Fill Ups, True False of Aldehydes, Ketones & Carboxylic Acids

Fill in the Blanks

Q.1. Formic acid when heated with conc. H_2SO_4 produces ....
(1983 - 1 Mark)

Ans. CO

Solution. $CO; \ HCOOH \xrightarrow[heat]{Conc.H_2SO_4} CO + H_2O$

Q.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)

Ans. sodium potassium tartarate

Solution. sodium potassium tartarate.

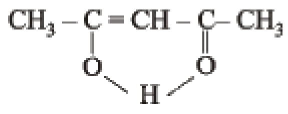
Q.3. The structure of the intermediate product, formed by the oxidation of toluene with CrO_3 and acetic anhydride, whose hydrolysis gives benzaldehyde is............... (1992 - 1 Mark)

Ans. $C_6H_5CH(OCOCH_3)_2$

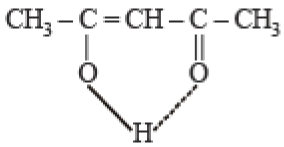
Solution. $C_6H_5CH(OCOCH_3)_2$ benzylidene acetate

Q.4. The structure of the enol form of $CH_3–CO–CH_2–CO–CH_3$ with intramolecular hydrogen bonding is .... (1993 - 1 Mark)

Ans.



Solution.



True / False

Q.1. Benzaldehyde undergoes aldol condensation in an alkaline medium. (1982 - 1 Mark)

Ans. False
Solution. False : Benzaldehyde has no a-hydrogen atom hence it does not undergo aldol condensation but undergoes Cannizzaro reaction.

Q.2. Hydrolysis of an ester in presence of a dilute acid is known as saponification. (1983 - 1 Mark)

Ans. False
Solution. False : Saponification is alkaline hydrolysis of esters.

Q.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)

Ans. True

Solution. True : Aldehydes (from primary alchols) may further be oxidised easily to acids as compared to ketones (from secondary alcohols).

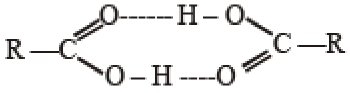
Q.4. The reaction of methyl magnesium iodide with acetone followed by hydrolysis gives secondary butanol. (1987 - 1 Mark)

Ans. False

Solution. False : Grignard reagents react with ketones to form teralcohols; hence here ter-butanol will be formed.

Q.5. The boiling point of propionic acid is less than that of n-butyl alcohol, an alcohol of comparable molecular weight. (1991 - 1 Mark)

Ans. False
Solution. False : H-bonding in propionic acid is stronger (carboxylic acids can form dimers) than that in butanol.



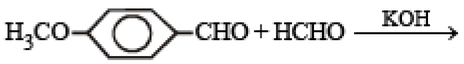
Subjective Ques of Aldehydes, Ketones & Carboxylic Acids, (Part - 1)

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

(iv) $\text{propanal} \xrightarrow[\text{heat}]{NaOH}$ **(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)

$CH_3-CH_2-COOH \xrightarrow[\text{bromine}]{\text{P and}} \overset{\textbf{A}}{\text{-----}}$

$\xrightarrow[2.\,H^+]{\text{1. alcoholic KOH (excess)}} \overset{\textbf{B}}{\text{-----}}$

(1995 - 2 Marks)

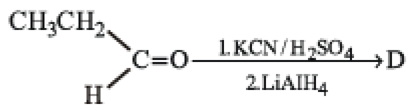
(ix) C_6H_5 - CHO + CH_3 - $COOC_2H5$ $\xrightarrow[C_2H_5OH\text{ and heat}]{NaOC_2H_5\text{ in absolute}} \overset{\textbf{D}}{\text{------}}$ **(1995 - 1 Mark)**

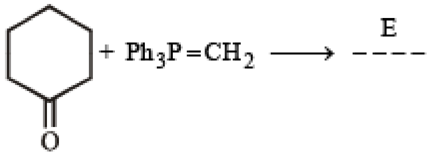
(x) o - HOOC - C_6H_4 - CH_2- C_6H_5

$\xrightarrow{SOCl_2} \overset{\textbf{G}}{\text{------}} \xrightarrow[AlCl_3]{\text{anhydrous}} \overset{\textbf{H}}{\text{------}}$

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

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

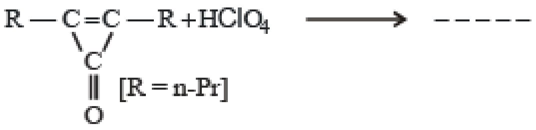


(xii) 

(1997 - 1 Mark)

(xiii) $(COOH)_2 + (CH_2OH)_2 +$ Conc.H_2SO_4

$\longrightarrow \overset{F}{----}$ **(1997 - 1 Mark)**

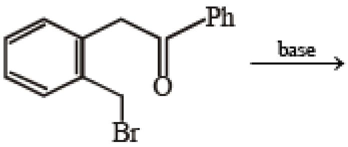
(xiv) 

(1997 - 1 Mark)

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

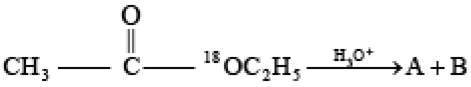
(xvi) $H_3CCOCOC_6H_5 + NaOH / H_3O^{\oplus} \rightarrow$ -- -- (1997 - 1 Mark)

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

(xviii) 

(2000 - 1 Mark)

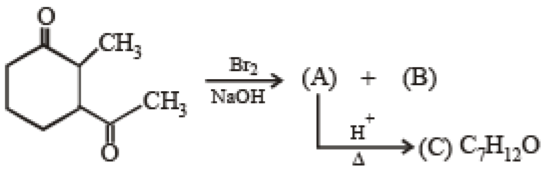
(xix) Write the structures of the products A and B.



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

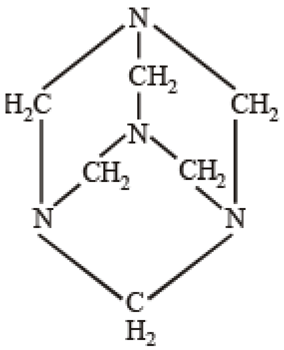
(2000 - 2 Marks)

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

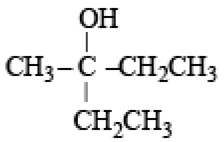


(2000 - 3 Marks)

Solution. (i)

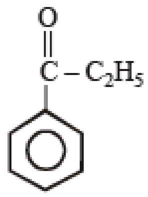


Hexamethylenetetramine (Urotropine)

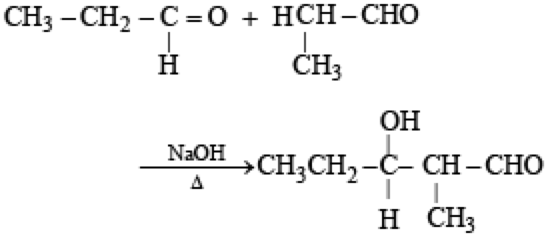
(ii) 

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

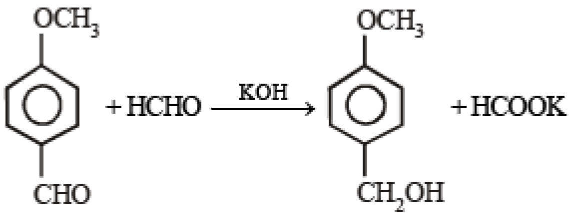
2−Ethylbutanol−2

(iii) 

Phenyl ethyl ketone

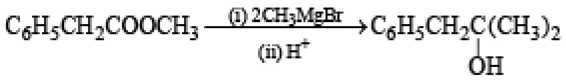
(iv) 

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

(v) 

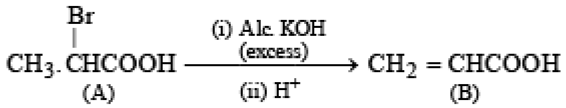
(vi) $C_6H_5COOH + CH_3MgI \longrightarrow CH_4 + C_6H_5COO\,MgI$

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



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

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



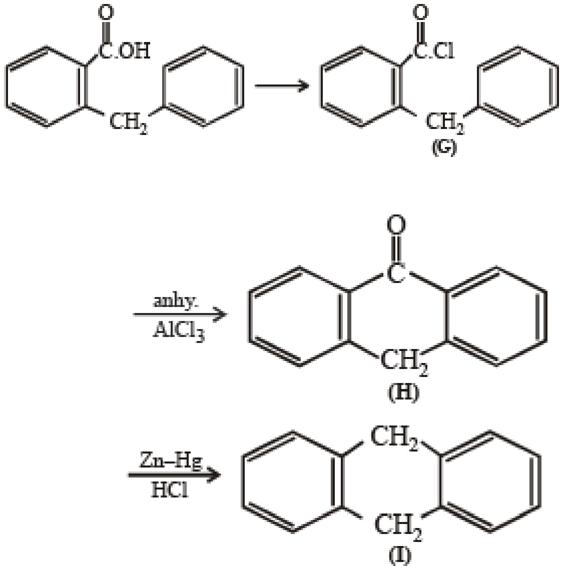
$$CH_3.\overset{\overset{Br}{|}}{C}HCOOH \ (A) \xrightarrow[\text{(ii) } H^+]{\text{(i) Alc. KOH (excess)}} CH_2 = CHCOOH \ (B)$$

(ix) $C_6H_5CHO + CH_3COOC_2H_5$

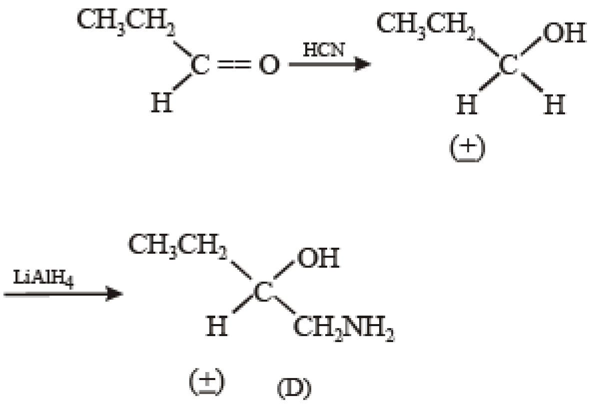
$$\xrightarrow[\text{absolute alcohol, heat}]{NaOC_2H_5 \text{ in}} C_6H_5CH = CHCOOC_2H_5 \ (D)$$

(Claisen condensation)

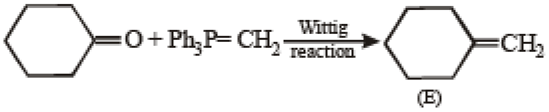
(x)

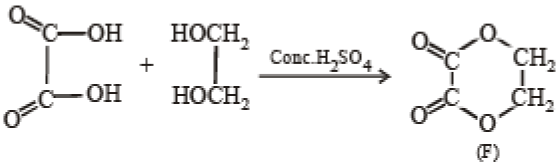


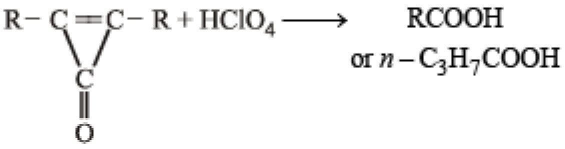
(xi) $KCN + H_2SO_4 \longrightarrow KHSO_4 + HCN$



