

**Chapter 11- Alcohols ,Phenols and Ethers****LEVEL-1 QUESTIONS**

1	<p><b>Haloalkanes undergo nucleophilic substitution reaction readily than haloarenes.</b></p> <p>Ans (a) Low bond dissociation enthalpy of R-X bond due to low s- character of C <math>sp^3</math></p> <p>(b) Stability of carbocation by hyper conjugation of neighboring alkyl groups.</p>
2	<p><b>The b.pt of isomeric haloalkanes decreases increasing in branching of carbon chains.</b></p> <p>Ans - As branching increases molecules becomes more compact and acquires a low surface area . Since strength of Vander waals forces are proportional to area of contact between molecules, attractive forces decreases with branching.</p>
3	<p><b>Alcohols have higher boiling point compared to hydrocarbons, ethers and halo compounds of comparable mass.</b></p> <p>Ans Due to presence of inter molecular H-bonding, which is either absent or very weak in other molecules.</p>
4	<p><b>Phenol is more acidic than alcohol</b></p> <p>Ans <math>C_6H_5-OH \rightleftharpoons C_6H_5O^- + H^+</math></p> <p><math>R-OH \rightleftharpoons RO^- + H^+</math></p> <p>The phenoxide ion is resonance stabilized due to (-) R effect of benzene ring. The alkoxide ion is less stable due to (+) I effect of -R group.</p>

5	<p><b>Aldehydes are more reactive than ketones towards nucleophilic addition reactions.</b></p> <p>Ans (a) inductive effect of R groups reduces the electrophilicity of the C atom of carbonyl group in ketones (b) steric hindrance: the approaching nucleophile suffers greater repulsion due to presence of two bulky-R groups in ketones.</p>
6	<p><b>Carboxylic acids have higher boiling points than aldehydes, ketones and alcohols of comparable molecular masses.</b></p> <p>Ans- The C.A molecules form dimers which do not separate into monomers even in vapour phase.</p>
7	<p><b>Gabriel Phthalimide synthesis is not suitable for preparation of secondary and tertiary amines.</b></p> <p>Ans- Since the reaction involves <math>S_N2</math> mechanism, only a primary alkyl group can approach the sterically hindered Phthalimide ring.</p>
8	<p><b><math>pK_b</math> of aniline is more than that of methylamine.</b></p> <p>Ans- Since the lone pair on the N-atom remains in conjugation with the benzene ring and is unavailable for donation. The basic character of methylamine is enhanced due to +I effect of <math>-CH_3</math> group.</p>
9	<p><b>Aniline does not undergo Friedel Crafts reaction.</b></p> <p>Ans- Aniline is basic and reacts with anhyd. <math>AlCl_3</math> to form a salt which deactivates the benzene ring towards electrophilic substitution.</p>
10	<p><b>During esterification, water must be removed as soon as it is formed.</b></p> <p style="text-align: center;"><math>H^+</math></p> <p>Ans- <math>RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O</math></p> <p>If the by-product is not removed, it will cause backward reaction. The ester formed will breakdown giving poor yield.</p>

### LEVEL-2 QUESTIONS

**Q1) Although phenoxide ion has more no. of resonating structures than carboxylate ion, even though carboxylic acid is a stronger acid why ?**

Ans:- The phenoxide ion has non equivalent resonance structures in which -ve charge is at less electronegative C atom and +ve charge is at more electronegative O-atom.

In carboxylate ion -ve charge is delocalized on two electronegative O-atoms hence resonance is more effective and a stronger acid.



**Q.2 Why Carboxylic acid have higher boiling point than alcohols as alcohol forms**

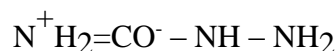
**strongest intermolecular hydrogen bonding?**

Ans. As Carboxylic acid forms a dimer due to which their surface area increases and forms strong intermolecular H-bonding having more boiling point than alcohols.

**Q.3 There are two-NH<sub>2</sub> group in semicarbazide. However only one is involved in formation of semicarbazones. Why?**

Ans.  $\text{NH}_2\text{-CO-NH-NH}_2$

Due to resonance one NH<sub>2</sub> group undergoes or involved in resonance and hence can't participate in the formation of semicarbazone.



Long pair of NH<sub>2</sub> group is not involved in resonance and is available for nucleophilic attack

**4 Why does solubility decrease with increasing molecular mass in carboxylic acid?**

Ans. Because of increase in alkyl chain length which is hydrophobic in nature. Hence solubility decreases.

**Q.5 Why are aldehydes more reactive than ketones when undergo nucleophilic addition reaction?**

Ans (a) + I effect:- The alkyl group in Ketones due to their e-releasing character decrease the +ve charge on C-Atom and thus reduce its reactivity.

