

ASSIGNMENT NO - 3

CH-Aldehyde, ketone and Acid.

(1)

(A) Give Reason for the following:

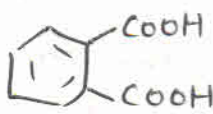
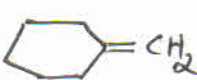
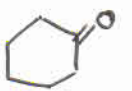
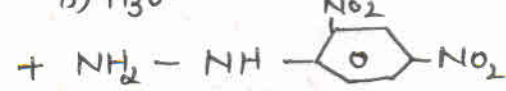


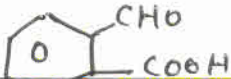
- (i) Oxidation of aldehydes is easier than ketones.
- (ii) $\text{CH}_2=\text{CH}-\text{COOH}$ is more acidic than $\text{CH}_3\text{CH}_2-\text{COOH}$
- (iii) Benzoic acid is a stronger acid than acetic acid.
- (iv) Methanal is more reactive toward nucleophilic addition reaction than ethanal.
- (v) Propanone is less reactive than ethanal towards nucleophilic addition reaction.
- (vi) $\text{O}_2\text{N}-\text{CH}_2-\text{COOH}$ has lower pK_a value than CH_3COOH .
- (vii) $(\text{CH}_3)_2\text{CH}-\text{CHO}$ undergoes aldol condensation while $(\text{CH}_3)_3\text{C}-\text{CHO}$ does not.
- (viii) The α -hydrogen atoms of aldehydes & ketones are acidic.
- (ix) Benzoic acid does not give Friedel-Crafts reaction.
- (x) $\text{Cl}-\text{CH}_2\text{COOH}$ is a stronger acid than CH_3COOH
- (xi) Carboxylic acids don't give reactions of carbonyl group.
- (xii) Out of $\text{CH}_3\text{CH}_2-\text{CO}-\text{CH}_2-\text{CH}_3$ and $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CO}-\text{CH}_3$, which give iodoform test?
- (xiii) Ethanal is more reactive than acetone towards nucleophilic addition reaction.
- (xiv) $(\text{CH}_3)_3\text{C}-\text{CHO}$ does not undergo aldol condensation.
- (xv) Carboxylic acids are higher boiling liquids than alcohols.
- (xvi) The boiling points of aldehydes and ketones are lower than of the corresponding acids.
- (xvii) The aldehydes and ketones undergo a number of addition reactions.
- (xviii) Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Give two reasons.
- (xix) Benzaldehyde reduces Tollen's reagent.
- (xx) Ethanoic acid is a weaker acid than benzoic acid.

(B) Explain the following Name Reactions!

- (i) Rosenmund Reduction (ii) Etard Reaction
 (iii) Gatterman-Koch Reaction (iv) Clemmensen Reduction
 (v) Wolff-Kishner Reduction (vi) Aldol Condensation
 (vii) Hell-Volhard-Zelinsky Rx. (viii) Stephen's Reduction
 (ix) Decarboxylation.

(3) Explain the mechanism of a nucleophilic attack on carbonyl group of an aldehyde or a ketone.

(4) Write structures of the following:

- (i) $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{PCC}} \text{A} \xrightarrow{\text{CH}_3\text{OH}/\text{dry HCl}} \text{B}$
- (ii) $\text{C}_6\text{H}_5\text{COCH}_3 \xrightarrow{\text{NaOI}} \text{A} + \text{B}$
- (iii) $\text{CH}_3\text{-BH} \xrightarrow{\text{Mg/Ether}} \text{(A)} \xrightarrow[\text{(ii) Water}]{\text{(i) CO}_2} \text{(B)} \xrightarrow[\Delta]{\text{CH}_3\text{OH}/\text{H}^+} \text{(C)}$
- (iv) $\text{CH}_3\text{-}\overset{\text{O}}{\parallel}\text{C}\text{-CH}_3 \xrightarrow[\text{(ii) H}_2\text{O}]{\text{(i) CH}_3\text{MgBH}} \text{(A)} \xrightarrow[\text{Ether}]{\text{Na Metal}} \text{(B)} \xrightarrow{\text{CH}_3\text{-BH}} \text{(C)}$
- (v) $\text{CH}_3\text{-}\overset{\text{O}}{\parallel}\text{C}\text{-CH}_3 \xrightarrow[\text{(ii) KOH/Glycol, \Delta}]{\text{(i) H}_2\text{N-NH}_2} ?$
- (vi) $\text{C}_6\text{H}_5\text{-CO-CH}_3 \xrightarrow{\text{NaOH/I}_2}$
- (vii) $\text{CH}_3\text{COONa} \xrightarrow[\Delta]{\text{NaOH/CaO}}$
- (viii)  $\xrightarrow[\text{Heat}]{\text{SOCl}_2}$
- (ix) $\text{C}_6\text{H}_5\text{CHO} \xrightarrow{\text{H}_2\text{NCONHNH}_2}$
- (x)  $\xrightarrow{?} \text{Cyclohexane ring with a -CHO group}$
- (xi) $\text{C}_6\text{H}_5\text{BH} \xrightarrow{\text{Mg/dry Ether}} \text{A} \xrightarrow[\text{ii) H}_3\text{O}^+]{\text{i) CO}_2} \text{(B)} \xrightarrow{\text{PCl}_5} \text{C}$
- (xii) $\text{CH}_3\text{CN} \xrightarrow[\text{b) H}_3\text{O}^+]{\text{a) SnCl}_2/\text{HCl}} \text{A} \xrightarrow{\text{dil. NaOH}} \text{B} \xrightarrow{\Delta} \text{C}$
- (xiii)  + $\text{NH}_2\text{-NH-}$  $\xrightarrow{\text{H}^+}$
- (xiv)  $\overset{\text{O}}{\parallel}\text{C-CH}_3$ + $\text{CH}_3\text{CH}_2\text{NH}_2 \xrightarrow{\text{H}^+}$
- (xv) 
- (xvi)  $\xrightarrow{\text{NaCN/Hg}} ?$

(5) Convert the following!

- (i) Ethyl benzene to benzene (ii) Acetaldehyde to Butan-1,3-diol
 (iii) Acetone to propene (iv) Ethanol to Acetone
 (v) Benzene to Acetophenone (vi) Benzoic acid to Benzaldehyde
 (vii) Propanone to propene (viii) Benzaldehyde to Benzophenone
 (ix) Ethanol to 3-hydroxybutanal (x) Toluene to Benzaldehyde
 (xi) Ethyl benzene to Benzoic acid (xii) Ethanol to But-2-enal
 (xiii) Propanone to Propene (xiv) Propene to Propan-2-ol

(6) Give chemical test to distinguish between:

- (i) Acetaldehyde and Benzaldehyde.
 (ii) Propanone and Propanol
 (iii) Ethanal and Propanal (iv) Phenol and Benzocack
 (v) Acetophenone and Benzophenone
 (vi) Propanal and Propanone
 (vii) Benzaldehyde and acetophenone
 (viii) pentan-2-one and pentan-3-one

(7) AN organic compound 'A' on treatment with ethylalcohol gives carboxylic acid 'B' and compound 'C'. Hydrolysis of 'C' under drastic conditions gives 'B' and 'D'. Oxidation of 'D' with KMnO_4 also gives 'B'. B on heating with Ca(OH)_2 gives E with M.F $\text{C}_3\text{H}_6\text{O}$. 'E' does not give Tollens test or reduce Fehling solution but forms 2,4-dinitrophenyl Hydrazone. Identify A, B, C, D, E.

(8) Give names of the reagents that bring about these rxns.

- (i) Hexan-1-ol to Hexanal
 (ii) p-Fluorotoluene to p-fluorobenzaldehyde
 (iii) Ethanenitrile to ethanol
 (iv) Allyl alcohol to propenal

(9) Draw the structures of the following derivatives

- (i) The 2,4-Dinitrophenyl Hydrazone of Benzaldehyde
 - (ii) Acetaldehyde dimethyl acetal
 - (iii) Cyclopropanone oxime
- (10) Arrange the following in order of the property indicated.
- (i) CH_3CHO , $\text{CH}_3\text{CH}_2\text{OH}$, CH_3OCH_3 , $\text{CH}_3\text{CH}_2\text{CH}_3$ (↑ing order of b.pt)
 - (ii) $(\text{CH}_3)_2\text{CHCOOH}$, $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$, $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH}$ (↑ing order of their acid strength)

11) An organic compound 'A' with molecular formula $\text{C}_5\text{H}_8\text{O}_2$ is reduced to n-pentane on treatment with Zn-Hg/HCl . 'A' forms a dioxime with hydroxylamine and give a positive Iodoform test and Tollen's test. Identify the compound A and deduce its structure.

12) Write the structures of A, B, C, D and E in the following rxns:

