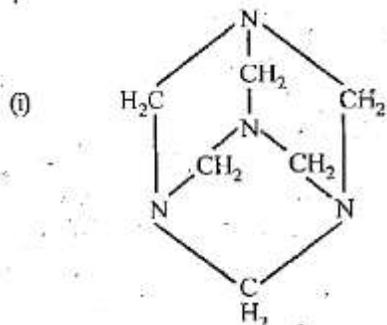


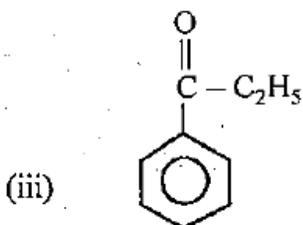
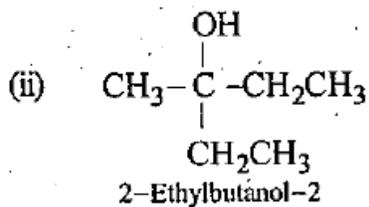
Aldehydes, Ketones and Carboxylic acids-Solutions

SUBJECTIVE PROBLEMS:

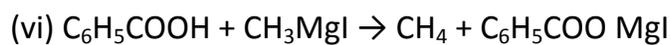
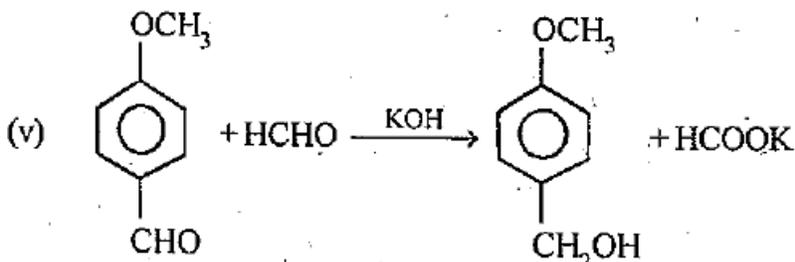
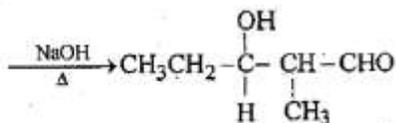
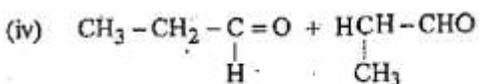
Sol 1



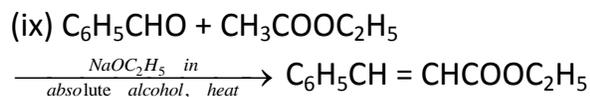
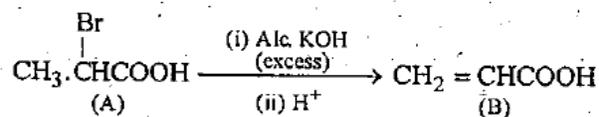
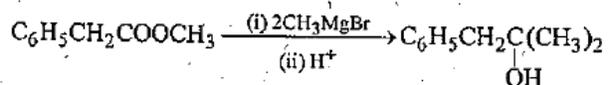
Hexamethylenetetramine (Urotropine)



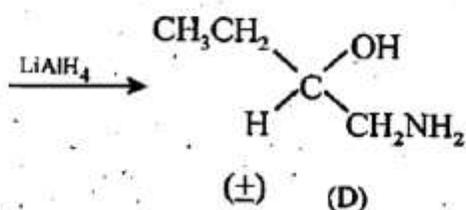
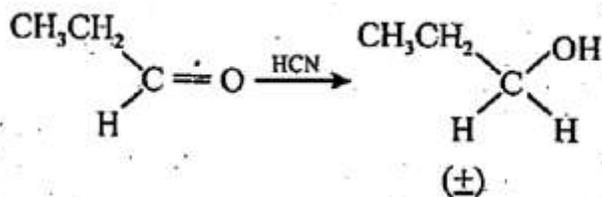
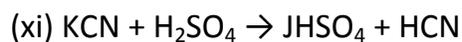
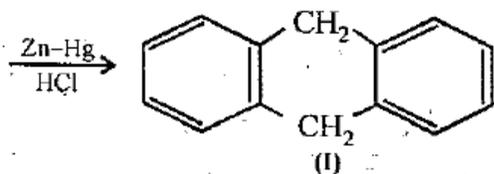
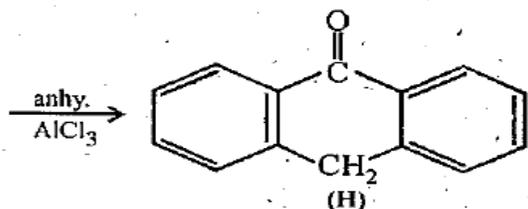
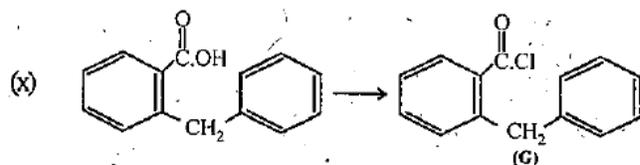
Phenyl ethyl ketone

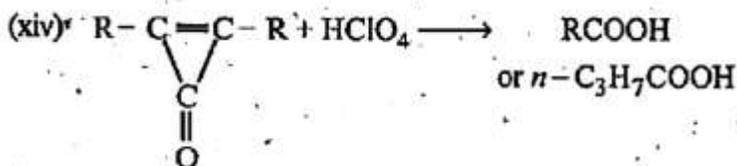
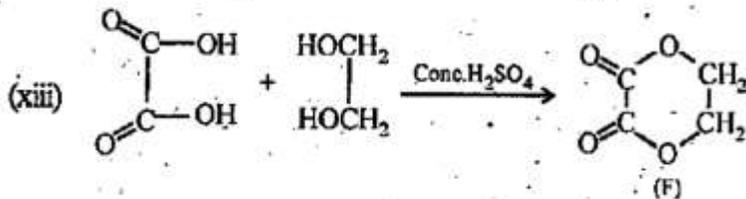
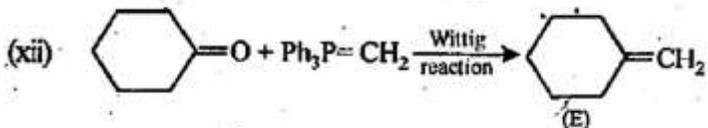


(vii) **NOTE** : Esters react with excess of RMgX to form 3° alcohols having two alkyl group corresponding to R of RMgX. Thus

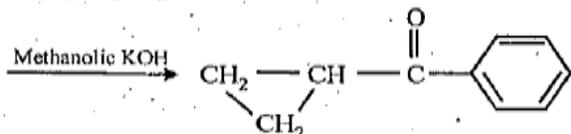


(Claisen condensation)

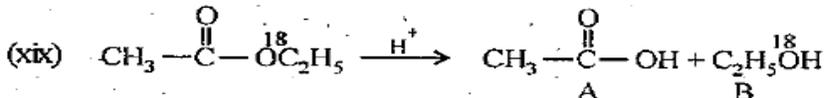
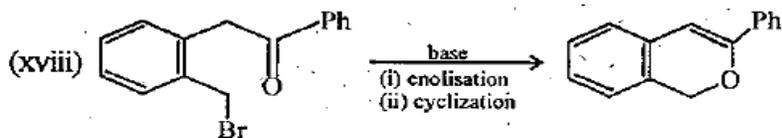
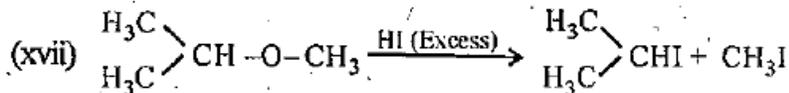




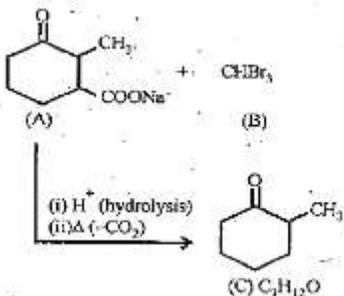
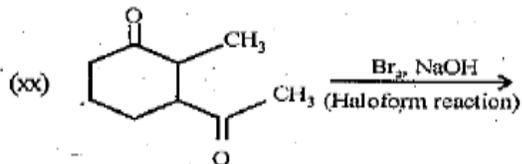
(xv) $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{COPh}$

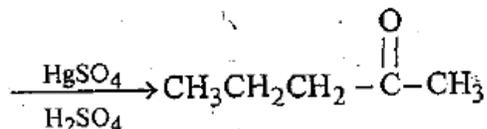
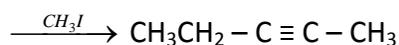
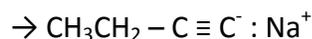
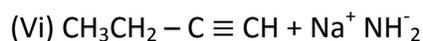
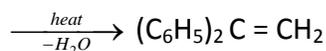
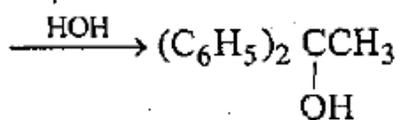
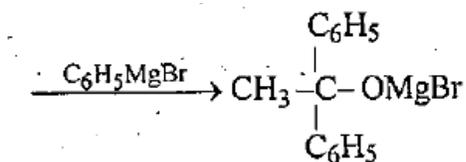


NOTE : The reaction is an example of benzyl-benzylic acid type rearrangement.