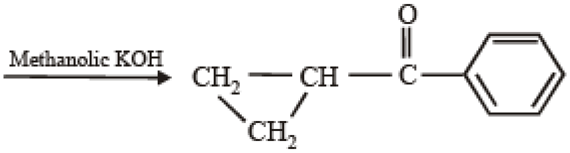
(xii)

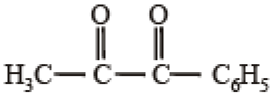


(xiii) 

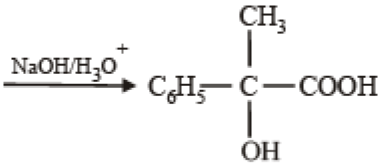
(xiv) 

(xv) $ClCH_2CH_2CH_2COPh$



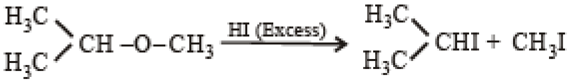
(xvi) 

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

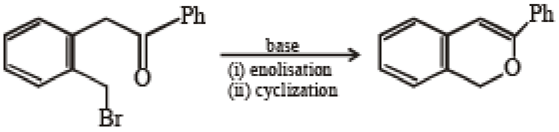


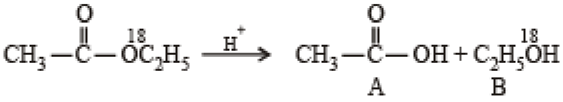
$\xrightarrow{NaOH/H_3O^+} C_6H_5-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-COOH$

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

(xvii) 

$(H_3C)_2CH-O-CH_3 \xrightarrow{HI\ (Excess)} (H_3C)_2CHI + CH_3I$

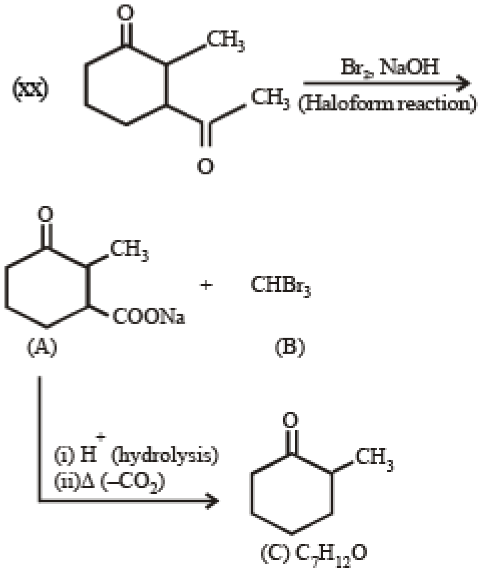
(xviii) 

(xix) 

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

(Ester hydrolysis involves acyl-oxygen fission)

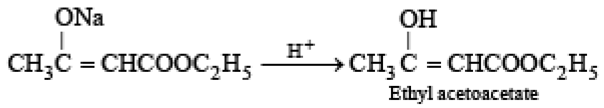
(xx)



Q.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)

Solution.

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



$$CH_3\overset{\overset{\displaystyle ONa}{|}}{C} = CHCOOC_2H_5 \xrightarrow{H^+} \underset{\text{Ethyl acetoacetate}}{CH_3\overset{\overset{\displaystyle OH}{|}}{C} = CHCOOC_2H_5}$$

Q.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) Eth anoic acid to a mixture of meth anoic acid and diphenyl ketone. (1990 - 2Marks)

(vi) Carry out the following transformation in not more than three steps. (1999 - 3 Marks)

Solution.

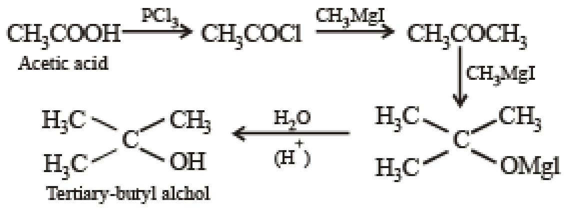
(i) $\underset{\text{Methanal}}{HCHO} \xrightarrow{[O]} HCOOH \xrightarrow{Ca(OH)_2}$

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

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

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

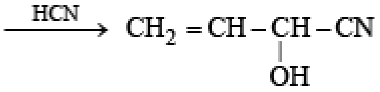
(iii)



(iv)

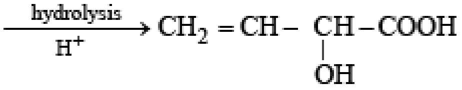
$$\underset{\text{ethanal}}{CH_3.CHO} \xrightarrow{HCHO/NaOH} \underset{OH}{\underset{|}{CH_2}}CH_2CHO$$

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



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

propenal cyanohydrin

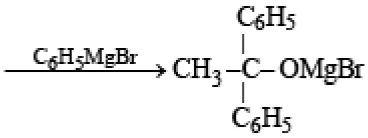


$$\xrightarrow[H^+]{\text{hydrolysis}} CH_2=CH-\underset{OH}{\underset{|}{CH}}-COOH$$

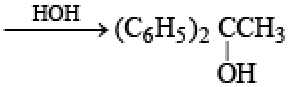
2−hydroxy−3− butenoic acid

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

$$\xrightarrow{C_6H_5MgBr} C_6H_5COCH_3$$



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



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

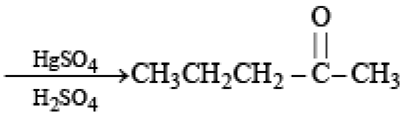
$$\xrightarrow[-H_2O]{\text{heat}} (C_6H_5)_2C=CH_2$$

$$\xrightarrow{CrO_3} C_6H_5COC_6H_5 + HCOOH$$

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

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

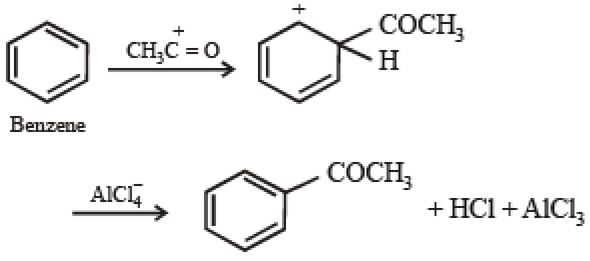
$$\xrightarrow{CH_3I} CH_3CH_2-C\equiv C-CH_3$$



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

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

Solution. $CH_3COCl + AlCl_3 \rightarrow CH_3C^+=O + AlCl_4^-$



Benzene

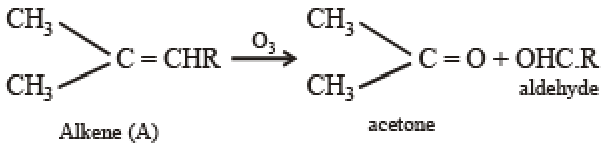
Acetophenone

Q.5. An alkene (A) on ozonolysis yields acet one 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)

Ans.

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

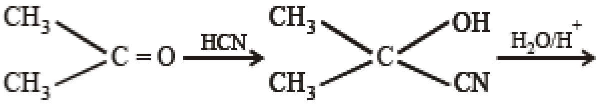
Solution. Ozonolysis of (A) to acetone and an aldehyde indicates the following part structure of alkene (A):

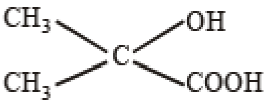


As per problem :

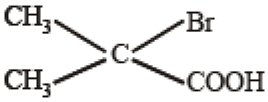
$$\mathrm{RCHO} \xrightarrow{[O]} \mathrm{RCOOH[B]} \xrightarrow{P/Br_2}$$

Bromo compound $[C] \xrightarrow{H_2O}$ Hydroxy acid [D] Structure of (D) is determined by the reaction:

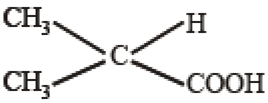



(D)

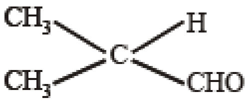
The compound (D) is obtained by hydrolysis of (C) with aqueous alkali since (C) is a bromo compound, therefore it has a bromo group where the compound (D) has a hydroxyl group. Therefore, structure of C is



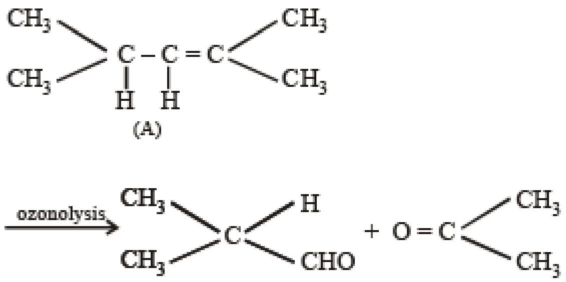
The compound (C) is formed by bromination of compound (B), therefore, the compound (B) is



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



Q.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)

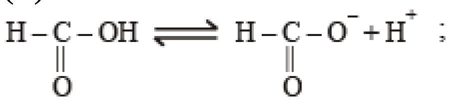
(v) Iodoform is obtained by the reaction of acetone with hypoiodite but not with iodide ion. (1991 - 1 Mark)

(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)

Solution. (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 a – H atoms) on which halogenation takes place.

(ii)

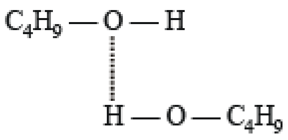


$$H-\underset{\underset{O}{\|}}{C}-OH \rightleftharpoons H-\underset{\underset{O}{\|}}{C}-O^- + H^+ \;;$$

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

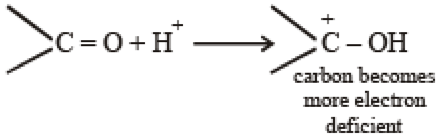
Presence of CH_3 gp in acetate ion shows +I effect and thereby intensifying charge on O^- of acetate ion which is thus destabilized. Thus formate ion is more stable than acetate ion or HCOOH loses proton more easily than CH_3COOH.

(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.



$$>C=O+H^+ \longrightarrow >\overset{+}{C}-OH$$

carbon becomes more electron deficient

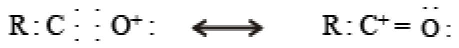
In strongly acidic medium (pH < 3.5), the unshared pair of electrons of N of the reagent is protonated with the result nucleophile (NH_2NH_2) is converted to an electrophile ($NH_2N^+H_3$)which cannot react. Hence in highly acidic medium, there is no protonation of the carbonyl group.

(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.

