NCERT Solution for Class 12 Chemistry

Chapter 8 - Aldehydes, Ketones and Carboxylic Acids

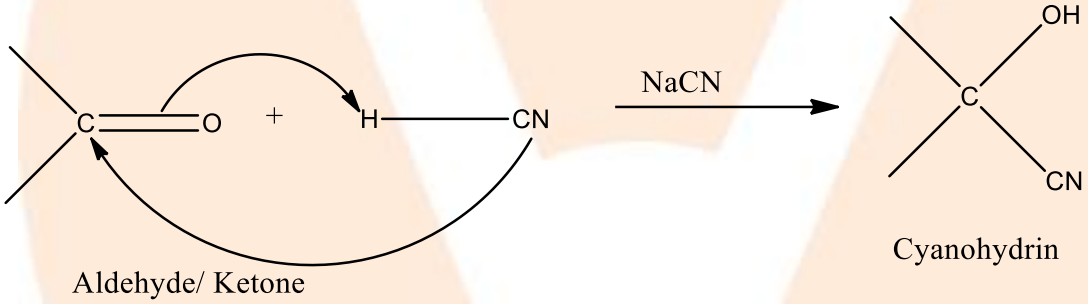
NCERT Exercise

1. What is meant by the following terms? Give an example of the reaction in each case.

(i) Cyanohydrin

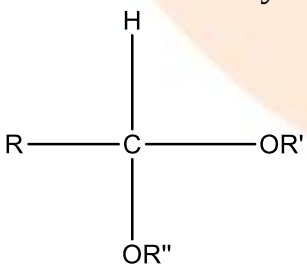
Ans: Cyanohydrins are organic, RR′(OH)CN chemicals, where R and R′s may be either alkyl or aryl.

In the presence of excess sodium cyanide (NaCN) as a catalyst in the field of cyanohydrin, aldehydes and ketones react with hydrogen cyanide (HCN). These are called cyanohydrins reactions. The reaction is given below:

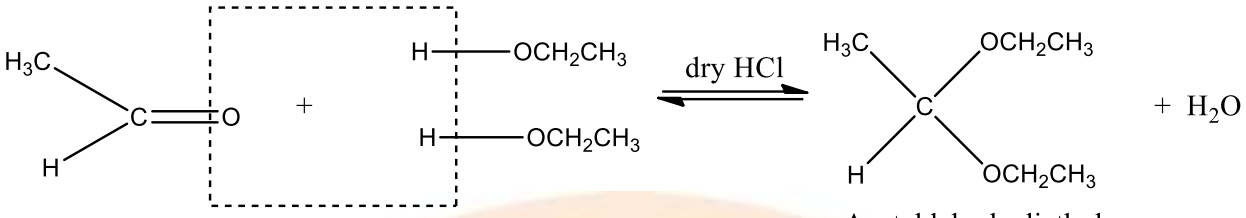


(ii) Acetal

Ans: Acetals are gem-dialkoxy alkanes in which the terminal carbon atom consists of two alcohol groups. There are connections between one bond and an alkyl group and the other with a hydrogen atom.



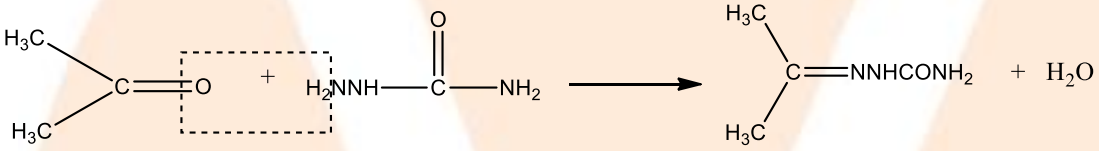
When two monohydrous alcohol equivalents are treated with dry HCl gas, the hemiacetals are generated which react further with another alkohol molecule to form acetal. The reaction is given below:



Acetaldehyde diethyl acetal

(iii) Semicarbazone

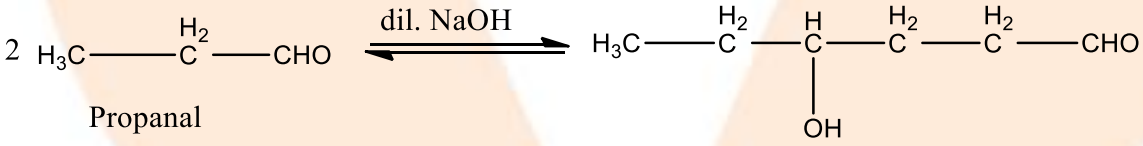
Ans: Semicarbazones are products of the condensation process of aldehydes and ketones generated by ketone or aldehyde and semicarbazide. An example of the formation of semicarbazone is given below:



Acetone Semicarbazide Acetone semicarbazone

(iv) Aldol

Ans: An aldol is recognised to be a β-hydroxy aldehyde or ketone. The condensation process in the presence of a base is generated between two molecules of one or two distinct aldehydes or ketones. An example of the formation of aldol is given below:

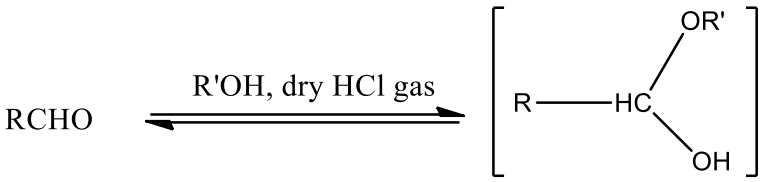


Propanal

4- Hydroxyhexanal (Aldol)

(v) Hemiacetal

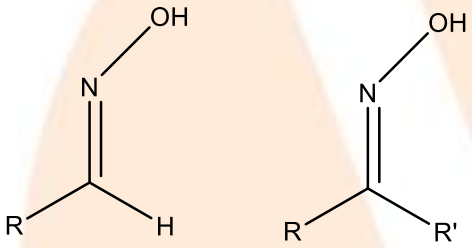
Ans: We can say that α-alkoxyalcohols are known as hemiacetals. In the presence of dry HCl gas, aldehyde interacts with a single molecule of monohydric alcohol. The reaction is given below:



Hemiacetal

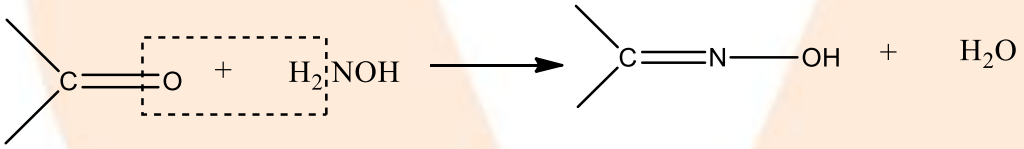
(vi) Oxime

Ans: Oximes have the common formula of RR′CNOH where R is an organic side chain, and R′ is a hydrogen or organic side chain. Oximes are organic chemicals. If R′ is H, the aldoxime is known and R′ is known as ketoxime if it is an organic side chain.



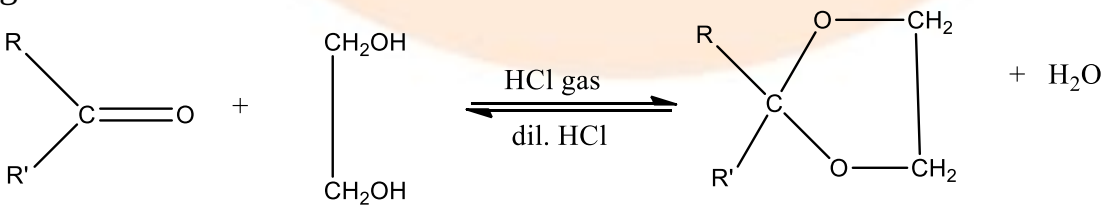
Aldoxime Ketoxime

Aldehydes or ketones formoximes are treated with hydroxylamine in a slightly acidic media. The reaction is given below:



(vii) Ketal

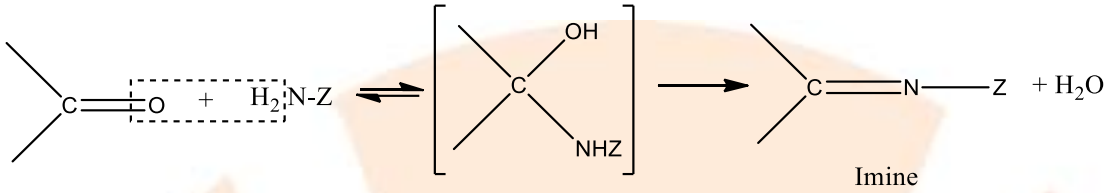
Ans: Ketals are gemodioxyalcanes in which the chain contains two alcoholic groups on the same carbon atom. The other two carbon bonds are linked to two groups of alkynes. In the presence of HCl dry gas, ketones react with ethylene glycol to a cyclic compound called ethylene glycol ketals. An example of the formation of a ketal is given below:



ketone ethylene glycol Ethylene glycol ketal

(viii) Imine

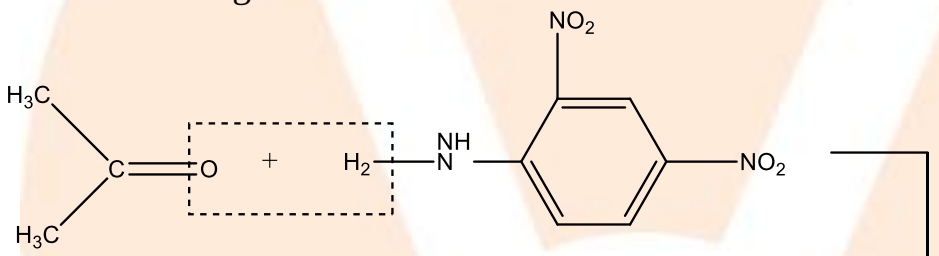
Ans: Imines are chemicals that have a double bond of carbon nitrogen. Imines are generated when ammonia and its derivatives are reacted by aldehydes and ketones. The reaction is given below:



Imine

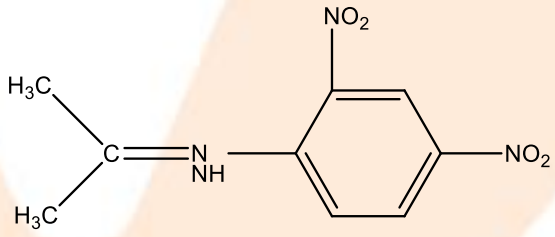
(ix) 2,4-DNP-derivative

Ans: 2, 4−dinitrophenylhydrazones 2, 4−DNP− derivatives that are made using 2, 4−dinitrophenylhydrazine in a low acidic medium in the case of aldehydes or ketones. The reaction is given below:



Acetone

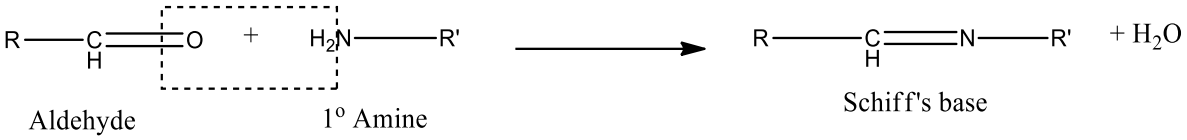
2, 4- Dinitrophenylhydrazine



Acetone 2, 4-dinitrophenylhydrazone

(x) Schiff's base

Ans: The Schiff's base (or azomethine) is a chemical molecule that has an aryl or alkyl group, but not hydrogen, carbon-nitrogen twice the atom of nitrogen. They have the usual R1R2C=NR3 formulation. As it is an imine and it is named after Hugo Schiff, a physicist. The reaction is given below:



2. Name the following compounds according to IUPAC system of nomenclature:

(i) $CH_3CH(CH_3)CH_2CH_2CHO$

Ans: The IUPAC name of the given compound is 4-Methylpentanal.

(ii) $CH_3CH_2COCH(C_2H_5)CH_2CH_2Cl$

Ans: The IUPAC name of the given compound is 6-Chloro-4-ethylhexan-3-one.

(iii) $CH_3CH=CHCHO$

Ans: The IUPAC name of the given compound is But-2-en-1-al.

(iv) $CH_3COCH_2COCH_3$

Ans: The IUPAC name of the given compound is Pentan-2,4-dione.

(v) $CH_3CH(CH_3)CH_2C(CH_3)_2COCH_3$

Ans: The IUPAC name of the given compound is 3,3,5-Trimethylhexan-2-one.

(vi) $(CH_3)_3CCH_2COOH$

Ans: The IUPAC name of the given compound is 3, 3-Dimethylbutanoic acid.

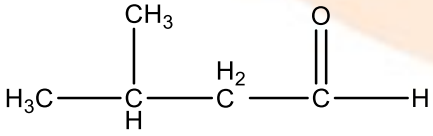
(vii) $OHCC_6H_4CHO$-p

Ans: The IUPAC name of the given compound is Benzene-1,4-dicarbaldehyde.

3. Draw the structures of the following compounds:

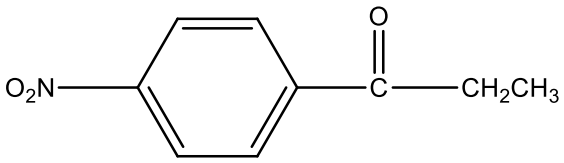
(i)3-Methylbutanal

Ans: The structure of 3-Methylbutanal is given below:



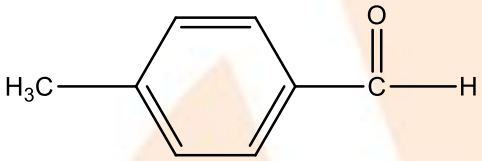
(ii) p-Nitropropiophenone

Ans: The structure of p-Nitropropiophenone is given below:



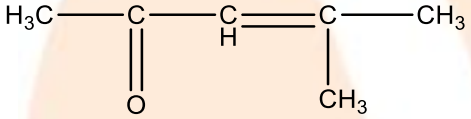
(iii) p-Methylbenzaldehyde

Ans: The structure of p-Methylbenzaldehyde is given below:



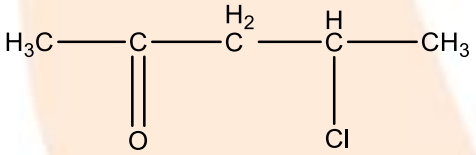
(iv) 4-Methylpent-3-en-2-one

Ans: The structure of 4-Methykpent-3-en-2-one is given below:



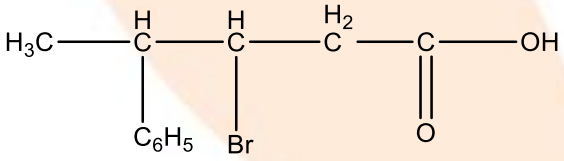
(v) 4-Chloropentan-2-one

Ans: The structure of 4-Chloropentan-2-one is given below:



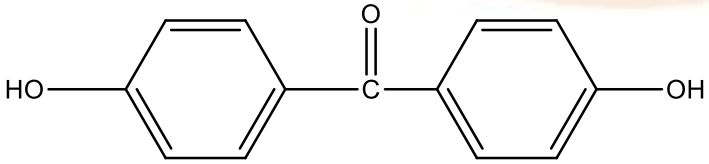
(vi) 3-Bromo-4-phenylpentanoic acid

Ans: The structure of 3-Bromo-4-phenylpentanoic acid is given below:



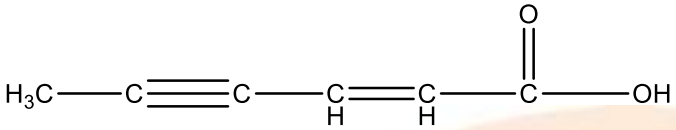
(vii) p,p'-Dihydroxybenzophenone

Ans: The structure of p,p'-Dihydroxybenzophenone is given below:



(viii) Hex-2-en-4-ynoic acid

Ans: The structure of Hex-2-en-4-ynoic acid is given below:



4. Write the IUPAC names of the following ketones and aldehydes. Whenever possible, give also common names.

(i) $CH_3CO(CH_2)_4CH_3$

Ans: The IUPAC name of the given compound is Heptan-2-one and its common name is Methyl n-pentyl ketone.

(ii) $CH_3CH_2CHBrCH_2CH(CH_3)CHO$

Ans: The IUPAC name of the given compound is 4-Bromo-2-methylhexanal and its common name is γ-Bromo-α-methylcaproaldehyde

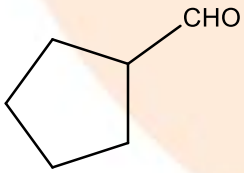
(iii) $CH_3(CH_2)_5CHO$

Ans: The IUPAC name of the given compound is Heptanal.

(iv) Ph-CH=CH-CHO

Ans: The IUPAC name of the given compound is 3-Phenylprop-2-enal and its common name is beta-phenylacrolein.

(v)



Ans: The IUPAC name of the given compound is Cyclopentanecarbaldehyde and its common name is also Cyclopentanecarbaldehyde.

