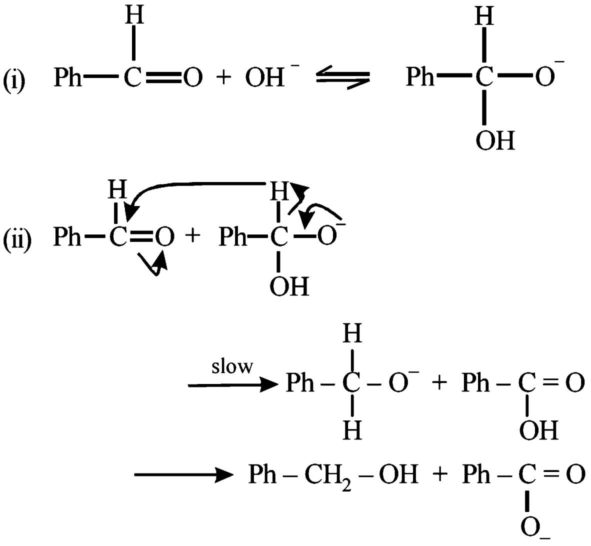
8. (b) **NOTE :** This reaction is known as Rosenmund's reaction.

$$C_6H_5COCl + H_2 \xrightarrow[BaSO_4]{Pd} C_6H_5CHO + HCl$$

9. (a) **TIPS/FORMULAE :**
$LiAlH_4$ is a reducing agent, it reduces $-COOH$ group to $-CH_2OH$ group.

$$C_6H_5COOH \xrightarrow{LiAlH_4} C_6H_5CH_2OH$$

10. (a) $C_6H_5OCH_3 \xrightarrow{HI} C_6H_5OH + CH_3I$
11. (b) The possible mechanism is



NOTE : The slowest step is the transfer of hydride to the carbonyl group as shown in step (ii).

12. (d) $C_2H_5COOH + NaH\overset{14}{C}O_3 \rightarrow$

$$C_2H_5COONa + H_2O + \overset{14}{C}O_2$$

13. (b) Remember that α - H's of carbonyl group are easily replaced by D of D_2O.
14. (a) Compound (a) undergoes dehydration easily as the product obtained is conjugated and thus more stable.
15. (c) $C_6H_5\,COOH + SOCl_2 \longrightarrow C_6H_5COCl + SO_2 + HCl$

16. **(b)** Zn(Hg), HCl cannot be used when acid sensitive group like –OH is present, but NH_2NH_2, OH^- can be used.

17. **(a)** **TIPS/Formulae :**

Both compounds do not contain α-hydrogen hence undergo Crossed Cannizzaro reaction.

Initially OH^- attacks at the carbonyl carbon of HCHO than that of PhCHO because carbonyl carbon of HCHO is

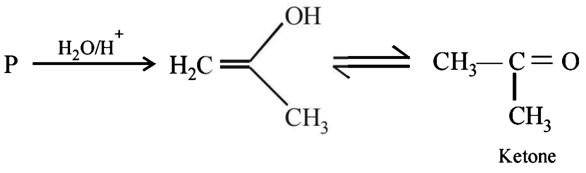
(i) more electrophilic

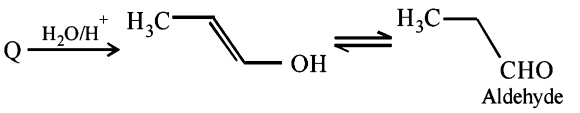
(ii) less sterically hindered to give hydroxyalkoxide which acts as hydride donor in next step to give sodium formate.

$$C_6H_5CHO + HCHO \xrightarrow{NaOH} HCOONa + C_6H_5CH_2OH$$

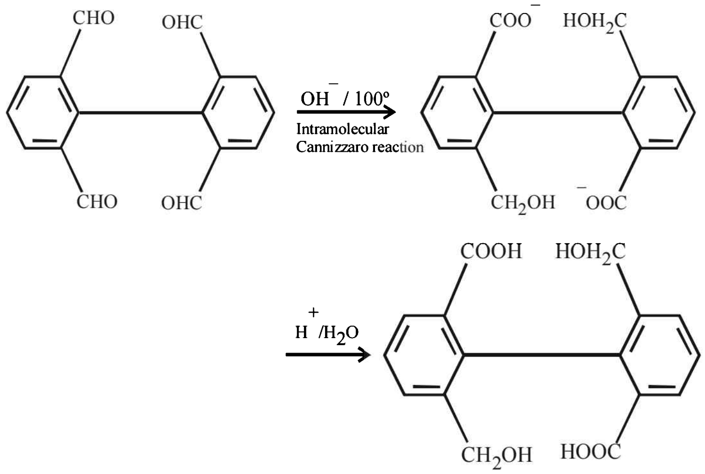
18. **(c)** **TIPS/Formulae :**

Ketone (non-reducing) and aldehyde (reducing) can be distinguished by Fehling solution.

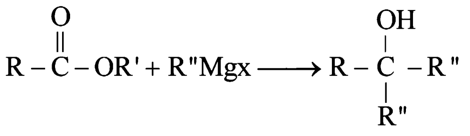




19. **(b)**



20. **(a)** Recall that, esters react with excess of Grignard reagents to form 3° alcohols having at least two identical alkyl groups corresponding to Grignard reagent.



$$R-\overset{O}{\overset{\|}{C}}-OR' + R''Mgx \longrightarrow R-\underset{R''}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-R''$$

Since here Grignard reagent is CH_3MgBr, the 3° alcohol should have at least two methyl groups

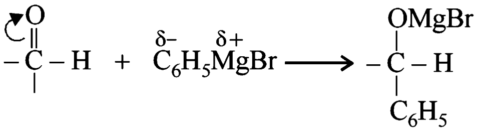
Thus, the choice with at least two methyl groups at the carbon linked with –OH group will be the correct choice.

Hence (a) is the correct choice.

21. **(a)** The optically active acid will react with *d* and *l* forms of alcohol present in the racemic mixture at different rates to form two diastereomers in unequal amounts leading to optical activity of the product.

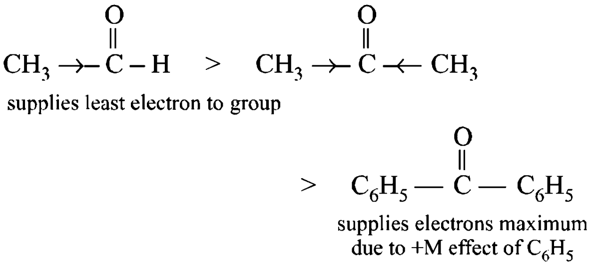
22. **(c)** **TIPS/Formulae :**

Reaction of PhMgBr with carbonyl compounds is an example of nucleophilic addition on carbonyl group which increases with the increase in electron-deficiency of carbonyl carbon.



$$-\underset{|}{\overset{O}{\overset{\|}{C}}}-H + \overset{\delta-}{C_6H_5}\overset{\delta+}{MgBr} \longrightarrow -\underset{C_6H_5}{\underset{|}{\overset{OMgBr}{\overset{|}{C}}}}-H$$

Thus acetaldehyde is most reactive while $C_6H_5COC_6H_5$ least



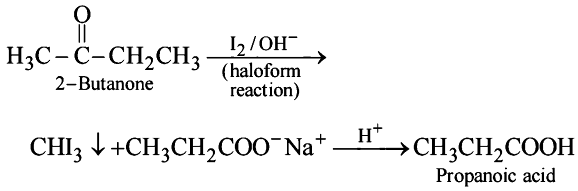
$$CH_3 \rightarrow\!\!-\overset{O}{\overset{\|}{C}}-H \;>\; CH_3 \rightarrow\!\!-\overset{O}{\overset{\|}{C}}\!\!\leftarrow CH_3$$

supplies least electron to group

$$> C_6H_5 — \overset{O}{\overset{\|}{C}} — C_6H_5$$

supplies electrons maximum due to +M effect of C_6H_5

23. **(c)**



$$H_3C-\overset{O}{\overset{\|}{C}}-CH_2CH_3 \xrightarrow[\text{(haloform reaction)}]{I_2/OH^-}$$

2–Butanone

$$CHI_3\downarrow + CH_3CH_2COO^-Na^+ \xrightarrow{H^+} CH_3CH_2COOH$$

Propanoic acid

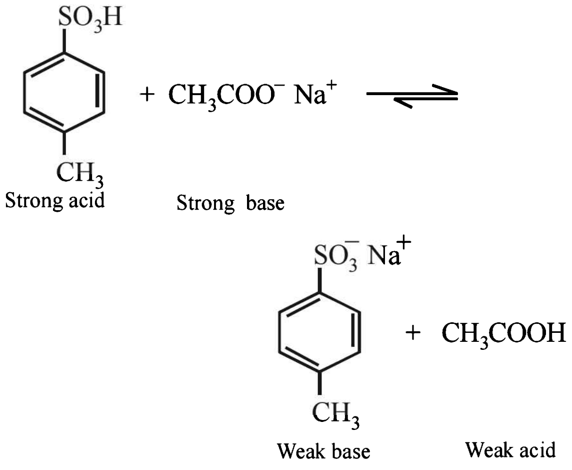
24. **(c)** **TIPS/Formulae :**

This reaction is an example of "Perkin reaction".

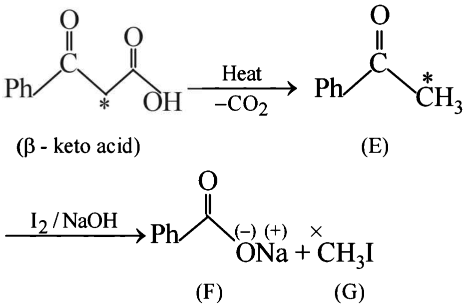
The compound X should be $(CH_3CO)_2O$.

In this step the carbanion is obtained by removal of an α–H atom from a molecule of an acid anhydride, the anion of the corresponding acid acting as a necessary base.

25. **(a)** This is simply an acid-base reaction.



26. **(c)**



(β - keto acid)

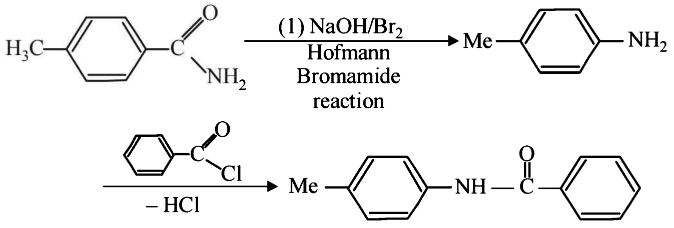
(E)

(F)

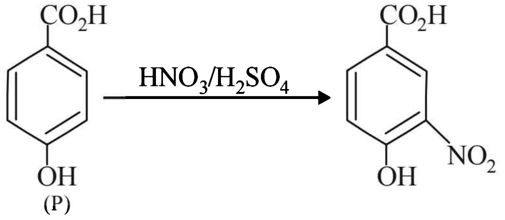
(G)

27. (a) Carboxylic acid is stronger acid than phenol. The presence of electron withdrawing group (e.g. Cl) increases acidic strength, while presence of electron donating group (e.g. CH_3) decreases acidic strength.

28. (c)

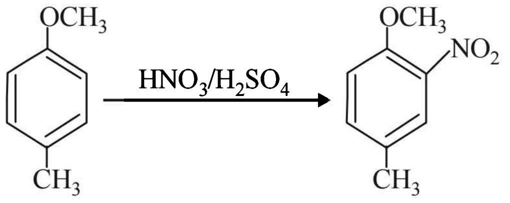


29. (c)



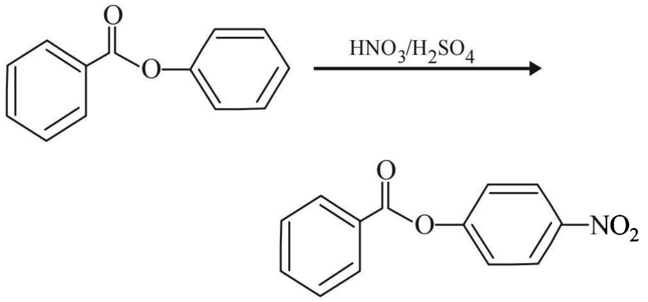
(P)

(OH group is activing)



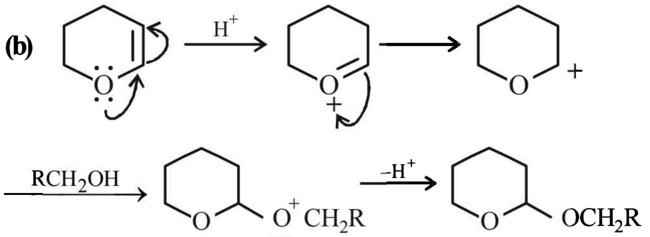
(Q)

(OCH_3 group is more activating)



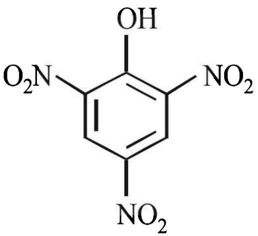
(Benzene ring having –O– is activated)

30. (b)

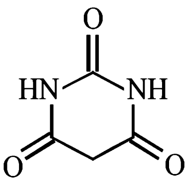


An acetal

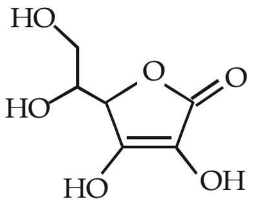
31. (d)



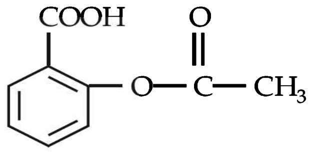
(Picric acid)



(Barbituric acid)

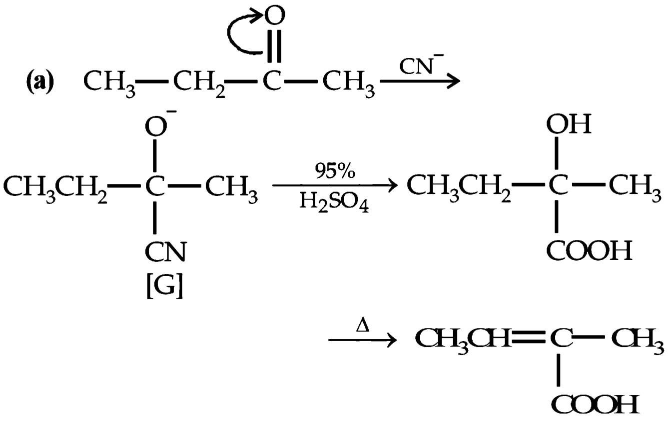


(Ascorbic acid)



(Aspirin)

32. (a)



$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{CN^-} CH_3CH_2-\underset{CN}{\overset{O^-}{C}}-CH_3 \xrightarrow[H_2SO_4]{95\%} CH_3CH_2-\underset{COOH}{\overset{OH}{C}}-CH_3$$

[G]

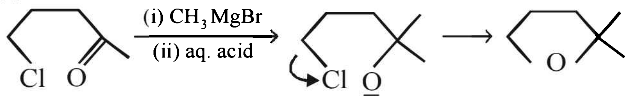
$$\xrightarrow{\Delta} CH_3CH=\underset{COOH}{C}-CH_3$$

[H]

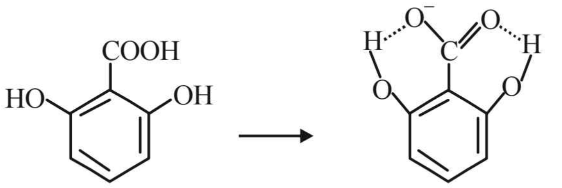
33. (b) β-Ketoacids undergo decarboxylation easily.

34. (d) Carbolic acid (Phenol) is weaker acid than carbonic acid and hence does not liberate CO_2 on treatment with aq. $NaHCO_3$ solution.