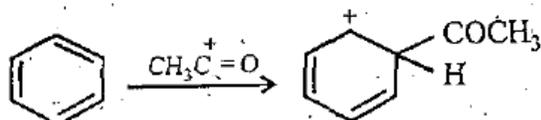
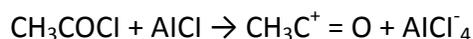


(Ester hydrolysis involves acyl-oxygen fission)

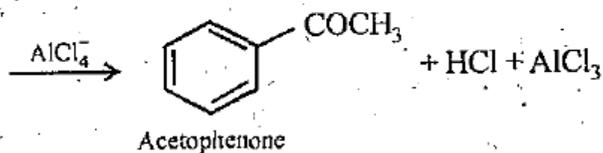




Sol 4.



Benzene

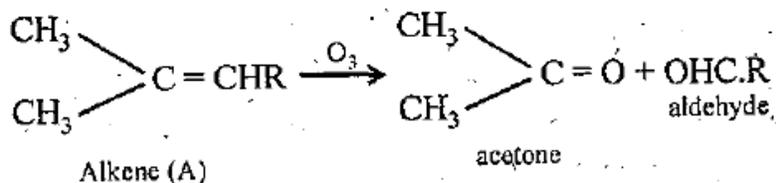


Acetophenone

Sol 5.

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

(A) :



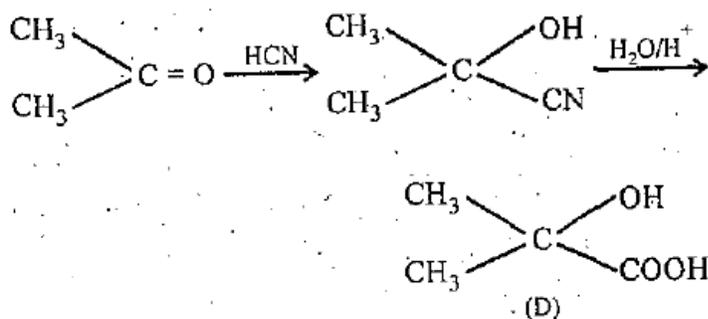
Alkene (A)

acetone

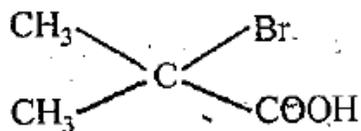
As per problem :



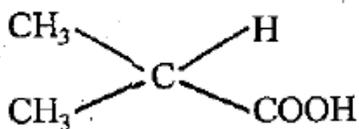
Bromo compound [C] $\xrightarrow{\text{H}_2\text{O}}$ Hydroxy acid [D] Structure of (D) is determined by the reaction :



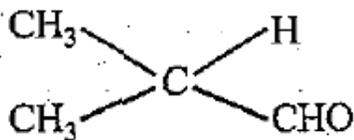
The compound (D) is obtained by hydrolysis of (C) with aqueous alkali since (C) is a bromo compound, therefore it has bromo group where the compound (D) has a hydroxyl group. Therefore, structure of C is



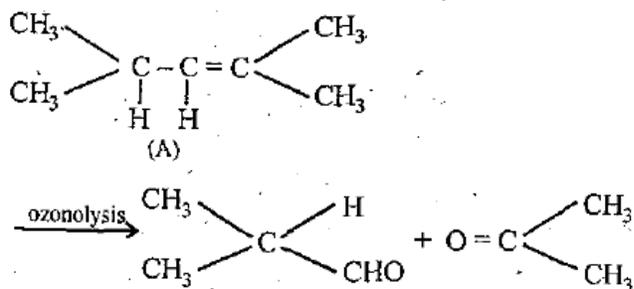
The compound (C) is formed by bromination of compound (B), therefore, the compound (B) is



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

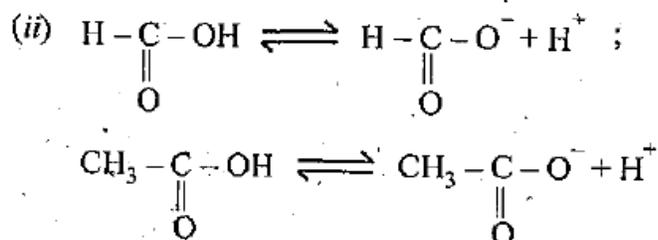


The aldehyde and acetone are formed by ozonolysis of alkene. Therefore, the double bond in alkene should be between the carbon atoms of the two carbonyl compounds (the aldehyde and acetone). Therefore, the compounds and the reactions are identified as



Sol 6.

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

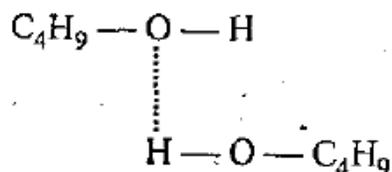


Presence of CH_3 gp in acetone ion shows +I effect and thereby intensifying charge on O^- of acetate ion which is thus destabilized. Thus formate ion is more stable than acetate ion or HCOOH loses proton more easily than CH_3COOH .

(iii) **NOTE :**

Alcohols show hydrogen bonding.

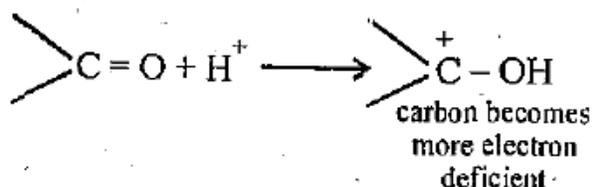
The boiling points of carbonyl compounds are lower than the corresponding alcohols since former do not show intermolecular H-bonding like alcohols.



H-bonding between two butanol molecules

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

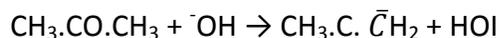
(iv) In weakly acidic medium carbonyl group is protonated to form conjugate acid.



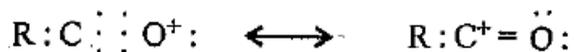
In strongly acidic medium ($\text{pH} < 3.5$), the unshared pair of electrons of N of the reagent is protonated with the result nucleophile (NH_2NH_2) is converted to an electrophile ($\text{NH}_2\text{H}^+\text{H}_3$) which cannot react. Hence in highly acidic medium, there is no protonation of the carbonyl group.

(v) **NOTE :** Hypiodite (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). Hypiodite ion being strong base than iodide ion, can easily remove acidic hydrogen atom.



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

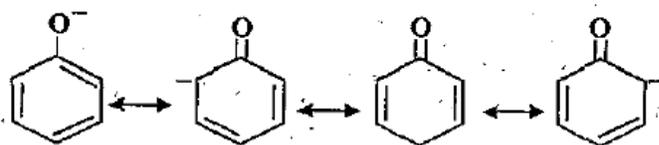


Acylium ion

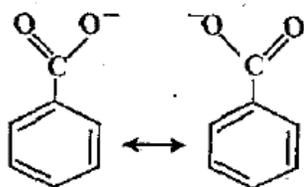
Carbonium ion

(Carbon has only six electrons)

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



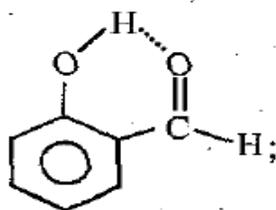
Resonating structures of phenoxide ion



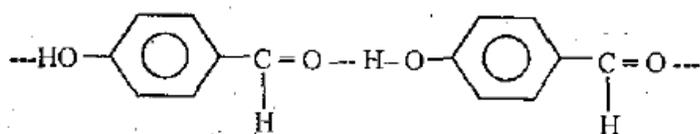
Resonating structure of benzoate ion

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.

