DAY THIRTY

Organic Compounds Containing Oxygen

Learning & Revision for the Day

- Alcohols
- Phenol
- Ethers
- Aldehydes and Ketones
- Carboxylic Acids

Alcohols and phenols are formed when a hydrogen atom from a hydrocarbon, aliphatic and aromatic respectively, is replaced by —OH group. The substitution of a hydrogen atom from a hydrocarbon by an alkoxy or aryloxy group (R—O / Ar—O) gives **ethers**. In **carboxylic acids** and their derivatives (esters, anhydrides), the carbonyl group is bonded to oxygen. In compounds such as amides and acyl halides, carbon is attached to —$CONH_2$ and —OX groups respectively.

Alcohols

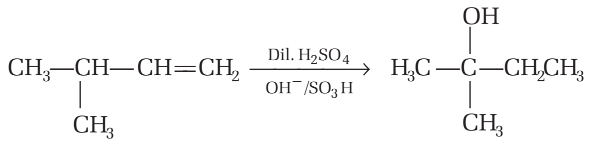
An alcohol contains one or more hydroxyl group(s) (—OH) directly attached to carbon atom(s) of an aliphatic system (like CH_3OH).

Preparation

These can be prepared by the following methods:

1. From Alkenes

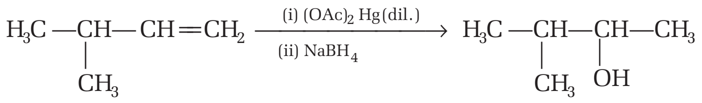
- Alkenes react with water in the presence of acid as catalyst to form alcohols by **acid catalysed hydration**.



$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH=CH_2 \xrightarrow[OH^-/SO_3H]{\text{Dil. } H_2SO_4} H_3C-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2CH_3$$

In this reaction, intermediate carbocation is formed and rearrange, therefore —OH gets attached at maximum degree of carbon.

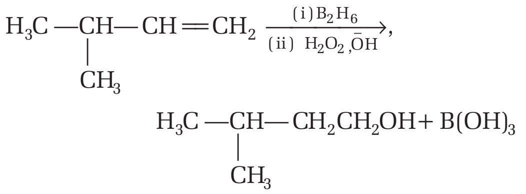
- **In oxymercuration demercuration reaction**, mercury (II) acetate reacts with alkene in presence of water to give β-hydroxy alkyl mercury (II) acetate which is treated directly with $NaBH_4$ to alcohol.



$$H_3C-\underset{\underset{CH_3}{|}}{CH}-CH=CH_2 \xrightarrow[\text{(ii) } NaBH_4]{\text{(i) } (OAc)_2\,Hg(\text{dil.})} H_3C-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-CH_3$$

Alcohol is formed according to Markownikoff's rule.

- Diborane reacts with alkenes to give trialkyl boranes as addition product. This is oxidised to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide. This reaction is called **hydroboration oxidation reaction.**



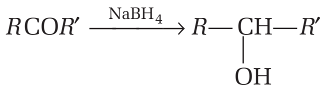
$$H_3C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH=CH_2 \xrightarrow[\text{(ii) } H_2O_2,\bar{O}H]{\text{(i) } B_2H_6}, \quad H_3C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2CH_2OH + B(OH)_3$$

The alcohol so formed looks as if it has been formed by the addition of water to the alkene in a way opposite to the Markownikoff's rule.

2. By Reduction of Carbonyl Compounds

Aldehydes on reduction give primary alcohols and ketones give secondary alcohols in the presence of weak reducing agent ($NaBH_4$) by addition of hydrogen in the presence of catalysts such as platinum, palladium or nickel.

$$RCHO + H_2 \xrightarrow{Pd} RCH_2OH$$



$$RCOR' \xrightarrow{NaBH_4} R-\underset{\displaystyle OH}{\underset{|}{CH}}-R'$$

3. By Reduction of Acid and Esters

Carboxylic acids and esters on reduction, in the presence of strong reducing agent ($LiAlH_4$), give primary alcohols.

$$RCOOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} RCH_2-OH$$

$$CH_3COOCH_2-CH_2-CH_3 \xrightarrow[+4H]{LiAlH_4} CH_3CH_2OH + CH_3CH_2CH_2OH$$

4. Hydrolysis of Haloalkanes

With aqueous sodium or potassium hydroxide, or carbonate or moist silver oxide results in the formation of alcohols.

$$CH_3-CH_2Br + NaOH(aq) \longrightarrow CH_3-CH_2-OH \ + NaBr$$

5. Aliphatic Primary Amines

Aliphatic primary amines react with nitrous acid to give primary alcohol.

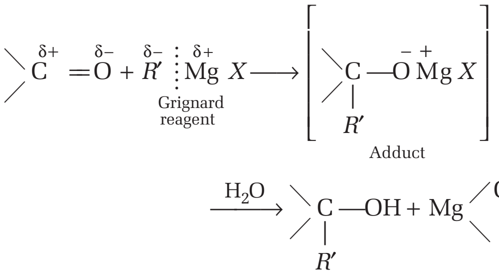
$$NaNO_2 + HCl \xrightarrow{0-5°C} HNO_2 + NaCl$$

$$R-NH_2 + HNO_2 \xrightarrow{0-5°C} R-OH + N_2\uparrow + H_2O$$

6. From Grignard Reagent

Grignard reagent ($R'MgX$) on reaction with aldehydes/ketones followed by hydrolysis gives alcohols.

If the reacting aldehyde is formaldehyde, primary alcohol ($-CH_2OH$) is obtained while other aldehydes give secondary alcohols ($-CHOH$) with Grignard reagent. Ketones give tertiary alcohols with Grignard reagent.



$$\overset{\delta+}{C}=\overset{\delta-}{O} + \overset{\delta-}{R'}\vdots\overset{\delta+}{Mg}X \longrightarrow \left[\underset{\displaystyle R'}{\underset{|}{C}}-\overset{-}{O}\overset{+}{Mg}X\right] \xrightarrow{H_2O} \underset{\displaystyle R'}{\underset{|}{C}}-OH + Mg\begin{matrix}OH\\X\end{matrix}$$

Physical Properties

- Alcohols have higher boiling point than haloalkanes of comparable molecular mass because alcohols form intermolecular hydrogen bonding.