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

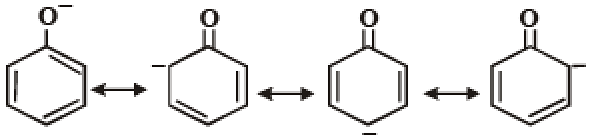
(vi) In the acylium ion ($R - C \equiv O^+$), each and every element has a complete octet, while in carbonium ion ($R - C^+ = O$), carbon bearing positive charge has uncomplete octet which makes it more reactive than the former.



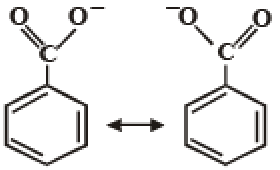
Acylium ion **Carbonium ion**

(Carbon has only six electrons)

(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

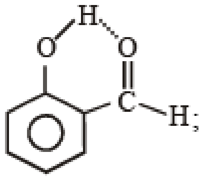


Resonating structures of benzoate ion

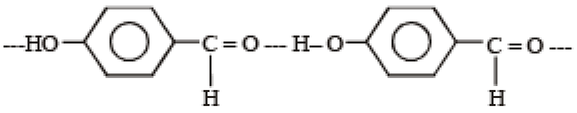
The benzoate ion is more stabilized because the negative charge on both structures is on the more electronegative oxygen atom, whereas in phenoxide ion, it is on the less electronegative carbon atoms.

(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)

Q.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)

Ans. $\underset{A}{CH_3.CH_2OH},\ \underset{B}{CH_2=CH_2},\ \underset{C}{CH\equiv CH},\ \underset{D}{CH_3.CHO}$

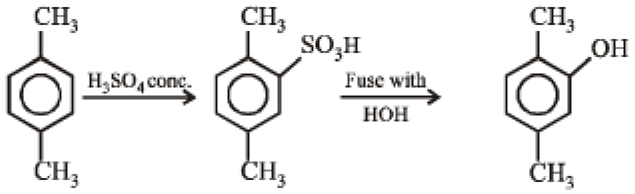
Solution.

(*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*) $CH_3I + KCN(alc) \xrightarrow{-KI} CH_3CN$

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

Solution.

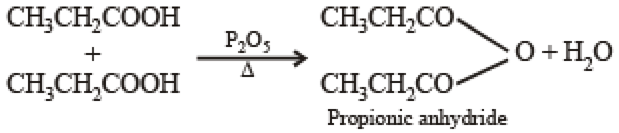


2, 5- Dimethylphenol

Q.9. Write down the reactions involved in the preparation of the following using the reagents indicated against it in parenthesis:
Propionic anhydride from propionaldehyde
$[AgNO_3/NH_4OH, P_2O,]$. (1984 - 2 Marks)

Solution.

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



$$\begin{matrix} CH_3CH_2COOH \\ + \\ CH_3CH_2COOH \end{matrix} \xrightarrow[\Delta]{P_2O_5} \begin{matrix} CH_3CH_2CO \\ CH_3CH_2CO \end{matrix} \!\!> O + H_2O$$

Propionic anhydride

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

Solution. 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.

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

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

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

Solution. 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:

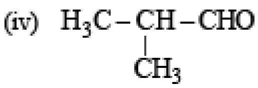
$$NH_2^- > OR^- > OCOR^- > Cl^-$$

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.

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

Q.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) 

$\underset{\displaystyle CH_3}{H_3C-\underset{|}{CH}-CHO}$

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

Ans. $\underset{A}{C_2H_5CH(Cl).CH(CH_3)_2}$, $\underset{B}{CH_3CH=CH.CH(CH_3)_2}$, $\underset{C}{C_2H_5CH=C(CH_3)_2}$

Solution. Let us summaries the given facts.

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

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

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

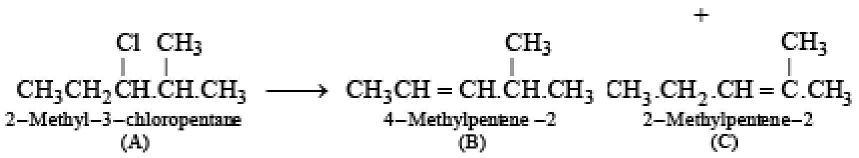
NOTE THIS STEP: With the help of structures of the four carbonyl compounds, (i) to (iv), we may write the structures of the two isomeric olefins (B) and (C).

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)]

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

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

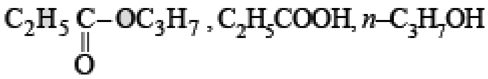
Thus the compound (A) should be a chloride that can eliminate a molecule of HCl to give B as well as C.



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

Q.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)

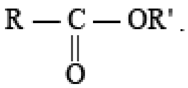
and (Z)? (1986 - 3 Marks)



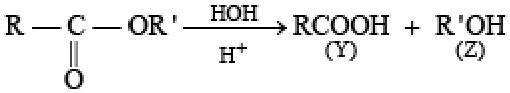
$\underset{\underset{O}{\|}}{C_2H_5\,C{-}OC_3H_7}$, C_2H_5COOH, $n{-}C_3H_7OH$

Ans. (X) (Y) (Z)

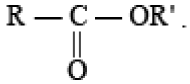
Solution. (X) is hydrolysed to give an acid (Y) and an alcohol (Z) and thus X is an ester;



$R - \underset{\underset{O}{\|}}{C} - OR'$.



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

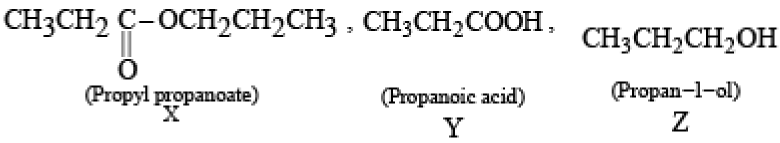


$R - \underset{\underset{O}{\|}}{C} - OR'$.

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

or $RCH_2OH \longrightarrow RCOOH$ ($\because$ R' is $R{-}CH_2$)

Hence X, Y and Z are



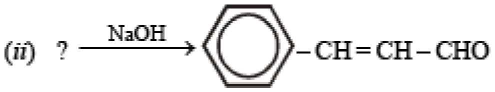
$\underset{\underset{O}{\|}}{CH_3CH_2\,C{-}OCH_2CH_2CH_3}$, CH_3CH_2COOH, $CH_3CH_2CH_2OH$

(Propyl propanoate) X (Propanoic acid) Y (Propan–1–ol) Z

Q.14. Complete the following with appropriate structures:

(*i*) $(CH_3CO)_2O \xrightarrow{C_2H_5OH} CH_3COOH + ?$ **(1986 - 1 Mark)**

(*ii*)



$? \xrightarrow{NaOH} C_6H_5{-}CH{=}CH{-}CHO$

(1986 - 1 Mark)

Solution.

(*i*) $\underset{\underset{O}{\|}}{CH_3\,C{-}OC_2H_5}$ (*iii*) $C_6H_5{-}CHO + CH_3CHO$

Q.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 disulphide addition compound and gives a positive iodoform test. What are the possible structures for the unknown

compound? (1987 - 5 Marks)

Solution. (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**

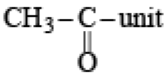
∴ Empirical formula of compound is $C_5H_{10}O$ and empirical formula wt. = 86.
Also molecular wt. = 86.

∴ 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



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

(v) Above facts reveal that the compound is

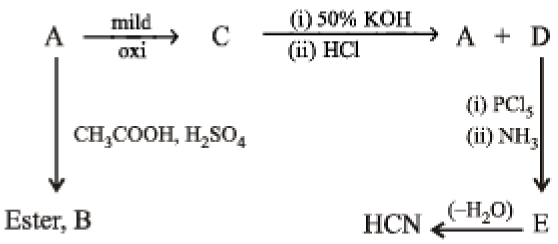
$\underset{\text{pentan-2-one}}{CH_3CH_2CH_2COCH_3}$ or $\underset{\text{3-methylbutan-2-one}}{(CH_3)_2CHCOCH_3}$

Subjective Ques of Aldehydes, Ketones & Carboxylic Acids, (Part - 2)

Q.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)

Ans. $\underset{A}{CH_3OH}, \underset{B}{CH_3COOCH_3}, \underset{C}{HCHO}, \underset{D}{HCOOH}, \underset{E}{HCONH_2}$

Solution. TIPS/Formulae:

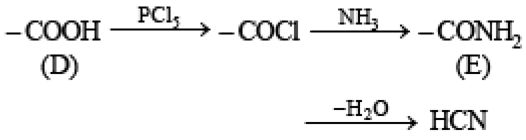


The above reactions lead to following conclusions.

(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.



$$\underset{(D)}{-COOH} \xrightarrow{PCl_5} -COCl \xrightarrow{NH_3} \underset{(E)}{-CONH_2} \xrightarrow{-H_2O} HCN$$

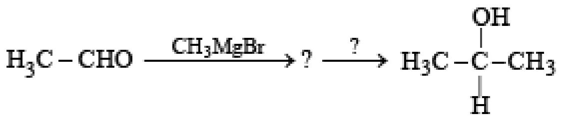
Formation of HCN by the dehydration of E establishes that E is $HCONH_2$ and hence D is HCOOH.

(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

Q.17. Complete the following reactions :

(i) 

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

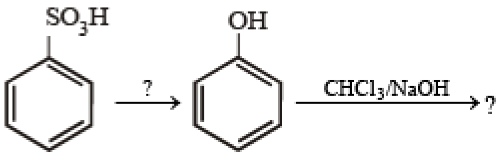
(1988 - 1 Marks)

(ii) $CH_3COOH \xrightarrow{?} ClCH_2COOH \xrightarrow{\text{excess ammonia}} ?$ **(1988 - 1 Marks)**

(iii) 

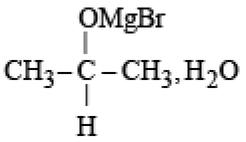
$$2CH_3\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow{\text{base catalyst}} ? \xrightarrow{\text{acid catalyst}} ?$$

(1988 - 1 Marks)

(iv) 

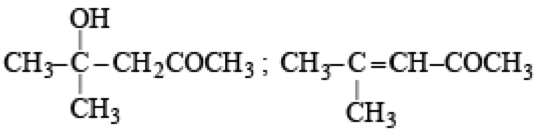
(1988 - 1 Marks)

Solution.

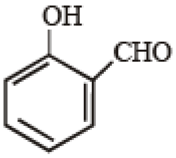
(i) 

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

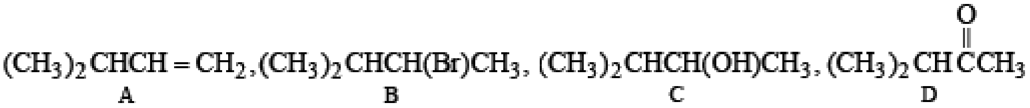
(ii) $P/Cl_2, NH_2CH_2COONH_4$

(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^+ ; 

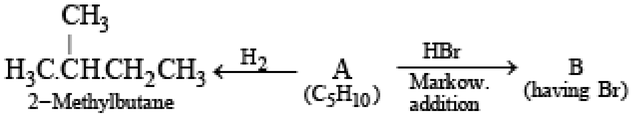
Q.18. A hydrocarbon A (molecular formula C_5H_{10}) yields 2-methylbutane on catalytic hydrogenation. A adds HBr (in accordance with Markownikoff's rule) to form a compound B which on reaction with silver hydroxide forms an alcohol C, $C_5H_{12}O$. Alcohol C on oxidation gives a ketone D. Deduce the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

Ans. 