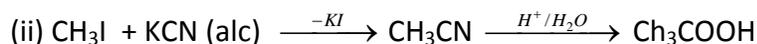
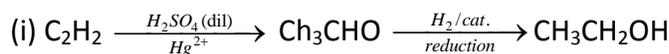
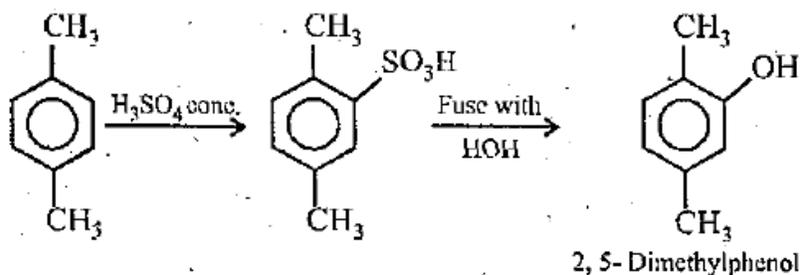
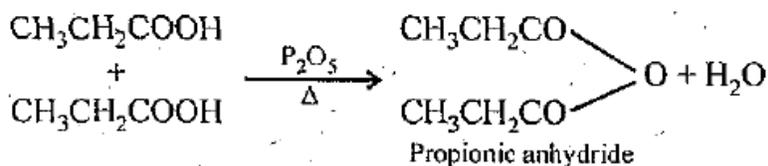
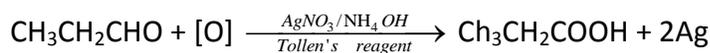
(viii) O-Hydroxybenzaldehyde has intramolecular H-bonding while the p-isomer has intermolecular H-bonding.



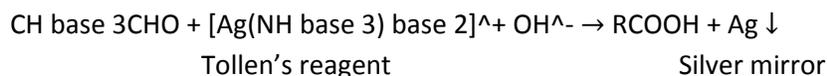
Intramolecular H-bonding in o-isomer



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

Sol 7.**Sol 8.****Sol 9.****SOL 10.**

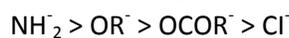
Acetaldehyde can be distinguished from acetone by using Tollen's reagent or Fehling solution or Schiff's reagent. Only acetaldehyde responds to all these tests.

**SOL 11.**

The weaker a base better is its leaving ability.

This is an example of nucleophilic substitution where the group X (Cl, OC₂H₅, OCOCH₃) is replaced by OH.

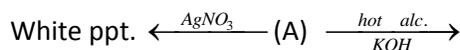
The decreasing basic character of the four concerned group is



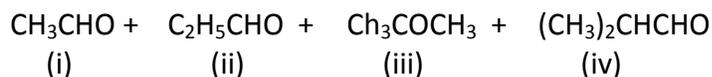
Hence Cl⁻ (the weakest base) will be lost most easily while NH₂⁻ (the strongest base) will be lost with most difficulty. Thus the order of hydrolysis becomes.

**Sol 12.**

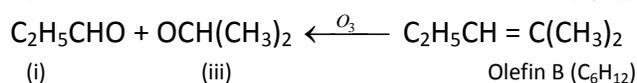
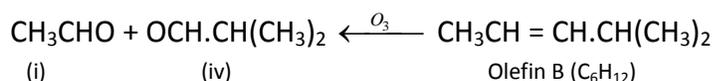
Let us summarise the given facts.



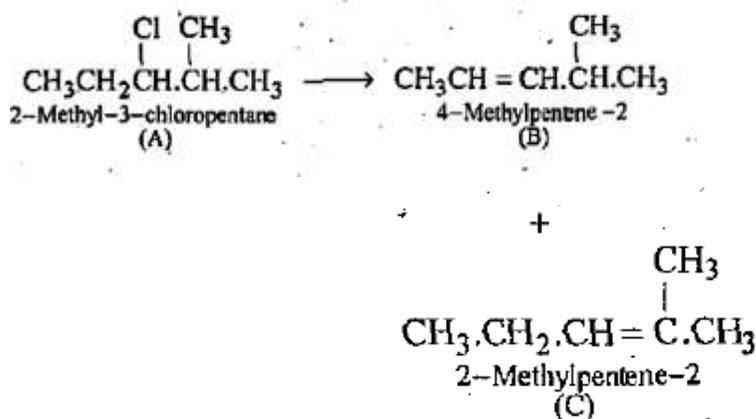
(Isomeric alkenes. C₆H₁₂)



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)].

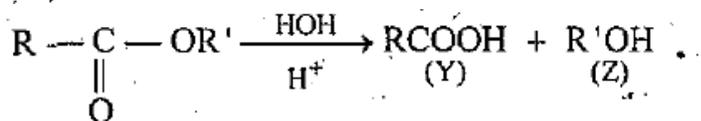
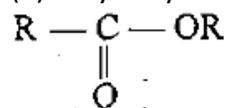


Thus the compound (A) should be a chloride that can eliminate a molecule of HCl to give B as well as C.

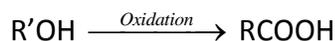


Sol 13.

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



Oxidation of alcohol (Z) gives acid (Y)

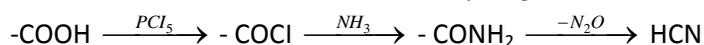


(Z)

or $\text{RCH}_2\text{OH} \rightarrow \text{RCOOH}$ (\because R' is $\text{R} - \text{CH}_2$)

Hence X, Y and Z are

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



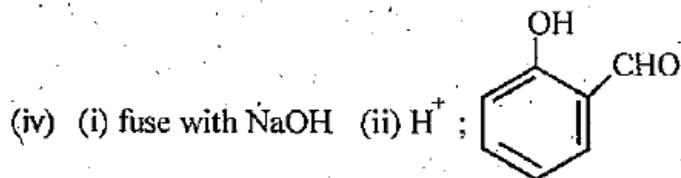
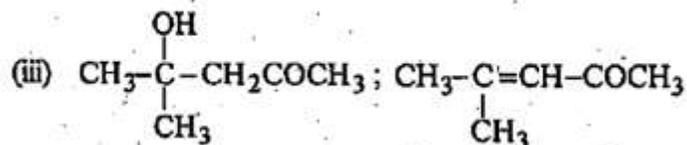
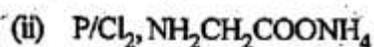
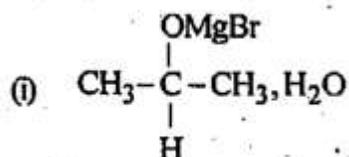
Formation of HCN by the dehydration of E establishes that E is HCONH_2 and hence D is HCOOH .

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

Thus the various compounds are as below :

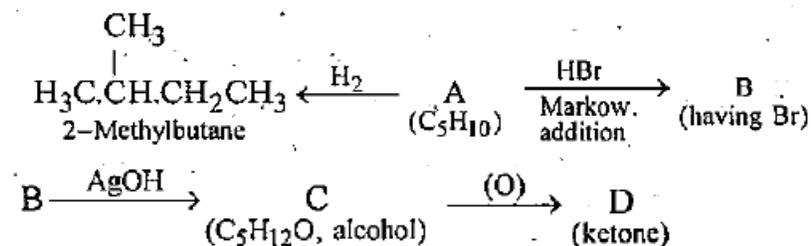
A	B	C	D	E
CH_3OH	$\text{CH}_3\text{COOCH}_3$	HCHO	HCOOH	HCONH_2
Methyl alcohol	Methyl acetate	Formaldehyde	Acid	Formamide

Sol 17.



Sol 18.

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

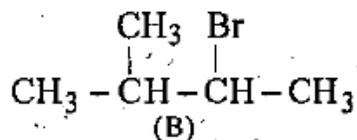


Let us draw some conclusions from the above set of reactions.

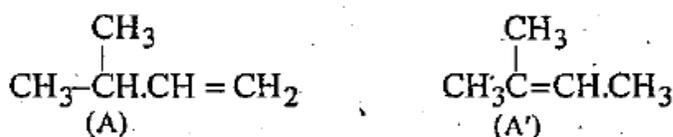
(i) The molecular formula C_5H_{10} (C_nH_{2n}) for A indicates that it is an alkene having one double bond.

(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.

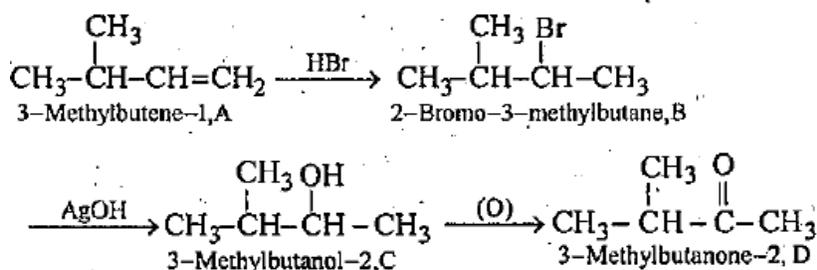
(iii) The structure of 2-methylbutane, the hydrogenated product of A, indicates that the secondary bromide must have following structure.



(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.



Thus the reaction involved can be represented as below:



Sol 19.

The compound A ketone, undergoes haloform reaction.