(b) Steric hindrance:- Due to steric hindrance in ketones they are less reactive.



**Q.6 Why PCC cannot oxidise methanol to methanoic acid and while KMnO<sub>4</sub> can?**

Ans. This is because PCC is a mild oxidising agent and can oxidise methanol to methanal only. While KMnO<sub>4</sub> being strong oxidising agent oxidises it to methanoic acid.

**Q.7 During preparation of esters from a carboxylic acid and an alcohol in the presence of acid catalyst water or ester formed should be removed as soon as it is formed.**

Ans. The formation of esters from a carboxylic acid and an alcohol in the presence of acid catalyst is a reversible reaction.



To shift the equilibrium in forward direction, the water or ester formed should be removed as fast as it is formed.

**8 Why HCOOH does not give HVZ reaction while CH<sub>3</sub>COOH does?**

Ans. CH<sub>3</sub>COOH contains  $\alpha$ -hydrogens and hence give HVZ reaction but HCOOH does not contain  $\alpha$ -hydrogen and hence does not give HVZ reaction.

**Q.9 Suggest a reason for the large difference in the boiling point of butanol and butanal although they have same solubility in water.**

Ans. Because Butanol has strong intermolecular H-bonding while butanal has weak dipole-dipole interaction. However both of them form H-bonds with water and hence are soluble.

**Q.10 Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reaction than propanal. Explain.**

Ans. C-atom of Carbonyl group of benzaldehyde is less electrophilic than C-atom of Carbonyl group in propanal.

Polarity of Carbonyl group in benzaldehyde is reduced due to resonance making it less reactive in nucleophilic addition reactions.

**Q.11 Why does methanal not give aldol condensation while ethanol gives?**

Ans. This is because only those compounds which have  $\alpha$ -hydrogen atoms can undergo aldol reaction. Ethanol possesses  $\alpha$ -hydrogen and undergoes aldol condensation. Methanal has no  $\alpha$ -hydrogen atoms hence does not undergo aldol condensation.

**Q.12 Why does methanal undergo Cannizzaro's reaction?**

Ans. because it does not possess  $\alpha$ -hydrogen atom.

**Q.13 Which acid is stronger and why?**

F<sub>3</sub>C-C<sub>6</sub>H<sub>4</sub>COOH and CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>COOH Ans. CF<sub>3</sub><sup>-</sup> has strong (-I) effect

Whereas, CH<sub>3</sub><sup>-</sup> has strong (+I) effect. Due to greater stability of F<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>COO<sup>-</sup> ion over CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>COO<sup>-</sup> ion, CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>COOH is much stronger acid than CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>COOH.

**Q.14 Explain why O-hydroxy benzaldehyde is a liquid at room temperature while p-hydroxy benzaldehyde is a high melting solid.**

Ans. Due to intramolecular H-bonding in O-hydroxy benzaldehyde exists as discrete molecule whereas due to intermolecular H-bonding p-hydroxy benzaldehyde exists as associated molecules.

To break this intermolecular H-bonds a large amount of energy is needed. Consequently P-isomer has a much higher m.p. and b.p. than that of O-isomer. As a result O-hydroxy benzaldehyde is liquid.

**Q.15 Why is the boiling point of an acid anhydride higher than the acid from which it is**

derived?

Ans. Acid anhydrides are bigger in size than corresponding acids have more surface area more van der Waals. Force of attraction hence have higher boiling point.

**Q.16 Why do Carboxylic acids not give the characteristic reactions of a carbonyl group?**

Ans. Due to resonance, It doesn't give the characteristic reactions of carbonyl group. It does not have free

C=O group

**Q.17 Cyclohexanone forms cyanohydrin in good yield but 2,2,6 trimethyl cyclo-hexanone does not. Why?**

Ans. In 2,2,6 trimethyl cyclohexanone there is steric hindrance of 3 methyl groups, It does not form cyanohydrin in good yield.

**Q.18 Why is carboxyl group in benzoic acid meta directing?**

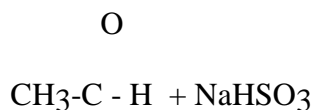
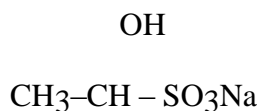
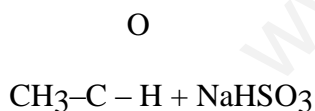
Ans. In benzoic acid the Carboxyl group is meta directing because it is electron-withdrawing. There is +ve charge on ortho and para positions. Electrophilic substitution takes place at meta position.

**Q.19 Treatment of Benzaldehyde with HCN gives a mixture of two isomers which cannot be separated even by careful fractional distillation. Explain why?**

Ans. It is because we get two optical isomers which have same physical properties. Cannot be separated by Fractional distillation.

