Chapter – 12 (Aldehydes, Ketones and Carboxylic Acids)

Exercise Questions:

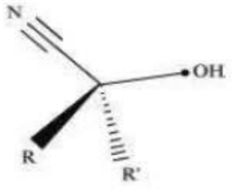
Question:1 What is meant by the following terms? Give an example of the reaction in each case.

- **i.) Cyanohydrin**
- **ii.) Acetal**
- **iii.) Semicarbazone**
- **iv.) Aldol**
- **v.) Hemiacetal**
- **vi.) Oxime**
- **vii.) Ketal**
- **viii.) Imine**
- **ix.) 2,4-DNP – derivative**
- **x.) Schiff's base**

Answer:

(i) Cyanohydrin:

Cyanohydrins are organic compounds having the formula RR“^{2}C(OH)CN, where R and R“^{2} can be alkyl or aryl groups.

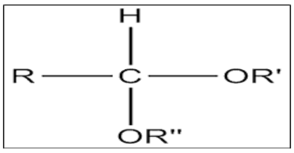


Aldehydes and ketones react with hydrogen cyanide (HCN) in the presence of excess sodium cyanide (NaCN) as a catalyst to field cyanohydrin. These reactions are known as cyanohydrin reactions.

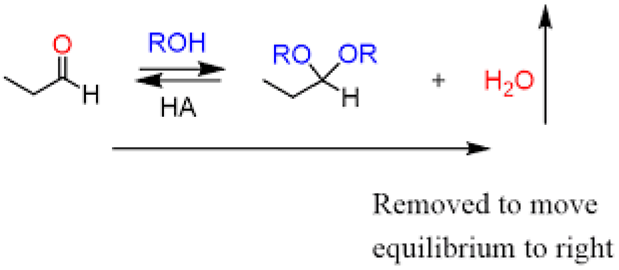
$RR'C = O + HCN \xrightarrow{NaCN} RR'C(OH)CN$

Cyanohydrins are useful synthetic intermediates.

(ii) Acetal:



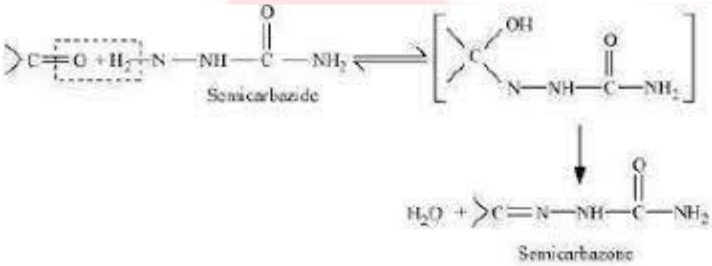
Acetals are gem - dialkoxy alkanes in which two alkoxy groups are present on the terminal carbon atom. One bond is connected to an alkyl group while the other is connected to a hydrogen atom.



When aldehydes are treated with two equivalents of a monohydric alcohol in the presence of dry HCl gas, hemiacetals are produced that further react with one more molecule of alcohol to yield acetal.

(iii) Semicarbarbazone:

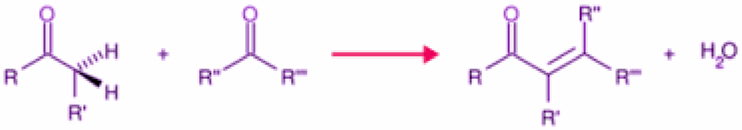
Semicarbazones are derivatives of aldehydes and ketones produced by the condensation reaction between a ketone or aldehyde and semicarbazide.



Semicarbazones are useful for identification and characterization of aldehydes and ketones.

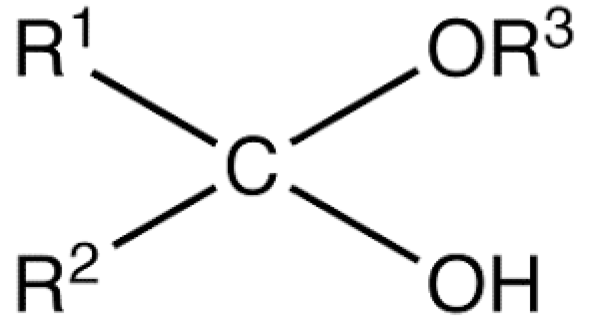
(iv) Aldol:

A β–hydroxy aldehyde or ketone is known as an aldol. It is produced by the condensation reaction of two molecules of the same or one molecule each of two different aldehydes or ketones in the presence of a base.



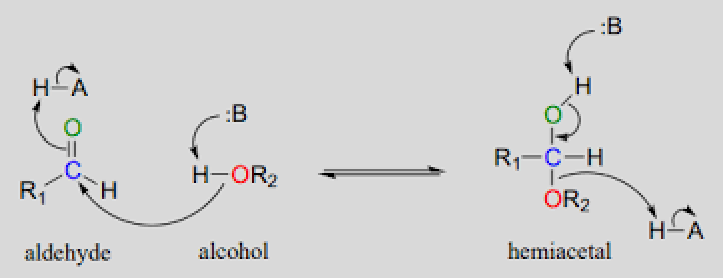
(v) Hemiacetal:

Hemiacetals are α - alkoxyalcohols



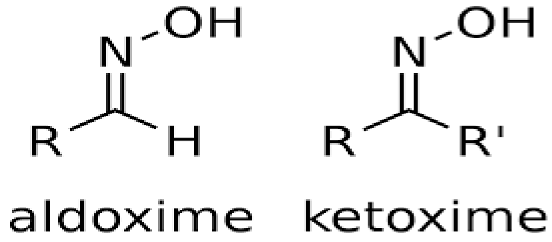
General structure of a hemiacetal

Aldehyde reacts with one molecule of a monohydric alcohol in the presence of dry HCl gas.



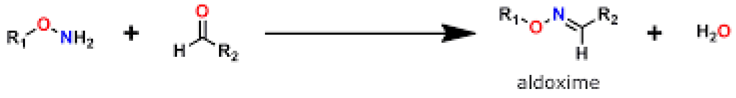
(vi) Oxime:

Oximes are a class of organic compounds having the general formula RR“^{2}CNOH, where R is an organic side chain and R“^{2} is either hydrogen or an organic side chain. If R“^{2} is H, then it is known as aldoxime and if R“^{2} is an organic side chain, it is known as ketoxime.



On treatment with hydroxylamine in a weakly acidic medium, aldehydes or ketones form oximes.

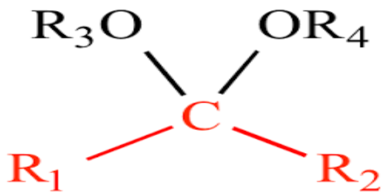
a.



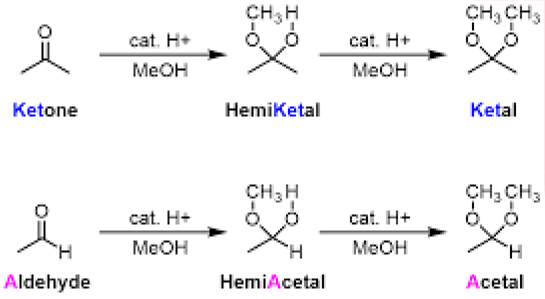
b.

(vii) Ketal:

Ketals are gem - dialkoxyalkanes in which two alkoxy groups are present on the same carbon atom within the chain. The other two bonds of the carbon atom are connected to two alkyl groups.



Ketones react with ethylene glycol in the presence of dry HCl gas to give a cyclic product known as ethylene glycol ketals.

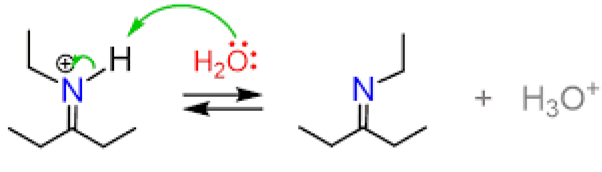


Note: The above hemiketal and hemiacetal *cannot* be isolated experimentally

(viii) Imine:

Imines are chemical compounds containing a carbon nitrogen double bond.

Imines are produced when aldehydes and ketones react with ammonia and its derivatives.

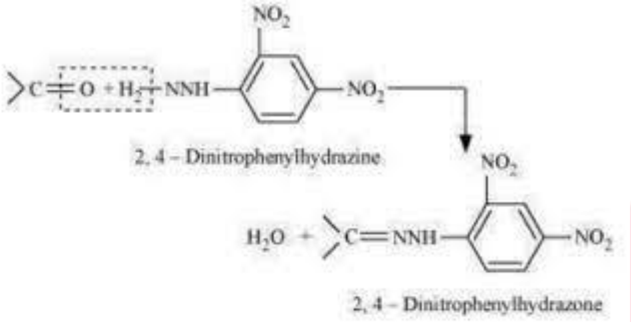


iminium ion

imine

(ix) 2, 4 - DNP - derivative:

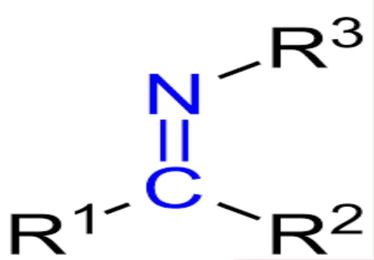
2, 4 - dinitrophenylhydragones are 2, 4 - DNP - derivatives, which are produced when aldehydes or ketones react with 2, 4 - dinitrophenylhydrazine in a weakly acidic medium.