  As the number of carbon atoms increases, boiling point increases. The boiling point decreases with increase of branching in carbon chain.
- Alcohols are soluble in water due to their ability to form hydrogen bonds with water molecules. As the number of carbon atoms increases, solubility decreases.

Chemical Properties

Alcohols react both as nucleophiles and electrophiles. As a result, the bond between $O-H$ and $C-O$ get broken. These are as follows:

1. Reactions Involving Cleavage of O—H Bond

- Alcohols react with active metals such as sodium, potassium and aluminium to yield corresponding alkoxide and hydrogen.

$$2R-OH + 2Na \longrightarrow 2R-\overset{-}{O}-\overset{+}{Na} + H_2$$

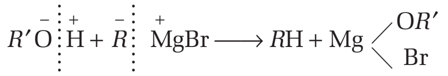
- Acidity of alcohols in decreasing order

$$1° > 2° > 3°$$

  Electron releasing group decreases the polarity of $-OH$ bond. This decreases the acidic strength.
- Alcohols when react with carboxylic acids, acid chlorides and acid anhydrides, form esters. This reaction is called **esterification.**

$$RO\vdots H + R'CO\vdots OH \xrightleftharpoons{H^+} R'COOR + H_2O$$

- Alcohols when react with Grignard reagent give alkanes.



$$R'\overset{-}{O}\vdots\overset{+}{H} + \overset{-}{R}\vdots\overset{+}{Mg}Br \longrightarrow RH + Mg\begin{matrix}OR'\\Br\end{matrix}$$

2. Reactions Involving Cleavage of Carbon Oxygen (C—OH) Bond

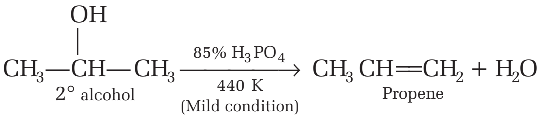
- Alcohols react with hydrogen halides to form alkyl halides.

$$ROH + HX \longrightarrow R-X + H_2O$$

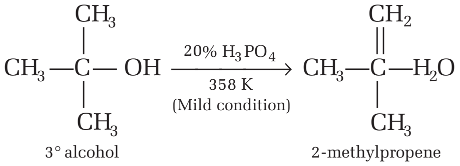
  Reactivity of alcohol in decreasing order 3° > 2° > 1°.

- **Dehydration of alcohol place** in the presence of protic acids like conc. H_2SO_4 or H_3PO_4 or in the presence of catalysts such as anhy. $ZnCl_2$ or Al_2O_3.

$$\underset{1^\circ\text{ alcohol}}{C_2H_5OH} \xrightarrow[443\text{ K}]{H_2SO_4} \underset{\text{Ethene}}{CH_2=CH_2} + H_2O$$



$$\underset{2^\circ\text{ alcohol}}{CH_3-\overset{\overset{OH}{|}}{C}H-CH_3} \xrightarrow[\substack{440\text{ K}\\ \text{(Mild condition)}}]{85\%\ H_3PO_4} \underset{\text{Propene}}{CH_3\,CH=CH_2} + H_2O$$



$$\underset{3^\circ\text{ alcohol}}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH} \xrightarrow[\substack{358\text{ K}\\ \text{(Mild condition)}}]{20\%\ H_3PO_4} \underset{\text{2-methylpropene}}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_2}{\|}}{C}}-H_2O}$$

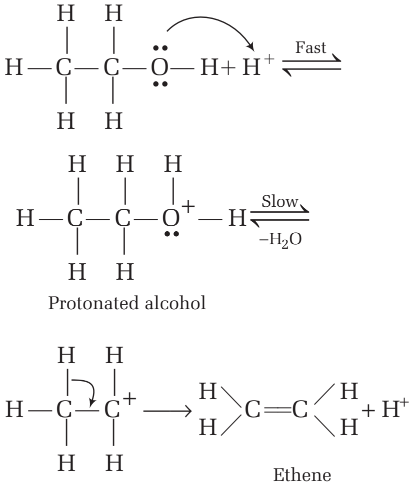
Relative ease of dehydration of alcohols 3° > 2° > 1°.

- Mechanism of **dehydration of ethanol** involves following steps.

  (i) Formation of protonated alcohol.

  (ii) Formation of carbocation

  (iii) Formation of ethene by elimination of proton.

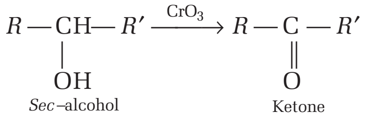


3. Oxidation of Alcohols

It involves the formation of a C—O double bond with cleavage of an O—H and C—H bonds.

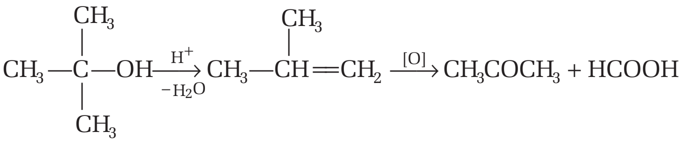
- $RCH_2OH \xrightarrow[\text{Acidified } KMnO_4]{[O]} R-CHO \xrightarrow{[O]} RCOOH$
- $RCH_2OH \xrightarrow{CrO_3} RCHO$
- $CH_3-CH=CH-CH_2OH \xrightarrow{PCC} CH_3-CH=CH-CHO$

  (PCC = pyridinium chloro chromate is a better reagent to convert 1° alcohol to aldehyde)

- 

$$\underset{Sec\text{–alcohol}}{R-\underset{\underset{OH}{|}}{C}H-R'} \xrightarrow{CrO_3} \underset{\text{Ketone}}{R-\underset{\underset{O}{\|}}{C}-R'}$$

Tertiary alcohols do not undergo oxidation reaction. In presence of strong oxidising agent ($KMnO_4$) and at high temperature, cleavage of C—C bond takes place and a mixture of carboxylic acids containing lesser number of carbon atoms is formed.

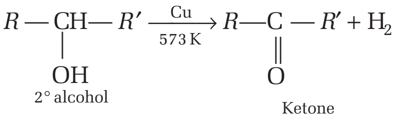


$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH \xrightarrow[-H_2O]{H^+} CH_3-\overset{\overset{CH_3}{|}}{C}H=CH_2 \xrightarrow{[O]} CH_3COCH_3 + HCOOH$$

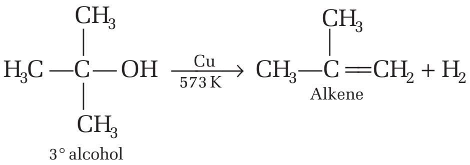
$$HCOOH \xrightarrow{[O]} H_2O + CO_2$$

4. Action of Heated Copper

$$\underset{1^\circ\text{ alcohol}}{RCH_2OH} \xrightarrow[573\text{ K}]{Cu} \underset{\text{Aldehyde}}{R-CHO} + H_2$$



$$\underset{2^\circ\text{ alcohol}}{R-\underset{\underset{OH}{|}}{C}H-R'} \xrightarrow[573\text{ K}]{Cu} \underset{\text{Ketone}}{R-\underset{\underset{O}{\|}}{C}-R'} + H_2$$



$$\underset{3^\circ\text{ alcohol}}{H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH} \xrightarrow[573\text{ K}]{Cu} \underset{\text{Alkene}}{CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2} + H_2$$

Identification of Primary, Secondary and Tertiary Alcohols

1. With Lucas reagent (conc. HCl and $ZnCl_2$)

- Tertiary alcohols give turbidity immediately.
- Secondary alcohols give turbidity with in five minutes.
- Primary alcohols do not produce turbidity at room temperature.

2. In Victor Meyer's test

- Blood red colour indicates 1° alcohols.
- Blue colour indicates 2° alcohols.
- Colourless solution indicates 3° alcohols.

Uses of Alcohols

- Methanol and ethanol are two commercially important alcohols. Methanol is used as a solvent in paints, varnishes and mainly for making formaldehyde.
- It is highly poisonous in nature. Ingestion of even small quantities of methanol can cause blindness and large quantities cause even death.
- Ethanol is used as a solvent in paint industry and in preparation of a number of carbon compounds.
- Commercial alcohol is made unfit for drinking by mixing $CuSO_4$ and pyridine **(denaturation of alcohol).**
- Ethanol is mainly used in alcoholic beverages.

Phenol (C_6H_5OH)

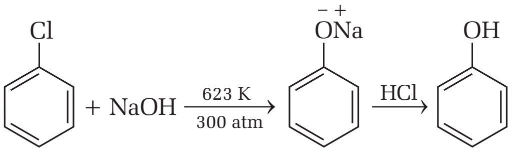
A phenol contains —OH group(s) directly attached to carbon atom(s) of an aromatic system (like C_6H_5OH).

Preparation

Some general and important **methods of preparation of phenol** are discussed below :

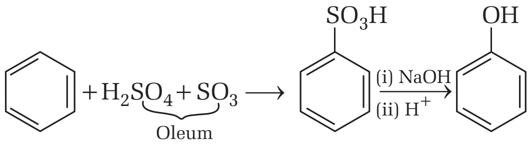
1. From Haloarenes (Dow's Process)

Chlorobenzene is fused with NaOH at 623K and 320 atmospheric pressure. Phenol is obtained by acidification of sodium phenoxide so produced.



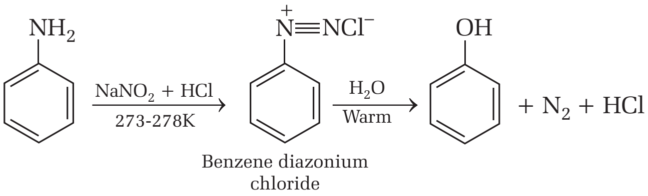
2. From Benzene Sulphonic Acid

Benzene is sulphonated with oleum and benzene sulphonic acid so formed is converted to sodium phenoxide on heating with molten NaOH. Acidification of sodium salt gives phenol.



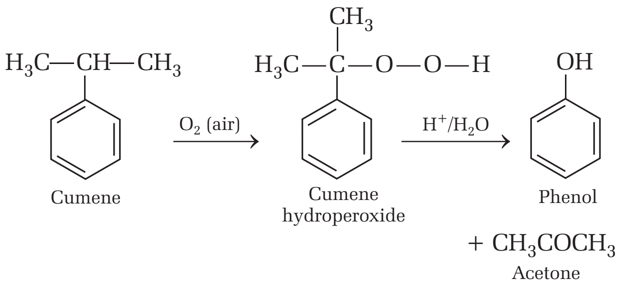
3. From Diazonium Salts

Diazonium salts are hydrolysed to phenols by warming with water or by treating with dilute acids.



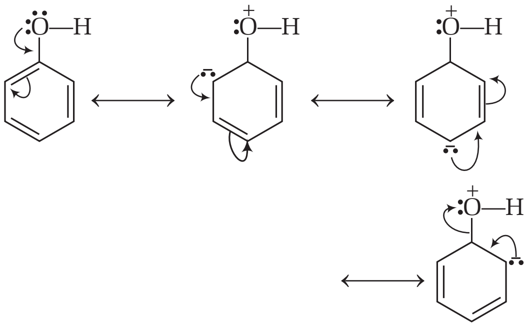
4. From Cumene

Phenol is manufactured from the hydrocarbon, cumene. Cumene is oxidised in presence of air to cumene hydroperoxide. It is converted to phenol and acetone by treating with dilute acid.