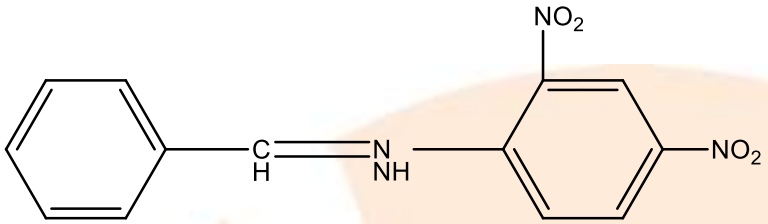
(vi) PhCOPh

Ans: The IUPAC name of the given compound is Diphenylmetthanone and its common name is Benzophenone.

5. Draw structures of the following derivatives.

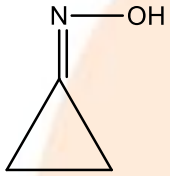
(i)The 2,4-dinitrophenylhydrazone of benzaldehyde

Ans: The structure of derivative of 2,4-dinitrophenylhydrazone of benzaldehyde will be:



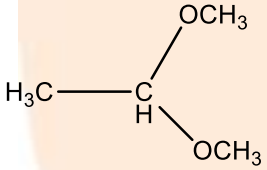
(ii) Cyclopropanone oxime

Ans: The structure of derivative of Cyclopropanone oxime is given below:



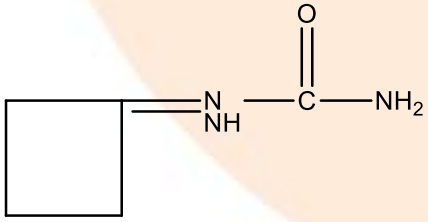
(iii)Acetaldehydedimethylacetal

Ans: The structure of derivative of Acetaldehydedimethylacetal is given below:



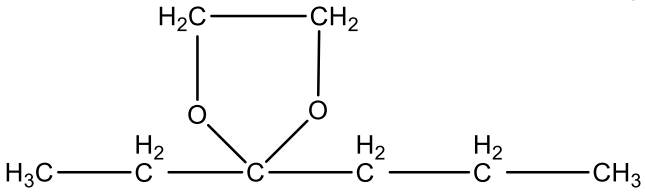
(iv)The semicarbazone of cyclobutanone

Ans: The structure of derivative of the semicarbazone of cyclobutanone is given below:



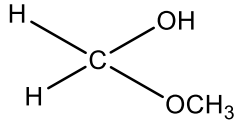
(v) The ethylene ketal of hexan-3-one

Ans: The structure of derivative of the ethylene ketal of hexan-3-one is given below:



(vi) The methyl hemiacetal of formaldehyde

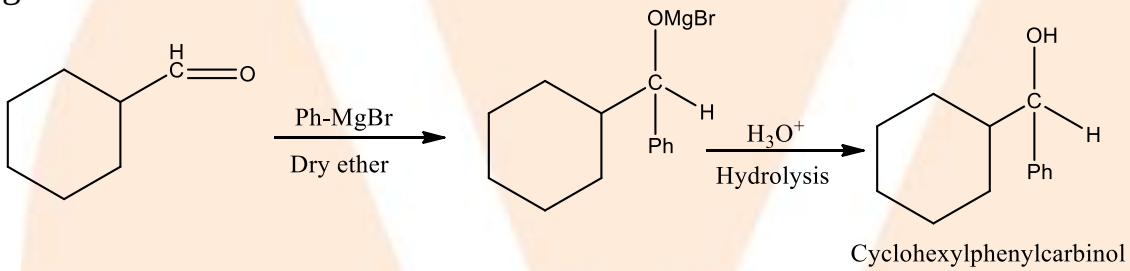
Ans: The structure of derivative of the methyl hemiacetal of formaldehyde is given below:



6. Predict the products formed when cyclohexanecarbaldehyde reacts with following reagents.

(i) PhMgBr and then H_3O^+

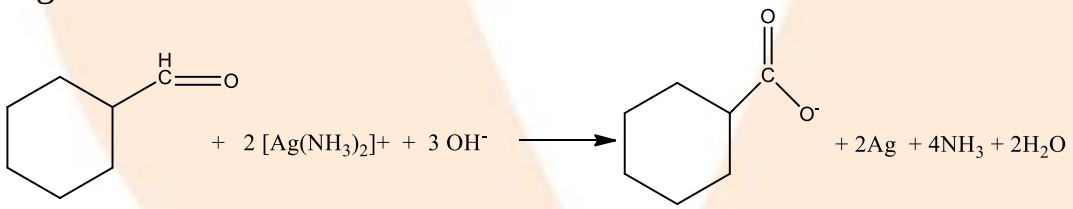
Ans: The product in this reaction will be Cyclohexylphenylcarbinol. The reaction is given below:



Cyclohexylphenylcarbinol

(ii) Tollens' reagent

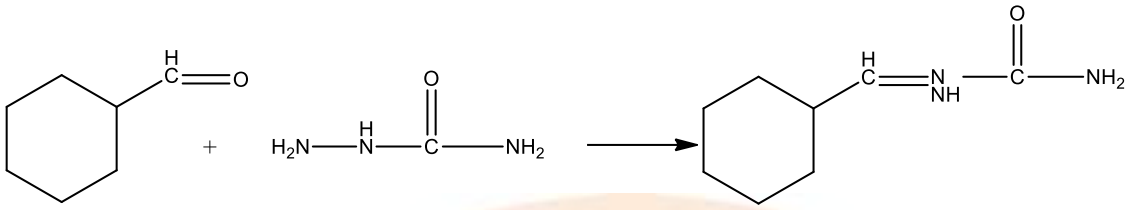
Ans: The product formed in this reaction is Cyclohexane-carboxylate ion. The reaction is given below:



Cyclohexane-carboxylate ion

(iii) Semicarbazide and weak acid

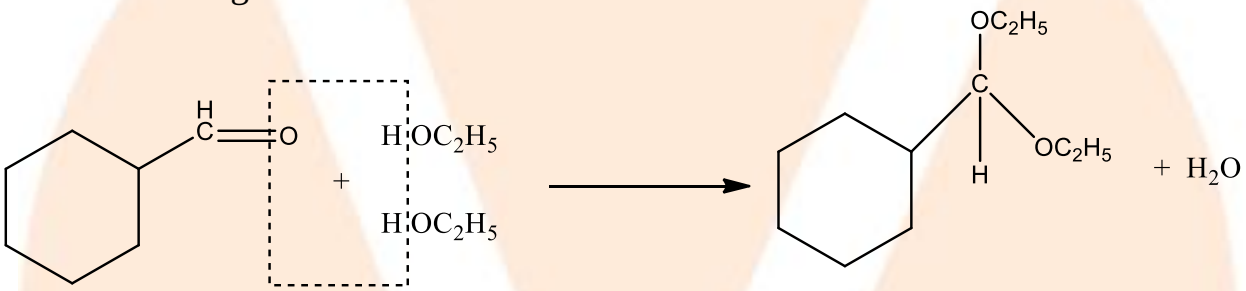
Ans: The product formed in this reaction is Cyclohexanecarbaldehyde semicarbazone. The reaction is given below:



Cyclohexanecarbaldehyde semicarbazone

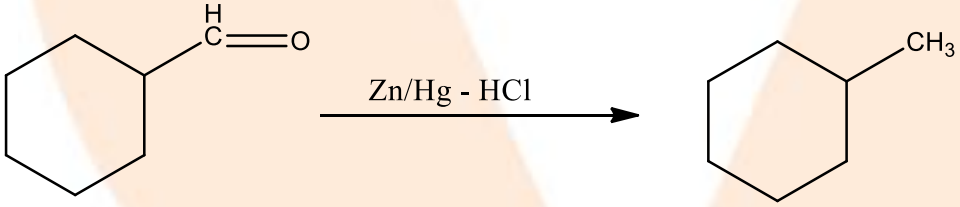
(iv) Excess ethanol and acid

Ans: The product formed in this reaction is Cyclohexanecarbaldehyde diethyl acetal. The reaction is given below:



(v) Zinc amalgam and dilute hydrochloric acid.

Ans: The product formed in this reaction will be Methylcyclohexane. The reaction is given below:



Methylcyclohexane

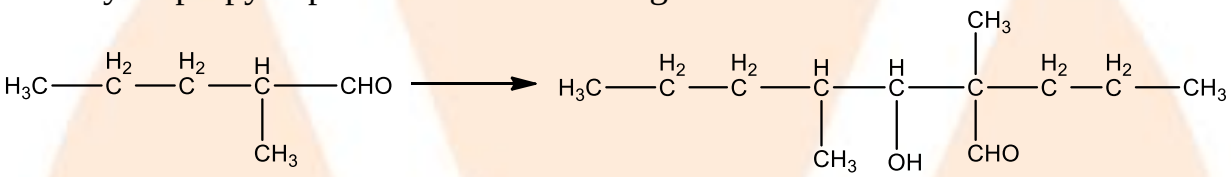
7. Which of the following compounds would undergo aldol condensation, which the Cannizzaro reaction and which neither? Write the structures of the expected products of aldol condensation and Cannizzaro reaction.

(i) Methanal
(ii) 2-Methylpentanal
(iii) Benzaldehyde
(iv) Benzophenone
(v) Cyclohexanone
(vi) 1-Phenylpropanone

(vii) Phenylacetaldehyde
(viii)Butan-1-ol
(ix) 2, 2-Dimethylbutanal

Ans: Aldehydes and ketones having at least one α-hydrogen undergo aldol condensation. The compounds (ii) 2−methylpentanal, (v) cyclohexanone, (vi) 1-phenylpropanone, and (vi) phenylacetaldehyde contain one or more α-hydrogen atoms. Therefore, these undergo aldol condensation.

The product formed by the aldol condensation of 2-Methylpentanal is 3-Hydroxy-2,4-dimethyl-2-propylheptanal. The reaction is given below:

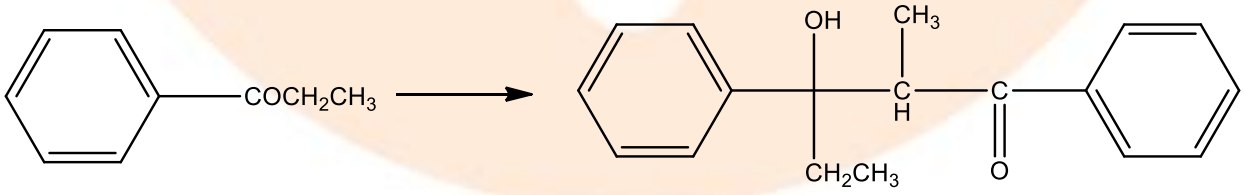


3- Hydroxy-2,4-dimethyl-2-propylheptanal

The product formed by the aldol condensation of cyclohexanone is 2-(1-Hydroxy-1-cyclohexyl)cyclohexane-1-one. The reaction is given below:

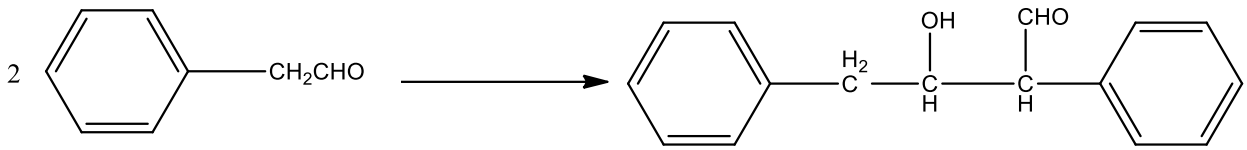
2-(1-Hydroxy-1-cyclohexyl) cyclohexane-1-one

The product formed by the aldol condensation of 1-Phenylpropanone is 3-Hydroxy-2-methyl-1,3-diphenylpentan-1-one. The reaction is given below:



3-Hydroxy-2-methyl-1,3-diphenylpentan-1-one

The product formed by the aldol condensation of Phenylacetyladehyde is 3-Hydroxy-2,4-diphenylbutanal. The reaction is given below:



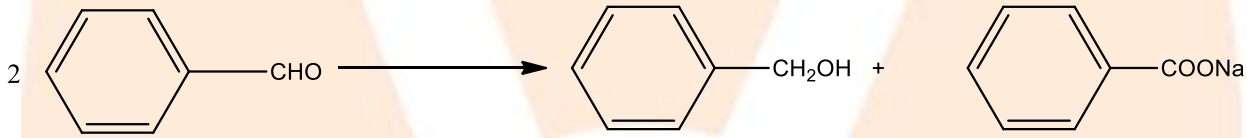
3-Hydroxy-2,4-diphenylbutanal

Aldehydes having no α-hydrogen atoms undergo Cannizzaro reactions. The compounds (i) Methanal, (iii) Benzaldehyde, and (ix) 2, 2-dimethylbutanal do not have any α-hydrogen .Therefore, these undergo cannizzaro reactions.

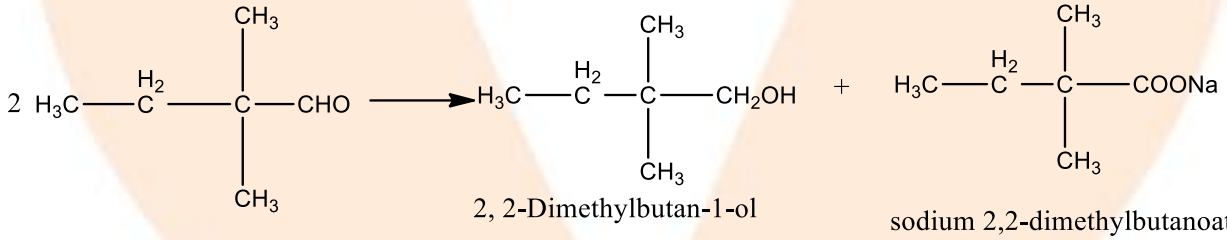
The products formed by the Cannizaro reaction of methanal are methanol and sodium methanoate. The reaction is given below:

$$2\ HCHO \xrightarrow{\text{conc. NaOH}} CH_3OH + HCOONa$$

The products formed by the Cannizaro reaction of benzaldehyde are benzyl alcohol and sodium benzoate. The reaction is given below:



The products formed by the Cannizaro reaction of 2,2-Dimethylbutanol are benzyl alcohol and sodium benzoate. The reaction is given below:



2, 2-Dimethylbutan-1-ol

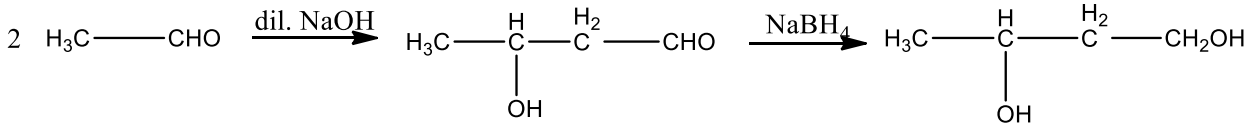
sodium 2,2-dimethylbutanoate

Compound (iv) Benzophenone is a ketone having no α-hydrogen atom and compound (viii) Butan-1-ol is an alcohol. Hence, these compounds do not undergo either aldol condensation or cannizzaro reactions.

8. How will you convert ethanal into the following compounds?

(i)Butane-1, 3-diol

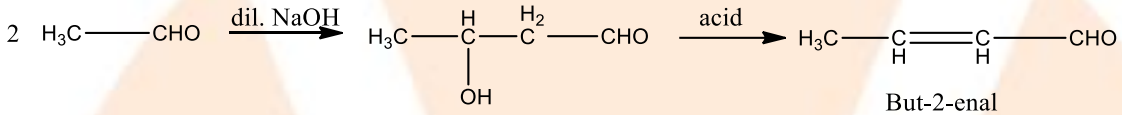
Ans: When ethanal reacts with dilute sodium hydroxide to form 3-Hydroxybutanal. Now, 3-Hydroxybutanal reacts with $NaBH_4$ to form butane-1, 3-diol. The reaction is given below:



Butane-1, 3-diol

(ii) But-2-enal

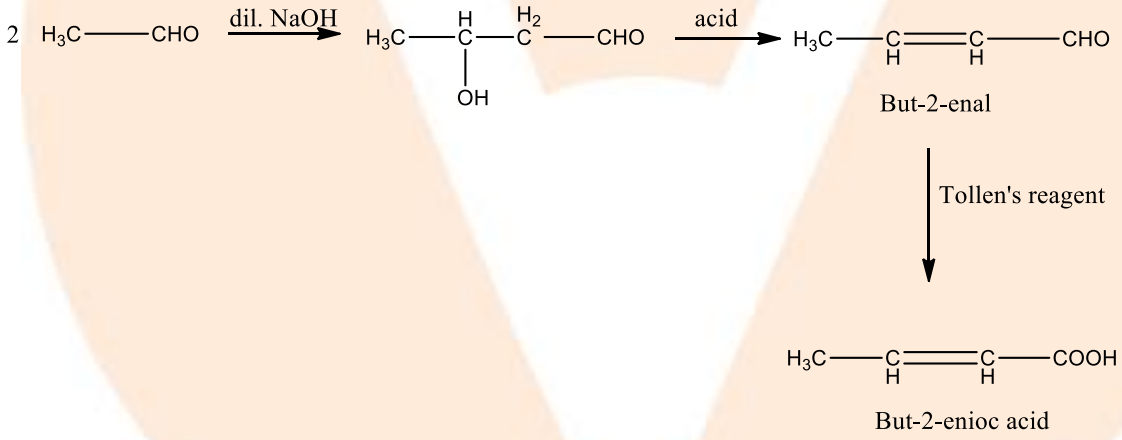
Ans: When ethanal reacts with dilute sodium hydroxide to form 3-Hydroxybutanal. Now, 3-Hydroxybutanal reacts with acid to form But-2-enal. The reaction is given below:



But-2-enal

(iii)But-2-enoic acid

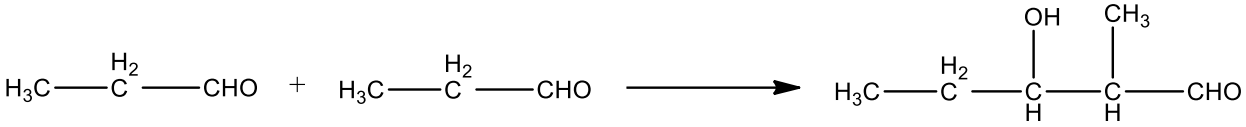
Ans: When ethanal reacts with dilute sodium hydroxide to form 3-Hydroxybutanal. Now, 3-Hydroxybutanal reacts with acid to form But-2-enal. Now, but-2-enal reacts with Tollen's reagent to But-2-enoic acid. The reaction is given below:



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.