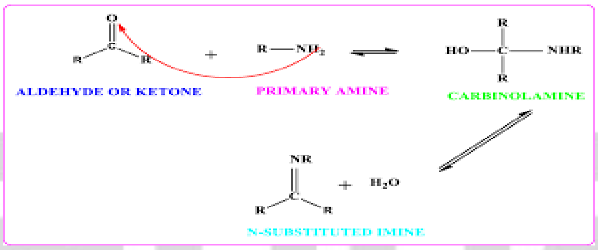
To identify and characterize aldehydes and ketones, 2, 4 - DNP derivatives are used.

(x) Schiff's base:

Schiff's base (or azomethine) is a chemical compound containing a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group-but not hydrogen. They have the general formula R1R2C = NR3. Hence, it is an imine.



It is named after a scientist, Hugo Schiff.



Aldehydes and ketones on treatment with primary aliphatic or aromatic amines in the presence of trace of an acid yields a Schiff's base.

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

- **i.)** $CH_3CH(CH_3)CH_2CH_2CHO$
- **ii.)** **CH3CH2COCH(C2H5)CH2CH2Cl**

- **iii.) CH3CH=CHCHO**
- **iv.) CH3COCH2COCH3**
- **v.) CH3CH(CH3)CH2C(CH3)2COCH3**
- **vi.) (CH3)3CCH2COOH**
- **vii.) OHCC6H4CHO-p**

Answer:

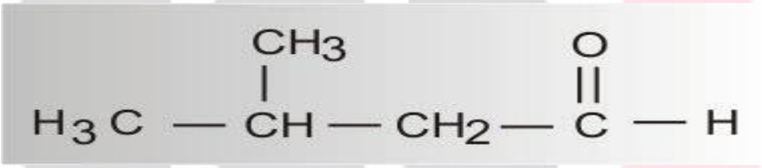
- i.) 4-Methylbutanal
- ii.) p-Nitropropiophenone
- iii.) p-Methylbenzaldehyde
- iv.) 4-Methylpent-3-en-2-one 4-chloropentan-2-one
- v.) 3-Bromo-4-phenylpentanoic acid
- vi.) p, p'-Dihydroxybenzophenone
- vii.) Hex-2-en-4-ynoic acid.

Question:3 Draw the structures of the following comp[ounds:

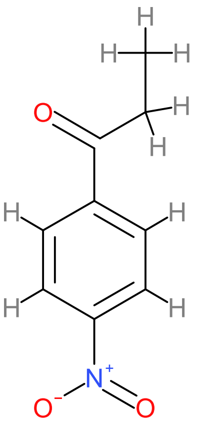
- **i.) 3 – Methylbutanal**
- **ii.) P-Nitropropiophenone**
- **iii.) p-Metylbenzaldehyde**
- **iv.) 4-Metylpent-3-en-2-one**
- **v.) 4-Chloropentan-2-one**
- **vi.) 3-Bromo-4-phenylpentanoic acid**
- **vii.) p,p'-Dihydroxybenzophenone**
- **viii.) Hex-2-en-4-ynoic acid**

Answer:

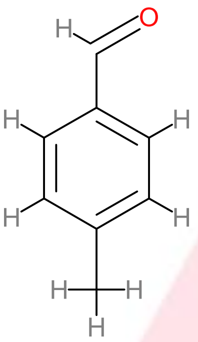
i.)



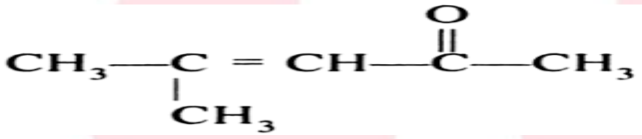
ii.)



iii.)

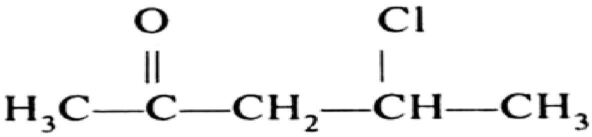


iv.)



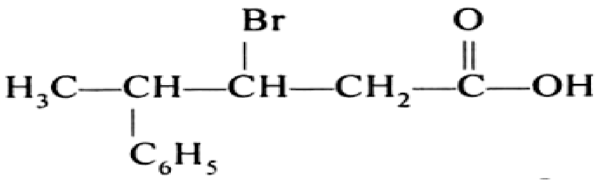
$$CH_3-\underset{CH_3}{\underset{|}{C}}=CH-\overset{O}{\overset{||}{C}}-CH_3$$

v.)

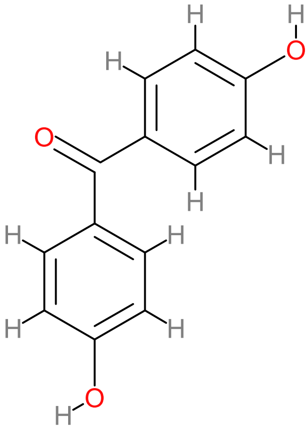


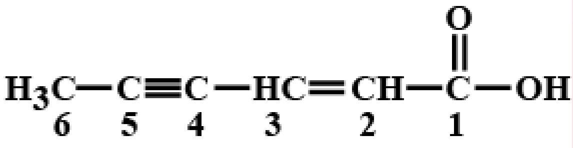
$$H_3C-\overset{O}{\overset{||}{C}}-CH_2-\overset{Cl}{\overset{|}{CH}}-CH_3$$

vi.)



$$H_3C-\underset{C_6H_5}{\underset{|}{CH}}-\overset{Br}{\overset{|}{CH}}-CH_2-\overset{O}{\overset{||}{C}}-OH$$

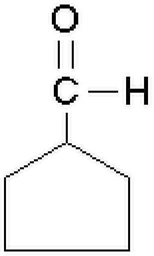
vii.) 

viii.) 

$$\underset{6}{H_3C}-\underset{5}{C}\equiv\underset{4}{C}-\underset{3}{HC}=\underset{2}{CH}-\underset{1}{\overset{\overset{\displaystyle O}{\|}}{C}}-OH$$

Question;4 Write the IUPAC names of the following ketones and aldehydes. Wherever possible give also common names.

- **i.)** **$CH3CO(CH2)4CH3$**
- **ii.)** **$CH3CH2CHBrCH2CH(CH3)CHO$**
- **iii.)** **$CH3(CH2)5CHO$**
- **iv.)** **Ph-CH=CH-CHO**
- **v.)**



- **vi.)** **PhCOPh**

Answer:

i.) IUPAC name: Heptan-2-one
Common name: Methyl n-propyl ketone

ii.) IUPAC name: 4-Bromo-2-methylhexanal
Common name: (γ-Bromo- α-methyl-caproaldehyde)

iii.) IUPAC name: Heptanal

iv.) IUPAC name: 3-phenylprop-2-enal
Common name: β-Phenolyacrolein

v.) IUPAC name: Cyclopentanecarbaldehyde

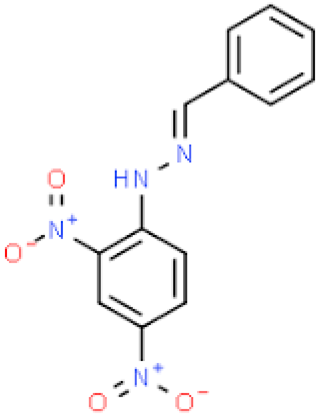
vi.) IUPAC name: Diphenylmethanone
Common name: Benzophenone

Question:5 Draw the structure of following derivatives:

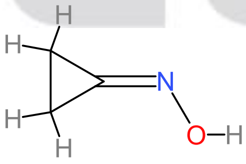
- **i.) The 2,4-dinitrophenylhydrazone of benzaldehyde**
- **ii.) Cyclopropanone oxime**
- **iii.) Acetaldehydedimethyllacetal**
- **iv.) The semicarbazone of cyclobutanone**
- **v.) The ethylene ketal of hexan-3-one**
- **vi.) The methyl hemiacetal of formaldehyde**

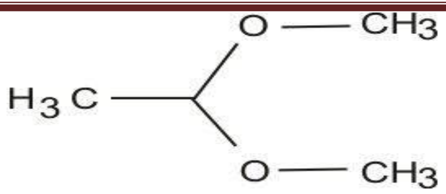
Answer:

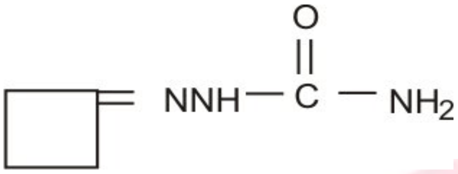
i.)

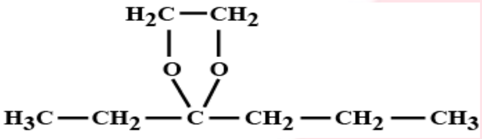


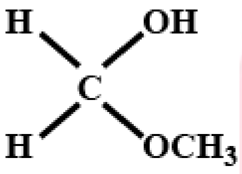
ii.)



iii.) 

iv.) 

v.) 