**Q.20 Sodium Bisulphite is used for the purification of aldehydes and Ketones. Explain.**

Ans. Aldehydes and Ketones form addition compounds with  $\text{NaHSO}_3$  whereas impurities do not. On hydrolysis we get pure aldehydes and Ketones back.



(P.U.  
R.E.)

**Q.21 Why pH of reaction should be carefully controlled while preparing ammonia derivatives of carbonyl compound?**

Ans. In strongly acidic medium ammonia derivatives being basic will react with acids and will not react with carbonyl compound. In basic medium,  $\text{OH}^-$  will attack carbonyl group. pH of a reaction should be carefully controlled.

**Q.22 Why formic acid is stronger acid than acetic acid?**

Ans. Due to +I effect,  $\text{CH}_3^-$  group in acetic acid increases  $e^-$  density on carbon atom which makes it a weak acid. While in formic acid no such pushing group is present, hence it is a stronger acid than acetic acid.

**Q.23 Why is oxidation of alcohols to get aldehydes carried out under controlled conditions?**

Ans. It is because aldehydes get further oxidised to acids, oxidation of alcohols to aldehydes needs to be controlled.

**Q.24 Why the oxidation of toluene to benzaldehyde with  $\text{CrO}_3$  is carried out in the presence of acetic anhydride.**

Ans. If acetic anhydride is not used we will get benzoic acid. Acetic anhydride is used to prevent oxidation of benzaldehyde to benzoic acid.

**Q.25 Melting point of an acid with even no. of carbon atoms is higher than those of its neighbour with odd no. of carbon atoms.**

Ans. They fit into crystal lattice more readily than odd ones that is why they have higher lattice energy and higher melting point.

**Q.26 Why do aldehydes have lower boiling point than corresponding alcohols?**

Ans. Alcohols have lower boiling point as they are not associated with intermolecular hydrogen bonding whereas alcohols are associated with intermolecular H-bonding. Aldehydes have lower B.p.

**Q.27 Why do aldehydes behave like polar compounds?**

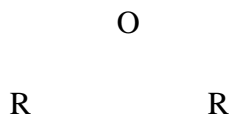
Ans. Due to presence of  $\text{C}=\text{O}$  group which is polar

**Q.28 Most aromatic acids are solids while acetic acid and others of this series are liquids. Explain why?**

Ans. Aromatic acids have higher molecular weight, More Van-der Waals force of attraction as compared to aliphatic acids. They are solids.

**Q.29 ethers possess a dipole moment even if the alkyl radicals in the molecule are identical. Why?**

Ans. It is because ethers are bent molecules, dipole do not get cancelled.



**Q.30 Why does acyl chlorides have lower boiling point than corresponding acids?**

Ans. Acyl chlorides are not associated with intermolecular H-bonding. They have lower boiling point.

**Q.31 Why ethers are stored in coloured bottles?**

Ans. They are stored in coloured bottles. In presence of sunlight they react with oxygen to form peroxides which may cause explosion.

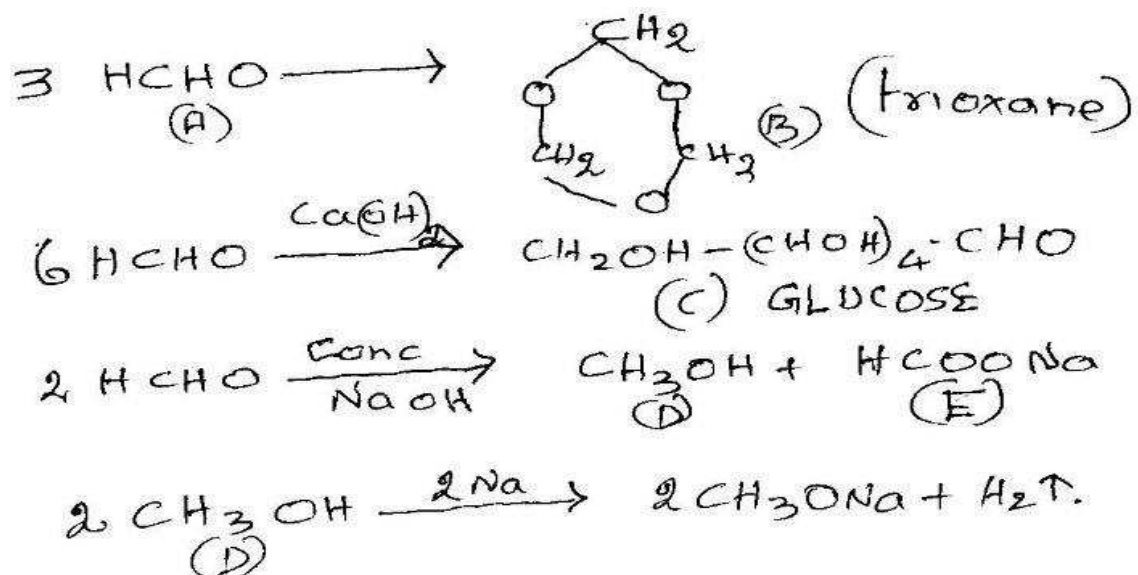
**Q.32 Why formaldehyde cannot be prepared by Rosenmund's reduction?**

Ans. Because the formyl chloride thus formed is unstable at room temperature. Cannot be prepared by Rosenmund reduction.