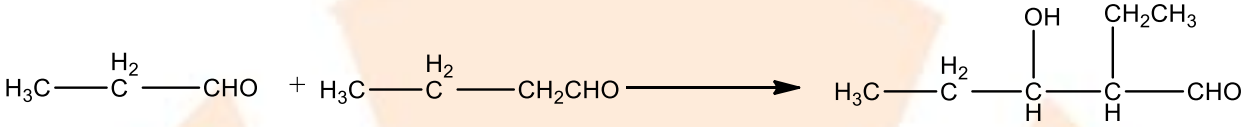
Ans:

(i) Taking propanal as nucleophile as well as electrophile. The product will be 3-Hydroxy-2-methylpentanal. The reaction is given below:



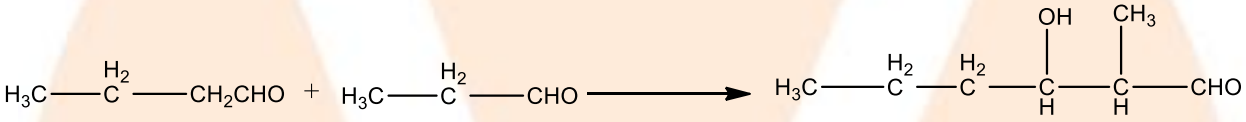
3- Hydroxy-2-methylpentanal

(ii) Taking propanal as electrophile and butanal as nucleophile. The product will be 2-Ethyl-3-hydroxypentanal. The reaction is given below:



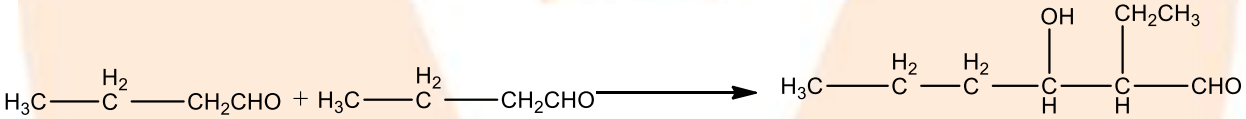
3- Hydroxy-2-methylpentanal

(iii) Taking butanal as electrophile and propanal as nucleophile. The product will be 3-Hydroxy-2-methylhexanal. The reaction is given below:



3-Hydroxy-2-methylhexanal

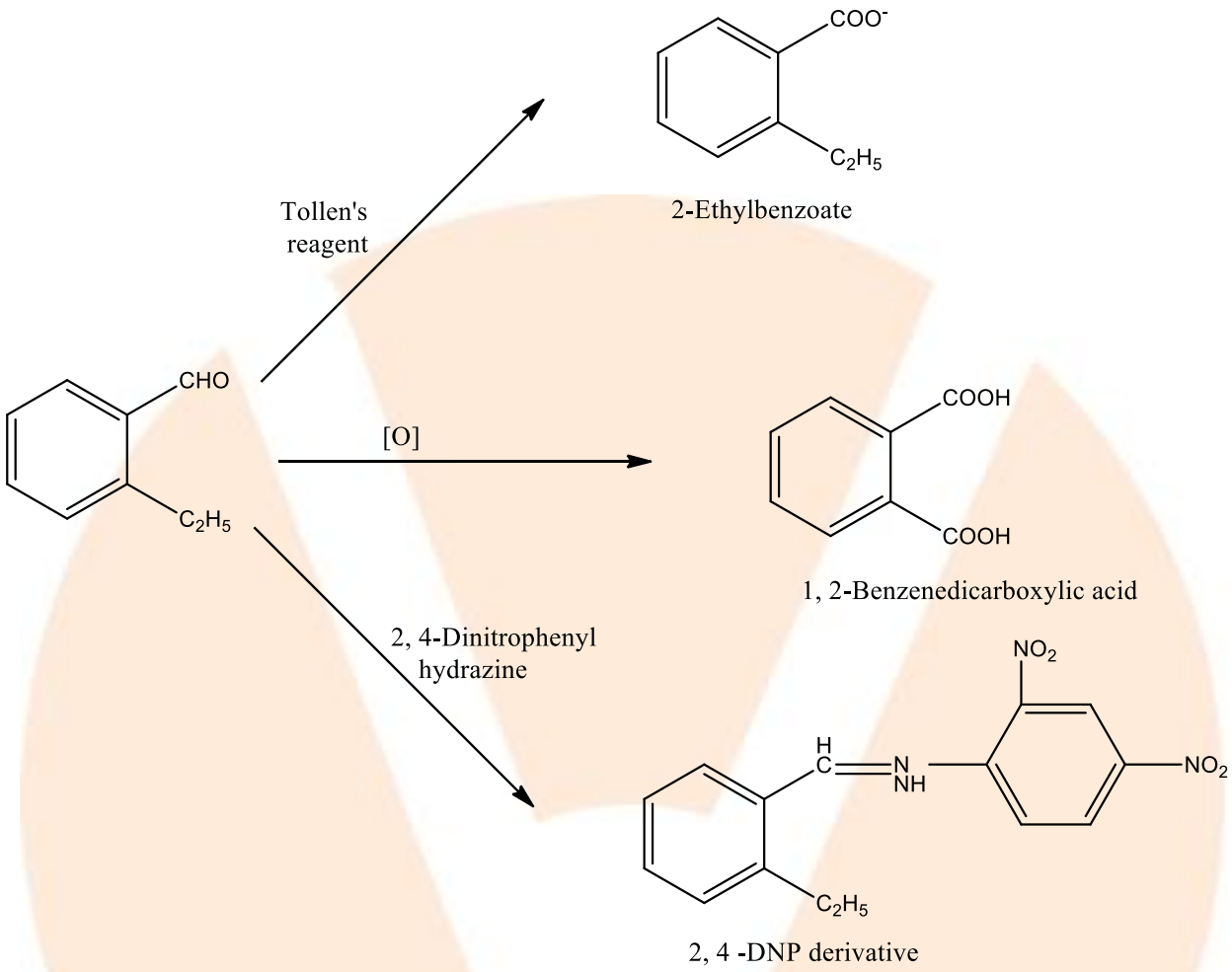
(iv) Taking butanal as nucleophile as well as electrophile. The product will be 2-Ethyl-3-hydroxyhexanal. The reaction is given below:



2-Ethyl-3-hydroxyhexanal

10. An organic compound with the molecular formula $C_9H_{10}O$ forms 2, 4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1, 2-benzenedicarboxylic acid. Identify the compound.

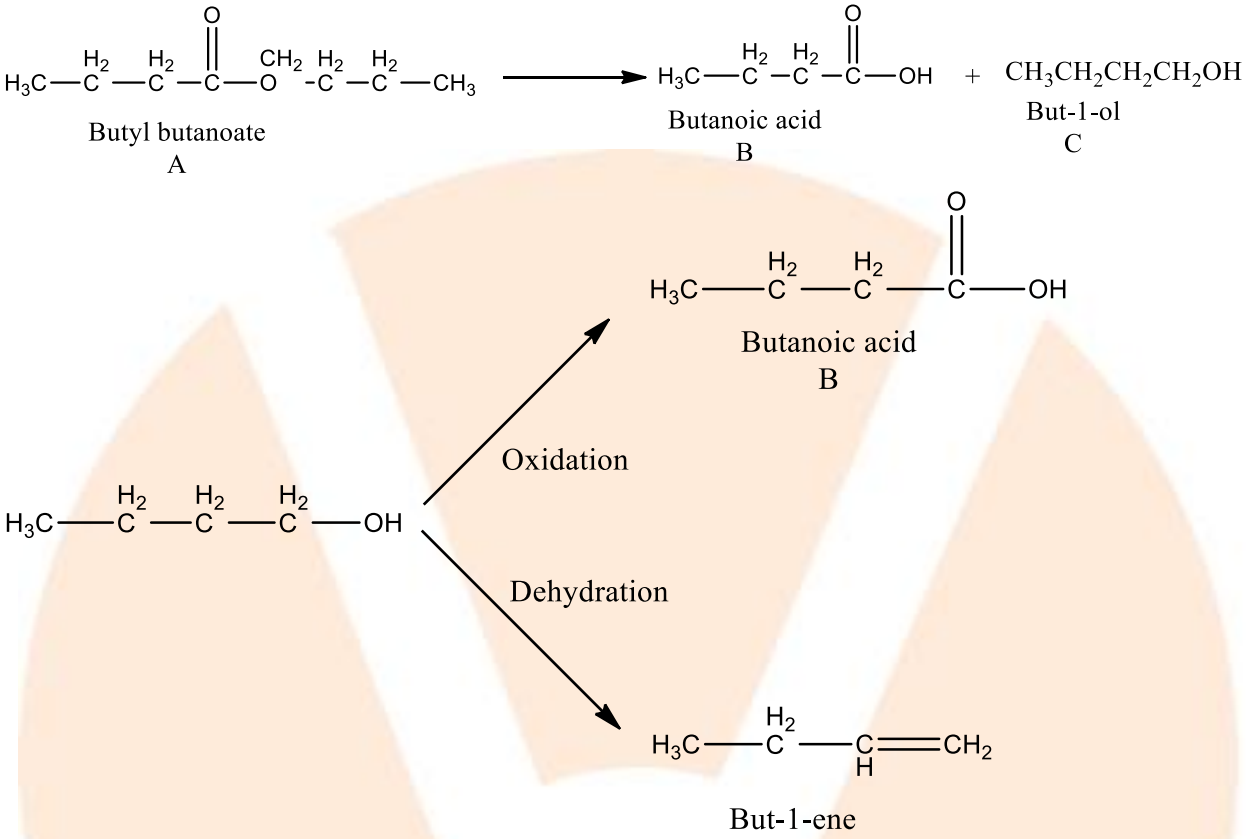
Ans: It is because the chemical ($C_9H_{10}O$) generates a derivative of 2, 4-dnp and reduces the reagent of Tollen. The chemical must thus be an aldehyde. The product is again subjected to cannizzaro's reaction and 1,2-benzenedicarboxylic acid is provided by oxidation. The −CHO group is therefore immediately connected to a benzene ring and ortho-substituted for this benzaldehyde. Thus, 2-ethylbenzaldehyde is the chemical.
The reactions given in the questions are given below:



11. An organic compound (A) (molecular formula $C_8H_{16}O_2$) was hydrolyzed with dilute sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (C) on dehydration gives but-1-ene.Write equations for the reactions involved.

Ans: A molecular molecular formula A molecule $C_8H_{16}O_2$ provides hydrolysis with dilute sulphuric acid carboxylic acid (B) and alcohol (C) Compound A therefore has to be an ester. Alcohol C also provides acid B for chromic acid oxidation. Therefore, the number of carbon atoms must be identical in B and C. Compound A has 8 carbon atoms, while 4 carbon atoms are included in each of B and C. Alcohol C again produces but-1-ene when it is dehydrated. C is thus straight and hence butane-1-ol. Butan-1-ol produces butanoic acid when oxidised. Therefore, butanoic acid is B acid. Thus, butyl butanoate is the molecular ester $C_8H_{16}O_2$.

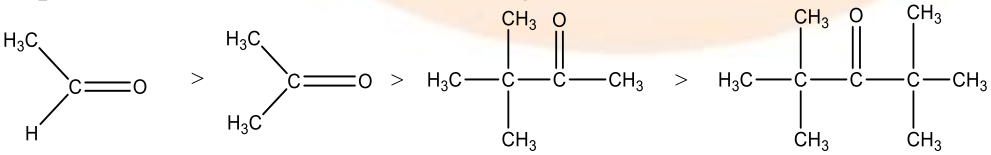
All the reactions in questions are given below:



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)

Ans: When HCN interacts with a molecule, the attacking species is nucleophile, CN^- Consequently, its reactivity to HCN diminishes as the negative charge of the compound rises. The +I effect rises in the given compounds as indicated below. The steric impediment also rises in this. It may be noticed.



Hence, the given compounds can be arranged according to their increasing reactivities toward HCN as:

Di-tert-butyl ketone < Methyl tert-butyl ketone < Acetone < Acetaldehyde.

(ii)

$CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$, $(CH_3)_2CHCOOH$, $CH_3CH_2CH_2COOH$ (acid strength)

Ans: Carboxylic acids are negatively charged after losing a proton, as illustrated:

$R\text{-}COOH \rightarrow R\text{-}COO^- + H^+$

Now any group which helps stabilise the negative load will enhance the carboxylic ion's stability and hence improve the acid strength. This will reduce the strength of acids in groups with +I effect and raise the strength of acids in groups with −I effect. The group $-CH_3$ exhibits +I and Br^- action in the following compounds. Br^- containing acids are hence stronger. Now, +I is more than the n-propyl isopropyl group effect.

Therefore, $(CH_3)_2CHCOOH$ is a weaker acid than $CH_3CH_2CH_2COOH$.

Also, the –I effect grows weaker as distance increases. Hence, $CH_3CH(Br)CH_2COOH$ is a weaker acid than $CH_3CH_2CH(Br)COOH$.

Hence, the order the strength is given below:

$CH_3CH(CH_3)COOH < CH_3CH_2CH_2COOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$

(iii) Benzoic acid, 4-Nitrobenzoic acid, 3,4-Dinitrobenzoic acid, 4-Methoxybenzoic acid (acid strength)

Ans: As we saw in the past case, electron-donor groups reduce acid strengths whereas electron-donor groups enhance acid strengths. Benefits of 4-methoxybenzoic acid is a lesser acid than benzoic acid as a group of electron-donor. Nitro group is a retracting electron group and increases acid strength. As it includes 2 nitrogen groups of 3,4-dinitrobenzoic acid, it is a little stronger than 4-nitrobenzoic acid.