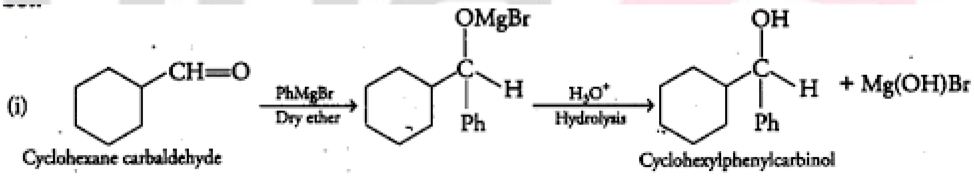
vi.) 

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

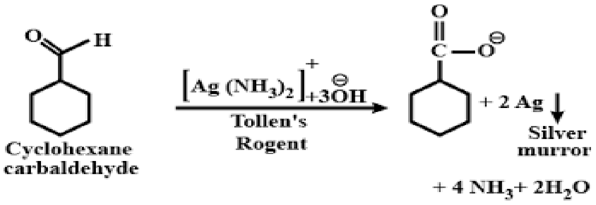
- **i.) PhMgBr and H3O$^+$**
- **ii.) Tollen's reagent**
- **iii.) Semicarbazide and weak acid**
- **iv.) Excess ethanol and acid**
- **v.) Zinc amalgam and dilute hydrochloric acid**

Answer:

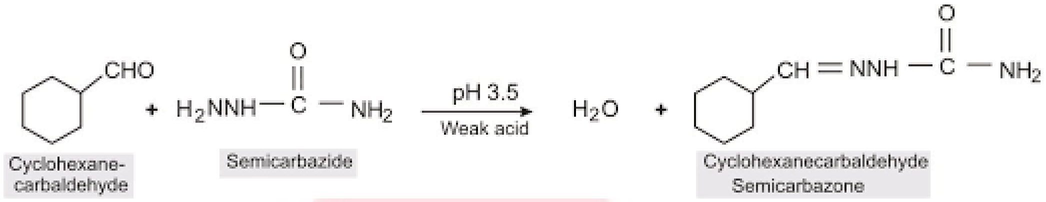
i.) The reaction of cyclohexanecarbaldehyde with PhMgBr followed by acid hydrolysis gives an alcohol.



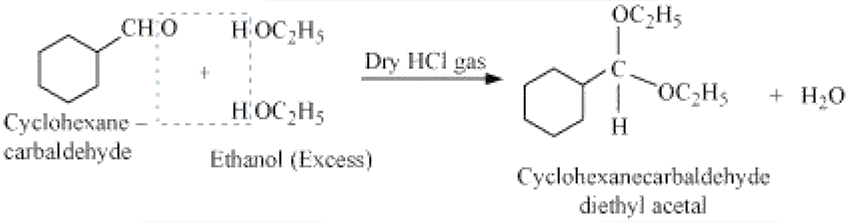
ii.) Oxidation of cyclohexane carbaldehyde with Tollen's reagent gives cyclohexane carboxylate ion.



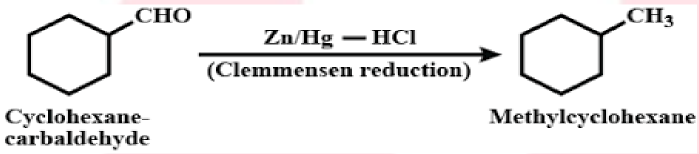
iii.) The reaction of cyclohexane carbaldehyde with semicarbazide and weak acid gives a semicarbazone.



iv.) The reaction of cyclohexane carbaldehyde with excess ethanol and acid gives an acetal.



v.)



Question: 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.

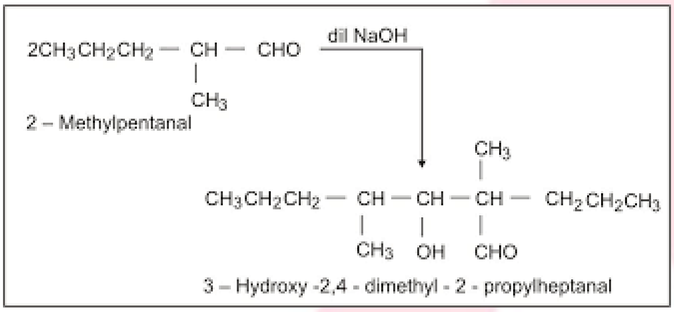
i.) Methanal
ii.) 2-Metylpantanal
iii.) Benzaldehyde
iv.) Bezophenone
v.) Cyclohexane
vi.) 1-Phenylpropanone
vii.) Phenylacetaldehyde
viii.) Butan-1-ol
ix.) 2,2-Dimethylbutanal

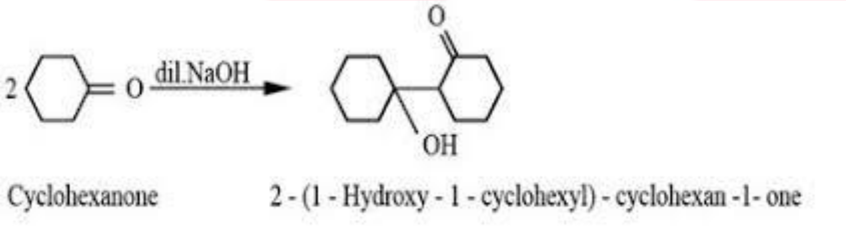
Answer:

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

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 atom and compounds viii.) Butan-1-ol is an alcohol. Hence, these compounds do not undergo either aldol condensation or cannizzaro reactions.

Aldol condensation: ii.)





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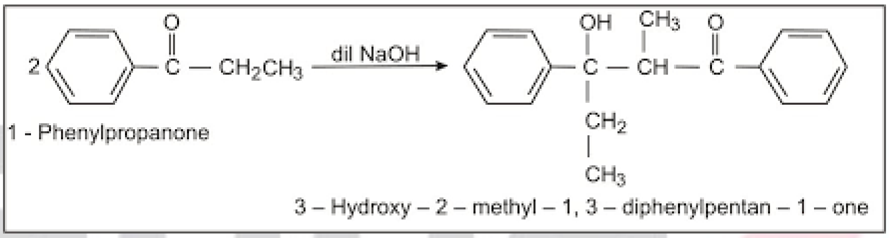

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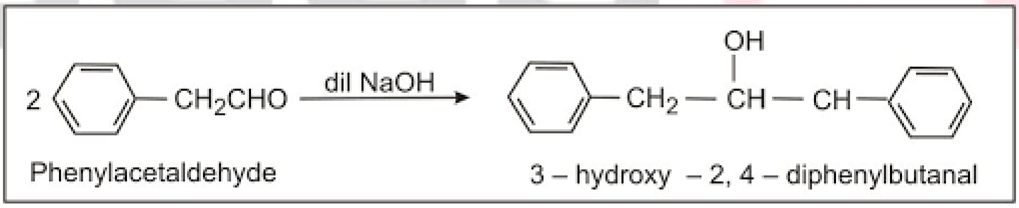
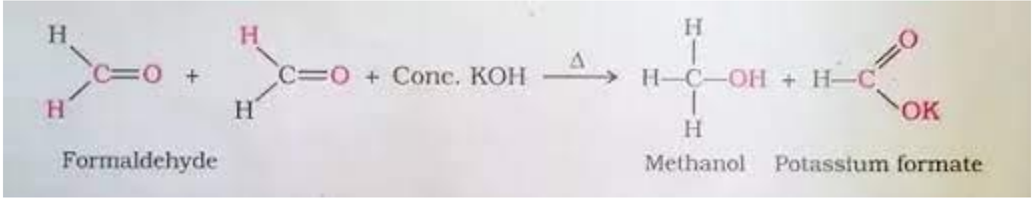
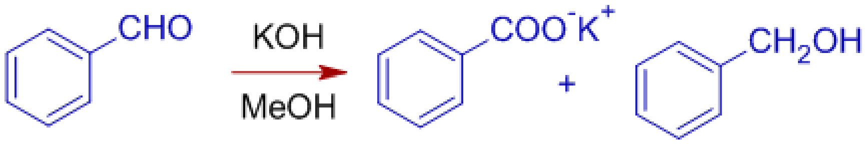


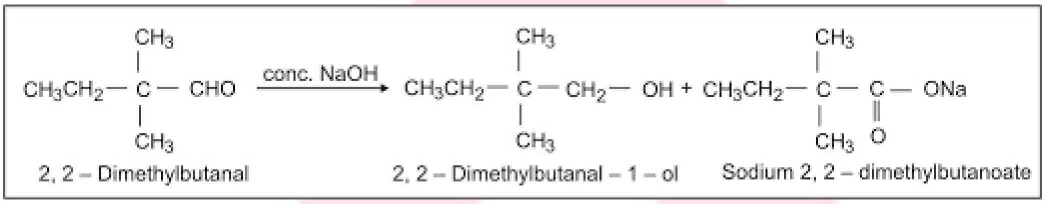
vii.

Cannizzaro reaction: (i.)





iii.



ix.

Question:8 How will you convert ethanal into the following compounds?