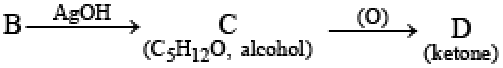
$$\underset{A}{(CH_3)_2CHCH=CH_2}, \underset{B}{(CH_3)_2CHCH(Br)CH_3}, \underset{C}{(CH_3)_2CHCH(OH)CH_3}, \underset{D}{(CH_3)_2CH\overset{\overset{O}{\|}}{C}CH_3}$$

Solution. TIPS/Formulae :

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



$$\underset{\text{2-Methylbutane}}{H_3C\overset{\overset{CH_3}{|}}{C}HCH_2CH_3} \xleftarrow{H_2} \underset{(C_5H_{10})}{A} \xrightarrow[\text{Markow. addition}]{HBr} \underset{\text{(having Br)}}{B}$$



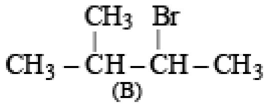
$$B \xrightarrow{AgOH} \underset{(C_5H_{12}O,\ \text{alcohol})}{C} \xrightarrow{(O)} \underset{\text{(ketone)}}{D}$$

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.



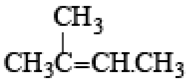
$$\underset{(B)}{CH_3-\overset{\overset{CH_3}{|}}{C}H-\overset{\overset{Br}{|}}{C}H-CH_3}$$

(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.

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

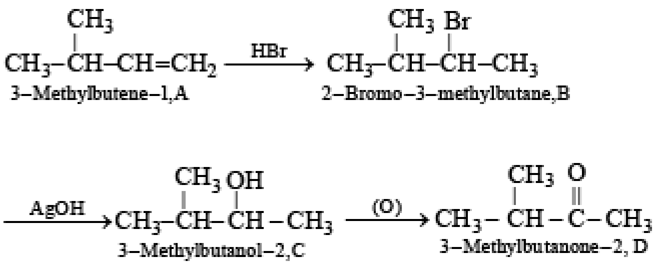
(A)



$CH_3\overset{CH_3}{\overset{|}{C}}=CHCH_3$

(A')

Thus the reaction involved can be represented as below:

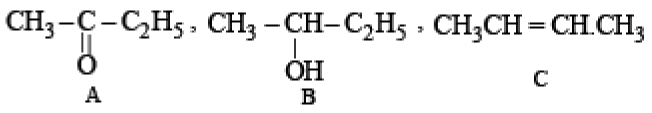


$$\underset{\text{3–Methylbutene–1,A}}{CH_3-\overset{CH_3}{\overset{|}{C}H}-CH=CH_2}\xrightarrow{HBr}\underset{\text{2–Bromo–3–methylbutane,B}}{CH_3-\overset{CH_3}{\overset{|}{C}H}-\overset{Br}{\overset{|}{C}H}-CH_3}$$

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

Q.19. A ketone 'A' which undergoes halo form 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)

Ans.



$$\underset{A}{CH_3-\underset{\underset{O}{||}}{C}-C_2H_5},\ \underset{B}{CH_3-\underset{\underset{OH}{|}}{C}H-C_2H_5},\ \underset{C}{CH_3CH=CHCH_3}$$

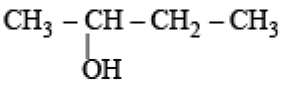
Solution. The compound A, a ketone, undergoes haloform reaction.

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,

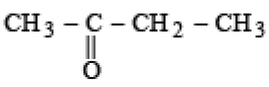
i.e. $CH_3 – CH = CH – CH_3$ (butene-2).

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



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

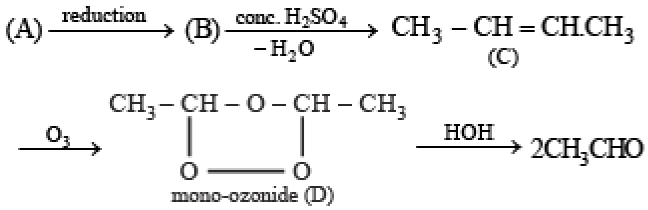
butan–2–ol (B)



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

butan–2–one (A)

The reactions involved:



Q.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)

Ans. 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

$$\%\text{ of H} = \frac{2}{18} \times \frac{0.08}{0.40} \times 100 = 2.22\%$$
$$\%\text{ of C} = \frac{12}{44} \times \frac{0.39}{0.40} \times 100 = 27.30\%$$
$$\%\text{ of O} = 100 - (2.22 + 27.30) = 71.48\%$$

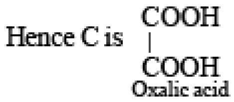
By usual method, empirical formula of acid C = CHO_2

$$\text{Eq. wt. of acid C} = \left(\frac{1.0}{0.71} \times 108\right) - 107 = 45$$

Mol. wt. of acid C = 45 × 2 = 90

∴ Mol. formula of C = $C_2H_2O_4$

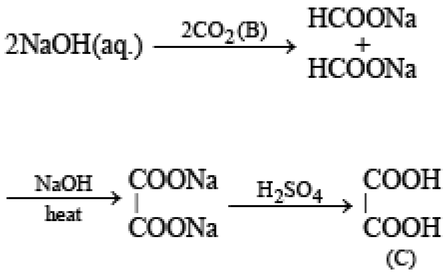
Since it is dicarboxylic acid, it must have two –COOH groups.



Hence C is $\begin{matrix} COOH \\ | \\ COOH \end{matrix}$ 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.



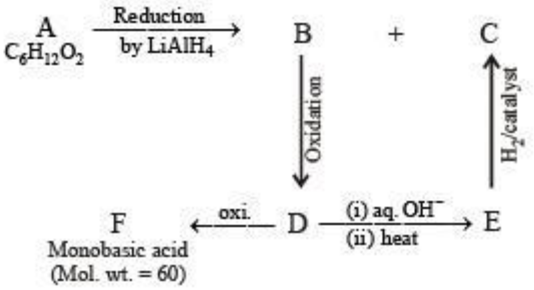
$$2NaOH(aq.) \xrightarrow{2CO_2(B)} \begin{matrix} HCOONa \\ + \\ HCOONa \end{matrix}$$

$$\xrightarrow[heat]{NaOH} \begin{matrix} COONa \\ | \\ COONa \end{matrix} \xrightarrow{H_2SO_4} \underset{(C)}{\begin{matrix} COOH \\ | \\ COOH \end{matrix}}$$

Q.21. Compound A ($C_6H_{12}O_2$) on reduction with LiAlH4 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)

Ans. $C_3H_7COOC_2H_5$, C_2H_5OH, C_4H_9OH, CH_3CHO

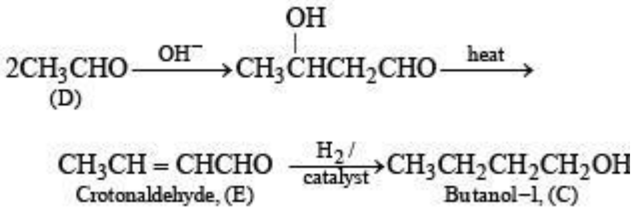
Solution. TIPS/FORMULAE :



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.

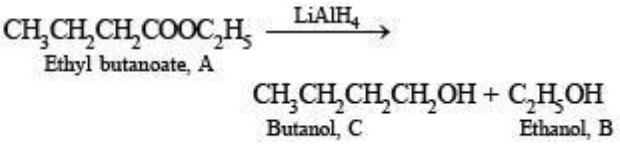
Acetaldehyde (D) on treating with aqueous alkali will undergo aldol condensation.



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

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

Nature of A. Thus it is evident that reduction of A with LiAlH4 gives two alcohols; B (ethanol) and C (butanol). Hence A must be an ester i.e., ethyl butanoate ($CH_3CH_2CH_2COOC_2H_5$).

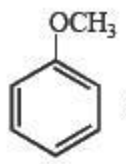


$$\underset{\text{Ethyl butanoate, A}}{CH_3CH_2CH_2COOC_2H_5} \xrightarrow{LiAlH_4}$$

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

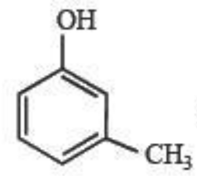
Q.22. An organic compound containing C, H and O exists in two isomeric forms A and B. An amount of 0.108 g of one of the isomers gives on combustion 0.308 g of CO_2 and 0.072 g of H_2O. A is insoluble in NaOH and $NaHCO_3$ while B is soluble in NaOH. A reacts with conc. HI to give compounds C and D. 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)

Ans.



Anisole (A)

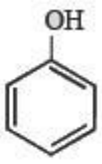
;



m-Cresol, (B)

; CH_3I ;

(C)



(D)

;

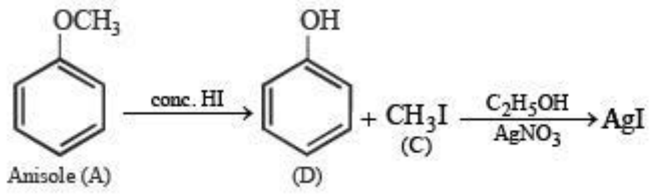
(E), $C_7H_5OBr_3$

Solution. Empirical formula of A and B.

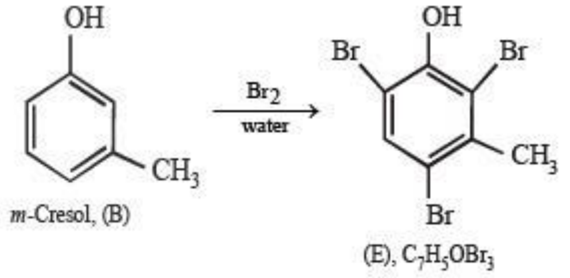
	Relative No. of atoms	Simplest ratio
$\% \text{ of } C = \frac{12}{44} \times \frac{0.308}{0.108} \times 100 = 77.77$	$\frac{77.77}{12} = 6.48$	$\frac{6.48}{0.92} = 7$
$\% \text{ of } H = \frac{2}{18} \times \frac{0.072}{0.108} \times 100 = 7.40$	$\frac{7.40}{1} = 7.40$	$\frac{7.40}{0.92} = 8$
$\therefore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

∴ Empirical formula of A and B = $C7H_8O$

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.



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.



