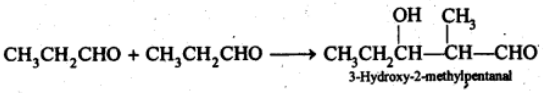
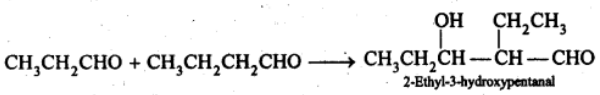
12.9. Write structural formulas and names of four possible aldol condensation products from propanal and butanal. In each case, indicate which aldehyde acts as nucleophile and which as electrophile.
Ans:

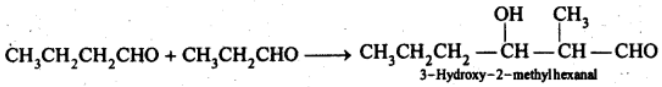
(a) Propanal acts as both nucleophile as well as electrophile.



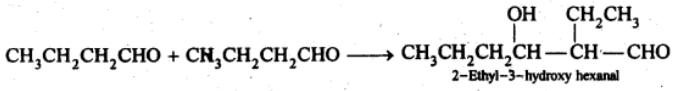
(b) Propanal as electrophile and butanal as nucleophile.



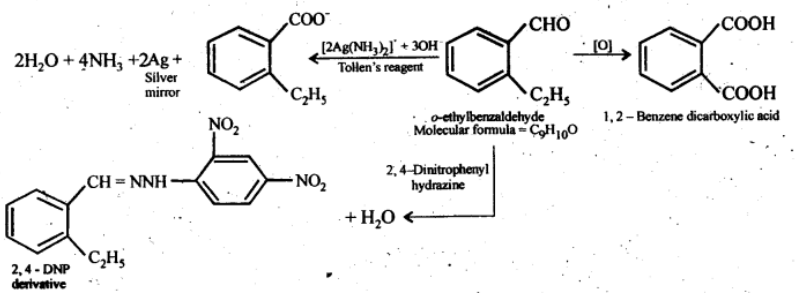
(c) Butanal as electrophile and propanal as nucleophile.



(d) Butanal acts as both nucleophile as well as an electrophile.

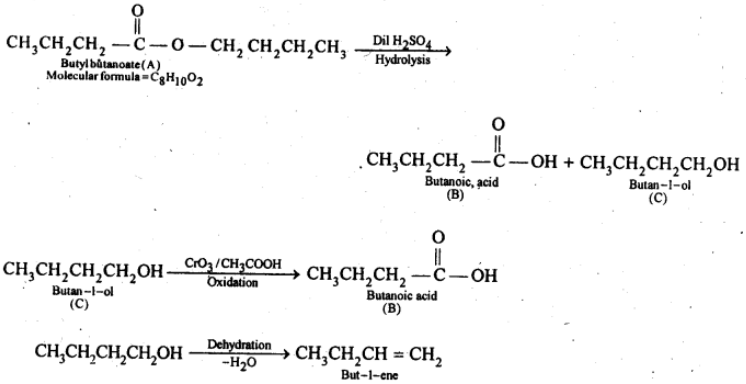


12.10. An organic compound with the molecular formula $C_9H_{10}O$ forms 2,4-DNP derivative, reduces Tollen's reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid. Identify the compound.
Ans: Since the given compound with molecular formula $C_9H_{10}O$ forms a 2,4-DNP derivative and reduces Tollen's reagent, it must be an aldehyde. Since it undergoes Cannizzaro reaction, therefore, CHO group is directly attached to die benzene ring.
Since on vigorous oxidation, it gives 1, 2-benzene dicarboxylic acid, therefore, it must be an ortho- substituted benzaldehyde. The only o-substituted aromatic aldehyde having molecular formula $C_9H_{10}O$ is o-ethyl benzaldehyde. Ail the reactions can now be explained on the basis of this structure.