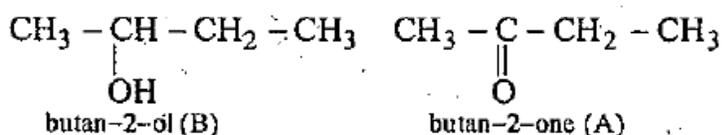
Thus, it must contain CH_3CO group.

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,

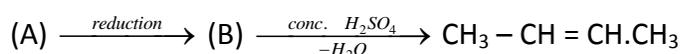
i.e. $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$ (butane-2).

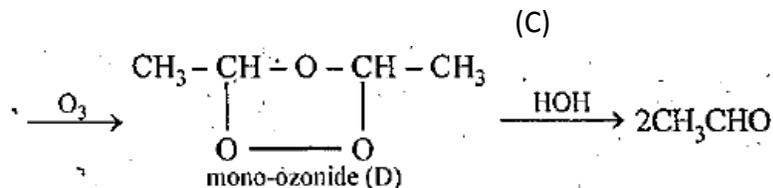
The compound B is obtained by the reduction of compound A (which contains CH_3CO group).

Hence, the compound B would be an alcohol, which on heating with H_2SO_4 gives (C). Hence B and A would be



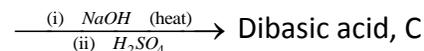
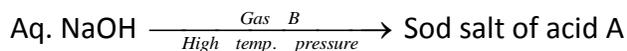
The reactions involved :





Sol 20.

The given set of reactions can be represented as below :



Calculation of molecular formula of C

$$\% \text{ of H} = \frac{2}{18} * \frac{0.08}{0.40} * 100 = 2.22\%$$

$$\% \text{ of C} = \frac{12}{44} * \frac{0.39}{0.40} * 100 = 27.30\%$$

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

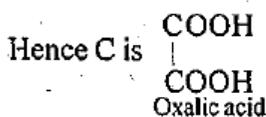
By usual method, empirical formula of acid C = CHO₂

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

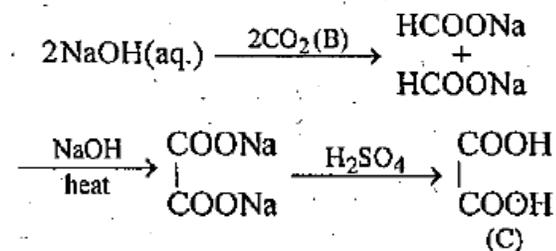
$$\text{Mol. wt. of acid C} = 45 * 2 = 90$$

$$\therefore \text{Mol. formula of C} = \text{C}_2\text{H}_2\text{O}_4$$

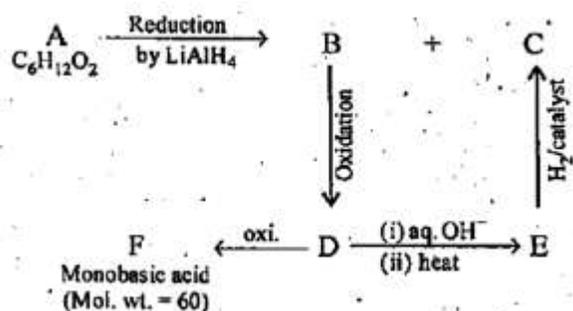
Since it is dicarboxylic acid, it must have two -COOH group



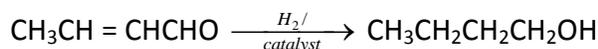
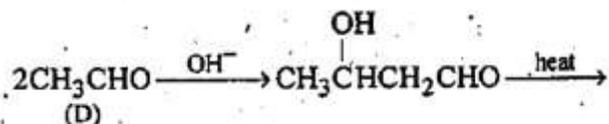
Going back, compound C must be produced from sodium oxalate which in turn is produced from sodium formate. Hence A is formic acid and B is CO₂. Thus the complete series of reactions can be written as below.



Sol 21.



Molecular weight of the monobasic acid (RCOOH) indicates that the R – should be CH₃-i.e., acid F should be acetic acid (CH₃COOH, mol. wt. 15+45). Thus compound D must be acetaldehyde CH₃CHO, and compound B which on oxidation gives CH₃CHO must be ethanol, CH₃CH₂OH. Acetaldehyde (D) on treating with aqueous alkali will undergo aldol condensation.

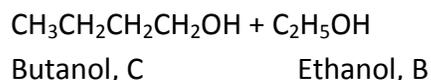


Crotonaldehyde, (E) Butanol – 1, (C)

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 (CH₃CH₂CH₂COOC₂H₅).



Ethyl butanoate, A



Sol 22.

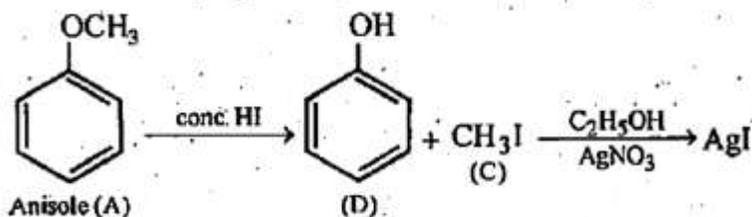
Empirical formula of A and B.

	Relative No. of atoms	Simplest 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 = $100 - (77.77 + 7.40) = 14.83$	$\frac{14.83}{16} = 0.92$	$\frac{0.92}{0.92} = 1$

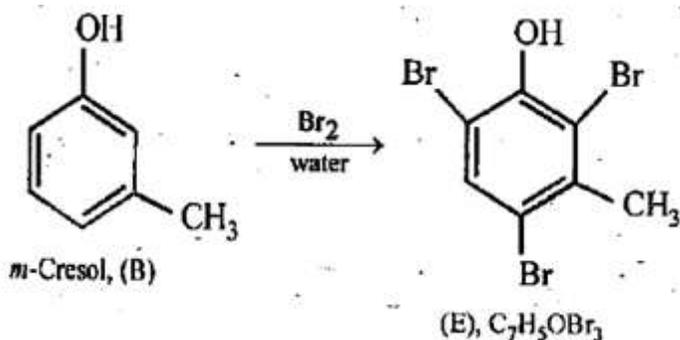
= 14.83

∴ Empirical formula of A and B = C₇H₈O

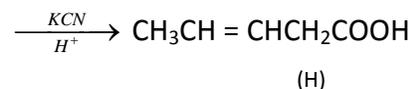
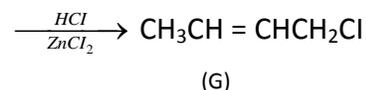
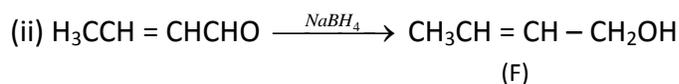
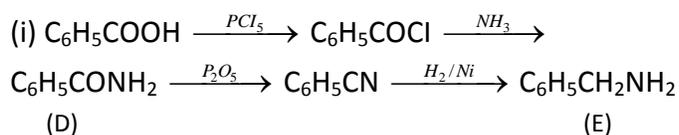
Nature of (A) : Since A is insoluble in NaOH and NaHCO₃, it can't have – OH and – COOH groups. Further the reaction of A with conc. HI to give compounds C and D separable by means of ammonical AgNO₃ and solubility of D in NaOH indicates that C and D are alkyl halide and phenol respectively. Thus A is an ether i.e. it is C₆H₅.O.CH₃ which explains all the given reactions.



Nature of (B) : Solubility of B (C₇H₈O) 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, C₇H₅OBr₃. Further bromination of B give tribromo product indicates that it is *m*-cresol.



Sol 23.



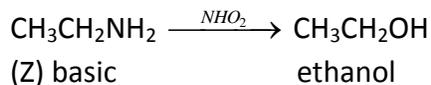
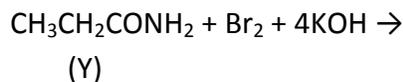
Sol 24.

For empirical formula of (Y)

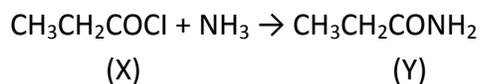
Element	%	Relative no. of atoms	Simple ratio
C	49.31	4.10	3
H	9.59	9.59	7
N	19.18	1.37	1

∴ Empirical formula of (Y) is C₃H₇NO.