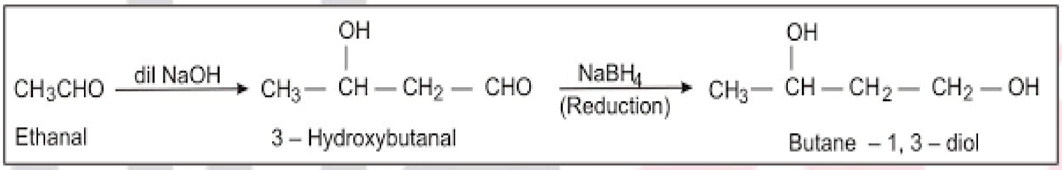
i.) Butane-1,3-diol

ii.) But-2-enal

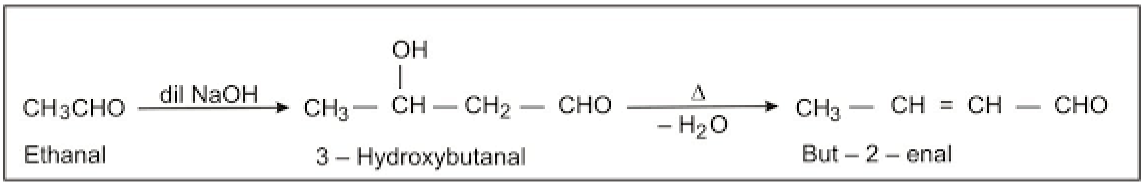
iii.) But-2-enoic acid

Answer:

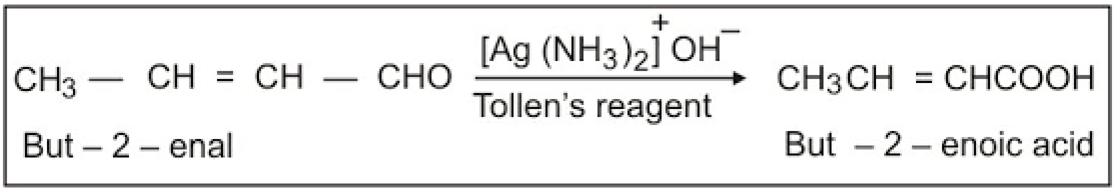
i.) On treatment with dilute alkali, ethanol produces 3-hydroxybutanal gives butane-1,3-diol on reduction.



ii.) On treatment with dilute alkali, ethanol gives 3-hydroxybutanal which on heating produces but-2-enal.



iii.) When treated with Tollen's reagent, But-2-enal produced in the above reaction produces but-2-enoic acid.



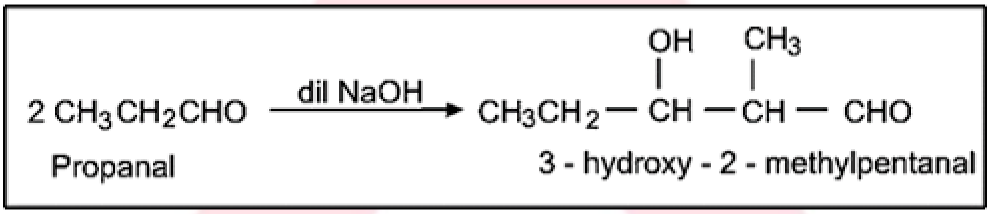
$$CH_3-CH=CH-CHO \xrightarrow[\text{Tollen's reagent}]{[Ag(NH_3)_2]^+OH^-} CH_3CH=CHCOOH$$

But – 2 – enal → But – 2 – enoic acid

Question: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.

Answer:

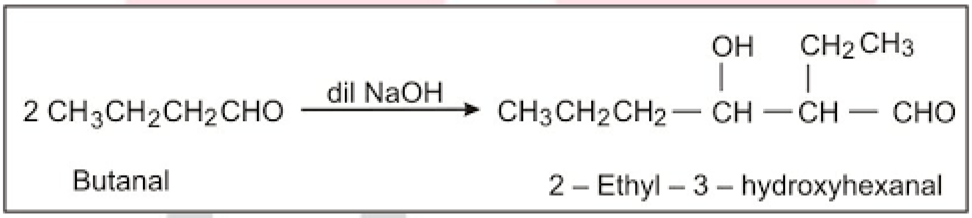
i.) Taking two molecules of propanal, one which acts as a nucleophile and the other as an electrophile.



$$2\,CH_3CH_2CHO \xrightarrow{\text{dil NaOH}} CH_3CH_2-\overset{OH}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-CHO$$

Propanal → 3 - hydroxy - 2 - methylpentanal

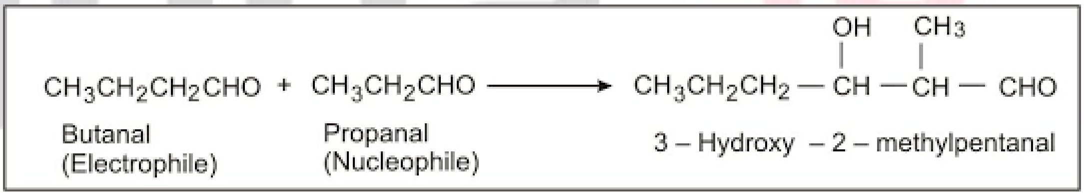
ii.) Taking two molecules of butanal, one which acts as a nucleophile and the other as an electrophile.



$$2\,CH_3CH_2CH_2CHO \xrightarrow{\text{dil NaOH}} CH_3CH_2CH_2-\overset{OH}{\overset{|}{CH}}-\overset{CH_2CH_3}{\overset{|}{CH}}-CHO$$

Butanal → 2 – Ethyl – 3 – hydroxyhexanal

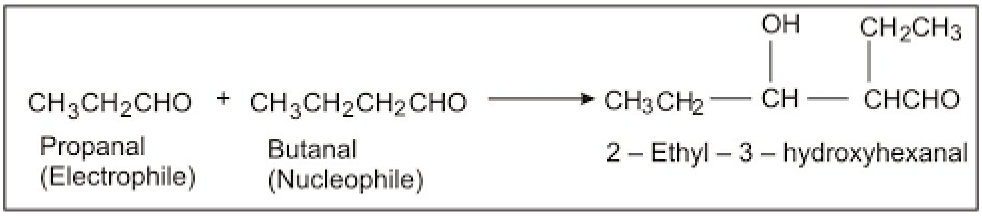
iii.) Taking one molecule each of propanal and butanal in which propanal acts a nucleophile and butane act as an electrophile.



$$CH_3CH_2CH_2CHO + CH_3CH_2CHO \longrightarrow CH_3CH_2CH_2-\overset{OH}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-CHO$$

Butanal (Electrophile) + Propanal (Nucleophile) → 3 – Hydroxy – 2 – methylpentanal

iv.) Taking one molecule each of propanal and butanal in which propanal acts an electrophile and butane act as a nucleophile.

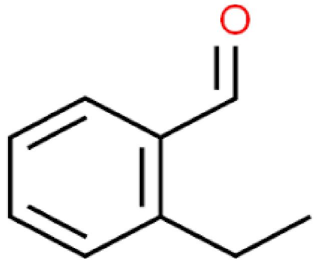


$$CH_3CH_2CHO + CH_3CH_2CH_2CHO \longrightarrow CH_3CH_2-\overset{OH}{\overset{|}{CH}}-\overset{CH_2CH_3}{\overset{|}{CH}}CHO$$

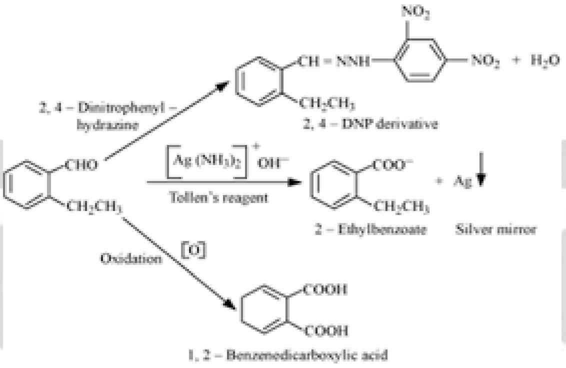
Question:10 An organic compound with the molecular formula C9H10O form 2,4-DNP derivative, reduces Tollen's reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid. Identify the compound.

Answer:

It is given that the compound forms 2,4-DNP derivatives and reduces Tollen's reagent. Therefore, the given compound must be an aldehyde. Again, the compound undergoes cannizzaro reaction and on oxidation gives 1,2-benzenedicarboxylic acid. Therefore, the –CHO group is directly attached to a benzene a ring and this benzaldehyde is ortho-substituted. Hence, the compound is 2-ethylbenzaldehyde.



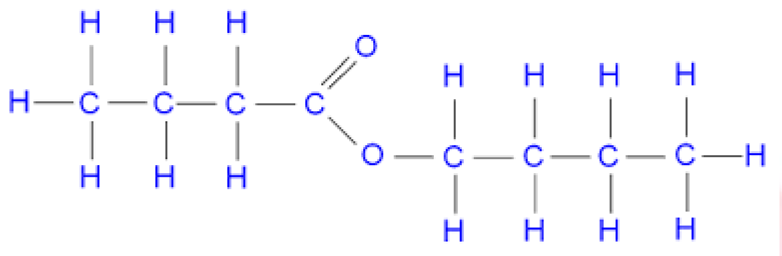
The given reactions can be explained by the following equations.