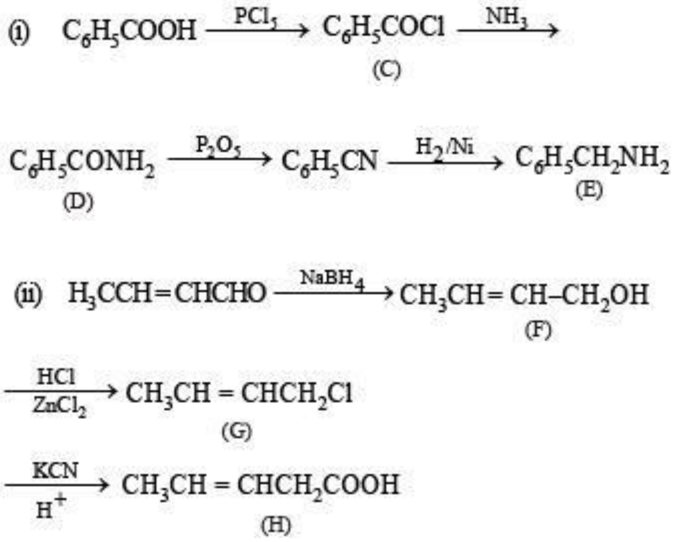
Q.23. (i) $C_6H_5COOH \xrightarrow{PCl_5} C \xrightarrow{NH_3} D \xrightarrow{P_2O_5} C_6H_5CN \xrightarrow{H_2/Ni} E;$

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)

Solution.



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

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

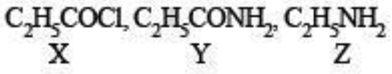
(ii) $H_3CCH{=}CHCHO \xrightarrow{NaBH_4} \underset{(F)}{CH_3CH{=}CH{-}CH_2OH}$

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

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

Q.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)

Ans.



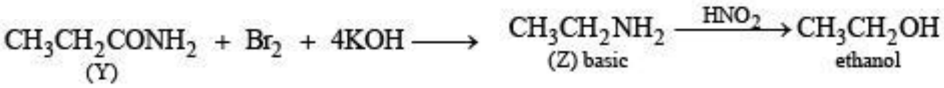
$\underset{X}{C_2H_5COCl}, \underset{Y}{C_2H_5CONH_2}, \underset{Z}{C_2H_5NH_2}$

Solution. 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

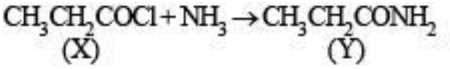
∴ Empirical formula of (Y) is C_3H_7NO.

(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.



$$\underset{(Y)}{CH_3CH_2CONH_2} + Br_2 + 4KOH \longrightarrow \underset{(Z)\text{ basic}}{CH_3CH_2NH_2} \xrightarrow{HNO_2} \underset{\text{ethanol}}{CH_3CH_2OH}$$

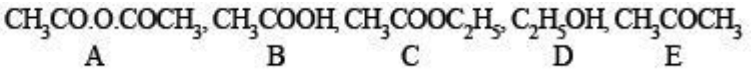
Y is formed from (X) having Cl on treatment with NH_3 and so (X) is CH_3CH_2COCl i.e. propanoyl chloride.



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

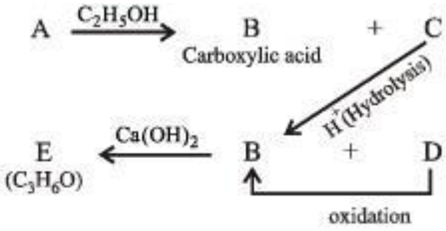
Q.25. An organic compound ‘A’ on treatment with ethyl alcohol gives a carboxylic acid ‘B’ and compound ‘C’. Hydrolysis of ‘C’ under acidic conditions gives ‘B’ and ‘D’. Oxidation of ‘D’ with $KMnO_4$ also gives ‘B’. ‘B’ on heating with $Ca(OH)_2$ gives ‘E’ (molecular formula, C_3H_6O). ‘E’ does not give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

Ans.



$$\underset{A}{CH_3CO.O.COCH_3},\ \underset{B}{CH_3COOH},\ \underset{C}{CH_3COOC_2H_5},\ \underset{D}{C_2H_5OH},\ \underset{E}{CH_3COCH_3}$$

Solution. TIPS/Formulae:



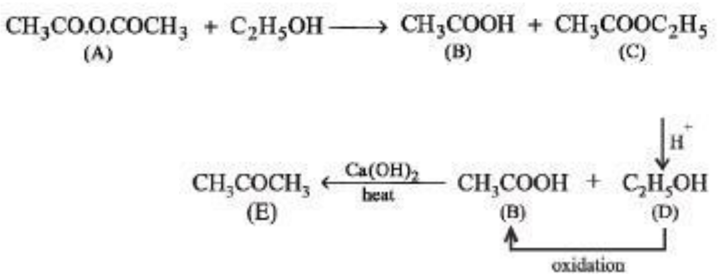
(i) Since E (C_3H_6O) forms a 2, 4-dinitrophenylhydrazone but does not reduce Tollen’s reagent and Fehling solution, it must be a ketone, $CH_3.CO.CH_3$.

(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.



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

$$\underset{(E)}{CH_3COCH_3} \xleftarrow[\text{heat}]{Ca(OH)_2} \underset{(B)}{CH_3COOH} + \underset{(D)}{C_2H_5OH}$$

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

$CH_3COCH_2CHO_3$ CH_3COCH_3, CH_3CHO, $CH_3COCH_2COCH_3$

Ans. $CH_3CHO < CH_3COCH_3 < CH_3COCH_2CHO < CH_3COCH_2COCH_3$

Solution. $CH_3CHO < CH_3COCH_3 < CH_3COCH_2COCH_3 < CH_3COCH_2CHO$

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

$$\begin{array}{cccccc} PCl_5 & + & SO_2 & \longrightarrow & A & + & B \\ A & + & CH_3COOH & \longrightarrow & C & + & SO_2 + HCl \\ 2C & + & (CH_3)_2Cd & \longrightarrow & 2D & + & CdCl_2 \end{array}$$

Ans. $\underset{A}{SOCl_2}, \underset{B}{POCl_3}, \underset{C}{CH_3COCl}, \underset{D}{CH_3COCH_3}$

Solution.

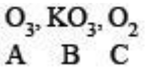
$$PCl_5 + SO_2 \longrightarrow \underset{(A)}{SOCl_2} + \underset{(B)}{POCl_3}$$

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

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

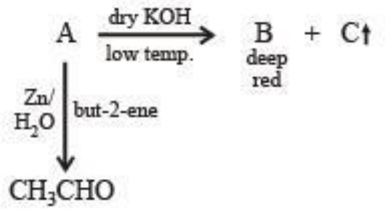
Q.28. When gas A is passed through dry KOH at low temperature, a deep red

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)**

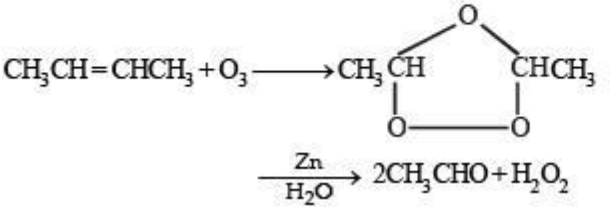
Ans. 

$\underset{A}{O_3}, \underset{B}{KO_3}, \underset{C}{O_2}$

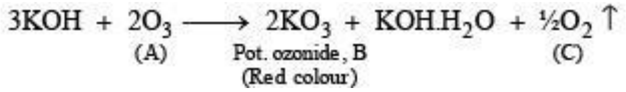
Solution. TIPS/Formulae :



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).

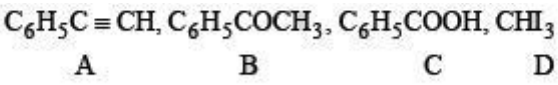


Reaction of ozone with KOH.



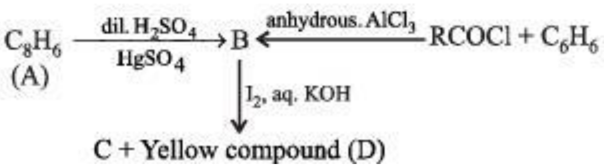
$3KOH + \underset{(A)}{2O_3} \longrightarrow \underset{\substack{\text{Pot. ozonide, B} \\ \text{(Red colour)}}}{2KO_3} + KOH.H_2O + \underset{(C)}{½O_2}\uparrow$

Q.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)**

Ans. 

$\underset{A}{C_6H_5C\equiv CH}, \underset{B}{C_6H_5COCH_3}, \underset{C}{C_6H_5COOH}, \underset{D}{CHI_3}$

Solution. TIPS/Formulae:



(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.

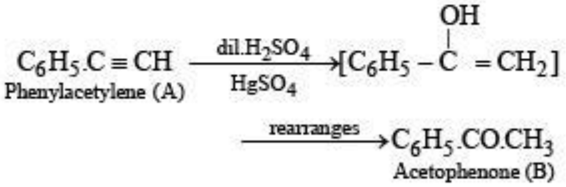
(ii) Further th e keton e (B) reacts with alkaline iodine forming yellow compound (D) (haloform reaction). This indicates that one of the alkyl groups in ketone B is – CH3. Hence it should be $C_6H_5.CO.CH$,.

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

Thus compounds (A) to (D) are

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

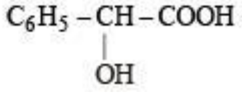
Formation of (B) from (A)



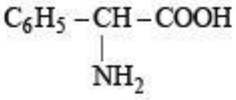
Q.30. Which of the following carboxylic acids under goes decarboxylation easily? Explain briefly. (1995 - 2 Marks)

(i) C_6H_5–CO–CH_2–COOH

(ii) C_6H_5–CO–COOH

(iii)


$C_6H_5-\underset{OH}{\underset{|}{CH}}-COOH$

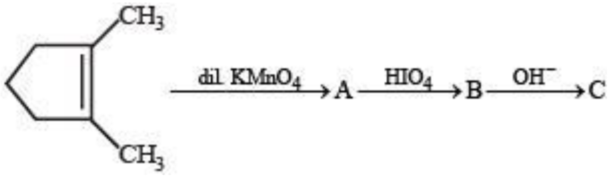
(iv)


$C_6H_5-\underset{NH_2}{\underset{|}{CH}}-COOH$

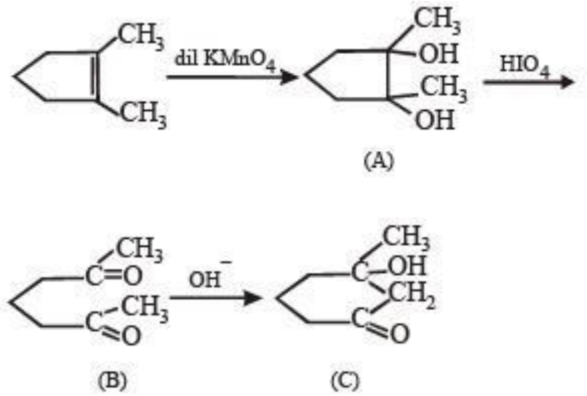
Solution. (i) β-Keto acids are unstable and undergo decarboxylation most readily.

Subjective Ques of Aldehydes, Ketones & Carboxylic Acids, (Part - 3)

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



Solution.