35. (d)

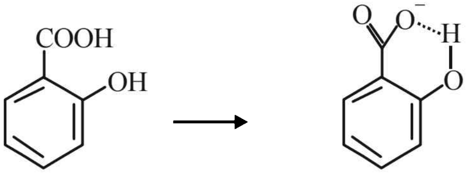


36. (a)



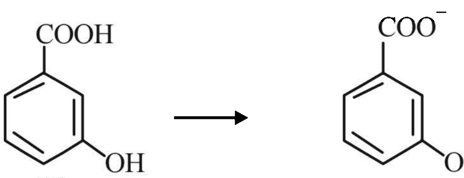
(I)

(stabilizes by more H-bonding)



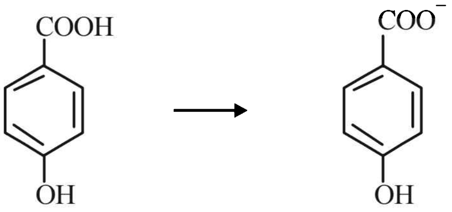
(II)

(stabilizes by H-bonding)



(III)

(stabilizes by –I effect)

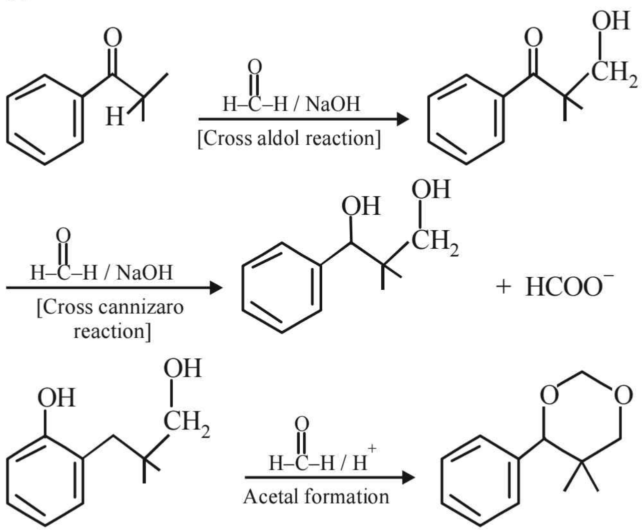


(IV)

(destabilizes by +M effect)

∴ acidity order is I > II > III > IV

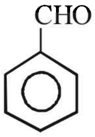
37. **(a)**



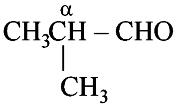
D. MCQs with ONE or More Than One Correct

1. **(a, c)** **TIPS/Formulae :**
Aldehydes having at least one α-hydrogen atom undergo aldol condensation.

$CH_3\overset{\alpha}{C}H_2CHO$
propionaldehyde
(a)

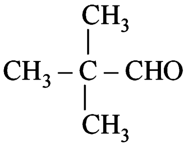


benzaldehyde
(no α- hydrogen atom)
(b)



$CH_3\overset{\alpha}{C}H(CH_3)-CHO$

2-methylpropionaldehyde
(c)



$CH_3-C(CH_3)_2-CHO$

2, 2-dimethylpropionaldehyde
(no α-hydrogen atom)
(d)

2. **(a, b)** **TIPS/Formulae :**
Iodoform reaction is given by the compounds containing $CH_3\!>\!C=O$, $CH_3\!>\!CHOH$ group, CH_3CHO and CH_3CH_2OH.
2-Hydroxypropane ($CH_3CHOHCH_3$) contains the grouping CH_3CHOH— and acetophenone ($C_6H_5COCH_3$) contains the grouping CH_3CO– linked to carbon and hence give yellow ppt. with I_2 and alkali—**iodoform test.**
In methyl acetate ($CH_3COOC_2H_5$) and acetamide ($CH_3CO–NH_2$), CH_3CO is attached to a hetero atom but not to carbon atom and hence both these compounds do not give iodoform test.

3. **(a,b,d)** **NOTE:**
Ethyl chloride and acetyl chloride react with alc. KCN by nucleophilic substitution reaction while benzaldehyde undergoes benzoin condensation :

$$C_2H_5Cl \xrightarrow{KCN\,(alc.)} C_2H_5CN + KCl$$

$$CH_3COCl \xrightarrow{KCN\,(alc.)} CH_3COCN + KCl$$

$$2\,C_6H_5CHO \xrightarrow{KCN\,(alc.)} C_6H_5CHOHCOC_6H_5$$

Thus only chlorobenzene does not react.

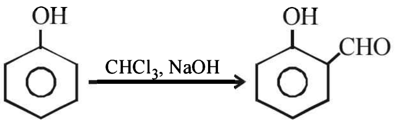
4. **(b,d)** Keto-enol tautomerism is shown in compounds having α-hydrogen on the C adjacent to the CO group.

5. **(a, b)** **NOTE :**
Aldehydes and ketones containing α-Hydrogen atom undergo aldol condensation.

6. **(b,d)** (a) $HCHO \xrightarrow{OH^-} CH_3OH + HCOO^-$
(No new C – C bond is formed)

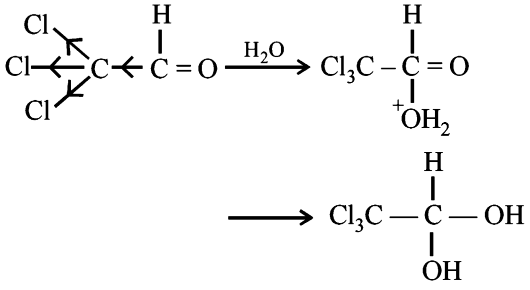
(b) $C_6H_6 + CH_3Cl \xrightarrow{AlCl_3} C_6H_5 - CH_3$
(New C – C bond is formed)

(c) $>C=O \xrightarrow[HCl]{Na/Hg} >CH_2$
(No new C – C bond is formed)

(d)


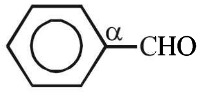
(New C – C bond is formed)

7. **(b)** **TIPS/Formulae :**
Three Cl of chloral makes its carbonyl carbon highly electron deficient, hence H_2O, a nucleophile easily adds on it forming chloral hydrate, $CCl_3CH(OH)_2$, which is quite stable due to intramolecular H–bonding between two –OH groups.



8. **(a,b,d)** **TIPS/Formulae :**
Carbonyl compounds having α – H or α - D undergo aldol condensation.

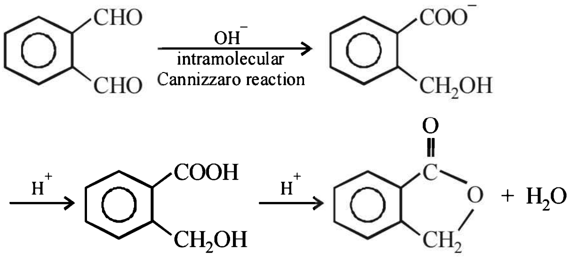
(a) $\overset{\alpha}{C}H_3CHO$ (b) $CH_3\overset{\alpha}{C}H_2CHO$

(c)


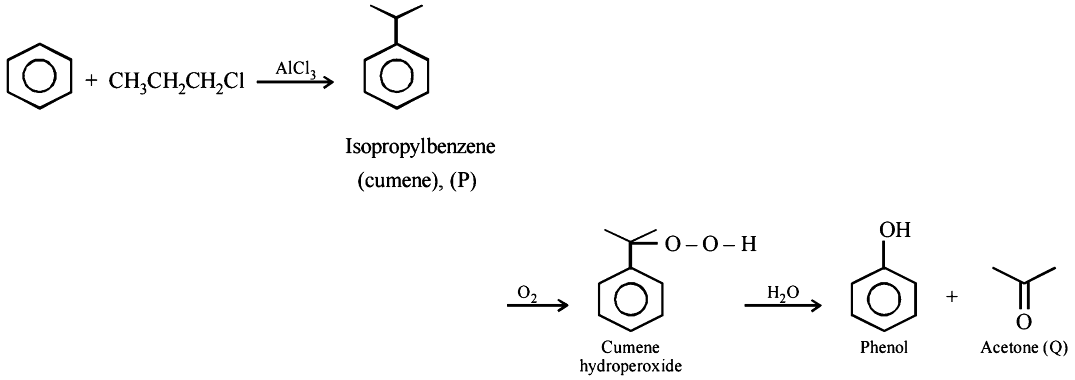
(No α – H)

(d) $\overset{\alpha}{C}D_3CHO$
(α – D present)

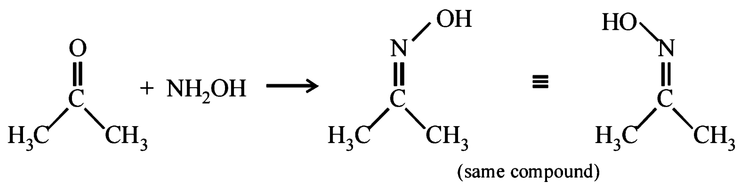
9. **(d)**

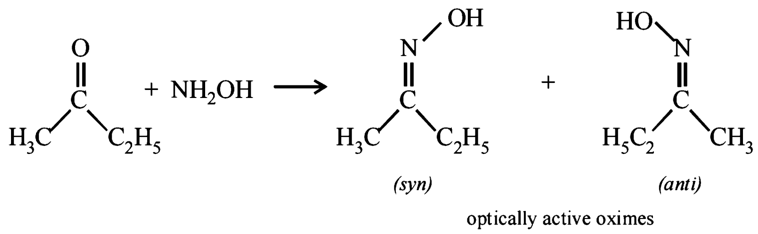


10. (c)



11. (b)





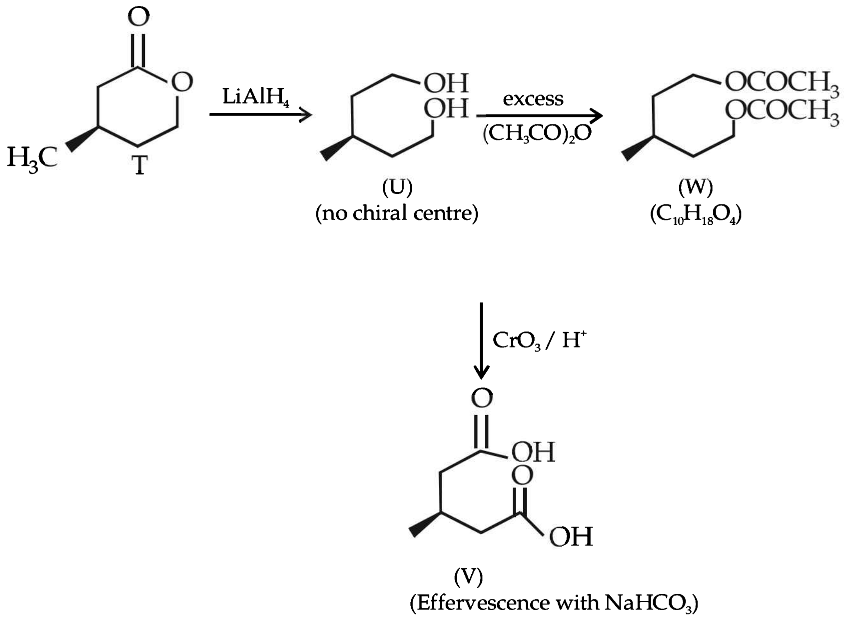
12. **(b,d)** (A) Both are soluble in NaOH, hence **inseparable**.

(B) Only benzoic acid (C_6H_5COOH) is soluble in NaOH and $NaHCO_3$, while benzyl alcohol ($C_6H_5CH_2OH$) is not. Hence, **separable**.

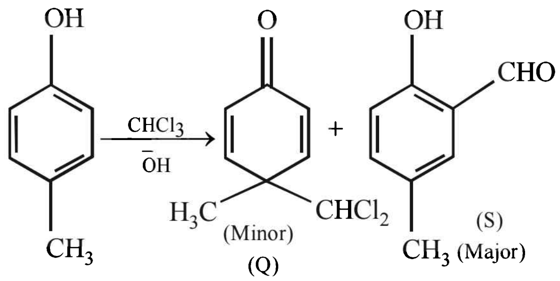
(C) Although NaOH can enable separation between benzyl alcohol ($C_6H_5CH_2OH$) and phenol (C_6H_5OH) as only the later is soluble in NaOH. However, in $NaHCO_3$, both are insoluble. Hence, **inseparable**.

(D) α-Phenylacetic acid ($C_6H_5CH_2COOH$) is soluble in NaOH and $NaHCO_3$. While benzyl alcohol ($C_6H_5CH_2OH$) is not. Hence, **separable**.

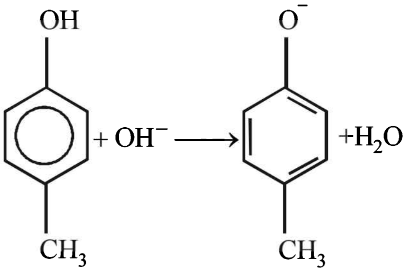
13. **(a, c, d)**

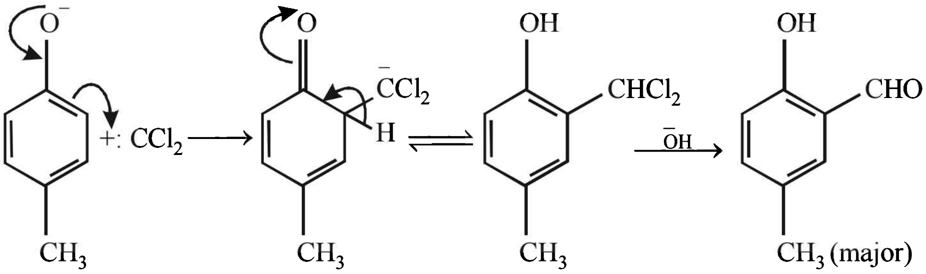


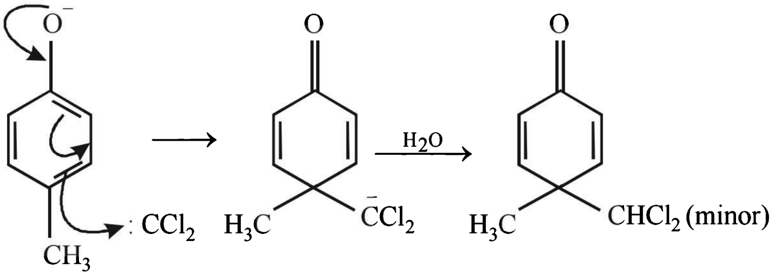
14. (b,d)



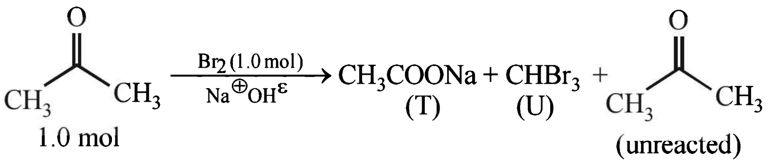
$CHCl_3 + \overset{-}{O}H \longrightarrow :CCl_2 + H_2O + Cl^-$



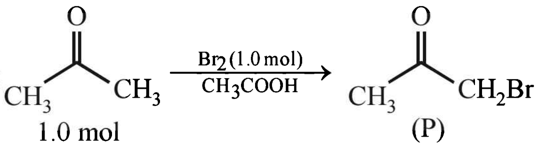




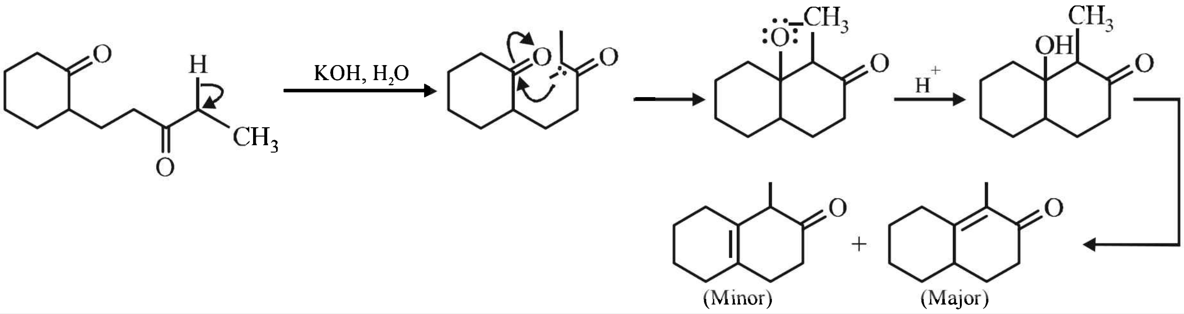
15. (c) Reaction I :



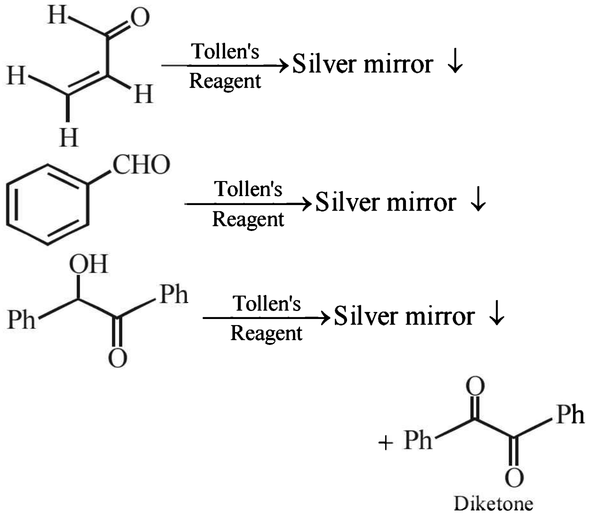
Reaction II :



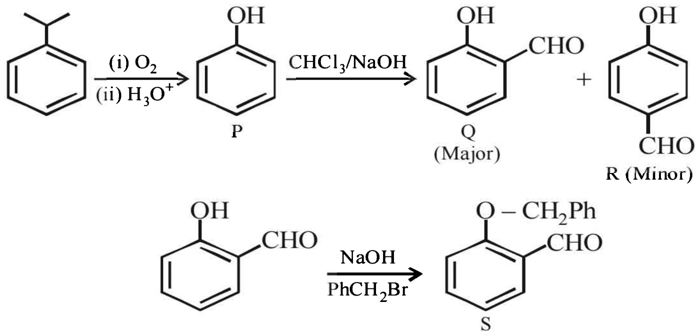
16. (a)



17. **(a, b, c)** Aldehydes and α-Hydroxyketones show positive Tollen's test.