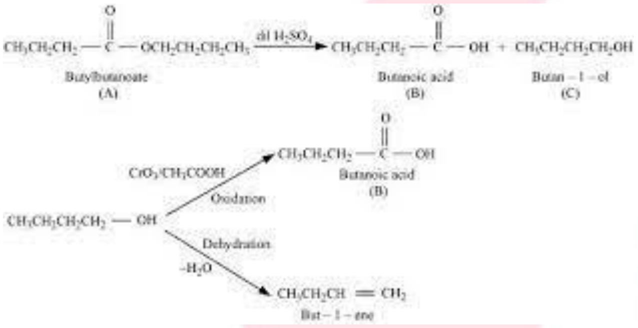
Question:11 An organic compound (A) (molecular formula C8H16O2) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B). (C) on dehydration gives but-1-en. Write equation for the reaction involved.

Answer:

An organic compound A with molecular formula C8H16O2 gives a carboxylic acid and an alcohol on hydrolysis with dilute sulphuric acid. Thus, compound A must be an ester. Further, alcohol C gives acid B on oxidation with chromic acid. Thus, B and C must contain equal number of carbon atoms. Since compound A contains a total of 8 carbon atoms, each of B and C contain 4 carbon atoms. Again, on dehydration, alcohol C gives but-1-ene. Therefore, C is straight chain and hence, it is butan-1-ol. On oxidation, Butan-1-ol gives butanoic acid. Hence, acid B is butanoic acid. Hence, the ester with molecular formula C8H16O2 is butylbutanoate.



All the given reactions can be explained by the following equations.



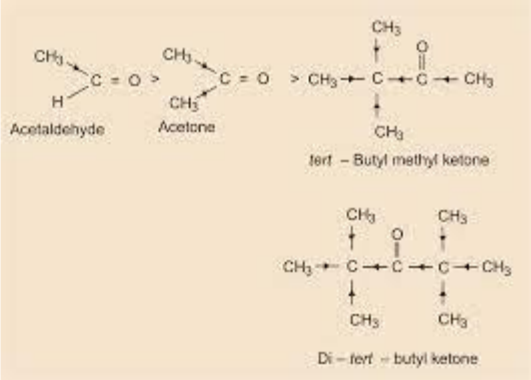
Question:12 Arrange the following compounds in increasing order of the their property indicated:

- **i.) Acetaldehyde, Acetone, Di-tert-butyl ketone, Methyl tert-butyl ketone(reactivity towards HCN)**
- **ii.) CH3CH2CH(Br)COOHJ, CH3CH(Br)CH2COOH, (CH3)2CHCOOH, CH3CH2CH2COOH (acid strength)**
- **iii.) Benzoic acid, 4-Nitrobenzoic acid, 3,4-Dinitrobenzoic acid, 4-Methoxybenzoic acid (acid strength)**

Answer:

(i) When HCN reacts with a compound, the attacking species is a nucleophile, CN - . Therefore, as the negative charge on the compound increases, its reactivity with HCN decreases. In the given compounds, the +I effect increases as shown below. It can be observed that steric hindrance also increases in the same

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) After losing a proton, carboxylic acids gain a negative charge as shown:

R-COOH →R-COO^- + H^+

Now, any group that will help stabilise the negative charge will increase the stability of the carboxyl ion and as a result, will increase the strength of the acid. Thus, groups having +I effect will decrease the strength of the acids and groups having - I effect will increase the strength of the acids. In the given compounds, - CH3group has +I effect and Br - group has - I effect. Thus, acids containing Br - are stronger.

Now, the +I effect of isopropyl group is more than that of n-propyl group. Hence, (CH3)2CHCOOH is a weaker acid than CH3CH2CH2COOH.

Also, the - I effect grows weaker as distance increases. Hence, CH3CH(Br)CH2COOH is a weaker acid than CH3CH2CH(Br)COOH.

Hence, the strengths of the given acids increase as:

(CH3)2CHCOOH < CH3CH2CH2COOH < CH3CH(Br)CH2COOH < CH3CH2CH(Br)COOH

(iii) As we have seen in the previous case, electron-donating groups decrease the strengths of acids, while electron-withdrawing groups increase the strengths of acids. As methoxy group is an electron-donating group, 4-methoxybenzoic acid is a weaker acid than benzoic acid. Nitro group is an electron-withdrawing group and will increase the strengths of acids. As 3,4-dinitrobenzoic acid contains two nitro groups, it is a slightly stronger acid 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

Question:13 Give simple chemical tests to distinguish b/w the following pairs of compounds.

i.) Propanal and propanone

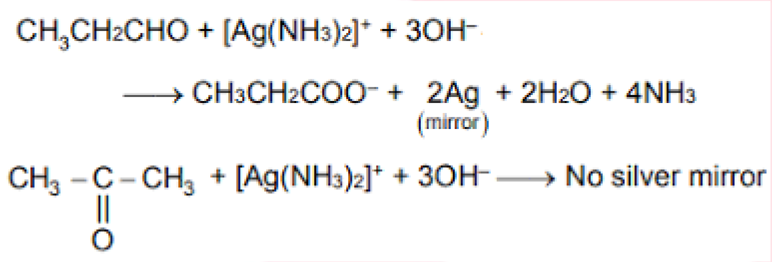
ii.) **Acetophenone and Benzophenone**
iii.) **Phenol and Benzoic acid**
iv.) **Benzoic acid and Ethyl benzoate**
v.) **Pentan-2-one and Pentan-3-one**
vi.) **Benzaldehyde and Acetophenone**
vii.) **Ethanol and Propanal**

Answer:

(i) Propanal and propanone can be distinguished by the following tests.

(a) Tollen's test

Propanal is an aldehyde. Thus, it reduces Tollen's reagent. But, propanone being a ketone does not reduce Tollen's reagent.



$$CH_3CH_2CHO + [Ag(NH_3)_2]^+ + 3OH^- \longrightarrow CH_3CH_2COO^- + \underset{(mirror)}{2Ag} + 2H_2O + 4NH_3$$

$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + [Ag(NH_3)_2]^+ + 3OH^- \longrightarrow \text{No silver mirror}$$

(b) Fehling's test

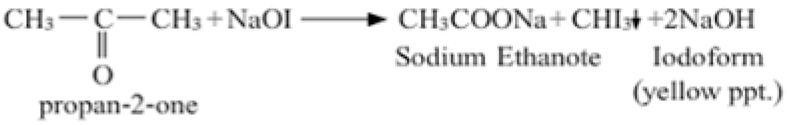
Aldehydes respond to Fehling's test, but ketones do not.

Propanal being an aldehyde reduces Fehling's solution to a red-brown precipitate of Cu2O, but propanone being a ketone does not.

$$\underset{\text{Methanal}}{H-CHO} + \underset{\substack{\text{Fehling's solution}\\ \text{(Blue colour)}}}{2\,Cu\,(OH)_2 + NaOH} \longrightarrow HCOONa + \underset{\substack{\text{Cuprous oxide}\\ \text{(Red ppt.)}}}{Cu_2O} + 3H_2O$$

(c) Iodoform test:

Aldehydes and ketones having at least one methyl group linked to the carbonyl carbon atom respond to iodoform test. They are oxidized by sodium hypoiodite (NaOI) to give iodoforms. Propanone being a methyl ketone responds to this test, but propanal does not.



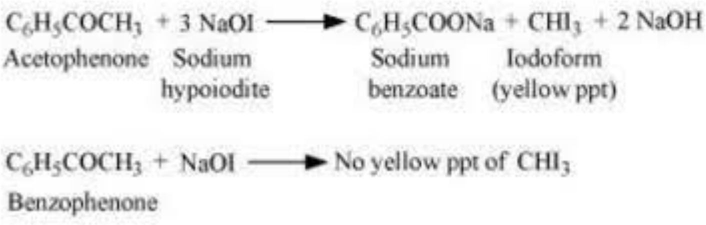
$$\underset{\text{propan-2-one}}{CH_3-\underset{\underset{O}{\|}}{C}-CH_3} + NaOI \longrightarrow \underset{\text{Sodium Ethanote}}{CH_3COONa} + \underset{\substack{\text{Iodoform}\\ \text{(yellow ppt.)}}}{CHI_3\downarrow} + 2NaOH$$

$$\underset{\text{propanal}}{CH_3-CH_2-CHO} + NaOI \longrightarrow \text{No yellow ppt-of Iodoform}$$

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

Iodoform test:

Methyl ketones are oxidized by sodium hypoiodite to give yellow ppt. of iodoform. Acetophenone being a methyl ketone responds to this test, but benzophenone does not.



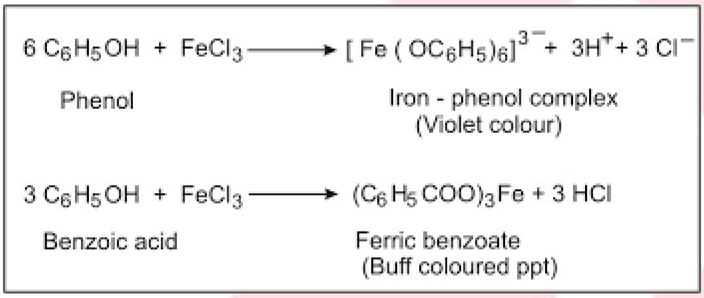
$$\underset{\text{Acetophenone}}{C_6H_5COCH_3} + \underset{\text{Sodium hypoiodite}}{3\,NaOI} \longrightarrow \underset{\text{Sodium benzoate}}{C_6H_5COONa} + \underset{\text{Iodoform (yellow ppt)}}{CHI_3} + 2\,NaOH$$

$$\underset{\text{Benzophenone}}{C_6H_5COCH_3} + NaOI \longrightarrow \text{No yellow ppt of } CHI_3$$

(iii) Phenol and benzoic acid can be distinguished by ferric chloride test.