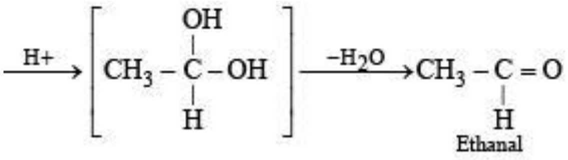
The last step is intramolecular aldol condensation.

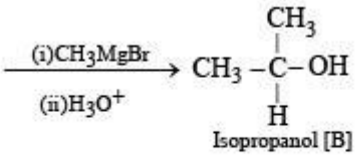
Q.32. An ester A ($C_4H_8O_2$), on treatment with excess methyl magnesium chloride followed by acidification, gives an alcohol B as the sole organic product. Alcohol B, on oxidation with NaOCl followed by acidification, gives acetic acid. Deduce the structures of A and B. Show the reactions involved.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

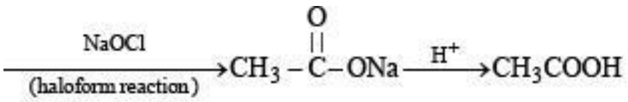
Ans.

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

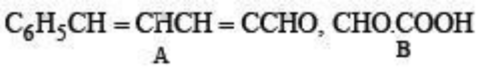
Solution. We know that esters on treatment with excess of methyl magnesium chloride either give secondary alcohols (from alkyl formats) or tertiary alcohols (from esters other than formats). However, tertiary alcohols are not easily oxidised, hence the alcohol should be secondary alcohol and thus ester is alkyl format. 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.







Q.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)

Ans. 

$$\underset{A}{C_6H_5CH=CHCH=CCHO},\ \underset{B}{CHO.COOH}$$

Solution. Following informations are provided by the problem.

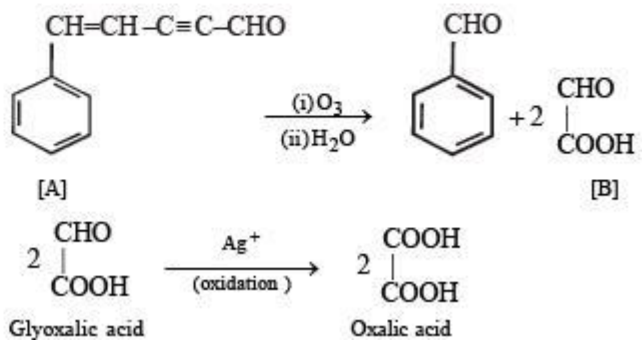
(i) Since aldehyde A ($C_{11}H_8O$) gives C_6H_5CHO on ozonolysis, it must have a benzene nucleus and a side chain. The side chain should have five carbon (C_{11}–C_6 =C_5), three hydrogen (H_8-H_5=H_3) and one oxygen atom, i.e., it should be C_5H_3O. Further the compound A has an aldehydic group, so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

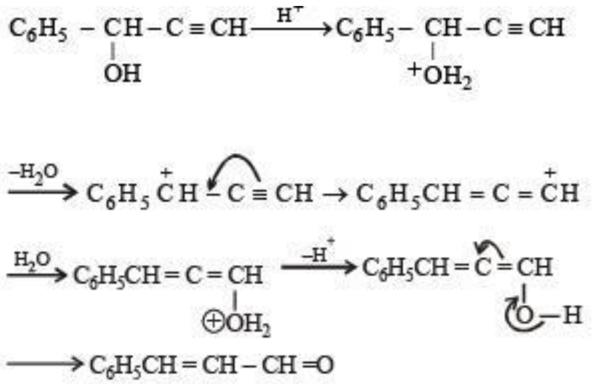
(v) Thus compound A should possess following structure which explains all the given reactions.



Q.34. Write the intermediate steps for the following reaction. (1998 - 2 Marks)

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

Solution.



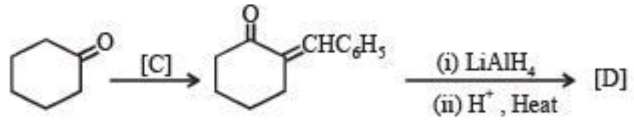
$$C_6H_5-\underset{OH}{\underset{|}{CH}}-C\equiv CH \xrightarrow{H^+} C_6H_5-\underset{^+OH_2}{\underset{|}{CH}}-C\equiv CH$$

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

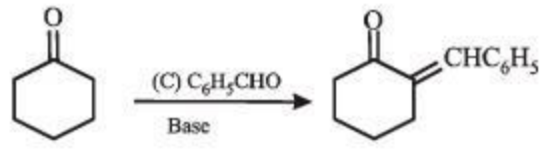
$$\xrightarrow{H_2O} C_6H_5CH=C=\underset{\oplus OH_2}{\underset{|}{CH}} \xrightarrow{-H^+} C_6H_5CH=C=\underset{O-H}{\underset{|}{CH}}$$

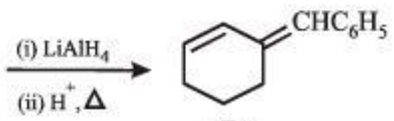
$$\longrightarrow C_6H_5CH=CH-CH=O$$

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



Solution.



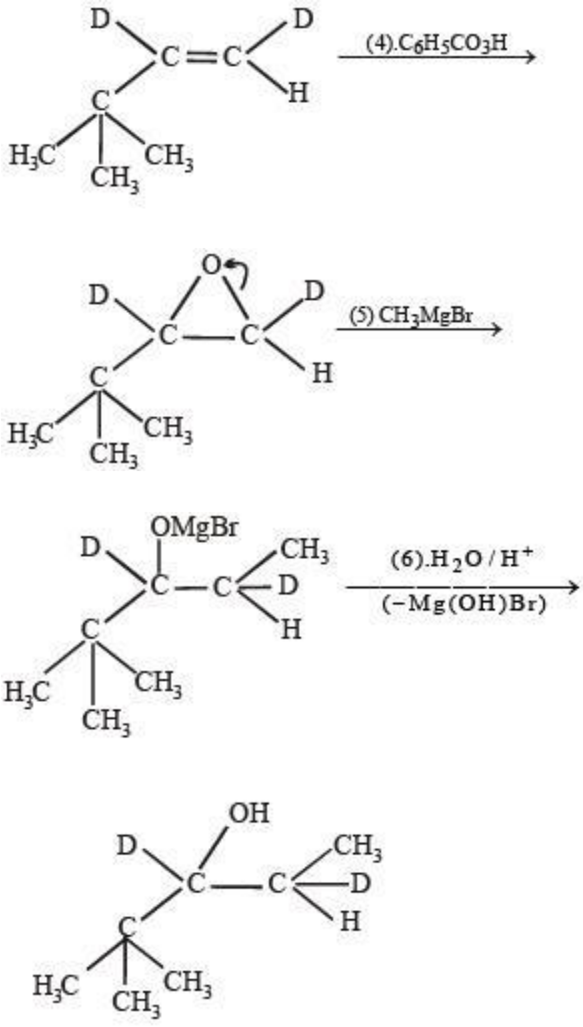


(D)

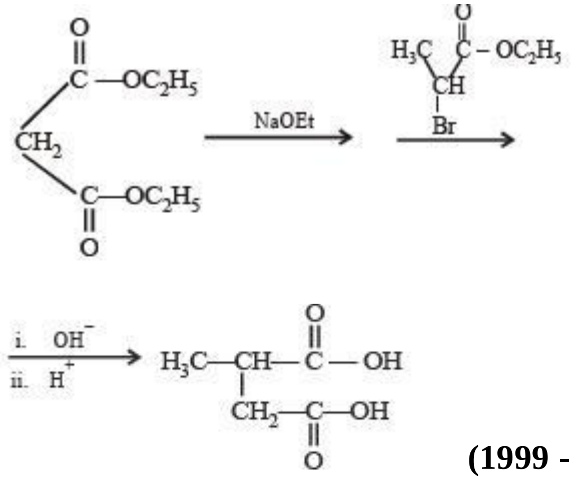
LiAlH$_4$ reduces only ketonic group to 2° alcoholic group without affecting double bond.

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

Solution.

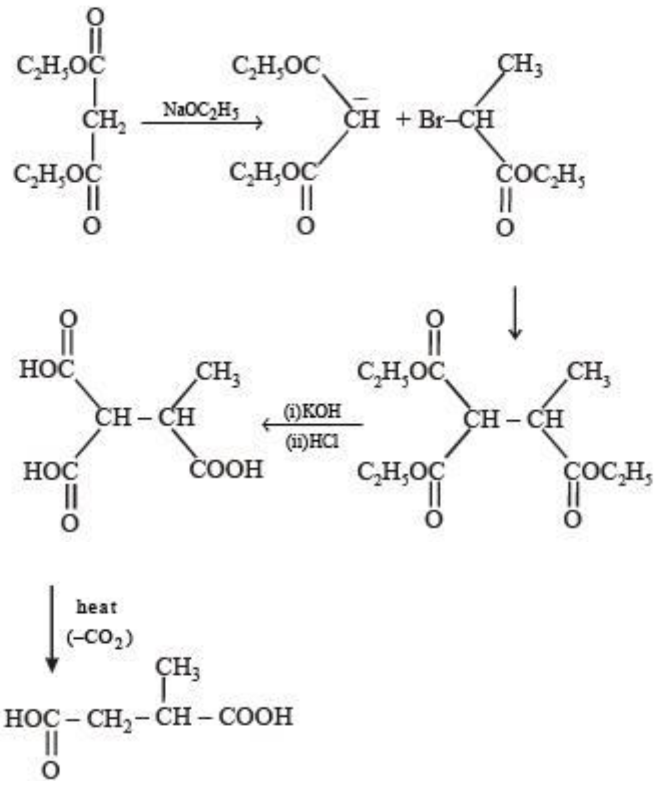


Q. 37. Explain briefly the formation of the products giving the structures of the intermediates.



(1999 - 5 Marks)

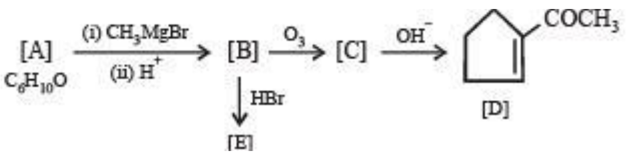
Solution.



Q.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)

Solution. TIPS/Formula:

The given reaction can be summarised as below :



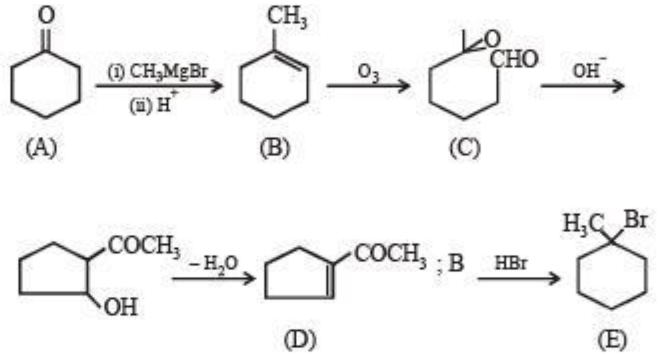
Conclusions from the set of reactions

(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.