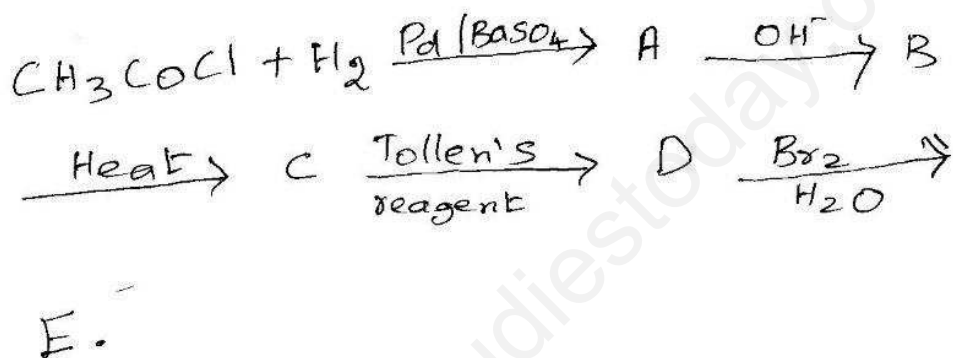
### LEVEL-3 QUESTIONS

1. A compound 'A' dissolves in water and its 40% aqueous solution is used as a preservative for zoological specimen. When its aq. solution is allowed to stand, it forms trimer 'B'. 6 moles of it react to give 'C' in presence of  $\text{Ca(OH)}_2$ . 'A' undergoes disproportionation reaction in presence of conc. Alkali to form 'D' and 'E'. 'D' liberates  $\text{H}_2(\text{g})$  with Na Metal. Identify 'A' to E writing the chemical equations involved

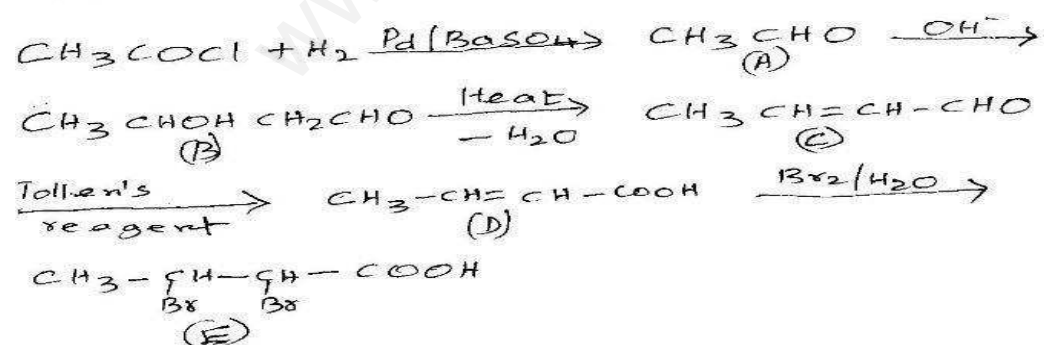
Ans: A is formaldehyde ( $\text{HCHO}$ ) (aq soln formalin is used as preservative)



2. Complete the following and identify from A to E.



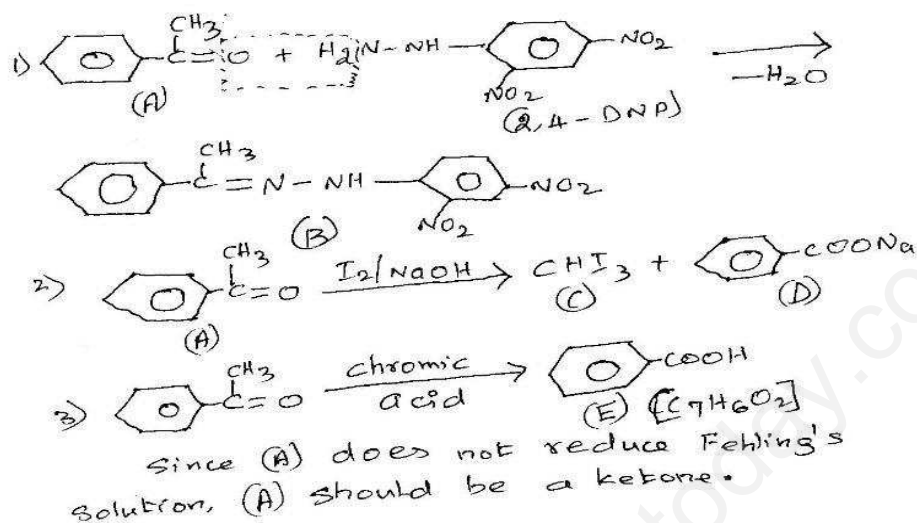
Solution:



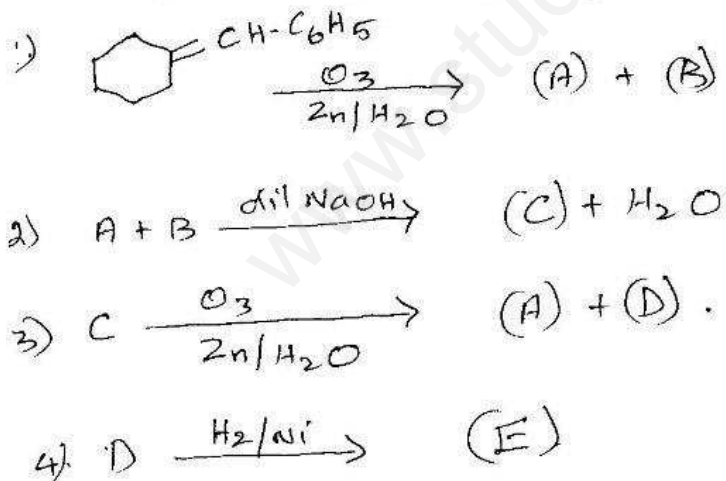


3. An organic compound (A) having MF  $C_8H_8O$  forms an orange red precipitate (ppt) (B) with 2,4-DNP. Compound (A) gives yellow ppt ('C'). When heated in presence of  $I_2$  and NaOH along with a colorless compound 'D'. 'A' does not reduce Fehling's solution and does not decolorize Bromine water. On drastic oxidation of 'A' with chromic acid, a carboxylic acid 'E' with mF  $C_7H_6O_2$  is formed. Deduce the structures of A to E. Also, write the reactions involved.

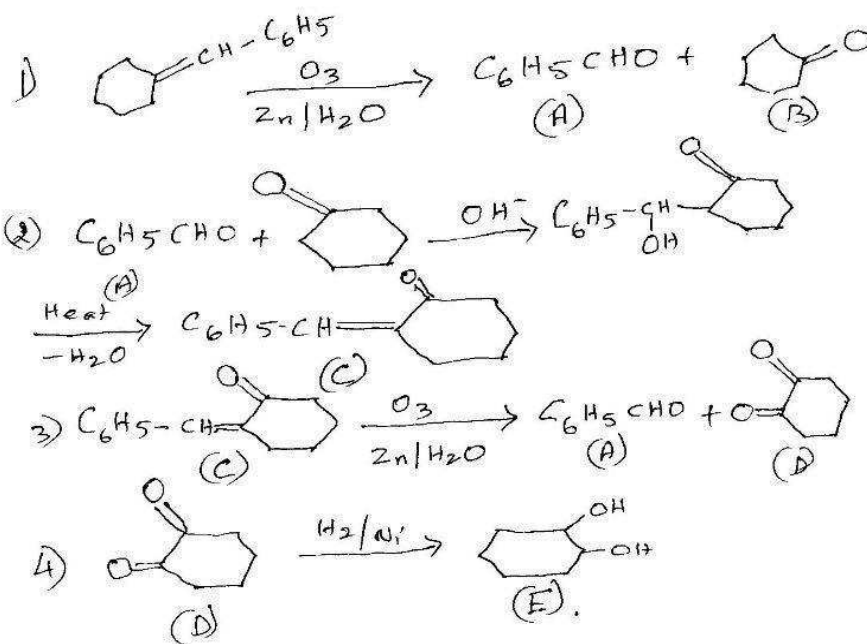
Ans:



4. Complete the following and identify the compounds A to E



Ans.

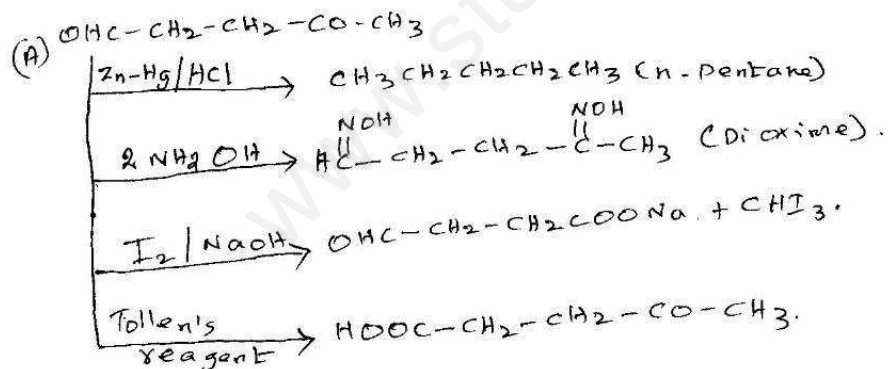


5. An organic compound A with mF  $C_5H_8O_2$  is reduced to n pentane on treatment with  $Zn-Hg/HCl$ . 'A' forms di-oxime with  $NH_2OH$  and gives a positive iodoform test and Tollen's reagent test. Identify the compound 'A' and deduce its structure

Ans: Contains  $CH_3CO-$  group.

- Gives positive Tollen's tests. Has  $-CHO$  group
- Gives n pentane on reduction. Should contain all 5 carbons in the same chain.

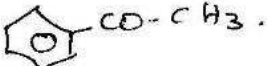
$\therefore$  The structure of (A) is  $OHC-CH_2-CH_2-CO-CH_3$ .

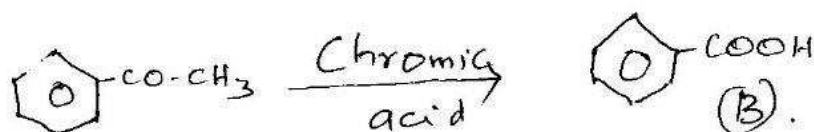
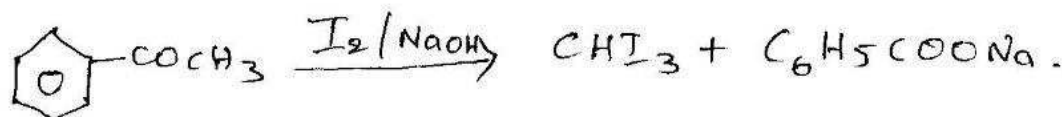
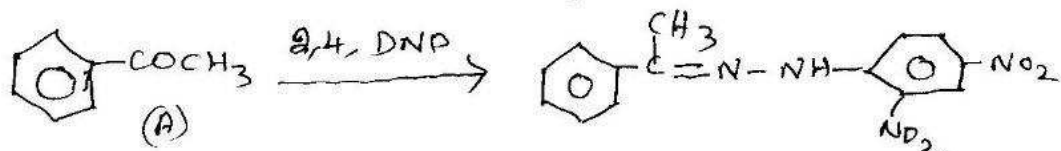


6. An organic compound 'A' with MF  $C_8H_8O$  gives positive iodoform and 2,4-DNP tests. It does not reduce Fehling's solution and does not decolorize  $Br_2/H_2O$ . On oxidation with chromic oxide, it gives a carboxylic acid 'B' with MF  $C_7H_6O_2$ . Deduce the structures of A and B

Ans: A is a carbonyl compound (gives 2,4 DNP test)

- Has  $\text{CH}_3\text{CO}$  group (Iodoform test)
- Is saturated (not decolorising  $\text{Br}_2$  water).

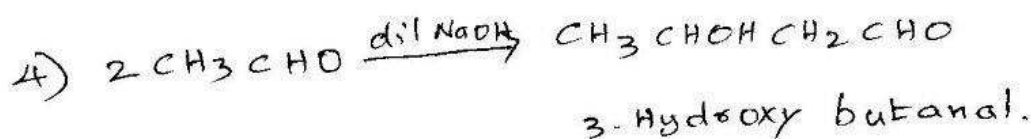
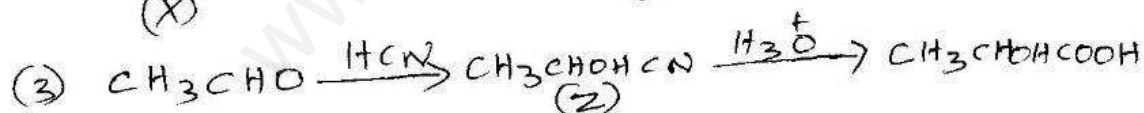
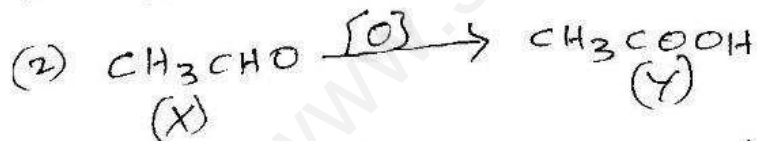
Structure of A is .