Ferric chloride test:

Phenol reacts with neutral FeCl3 to form an iron-phenol complex giving violet colouration.



$$\underset{\text{Phenol}}{6\,C_6H_5OH} + FeCl_3 \longrightarrow \underset{\substack{\text{Iron - phenol complex}\\ \text{(Violet colour)}}}{[Fe(OC_6H_5)_6]^{3-}} + 3H^+ + 3\,Cl^-$$

$$\underset{\text{Benzoic acid}}{3\,C_6H_5OH} + FeCl_3 \longrightarrow \underset{\substack{\text{Ferric benzoate}\\ \text{(Buff coloured ppt)}}}{(C_6H_5COO)_3Fe} + 3\,HCl$$

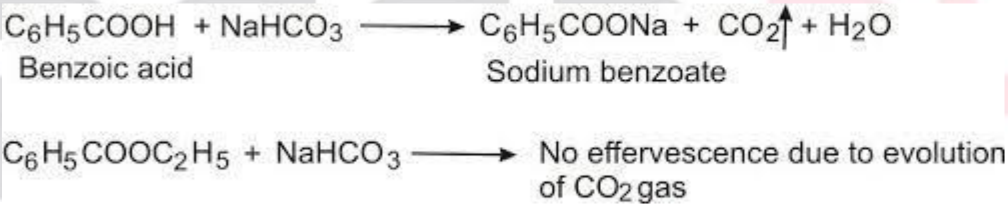
But benzoic acid reacts with neutral FeCl3 to give a buff coloured ppt. of ferric benzoate.

(iv) Benzoic acid and Ethyl benzoate can be distinguished by sodium bicarbonate test.

Sodium bicarbonate test:

Acids react with NaHCO3 to produce brisk effervescence due to the evolution of CO2 gas.

Benzoic acid being an acid responds to this test, but ethylbenzoate does not.



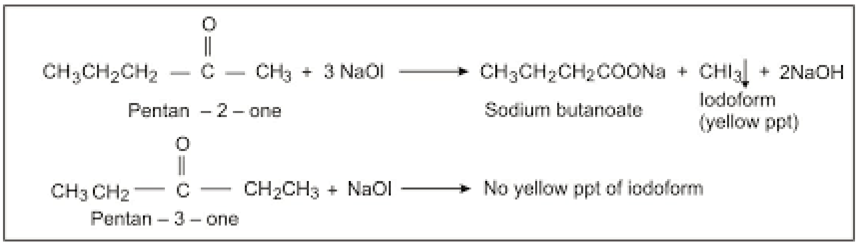
$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + NaHCO_3 \longrightarrow \underset{\text{Sodium benzoate}}{C_6H_5COONa} + CO_2\uparrow + H_2O$$

$$C_6H_5COOC_2H_5 + NaHCO_3 \longrightarrow \text{No effervescence due to evolution of } CO_2 \text{ gas}$$

(v) Pentan-2-one and pentan-3-one can be distinguished by iodoform test.

Iodoform test:

Pentan-2-one is a methyl ketone. Thus, it responds to this test. But pentan-3-one not being a methyl ketone does not respond to this test.



$$\underset{\text{Pentan}-2-\text{one}}{CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-CH_3} + 3\,NaOI \longrightarrow \underset{\text{Sodium butanoate}}{CH_3CH_2CH_2COONa} + \underset{\substack{\text{Iodoform}\\ \text{(yellow ppt)}}}{CHI_3\downarrow} + 2NaOH$$

$$\underset{\text{Pentan}-3-\text{one}}{CH_3CH_2-\overset{\overset{O}{\|}}{C}-CH_2CH_3} + NaOI \longrightarrow \text{No yellow ppt of iodoform}$$

(vi) Benzaldehyde and acetophenone can be distinguished by the following tests.

(a) Tollen's Test

Aldehydes respond to Tollen's test. Benzaldehyde being an aldehyde reduces Tollen's reagent to give a red-brown precipitate of Cu2O, but acetophenone being a ketone does not.

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Tollen's reagent}}{[Ag(NH_3)_2]^+ + 3\,OH^-} \longrightarrow \underset{\text{Benzoate ion}}{C_6H_5COO^-} + \underset{\text{Silver mirror}}{Ag\downarrow} + 4NH_3 + 2H_2O$$

(b) Iodoform test

Acetophenone being a methyl ketone undergoes oxidation by sodium hypoiodite (NaOI) to give a yellow ppt. of iodoform. But benzaldehyde does not respond to this test.

$$\underset{\text{Acetophenone}}{C_6H_5COCH_3} + 3\,NaOI \longrightarrow \underset{\text{Sodium benzoate}}{C_6H_5COONa} + \underset{\substack{\text{Iodoform}\\ \text{(yellow ppt)}}}{CHI_3} + 2\,NaOH$$

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

Iodoform test

Aldehydes and ketones having at least one methyl group linked to the carbonyl carbon atom responds to the iodoform test. Ethanal having one methyl group linked to the carbonyl carbon atom responds to this test. But propanal does not have a methyl group linked to the carbonyl carbon atom and thus, it does not respond to

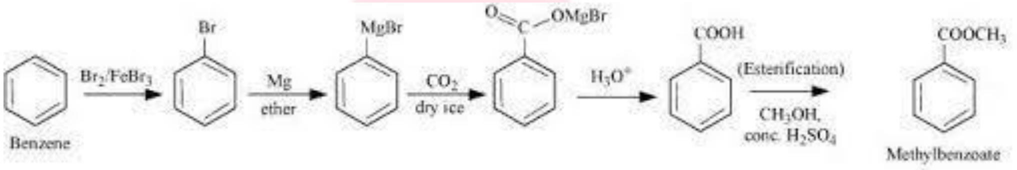
$$\underset{\text{Ethanal}}{CH_3CHO} + 3\,NaOI \longrightarrow \underset{\substack{\text{Sodium}\\ \text{methanoate}}}{HCOONa} + \underset{\substack{\text{Iodoform}\\ \text{(yellow ppt)}}}{CH_3} + 2\,NaOH$$

Question: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

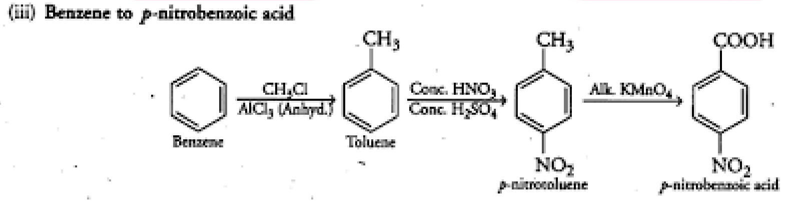
i.) **Methyl benzoate**
ii.) **M-Nitrobenzoic acid**
iii.) **p-nitrobenzoic acid**
iv.) **p-Nitrobenzaldehyde.**

Answer:

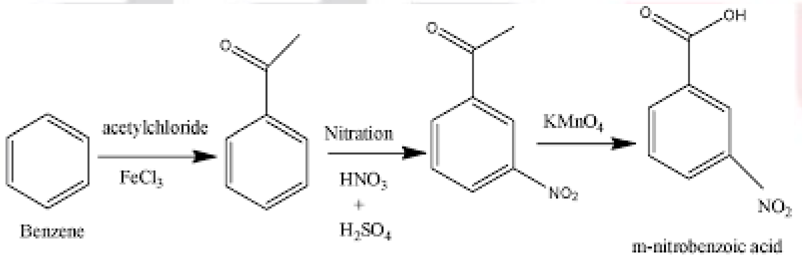
i.) Methyl benzoate is the ester of benzene. It can easily be prepared after preparing benzoic acid. So, we can form benzoic acid by Friedel Craft alkylation and then form an ester, we can just oxidize the formed acid to get methyl benzoate. The process is called esterification.



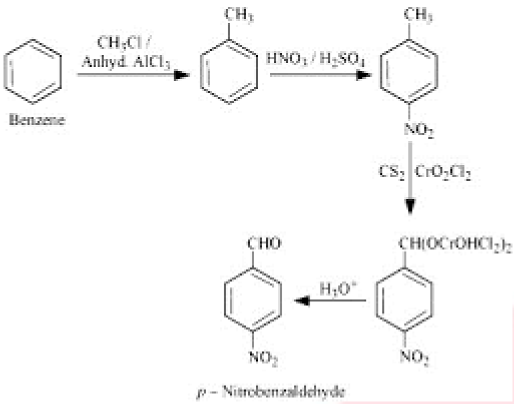
ii.) One of the many possible ways to prepare m-nitrobenzoic acid is by first forming acetophenone by Friedel Craft acylation and then form nitroacetophenone by nitration of the compound. Oxidation of the compound gives us our desired product.



iii.) To form p-nitrobenzoic acid, first, perform Friedel Craft alkylation to get toluene and then form p-nitrotoluene by nitration. Minor products can be eliminated by filtration. Oxidation of the compound gives us p-nitrobenzoic acid.



iv.) p-Nitrobenzaldehyde has been prepared from p-nitrotoluene by treatment with isoamyl nitrite in the presence of sodium methoxide or by oxidation with chromyl chloride, cerium dioxide, or chromium trioxide in the presence of acetic anhydride.