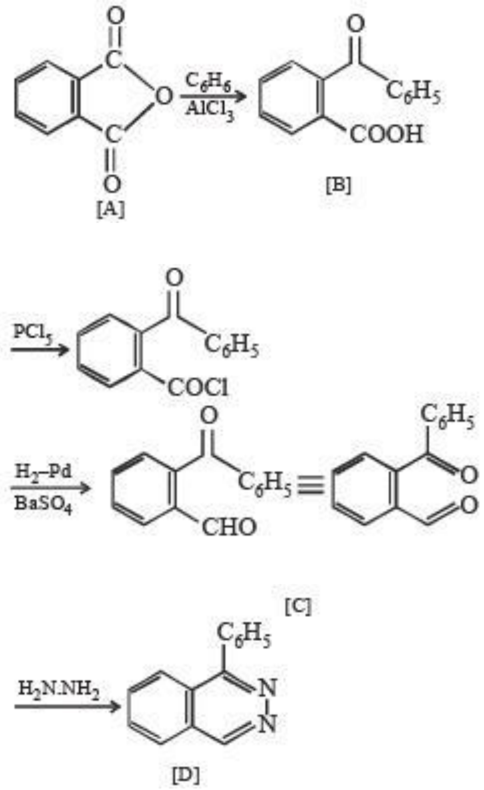
(iii) As B undergoes ozonolysis to form C, It must have a double bond, and C must have two carbonyl groups.

(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.

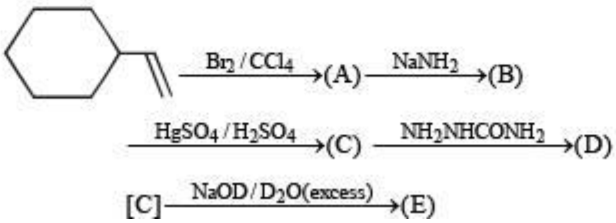


Q.39. An organic compound A, $C_8H_4O_3$, in dry benzene in the presence of anhydrous $AlCl_3$gives compound B. The compound B on treatment with PCl_5, followed by reaction with H_2/Pd ($BaSO_4$) gives compound C, which on reaction with hydrazine gives a cyclic compound D ($C_{14}H_{10}N_2$).
Identify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

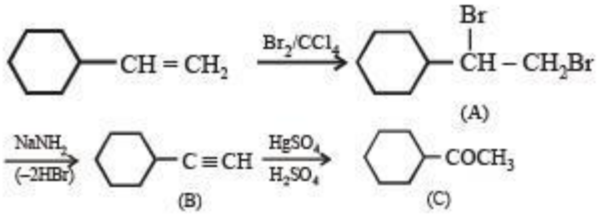
Solution.

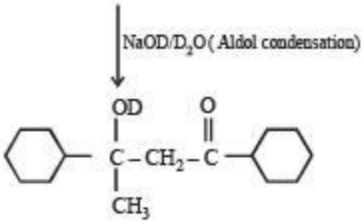


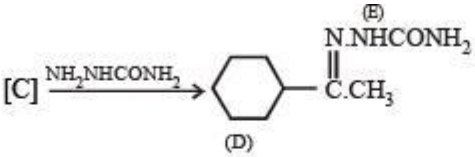
Q.40. Identify (A), (B), (C), (D) and (E) in the following schemes and write their structures:



Solution.







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

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

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

(2001 - 5 Marks)

Explain the formation of labelled formaldehyde (H$_2$C*O) as one of the products when compound (Z) is treated with HBr and subsequently ozonolysed. Mark the C* carbon in the entire scheme.

Ans. $\underset{X}{\overset{*}{C}O_2}$, $\underset{Y}{CH_2=CH\overset{*}{C}OOH}$, $\underset{Z}{CH_2=CH\overset{*}{C}H_2OH}$

Solution.

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

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

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

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

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

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

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

Q.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)

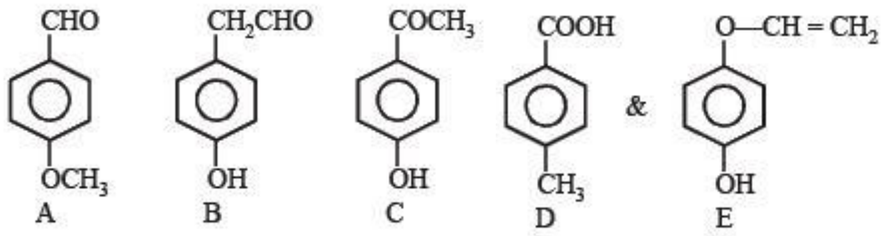
(i) Both A and B form a silver mirror with Tollen's reagent; also B gives a positive test with $FeCl_3$ solution.

(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.

Ans.

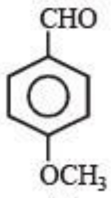


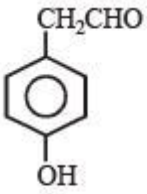
Solution. (i) As both the compounds A and B form a silver mirror with Tollen's reagent, they have aldehydic group in their structure. In these compounds, B gives positive test with $FeCl_3$ solution, so it must also have phenolic group in its structure. Hence, compound A is p-methoxybenzaldehyde and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

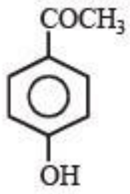
(ii) Compound C gives positive iodoform test, so it must have CH_3CO– group in its structure. Hence compound C is p-hydroxyphenylmethyl ketone.

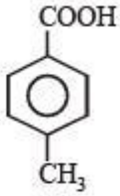
(iii) Compound D is readily extracted in aqueous $NaHCO_3$, so it must have -COOH group in its structure. So, compound D is p-methylbenzoic acid.

(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 :

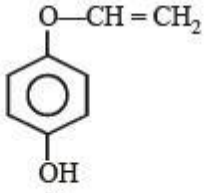

'A'


'B'


'C'


'D'

&

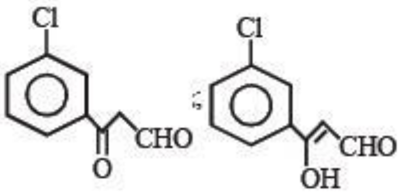

'E'

Q.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?

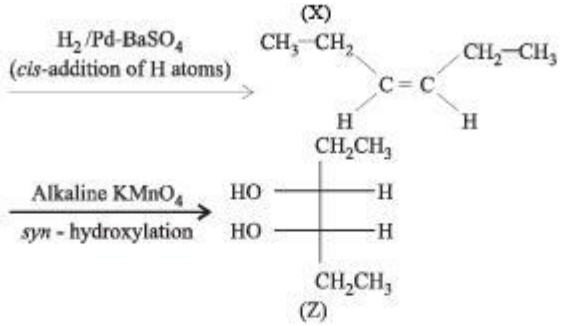


Ans.

Solution. TIPS/Formulae : Meso forms are optically inactive.

$$CH_3CH_2-C\equiv C-H$$

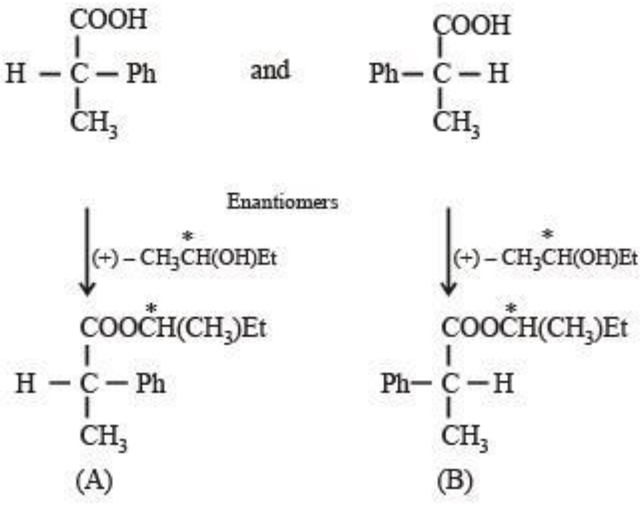
$$\xrightarrow[\text{(ii) } CH_3CH_2Br]{\text{(i) } NaNH_2} CH_3CH_2-C\equiv C-CH_2CH_3$$



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.

Q.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)

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



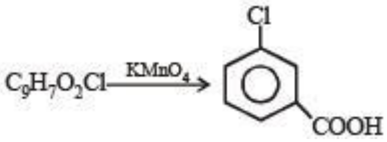
(A) and (B) are diasteromers.

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.

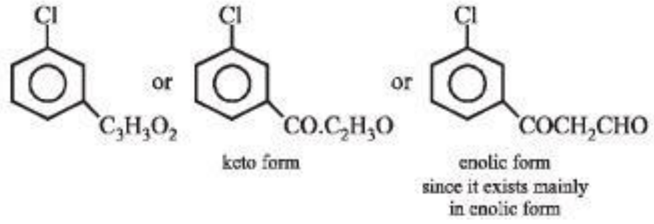
Q.45. Compound A of molecular formula $C_9H_7O_2Cl$ exists in keto form and predominantly in enolic form 'B'. On oxidation with $KMnO_4$, 'A' gives m–

chlorobenzoic acid. Identify 'A' and 'B'. (2003 - 2 Marks)

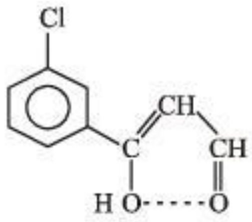
Solution.



Hence compound should have following part structure



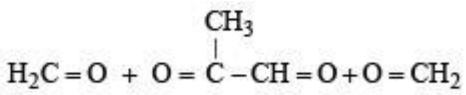
The enolic form of the compound is more stable than the keto form due to hydrogen bonding.



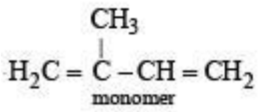
Q.46. A monomer of a polymer on ozonolysis gives two moles of CH_2O and one mole of CH_3COCHO. Write the structure of monomer and write all – 'cis' configuration of polymer chain.

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

Solution.

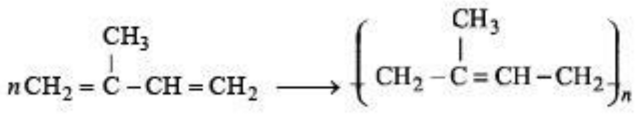


$$H_2C=O + O=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH=O+O=CH_2$$



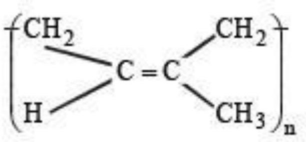
$$\underset{\text{monomer}}{H_2C=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH=CH_2}$$

Thus the possible polymer should be



$$n\,CH_2=\overset{CH_3}{\overset{|}{C}}-CH=CH_2 \longrightarrow \left[CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\right]_n$$

Structure of all cis configuration of the polymer.

