

# Aldehydes, Ketones and Carboxylic acids-Solutions

#### **SUBJECTIVE PROBLEMS:**



(vi)  $C_6H_5COOH + CH_3MgI \rightarrow CH_4 + C_6H_5COO MgI$ 



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



Educational Material Downloaded from http://www.evidyarthi.in/ Get CBSE Notes, Video Tutorials, Test Papers & Sample Papers





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



(Ester hydrolysis involves acyl-oxygen fission)





## Sol 2. $Ch_3COOC_2H_5 + H_3CCOOC_2H_2 \xrightarrow{C_2H_5ONa}_{C_2H_5OH}$ $CH_{3}C = CHCOOC_{2}H_{5} \xrightarrow{H^{+}} CH_{3}C = CHCOOC_{2}H_{5}$ Ethyl acetoacetate Sol 3. (i) HCNO $\xrightarrow{[O]}$ HCOOH $\xrightarrow{Ca (OH)_2}$ Methanal $(\mathsf{HCOO})_2\mathsf{Ca} \xrightarrow[heat]{(CH_3COO)_2Ca} 2 \mathsf{CH}_3 \mathsf{CHO}$ Ethanal (ii) $CH \equiv CH \xrightarrow{H_2SO_4} Ch_3CHO \xrightarrow{KMnO_4} CH_3COOH$ Acetylene $\xrightarrow{Ca(OH)_2}$ (CH<sub>3</sub>COO)<sub>2</sub> $\xrightarrow{distili}$ (CH<sub>3</sub>)<sub>2</sub>CO Acetone $\xrightarrow{\text{PCl}_3} \text{CH}_3\text{COCl} \xrightarrow{\text{CH}_3\text{Mgl}} \text{CH}_3\text{COCH}_3$ (iii) CH<sub>2</sub>COOH-Acetic acid $C \stackrel{CH_3}{\longleftarrow} \stackrel{H_2O}{\stackrel{(H^+)}{\longleftarrow}} \stackrel{H_3C}{\stackrel{H_3C}{\longleftarrow}}$ H<sub>3</sub>C H<sub>2</sub>C Tertiary-butyl alchol HCHO/NaOH → GH2CH2CHO CH<sub>3</sub>.CHO (iv) ethanal OH Dehydration CH<sub>2</sub> = CHCHO propenal (heat) HCN $CH_2 = CH -$ CH - CNOH propenal cyanohydrin $\rightarrow CH_2 \approx CH - CH - COOH$ hydrolysis OH 2-hydroxy-3- butenoic acid (v) CH<sub>3</sub>COOH $\xrightarrow{PCI_5}$ Ch<sub>3</sub>COCI $C_6H_5MgBr \rightarrow C_6H_5COCH_3$





## <u>Sol 4.</u>



## <u>Sol 5.</u>

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



## 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 :





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



The compound (C) is forged 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





## <u>Sol 6.</u>

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

(*ii*) 
$$H - C - OH \implies H - C - O^{-} + H^{+}$$
;  
 $H = O = OH \implies O$   
 $CH_3 - C - OH \implies CH_3 - C - O^{-} + H^{+}$   
 $O = OH \implies O$ 

Presence of  $CH_3$  gp in acetone ion shows +I effect and thereby intensifying charge on O<sup>-</sup> 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 due to hydrogen bonding between butanol and water molecules (similarity to butanol).

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

$$>C = O + H^{+} \xrightarrow{+} C - OH$$
carbon becomes
more electron
deficient

In strongly acidic medium (pH < 3.5), the unshared pair of electrons of N of the reagent is protonated with the result nucleophile (NH<sub>2</sub>NH<sub>2</sub>) is converted to an electrophile (NH<sub>2</sub>H<sup>+</sup>H<sub>3</sub>) which cannot react. Hence in highly acidic medium, there is no protonation of the carbonyl group.

(v) **BOTE :** Hypoiodite ( $^{-}$ OI) is 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.



## $CH_3.CO.CH_3 + OH \rightarrow CH_3.C. \overline{C}H_2 + HOI$

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

$$R:C \to O^+: \longleftrightarrow R:C^+=O:$$



Carbonium ion

(Carbon has only six electrons)

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



Resonating structures of phenoxide ion



Resonating structure 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) 0-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)





## <u>SOL 10.</u>

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 base 3CHO + [Ag(NH base 3) base 2]^+ OH^-  $\rightarrow$  RCOOH + Ag  $\downarrow$ Tollen's reagent Silver mirror

#### <u>SOL 11.</u>

The weaker a base better is its leavability.

This is an example of nucleophilic substitution where the group X (CI,  $OC_2H_5$ ,  $OCOCH_3$ ) is replaced by OH.

The decreasing basic character of the four concerned group is

 $NH_2^2 > OR^2 > OCOR^2 > Cl^2$ 

Hence Cl<sup>-</sup> (the weakest base) will be lost most easily while NH<sup>-</sup><sub>2</sub> (the strongest base) will be lost with most difficulty. Thus the order of hydrolysis becomes.

 $CH_3CONH_2 < CH_3COOC_2H_5 < (CH_3CO)_2O < CH_3COCI.$ 

#### <u>Sol 12.</u>

Let us summarise the given facts.

White ppt.  $\xleftarrow{AgNO_3}$  (A)  $\xleftarrow{hot alc.}{KOH}$   $C_6H_{13}CI$ (B) + (C)  $\xrightarrow{O_3}$ 

(Isomeric alkenes. C<sub>6</sub>H<sub>12</sub>)



 $\begin{array}{cccc} CH_{3}CHO + & C_{2}H_{5}CHO + & Ch_{3}COCH_{3} + & (CH_{3})_{2}CHCHO \\ (i) & (ii) & (iii) & (iv) \end{array}$ 

**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)].

 $\begin{array}{ccc} \mathsf{CH}_3\mathsf{CHO} + \mathsf{OCH}.\mathsf{CH}(\mathsf{CH}_3)_2 & \xleftarrow{O_3} & \mathsf{CH}_3\mathsf{CH} = \mathsf{CH}.\mathsf{CH}(\mathsf{CH}_3)_2 \\ (i) & (iv) & \text{Olefin B} (\mathsf{C}_6\mathsf{H}_{12}) \\ \mathsf{C}_2\mathsf{H}_5\mathsf{CHO} + \mathsf{OCH}(\mathsf{CH}_3)_2 & \xleftarrow{O_3} & \mathsf{C}_2\mathsf{H}_5\mathsf{CH} = \mathsf{C}(\mathsf{CH}_3)_2 \\ (i) & (iii) & \text{Olefin B} (\mathsf{C}_6\mathsf{H}_{12}) \end{array}$ 

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

 $\begin{array}{ccc} Cl & CH_3 & CH_3 \\ l & l \\ CH_3CH_2CH.CH.CH_3 & \longrightarrow & CH_3CH = CH.CH.CH_3 \\ 2-Methyl-3-chloropentane & & 4-Methylpenene -2 \\ (A) & (B) \end{array}$ 

## <u>Sol 13.</u>

(X) is hydrolysed to give an acid (Y) and an alcohol (Z) and thus X is an ester:

$$\begin{array}{c} R \longrightarrow C \longrightarrow OR \\ \parallel \\ O \end{array} \\ R \longrightarrow C \longrightarrow OR' \longrightarrow RCOOH + R'OH \\ \parallel \\ O \end{array} \\ H^+ \qquad (Y) \qquad (Z) \end{array}$$
Oxidation of alcohol (Z) gives acid (Y)
$$\begin{array}{c} R'OH \longrightarrow RCOOH \\ (Z) \end{array}$$

or  $RCH_2OH \rightarrow RCOOH$  (:: R' is  $R - CH_2$ )

Hence X, Y and Z are



CH<sub>3</sub>CH<sub>2</sub> C-OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>COOH, О (Propyl propanoate) (Propanoic acid) Y CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH

(Propan – 1 - ol) Z

Sol 14.

(i)  $CH_3$ HO+CH,CHO

#### SOL 15.

(i)Empirical formula can be calculated as

Element	Percentage	Relative no. of atoms	Simplest ratio
С	69.777	5.81	5
Н	11.63	11.63	10
0	18.60	1.16	1

 $\therefore$  Empirical formula of compound is C base 5H base 10O and empirical formula wt. = 86.

Also molecular wt. = 86.

(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

## Sol 16.



#### 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.

-COOH  $\xrightarrow{PCI_5}$  - COCI  $\xrightarrow{NH_3}$  - CONH<sub>2</sub>  $\xrightarrow{-N_2O}$  HCN

Formation of HCN by the dehydration of E establishes that E is HCONH<sub>2</sub> and hence D is HCOOH.