Hence, the strengths of the given acids increase as:

4-Methoxybenzoic acid < Benzoic acid < 4-Nitrobenzoic acid < 3,4-Dinitrobenzoic acid

13. Give simple chemical tests to distinguish between the following pairs of compounds.

(i) Propanal and Propanone

Ans:

(a) Tollen's test

An aldehyde is Propanal. It reduces the reagent of Tollen. But, propanone being a ketone does not reduce Tollens reagent.

$$CH_3CH_2CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \rightarrow CH_3CH_2COO^- + Ag\downarrow + 4NH_3 + 2H_2O$$

(b) Fehling's test

Aldehydes are answering the test of Fehling, while ketones are not. Aldehyde-propanal converts the solution to a red-brown Cu2O precipitate, although propanone does not.

$$CH_3CH_2CHO + 2Cu^{2+} + 5OH^- \rightarrow CH_3CH_2COO^- + Cu_2O + 3H_2O$$

(c) Iodoform test

As one methyl group associated with the carbonyl carbon atom reacts to the iodoform test, with aldehydes and ketones. They are oxidised to yield iodoform using sodium hypoiodite (NaOI). Propanone is a methyl ketone, while propanal is not.

$$CH_3COCH_3 + 3NaOI \rightarrow CH_3COONa + CHI_3 + 2NaOH$$

(ii) Acetophenone and Benzophenone

Ans: Iodoform test

Acetophenone will give the Iodoform test but benzophenone will not.

$$C_6H_5COCH_3 + 3NaOI \rightarrow C_6H_5COONa + CHI_3 + 2NaOH$$

(iii)Phenol and Benzoic acid

Ans: Ferric chloride test

Phenol will give the violet coloration with neutral ferric chloride.

$$6C_6H_5OH + FeCl_3 \rightarrow \underset{\text{Violet color}}{[Fe(OC_6H_5)_6]^{3-}} + 3H^+ + 3Cl^-$$

Benzoic acid will give the buff coloration with neutral ferric chloride.

$$3C_6H_5COOH + FeCl_3 \rightarrow \underset{\text{buff color}}{[Fe(OOC_6H_5)_3]^{3-}} + 3H^+ + 3Cl^-$$

(iv)Benzoic acid and Ethyl benzoate

Ans: Sodium bicarbonate test

Benzoic acid will react with sodium bicarbonate and will evolve carbon dioxide.

$$C_6H_5COOH + NaHCO_3 \rightarrow C_6H_5COONa + CO_2 + H_2O$$

(v) Pentan-2-one and Pentan-3-one

Ans: Iodoform test

Pentan-2-one will react to the Iodoform test but Pentan-3-one will not react.
$CH_3CH_2CH_2COCH_3 + 3NaOI \rightarrow CH_3CH_2CH_2COONa + CHI_3 + 2NaOH$

(vi) Benzaldehyde and Acetophenone

Ans: Iodoform test

Acetophenone will give the Iodoform test but benzaldehyde will not.
$C_6H_5COCH_3 + 3NaOI \rightarrow C_6H_5COONa + CHI_3 + 2NaOH$

(vii) Ethanal and Propanal

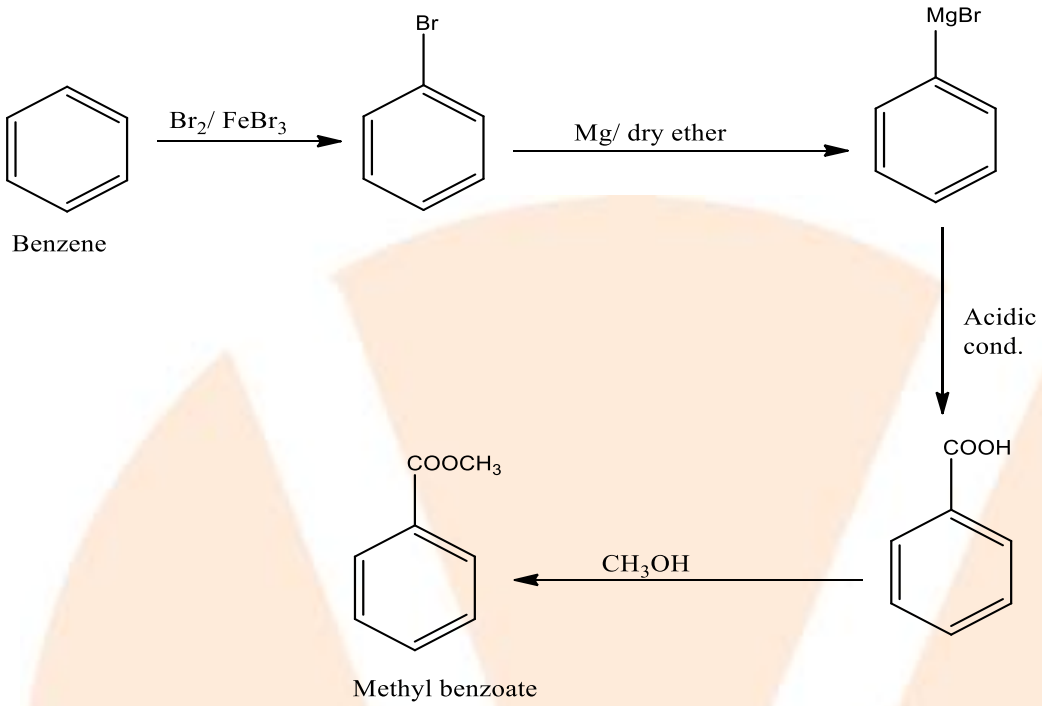
Ans: Iodoform test

The iodoform test responds to aldehydes and ketones with a minimum of a methyl group associated with the carbonyl carbon atom. This test is followed by ethanal with one methyl group attached to the carbonyl atom. But propanal doesn't contain a carbonyl carbon dioxide-related methyl group and does not thus respond to this condition.
$CH_3CHO + 3NaOI \rightarrow HCOONa + CHI_3 + 2NaOH$

14. How 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.

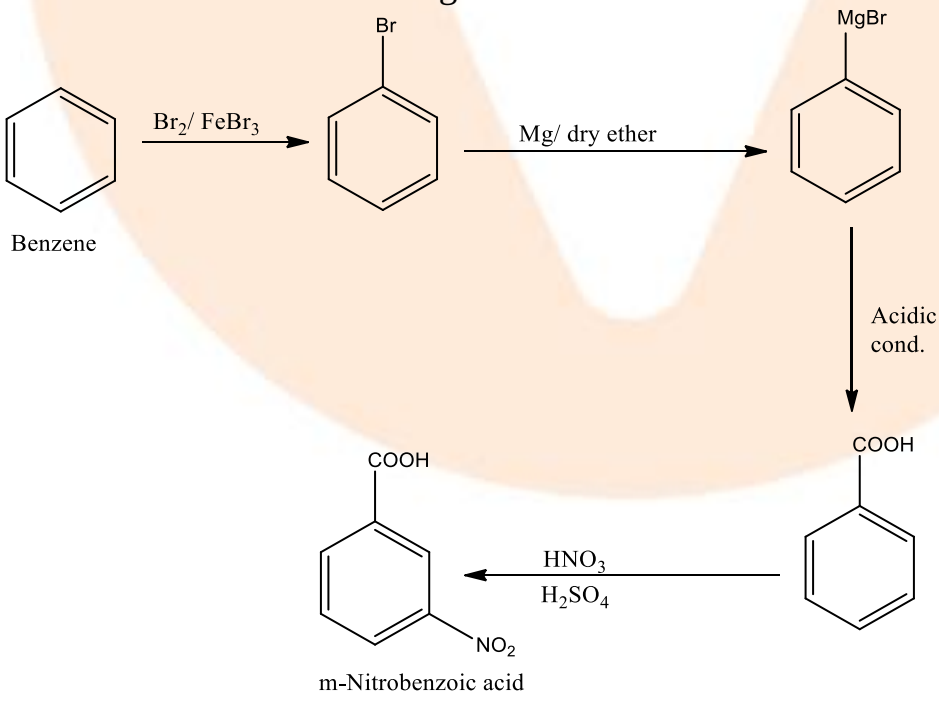
(i) Methyl benzoate

Ans: Benzene will react with bromine to form Bromobenzene. This bromobenzene will be converted into benzoic acid. Now, this benzoic acid will be converted into Methyl benzoate. The reaction is given below:



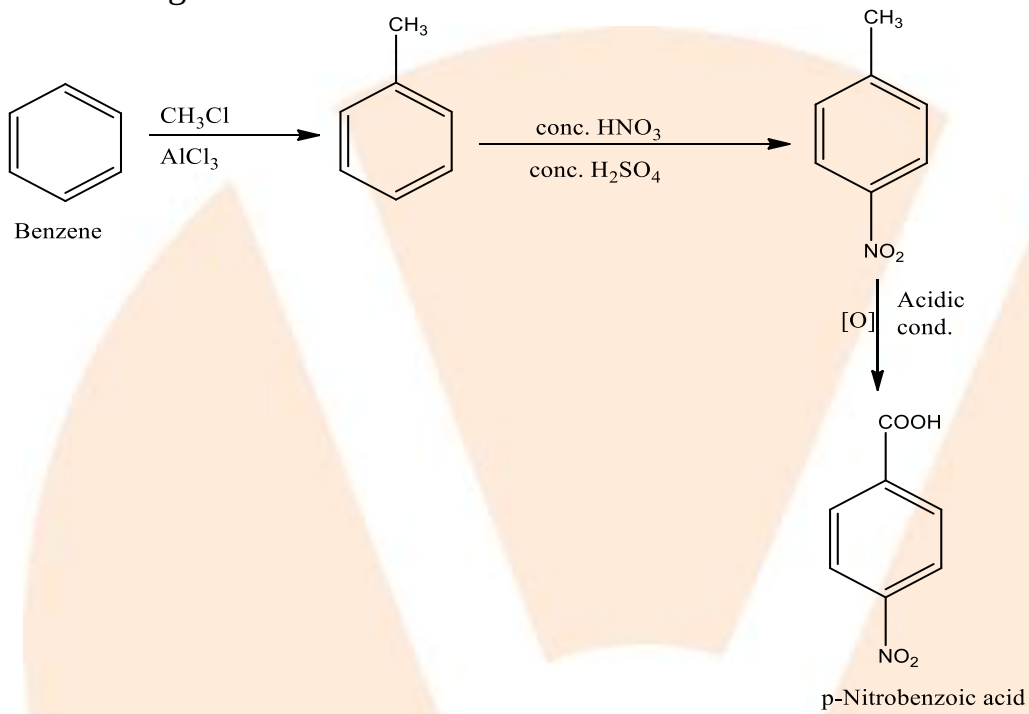
(ii) m-Nitrobenzoic acid.

Ans: Benzene will react with bromine to form Bromobenzene. This bromobenzene will be converted into benzoic acid. Now, this benzoic acid will be converted into m-Nitro benzoic acid. The reaction is given below:



(iii)p-Nitrobenzoic acid

Ans: Benzene will be converted into toluene. Now, Toluene will be converted into p-nitrotoluene. Now, this p-nitrotoluene on oxidation will form p-nitrobenzoic acid. The reaction is given below:

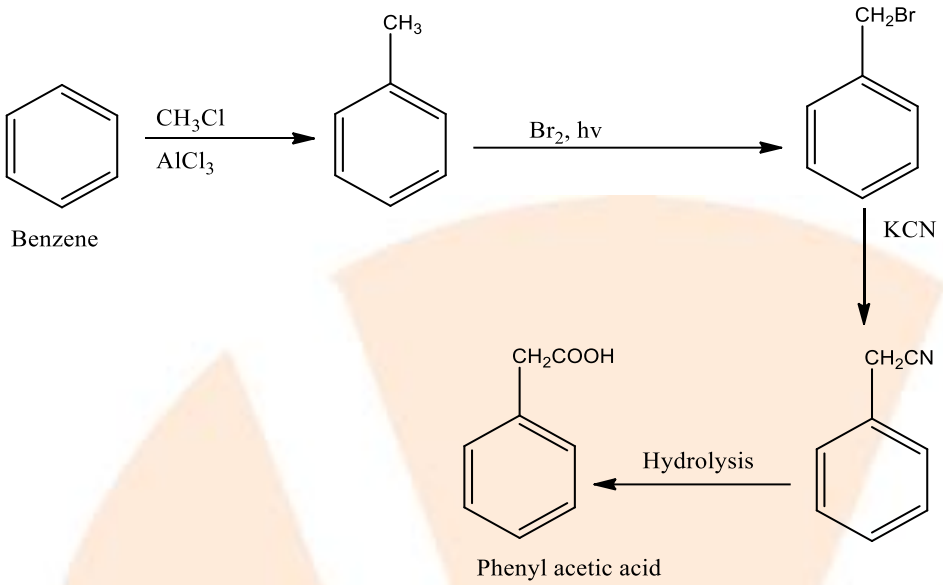


Benzene

p-Nitrobenzoic acid

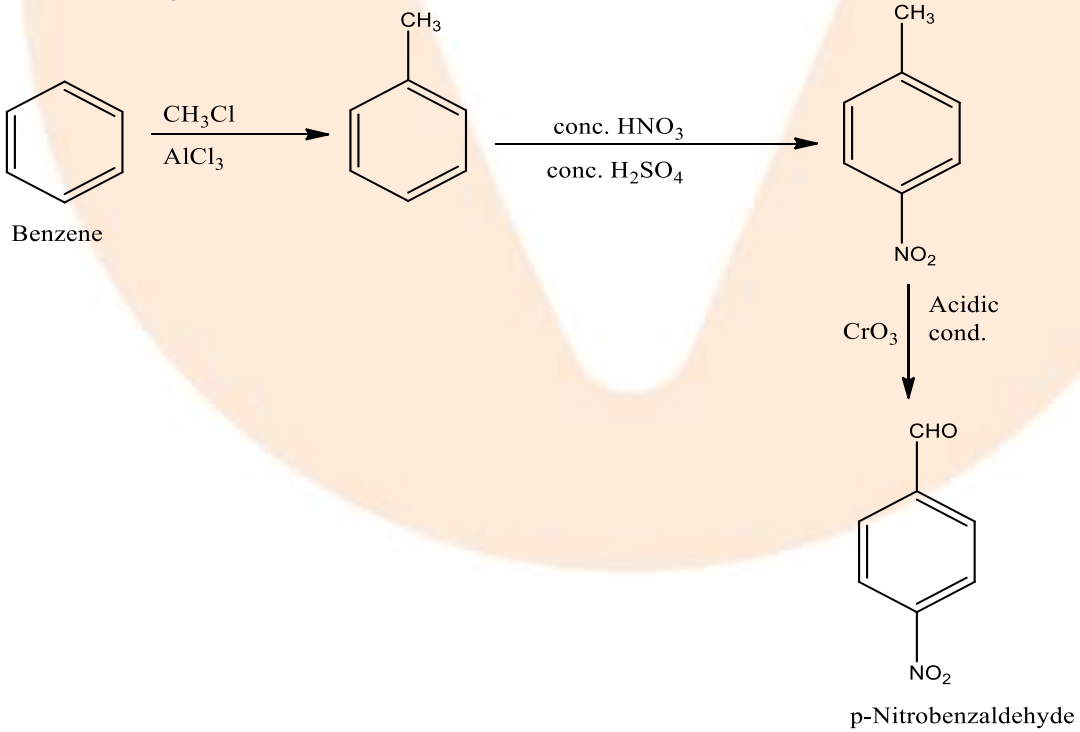
(iv)Phenylacetic acid

Ans: Benzene will be converted into toluene. Now, Toluene will be converted into Benzyl bromide; this will be further converted into benzyl cyanide. Benzyl cyanide will be hydrolyzed to Phenylacetic acid. The reaction is given below:



(v) p-Nitrobenzaldehyde

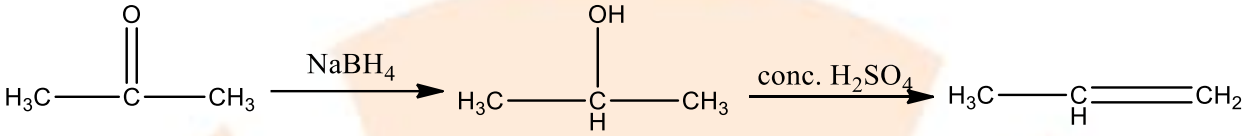
Ans: Benzene will be converted into toluene. Now, Toluene will be converted into p-nitrotoluene. Now, this p-nitrotoluene on oxidation will form p-nitrobenzaldehyde. The reaction is given below:



15. How will you bring about the following conversions in not more than two steps?

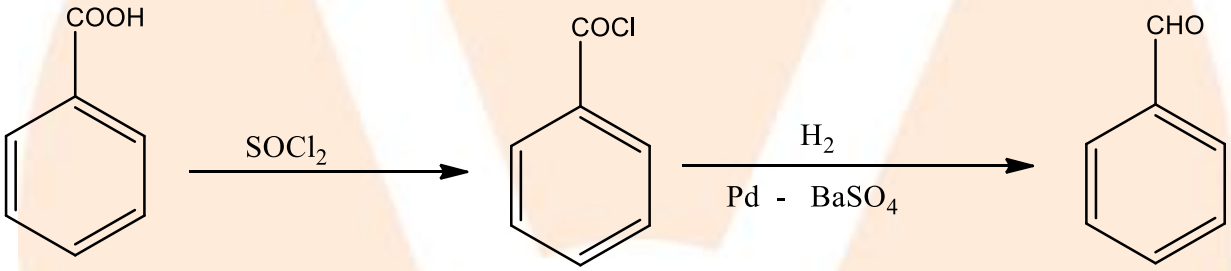
(i) Propanone to Propene

Ans: Propanone will react with $NaBH_3$ to form 2-Propanol. When 2-propanol will react with concentrated sulfuric acid to form propene. The reaction is given below:



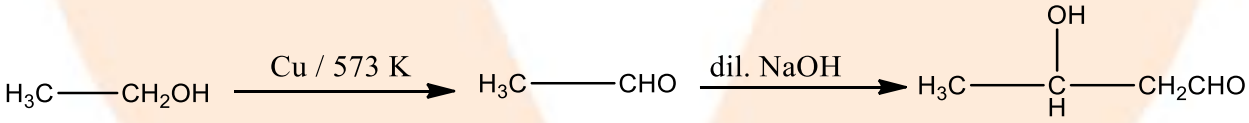
(ii) Benzoic acid to Benzaldehyde

Ans: Benzoic acid will be converted into Benzoyl chloride which will react with hydrogen and barium sulphate to give Benzaldehyde. The reaction is given below:



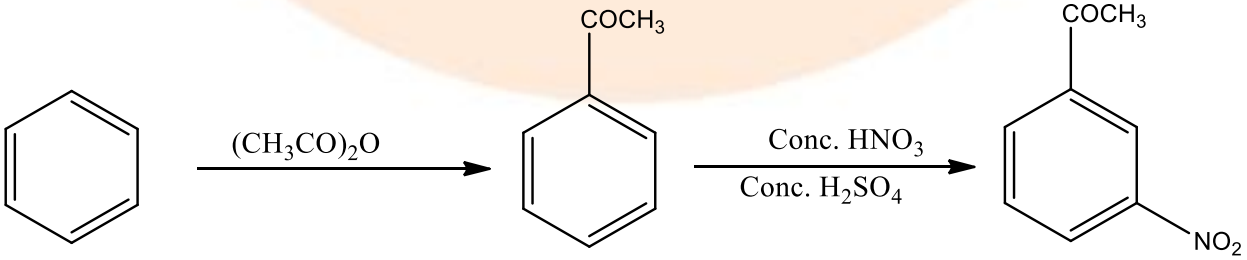
(iii)Ethanol to 3-Hydroxybutanal

Ans: Ethanol will be converted into ethanal which will react with dilute NaOH to form 3-Hydroxybutanal. The reaction is given below:



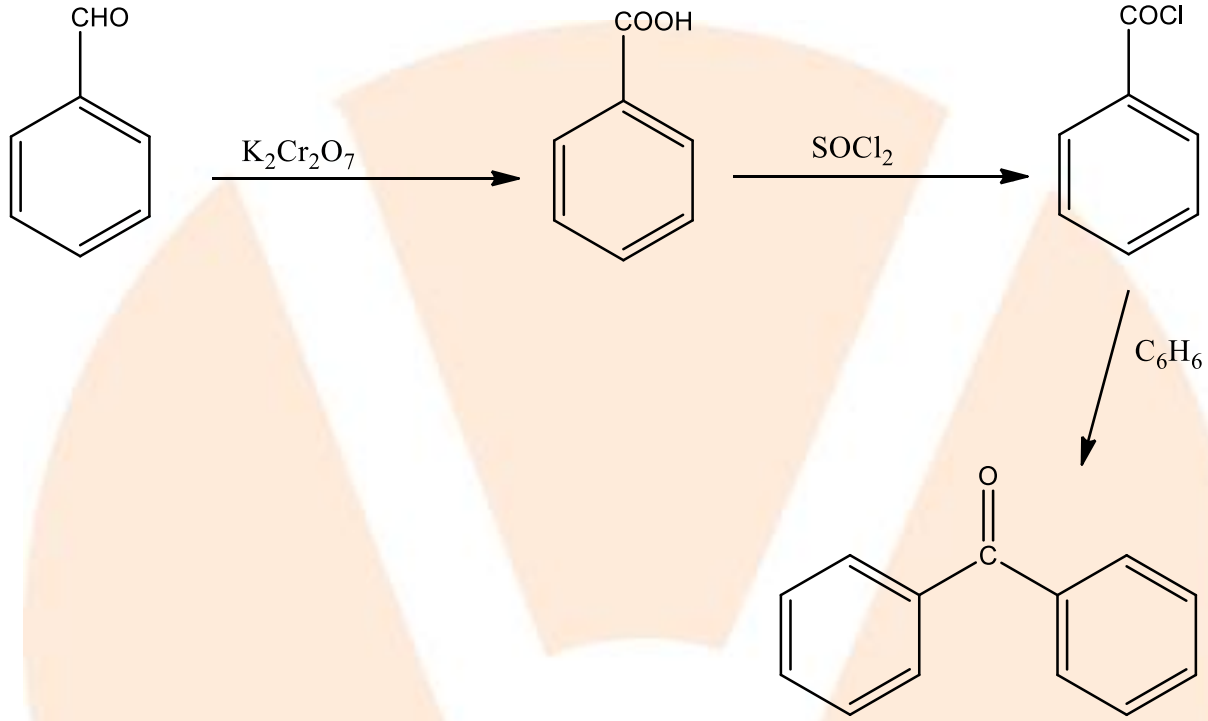
(iv)Benzene to m-Nitroacetophenone

Ans: Benzene will be converted into acetophenone which will react with concentrated nitric acid and sulfuric acid to form m-Nitroacetophenone. The reaction is given below:



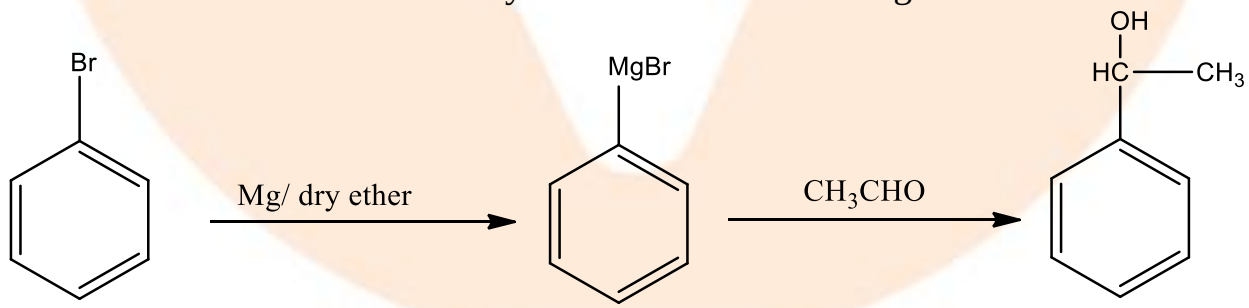
(v) Benzaldehyde to Benzophenone

Ans: Benzaldehyde will be converted into benzoic acid. The benzoic acid will be converted into benzoyl chloride which will react with benzene to form Benzophenone. The reaction is given below:



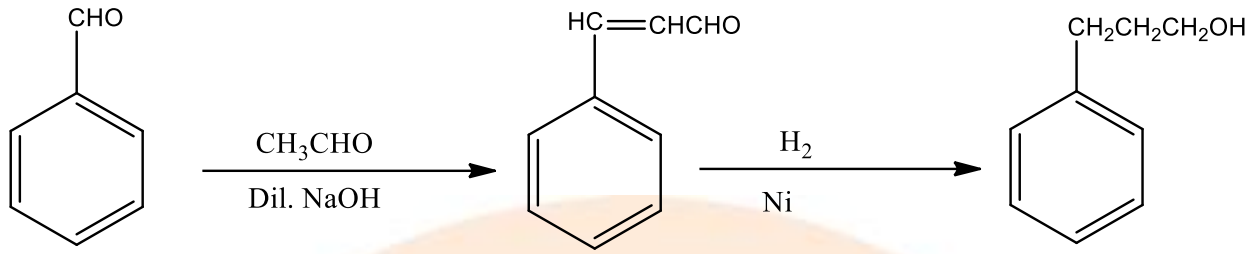
(vi)Bromobenzene to 1-Phenylethanol

Ans: Bromobenzene will be converted into Phenyl magnesium bromide which will react with ethanal to form 1-Phenylethanol. The reaction is given below:



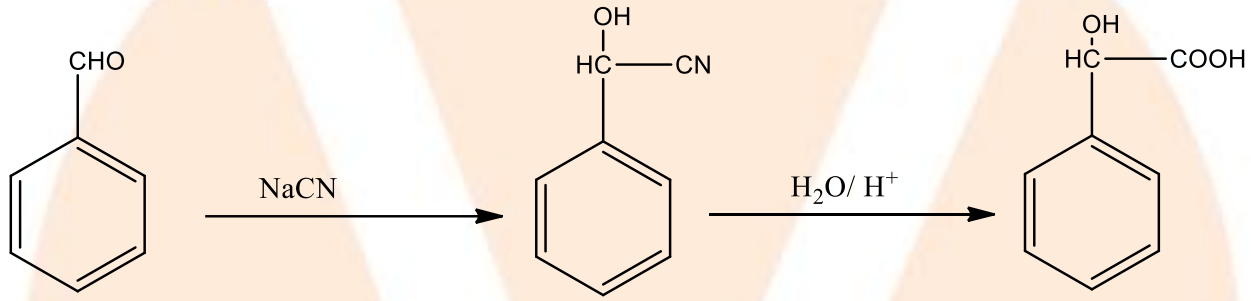
(vii) Benzaldehyde to 3-Phenylpropan-1-ol

Ans: Benzaldehyde will be converted into 3-Phenylprop-2-enal which will react with hydrogen to form 3-Phenylpropan-1-ol. The reaction is given below:



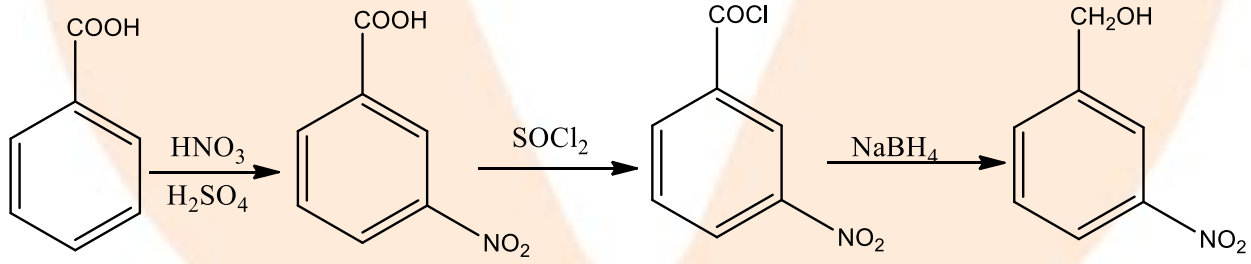
(viii) Benazaldehyde to α-Hydroxyphenylacetic acid

Ans: Benzaldehyde will be converted into Benzaldehyde cyanohydrin which will react with acidic water to form α-Hydroxyphenylacetic acid . The reaction is given below:



(ix)Benzoic acid to m- Nitrobenzyl alcohol

Ans: Benzoic acid will be converted into m-nitrobenzoic acid which will be further converted into m-Nitrobenzoyl chloride. m-Nitrobenzoyl chloride will react with $NaBH_4$ to form m-Nitrobenzyl alcohol. The reaction is given below:



16. Describe the following:

(i) Acetylation

Ans: Acetyl functional group is referred to as acetylation in the organic molecule. It is generally done with a basis such as pyridine, dimethylaniline, etc. This includes replacing an active hydrogen atom with a group of acetyls. The most popular acetylating agents include acetyl chloride and acetic anhydroid. For example, ethanol acetylation generates ethyl acetate.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + \underset{\text{Acetyl Chloride}}{CH_3COCl} \xrightarrow{\text{pyridine}} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + HCl$$

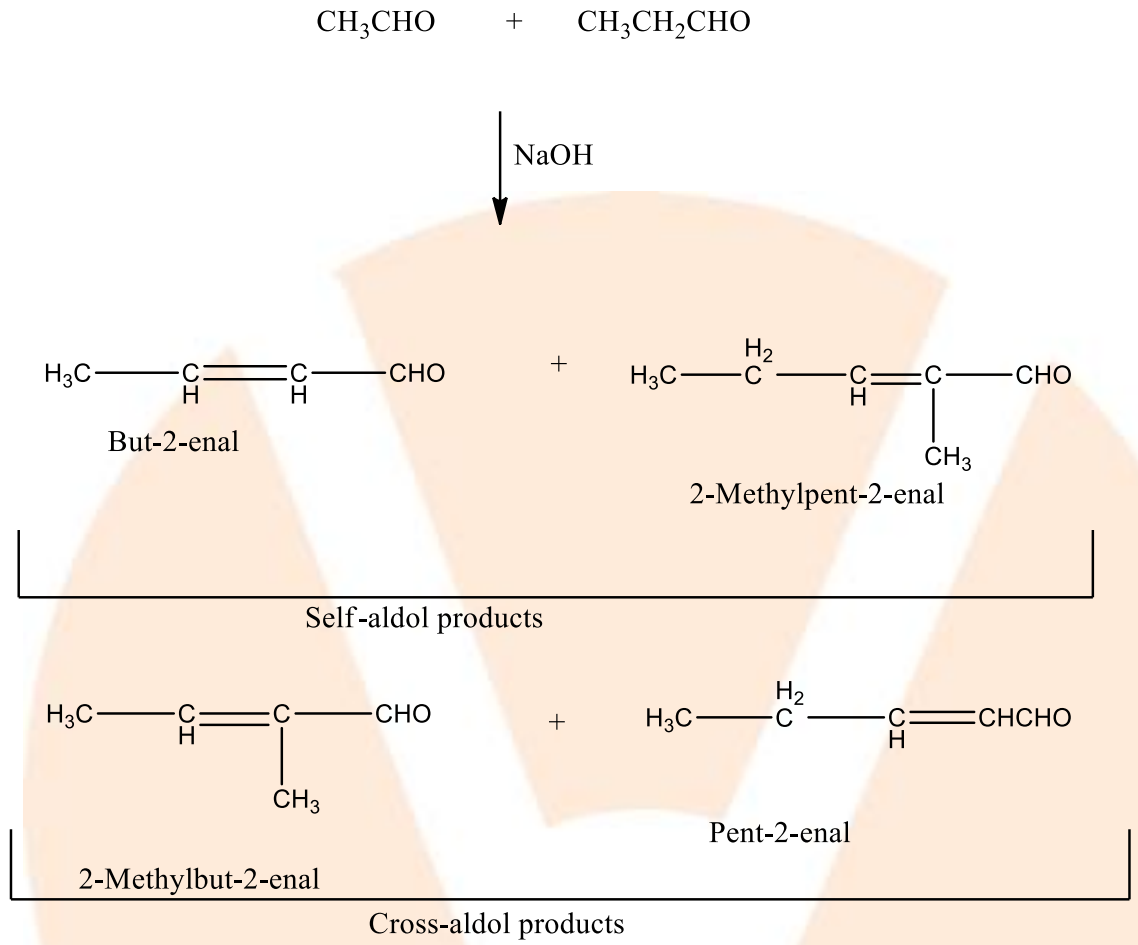
(ii) Cannizzaro reaction

Ans: The reaction of aldehydes that have no α-hydrogen to concentrated alkalis is sometimes called the Cannizzaro Reaction or Self-oxidation-reduction (disproportion). Two aldehyde molecules are involved in this process, one reduced to alcohol and the other to carboxylic acid oxidised.

Ethanol and potassium ethanoate are, for example, produced when treated with concentrated potassium hydroxide.

(iii)Cross aldol condensation

Ans: The reaction is called a cross-aldol condensation if aldol condensation is carried out by two distinct aldehydes or two separate ketones or an aldehyde and a ketone. If the α-hydrogen is present in the two reactants, four compound products are produced. Ethanal and propanal, for example, respond to four products.



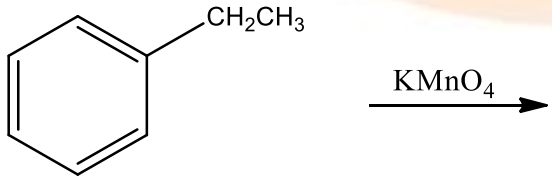
(iv) Decarboxylation

Ans: Decarboxylation is the reaction in which carboxylic acids, when their salts are heated by soda-lime, lose carbon dioxide in order to produce hydrocarbons.