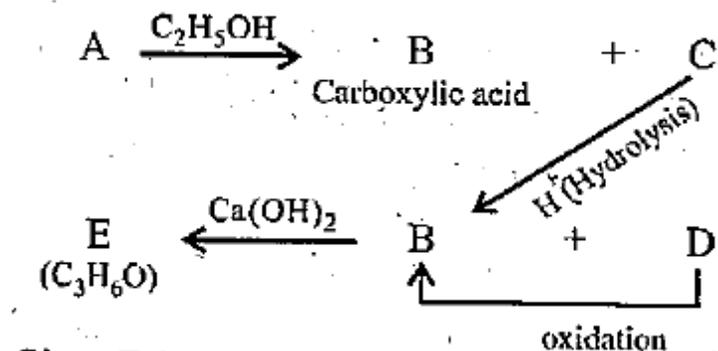
(Y) reacts with Br₂ and NaOH to give (Z) and (Z) reacts with HNO₂ to give ethanol and thus (Y) seems to have – CONH₂ group.



Y is formed from (X) having Cl on treatment with NH₃ and so (X) is CH₃CH₂COCl i.e. propanoyl chloride.



Sol 25.

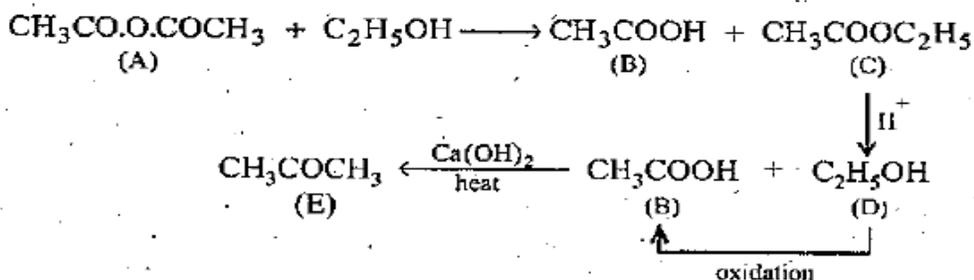


(i) Since E (C₃H₆O) forms a 2, 4-dinitrophenylhydrazone but does not reduce Tollen’s reagent and Fehling solution, it must be a ketone, CH₃.CO.CH₃.

(ii) The compound E (established as ketone) is obtained by heating compound B with Ca(OH)₂, B must be CH₃COOH.

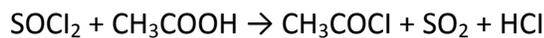
(iii) Compound B is obtained by the oxidation of D, the latter must be ethyl alcohol, C₂H₅OH and hence C must be ethyl acetate, CH₃COOC₂H₅.

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

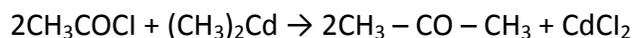


Sol 26.**Sol 27.**

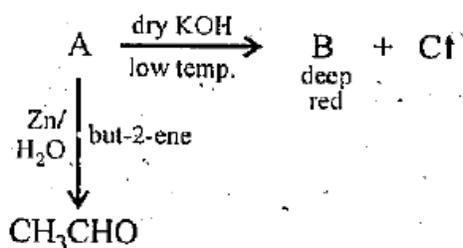
(A) (B)



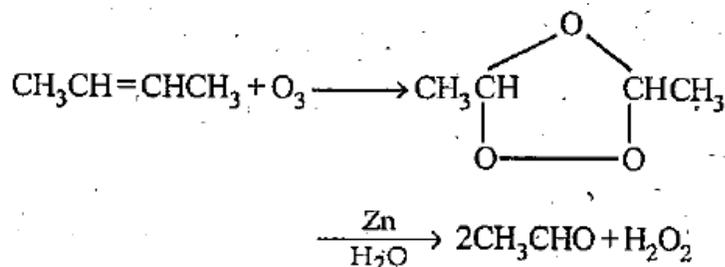
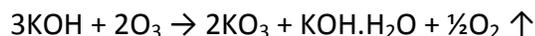
(A) (C)



(C)

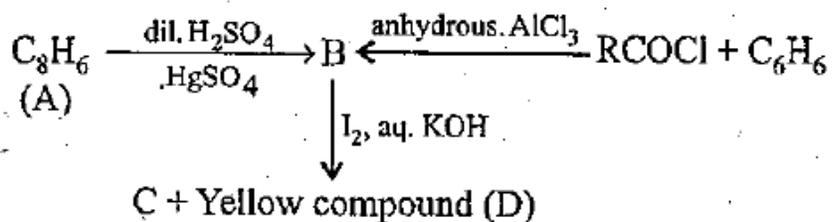
Sol 28.

The reaction of gas (A) with but-2-ene followed by treatment with Zn/H₂O gives CH₃CHO. This shows that the gas (A) is ozone (O₃).

**Reaction of ozone with KOH.**

(A) Pot. Ozonide, B (C)

(Red colour)

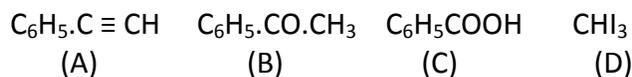
Sol 29.

(i) Formation of (B) from benzene and acid chloride in presence of anhydrous AlCl₃ (Friedel-Craft reaction) indicates that it is a ketone, C₆H₅COR.

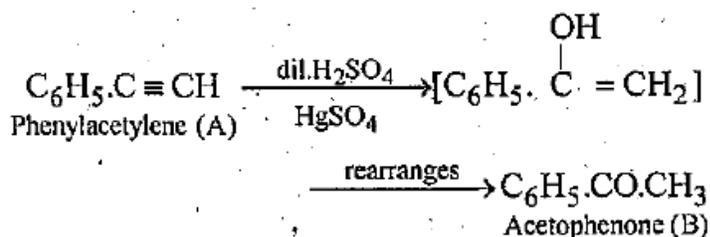
(ii) Further the ketone (B) reacts with alkaline iodine forming yellow compound (D) (haloform reaction). This indicates that one of the alkyl groups in ketone B is $-\text{CH}_3$. Hence it should be $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}_3$.

(iii) Since ketone (B) is also formed from the hydrocarbon C_8H_6 (A) by reaction with $\text{dil. H}_2\text{SO}_4$ and HgSO_4 , the hydrocarbon (A) must have an acetylenic hydrogen atom, i.e. $\equiv\text{C}-\text{H}$ grouping. Hence (A) must be $\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$.

Thus compounds (A) to (D) are



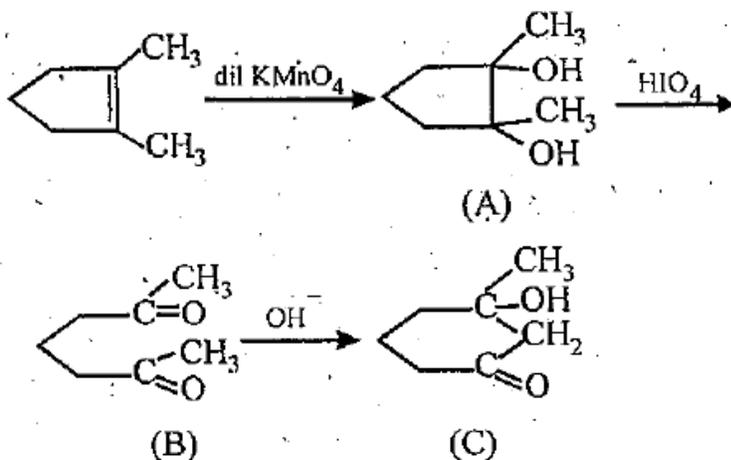
Formation of (B) from (A)



Sol 30.

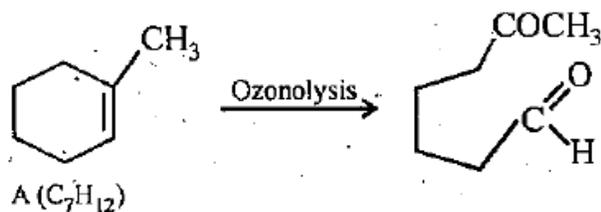
(i) β -Keto acids are unstable and undergo decarboxylation most readily

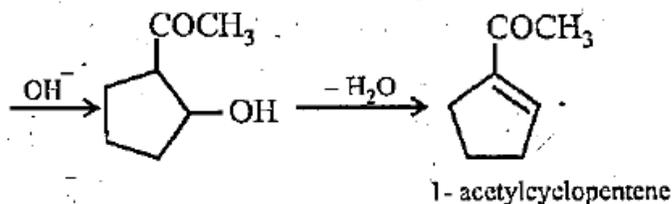
Sol 31.



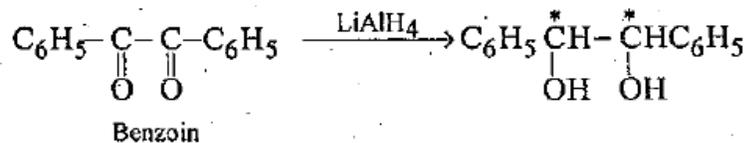
The last step is intramolecular aldol condensation

Sol 32.





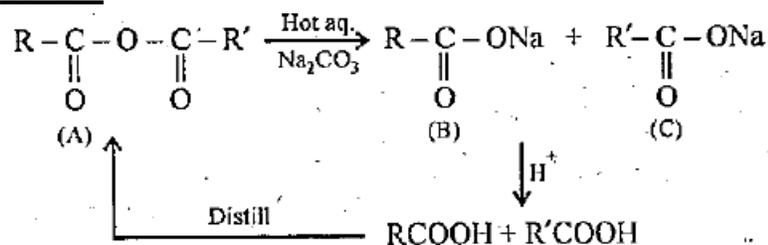
Sol 33.



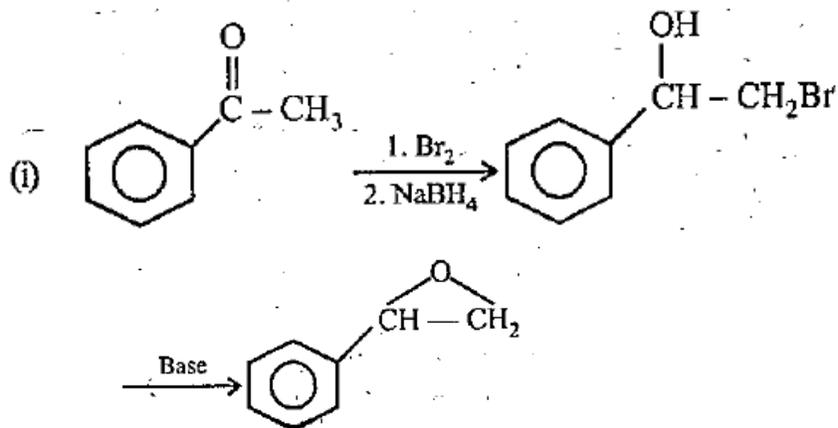
The molecule after reduction possesses two asymmetric carbon (*) with symmetry in molecule.

∴ No. of stereoisomers (d, l and m) = 3

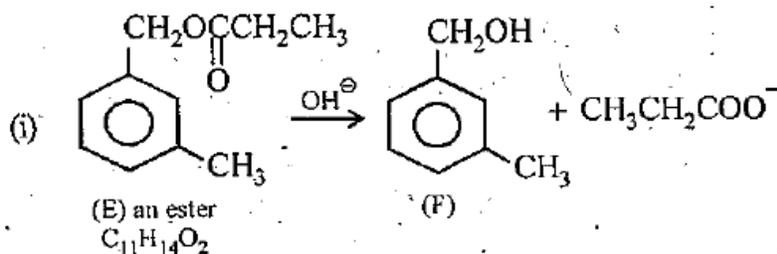
Sol 34.

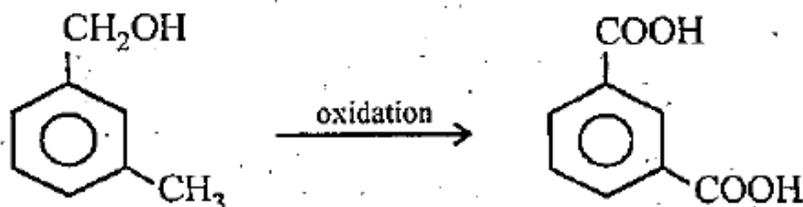


Sol 35.



Sol 36.

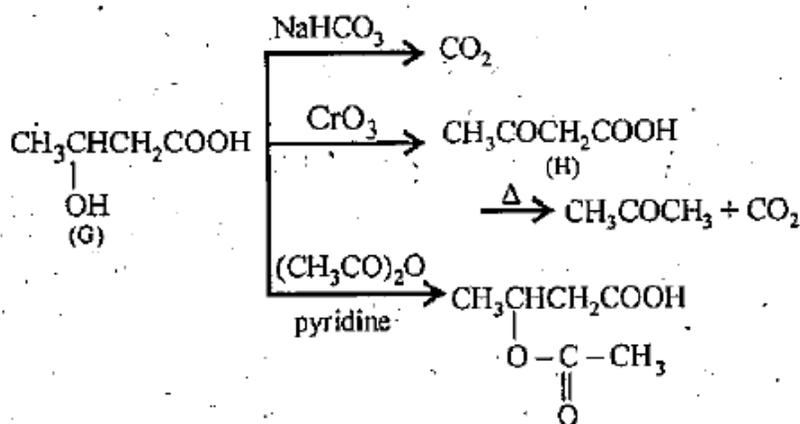




(ii) (a) Reaction of G with NaHCO_3 to give CO_2 indicates that it has $-\text{COOH}$ group.

(b) Reaction of G with acetic anhydride indicates that it has $-\text{OH}$ group.

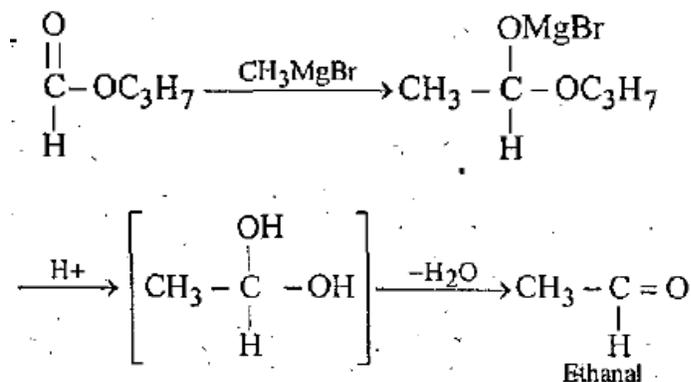
(c) Decarboxylation of (H), oxidized product of G indicates H is β -keto acid hence it should be β -hydroxy acid. Thus G should be

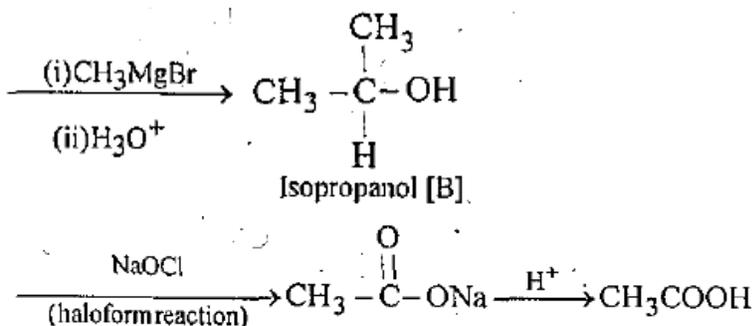


Thus G should be $\text{CH}_3\text{CHOHCH}_2\text{COOH}$.

Sol 37.

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 ($\text{C}_4\text{H}_8\text{O}_2$) should be HCOOC_3H_7 . Thus the various reactions and nature of compound B can be established as below.





Sol 38.

Following information are provided by the problem.

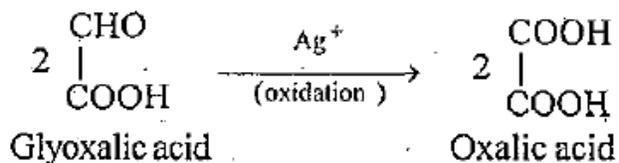
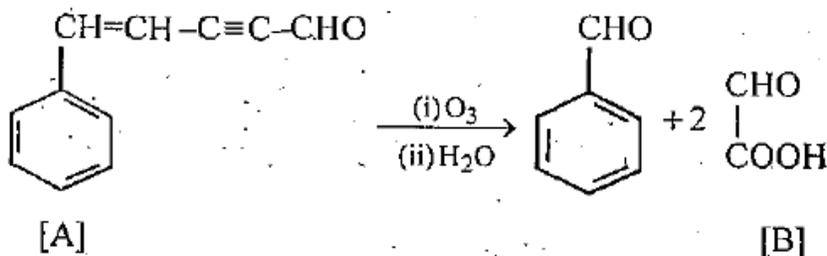
(i) Since aldehyde A ($\text{C}_{11}\text{H}_8\text{O}$) gives $\text{C}_6\text{H}_5\text{CHO}$ on ozonolysis, it must have a benzene nucleus and a side chain. The side chain should have five carbon ($\text{C}_{11}-\text{C}_6=\text{C}_5$), three hydrogen ($\text{H}_8-\text{H}_5=\text{H}_3$) and one oxygen atom, i.e., it should be $\text{C}_5\text{H}_3\text{O}$. Further the compound A has an aldehydic group, so the side chain can be written as $\text{C}_4\text{H}_2\text{CHO}$.

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

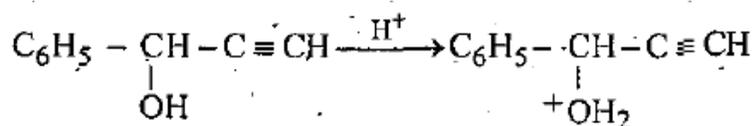
(iii) Further since the aldehyde A does not undergo aldol condensation, α - hydrogen is absent and hence triple bond should be present between C_2 and C_3 .