Physical Properties of Phenol

- Phenol has higher boiling point and soluble in water due to its ability to form hydrogen bonding with water.
- **Phenol is acidic in nature**, even more acidic than alcohols due to conjugation between lone pair of oxygen and benzene nucleus, i.e.



Presence of electron releasing groups like $—CH_3$, $—C_2H_5$ over benzene nucleus destabilises the phenoxide ion, thus, decreases the acidity of phenol whereas presence of electron withdrawing groups like $—NO_2$, —CN, etc., stabilises the phenoxide ion and thus, increases the acidity of phenol.

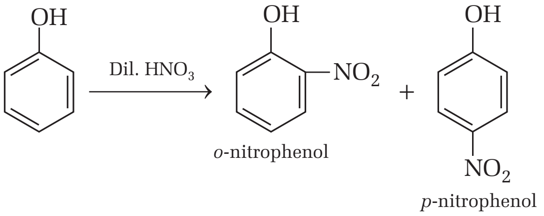
Chemical Properties

Various chemical properties of phenols are as follows:

1. Electrophilic Substitution Reactions

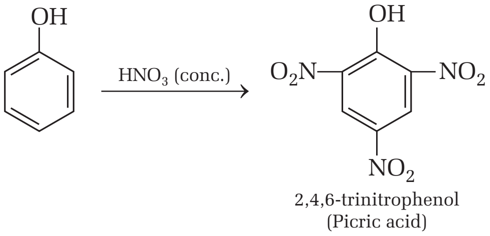
- In phenol, the —OH group shows $+R$ and $-I$-effect and hence, highly activates the benzene ring towards electrophilic substitution reaction. It is *ortho* and *para* directing group.

Nitration

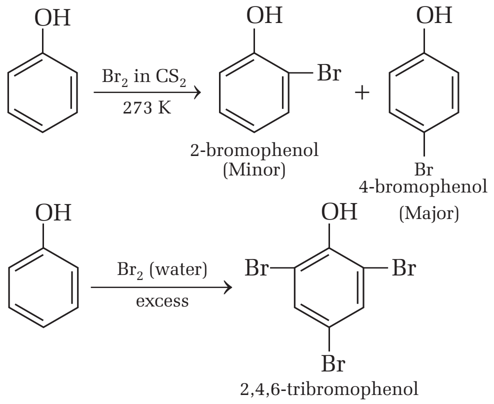


The *ortho* and *para* isomers can be separated by steam distillation.

- With conc. HNO_3, phenol is converted to 2, 4, 6-trinitrophenol

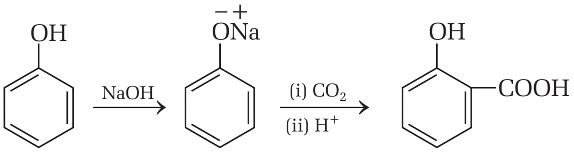


Halogenation



Kolbe's Reaction

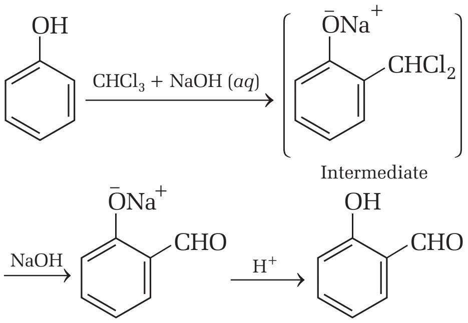
Phenoxide ion undergoes electrophilic substitution with carbon dioxide, a weak electrophile. Here, *ortho*-hydroxybenzoic acid is formed as main product.



2-hydroxybenzoic acid (Salicylic acid)

2. Reimer-Tiemann Reaction

Phenol on reaction with chloroform in presence of NaOH, produces a — CHO group at *ortho*-position of benzere ring.

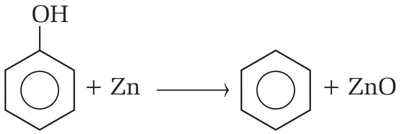


Salicylaldehyde

NOTE Electrophile is CCl_2 (dichlorocarbene)

3. Reaction of Phenol with Zinc Dust

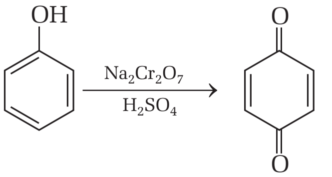
Phenol is connected to benzene on heating with zinc dust.



Benzene

4. Oxidation

Oxidation of phenol with chromic acid produces a conjugated diketone known as benzoquinone



Benzoquinone

Uses of Phenols

- Phenol is used in the manufacture of bakelite, soaps, lotions etc.
- It is used in the manufacture of drugs like aspirin, salol, phenacetin etc.

Ethers

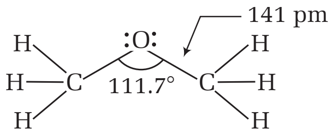
Organic compounds having —O— functional group are called ethers.

- In other words, ethers are the derivatives of water as these are obtained when both the H-atoms of H_2O are replaced by —*R* groups. The —*R* groups may be same or different. When both the —*R* groups (alkyl groups) are same, the ethers are called **simple** or **symmetrical ether** and when both the —*R* groups are different, the ethers are called **mixed** or **unsymmetrical ethers,** e.g.

CH_3-O-CH_3 and $CH_3OC_2H_5$

(Simple or symmetrical ethers) (Mixed ether)

- In ethers, two bond pairs and two lone pairs of electrons on oxygen are arranged approximately in tetrahedral manner. The bond angle is slightly greater than tetrahedral angle due to the repulsive forces between the two bulky alkyl groups.



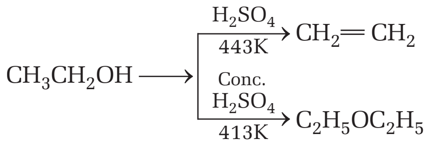
Structure of methoxymethane

Preparation

General methods used to synthesis ethers are as follows:

1. By the Dehydration of Alchols

Alcohols undergo **dehydration** in the presence of protic acids. The formation of the reaction product, alkene or ether depends on the reaction conditions.