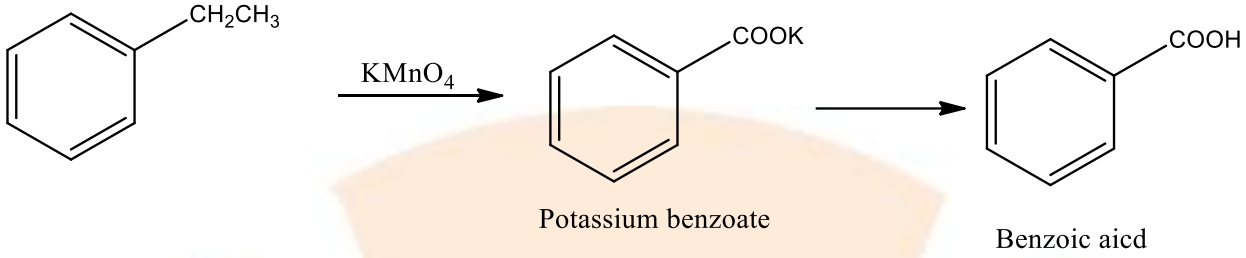
$CH_3\text{-}COONa \xrightarrow{\text{Soda lime}} CH_4 + Na_2CO_3$

17. Complete each synthesis by giving missing starting material, reagent or products.

(i)



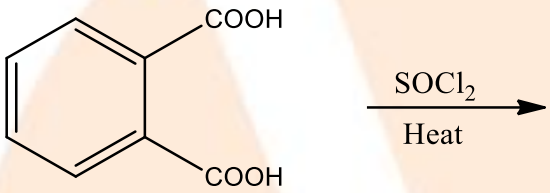
Ans: The products formed in this reaction are potassium benzoate and then benzoic acid. The reaction is given below:



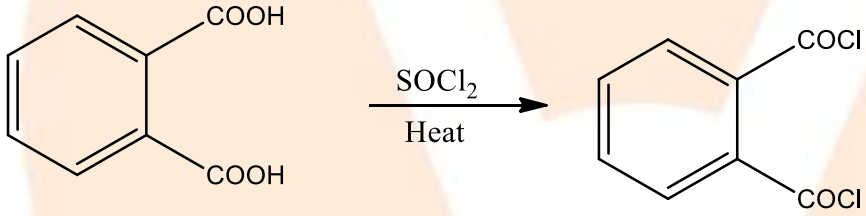
Potassium benzoate

Benzoic aicd

(ii)



Ans: The product formed in this reaction is Phthaloyl chloride. The reaction is given below:



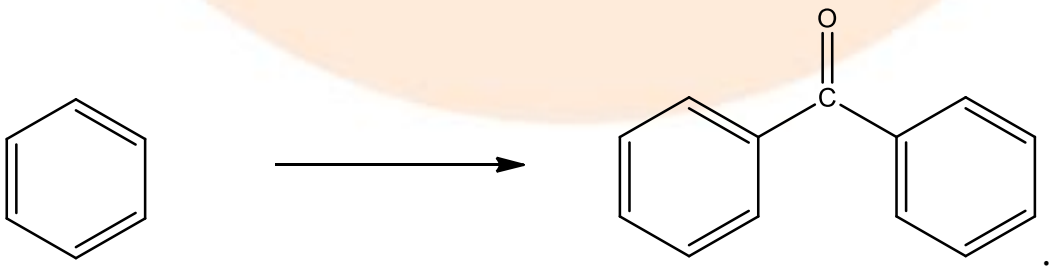
Phthalonyl chloride

(iii) $\mathbf{C_6H_5CHO \xrightarrow{H_2NCONHNH_2}}$

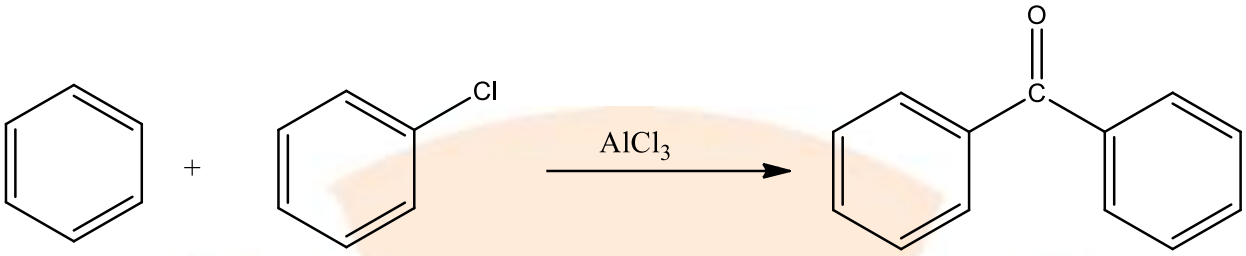
Ans: The product formed in this reaction will be Benzaldehyde semicarbazone. The reaction is given below:

$$C_6H_5CHO \xrightarrow{H_2NCONHNH_2} C_6H_5CH{=}NNHCONH_2 + H_2O$$

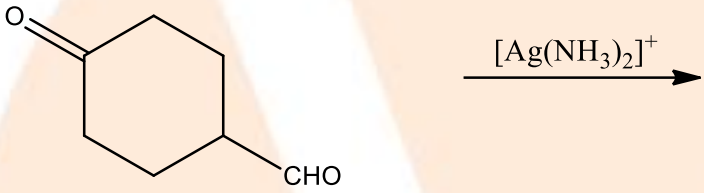
(iv)



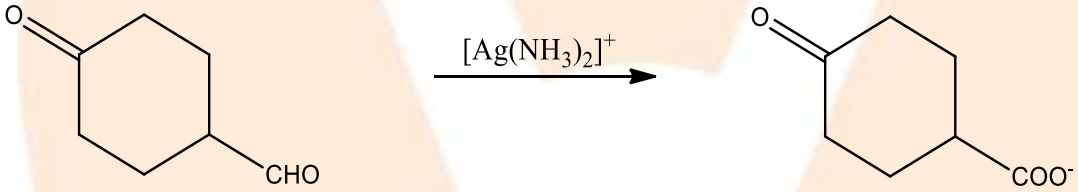
Ans: In this reaction, another reactant is benzoyl chloride and the catalyst is aluminium chloride. The reaction is given below:



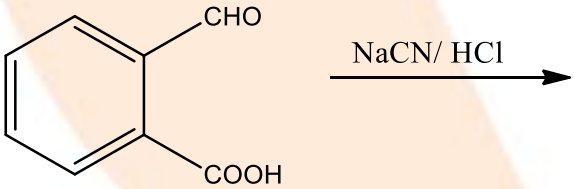
(v)



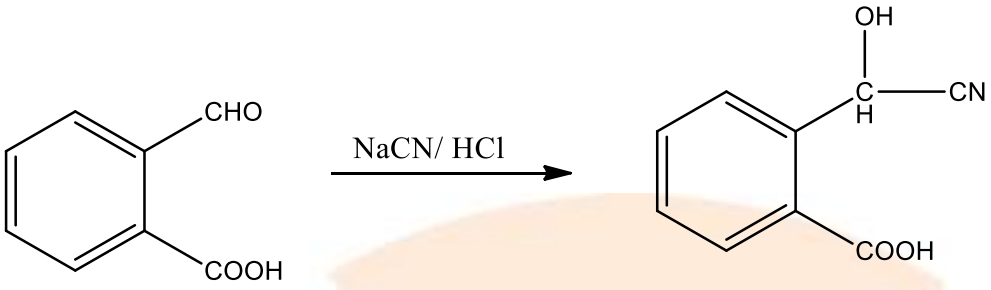
Ans: The tollen's reagent will only reduce the aldehyde part. The reaction is given below:



(vi)



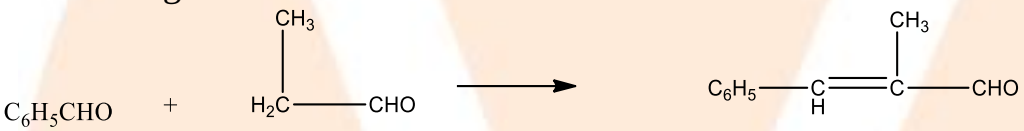
Ans: The product formed in this reaction will be 2-[1-Hydroxycyanomethyl] benzoic acid. The reaction is given below:



2-[1-Hydroxycyanomethyl] benzoic acid

(vii) $C_6H_5CHO + CH_3CH_2CHO \xrightarrow{\text{dil.NaOH}}$

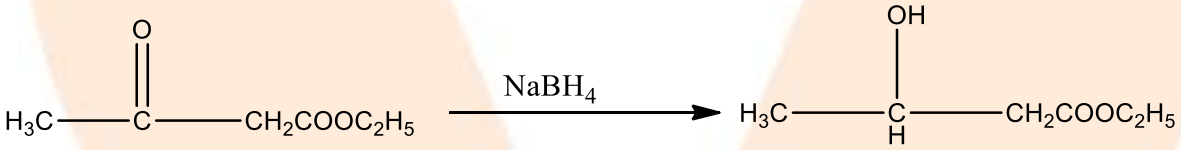
Ans: The product formed in this reaction will be 2-Methyl-3-phenylprop-2-enal. The reaction is given below:



2-Methyl-3-phenylprop-2-enal

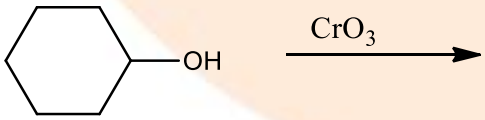
(viii) $CH_3COCH_2COOC_2H_5 \xrightarrow[(ii)H^+]{(i)NaBH_4}$

Ans: The product formed in this reaction is Ethyl-3-hydroxybutanoate. The reaction is given below:

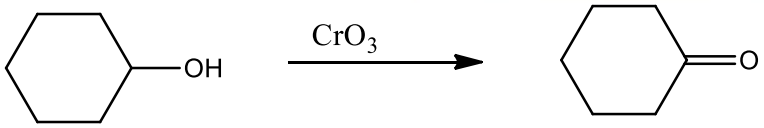


Ethyl 3-hydroxybutanoate

(ix)

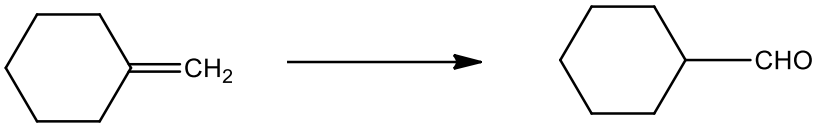


Ans: The product formed in this reaction will be Cyclohexanone. The reaction is given below:

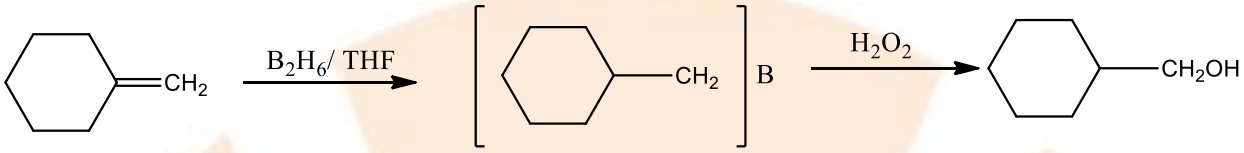


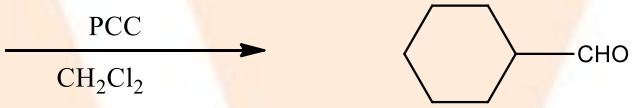
Cyclohexanone

(x)

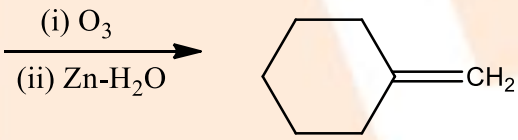


Ans: The complete reaction is given below:

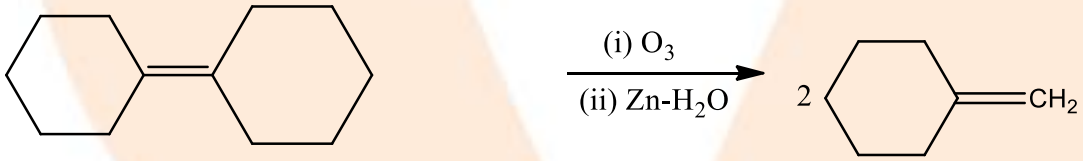




(xi)



Ans: The reactant for this reaction will be Cyclohexylidenecyclohexane. The reaction is given below:

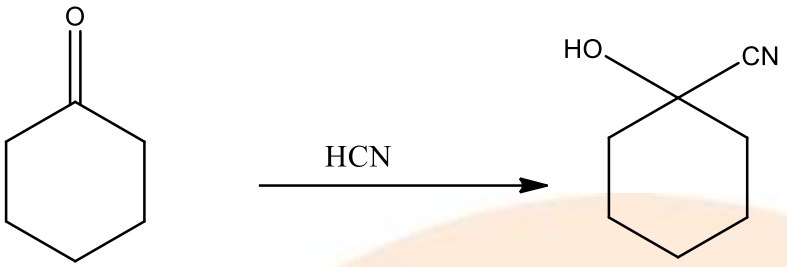


Cyclohexylidenecyclohexane

18. Give plausible explanation for each of the following:

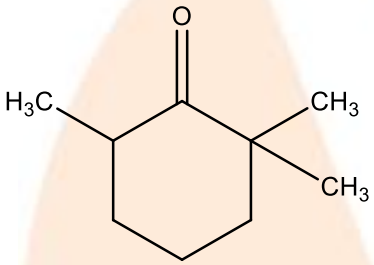
(i) Cyclohexanone forms cyanohydrin in good yield but 2, 2, 6-trimethylcyclohexanone does not.

Ans: Cyclohexanones form cyanohydrins according to the following equation.



Cyclohexanone Cyclohydrin

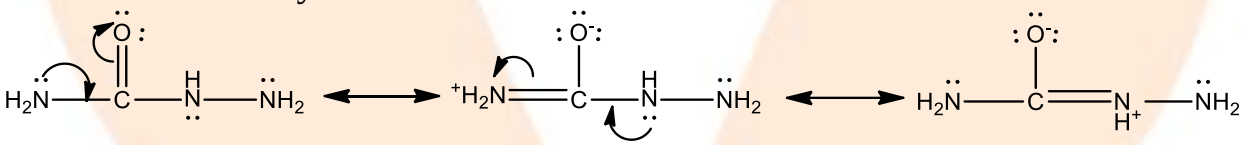
In this scenario, nucleophile CN^- can approach freely without steric obstruction. But for 2-2, 6-trimethylcyclohexanone, α-positioned methyl groups present steric barriers and as a result CN^- cannot successfully attack.



That's why it cannot form cyanohydrins.

(ii) There are two $-NH_2$ groups in semicarbazide. However, only one is involved in the formation of semicarbazones.

Ans: Semicarbazide is resonant with just one of two groups $-NH_2$ which is immediately linked to the carbonyl carbon atom.



Consequently, the electron density at $-NH_2$ likewise decreases with the resonance. It cannot therefore operate as a nucleophile. Since the other group $-NH_2$ does not engage itself in resonance, it may function as a nucleophile and can attack aldehydrogen and ketone carbonyl atoms to generate semicarbazones.

(iii)During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as soon as it is formed.

Ans: In presence of acid, ester along with water is reversibly made of carboxylic acid and alcohol.

$$RCOOH+R'OH \xrightarrow{H^+} RCOOR'+H_2O$$

If water or ester is not eliminated as it forms, then the reactants react to the reversibility of the reaction. Therefore, one of the two should be eliminated to push the balance forward in a more ester way.

19. An organic compound contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollens' reagent but forms an additional compound with sodium hydrogen sulphite and gives a positive iodoform test. On vigorous oxidation it gives ethanoic and propanoic acid. Write the possible structure of the compound.

Ans: The percentage of carbon atom = 69.77%

The percentage of hydrogen atom = 11.63%

The percentage of oxygen atom = 100 – (69.77 + 11.63) = 18.6%

Thus, the ratio of the number of carbon, hydrogen, and oxygen atoms in the organic compound can be given as:

$$C : H : O = \frac{69.77}{12} : \frac{11.63}{1} : \frac{18.6}{16}$$

= 5.81 : 11.63 : 1.16

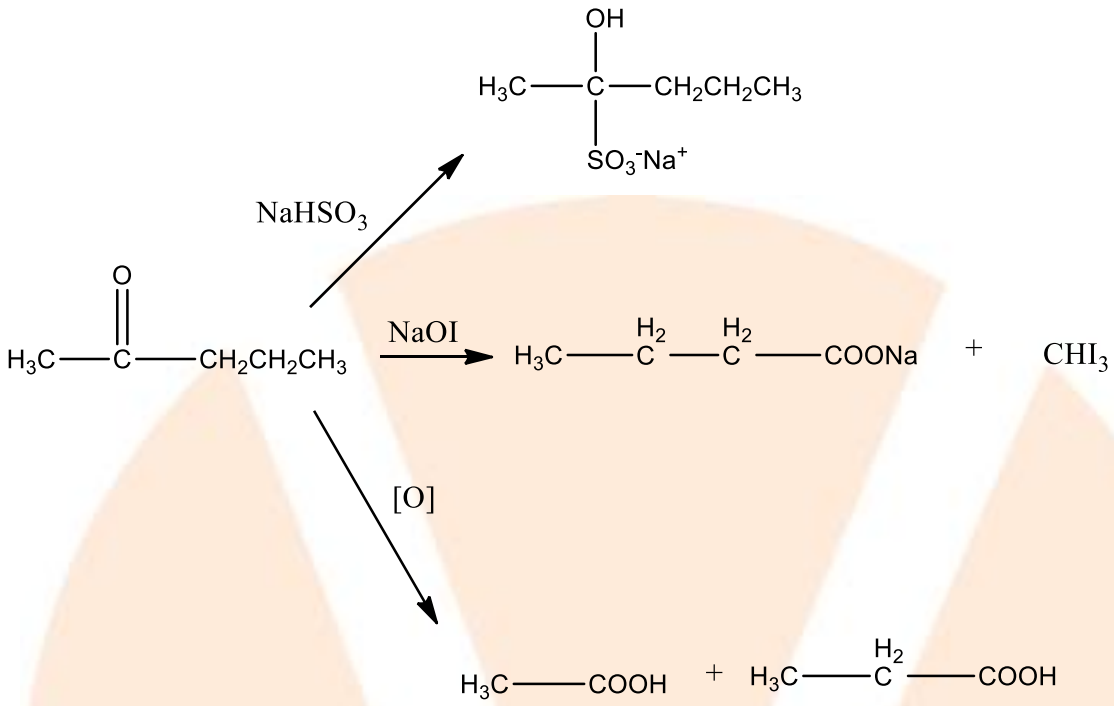
= 5 : 10 : 1

Hence the empirical formula of the compound is $C_5H_{10}O$. So, the mass of the compound is = 5 × 12 + 10 × 1 + 1 × 16 = 86

Since the given molecular mass is also 86. The molecular formula is also $C_5H_{10}O$.