18. **(b, c)**



Q is steam volatile not R.

Q and R show positive test with 1% aqueous $FeCl_3$ solution.

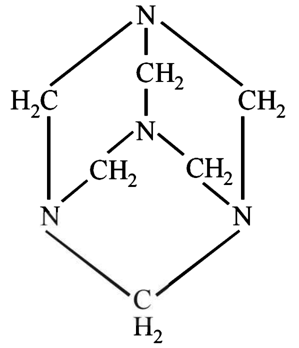
Q, R, S give yellow precipitate with 2, 4-dinitrophenyl hydrazine.

19. **(c, d)**

$LiAlH_4/(C_2H_5)_2O$	: Reduces to esters, carboxylic acid, epoxides and aldehydes and ketones.
BH_3 in T.H.F	: Reduces to –COOH and aldehydes into alcohols but do not reduce to esters and epoxides.
$NaBH_4$ in C_2H_5OH	: Reduces only aldehydes and ketones into alcohols but not to others.
Raney Ni in T.H.F.	: Do not reduce to –COOH, –COOR and epoxide but it can reduce aldehyde into alcohols.

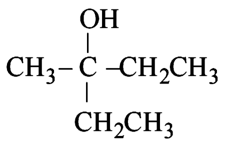
E. Subjective Problems

1. (i)



Hexamethylenetetramine (Urotropine)

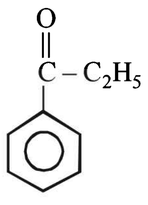
(ii)



$CH_3-\underset{CH_2CH_3}{\overset{OH}{C}}-CH_2CH_3$

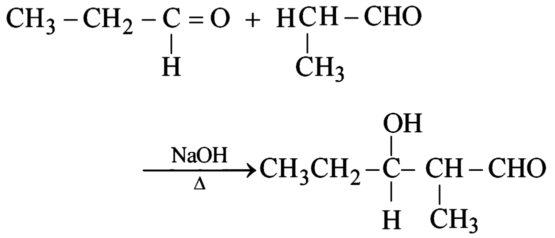
2–Ethylbutanol–2

(iii)



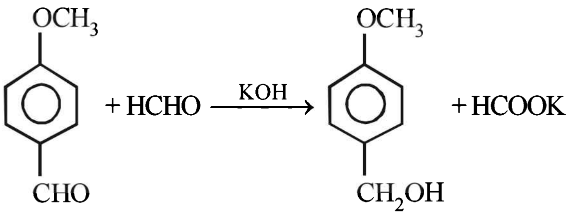
Phenyl ethyl ketone

(iv)



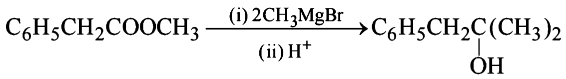
$CH_3-CH_2-\underset{H}{C}=O + H\underset{CH_3}{C}H-CHO \xrightarrow[\Delta]{NaOH} CH_3CH_2-\underset{H}{\overset{OH}{C}}-\underset{CH_3}{CH}-CHO$

(v)



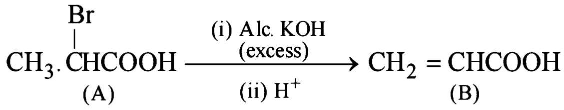
(vi) $C_6H_5COOH + CH_3MgI \longrightarrow CH_4 + C_6H_5COOMgI$

(vii) **NOTE :** Esters react with excess of RMgX to form 3° alcohols having two alkyl groups corresponding to R of RMgX. Thus



$C_6H_5CH_2COOCH_3 \xrightarrow[(ii)\ H^+]{(i)\ 2CH_3MgBr} C_6H_5CH_2\underset{OH}{C}(CH_3)_2$

(viii) $CH_3CH_2COOH \xrightarrow[\text{HVZ reaction}]{P \text{ and } Br_2}$

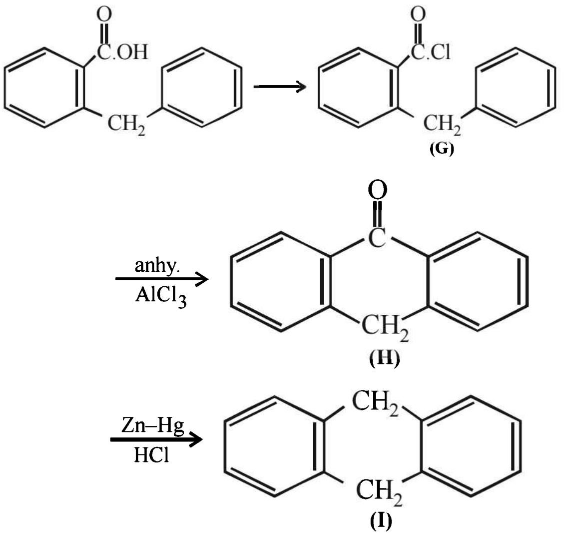


$\underset{(A)}{CH_3.\overset{Br}{C}HCOOH} \xrightarrow[(ii)\ H^+]{(i)\ \text{Alc. KOH (excess)}} \underset{(B)}{CH_2=CHCOOH}$

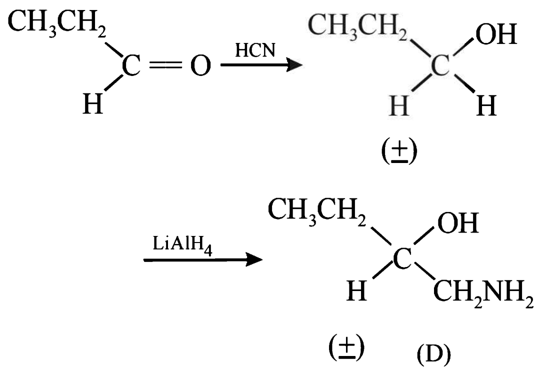
(ix) $C_6H_5CHO + CH_3COOC_2H_5 \xrightarrow[\text{absolute alcohol, heat}]{NaOC_2H_5 \text{ in}} \underset{(D)}{C_6H_5CH=CHCOOC_2H_5}$

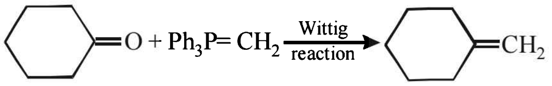
(Claisen condensation)

(x)

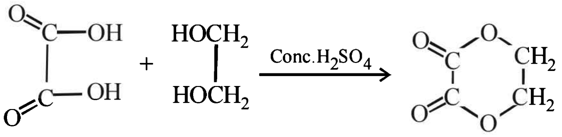


(xi) $KCN + H_2SO_4 \longrightarrow KHSO_4 + HCN$

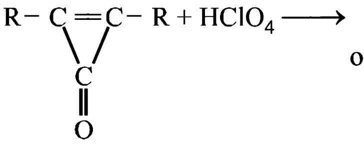


(xii)


(E)

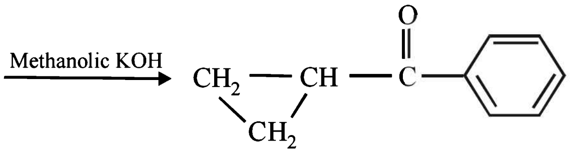
(xiii)


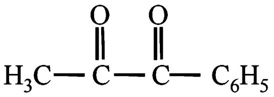
(F)

(xiv)


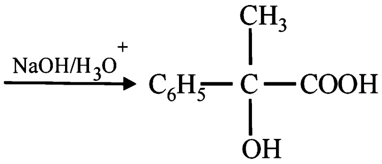
RCOOH
or $n-C_3H_7COOH$

(xv) $ClCH_2CH_2CH_2COPh$



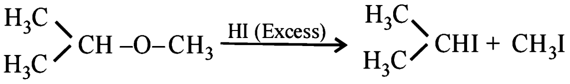
(xvi)


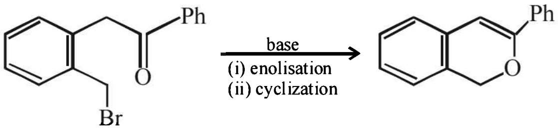
$H_3C-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-C_6H_5$

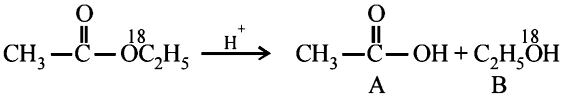


$\xrightarrow{NaOH/H_3O^+} C_6H_5-\underset{OH}{\overset{CH_3}{C}}-COOH$

NOTE : The reaction is an example of benzil-benzilic acid type rearrangement.

(xvii)


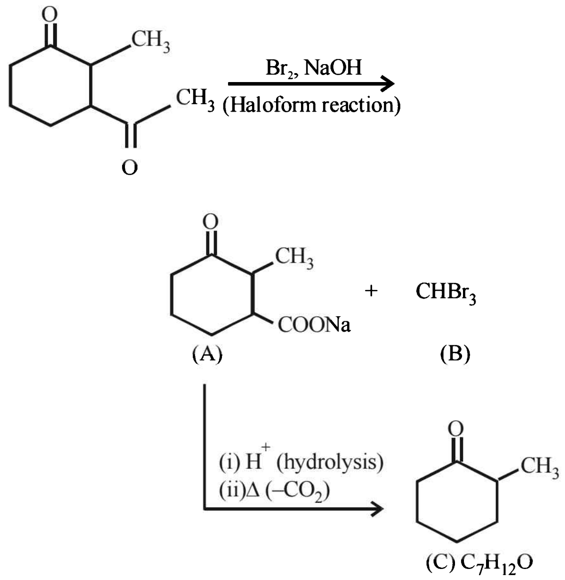
(xviii)


(xix)


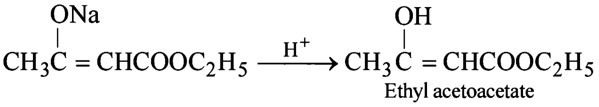
$CH_3-\overset{O}{\overset{\|}{C}}-\overset{18}{O}C_2H_5 \xrightarrow{H^+} CH_3-\overset{O}{\overset{\|}{C}}-OH + C_2H_5\overset{18}{O}H$

A B

(Ester hydrolysis involves acyl-oxygen fission)

(xx)


2. $CH_3COOC_2H_5 + H_3CCOOC_2H_5 \xrightarrow[C_2H_5OH]{C_2H_5ONa}$



$CH_3\overset{ONa}{\overset{|}{C}} = CHCOOC_2H_5 \xrightarrow{H^+} CH_3\overset{OH}{\overset{|}{C}} = CHCOOC_2H_5$

Ethyl acetoacetate

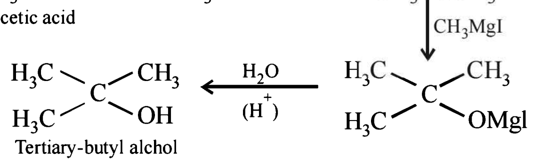
3. (i) $HCHO \xrightarrow{[O]} HCOOH \xrightarrow{Ca(OH)_2}$
Methanal

$(HCOO)_2Ca \xrightarrow[heat]{(CH_3COO)_2Ca} 2\ CH_3CHO$
Ethanal

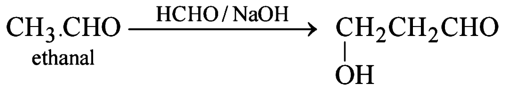
(ii) $CH \equiv CH \xrightarrow[Hg^{2+}]{H_2SO_4} CH_3CHO \xrightarrow[(Oxi.)]{KMnO_4} CH_3COOH$
Acetylene

$\xrightarrow{Ca(OH)_2} (CH_3COO)_2Ca \xrightarrow{distil} (CH_3)_2CO$
Acetone

(iii) $CH_3COOH \xrightarrow{PCl_3} CH_3COCl \xrightarrow{CH_3MgI} CH_3COCH_3$
Acetic acid

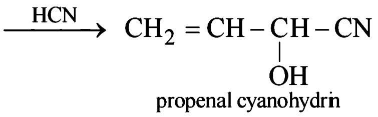


Tertiary-butyl alchol

(iv)


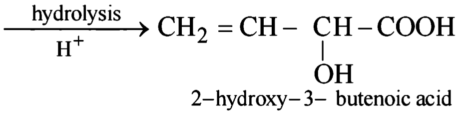
$CH_3.CHO \xrightarrow{HCHO/NaOH} \underset{OH}{\underset{|}{CH_2}}CH_2CHO$
ethanal

$\xrightarrow[(heat)]{Dehydration} CH_2 = CHCHO$
propenal



$\xrightarrow{HCN} CH_2 = CH-\underset{OH}{\underset{|}{CH}}-CN$

propenal cyanohydrin

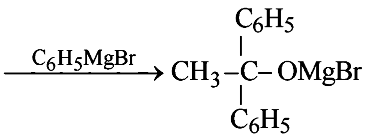


$\xrightarrow[H^+]{hydrolysis} CH_2 = CH-\underset{OH}{\underset{|}{CH}}-COOH$

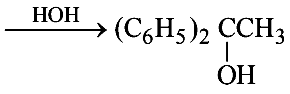
2–hydroxy–3– butenoic acid

(v) $CH_3COOH \xrightarrow{PCl_5} CH_3COCl$

$\xrightarrow{C_6H_5MgBr} C_6H_5COCH_3$



$$\xrightarrow{C_6H_5MgBr} CH_3-\underset{C_6H_5}{\overset{C_6H_5}{\overset{|}{\underset{|}{C}}}}-OMgBr$$



$$\xrightarrow{HOH} (C_6H_5)_2\underset{OH}{\underset{|}{C}}CH_3$$

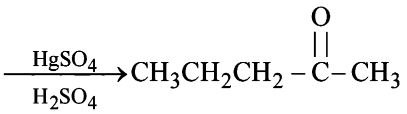
$\xrightarrow[-H_2O]{heat} (C_6H_5)_2C=CH_2$

$\xrightarrow{CrO_3} C_6H_5COC_6H_5 + HCOOH$

(vi) $CH_3CH_2-C\equiv CH + Na^+\ NH_2^-$

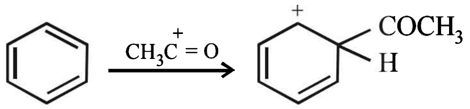
$\longrightarrow CH_3CH_2-C\equiv C^- : Na^+$

$\xrightarrow{CH_3I} CH_3CH_2-C\equiv C-CH_3$

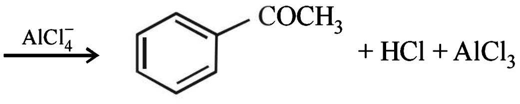


$$\xrightarrow[H_2SO_4]{HgSO_4} CH_3CH_2CH_2-\overset{O}{\overset{||}{C}}-CH_3$$

4. $CH_3COCl + AlCl_3 \rightarrow CH_3C^+{=}O + AlCl_4^-$

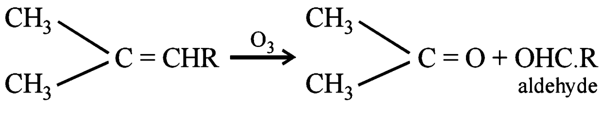


Benzene



Acetophenone

5. Ozonolysis of (A) to acetone and an aldehyde indicates the following part structure of alkene (A) :



Alkene (A)

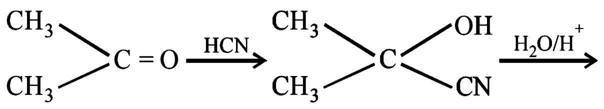
acetone

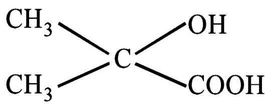
As per problem :

$RCHO \xrightarrow{[O]} RCOOH[B] \xrightarrow{P/Br_2}$

Bromo compound [C] $\xrightarrow{H_2O}$ Hydroxy acid [D]

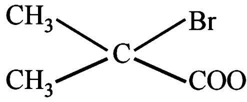
Structure of (D) is determined by the reaction :



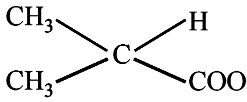


(D)

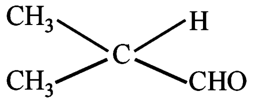
The compound (D) is obtained by hydrolysis of (C) with aqueous alkali since (C) is a bromo compound, therefore it has a bromo group where the compound (D) has a hydroxyl group. Therefore, structure of C is



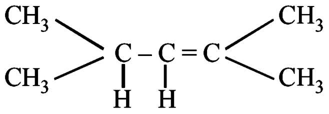
The compound (C) is formed by bromination of compound (B), therefore, the compound (B) is



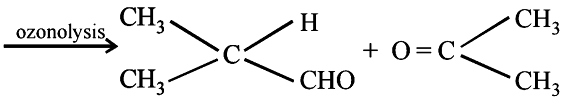
The compound (B) is formed by oxidation of an aldehyde therefore the structure of the aldehyde is



The aldehyde and acetone are formed by ozonolysis of alkene. Therefore, the double bond in alkene should be between the carbon atoms of the two carbonyl compounds (the aldehyde and acetone). Therefore, the compounds and the reactions are identified as



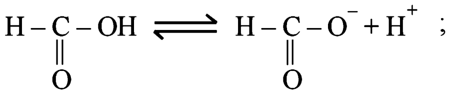
(A)



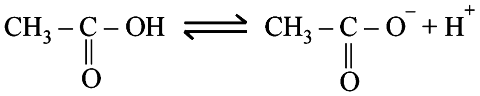
6. (*i*) **TIPS/Formulae :**

Formic acid has no alkyl group i.e no α – H atom, hence it does not undergo halogenation, while acetic acid has a methyl group (i.e three α – H atoms) on which halogenation takes place.