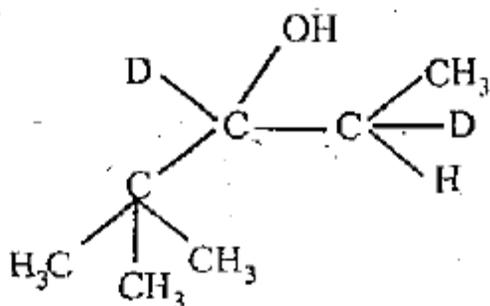
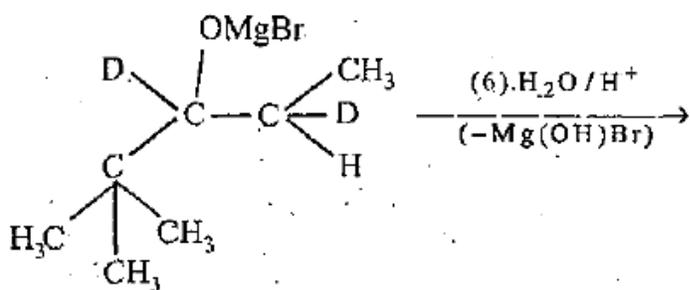
(iv) Thus the side chain $\text{C}_4\text{H}_2\text{CHO}$ of A can be written as $-\text{CH}=\text{CH}-\text{C}\equiv\text{C}-\text{CHO}$.

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

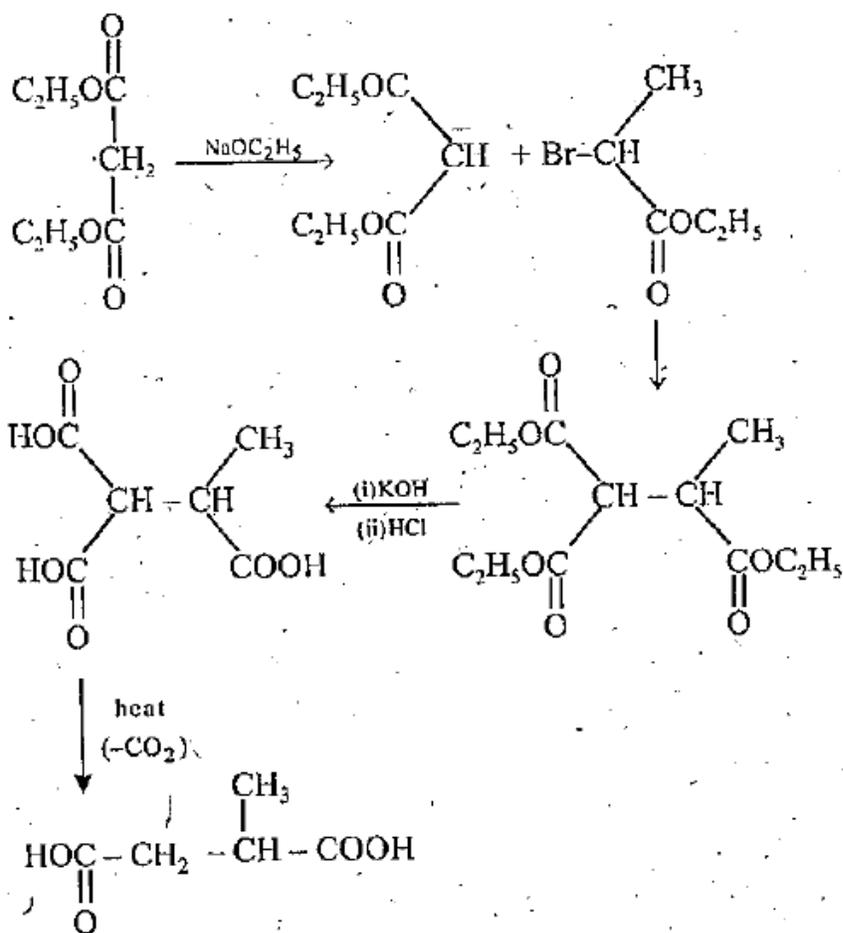


Sol 39.



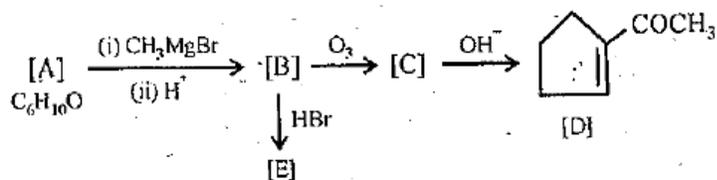


Sol 42.



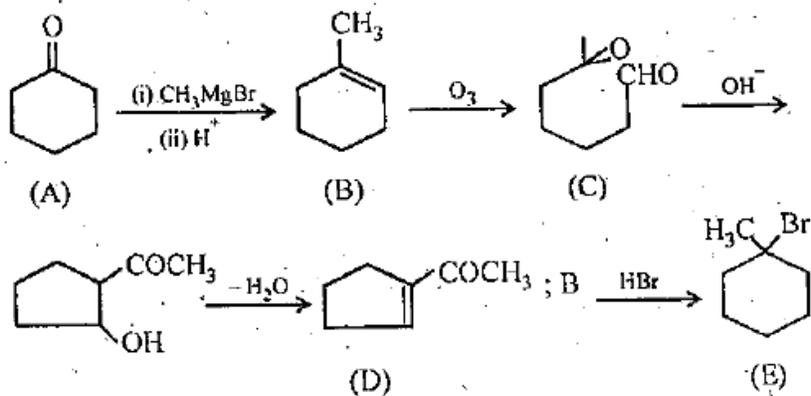
Sol 43.

The given reaction can be summarized as below :

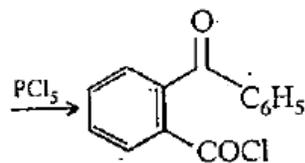
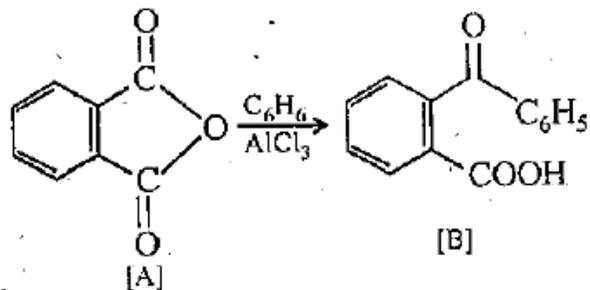


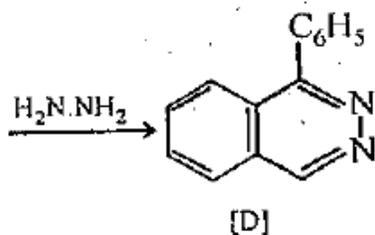
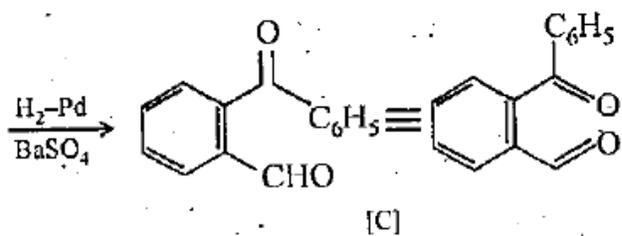
Conclusions from the set of reactions

- (i) Carbon-hydrogen ratio of A indicates that it is a cyclic compound
- (ii) Reaction of A with CH₃MgBr 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.

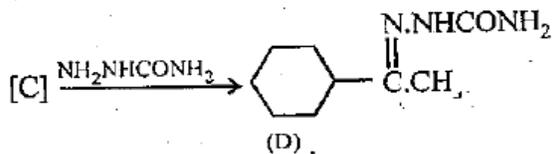
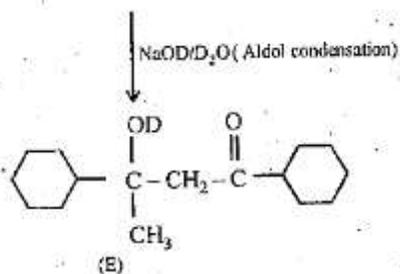
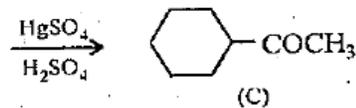
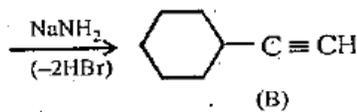
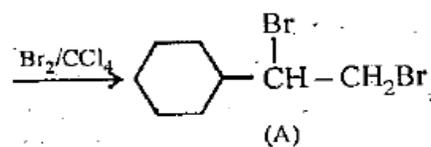
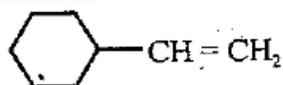


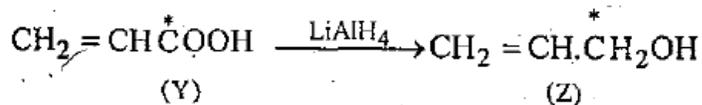
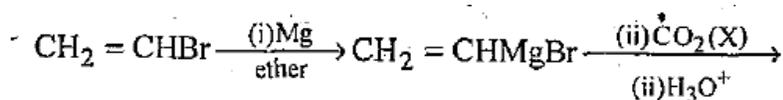
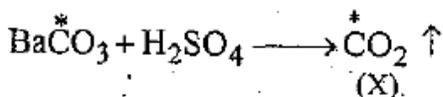
Sol 44.