7. A compound 'X' with MF  $\text{C}_2\text{H}_4\text{O}$  on oxidation gives Y with MF  $\text{C}_2\text{H}_4\text{O}_2$ . X undergoes haloform reaction. On treatment with  $\text{HCN}$ , X gives Z which on hydrolysis gives 2-hydroxy propanoic acid. Write down the structures of X, Y and Z. Name the product when X reacts with diluted  $\text{NaOH}$ .

Ans: Y Has 2 carbon atoms . Hence not Ketone

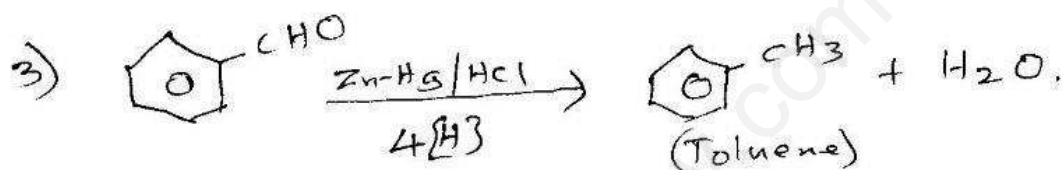
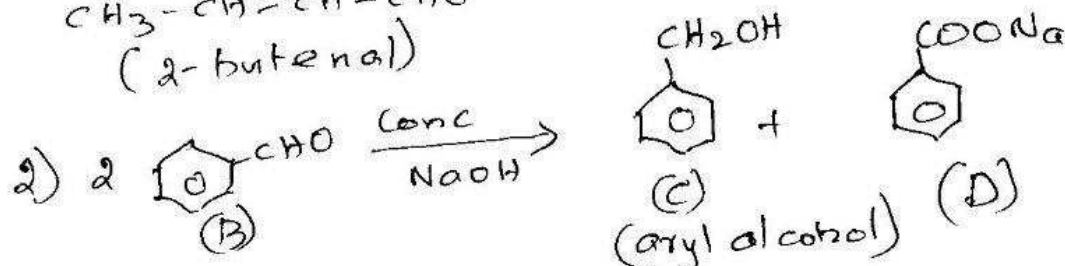
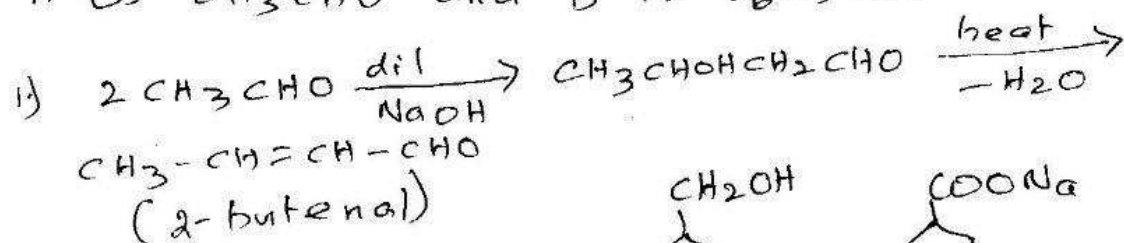
- X is  $\text{CH}_3\text{CHO}$  (gives haloform reaction)



8. An unknown aldehyde A on reaction with alkali gives B-hydroxy aldehyde which loses  $\text{H}_2\text{O}$  forming an unsaturated aldehyde 2-butenal. Another aldehyde B undergoes disproportionation reaction in the presence of con. Alkali to produce C and D. C is an

aryl alcohol with MF  $C_7H_8O$ . Write the sequence of reactions involved. Identify A to D. Name the product when B reacts with  $Zn-Hg/HCl$

A is  $CH_3CHO$  and B is  $C_6H_5CHO$

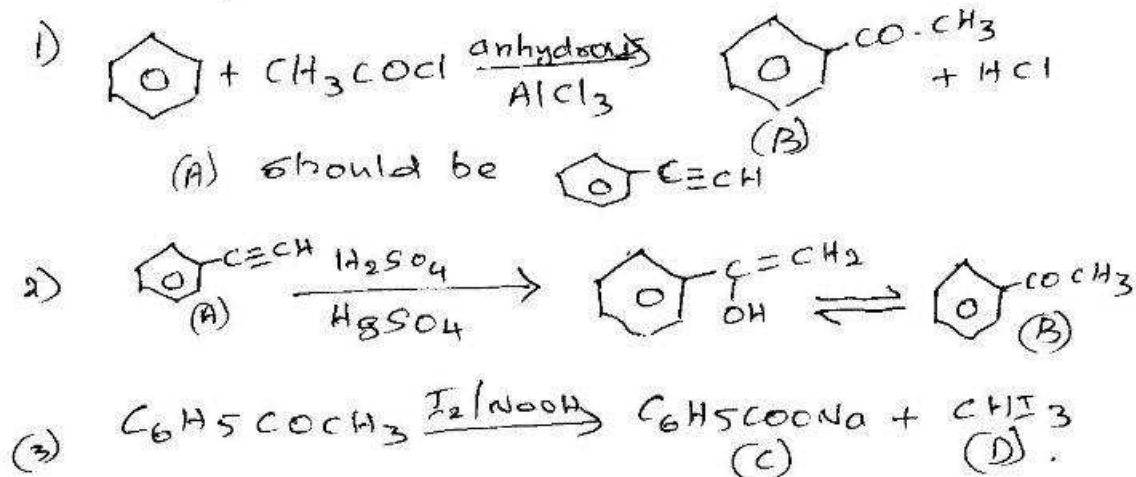


Ans:

9. An organic compound A ( $C_8H_6$ ) on treatment with  $H_2SO_4$  and  $HgSO_4$  gives B which also can be obtained from the reaction b/w benzene and an acid chloride in presence of  $AlCl_3$  (anhydrous). B on treatment with  $I_2/NaOH$  gives C and a yellow compound D. Identify from A to D. Write the sequence of reactions

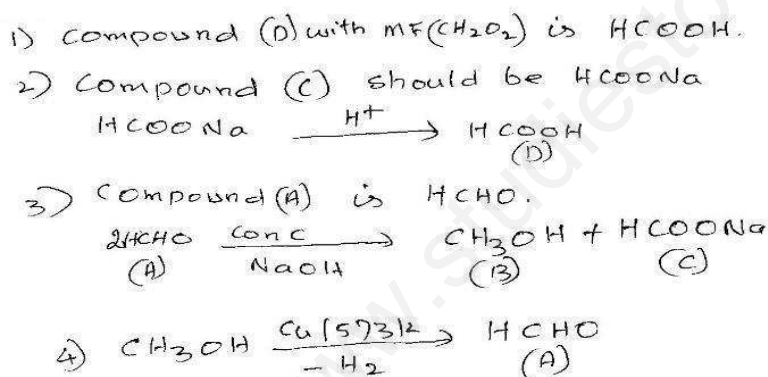
Ans: B has  $CH_3CO$  group (iodoform test)

- B is obtained from benzene and acid chloride in presence of anhyd.  $AlCl_3$  (FC reaction)



10. Two moles of an organic compound A on treatment with strong base gives compounds B and C. Compound B on dehydrogenation with Cu gives A while on acidification gives a carboxylic acid D with MF  $\text{CH}_2\text{O}_2$ . Identify A to D and write the sequence of reactions

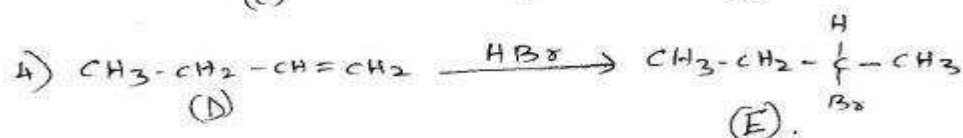
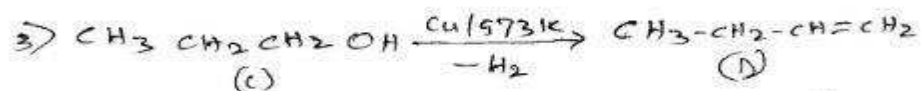
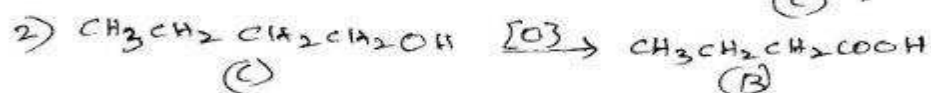
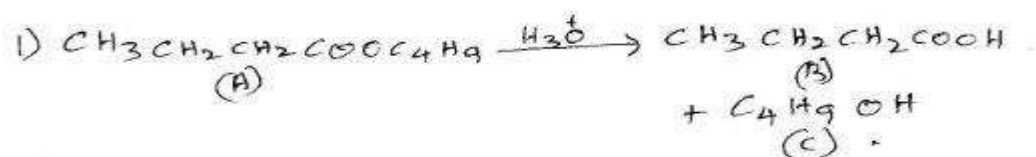
Ans:



11. An organic compd A ( $\text{C}_8\text{H}_{16}\text{O}_2$ ) was hydrolysed with dil  $\text{H}_2\text{SO}_4$  to yield a carboxylic acid B and an alcohol C. Oxidation of C with chromic acid gives compound B. C on dehydration gives D which reacts with  $\text{HBr}$  to give optically active compound E. Identify A to E with the help of equations.

Ans: A is an ester (on hydrolysis gives Carboxylic acid and alcohol)

- C and B have same number of Carbon atoms (C on oxidation gives B)



E is optically active since it contains a chiral carbon.