(*ii*)



$$H-\underset{O}{\underset{||}{C}}-OH \rightleftharpoons H-\underset{O}{\underset{||}{C}}-O^- + H^+ \;;$$



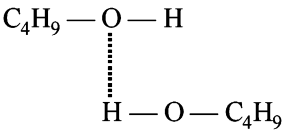
$$CH_3-\underset{O}{\underset{||}{C}}-OH \rightleftharpoons CH_3-\underset{O}{\underset{||}{C}}-O^- + H^+$$

Presence of CH_3 gp in acetate ion shows +I effect and thereby intensifying charge on O^- of acetate ion which is thus destabilized. Thus formate ion is more stable than acetate ion or HCOOH loses proton more easily than CH_3COOH.

(*iii*) **NOTE :**

Alcohols show hydrogen bonding.

The boiling points of carbonyl compounds are lower than the corresponding alcohols since former do not show intermolecular H-bonding like alcohols.

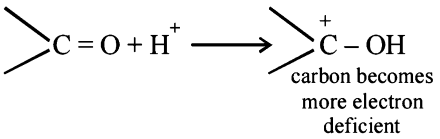


H-bonding between two butanol molecules

Solubility of butanol in water is due to hydrogen bonding between butanol and water molecules (similarity to butanol).

(*iv*) **TIPS/Formulae :**

In weakly acidic medium carbonyl group is protonated to form conjugate acid.



In strongly acidic medium (pH < 3.5), the unshared pair of electrons of N of the reagent is protonated with the result nucleophile (NH_2NH_2) is converted to an electrophile ($NH_2N^+H_3$)which cannot react. Hence in highly acidic medium, there is no protonation of the carbonyl group.

(*v*) **NOTE :** Hypoiodite (^-OI) is a strong base than iodide ion. (O is more electronegative thus easily accommodate negative charge than I in I^-).

Haloform reaction is base-promoted reaction (the first step involves removal of acidic hydrogen atom of acetone by base). Hypoiodite ion being strong base than iodide ion, can easily remove acidic hydrogen atom.

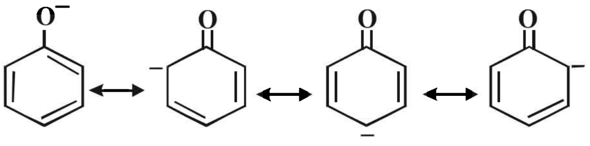
$$CH_3.CO.CH_3 + {}^-OI \rightarrow CH_3.CO.\overline{C}H_2 + HOI$$

(*vi*) In the acylium ion ($R-C\equiv O^+$), each and every element has a complete octet, while in carbonium ion ($R-C^+=O$), carbon bearing positive charge has uncomplete octet which makes it more reactive than the former.

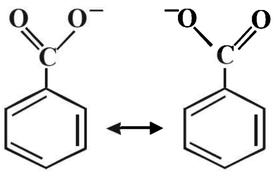
$$\underset{\textbf{Acylium ion}}{R:C\,\vdots\,\vdots\,O^+:} \longleftrightarrow \underset{\substack{\textbf{Carbonium ion}\\ \text{(Carbon has only six electrons)}}}{R:C^+=\ddot{O}:}$$

(*vii*) **TIPS/Formulae :**

Both of the resonating structures of benzoate ion are equivalent, while it is not so in phenoxide ion.



Resonating structures of phenoxide ion

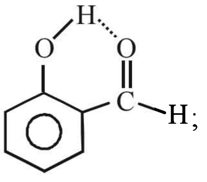


Resonating structures of benzoate ion

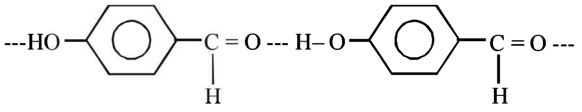
The benzoate ion is more stabilized because the negative charge on both structures is on the more electronegative oxygen atom, whereas in phenoxide ion, it is on the less electronegative carbon atoms.

(*viii*) **TIPS/Formulae :**

o-Hydroxybenzaldehyde has intramolecular H-bonding while the *p*-isomer has intermolecular H-bonding.



Intramolecular H-bonding in o-isomer

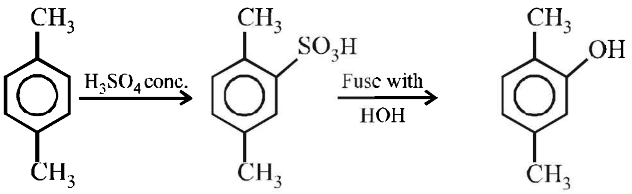


Intermolecular H-bonding in the *p*-isomer (association)

7. (*i*) $C_2H_2 \xrightarrow[Hg^{2+}]{H_2SO_4(\text{dil.})} CH_3CHO \xrightarrow[\text{reduction}]{H_2/\text{cat.}} CH_3CH_2OH$

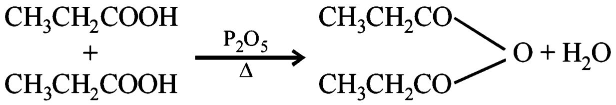
(*ii*) $CH_3I + KCN\,(alc) \xrightarrow{-KI} CH_3CN \xrightarrow{H^+/H_2O} CH_3COOH$

8.



2, 5- Dimethylphenol

9. $CH_3CH_2CHO + [O] \xrightarrow[\text{Tollen's reagent}]{AgNO_3/NH_4OH} CH_3CH_2COOH + 2Ag$



$CH_3CH_2COOH + CH_3CH_2COOH \xrightarrow[\Delta]{P_2O_5} (CH_3CH_2CO)_2O + H_2O$

Propionic anhydride

10. **TIPS/Formulae :**

Acetaldehyde can be distinguished from acetone by using Tollen's reagent or Fehling solution or Schiff's reagent. Only acetaldehyde responds to all these tests.

$$CH_3CHO + \underset{\text{Tollen's reagent}}{[Ag(NH_3)_2]^+OH^-} \rightarrow RCOOH + \underset{\text{Silver mirror}}{Ag\downarrow}$$

11. **TIPS/Formulae :**

The weaker a base better is its leavability.

This is an example of nucleophilic substitution where the group X (Cl, NH_2, OC_2H_5, $OCOCH_3$) is replaced by OH. The decreasing basic character of the four concerned groups is:

$$NH_2^- > OR^- > OCOR^- > Cl^-$$

Hence Cl^- (the weakest base) will be lost most easily while

NH_2^- (the strongest base) will be lost with most difficulty.

Thus the order of hydrolysis becomes.

$CH_3CONH_2 < CH_3COOC_2H_5 < (CH_3CO)_2O < CH_3COCl$.

12. Let us summarise the given facts.

$$\text{White ppt.} \xleftarrow{AgNO_3} \underset{C_6H_{13}Cl}{(A)} \xrightarrow[KOH]{\text{hot alc.}}$$

$$\underset{\text{(Isomeric alkenes, }C_6H_{12})}{(B)+(C)} \xrightarrow{O_3}$$

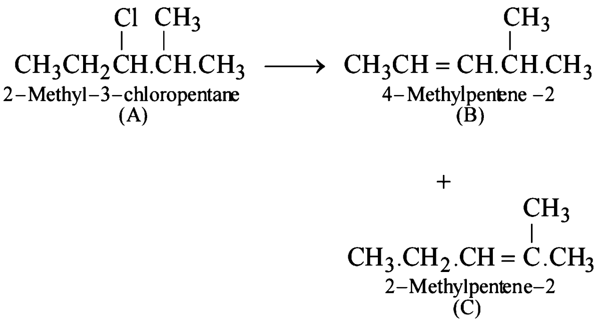
$$\underset{(i)}{CH_3CHO} + \underset{(ii)}{C_2H_5CHO} + \underset{(iii)}{CH_3COCH_3} + \underset{(iv)}{(CH_3)_2CHCHO}$$

NOTE THIS STEP: With the help of structures of the four carbonyl compounds, (*i*) to (*iv*), we may write the structures of the two isomeric olefins (B) and (C). The two carbonyl compounds should be joined in such a way that the parent olefin has 6 carbon atoms. Two such possibilities are the combination of carbonyl compounds having 2+4 carbon atoms [*i.e.* (*i*) + (*iv*)] and 3+3 carbon atom [*i.e.* (*ii*) + (*iii*)].

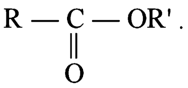
$$\underset{(i)}{CH_3CHO} + \underset{(iv)}{OHC.CH(CH_3)_2} \xleftarrow{O_3} \underset{\text{Olefin B }(C_6H_{12})}{CH_3CH{=}CH.CH(CH_3)_2}$$

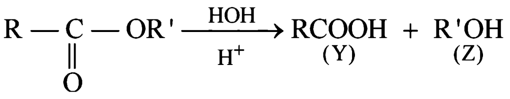
$$\underset{(ii)}{C_2H_5CHO} + \underset{(iii)}{OC(CH_3)_2} \xleftarrow{O_3} \underset{\text{Olefin }(C_6H_{12})}{C_2H_5CH{=}C(CH_3)_2}$$

Thus the compound (A) should be a chloride that can eliminate a molecule of HCl to give B as well as C.



$$\underset{\substack{\text{2-Methyl-3-chloropentane}\\(A)}}{CH_3CH_2\overset{\overset{Cl}{|}}{C}H.\overset{\overset{CH_3}{|}}{C}H.CH_3} \longrightarrow \underset{\substack{\text{4-Methylpentene-2}\\(B)}}{CH_3CH=CH.\overset{\overset{CH_3}{|}}{C}H.CH_3} + \underset{\substack{\text{2-Methylpentene-2}\\(C)}}{CH_3.CH_2.CH=\overset{\overset{CH_3}{|}}{C}.CH_3}$$

13. (X) is hydrolysed to give an acid (Y) and an alcohol (Z) and thus X is an ester;  $R-\underset{\underset{O}{\|}}{C}-OR'$.



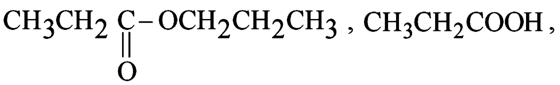
$$R-\underset{\underset{O}{\|}}{C}-OR' \xrightarrow[H^+]{HOH} \underset{(Y)}{RCOOH} + \underset{(Z)}{R'OH}$$

Oxidation of alcohol (Z) gives acid (Y).

$$\underset{(Z)}{R'OH} \xrightarrow{\text{Oxidation}} RCOOH$$

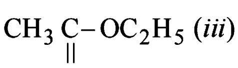
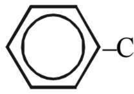
or $RCH_2OH \longrightarrow RCOOH$ ($\because$ R' is R—CH_2)

Hence X, Y and Z are



$$\underset{\substack{\text{(Propyl propanoate)}\\X}}{CH_3CH_2\underset{\underset{O}{\|}}{C}-OCH_2CH_2CH_3}\ ,\ \underset{\substack{\text{(Propanoic acid)}\\Y}}{CH_3CH_2COOH},$$

$$\underset{\substack{\text{(Propan-1-ol)}\\Z}}{CH_3CH_2CH_2OH}$$

14. (*i*)  $CH_3\underset{\underset{O}{\|}}{C}-OC_2H_5$ (*iii*) —CHO + CH_3CHO

15. (i) Empirical formula can be calculated as

Element	Percentage	Relative no. of atoms	Simplest ratio
C	69.77	5.81	5
H	11.63	11.63	10
O	18.60	1.16	1

$\therefore$ Empirical formula of compound is $C_5H_{10}O$ and empirical formula wt. = 86.

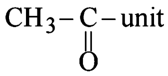
Also molecular wt. = 86.

$\therefore$ Molecular formula of compound is $C_5H_{10}O$.

(ii) Compound forms bisulphite addition compound and thus has carbonyl gp, *i.e.* aldehyde or ketone.

(iii) It does not reduce Fehling solution and thus it is not an aldehyde but a ketone.

(iv) It gives positive iodoform test and thus it has



$$CH_3-\underset{\underset{O}{\|}}{C}-\text{unit}$$

(v) Above facts reveal that the compound is

$\underset{\text{pentan-2-one}}{CH_3CH_2CH_2COCH_3}$ or $\underset{\text{3-methylbutan-2-one}}{(CH_3)_2CHCOCH_3}$

16. **TIPS/Formulae :**

$$\begin{tikzcd} A \arrow[r, "\text{mild}", "\text{oxi}"'] \arrow[d, "CH_3COOH,\ H_2SO_4"] & C \arrow[r, "\text{(i) 50\% KOH}", "\text{(ii) HCl}"'] & A + D \arrow[d, "\text{(i) }PCl_5", "\text{(ii) }NH_3"'] \\ \text{Ester, B} & HCN & E \arrow[l, "(-H_2O)"'] \end{tikzcd}$$

The above reactions lead to following conclusions.

(i) Reaction of A with CH_3COOH in presence of H_2SO_4 to form ester B indicates that A is an alcohol.

(ii) Reaction of C with 50% KOH followed by acidification to give alcohol A and the compound D seems to be the Cannizzaro reaction. Hence C must be an aldehyde and D must be an acid. The nature of C as aldehyde is again in consistent with the fact that it is obtained by the mild oxidation of A which has been established as an alcohol.

(iii) Structure of acid D is established by its given facts.

$$\underset{(D)}{-COOH} \xrightarrow{PCl_5} -COCl \xrightarrow{NH_3} \underset{(E)}{-CONH_2}$$

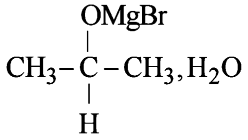
$$\xrightarrow{-H_2O} HCN$$

Formation of HCN by the dehydration of E establishes that E is $HCONH_2$ and hence D is HCOOH.

(iv) Thus the alcohol A produced along with HCOOH during Cannizzaro reaciton of C must be CH_3OH and hence C must be HCHO.

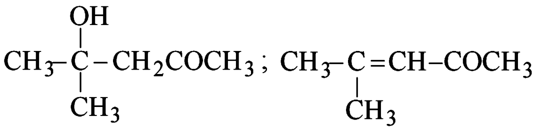
Thus the various compounds are as below :

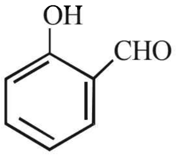
A	B	C	D	E
CH_3OH	CH_3COOCH_3	HCHO	HCOOH	$HCONH_2$
Methyl alcohol	Methyl acetate	Formaldehyde	Formic acid	Formamide

17. (i) 

$$CH_3-\overset{\overset{OMgBr}{|}}{\underset{\underset{H}{|}}{C}}-CH_3, H_2O$$

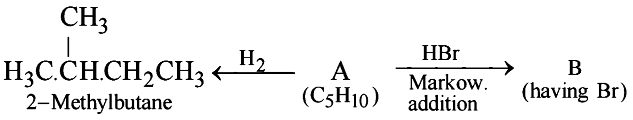
(ii) $P/Cl_2, NH_2CH_2COONH_4$

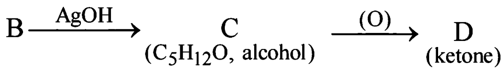
(iii) 
$CH_3-\underset{CH_3}{\overset{OH}{C}}-CH_2COCH_3$; $CH_3-\underset{CH_3}{C}=CH-COCH_3$

(iv) (i) fuse with NaOH (ii) H^+ ; 

18. TIPS/Formulae :

For this type of problem, students are advised to summarise the whole problem in the form of reactions.


$$\underset{\text{2-Methylbutane}}{H_3C.\overset{CH_3}{C}H.CH_2CH_3} \xleftarrow{H_2} \underset{(C_5H_{10})}{A} \xrightarrow[\text{Markow. addition}]{HBr} \underset{\text{(having Br)}}{B}$$

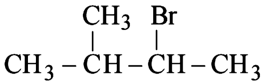

$$B \xrightarrow{AgOH} \underset{(C_5H_{12}O,\ \text{alcohol})}{C} \xrightarrow{(O)} \underset{\text{(ketone)}}{D}$$

Let us draw some conclusions from the above set of reactions.

(i) The molecular formula C_5H_{10} (C_nH_{2n}) for A indicates that it is an alkene having one double bond.

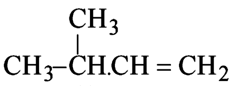
(ii) Since the alcohol C on oxidation gives a ketone D, C must be a secondary alcohol and hence B must be a secondary bromide.

(iii) The structure of 2-methylbutane, the hydrogenated product of A, indicates that the secondary bromide must have following structure.

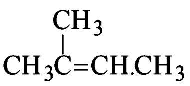

$CH_3-\overset{CH_3}{C}H-\overset{Br}{C}H-CH_3$

(B)

(iv) Thus the corresponding olefin A must have structure A which on Markownikoff addition of HBr gives the bromide B, the other possible alkene A' will not give B when HBr is addd on it according to Markownikoff rule.

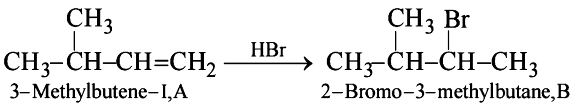

$CH_3-\overset{CH_3}{C}H.CH=CH_2$

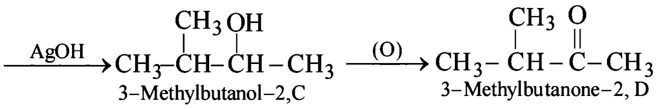
(A)


$CH_3\overset{CH_3}{C}=CH.CH_3$

(A′)

Thus the reaction involved can be represented as below:

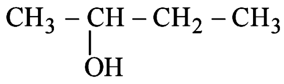

$$\underset{\text{3-Methylbutene-I,A}}{CH_3-\overset{CH_3}{C}H-CH=CH_2} \xrightarrow{HBr} \underset{\text{2-Bromo-3-methylbutane,B}}{CH_3-\overset{CH_3}{C}H-\overset{Br}{C}H-CH_3}$$


$$\xrightarrow{AgOH} \underset{\text{3-Methylbutanol-2,C}}{CH_3-\overset{CH_3}{C}H-\overset{OH}{C}H-CH_3} \xrightarrow{(O)} \underset{\text{3-Methylbutanone-2, D}}{CH_3-\overset{CH_3}{C}H-\overset{O}{\overset{\|}{C}}-CH_3}$$

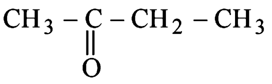
19. The compound A, a ketone, undergoes haloform reaction. Thus, it must contain CH_3CO group.

The compound C gives mono-ozonide D, which shows that the compound C contains a double bond. Since the hydrolysis of D gives only acetaldehyde, the compound C would be an alkene having four carbon atoms, *i.e.* $CH_3-CH=CH-CH_3$ (butene-2).

The compound B is obtained by the reduction of compound A (which contains CH_3CO group). Hence, the compound B would be an alcohol, which on heating with H_2SO_4 gives (C). Hence B and A would be

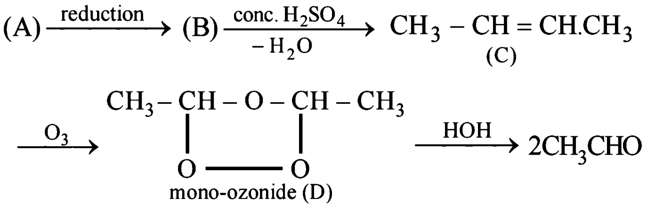

$CH_3-\underset{OH}{C}H-CH_2-CH_3$

butan-2-ol (B)


$CH_3-\underset{O}{\underset{\|}{C}}-CH_2-CH_3$

butan-2-one (A)

The reactions involved :


$$(A) \xrightarrow{\text{reduction}} (B) \xrightarrow[-H_2O]{\text{conc. } H_2SO_4} \underset{(C)}{CH_3-CH=CH.CH_3}$$
$$\xrightarrow{O_3} \underset{\text{mono-ozonide (D)}}{\begin{array}{c}CH_3-CH-O-CH-CH_3\\ |\qquad\qquad |\\ O\ \text{———}\ O\end{array}} \xrightarrow{HOH} 2CH_3CHO$$

20. TIPS/Formulae :

The given set of reactions can be represented as below :

$$\text{Aq. NaOH} \xrightarrow[\text{High temp., pressure}]{\text{Gas B}} \text{Sod. salt of acid A}$$
$$\xrightarrow[\text{(ii) } H_2SO_4]{\text{(i) NaOH (heat)}} \text{Dibasic acid, C}$$

Calculation of molecular formula of C

$$\%\text{ of H}=\frac{2}{18}\times\frac{0.08}{0.40}\times100=2.22\%$$

$$\%\text{ of C}=\frac{12}{44}\times\frac{0.39}{0.40}\times100=27.30\%$$

$$\%\text{ of O}=100-(2.22+27.30)=71.48\%$$

By usual method, empirical formula of acid $C=CHO_2$

$$\text{Eq. wt. of acid } C=\left(\frac{1.0}{0.71}\times108\right)-107=45$$

Mol. wt. of acid $C=45\times2=90$

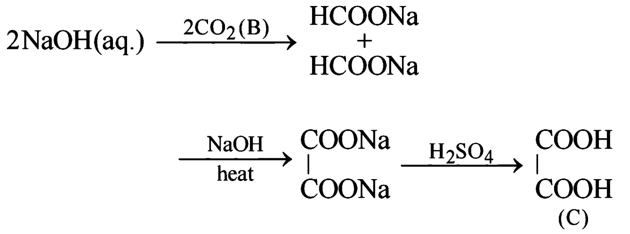
$\therefore$ Mol. formula of $C=C_2H_2O_4$

Since it is dicarboxylic acid, it must have two –COOH groups.

Hence C is 
$\begin{array}{l}COOH\\ |\\ COOH\end{array}$

Oxalic acid

Going back, compound C must be produced from sodium oxalate which in turn is produced from sodium formate. Hence A is formic acid and B is CO_2. Thus the complete series of reactions can be written as below.


$$2NaOH(aq.) \xrightarrow{2CO_2(B)} \begin{array}{c}HCOONa\\ +\\ HCOONa\end{array}$$
$$\xrightarrow[\text{heat}]{NaOH} \begin{array}{c}COONa\\ |\\ COONa\end{array} \xrightarrow{H_2SO_4} \underset{(C)}{\begin{array}{c}COOH\\ |\\ COOH\end{array}}$$

21. TIPS/FORMULAE:

$$\begin{tikzcd} \underset{C_6H_{12}O_2}{A} \arrow[r, "\text{Reduction}", "\text{by } LiAlH_4"'] & B \arrow[d, "\text{Oxidation}"] & + & C \\ \underset{\substack{\text{Monobasic acid} \\ \text{(Mol. wt. = 60)}}}{F} & D \arrow[l, "\text{oxi.}"'] \arrow[rr, "\text{(i) aq. } OH^-", "\text{(ii) heat}"'] & & E \arrow[u, "H_2/\text{catalyst}"'] \end{tikzcd}$$

Molecular weight of the monobasic acid (RCOOH) indicates that the R– should be CH_3– i.e., acid F should be acetic acid (CH_3COOH, mol. wt. 15+45). Thus compound D must be acetaldehyde CH_3CHO, and compound B which on oxidation gives CH_3CHO must be ethanol, CH_3CH_2OH.

Acetaldehyde (D) on treating with aqueous alkali will undergo aldol condensation.

$$\underset{(D)}{2CH_3CHO} \xrightarrow{OH^-} CH_3\overset{\overset{OH}{|}}{C}HCH_2CHO \xrightarrow{\text{heat}}$$

$$\underset{\text{Crotonaldehyde, (E)}}{CH_3CH = CHCHO} \xrightarrow[\text{catalyst}]{H_2/} \underset{\text{Butanol–1, (C)}}{CH_3CH_2CH_2CH_2OH}$$

Nature of A. Thus it is evident that reduction of A with $LiAlH_4$ gives two alcohols; B (ethanol) and C (butanol). Hence A must be an ester i.e., ethyl butanoate ($CH_3CH_2CH_2COOC_2H_5$).

$$\underset{\text{Ethyl butanoate, A}}{CH_3CH_2CH_2COOC_2H_5} \xrightarrow{LiAlH_4}$$

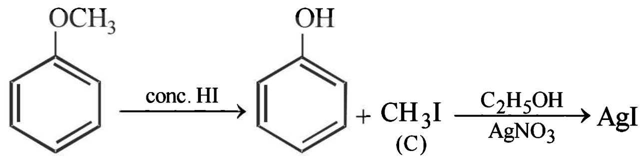
$$\underset{\text{Butanol, C}}{CH_3CH_2CH_2CH_2OH} + \underset{\text{Ethanol, B}}{C_2H_5OH}$$

22. Empirical formula of A and B.

	Relative No. of atoms	Simplest ratio
$\% \text{ of } C = \frac{12}{44} \times \frac{0.308}{0.108} \times 100 = 77.77$	$\frac{77.77}{12} = 6.48$	$\frac{6.48}{0.92} = 7$
$\% \text{ of } H = \frac{2}{18} \times \frac{0.072}{0.108} \times 100 = 7.40$	$\frac{7.40}{1} = 7.40$	$\frac{7.40}{0.92} = 8$
$\therefore \% \text{ of } O = 100 - (77.77 + 7.40) = 14.83$	$\frac{14.83}{16} = 0.92$	$\frac{0.92}{0.92} = 1$

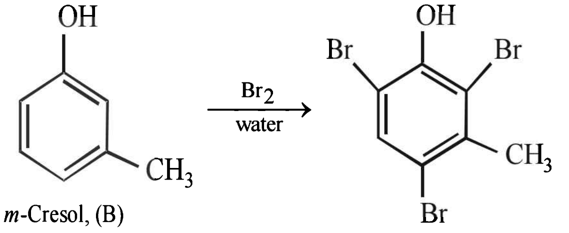
∴ Empirical formula of A and B = C_7H_8O

Nature of (A) : Since A is insoluble in NaOH and $NaHCO_3$, it can't have –OH and –COOH groups. Further the reaction of A with conc. HI to give compounds C and D separable by means of ammonical $AgNO_3$ and solubility of D in NaOH indicates that C and D are alkyl halide and phenol respectively. Thus A is an ether i.e. it is $C_6H_5.O.CH_3$ which explains all the given reactions.



Anisole (A) (D)

Nature of (B) : Solubility of B (C_7H_8O) in NaOH indicates that it is a phenol which is further confirmed by its reaction with bromine water to give compound E of molecular formula, $C_7H_5OBr_3$. Further bromination of B to give tribromo product indicates that it is *m*-cresol.



m-Cresol, (B) (E), $C_7H_5OBr_3$

23. (i) $C_6H_5COOH \xrightarrow{PCl_5} \underset{(C)}{C_6H_5COCl} \xrightarrow{NH_3}$

$$\underset{(D)}{C_6H_5CONH_2} \xrightarrow{P_2O_5} C_6H_5CN \xrightarrow{H_2/Ni} \underset{(E)}{C_6H_5CH_2NH_2}$$

(ii) $H_3CCH{=}CHCHO \xrightarrow{NaBH_4} \underset{(F)}{CH_3CH{=}CH\text{–}CH_2OH}$

$$\xrightarrow[ZnCl_2]{HCl} \underset{(G)}{CH_3CH = CHCH_2Cl}$$

$$\xrightarrow[H^+]{KCN} \underset{(H)}{CH_3CH = CHCH_2COOH}$$

24. For empirical formula of (Y)

Element	%	Relative no. of atoms	Simplest ratio
C	49.31	4.10	3
H	9.59	9.59	7
N	19.18	1.37	1
O	21.92	1.37	1

∴ Empirical formula of (Y) is C_3H_7NO.

(Y) reacts with Br_2 and NaOH to give (Z) and (Z) reacts with HNO_2 to give ethanol and thus (Y) seems to have —$CONH_2$ group.

$$\underset{(Y)}{CH_3CH_2CONH_2} + Br_2 + 4KOH \longrightarrow$$

$$\underset{\text{(Z) basic}}{CH_3CH_2NH_2} \xrightarrow{HNO_2} \underset{\text{ethanol}}{CH_3CH_2OH}$$

Y is formed from (X) having Cl on treatment with NH_3 and so (X) is CH_3CH_2COCl i.e. propanoyl chloride.

$$\underset{(X)}{CH_3CH_2COCl} + NH_3 \rightarrow \underset{(Y)}{CH_3CH_2CONH_2}$$

25. TIPS/Formulae :

$$\begin{tikzcd} A \arrow[r, "C_2H_5OH"] & \underset{\text{Carboxylic acid}}{B} & + & C \arrow[dll, "H^+ \text{(Hydrolysis)}"'] \\ \underset{(C_3H_6O)}{E} & B \arrow[l, "Ca(OH)_2"'] & + & D \arrow[ll, bend left, "\text{oxidation}"] \end{tikzcd}$$

(*i*) Since E (C_3H_6O) forms a 2, 4-dinitrophenylhydrazone but does not reduce Tollen's reagent and Fehling solution, it must be a ketone, $CH_3.CO.CH_3$.

(*ii*) The compound E (established as ketone) is obtained by heating compound B with $Ca(OH)_2$, B must be CH_3COOH.

(*iii*) Compound B is obtained by the oxidation of D, the latter must be ethyl alcohol, C_2H_5OH and hence C must be ethyl acetate, $CH_3COOC_2H_5$.

(*iv*) Since compound A when treated with ethyl alcohol gives acetic acid (B) and ethyl acetate (C), it must be acetic anhydride.

$$\underset{(A)}{CH_3CO.O.COCH_3} + C_2H_5OH \longrightarrow \underset{(B)}{CH_3COOH} + \underset{(C)}{CH_3COOC_2H_5}$$

$$\begin{tikzcd} & & \underset{(C)}{CH_3COOC_2H_5} \arrow[d, "H^+"] \\ \underset{(E)}{CH_3COCH_3} & \underset{(B)}{CH_3COOH} \arrow[l, "Ca(OH)_2", "heat"'] & + \ \underset{(D)}{C_2H_5OH} \arrow[l, bend left, "oxidation"] \end{tikzcd}$$

26. $CH_3CHO < CH_3COCH_3 < CH_3COCH_2COCH_3 < CH_3COCH_2CHO$

27. $PCl_5 + SO_2 \longrightarrow \underset{(A)}{SOCl_2} + \underset{(B)}{POCl_3}$

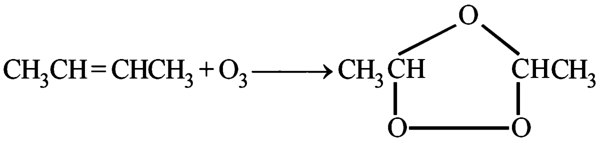
$$\underset{(A)}{SOCl_2} + CH_3COOH \longrightarrow \underset{(C)}{CH_3COCl} + SO_2 + HCl$$

$$\underset{(C)}{2CH_3COCl} + (CH_3)_2Cd \longrightarrow 2CH_3 - \underset{(D)}{CO} - CH_3 + CdCl_2$$

28. **TIPS/Formulae :**

$$\begin{tikzcd} A \arrow[r, "dry\ KOH", "low\ temp."'] \arrow[d, "Zn/H_2O"', "but\text{-}2\text{-}ene"] & \underset{\substack{deep\\red}}{B} + C\uparrow \\ CH_3CHO & \end{tikzcd}$$

The reaction of gas (A) with but-2-ene followed by treatment with Zn/H_2O gives CH_3CHO. This shows that the gas (A) is ozone (O_3).



$$\xrightarrow[H_2O]{Zn} 2CH_3CHO + H_2O_2$$

Reaction of ozone with KOH.

$$3KOH + \underset{(A)}{2O_3} \longrightarrow \underset{\substack{\text{Pot. ozonide, B}\\\text{(Red colour)}}}{2KO_3} + KOH.H_2O + \underset{(C)}{½O_2\uparrow}$$

29. **TIPS/Formulae :**

$$\begin{tikzcd} \underset{(A)}{C_8H_6} \arrow[r, "dil.\ H_2SO_4", "HgSO_4"'] & B \arrow[d, "I_2,\ aq.\ KOH"] & RCOCl + C_6H_6 \arrow[l, "anhydrous.\ AlCl_3"'] \\ & C + \text{Yellow compound (D)} & \end{tikzcd}$$

(i) Formation of (B) from benzene and acid chloride in presence of anhydrous $AlCl_3$ (Friedel-Craft reaction) indicates that it is a ketone, C_6H_5COR.

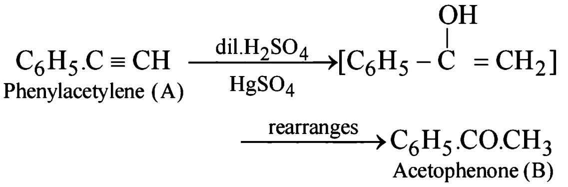
(ii) Further the ketone (B) reacts with alkaline iodine forming yellow compound (D) (haloform reaction). This indicates that one of the alkyl groups in ketone B is – CH_3. Hence it should be $C_6H_5.CO.CH_3$.