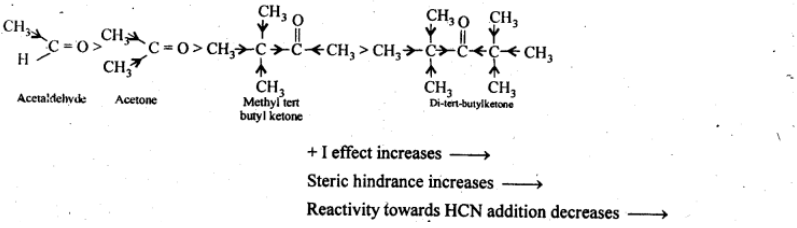


12.11. An organic compound (A) (molecular formula $C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (Q on dehydration gives but-l-ene. Write equations for the reactions involved.
Ans: Since an ester A with molecular formula $C_8H_{16}O_2$ upon hydrolysis gives carboxylic acid B and the alcohol C and oxidation

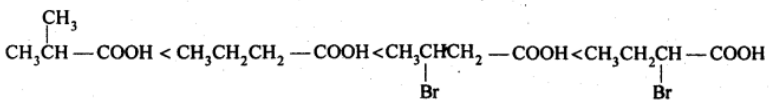
of C with chromic acid produces the acid B, therefore, both the carboxylic acid B and alcohol C must contain the same number of carbon atoms.
Further, since ester A contains eight carbon atoms, therefore, both the carboxylic acid B and the alcohol C must contain four carbon atoms each.
Since the alcohol C on dehydration gives but-l-ene, therefore, C must be a straight chain alcohol, i.e., butan-l-ol.
If C is butan-l-ol, then the acid B must be butanoic acid and the ester A must be butyl butanoate.The chemical equations are as follows:



12.12. Arrange the following compounds in increasing order of their property as indicated:
(i) Acetaldehyde, Acetone, Di-tert butyl ketone, Methyl tert-butyl ketone (reactivity towards HCN)
(ii) $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$, $(CH_3)_2CH$ $COOH$,$CH_3CH_2CH_2COOH$ (acid strength).
(iii) Benzoic acid, 4-Nitrobenzoic acid, 3,4-Dinitrobenzoic add, 4-Methoxybenzok acid (acid strength).
Ans:
(i) The reactivity of aldehydes and ketones towards HCN addition decreases as the +1 - effect of the alkyl groups increases. Secondly it decreases with increase in steric hindrance to the nucleophilic attack byCN^- at the carbonyl carbon. Thus the decreasing order of reactivity towards HCN is,



(ii) We know that + I-effect decreases while -I-effect increases the acidic strength of carboxylic acids. Since + I-effect of isopropyl group is more than that of propyl group, therefore, $(CH_3)_2CHCOOH$ is a weaker acid than $CH_3CH_2CH_2COOH$. Further since -I-effect decreases with distance, therefore $CH_3CH_2CHBrCOOH$ is a stronger acid than $CH_3CHBrCH_2COOH$. Thus, the overall acid strength increases in the order:



(iii) Since electron-donating groups decreases the acidic strength, therefore, 4-methoxy benzoic acid is a weaker acid than benzoic acid. Further since electron withdrawing groups increase the acidic strength, therefore, both 4-nitrobenzoic acid and 3,4-dinitrobenzoic acid are stronger acids than benzoic acid. Further due to the presence of an additional $-NO_2$ group at /w-position with respect to -COOH group, 3,4-dinitrobenzoic acid is a stronger acid than 4-

nitrobenzoic acid. Thus, the overall acidic strength increases in the order:4-methoxy benzoic acid < benzoic acid < 4-nitrobenzoic acid < 3,4-dinitrobenzoic acid.