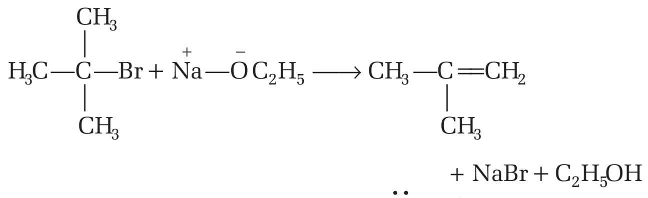


2. Williamson's Synthesis

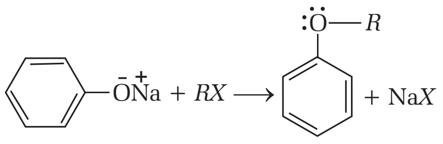
Only primary alkyl halides when react with sodium alkoxide give ether while tertiary alkyl halide give alkene due to steric hindrance.

$$CH_3CH_2Br + CH_3CH_2\overset{-}{O}\overset{+}{N}a \longrightarrow CH_3CH_2OCH_2CH_3 + NaBr$$

If a tertiary alkyl halide is used, and alkene is the only reaction product.



$$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-Br + \overset{+}{Na}-\overset{-}{O}C_2H_5 \longrightarrow CH_3-\underset{CH_3}{C}=CH_2 + NaBr + C_2H_5OH$$



Alkoxy benzene

Physical Properties

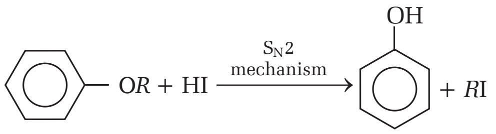
- Ethers are polar but insoluble in H_2O and have low boiling point than alcohols (having comparable molecular mass) because ethers do not form hydrogen bond with water.
- Low ethers (upto three carbon atoms) are soluble in water and their miscibility with water resembles those of alcohols of the same molecular mass.

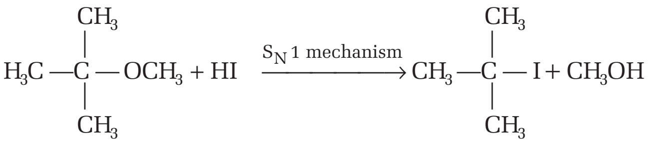
Chemical Properties

The **reactions of ethers** are mainly due to lone pair of ethereal O, cleavage of C—O bond and —R group:

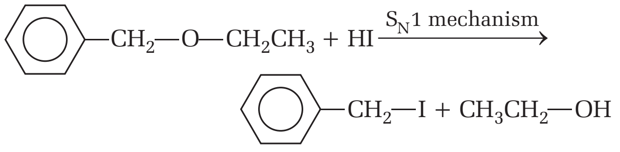
1. **Reactions Involving Cleavage of C—O Bonds** Ethers are least reactive of the functional groups. The cleavage of C—O bond in ethers takes place under drastic conditions.

$$CH_3-CH_2-\ddot{\underset{..}{O}}-CH_3 + HI \xrightarrow{S_N2 \text{ mechanism}} CH_3-CH_2-OH + CH_3I$$



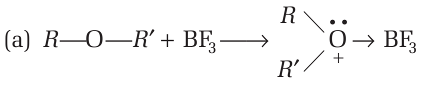


$$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-OCH_3 + HI \xrightarrow{S_N1 \text{ mechanism}} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-I + CH_3OH$$



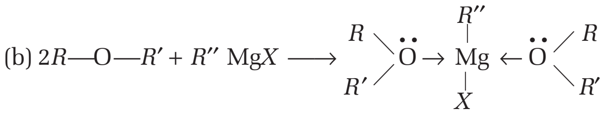
2. Some important **addition reactions** given by ethers are as follows:

(a)



$$R-O-R' + BF_3 \longrightarrow \overset{R}{\underset{R'}{}}\overset{..}{\underset{+}{O}} \rightarrow BF_3$$

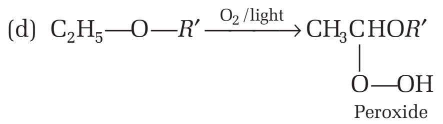
(b)



$$2R-O-R' + R''MgX \longrightarrow \overset{R}{\underset{R'}{}}\ddot{O} \rightarrow \underset{X}{\overset{R''}{Mg}} \leftarrow \ddot{O}\overset{R}{\underset{R'}{}}$$

(c) $R-O-R' \xrightarrow[425\,K]{CO/BF_3} \underset{\text{Ester}}{RCOOR'}$

(d)

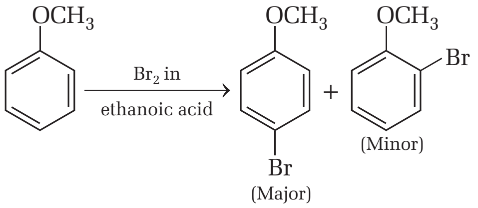


$$C_2H_5-O-R' \xrightarrow{O_2/light} CH_3\underset{O-OH}{\underset{|}{C}}HOR'$$

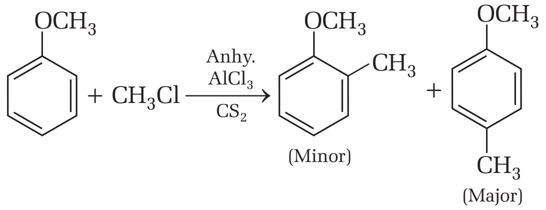
Peroxide

3. **Electrophilic Substitution Reactions** —OR is *ortho, para* directing group and activates the aromatic ring towards electrophilic substitution reaction.

