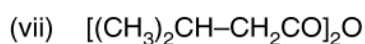
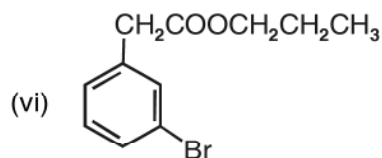
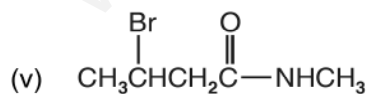
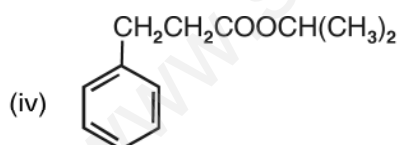
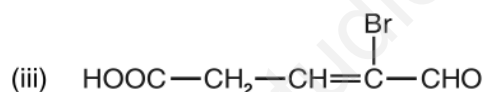
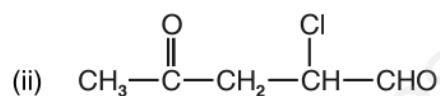
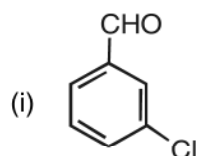


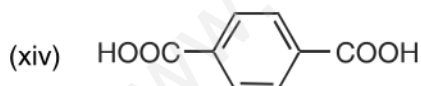
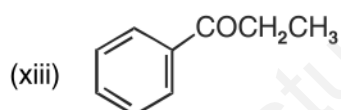
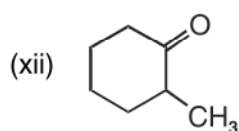
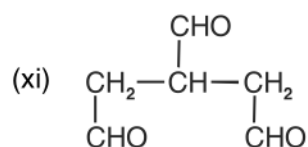
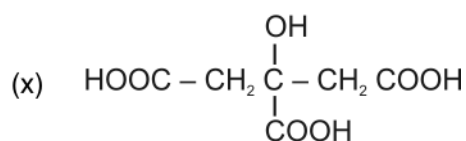
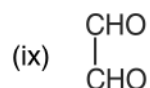
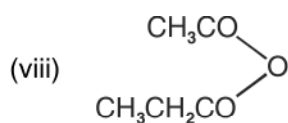
## Unit - 12

## ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

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1. Indicate the electrophilic and nucleophilic centres in acetaldehyde.
2. Write the IUPAC names of the following organic compounds :





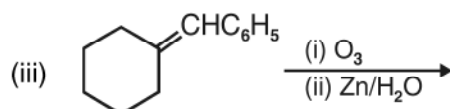
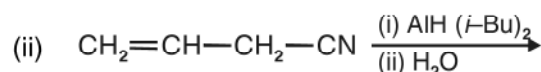
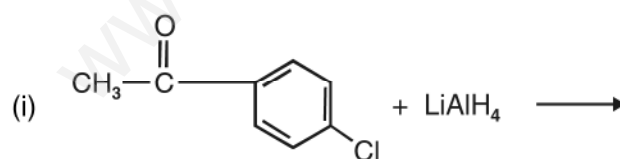
3. Explain the following reactions giving one example of each :
- (i) Rosenmund reduction reaction
  - (ii) Stephen reaction
  - (iii) Etard reaction
  - (iv) Gatterman-Koch reaction
  - (v) Aldol condensation
  - (vi) Cross aldol condensation
  - (vii) Cannizzaro reaction
  - (viii) Decarboxylation reaction

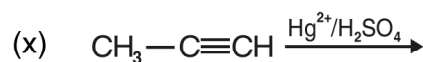
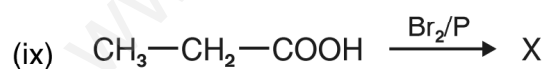
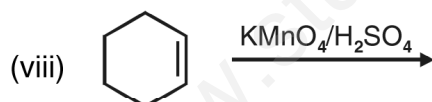
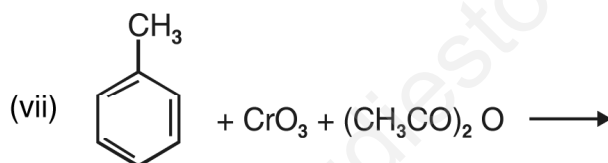
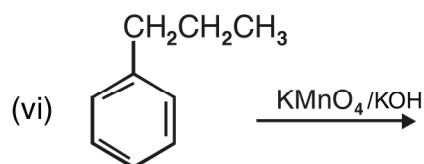
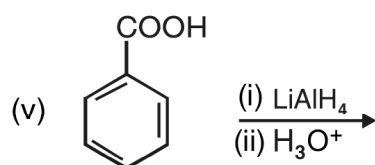
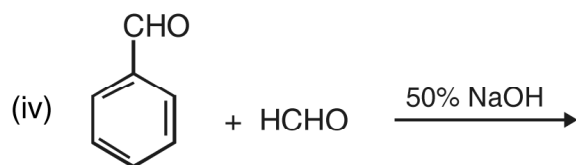
- (ix) Kolbe's reaction
- (x) Hell-Volhard-Zelinsky reaction
- (xi) Clemmensen reduction
- (xii) Wolff-Kishner reduction
- (xii) Haloform reaction.