12.13. Give simple chemical tests to distinguish between the following pairs of compounds.
(i) PropanalandPropanone
(ii) Acetophenone and Benzophenone
(iii) Phenol and Benzoic acid
(iv) Benzoic acid and Ethyl benzoate
(v) Pentan-2-one and Pentan-3-one
(vi) Benzaldehyde and Acetophenone.
(vii) EthanalandPropanal
Ans:

(i) Propanal and Propanone can be distinguished by iodoform test.

$$CH_3COCH_3 + 3NaOI \longrightarrow \underset{\text{Iodoform (Yellow ppt.)}}{CH_3I\downarrow} + CH_3COONa + 2NaOH$$

This test is given by aldehydes containing —$COCH_3$ group. Propanal does not have —$COCH_3$ group thus it does not give iodoform test

(ii) Acetophenone and Benzophenone can be distinguished by iodoform test.

$$C_6H_5COCH_3 + 3NaOI \longrightarrow C_6H_5COONa + \underset{\text{Iodoform (Yellow ppt.)}}{CH_3I\downarrow} + 2NaOH$$

$$C_6H_5COC_6H_5 \xrightarrow{NaOI} \text{No yellow ppt.}$$

This test is given by aldehydes and ketones containing –$COCH_3$ group

(iii) Phenol and Benzoic acid can be distinguished by $FeCl_3$ test

$$3C_6H_5OH + FeCl_3 \longrightarrow \underset{\text{Violet colouration}}{(C_6H_5O)_3Fe} + 3HCl$$

$$3C_6H_5COOH + FeCl_3 \longrightarrow \underset{\text{Buff-colouration ppt.}}{(C_6H_5COO)_3Fe} + 3HCl$$

(iv) Benzoic acid and Ethyl benzoate— By $NaHCO_3$ test

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + NaHCO_3 \longrightarrow \underset{\text{Sodiumbenzoate}}{C_6H_5COONa} + H_2O + CO_2\uparrow$$

$$C_6H_5COOC_2H_5 + NaHCO_3 \longrightarrow \text{No } CO_2 \text{ is formed}$$

(v) Pentan-2-one and Pentan-3-one can be distinguished by $NaHSO_3$ test

$$\begin{matrix} CH_3 \\ CH_3CH_2CH_2 \end{matrix}\!\!>\!C=O + NaHSO_3 \longrightarrow \begin{matrix} CH_3 \\ CH_3CH_2CH_2 \end{matrix}\!\!>\!C\!<\!\begin{matrix} OH \\ SO_3Na \end{matrix}$$

(Solid adduct)

$$CH_3CH_2COCH_2CH_3 + NaHSO_3 \longrightarrow \text{No solid adduct.}$$

Only methyl and cyclic ketones react with $NaHSO_3$ to give solid adduct.

(vi) Benzaldehyde and Acetophenone can be distinguished by iodoform test.

$$C_6H_5COCH_3 + 3NaOI \longrightarrow C_6H_5COONa + \underset{\text{(Yellow ppt.)}}{CH_3I\downarrow} + 2NaOH$$