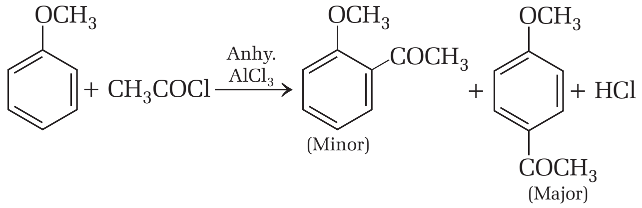
(a) **Halogenation**



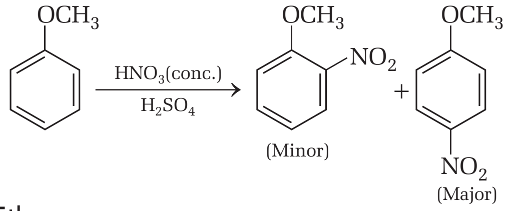
(b) **Friedel-Crafts' Alkylation**



(c) **Friedel-Crafts' Acylation**



(d) **Nitration**



Uses of Ethers

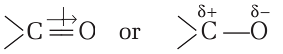
(i) Ethers are used as a solvent for oils, fats and Grignard reagent, etc.
(ii) It is used as general anaesthetic. It provides inert and moisture free medium for various reactions.

Aldehydes and Ketones

The organic compounds containing carbon-oxygen double bond, i.e. $>C=O$ group are called **carbonyl compounds.**

Nature of Carbopnyl Group

In carbonyl group, π-electron cloud is displaced towards more electronegative oxygen atom thus, causing polarisation of the bond so that carbon acquires partially positive and oxygen acquires partially negative charge.



In resonance terms, electron delocalisation in the carbonyl group is represented by contributions from two principal resonance forms.

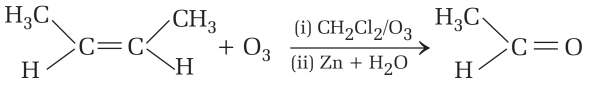
Preparation of Aldehydes and Ketones

There are several method from which aldehydes as well as ketones can be synthesised.

These methods are as follows:

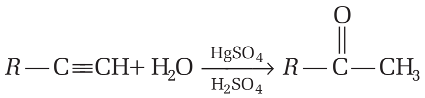
1. **Ozonolysis of alkenes** followed by reaction with zinc dust and water gives aldehyde, ketones and a mixture of both.

$$CH_2 = CH_2 \xrightarrow[\text{(ii) Zn + H}_2\text{O}]{\text{(i) O}_3\text{/CH}_2\text{Cl}_2} 2HCHO$$



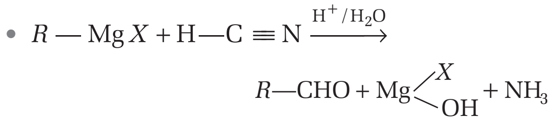
2. Acetylene on hydration in presence of H_2SO_4 and $HgSO_4$ gives acetaldehyde while other **alkynes on hydration** gives ketones.

$$\underset{\text{Acetylene}}{CH \equiv CH} + H_2O \xrightarrow[H_2SO_4]{HgSO_4} CH_3CHO$$

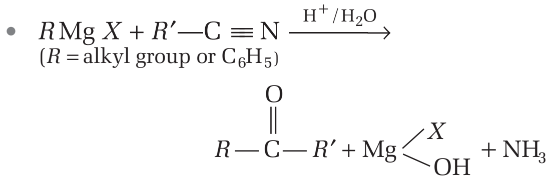


$$R—C \equiv CH + H_2O \xrightarrow[H_2SO_4]{HgSO_4} R—\overset{\overset{\displaystyle O}{\|}}{C}—CH_3$$

3. HCN when reacts with **Grignard reagent** and then subjected to hydrolysis, gives aldehydes while *R*CN gives ketone.



- $R—MgX + H—C \equiv N \xrightarrow{H^+/H_2O} R—CHO + Mg\begin{smallmatrix} X \\ OH \end{smallmatrix} + NH_3$



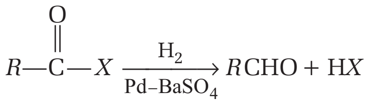
- $RMgX + R'—C \equiv N \xrightarrow{H^+/H_2O} R—\overset{\overset{\displaystyle O}{\|}}{C}—R' + Mg\begin{smallmatrix} X \\ OH \end{smallmatrix} + NH_3$

(R = alkyl group or C_6H_5)

Preparation of Aldehyde

The methods given below can be employed for the synthesis of only aldehydes.

1. **From Acyl Chloride** Acyl chloride is hydrogenated over catalyst, palladium on barium sulphate.



$$R—\overset{\overset{\displaystyle O}{\|}}{C}—X \xrightarrow[\text{Pd–BaSO}_4]{H_2} RCHO + HX$$

(R-alkyl group or C_6H_5)

This reaction is called **Rosenmund reduction**.

Formaldehyde cannot be obtained by this reaction because formyl chloride is unstable at room temperature.

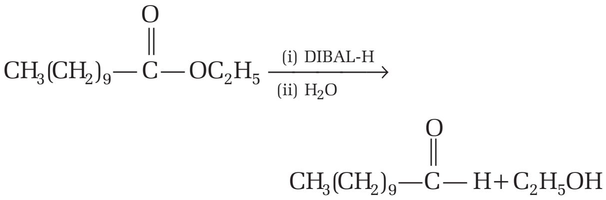
2. **From Nitriles and Esters** Stephen reaction involves the reduction of nitriles to corresponding imine with stannous chloride in presence of HCl, which on hydrolysis gives corresponding aldehyde.

$$R—CN + SnCl_2 + HCl \longrightarrow \underset{\text{Iminochloride}}{RCH = NH \cdot HCl}$$

$$\xrightarrow{H_3O^+} RCHO + NH_4Cl + H_2O$$

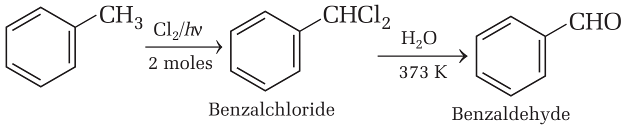
Nitriles are selectively reduced by diisobutyl aluminium hydride (DIBAL-H) and gives aldehydes.