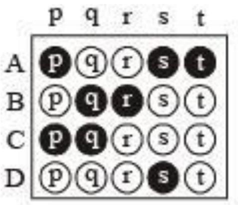


All *cis* form

Match the Following of Aldehydes, Ketones & Carboxylic Acids

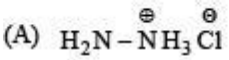
Match the Following

Q.1. 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.



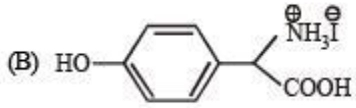
Q.1. Match the entries in Column I with the correctly related quantum number(s) in Column II. Indicate your answer by darkening the appropriate bubbles of the 4 × 4 matrix given in the ORS

Column I **Column II**



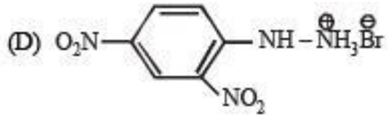
(A) $H_2N-\overset{\oplus}{N}H_3\overset{\ominus}{Cl}$

(p) sodium fusion extract of the compound gives Prussian blue colour with $FeSO_4$



(q) gives positive $FeCl_3$ test

(r) gives white precipitate with $AgNO_3$



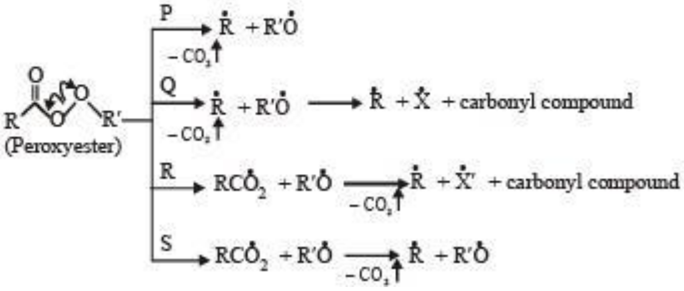
(s) reacts with aldehydes to form the corresponding hydrazone derivative

Ans. (A) - r, s; (B) - p, q; (C) - p, q, r; (D) - p, s

Solution. Compound (A) does not have carbon, hence does not responds (p) test.

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.

Q.2. Different possible <u>thermal</u> 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.



List-I

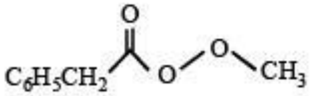
P. Pathway P

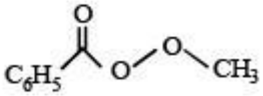
Q. Pathway Q

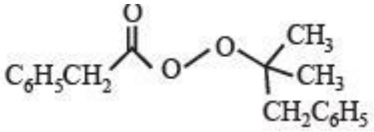
R. Pathway R

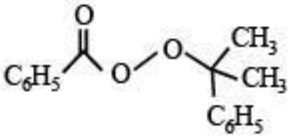
S. Pathway S

List-II

1.


2.


3.


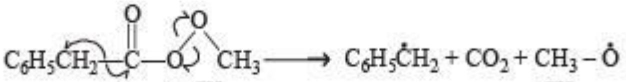
4.


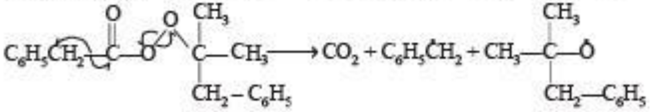
Code :

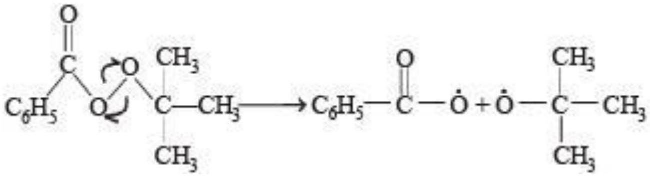
	P	Q	R	S
(a)	1	3	4	2
(b)	2	4	3	1
(c)	4	1	2	3
(d)	3	2	1	4

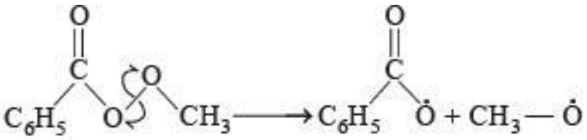
Ans. (a)

Solution.

(1) 

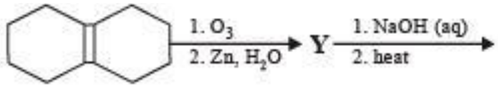
(3) 

(4) 

(2) 

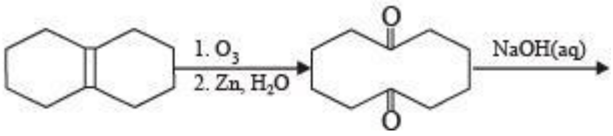
Integer Value Correct Type of Aldehydes, Ketones & Carboxylic Acids

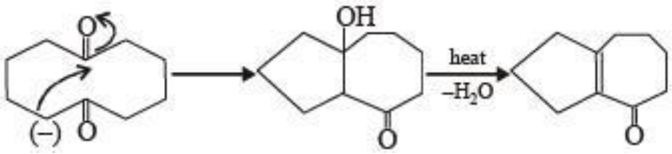
Q.1. In the scheme given below, the total number of intramolecular aldol condensation products formed from 'Y' is



Ans. 1

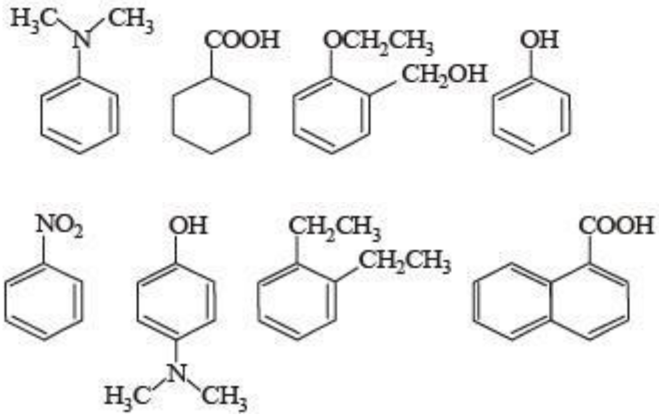
Solution.





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

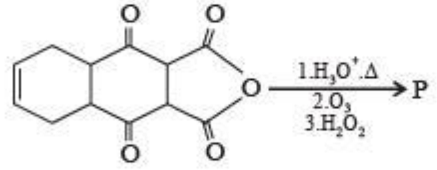
Q.2. Amongst the following, the total number of compounds soluble in aqueous NaOH is



Ans. 4

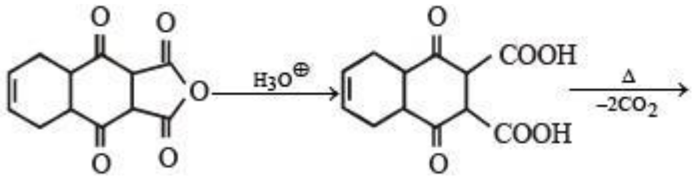
Solution. All carboxylic acids and phenols are soluble in aqueous NaOH. Four compounds are soluble in aqueous NaOH.

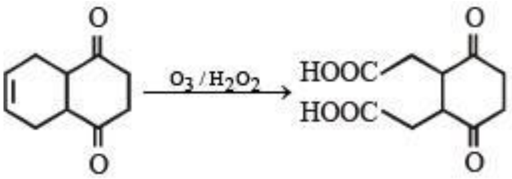
Q.3. The total number of carboxylic acid groups in the product P is



Ans. 2

Solution.





No. of –COOH group is '2'

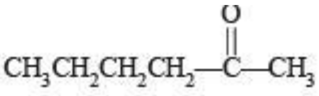
Q.4. Consider all possible isomeric ketones, including stereoisomers of MW = 100. All these isomers are independently reacted with $NaBH_4$ (NOTE: stereoisomers are also reacted separately). The total number of ketones that give a racemic product(s) is/are

Ans. 5

Solution. General molecular formula for ketones is C_nH2_nO

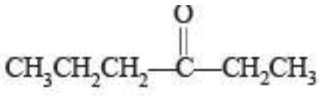
∴ $C_nH_{2n}O = 100$ or $12n + 2n + 16 = 100$, $n = 6$

Possible isomeric ketones with 6 carbon atoms are



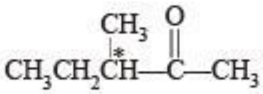
$CH_3CH_2CH_2CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

(I)



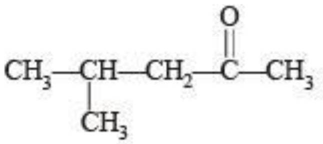
$CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-CH_2CH_3$

(II)



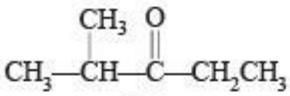
$CH_3CH_2\overset{CH_3}{\overset{|}{\overset{*}{C}H}}-\overset{O}{\overset{\|}{C}}-CH_3$

(III)



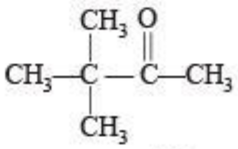
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

(IV)



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

(V)

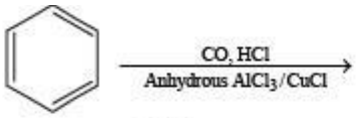


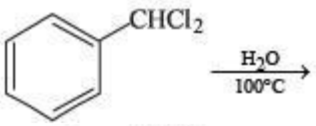
$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\overset{O}{\overset{\|}{C}}-CH_3$

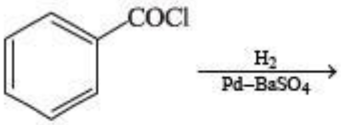
(VI)

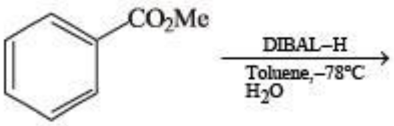
Note that only isomer III has a chiral carbon so on reduction with $NaBH_4$ it will give diastereomeric alcohols, while all other five isomers will give racemic mixture.

Q.5. Among the following, the number of reaction (s) that produce(s) benzaldehyde is

I. 

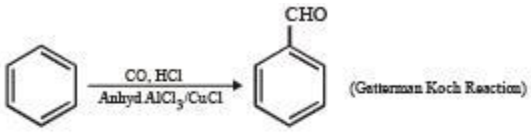
II. 

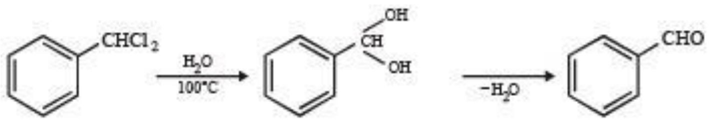
III. 

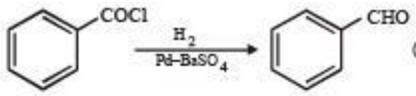
IV. 

Ans. 4

Solution.







(Rosenmund Reduction)