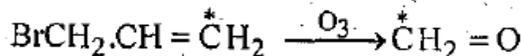
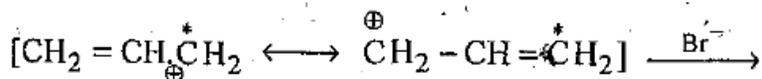
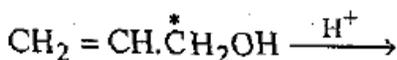


Sol 45.



Sol 46.

Formation of CH_2O from (Z)

**Sol 47.**

(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.

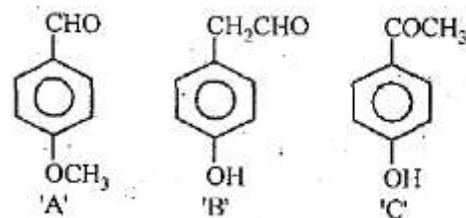
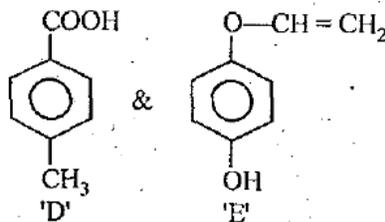
Hence compound C is p-hydroxyphenylmethyl ketone.

(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.

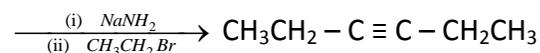
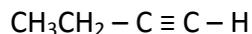
So, compound E is p-hydroxyphenyl vinyl ether.

Hence the structures of all the five compounds are :

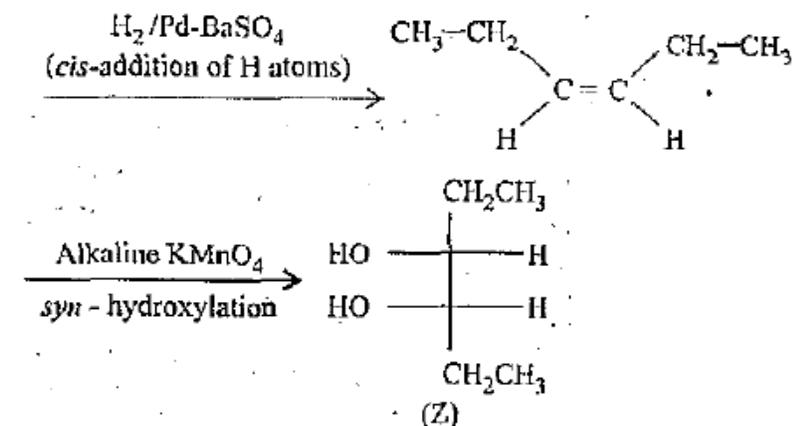


Sol 48.

Meso forms are optically inactive.



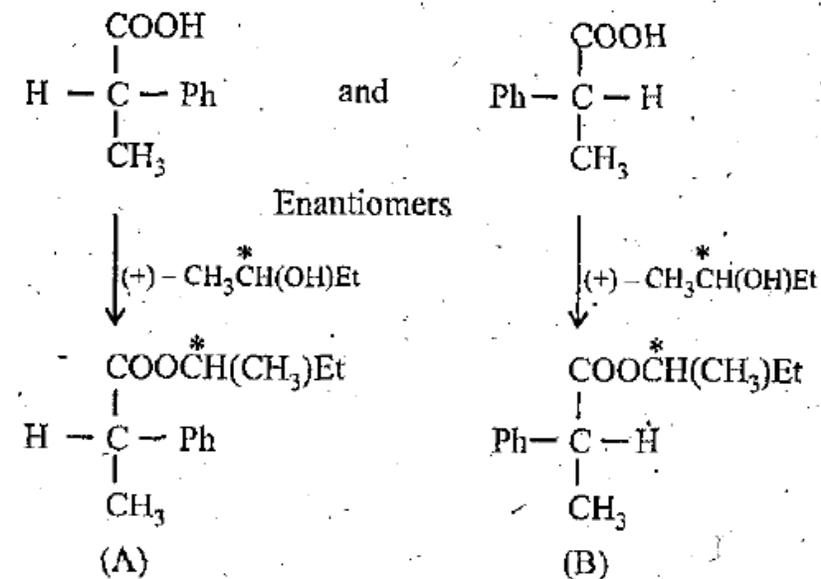
(X)



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.

Sol 49.

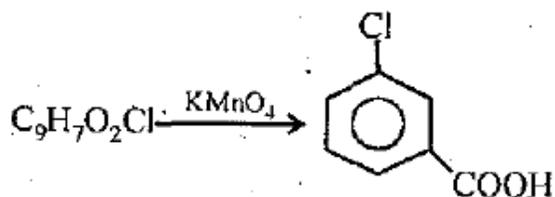
The two enantiomers of 2-phenylpropanoic acid in the racemic mixture react with (+) – alcohol to form two diastereomers.



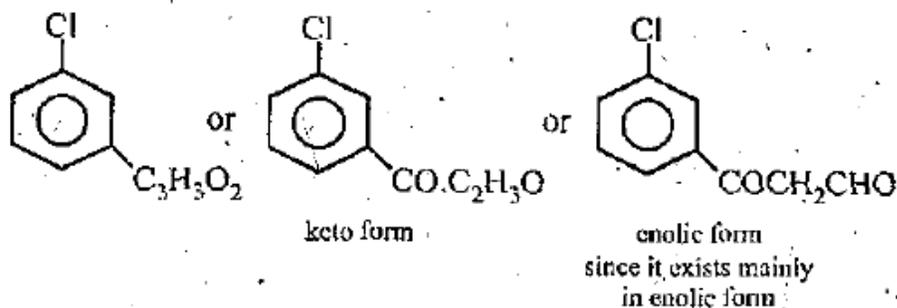
(A) and (B) are diastereomers.

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 (+)-(+)–ester, while (-) acid reacts with (+) alcohol to give (-)-(+)–ester. These two esters are diastereoisomers.

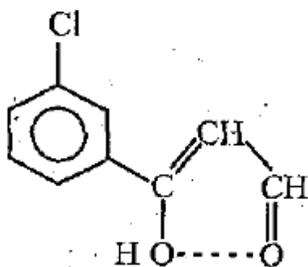
Sol 50.



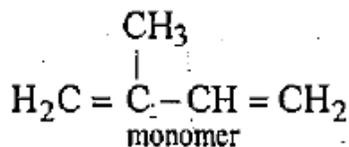
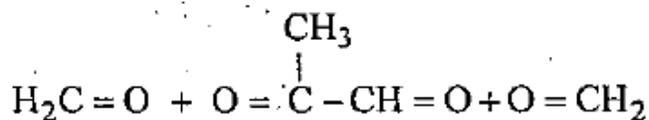
Hence compound should have following part structure



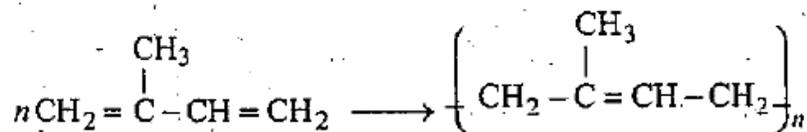
The enolic form of the compound is more stable than the keto form due to hydrogen bonding



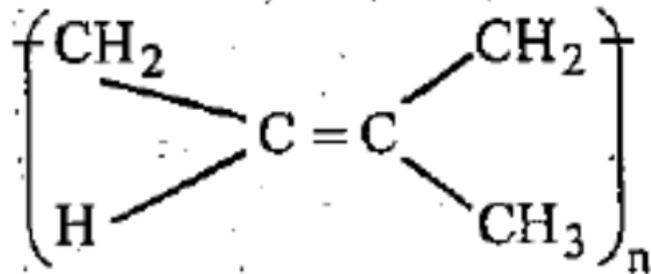
Sol 51.



Thus the possible polymer should be



Structure of all cis configuration of the polymer



All *cis* form