(iv) Thus the alcohol A produced along with HCOOH during Cannozzaro reaction of C must be  $CH_2OH$  hence C must be HCHO.

Thus the various compounds are as below :

А	В	С	D	E
CH₃OH	CH₃COOCH₃	НСНО	НСООН	HCONH <sub>2</sub>
Methyl	Methyl acetate	Formal dehyde	Acid	Form amide
alcohol				

## <u>Sol 17.</u>



## <u>Sol 18.</u>

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



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.

$$CH_3 Br$$

$$H_3 - CH - CH - CH_3$$
(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 add on it according to Markownikoff rule.

$$CH_{3} \qquad CH_{3} \qquad CH_{3} \\ CH_{3}-CH.CH = CH_{2} \qquad CH_{3}C=CH.CH_{3} \\ (A) \qquad (A')$$

Thus the reaction involved can be represented as below:

$$\begin{array}{c} CH_{3} & CH_{3} Br \\ I & I \\ CH_{3}-CH-CH=CH_{2} \xrightarrow{HBr} CH_{3}-CH-CH-CH_{3} \\ 3-Methylbutene-1,A & 2-Bromo-3-methylbutane,B \\ \end{array}$$

$$\begin{array}{c} CH_{3} OH \\ I & I \\ \hline AgOH \\ AgOH \\ \hline AgOH \\ 3-Methylbutanol-2,C \end{array} \xrightarrow{(O)} CH_{3}-CH-C-CH_{3} \\ \hline 3-Methylbutanone-2,D \end{array}$$

## <u>Sol 19.</u>

The compound A ketone, undergoes haloform reaction.

Thus, it must contain CH<sub>3</sub>CO 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.  $CH_3 - CH = CH - CH_3$  (butane-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

$$\begin{array}{ccc} CH_3 - CH - CH_2 - CH_3 & CH_3 - C - CH_2 - CH_3 \\ & & \parallel \\ OH & O \\ butan - 2 - ol (B) & butan - 2 - one (A) \end{array}$$

The reactions involved :

(A) 
$$\xrightarrow{reduction}$$
 (B)  $\xrightarrow{conc. H_2SO_4}$   $CH_3 - CH = CH.CH_3$ 





## <u>Sol 20.</u>

The given set of reactions can be represented as below :

Aq. NaOH  $\xrightarrow[(i)]{Gas \ B}$  Sod salt of acid A  $\xrightarrow[(i)]{MaOH} (heat)$  Dibasic acid, C

Calculation of molecular formula of C

% of H = 
$$\frac{2}{18} * \frac{0.08}{0.40} * 100 = 2.22\%$$
  
% of C =  $\frac{12}{44} * \frac{0.39}{0.40} * 100 = 27.30\%$ 

% of O = 100 - (2.22 + 27.30) = 71.48%

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

Eq. wt. of acid C = 
$$\left(\frac{.0}{0.71} * 1108\right)$$
 - 107 = 45

Mol. wt. of acid C = 45 \* 2 = 90

 $\therefore$  Mol. formula of C = C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>

Since it is dicarboxylic acid, it must have two -COOH group

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<sub>2</sub>. Thus the complete series of reactions can be written as below.







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.

$$2CH_{3}CHO \xrightarrow{OH^{-}} CH_{3}CHCH_{2}CHO \xrightarrow{heat}$$
(D)

OH

 $CH_{3}CH = CHCHO \xrightarrow[catalyst]{H_{2}/} CH_{3}CH_{2}CH_{2}CH_{2}OH$ 

Crotonaldehyde, (E) Butanol – 1, (C)

Nature of A. Thus it is evident that reduction of A with  $LiAIH_4$  gives two alcohols; B (ethanol) and C (butanol). Hence A must be an ester i.e., ethyl butanoate ( $CH_3CH_2CH_2COOC_2H_5$ ).

 $CH_3CH_2CH_2COOC_2H_5 \xrightarrow{LiAIH_4} \rightarrow$ 

Ethyl butanoate, A

 $CH_{3}CH_{2}CH_{2}CH_{2}OH + C_{2}H_{5}OH$ Butanol, C Ethanol, B

## <u>Sol 22.</u>

Empirical formula of A and B.

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

 $\therefore$  Empirical formula of A and B = C<sub>7</sub>H<sub>8</sub>O



**Nature of (A) :** Since A is insoluble in NaOH and NaHCO<sub>3</sub>, 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<sub>3</sub> 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<sub>3</sub> which explains all the given reactions.