4. How will you convert :

- (i) Isopropyl chloride to 2-methylpropionaldehyde.
- (ii) benzene to benzaldehyde
- (iii) benzoic acid to acetophenone
- (iv) propene to propanal
- (v) butanoic acid to 2-hydroxybutanoic acid
- (vi) benzoic acid to m-nitrobenzyl alcohol
- (vii) propanol to propene
- (viii) propanol to butan-2-one.
- (ix) methyl magnesium bromide to ethanoic acid
- (x) benzoic acid to benzyl chloride
- (xi) acetone to chloroform
- (xii) acetylene to acetic acid
- (xiii) formaldehyde to propanol
- (xiv) acetophenone to 2-phenylbutan-2-ol

5. Complete the following reactions :



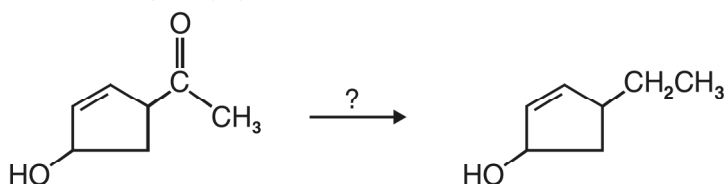


6. How will you prepare the following derivatives of acetone?

- (i) 2, 4-DNP derivative
- (ii) Schiff's base
- (iii) Oxime

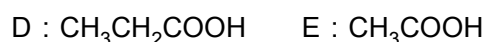
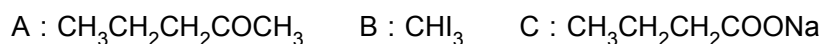
7. Arrange the following in the increasing order of the property indicated
- $\text{CH}_3\text{CHO}$ ,  $\text{HCHO}$ ,  $\text{CH}_3\text{COCH}_3$ ,  $\text{C}_6\text{H}_5\text{CHO}$  (reactivity towards  $\text{HCN}$ )
  - propan-1-ol, propanone, propanal (boiling point)
8. Give the reaction mechanism for following reactions :
- $\text{CH}_3\text{CHO} + \text{HCN} \longrightarrow \text{CH}_3-\text{CH} \begin{array}{l} \text{OH} \\ \text{CN} \end{array}$
  - $\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{H}_2\text{SO}_4} \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$
  - $\text{CH}_3\text{COCH}_3 \xrightarrow[\text{(ii) H}_2\text{O}]{\text{(i) CH}_3\text{MgBr}} \text{CH}_3-\text{C} \begin{array}{l} \text{OH} \\ | \\ \text{CH}_3 \end{array} -\text{CH}_3$
9. Give one chemical test to distinguish between following pair of compounds: Write the chemical reaction involved.
- propan-2-ol and propanone
  - ethyl acetate and methyl acetate
  - benzaldehyde and benzoic acid
  - benzaldehyde and acetaldehyde
  - formic acid and acetic acid
  - propanal and propan-1-ol
  - ethanoic acid and ethylethanoate
  - $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{COCH}_3$
  - $\text{CH}_3\text{CHO}$  and  $\text{HCHO}$
  - acetophenone and benzophenone
10. Give reason for the following
- cyclohexanone form cyanohydrin in good yield but 2, 2, 6 – trimethylcyclohexanone does not.
  - Benzaldehyde does not give Fehling's test.
  - The alpha H atoms in ethanal are acidic in nature.
  - p-nitrobenzaldehyde is more reactive than benzaldehyde towards nucleophilic addition reactions.