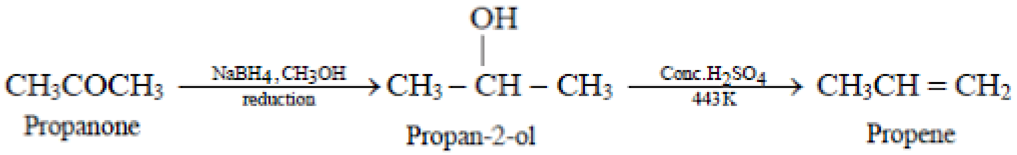


Quiestion:15 How will you bring about following conversion in not more than two steps?

- **i.) Propanone to Propene**
- **ii.) Benzoic acid to Benzaldehyde**
- **iii.) Ethanol to 3-Hydroxybutanal**
- **iv.) Benzene to m-Nitroacetophenone**
- **v.) Benzaldehyde to Benzophenone**
- **vi.) Bromobenzene to 1-Phenyletahnol**
- **vii.) Benzaldehyde to 3-Phenylpropan-1-ol**
- **viii.) Benzaldehyde to α-Hydroxyphenylacetic acid**
- **ix.) Benzoic acid m-Nitrobenzyl alcohol**

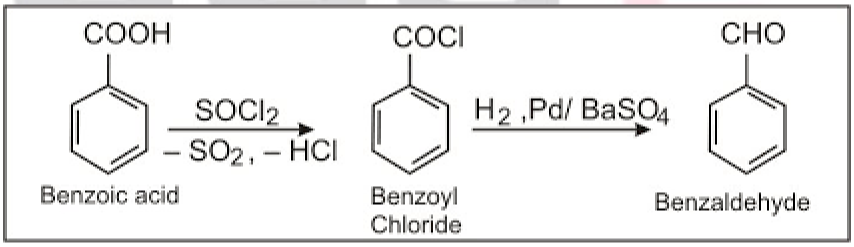
Answer:

i.)

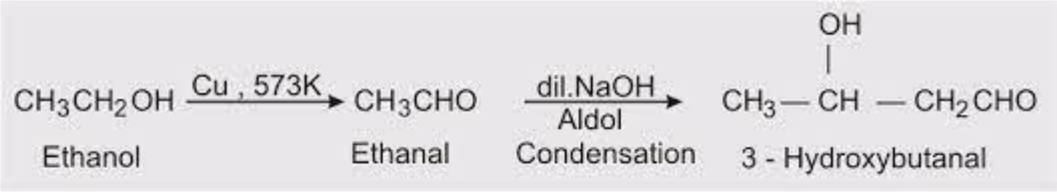


$$\underset{\text{Propanone}}{CH_3COCH_3} \xrightarrow[\text{reduction}]{NaBH_4, CH_3OH} \underset{\text{Propan-2-ol}}{CH_3-\overset{OH}{\overset{|}{CH}}-CH_3} \xrightarrow[443K]{Conc.H_2SO_4} \underset{\text{Propene}}{CH_3CH=CH_2}$$

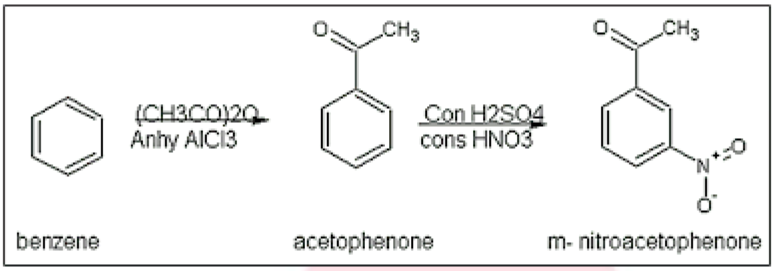
ii.)



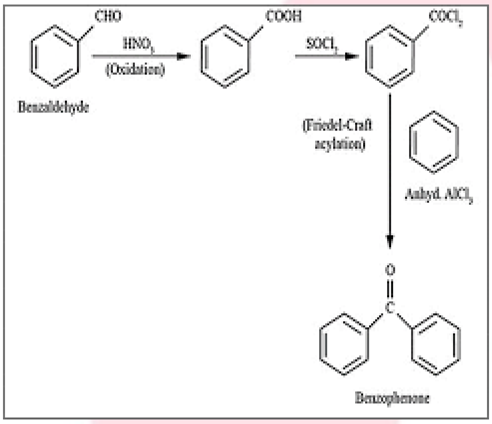
iii.)



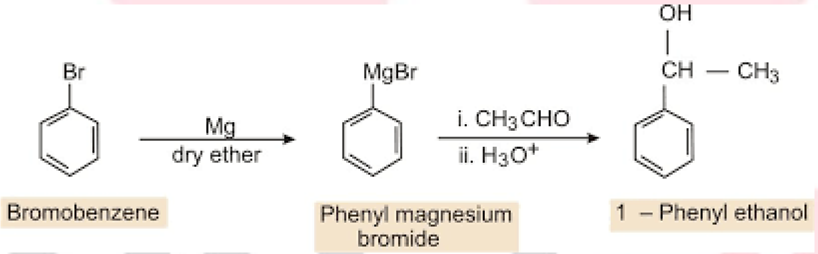
iv.)



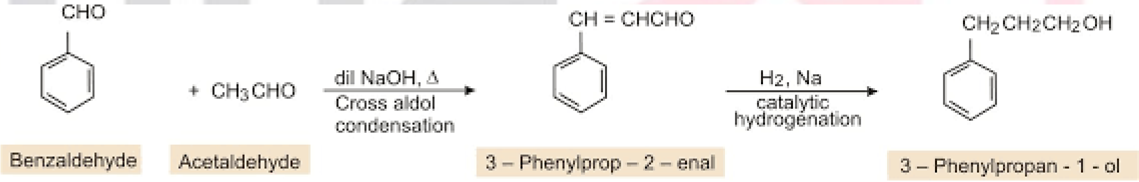
v.)



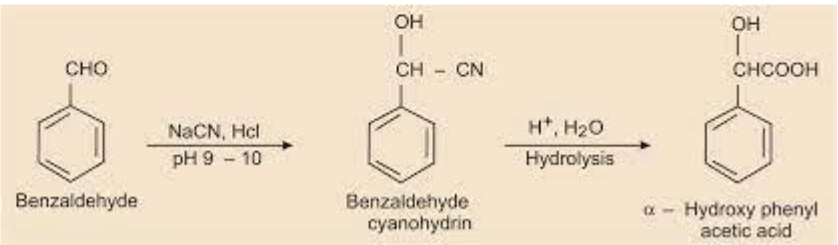
vi.)



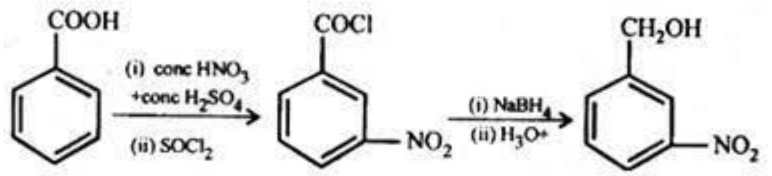
vii.)



viii.)



ix.)



Question:16 Describe the following:

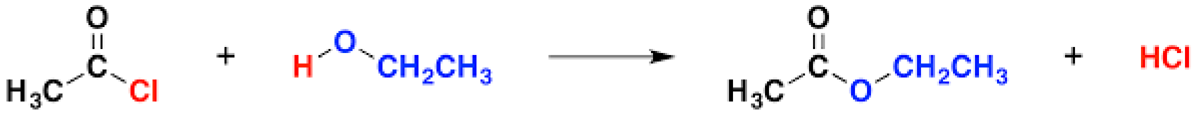
- **i.) Acetylation**
- **ii.) Cannizzaro reaction**
- **iii.) Cross aldol aondensation**
- **iv.) Decarboxylation**

Answer:

i.) Acetylation:

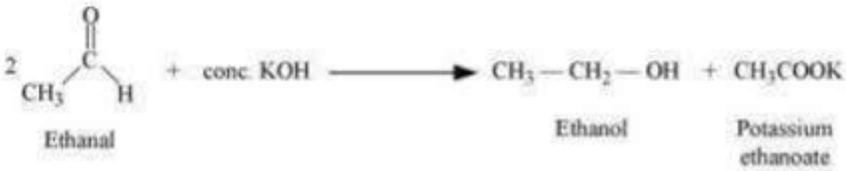
The introduction of an acetyl functional group into an organic compounds is known as acetylation. It is usually carried out in the presence of a base such as pyridine, dimethylaniline, etc. This process involves the substitution of an acetyl group for an active hydrogen atom. Acetyl chloride and acetic anhydride are commonly used as acetylating agents.