$$CH_3CH=CHCH_2CH_2CN \xrightarrow[\text{(ii) H}_2\text{O}]{\text{(i) AlH }(i\text{–Bu})_2} CH_3CH=CHCH_2CH_2CHO$$

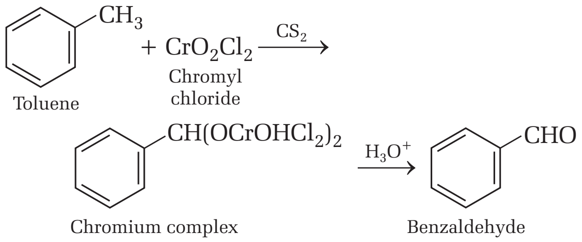


$$CH_3(CH_2)_9—\overset{\overset{\displaystyle O}{\|}}{C}—OC_2H_5 \xrightarrow[\text{(ii) H}_2\text{O}]{\text{(i) DIBAL-H}} CH_3(CH_2)_9—\overset{\overset{\displaystyle O}{\|}}{C}—H + C_2H_5OH$$

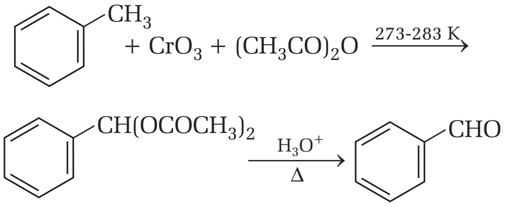
3. **By Side Chain Chlorination followed by Hydrolysis** Toluene gives benzalchloride which on hydrolysis gives benzaldehyde.



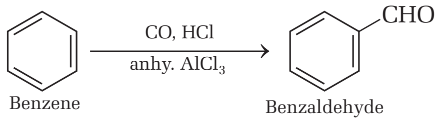
4. **Use of Chromyl Chloride (CrO_2Cl_2)** Chromyl chloride oxidises methyl group to a chromium complex, which on hydrolysis gives benzaldehyde. This reaction is called **Etard reaction**.



5. **Use of Chromic Oxide (CrO_3)** Toluene or substituted toluene is converted to benzylidene diacetate on treating with chromic oxide in acetic anhydride. The benzylidene diacetate can be hydrolysed to corresponding benzaldehyde with aqueous acid.



6. **By Gattermann-Koch Reaction** In Gattermann-Koch reaction benzene or its derivative is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminium chloride or cuprous chloride, it gives benzaldehyde or substituted benzaldehyde.



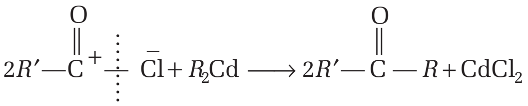
Preparation of Ketones

- The following methods are used to synthesise only ketones.

1. From Acyl Chlorides

Treatment of acyl chlorides with dialkyl cadmium prepared by the reaction of cadmium chloride with Grignard reagent, gives ketones.

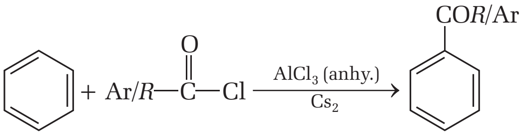
$$2R\,MgX + CdCl_2 \longrightarrow R_2Cd + 2Mg(X)Cl$$



$$2R'-\overset{O}{\overset{\|}{C}}{}^{+}\;\vdots\;\overset{-}{Cl} + R_2Cd \longrightarrow 2R'-\overset{O}{\overset{\|}{C}}-R + CdCl_2$$

2. From Benzene or Substituted Benzene

In **Friedel-Crafts acylation**, acid is treated with acid chloride in the presence of anhyd. $AlCl_3$.



Physical Properties of Aldehydes and Ketones

Physical properties of aldehydes and ketones are as follows:

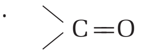
- Methanal is a gas at room temperature. Ethanal is a volatile liquid. Other aldehydes and ketones are liquid or solid at room temperature.
- The boiling points of aldehydes and ketones are higher than ethers of comparable molecular masses.
- The lower members of aldehydes and ketones such as methanal, ethanal and propanone are miscible with water in all proportions because they form hydrogen bond with water. However, the solubility of aldehydes and ketones decreases rapidly on increasing the length of alkyl chain.

Chemical Properties of Aldehydes and Ketones

The aldehydes and ketones because of the presence of polar carbonyl group exhibit the following **chemical reaction.**

1. Nucleophilic Addition Reactions

A nucleophile attacks at the electrophilic carbon atom of the polar carbonyl group.



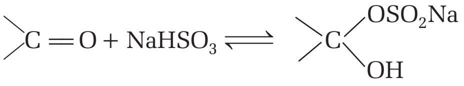
sp^2, carbonyl group

- As the number of carbon atoms/number of alkyl groups increases, reactivity decreases due to steric hindrance. Hence, the order of reactivity is
$HCHO > CH_3CHO > CH_3COCH_3 > C_2H_5COC_2H_5$.
- Various nucleophilic addition reactions are as follows:

(a) **Addition of Hydrogen Cyanide**

Cyanohydrin

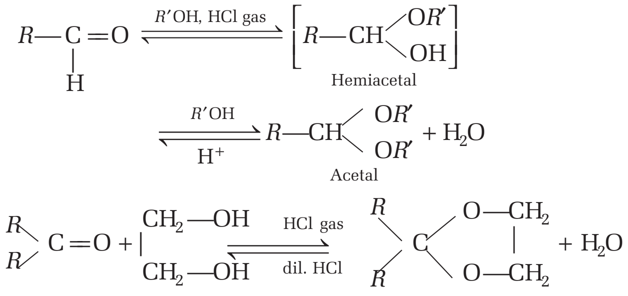
(b) **Addition of Sodium Hydrogen Sulphite**