**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 give tribromo product indicates that it is *m*-cresol.



## <u>Sol 23.</u>

(i) 
$$C_6H_5COOH \xrightarrow{PCI_5} C_6H_5COCI \xrightarrow{NH_3} C_6H_5CONH_2 \xrightarrow{P_2O_5} C_6H_5CN \xrightarrow{H_2/Ni} C_6H_5CH_2NH_2$$
  
(D) (E)  
(ii)  $H_3CCH = CHCHO \xrightarrow{NaBH_4} CH_3CH = CH - CH_2OH$   
(F)  
 $\xrightarrow{HCI} CH_3CH = CHCH_2CI$   
(G)  
 $\xrightarrow{KCN} H^+ CH_3CH = CHCH_2COOH$ 

## <u>Sol 24.</u>

For empirical formula of (Y)

Element	%	Relative no.	Simple ratio
С	49.31	4.10	3
Н	9.59	9.59	7
Ν	19.18	1.37	1





(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.





Sol 26. CH<sub>3</sub>CHO < CH<sub>3</sub>COCH<sub>3</sub> < CH<sub>3</sub>COCH<sub>2</sub>COCH<sub>3</sub> < CH<sub>3</sub>COCH<sub>2</sub>CHO Sol 27. PCI<sub>5</sub> + SO<sub>2</sub> → SOCI<sub>2</sub> + POCI<sub>3</sub> (A) (B) SOCI<sub>2</sub> + CH<sub>3</sub>COOH → CH<sub>3</sub>COCI + SO<sub>2</sub> + HCI (A) (C) 2CH<sub>3</sub>COCI + (CH<sub>3</sub>)<sub>2</sub>Cd → 2CH<sub>3</sub> - CO - CH<sub>3</sub> + CdCI<sub>2</sub> (C)

## <u>Sol 28.</u>

$$\begin{array}{c|c} A & \xrightarrow{dry \ KOH} & B & + \ Ct \\ \hline \\ \hline \\ Zn/ \\ H_2O \\ \hline \\ Dut-2-ene \\ CH_3CHO \end{array}$$

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 ( $O_3$ ).

$$CH_{3}CH = CHCH_{3} + O_{3} \longrightarrow CH_{3}CH \xrightarrow{O} O$$

$$CH_{3}CH \xrightarrow{O} O$$

$$CHCH_{3} \xrightarrow{O} O$$

$$-\frac{Zn}{H_{2}O} \rightarrow 2CH_{3}CHO + H_{2}O_{2}$$

Reaction of ozone with KOH.

 $3\text{KOH} + 2\text{O}_3 \rightarrow 2\text{KO}_3 + \text{KOH}.\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \uparrow$ 

(A) Pot. Ozonide, B (C) (Red colour)

<u>Sol 29.</u>

$$\begin{array}{c} C_{8}H_{6} \xrightarrow{\text{dil.} H_{2}SO_{4}} B \xleftarrow{\text{anhydrous. AlCl}_{3}} RCOCI + C_{6}H_{6} \\ (A) & \downarrow I_{2}, \text{ay. KOH} \\ C + Yellow compound (D) \end{array}$$

(i) Formation of (B) from benzene and acid chloride in presence of anhydrous  $AICI_3$  (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<sub>3</sub>.

(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 hydrocarbon (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

 $\begin{array}{cccc} C_6H_5.C \equiv CH & C_6H_5.CO.CH_3 & C_6H_5COOH & CHI_3 \\ (A) & (B) & (C) & (D) \end{array}$  Formation of (B) from (A)

$$C_{6}H_{5}C \equiv CH \xrightarrow{dil.H_{2}SO_{4}} [C_{6}H_{5}.C = CH_{2}]$$
Phenylacetylene (A) HgSO<sub>4</sub>

$$\xrightarrow{rearranges} C_{6}H_{5}.CO.CH_{3}$$
Acetophenone (B)

## <u>Sol 30.</u>

(i)  $\beta$ -Keto acids are unstable and undergo decarboxylation most readily

#### Sol 31.



The last step is intramolecular aldol condensation

## <u>Sol 32.</u>







Sol 33.



The molecular after reduction possesses two asymmetric carbon (\*) with symmetry in molecule.

 $\therefore$  No. of stereoisomers (d, l and m) = 3



Sol 35.



Sol 36.