(iii) Since ketone (B) is also formed from the hydrocarbon C_8H_6 (A) by reaction with dil. H_2SO_4 and $HgSO_4$, the hydrocabon (A) must have an acetylenic hydrogen atom, i.e. $\equiv C - H$ grouping. Hence (A) must be $C_6H_5C\equiv CH$.

Thus compounds (A) to (D) are

$$\underset{(A)}{C_6H_5.C\equiv CH} \quad \underset{(B)}{C_6H_5.CO.CH_3} \quad \underset{(C)}{C_6H_5COOH} \quad \underset{(D)}{CHI_3}$$

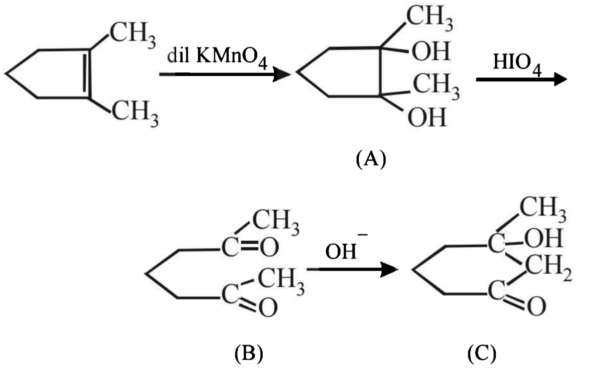
Formation of (B) from (A)



$$\underset{\text{Phenylacetylene (A)}}{C_6H_5.C\equiv CH} \xrightarrow[HgSO_4]{dil.H_2SO_4} [C_6H_5 - \overset{\overset{OH}{|}}{C} = CH_2] \xrightarrow{rearranges} \underset{\text{Acetophenone (B)}}{C_6H_5.CO.CH_3}$$

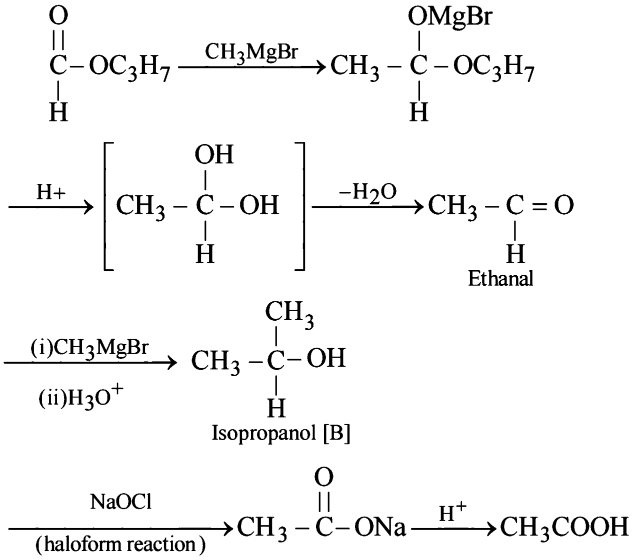
30. **(i)** β-Keto acids are unstable and undergo decarboxylation most readily.

31.



The last step is intramolecular aldol condensation.

32. We know that esters on treatment with excess of methyl magnesium chloride either give secondary alcohols (from alkyl formates) or tertiary alcohols (from esters other than formates). However, tertiary alcohols are not easily oxidised, hence the alcohol should be secondary alcohol and thus ester is alkyl formate. Hence ester A ($C_4H_8O_2$) should be $HCOOC_3H_7$. Thus the various reactions and nature of compound B can be established as below.



$$\overset{\overset{O}{||}}{\underset{\underset{H}{|}}{C}} - OC_3H_7 \xrightarrow{CH_3MgBr} CH_3 - \overset{\overset{OMgBr}{|}}{\underset{\underset{H}{|}}{C}} - OC_3H_7$$

$$\xrightarrow{H+} \left[CH_3 - \overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}} - OH \right] \xrightarrow{-H_2O} \underset{\text{Ethanal}}{CH_3 - \underset{\underset{H}{|}}{C} = O}$$

$$\xrightarrow[(ii)H_3O^+]{(i)CH_3MgBr} \underset{\text{Isopropanol [B]}}{CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}} - OH}$$

$$\xrightarrow[\text{(haloform reaction)}]{NaOCl} CH_3 - \overset{\overset{O}{||}}{C} - ONa \xrightarrow{H^+} CH_3COOH$$

33. Following informations are provided by the problem.

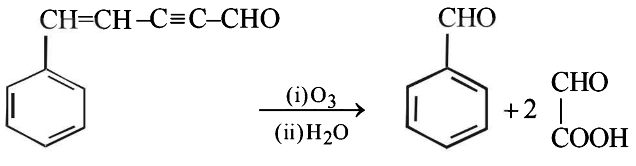
(i) Since aldehyde A ($C_{11}H_8O$) gives C_6H_5CHO on ozonolysis, it must have a benzene nucleus and a side chain. The side chain should have five carbon (C_{11}–C_6=C_5), three hydrogen (H_8-H_5=H_3) and one oxygen atom, i.e., it should be C_5H_3O. Further the compound A has an aldehydic group, so the side chain can be written as C_4H_2CHO.

(ii) Formation of two moles of B from one mole of A by ozonolysis indicates that the side chain must possess two unsaturated linkages, one of which must be alkyne type, suggested by very low number of hydrogen atoms.

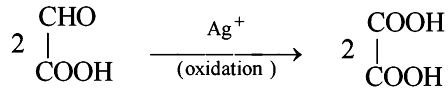
(iii) Further since the aldehyde A does not undergo aldol condensation, α-hydrogen is absent and hence triple bond should be present between C_2 and C_3.

(iv) Thus the side chain C_4H_2CHO of A can be written as – $CH=CH-C\equiv C-CHO$.

(v) Thus compound A should possess following structure which explains all the given reactions.

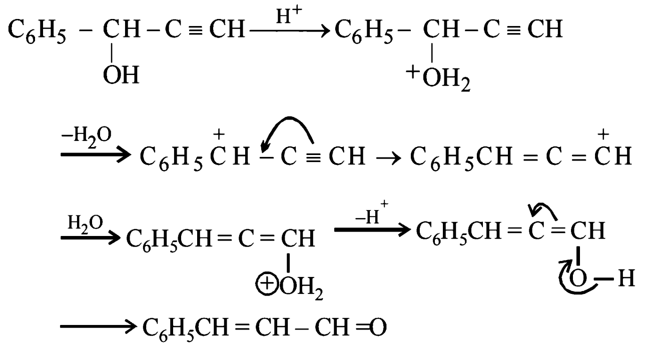


[A] [B]



Glyoxalic acid Oxalic acid

34.



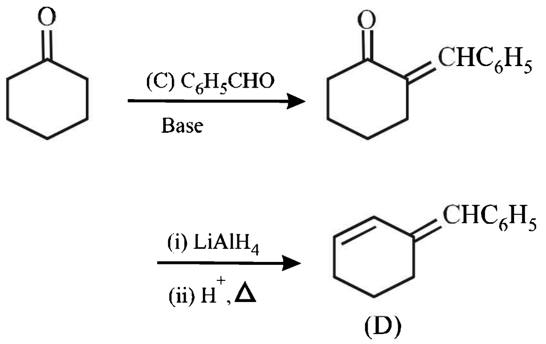
$$C_6H_5-\underset{OH}{\underset{|}{CH}}-C\equiv CH \xrightarrow{H^+} C_6H_5-\underset{^+OH_2}{\underset{|}{CH}}-C\equiv CH$$

$$\xrightarrow{-H_2O} C_6H_5\overset{+}{C}H-C\equiv CH \rightarrow C_6H_5CH=C=\overset{+}{C}H$$

$$\xrightarrow{H_2O} C_6H_5CH=C=\underset{\oplus OH_2}{\underset{|}{CH}} \xrightarrow{-H^+} C_6H_5CH=C=\underset{O-H}{\underset{|}{CH}}$$

$$\longrightarrow C_6H_5CH=CH-CH=O$$

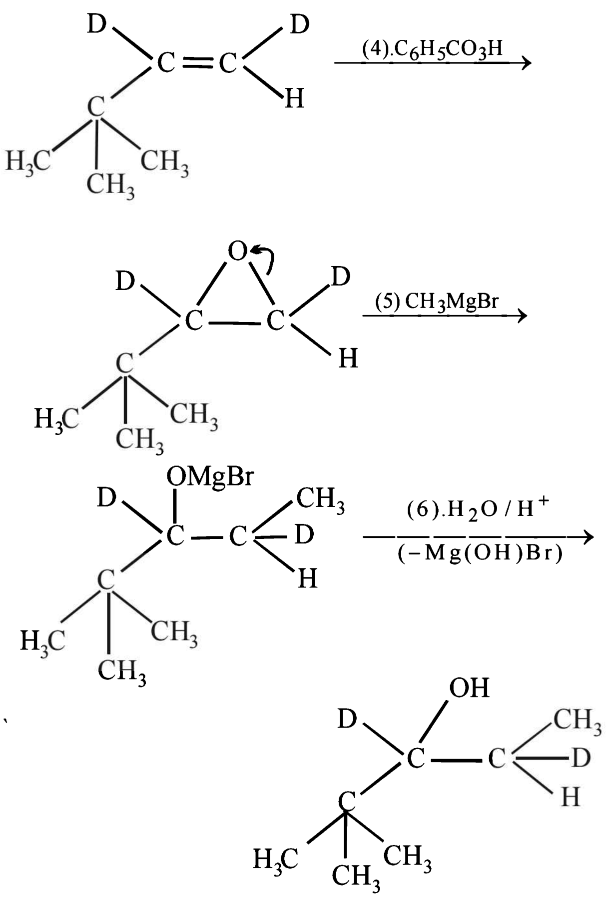
35.



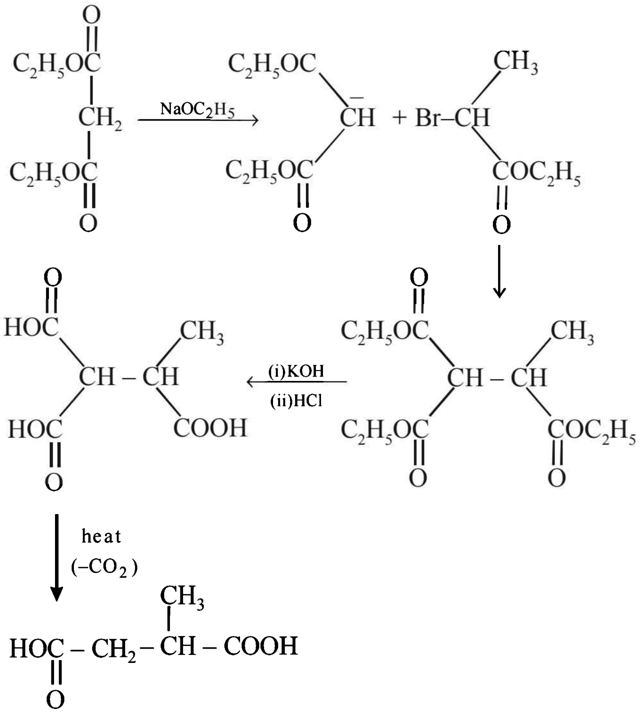
(D)

$LiAlH_4$ reduces only ketonic group to 2° alcoholic group without affecting double bond.

36.

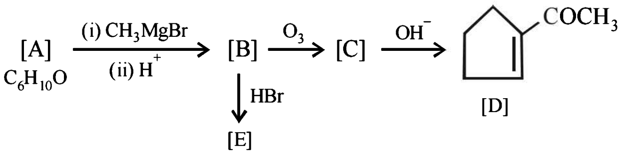


37.



38. **TIPS/Formulae :**

The given reaction can be summarised as below :



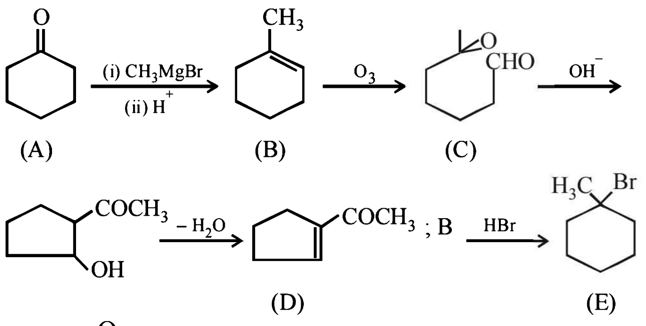
Conclusions from the set of reactions

(i) Carbon-hydrogen ratio of A indicates that it is a cyclic compound

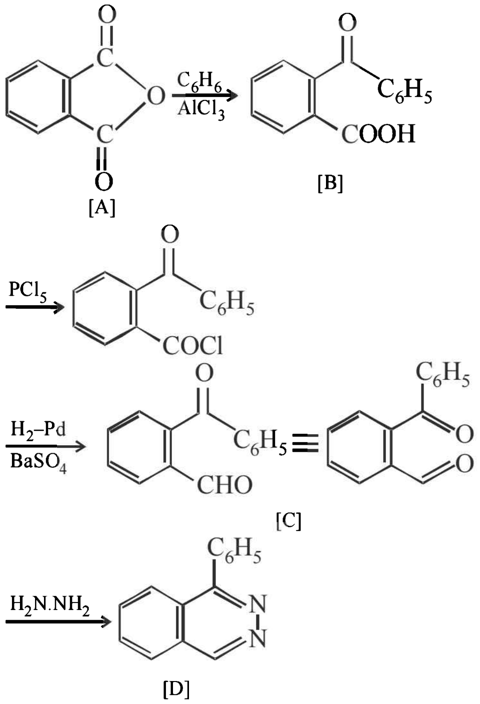
(ii) Reaction of A with CH_3MgBr indicates that it should have a ketonic group.

(iii) As B undergoes ozonolysis to form C, It must have a double bond, and C must have two carbonyl groups.

(iv) Reaction of C (a dicarbonyl compound) with a base gives a cyclic compound, it indicates that intramolecular condensation have occurred during this conversion. Thus A is cyclohexanone which explains all the given reactions.



39.



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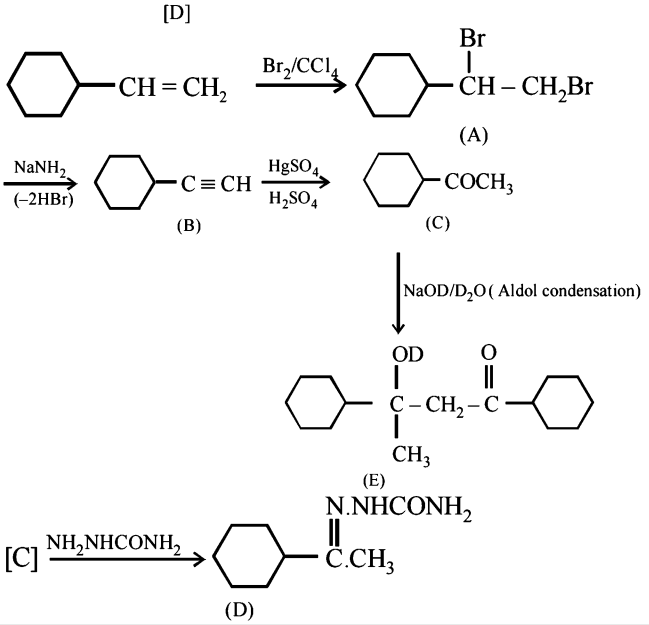


41. $$Ba\overset{*}{C}O_3 + H_2SO_4 \longrightarrow \underset{(X)}{\overset{*}{C}O_2} \uparrow$$

$$CH_2=CHBr \xrightarrow[\text{ether}]{\text{(i)Mg}} CH_2=CHMgBr \xrightarrow[\text{(ii)}H_3O^+]{\text{(ii)}\overset{*}{C}O_2(X)}$$

$$\underset{(Y)}{CH_2=CH\overset{*}{C}OOH} \xrightarrow{LiAlH_4} \underset{(Z)}{CH_2=CH.\overset{*}{C}H_2OH}$$

Formation of $\overset{*}{C}H_2O$ from (Z)

$$CH_2=CH.\overset{*}{C}H_2OH \xrightarrow{H^+}$$

$$[CH_2=\underset{\oplus}{CH.\overset{*}{C}H_2} \longleftrightarrow \overset{\oplus}{C}H_2-CH=\overset{*}{C}H_2] \xrightarrow{Br^-}$$

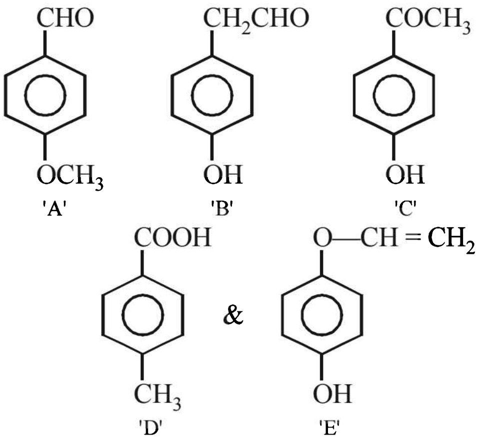
$$BrCH_2.CH=\overset{*}{C}H_2 \xrightarrow{O_3} \overset{*}{C}H_2=O$$

42. (i) As both the compounds **A** and **B** form a silver mirror with Tollen's reagent, they have aldehydic group in their structure. In these compounds, **B** gives positive test with $FeCl_3$ solution, so it must also have phenolic group in its structure.
Hence, compound **A** is *p*-methoxybenzaldehyde and **B** is *p*-hydroxyphenylacetaldehyde.