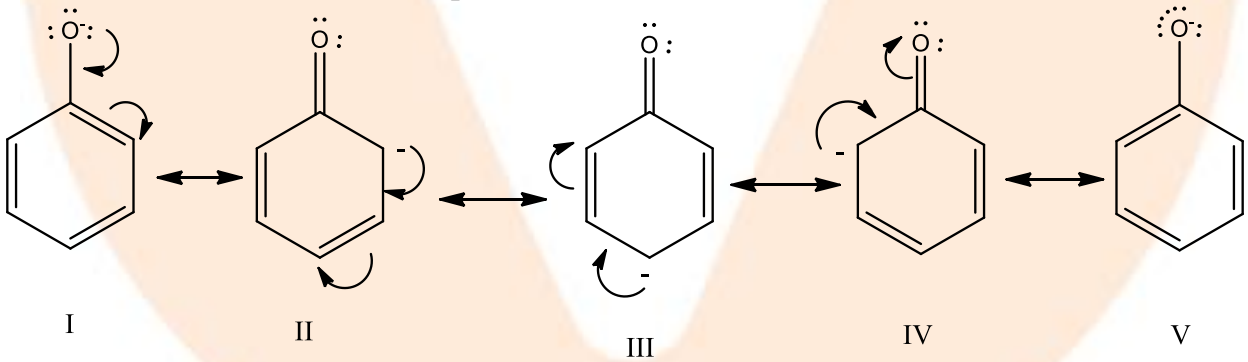
As Tollen's reagent is not reduced by that molecule, it is not an aldehyde. The chemical once again provides a positive Iodoform test to form sodium hydrogen sulphate supplements. The molecule must be a methyl ketone, because it is not an aldehyde. A combination of ethanoic acid and propanoic acid also results in the given chemical. The chemical is thus pentan−2−ol.

The reactions in the question are given below:



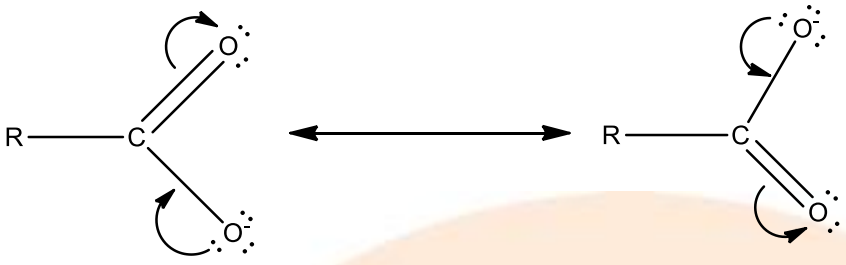
20. Although phenoxide ions have more resonating structures than carboxylate ions, carboxylic acid is a stronger acid than phenol. Why?

Ans: Resonance structures of phenoxide ion are:



Resonance structures of phenoxide ions may be shown to have a negative charge for fewer electronegative carbon atoms in II, III and IV. Those three configurations therefore make a negligible contribution to the phenoxide ion's resonance stability. Such constructions can thus be removed. The most electronegative oxygen atom carries a negative load only in structures I and V.

The resonating structures of carboxylate ion are given below:



I' II'

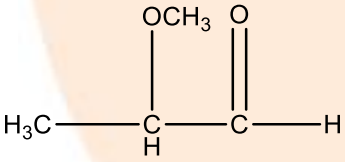
In the case of carboxylate ions, resonating structures I′ and II′ contain a charge carried by a more electronegative oxygen atom. Further, in resonating structures I′ and II′, the negative charge is delocalized over two oxygen atoms. But in resonating structures I and V of the phenoxide ion, the negative charge is localized on the same oxygen atom. Therefore, the resonating structures of carboxylate ions contribute more towards its stability than those of phenoxide ions. As a result, carboxylate ions are more resonance-stabilized than phenoxide ions. Hence, carboxylic acid is a stronger acid than phenol.

INTEXT SOLUTIONS

1. Write the structures of the following compounds.

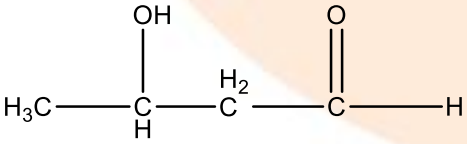
(i) α-Methoxypropionaldehyde

Ans: The structure of α-Methoxypropionaldehyde is given below:



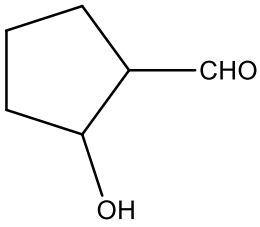
(ii) 3-Hydroxybutanal

Ans: The structure of 3-Hydroxybutanal is given below:



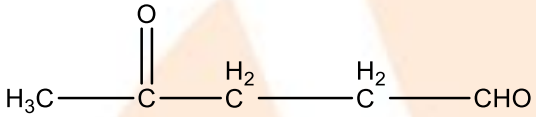
(iii)2-Hydroxycyclopentane carbaldehyde

Ans: The structure of 2-Hydroxycyclopentane carbaldehyde is given below:



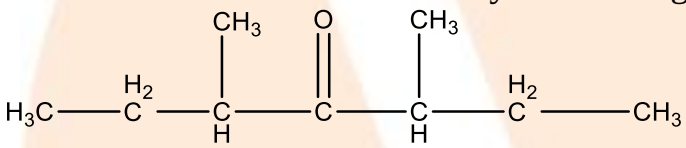
(iv) 4-Oxopentanal

Ans: The structure of 4-Oxopentanal is given below:



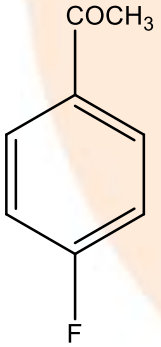
(v) Di-sec-butyl ketone

Ans: The structure of Di-sec-butyl ketone is given below:



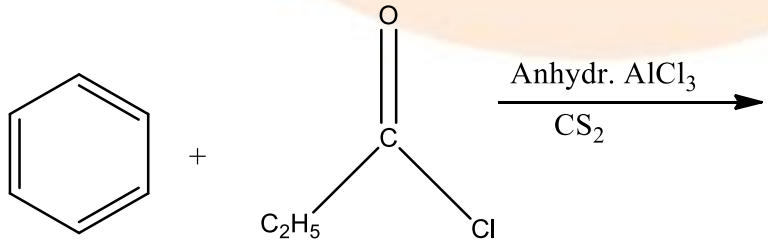
(vi) 4-Fluoroacetophenone

Ans: The structure of 4-Fluoroacetophenone is given below:

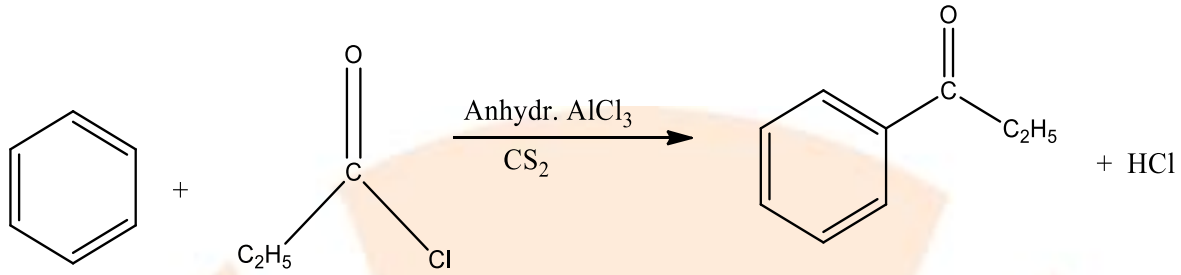


2. Write the structures of products of the following reactions;

(i)



Ans: The product formed in this reaction is Propiophenone. The reaction is given below:



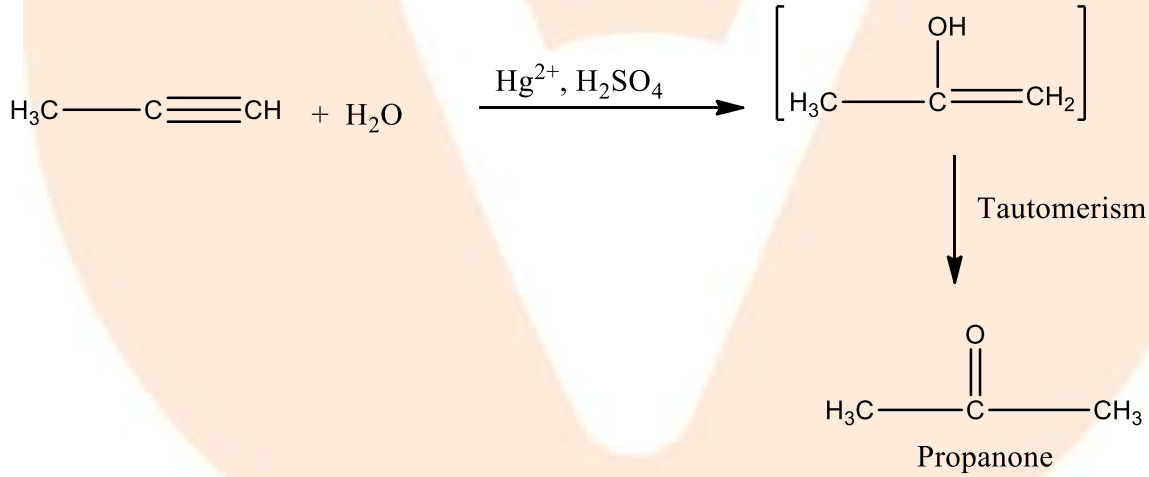
(ii) $(C_6H_5CH_2)_2Cd + 2CH_3COCl \rightarrow$

Ans: The product formed in this reaction is 1-Phenylpropan-2-one. The reaction is given below:

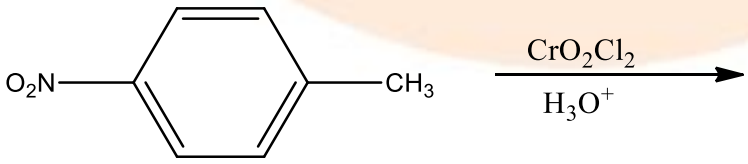
$(C_6H_5CH_2)_2Cd + 2CH_3COCl \rightarrow 2CH_3COCH_2C_6H_5 + CdCl_2$

(iii) $CH_3\text{-}C \equiv CH \xrightarrow{Hg^{2+},H_2SO_4}$

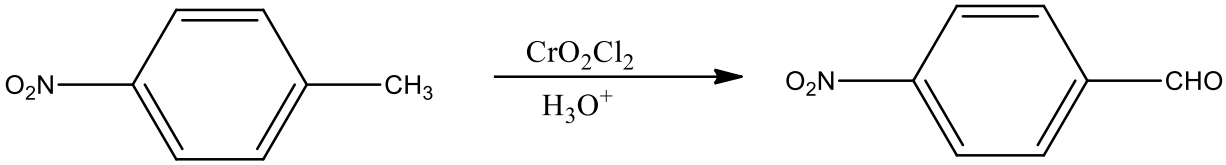
Ans: The product formed in this reaction is Propanone. The reaction is given below:



(iv)



Ans: The product formed in this reaction is p-Nitrobenzaldehyde. The reaction is given below:



p-Nitrobenzaldehyde

3. Arrange the following compounds in increasing order of their boiling points.
CH_3CHO, CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$

Ans: The molecular masses are in the range 44 to 46 of the listed compounds. CH_3CH_2OH has the greatest boiling point is consequently subjected to substantial, intermolecular H-bonding, culminating in the combination between molecules.

CH_3CHO is more polar than CH_3OCH_3, thus the dipole is greater than CH_3OCH_3, and $CH_3CH_2CH_3$ is weaker than the van der Waals.

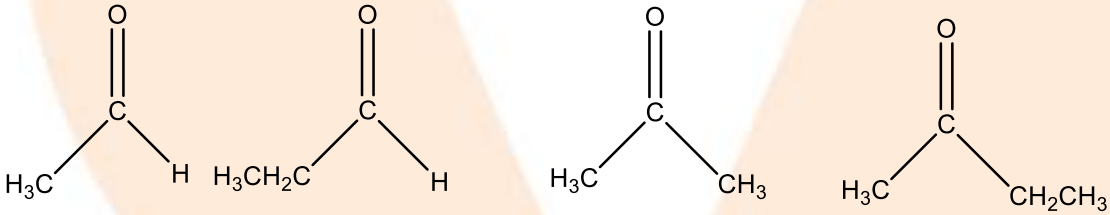
The order will be:

$CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$

4. Arrange the following compounds in increasing order of their reactivity in Nucleophilic addition reactions.

(i) Ethanal, Propanal, Propanone, Butanone.

Ans: The structures of all the compounds are given below:



Ethanal Propanal Propanone Butanone

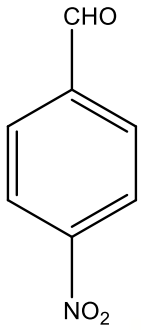
The alkyl group +I impact increases:

Ethanal < Propanal < Propanone < Butanone

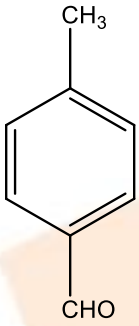
With the +I effect increasing, the electron density of carbonyl carbon rises. As a consequence, the possibilities of a nucleophile attack are reduced. Thus, in nucleophilic addition reactions, the increasing order of reactivities of given carbonyl compounds is Butanone < Propanone < Propanal < Ethanal.

(ii) Benzaldehyde, p-Tolualdehyde, p-Nitrobenzaldehyde, Acetophenone

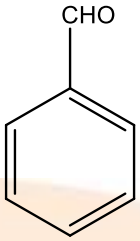
Ans: The structure of the following compounds is given below:



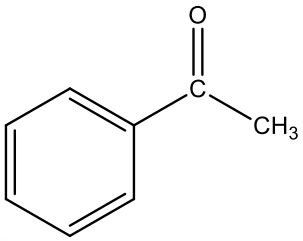
p-Nitrobenzaldehyde



p-Tolualdehyde



Benzaldehyde



Acetophenone

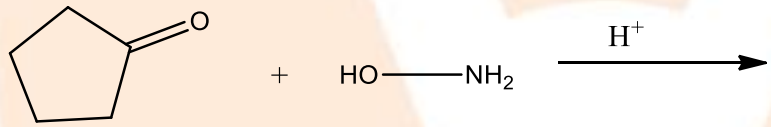
The impact of +I in ketone is higher than aldehyde. Acetophenone is therefore the least reactive in nuclear processes. The +I effect in p-tolualdehyde is greatest among aldehys, due to the electron-donating group $-CH_3$ and the presence of the electron-donating group $-NO_2$ and the existence of the p-nitrobezaldehyde.

Therefore, the increasing order of the compound reactivities is:

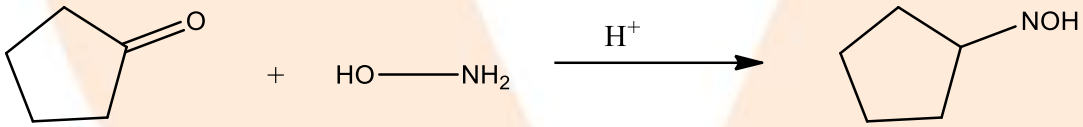
Benzaldehyde < p-Nitrobenzaldehyde < Acetophenone < p-tolualdehyde.