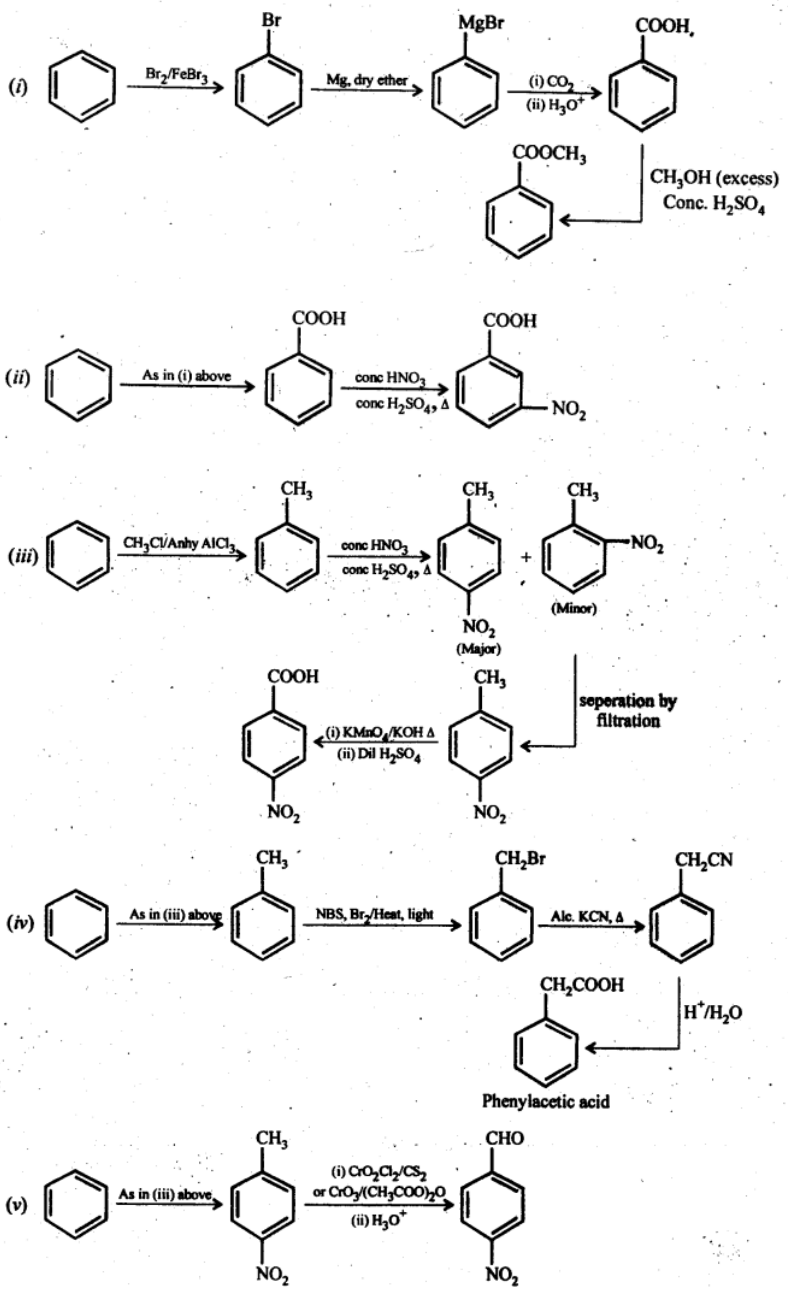
$$C_6H_5CHO + NaOI \longrightarrow \text{No yellow ppt.}$$

(vii) Ethanal and propanal can be distinguished by Iodoform test.

$$CH_3CHO + 3NaOI \longrightarrow HCOONa + \underset{\text{(Yellow ppt.)}}{CH_3I\downarrow} + 2NaOH$$

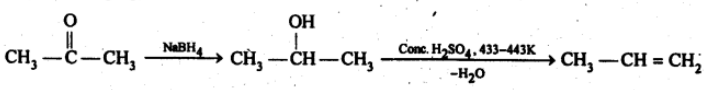
$$CH_3CH_2CHO \xrightarrow{I_2/NaOH} \text{No yellow ppt.}$$

12.14. Row will you prepare the following compounds from benzene? You may use any inorganic reagent and any organic reagent having not more than one carbon atom.
(i) Methyl benzoate
(ii) m-nitrobenzoic acid
(iii) p-nitrobenzoic acid
(iv) Phenylaceticacid
(v) p-nitrobenzaldehyde
Ans:

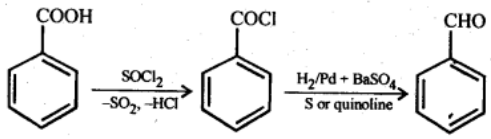


12.15. How will you bring about the following conversions in not more than two steps?
(i) PropanonetoPropene
(ii) Benzoic acid to Benzaldehyde
(iii) Ethanol to 3-Hydroxybutanal
(iv) Benzene to m-Nitroacetophenone
(v) Benzaldehyde to Benzophenone -
(vi) Bromobenzeneto 1-PhenylethanoL
(vii) Benzaldehyde to 3-Phenylpropan-1-ol.
(viil) Benzaldehyde to α Hydroxyphenylacetk acid
(ix) Benzoic acid to m-Nitrobenzy 1 alcohol
Ans:

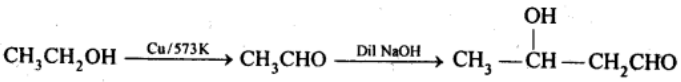
(i) Propanone to propene:



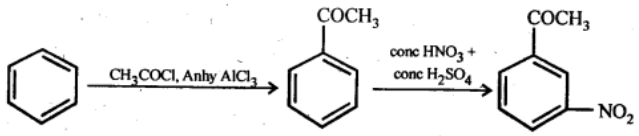
(*ii*) Benzoic acid to benzaldehyde:



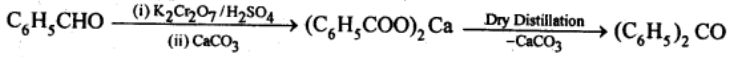
(*iii*) Ethanol to 3-hydroxy butanal:



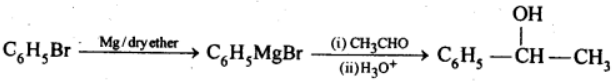
(*iv*) Benzene to *m*-nitroacetophenone:



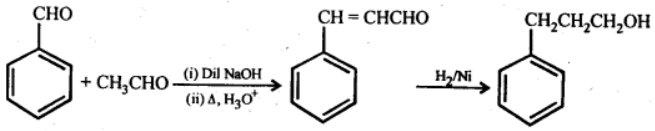
(*v*) Benzaldehyde to benzophenone:



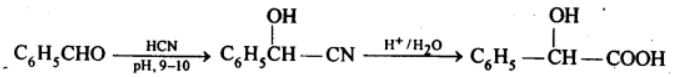
(*vi*) Bromobenzene to 1-phenylethanol



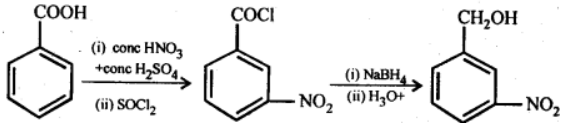
(*vii*) Benzaldehyde to 3-phenylpropan-1-ol



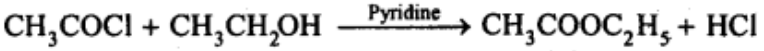
(*viii*) Benzaldehyde to α-hydroxyphenylacetic acid:



(*ix*) Benzoic acid to *m*-nitrobenzyl alcohol:

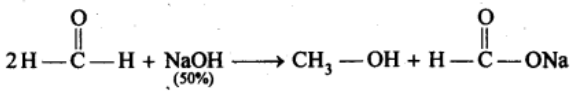


12.16 Describe the following:
(i) Acetylation
(ii) Cannizzaro reaction
(iii) Cross aldol condensation
(iv) Decarboxylation
Ans:
(i) Acetylation refers to the process of introducing an acetyl group into a compound namely, the substitution of an acetyl group for an active hydrogen atom. Acetylation is usually carried out in presence of a base such as pyridine, dimethylanitine, etc.

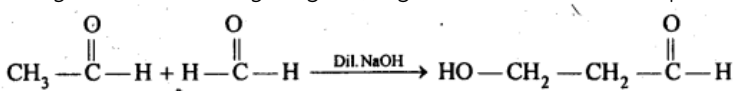


(ii) Cannizzaro reaction : Aldehydes which do not contain an a-hydrogen atom, when treated with concentrated alkali solution undergo disproportionation, i.e., self oxidation reduction. As a result, one molecule of the aldehyde is reduced to the corresponding alcohol at the cost of the other which is oxidised to the corresponding carboxylic acid. This reaction is called Cannizzaro reaction.

e.g.,



(iii) Cross aldol condensation: Aldol condensation between two different aldehydes is called cross aldol condensation.If both aldehydes contain a-hydrogens, It gives a mixture of four products.



(iv) Decarboxylation: The process of removal of a molecule of CO_2 from a carboxylic acid is called decarboxylation. Sodium salts of carboxylic acids when heated with soda-lime undergoes decarboxylation to yield alkanes.

$$CH_3CH_2COONa + NaOH \xrightarrow{CaO,\ 630\ K} CH_3 - CH_3 + Na_2CO_3$$

********** END **********