(ii) Compound **C** gives positive iodoform test, so it must have CH_3CO– group in its structure. Hence compound **C** is p-hydroxyphenylmethyl ketone.

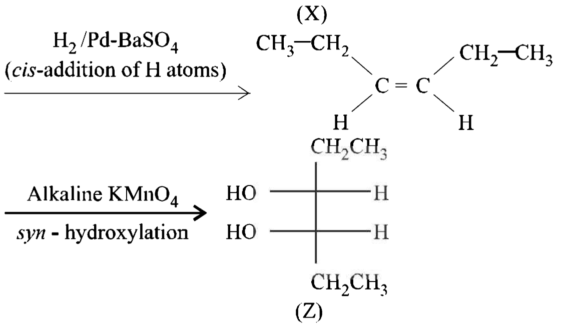
(iii) Compound **D** is readily extracted in aqueous $NaHCO_3$, so it must have -COOH group in its structure. So, compound **D** is *p*-methylbenzoic acid.

(iv) Compound **E** on hydrolysis gives 1,4-dihydroxybenzene. So, compound **E** is *p*-hydroxyphenyl vinyl ether.
Hence the structures of all the five compounds are :



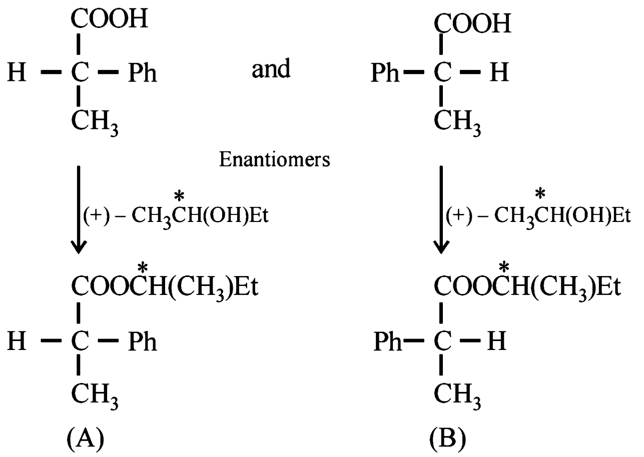
43. **TIPS/Formulae :**
Meso forms are optically inactive.

$$CH_3CH_2-C\equiv C-H \xrightarrow[\text{(ii) }CH_3CH_2Br]{\text{(i) }NaNH_2} CH_3CH_2-C\equiv C-CH_2CH_3$$



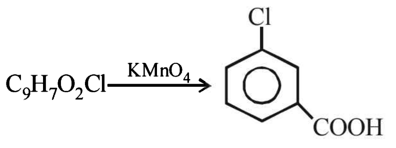
Z is in meso form having plane of symmetry. The upper half molecule is mirror image of the lower half molecule. The molecule is, therefore, optically inactive due to internal compensation.

44. The two enantiomers of 2-phenylpropanoic acid in the racemic mixture react with (+) – alcohol to form two diastereomers.

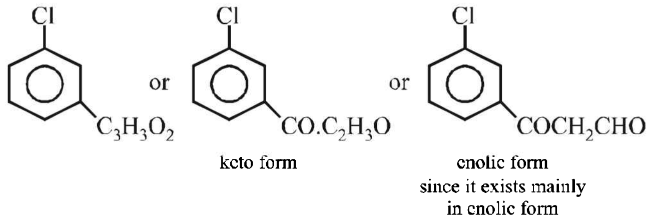


(A) and (B) are diasteromers.

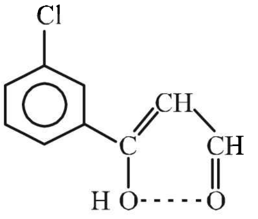
The bonds attached to the chiral carbon in both the molecules are not broken during the esterification reaction. (+) – Acid reacts with (+) –alcohol to give an (+)–(+)–easter, while (–) acid reacts with (+) alcohol to give (–)–(+)–ester. These two esters are diastereoisomers.

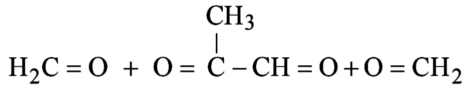
45. 

Hence compound should have following part structure

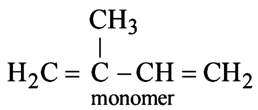


The enolic form of the compound is more stable than the keto form due to hydrogen bonding.



46. 

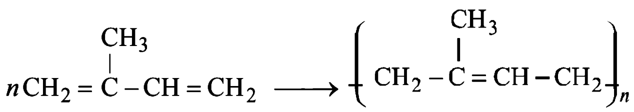
$$H_2C=O + O=\underset{}{\overset{CH_3}{C}}-CH=O+O=CH_2$$



$$H_2C=\overset{CH_3}{C}-CH=CH_2$$

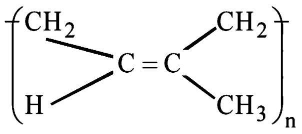
monomer

Thus the possible polymer should be



$$nCH_2=\overset{CH_3}{C}-CH=CH_2 \longrightarrow \left(CH_2-\overset{CH_3}{C}=CH-CH_2\right)_n$$

Structure of all *cis* configuration of the polymer.

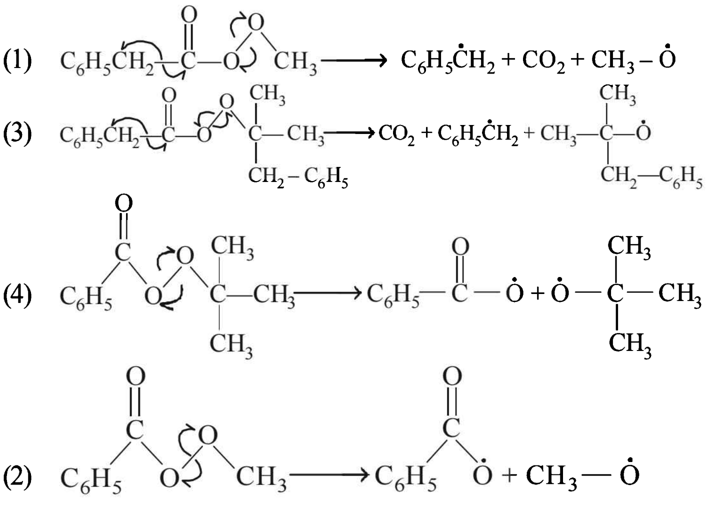


All *cis* form

F. Match the Following

1. **(A) - r, s; (B) - p, q; (C) - p, q, r; (D) - p, s**
compound (A) does not have carbon, hence does not responds (*p*) test.

2. **(a)**

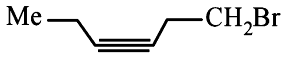


G. Comprehension Based Questions

1. **(d)** $CH_3-CH_2-C\equiv C-CH_2-CHO$

Hex-3-ynal

$$\xrightarrow[2.PBr_3]{1.NaBH_4} CH_3-CH_2-C\equiv C-CH_2-CH_2Br$$

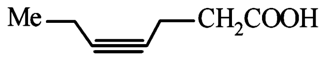
or 

Product 'I'

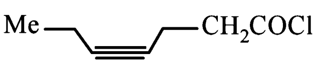
Sodium borohydride reduces –CHO
Selectively into –CH_2OH

2. **(a)** 

"I"

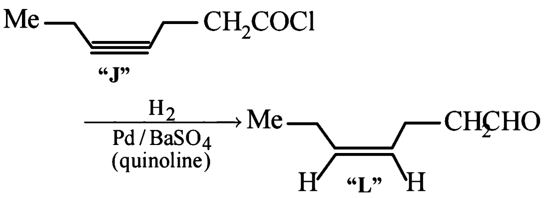
$\xrightarrow[3.H_3O^+]{1.Mg/Ether \; 2.CO_2}$ 

"J"

$\xrightarrow{"K"}$ 

Thus "K" is $SOCl_2$

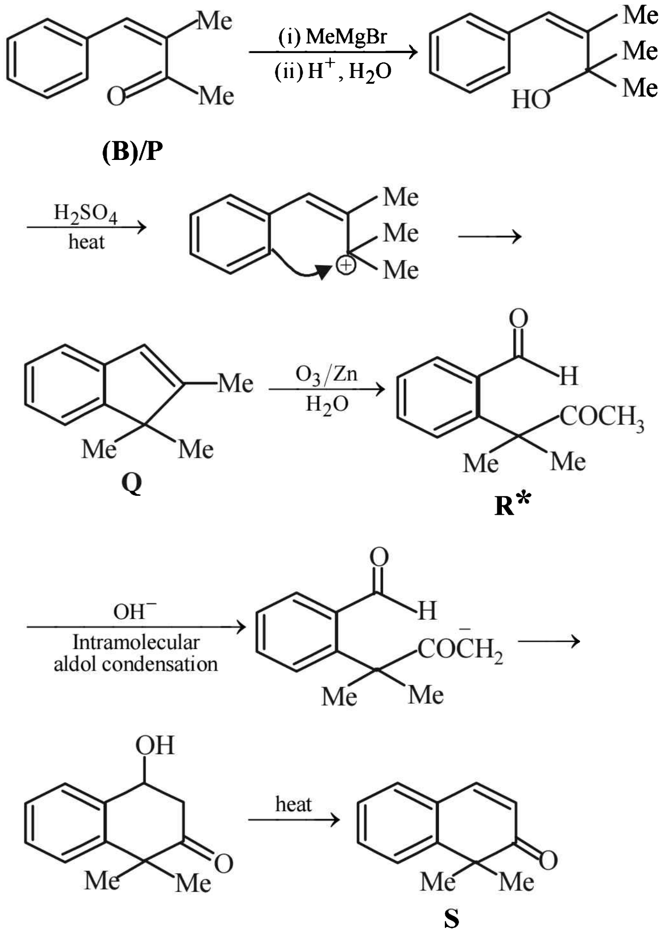
3. **(c)**



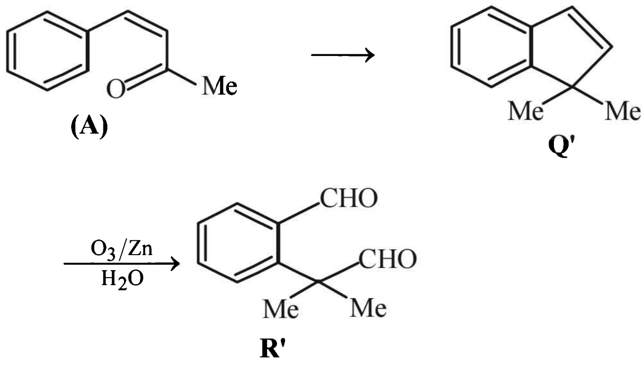
It is Rosemmund reaction. Simultaneously the reagent H_2-Pd also reduces carbon-carbon triple bond to double bond (*syn* -addition) giving *cis* product.

For 4-6.

Iodoform test of compound **P** points out that **P** has – $COCH_3$ group which shows that it may be either option (a) or (b) of Q. 16. Further since the dicarbonyl compound **R** has at least one α-H atom w.r.t to one of the carbonyl groups which is possible when **R** is produced from (b) of Q. 18; (a) option of Q. 16 will give dicarbonyl compound having two –CHO, none of which has α-H atom.

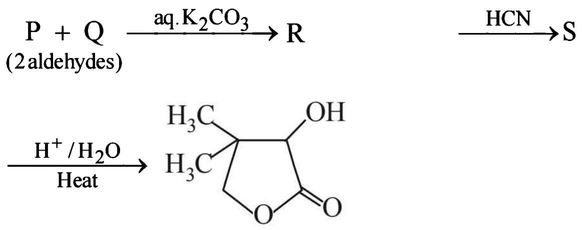


* Structure of **R** would be **R'** when **P** is (A)

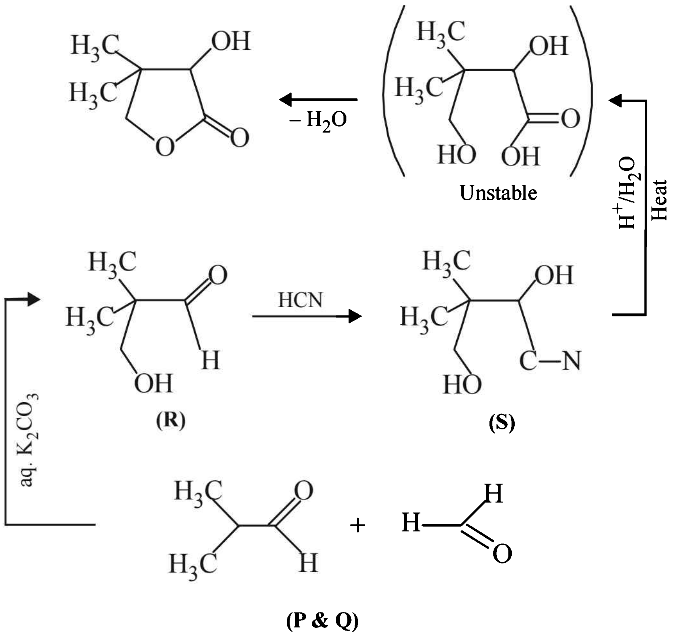


4. **(b)** **5.** **(a)** **6.** **(b)**

For 7-9. Let us summarize the given facts of the problem.



Structures of P, Q, R and S can be established on going backward from the known final product.

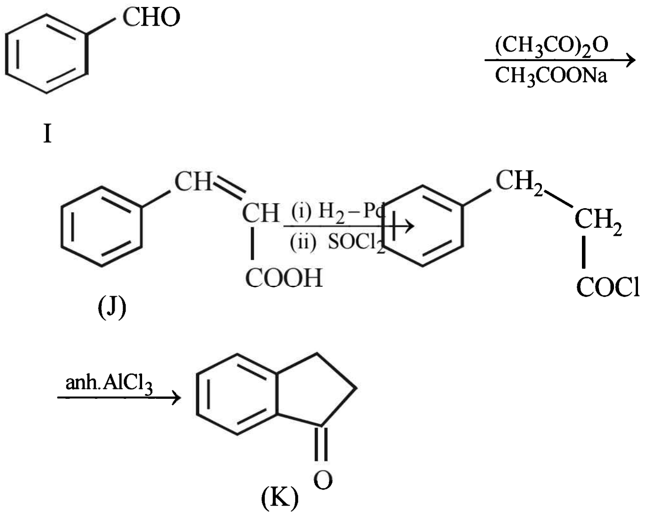


7. **(b)** **8.** **(a)** **9.** **(d)**

For 10 - 11

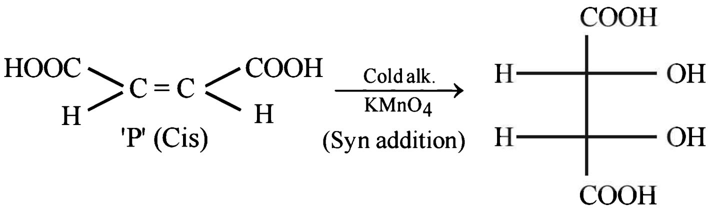
10. **(c)** **11.** **(a)**

Reactions of compound J ($C_9H_8O_2$) indicates that it has C = C linkage and – COOH group. Thus, J can be written as $C_6H_5CH = CH\ COOH$. Since, J is unsaturated carboxylic acid and it is formed by the reactions of compound I with $(CH_3CO)_2O$ and CH_3COONa, compound I should be an aldehyde (recall Perkin reaction). Thus the whole series of reactions can be written as below.

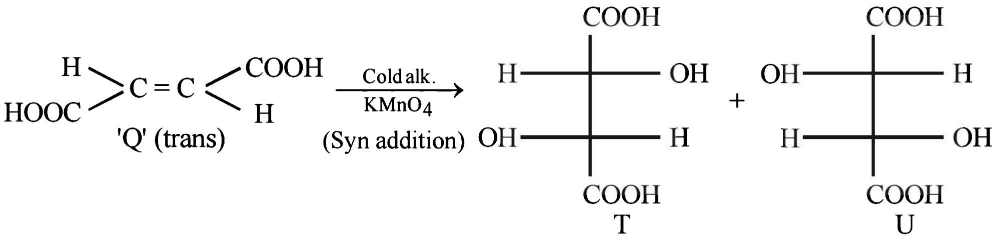


For 12-13.