- (v) Acetic acid does not give sodium bisulphite addition product.
- (vi) For the formation of ethyl acetate from acetic acid and ethanol in presence of sulphuric acid, the reaction mixture is heated to remove water as fast as it is formed.
- (vii) Chloroacetic acid has lower pka value than acetic acid.
- (viii) Monochloroethanoic acid is a weaker acid than dichloroethanoic acid.
- (ix) Benzoic acid is stronger acid than ethanoic acid.
- (x) Aldehydes are more reactive towards nucleophilic reagents than ketones .
- (xi) Benzaldehyde does not undergo aldol condensation.
- (xii) Formic acid reduces Tollens' reagent.
- (xiii) Electrophilic substitution in benzoic acid takes place at m-position.
- (xiv) Carboxylic acids do not give characteristic reactions of carbonyl group.
- (xv) Formaldehyde gives Cannizzaro reaction whereas acetaldehyde does not.
- (xvi) tert-butyl benzene cannot be oxidised with  $\text{KMnO}_4$ .
- (xviii) There are two  $-\text{NH}_2$  groups in semicarbazide. However, only one  $-\text{NH}_2$  group is involved in the formation of semicarbazones.
- (xix) Benzoic acid is less soluble in water than acetic acid.
- (xx) Formic acid is a stronger acid than acetic acid.
- \*11. You are given four different reagents  $\text{Zn-Hg/HCl}$ ,  $\text{NH}_2\text{NH}_2/\text{OH}^-$  in Glycol,  $\text{H}_2/\text{Ni}$  and  $\text{NaBH}_4$ . Select one reagent for the following transformation and give reasons to justify your answer.

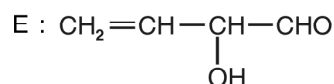
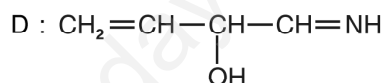
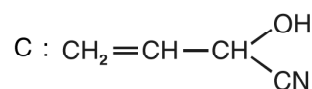
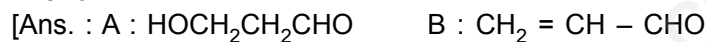


**[Hint :** OH group and alkene are sensitive groups to HCl so clemmeson reduction cannot be used. Hence  $\text{NH}_2\text{NH}_2/\text{OH}^-$  in glycol will be used.

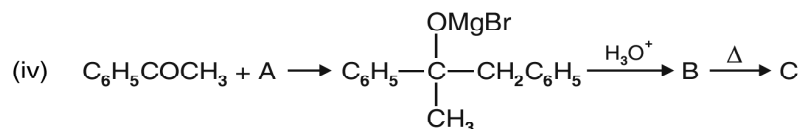
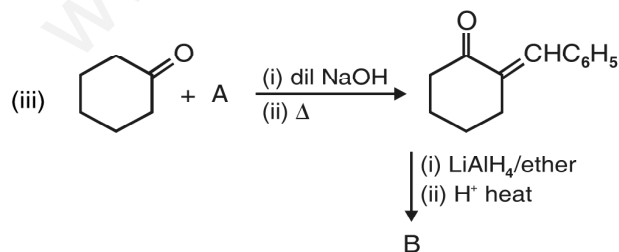
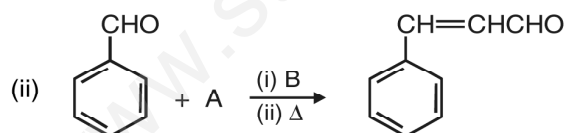
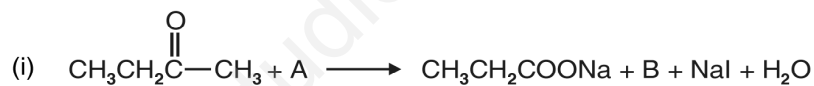
- \*12. An organic compound (A) having molecular formula  $C_5H_{10}O$  gives a positive 2, 4-DNP test. It does not reduce Tollens' reagent but forms an addition compound with sodium hydrogen sulphite. On reaction with  $I_2$  in alkaline medium, it forms a yellow precipitate of compound B and another compound C having molecular formula  $C_4H_7O_2Na$ . On oxidation with  $KMnO_4$ , [A] forms two acids D and E having molecular formula  $C_3H_6O_2$  and  $C_2H_4O_2$  respectively. Identify A, B, C, D and E.



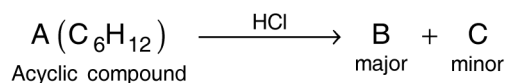
- \*13. Formaldehyde and acetaldehyde on treatment with dil. NaOH form A which on heating changes to B. When B is treated with HCN, it forms C. Reduction of C with DIBAL-H yields D which on hydrolysis gives E. Identify A, B, C, D and E.



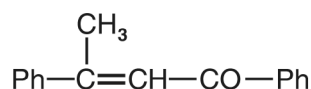
- \*14. Identify the missing reagent/products in the following reactions :



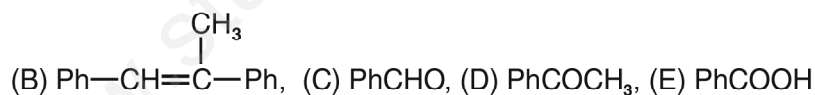
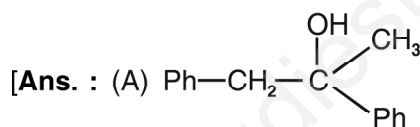
15. Identify A, B, C, D and E in the following sequences of reactions :



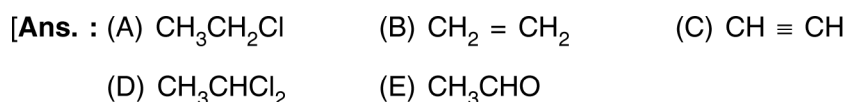
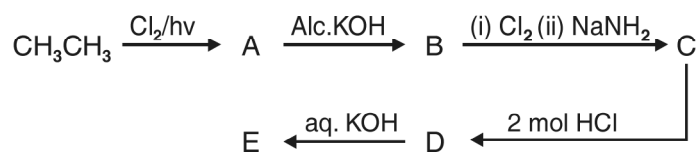
\*16. A tertiary alcohol 'A' on acid catalyzed dehydration gave product 'B'. Ozonolysis of 'B' gives compounds 'C' and 'D'. Compound 'C' on reaction with KOH gives benzyl alcohol and compound 'E'. Compound 'D' on reaction with KOH gives  $\alpha,\beta$  - unsaturated ketone having the following structure.



Identify A, B, C, D and E



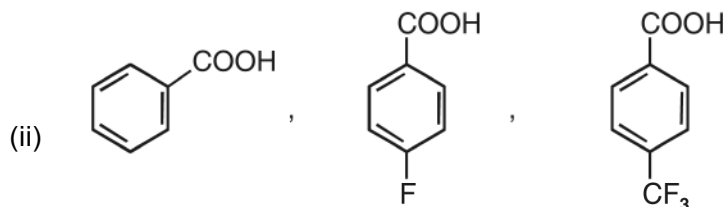
\*17. Identify A, B, C, D and E in the following sequence of reactions :





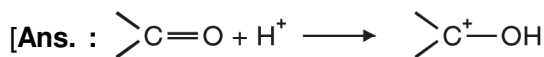
\*18. Arrange the following acids in the order of increasing acid strength

(i) formic acid, benzoic acid, acetic acid



(iii)  $\text{CH}_3\text{CH}_2\text{COOH}$ ,  $\text{C}_6\text{H}_5\text{COOH}$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$

\*19. During the reaction of a carbonyl compound with a weak nucleophile,  $\text{H}^+$  ions are added as catalyst. Why?



$\text{H}^+$  ions get attached to oxygen atom and make carbonyl carbon more electrophilic in nature.]

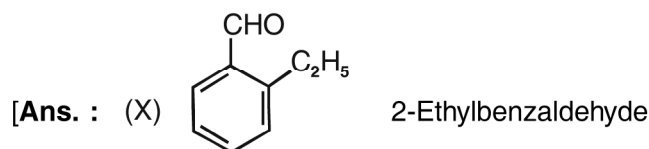
\*20. During reaction of carbonyl compound with 2, 4-DNP reagent, the pH of the reaction mixture has to be maintained between 3 and 4. Why?

[Ans. :  $\text{H}^+$  ions increase the electrophilicity of carbonyl carbon. When  $\text{H}^+$  ions are in excess, they protonate the  $\text{NH}_2$  group of 2, 4-DNP. After protonation  $-\text{N}^+\text{H}_3$  group does not act as nucleophile.]

\*21. An aromatic compound X with molecular formula  $\text{C}_9\text{H}_{10}$  gives the following chemical tests :

- Forms 2, 4-DNP derivative
- Reduces Tollens' reagent
- Undergoes Cannizzaro reaction
- On vigorous oxidation gives 1, 2-benzenedicarboxylic acid.

Identify X and write its IUPAC name. Also write the reactions involved in the formation of above mentioned products.



22. Iodoform can be prepared from, all except.

- |                           |                        |            |
|---------------------------|------------------------|------------|
| (i) Ethyl methyl ketone   | (ii) Isopropyl alcohol |            |
| (iii) 3-methylbutan-2-one | (iv) Isobutyl alcohol  | Ans : (iv) |