5. Predict the products of the following reactions:

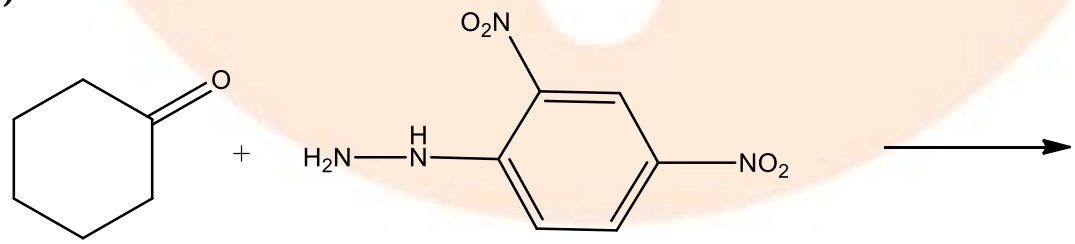
(i)



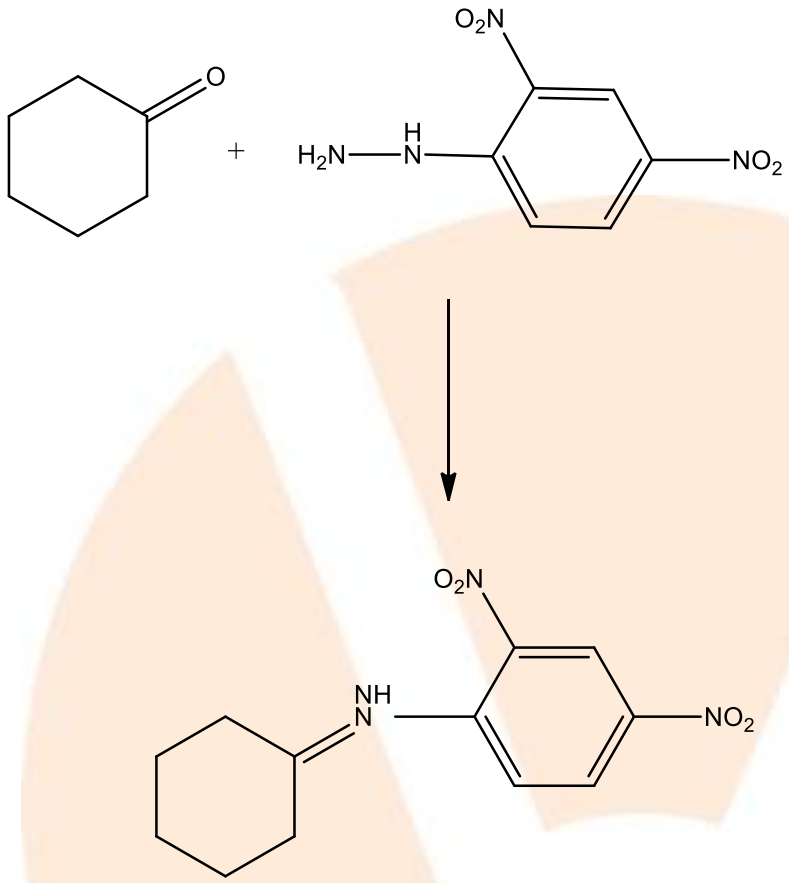
Ans: The complete reaction is given below:



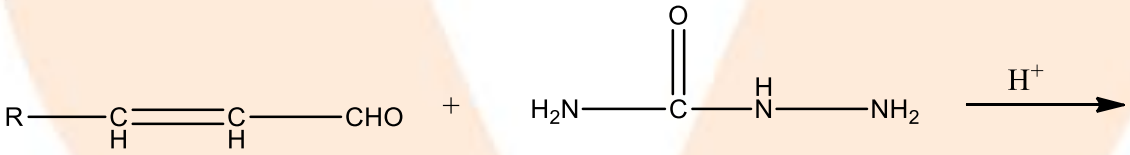
(ii)



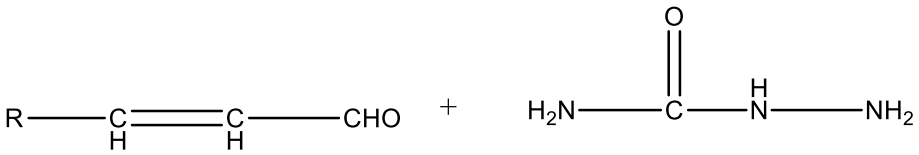
Ans: The complete reaction is given below:

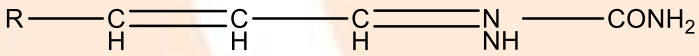


(iii)

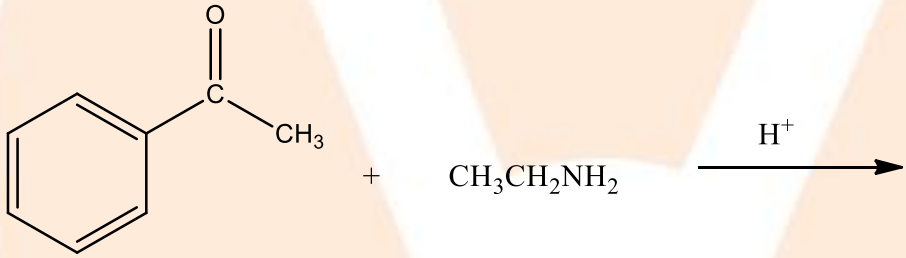


Ans: The complete reaction is given below:

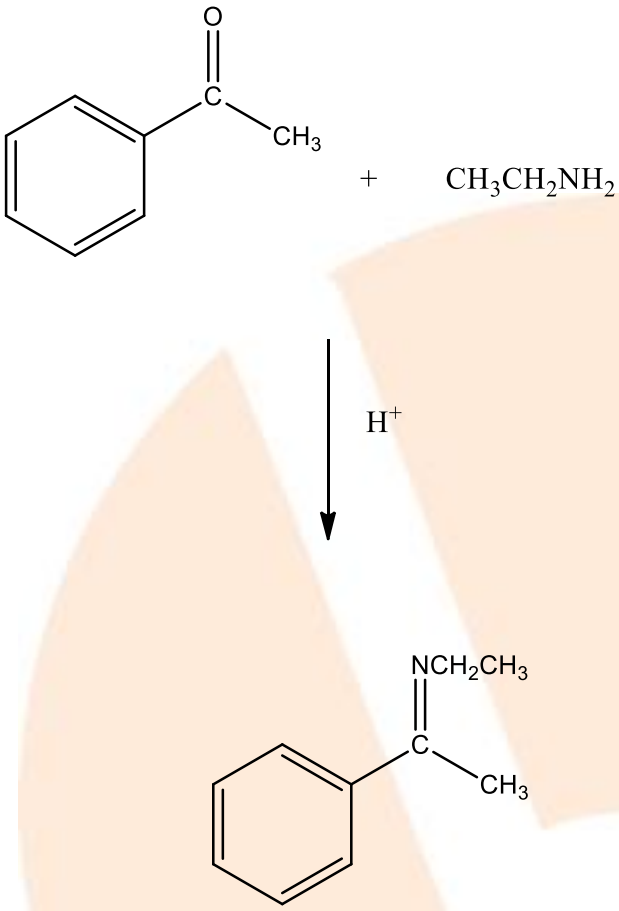




(iv)



Ans: The complete reaction is given below:



6. Give the IUPAC names of the following compounds:

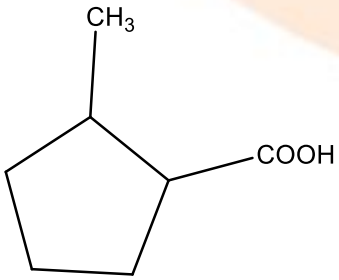
(i) $PhCH_2CH_2COOH$

Ans: The IUPAC name of the compound is 3-Phenylpropanoic acid.

(ii) $(CH_3)_2C=CHCOOH$

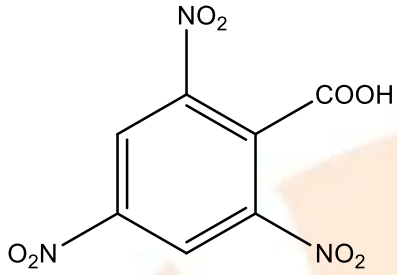
Ans: The IUPAC name of the compound is 3-Methylbut-2-enoic acid.

(iii)



Ans: The IUPAC name of the compound is 2-Methylcyclopentanecarboxylic acid.

(iv)

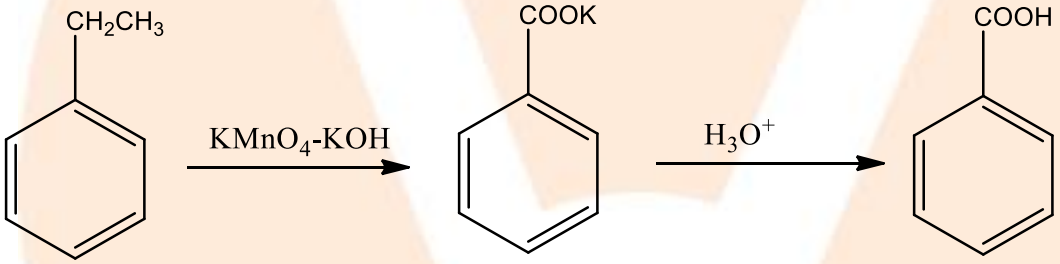


Ans: The IUPAC name of the compound is 2, 4, 6-Trinitrobenzoic acid.

7. Show how each of the following compounds can be converted to benzoic acid.

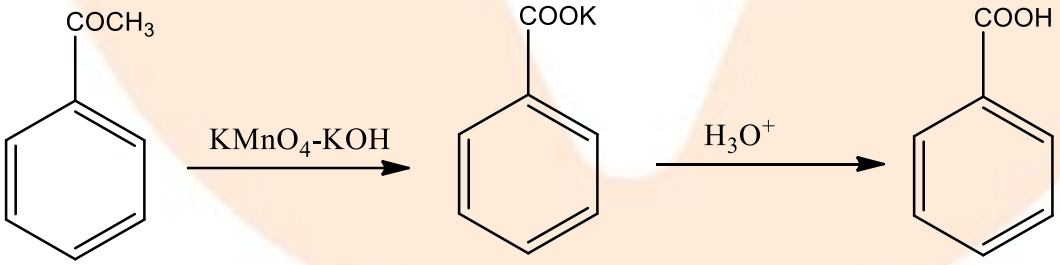
(i)Ethylbenzene

Ans: Ethylbenzene will convert into potassium benzoate. Now, this potassium benzoate will be hydrolyzed to form benzoic acid. The reaction is given below:



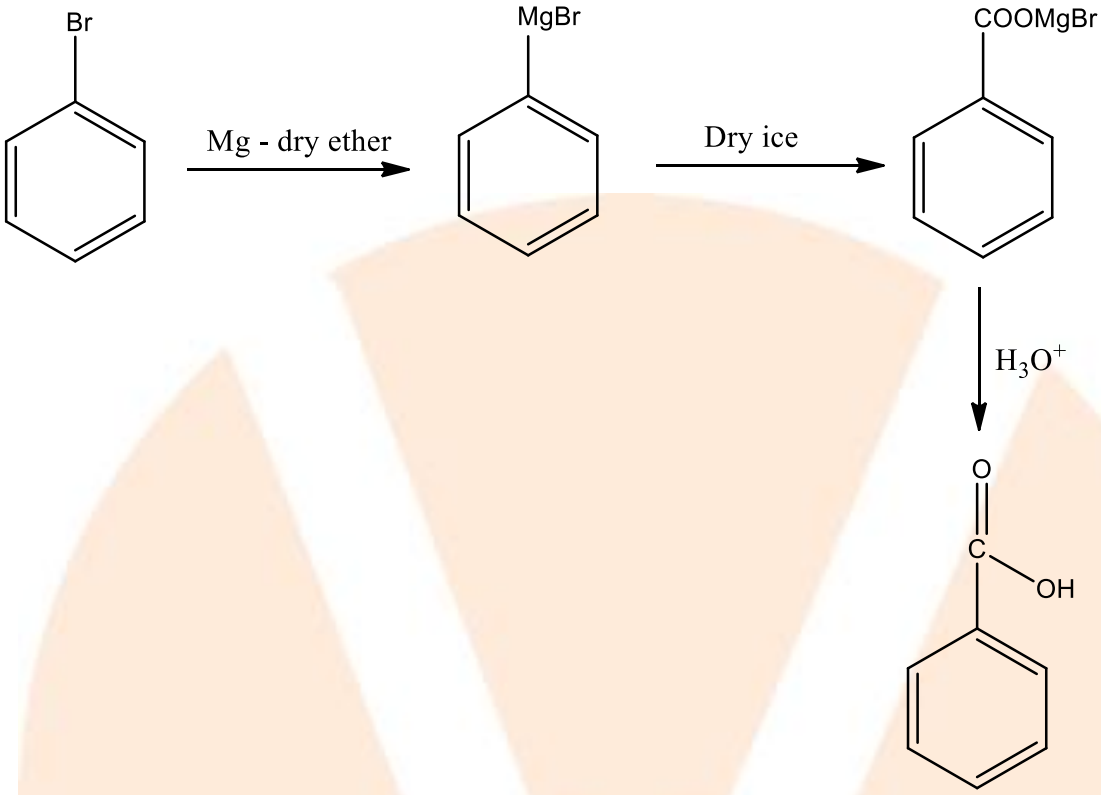
(ii) Acetophenone

Ans: Acetophenone will convert into potassium benzoate. Now, this potassium benzoate will be hydrolyzed to form benzoic acid. The reaction is given below:



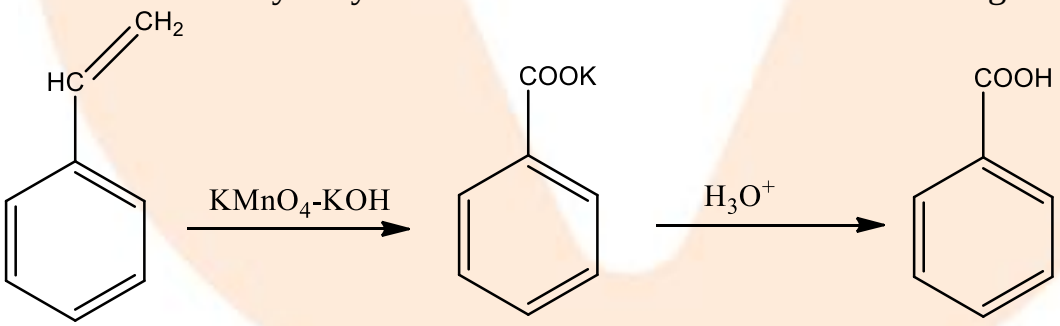
(iii)Bromobenzene

Ans: Bromobenzene will react with magnesium to form Phenyl magnesium bromide. This will be converted into benzoic acid. The reaction is given below:



(iv) Phenylethene (Styrene)

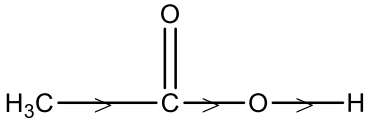
Ans: Phenylethene will convert into potassium benzoate. Now, this potassium benzoate will be hydrolyzed to form benzoic acid. The reaction is given below:

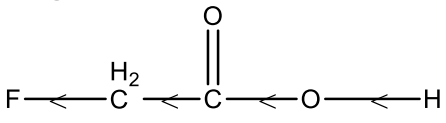


8. Which acid of each pair shown here would you expect to be stronger?

(i) CH_3CO_2H o rCH_2FCO_2H

Ans: The structures of the compounds are given below:





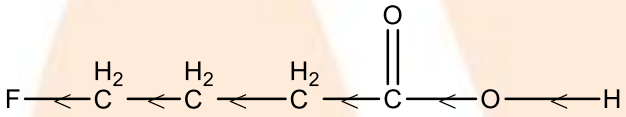
The $-CH_3$ Group's +I action increases the electron density on the O-H connection. Thus, it is tough to release the proton. The −I impact of F on the O-H bond, on the other hand, reduces the electron density. Proton may therefore readily be released. CH_2FCO_2H is hence stronger than CH_3CO_2H.

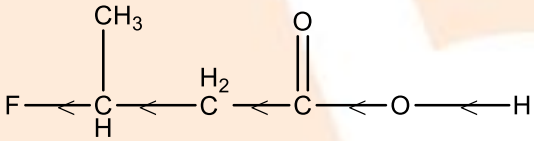
(ii) CH_2FCO_2H or CH_2ClCO_2H

Ans: F has stronger −I effect than Cl. Therefore, CH_2FCO_2H can release proton more easily than CH_2ClCO_2H. Hence, CH_2FCO_2H is stronger acid than CH_2ClCO_2H.

(iii) $CH_2FCH_2CH_2CO_2H$ or $CH_3CHFCH_2CO_2H$

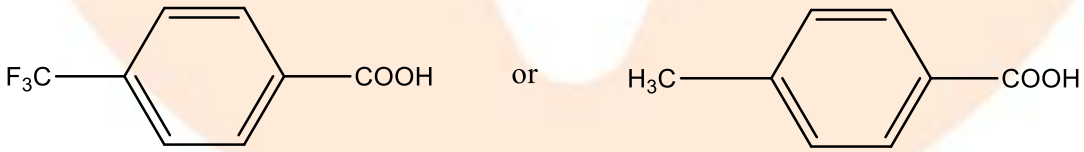
Ans: The structures of the compounds are given below:





Inductive effect decreases with increase in distance. Hence, the +I effect of F in $CH_3CHFCH_2CO_2H$ is more than it is in $CH_2FCH_2CH_2CO_2H$. Hence, $CH_3CHFCH_2CO_2H$ is stronger acid than $CH_2FCH_2CH_2CO_2H$.

(iv)



Ans: Due to the −I action of F, the release of proton for the chemical is simpler (A). However, proton release is problematic in the case of compound (B), because of the +I action of a group of $-CH_3$. (A) is hence stronger than acid (B).