(ii) (a) Reaction of G with NaHCO<sub>3</sub> to give  $CO_3$  to give  $CO_2$  indicates that it has –COOH group.

(b) Reaction of G with acetic anhydride indicates that it has –OH group.

(c) Decarboxylation of (H), oxidized product of G indicates H is  $\beta$ -keto acid hence it should be  $\beta$ -hydroxy acid. Thus G should be

CH<sub>3</sub>CHOHCH<sub>2</sub>COOH



Thus G should be CH<sub>3</sub>CHOHCH<sub>2</sub>COOH.

## <u>Sol 37.</u>

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 oxidized, hence the alcohol should be secondary alcohol and thus ester is alkyl formate. Hence ester A ( $C_4H_8O_2$ ) should be HCOOC<sub>3</sub>H<sub>7</sub>. Thus the various reactions and nature of compound B can be established as below.







### <u>Sol 38.</u>

Following information 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 slide 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,  $\alpha$  – hydrogen is absent and hence triple bond should be present between C<sub>2</sub> and C<sub>3</sub>.

(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.



$$C_{6}H_{5} - CH - C \equiv CH \xrightarrow{H^{+}} C_{6}H_{5} - CH - C \equiv CH$$





Sol 40.



LiAlH<sub>4</sub> reduces only ketonic group to  $2^{\circ}$  alcoholic group without affecting double bond











## <u>Sol 43.</u>

The given reaction can be summarized 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<sub>3</sub>MgBr indicates that it should have a ketonic group.

(iii) As B underegoes 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.



Sol 44.









Sol 46.  
BaČO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub> 
$$\longrightarrow$$
 CO<sub>2</sub> î  
(X).  
CH<sub>2</sub> = CHBr  $\xrightarrow{(i)Mg}_{ether}$  CH<sub>2</sub> = CHMgBr  $\xrightarrow{(ii)CO_2(X)}_{(ii)H_3O^+}$   
CH<sub>2</sub> = CHČOOH  $\xrightarrow{\text{LiAlH}_4}$  CH<sub>2</sub> = CH.CH<sub>2</sub>OH  
(Y) (Z)  
Formation of CH<sub>2</sub>O from (Z)  
CH<sub>2</sub> = CH.CH<sub>2</sub>OH  $\xrightarrow{H^+}$   
[CH<sub>2</sub> = CH.CH<sub>2</sub>OH  $\xrightarrow{H^+}$   
[CH<sub>2</sub> = CH.CH<sub>2</sub>OH  $\xrightarrow{H^+}$   
[CH<sub>2</sub> = CH.CH<sub>2</sub>OH  $\xrightarrow{H^+}$   $\xrightarrow{\oplus}$  CH<sub>2</sub> - CH =  $\stackrel{\bullet}{\leftarrow}$ CH<sub>2</sub>]  $\xrightarrow{Br^-}$   
BrCH<sub>2</sub>.CH =  $\stackrel{\bullet}{\leftarrow}$ H<sub>2</sub>  $\xrightarrow{O_3}$   $\stackrel{\bullet}{\leftarrow}$ H<sub>2</sub> = O

## <u>Sol 47.</u>

(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<sub>3</sub> solution, so it must also have phenolic group in its structure.

Hence, compound A is p-methoxybenzaldehyde and B is p-hydroxyphenylacetaldehyde.

(ii) Compond 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<sub>3</sub>, 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 :







Sol 48. Meso forms are optically inactive.  $CH_3CH_2 - C \equiv C - H$   $\xrightarrow{(i) \ CH_3CH_2Br} CH_3CH_2 - C \equiv C - CH_2CH_3$ (X)



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.

## <u>Sol 49.</u>

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 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.

#### <u>Sol 50.</u>



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



#### <u>Sol 51.</u>

$$CH_3$$

$$H_2C = O + O = C - CH = O + O = CH_2$$

$$CH_3$$

$$H_2C = C - CH = CH_2$$
monomer

Thus the possible polymer should be

$${}^{\text{CH}_3}_{n \text{CH}_2 = \overset{\text{CH}_3}{\text{CH}_2 - \text{CH} = \text{CH}_2} \longrightarrow \begin{pmatrix} \overset{\text{CH}_3}{|} \\ \overset{\text{CH}_2 - \overset{\text{CH}_3}{|} \\ & \overset{\text{CH}_3 - \overset{\text{CH}_3 - \overset{\text{CH}_3}{|} \\ & \overset{\text{CH}_3 - \overset{\text{$$