12. (b)

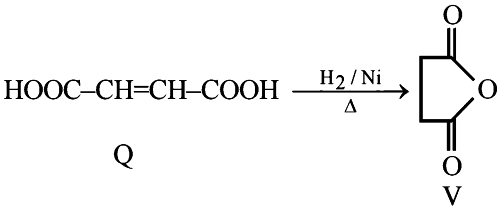


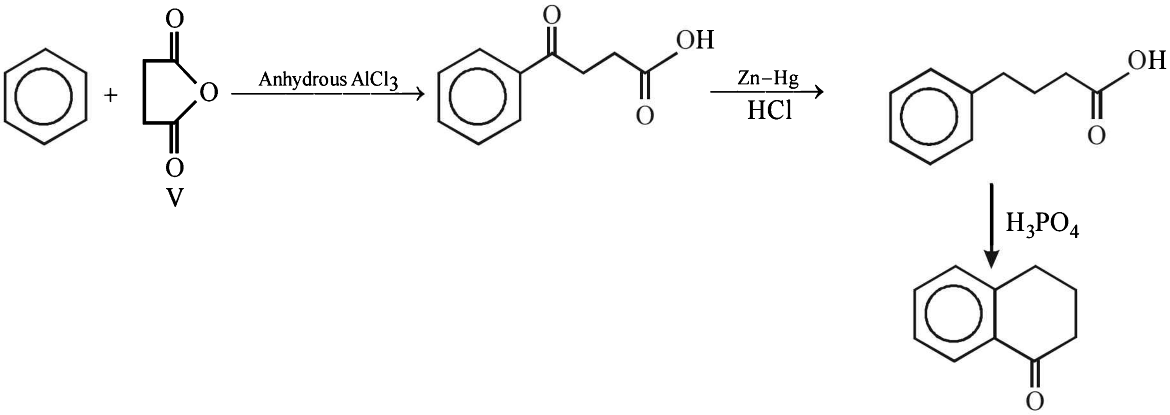
Meso (S), optically inactive



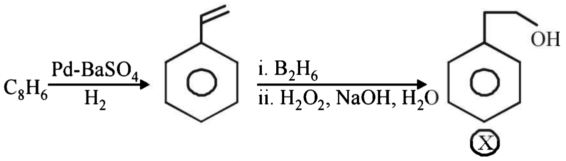
(Racemic Mixture), optically inactive

13. (a)

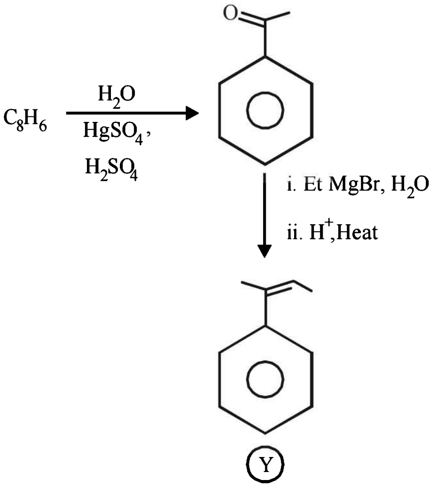




14. (c)



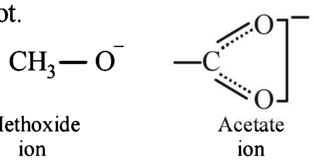
15. (d)



H. Assertion & Reason Type Questions

1. (d) TIPS/Formulae :

Acetate ion is reasonance stabilized while methoxide ion is not.

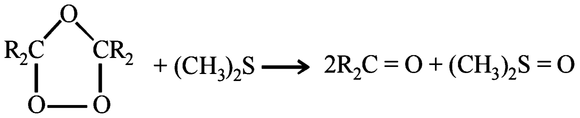


Hence, acetate ion is less basic than methoxide ion.

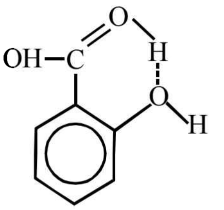
2. (c) Haloform reaction is undergone only by ketones, CH_3COOH has 3 α-hydrogens.

3. (a) TIPS/Formulae :

Ozonide can be reduced by $(CH_3)_2S$ to give carbonyl compounds and dimethyl sulphoxide.

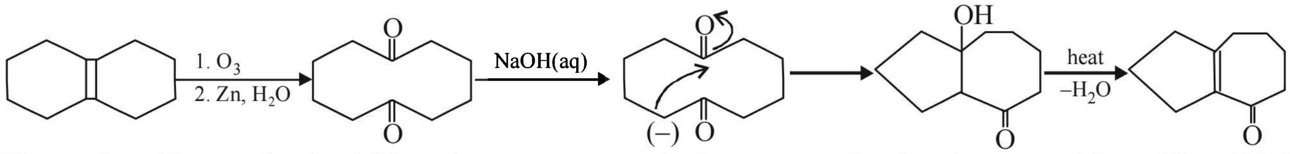


4. **(d)** *p*-Hydroxybenzoic acid has higher boiling point than *o*-hydroxybenzoic acid due to intermolecular hydrogen bonding. Thus, statement-1 is false. o-Hydroxybezoic acid shows intramolecular H-bonding thus, statement-2 is true.



I. Integer Value Correct Type

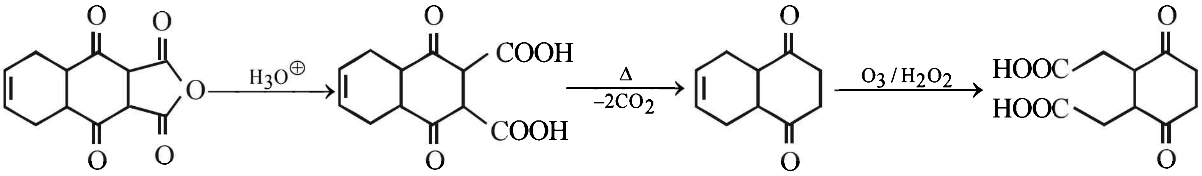
1.



The number of intra molecular aldol condensation products (α, β –unsaturated carbonyl compound formed from **Y** is 1.

2. All carboxylic acids and phenols are soluble in aqueous NaOH. Four compounds are soluble in aqueous NaOH.

3. **(2)**

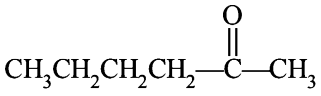


No. of –COOH group is '2'

4. **(5)** General molecular formula for ketones is $C_nH_{2n}O$

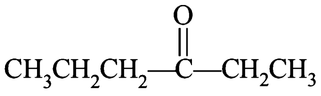
$\therefore\ C_nH_{2n}O = 100$ or $12n + 2n + 16 = 100, n = 6$

Possible isomeric ketones with 6 carbon atoms are



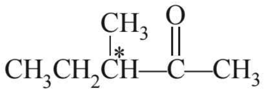
$CH_3CH_2CH_2CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

(I)



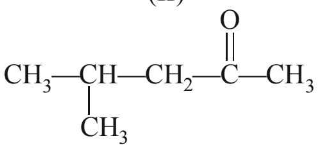
$CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-CH_2CH_3$

(II)



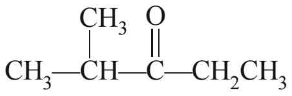
$CH_3CH_2\overset{CH_3}{\overset{|*}{C}}H-\overset{O}{\overset{\|}{C}}-CH_3$

(III)



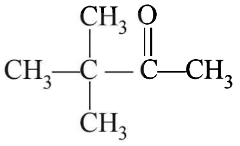
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

(IV)



$CH_3-\overset{CH_3}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}-CH_2CH_3$

(V)

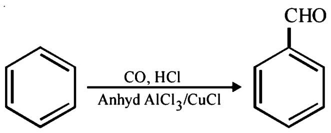


$CH_3-\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-\overset{O}{\overset{\|}{C}}-CH_3$

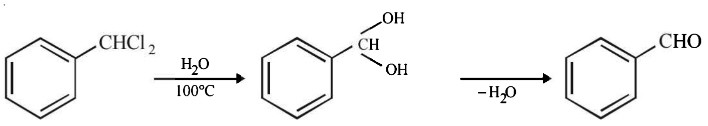
(VI)

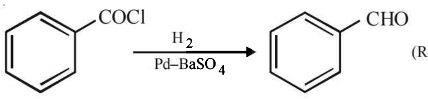
Note that only isomer III has a chiral carbon so on reduction with $NaBH_4$ it will give diastereomeric alcohols, while all other five isomers will give racemic mixture.

5. **(4)**

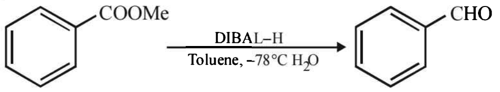


(Gatterman Koch Reaction)





(Rosenmund Reduction)



Section-B JEE Main/ AIEEE

1. (c) $CH_3CH_2COOH \xrightarrow[\text{red P}]{Cl_2} CH_3CHClCOOH$

$$\xrightarrow[-HCl]{\text{alc.KOH}} \underset{\text{Acrylic acid}}{CH_2{=}CHCOOH}$$

2. (b) Aldehydic group gets oxidised to carboxylic group. Double bond breaks and carbon gets oxidised to carboxylic group.

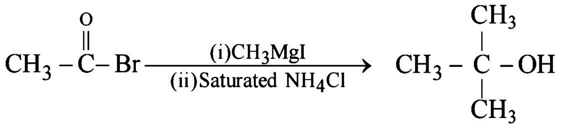
3. (c) 2,4,6-trinitrophenol is also known as picric acid.

4. (a) $LiAlH_4$ can reduce COOH group and not the double bond.

$$CH_2 = CH - COOH \xrightarrow{LiAlH_4} CH_2 = CH - CH_2OH$$

5. (c) There is no reaction hence the resultant mixture contains $CH_3COOC_2H_5 + NaCl$.

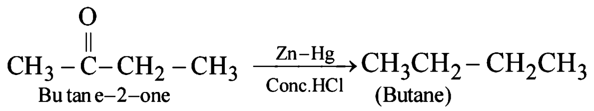
6. (a)



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Br \xrightarrow[\text{(ii)Saturated } NH_4Cl]{\text{(i)}CH_3MgI} CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-OH$$

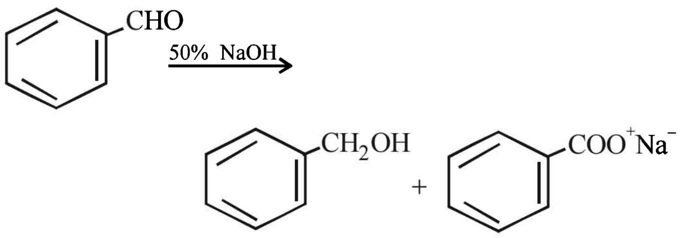
2–methyl–2–propanol

7. (d) It is Clemmensen's reduction



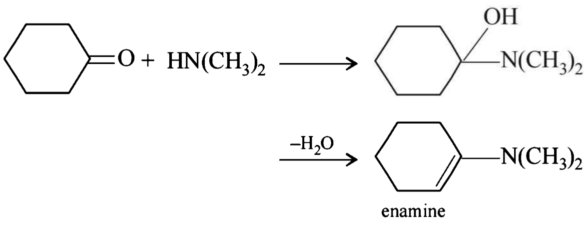
$$\underset{\text{Butane–2–one}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_3} \xrightarrow[\text{Conc.HCl}]{\text{Zn–Hg}} \underset{\text{(Butane)}}{CH_3CH_2-CH_2CH_3}$$

8. (b) This reaction is known as cannizzaro's reaction. In this reaction benzaldehyde in presence of 50%. NaOH undergoes disproportionation reaction and form one mol of Benzyl alcohol (Red. product) and one mole of sod. benzoate (ox. product)



9. (c) $pK_a = -\log K_a$; HCOOH is the strongest acid and hence it has the highest K_a or lowest pK_a value.

10. (c)



11. (a) **NOTE :** Addition of HCN to carbonyl compounds is nucleophilic addition reaction. The order of reactivity of carbonyl compounds is

Aldehydes (smaller to higher) Ketones (smaller to higher), Then

$$HCHO > CH_3COCH_3 > Ph.COCH_3 > PhCOPh$$

NOTE : The lower reactivity of Ketones is due to presence of two alkyl group which shows +I effect. The reactivity of Ketones decreases as the size of alkyl group increases.

12. (a) The correct order of increasing acid strength

$$CF_3.COOH > MeOCH_2COOH > CH_3COOH > (Me)_2CH.COOH$$

[**NOTE :** Electron withdrawing groups increase the acid strength and electron donating groups decrease the acid strength.]

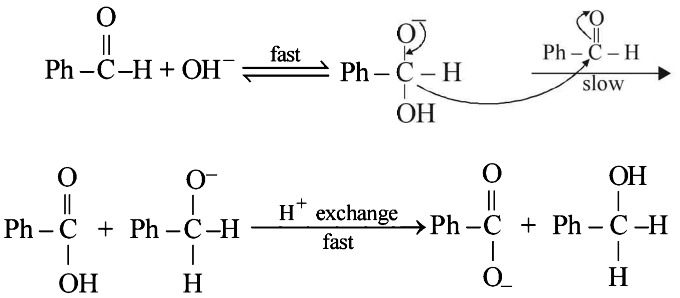
13. (c) Fruity smell is due to ester formation which is formed between ethanol and acid.

$$CH_3COOH + C_2H_5OH \xrightarrow{\text{Conc.} H_2SO_4} CH_3COOC_2H_5 + H_2O.$$

14. (c) $CH_3CHCl_2 \xrightarrow{\text{aq.KOH}} CH_3CH(OH)_2$

$$\xrightarrow{-H_2O} CH_3CHO$$

15. (a)



$$Ph-\overset{\overset{\displaystyle O}{\|}}{C}-H + OH^- \underset{}{\overset{\text{fast}}{\rightleftharpoons}} Ph-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle O^-}{|}}{C}}-H \xrightarrow[\text{slow}]{Ph-\overset{\overset{\displaystyle O}{\|}}{C}-H}$$

$$Ph-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle O}{\|}}{C}} + Ph-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle O^-}{|}}{C}}-H \xrightarrow[\text{fast}]{H^+ \text{ exchange}} Ph-\underset{\underset{\displaystyle O^-}{|}}{\overset{\overset{\displaystyle O}{\|}}{C}} + Ph-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-H$$

16. (d) Phenol gives a violet colour with neutral ferric chloride solution whereas benzoic acid does not give this test.

17. (a) $CCl_3CHO + NaOH \longrightarrow \underset{2,2,2-\text{trichloroethanol}}{CCl_3CH_2OH} + CCl_3COONa$

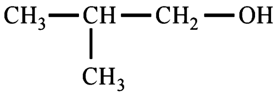
In Cannizzaro's reaction the compounds which do not contain α-hydrogen atoms undergo oxidation and reduction simultaneously i.e undergo disproportionation and form one molecule of sodium salt of carboxylic acid as oxidation product and one molecule of alcohol as reduction product.

18. (c) The electron withdrawing (–I) group – Cl withdraws electrons from O – H bond and thus helps the cleavage of the O – H bond releasing hydrogen as H^+.

19. **(d)** $$\underset{\text{ethanoyl chloride}}{CH_3CO\boxed{Cl + Na}} \underset{\text{sodium ethoxide}}{OC_2H_5} \longrightarrow \underset{\text{ethyl ethanoate}}{CH_3COOC_2H_5} + NaCl$$

20. **(a,c)** Both formaldehyde and acetaldehyde give silver mirror with Tollen's reagent.

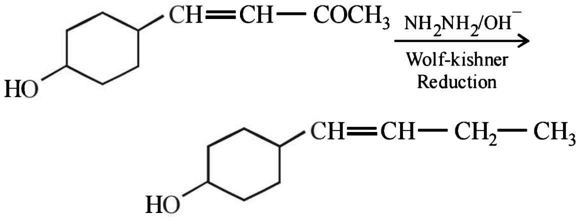
21. **(d)** Iodoform test is given by methyl ketones, acetaldehyde and methyl secondary alcohols.



$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-OH$$

isobutyl alcohol is a primary alcohol hence does'nt give positive iodoform test.

22. **(a)** Aldehydes and ketones can be reduced to hydrocarbons by the action (i) of amalgamated zinc and concentrated hydrochloric acid (Clemmensen reduction), or (b) of hydrazine (NH_2NH_2) and a strong base like NaOH, KOH or potassium *tert*-butoxide in a high-boiling alcohol like ethylene glycol or triethylene glycol (Wolf-Kishner reduction)



–OH group and alkene are acid-sensitive groups so clemmensen reduction can not be used. Acid sensitive substrate should be reacted in the Wolf-Kishner reduction which utilise strongly basic conditions.

23. **(d)** An excellent reagent for oxidation of 1° alcohols to aldehydes is PCC.

$$R-CH_2-OH \xrightarrow{PCC} R-CHO$$

24. **(c)** $$CH_3COOH \xrightarrow{LiAlH_4} \underset{(A)}{CH_3CH_2OH} \xrightarrow{PCl_5} \underset{(B)}{CH_3CH_2Cl} \xrightarrow{\text{Alc. KOH}} \underset{(C)}{CH_2=CH_2}$$

Hence the product (C) is ethylene.

25. **(b)**