For example, acetylation of ethanol produces ethyl acetate.



ii.) Cannizzaro reaction:

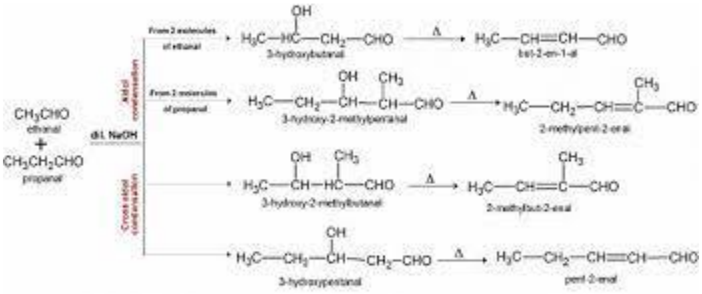
The self oxidation – reduction reaction of aldehydes having no α – hydrogen's on treatment with concentrated alkalis is known as the cannizzaro reaction. In this reaction, two molecules of aldehydes participates where one is reduced to alcohol and the other is oxidised to carboxylic acid. For example, when ethanol is treated with concentrated potassium hydroxide, ethanol and potassium ethanoate are produced.



iii.) Cross – aldol condensation:

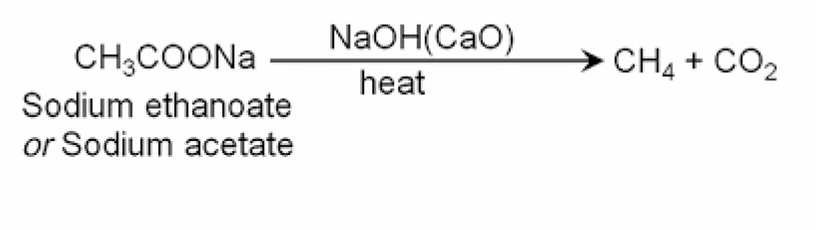
When aldol condensation is carried out between two different aldehydes, or two different ketones, or an aldehyde and a ketones, then the reaction is called a cross – aldol condensation. If both the reactants contain α – hydrogen, four compounds are obtained as products.

For example, ethanol and propanal react to give four products.



iv.) Decarboxylation:

Decarboxylation refers to the reaction in which carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with soda – lime.



$$CH_3COONa \xrightarrow[\text{heat}]{NaOH(CaO)} CH_4 + CO_2$$

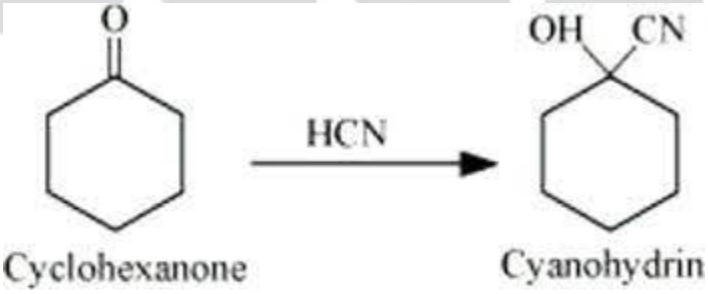
Decarboxylation also takes place when aqueous solutions of alkali metal salts of carboxylic acids are electrolyzed. This electrolytic process is known as Kolbe's electrolysis.

Question:17 Give plausible explanation for each of the following:

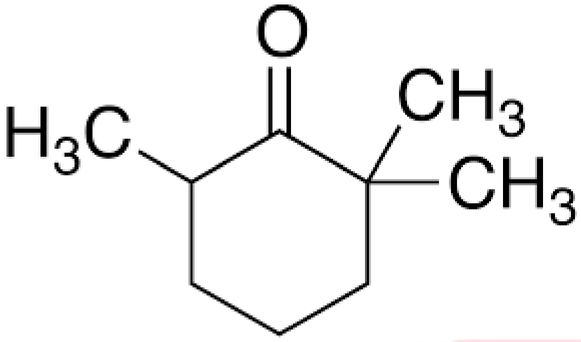
- **i.) Cyclohexanone forms cyanohydrin in good yield nut 2,2,6-trimethylcyclohexanone does not.**
- **ii.) There are two –NH2 groups in semicarbazide. However, onl;y one is involved in the formation of semicarbazones.**
- **iii.) During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as soon as it is formed.**

Answer:

i.) Cyclohexanones form cyanohydrins according to the following equation.

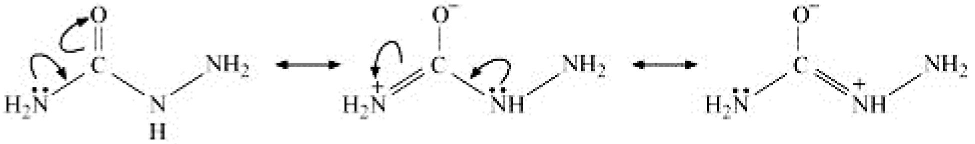


In this case, the nucleophile CN^- cab easily attack without any steric hindrance. However, in the case of 2, 2, 6- trimethylcyclohexanone, methyl groups at α-positions offer steric hindrance and a s result, CN^- cannot attack effectively.



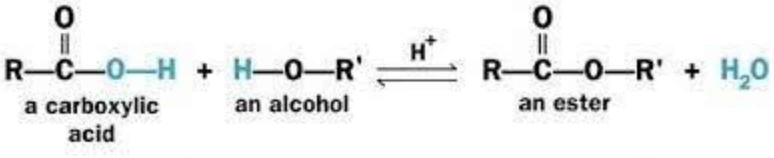
For this reason, it does not form a cyanohydrin.

ii.) Semicarbazide undergoes resonance involving only one of the two –NH2 groups, which is attached directly to the carbonyl – carbon atom.



Therefore, the electron density on –NH2 group involved in the resonance also decreases. As a result, it cannot act as a nucleophile. Since, the other –NH2 group is not involved in resonance; it can act as nucleophile and can attack carbonyl – carbon atoms of aldehydes and ketones tom produce semicarbazones.

iii.) Ester along with water is formed reversibly from a carboxylic acid and an alcohol in presence of an acid.



$$R{-}\overset{\overset{\large O}{\|}}{C}{-}O{-}H + H{-}O{-}R' \overset{H^+}{\rightleftharpoons} R{-}\overset{\overset{\large O}{\|}}{C}{-}O{-}R' + H_2O$$

(Where R and R' are general hydrocarbon groups)

If either water or ester is not removed as soon as it is formed, then it reacts to give back the reactants as the reaction is reversible. Therefore, to shift the equilibrium in the forward direction i.e., to produce more ester, either of the two should be removed.

Question: 18 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 tollen's reagent nut forms an addition compound with sodium hydroigensulphite and give positive idoform test. On vigorous oxidation it gives ethanoic and propanoic acid. Write the possible structure of the compound.

Answer:

% of carbon = 69.77 %

% of hydrogen = 11.63 %

% of oxygen = {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:

= 5.81:11.63:1.16

= 5:10:1

Therefore, the empirical formula of the compound is C5H10O. Now, the empirical formula mass of the compound can be given as:

5 × 12 + 10 ×1 + 1 × 16

= 86

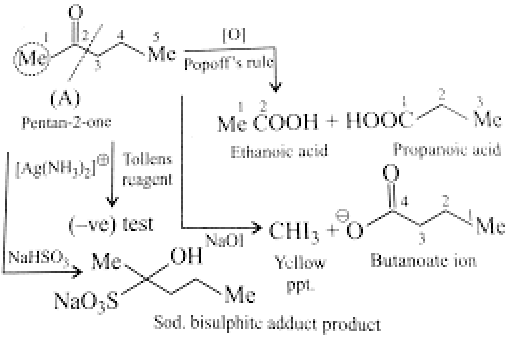
Molecular mass of the compound = 86

Therefore, the molecular formula of the compound is given by C5H10O.

Since the given compound does not reduce Tollen's reagent, it is not an aldehyde. Again, the compound forms sodium hydrogen sulphate addition products and gives a positive iodoform test. Since the compound is not an aldehyde, it must be a methyl ketone.

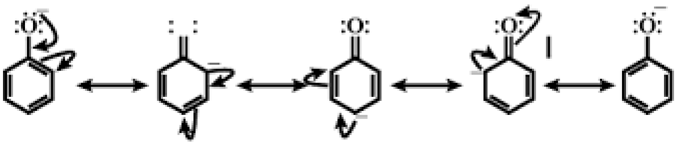
The given compound also gives a mixture of ethanoic acid and propanoic acid.

Hence, the given compound is Pentan-2-one



Question:19 Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Why?

Answer:



i.) Phenoxide ion has non-equivalent resonance structures in which the negative charge is at the less electronegative carbon atom whereas in case of carboxylate ion both the resonating structures are equivalent.

ii.) The negative charge is delocalised over two electronegative oxygen atoms in carboxylate ion whereas in phenoxide ion the negative charge less effectively delocalises over one oxygen atom and less electronegative carbon atoms. So the carboxylate ion is more resonance stabilised than phenoxide ion. Thus, the release of proton from carboxylic acid is much easier than from phenol. Hence, carboxylic acid is a stronger acid than phenol**.**