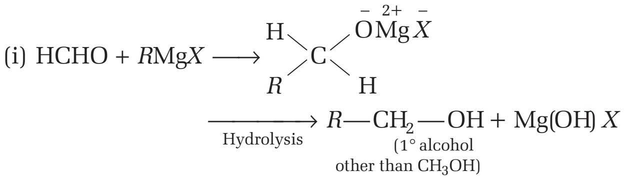
White crystalline solid

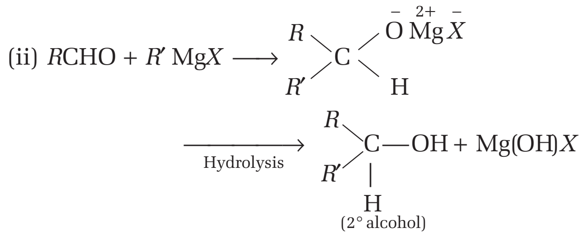
This reaction is used for the separation and purification of aldehydes and ketones. The reason for this is that the hydrogen sulphite addition compound formed is water soluble and can be converted back to the original carbonyl compound by treating with dilute mineral acid or alkali.

(c) **Addition of Lower Alcohols**



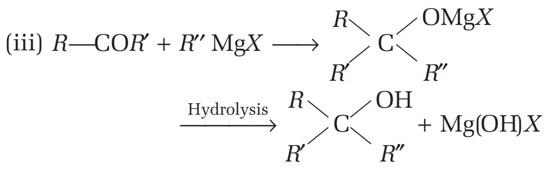
(d) **Addition of Grignard reagent** is used to distinguish aldehyde and ketone. The reactions are as follows:



(ii) 

$$RCHO + R'MgX \longrightarrow \underset{R'}{\overset{R}{>}}C\underset{H}{\overset{\overset{-\ \ 2+\ \ -}{O\,Mg\,X}}{<}} \xrightarrow{\text{Hydrolysis}} \underset{R'}{\overset{R}{>}}\underset{\underset{H}{|}}{C}-OH + Mg(OH)X$$

(2° alcohol)

(iii) 

$$R-COR' + R''MgX \longrightarrow \underset{R'}{\overset{R}{>}}C\underset{R''}{\overset{OMgX}{<}} \xrightarrow{\text{Hydrolysis}} \underset{R'}{\overset{R}{>}}C\underset{R''}{\overset{OH}{<}} + Mg(OH)X$$

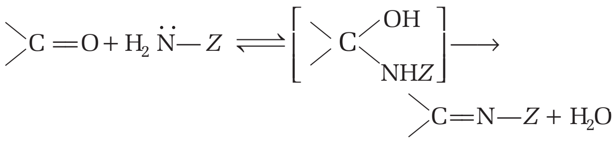
(3° alcohol)

Nucleophilic Addition Elimination Reaction

These are two step reactions involving addition followed by elimination of some small molecules.

Addition Reactions with Derivatives of Ammonia

It is reversible reaction and catalysed by acid (pH ≈ 4). The equilibrium favours the product formation due to rapid dehydration of the intermediate to form $>C=N-Z$.



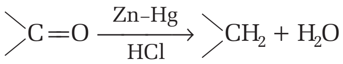
$$>C=O + H_2\ddot{N}-Z \rightleftharpoons \left[>C\underset{NHZ}{\overset{OH}{<}}\right] \longrightarrow >C=N-Z + H_2O$$

where, Z = alkyl, aryl, —OH, $-NH_2$, C_6H_5NH-, $-NHCONH_2$ etc.

Formaldehyde reacts with ammonia to form urotropine while acetaldehyde reacts with ammonia to form acetaldimine. While acetone react with ammonia to form diacetonamine.

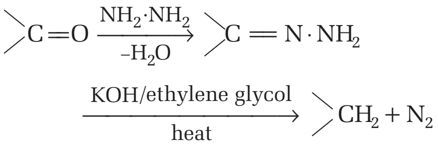
Reduction

Aldehydes and ketones are reduced to alkanes.



$$>C=O \xrightarrow[\text{HCl}]{\text{Zn–Hg}} >CH_2 + H_2O$$

(Clemmensen reduction)



$$>C=O \xrightarrow[-H_2O]{NH_2\cdot NH_2} >C=N\cdot NH_2 \xrightarrow[\text{heat}]{\text{KOH/ethylene glycol}} >CH_2 + N_2$$

(Wolff-Kishner reduction)

Oxidation

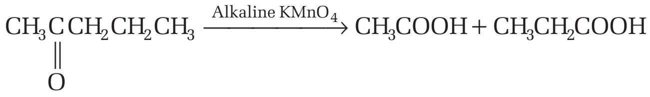
Aldehydes are easily **oxidised** to carboxylic acids on treatment with strong oxidising agents (HNO_3, $K_2Cr_2O_7$, $KMnO_4$, etc.). Even mild oxidising agents, mainly Tollen's reagent and Fehling's reagent also oxidise aldehydes.

$$\underset{(R\text{-alkyl or }C_6H_5\text{ group})}{RCHO} + \underset{\text{Tollen's reagent}}{2[Ag(NH_3)_2]^+ + 3OH^-} \longrightarrow RCOO^- + \underset{\text{Silver mirror}}{2Ag\downarrow} + 2H_2O + 4NH_3$$

$$R-CHO + \underset{\text{Fehling solution}}{2Cu^{2+} + 5OH^-} \longrightarrow RCOO^- + \underset{\text{Red brown ppt}}{Cu_2O} + 3H_2O$$

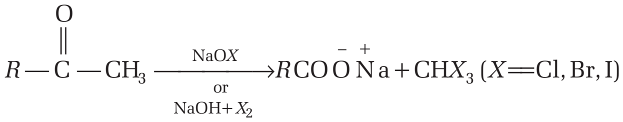
This reaction is not given by aromatic aldehydes.

- **Ketones cannot be oxidised by weak oxidising agents** such as Tollen's reagent and Fehling's solution. They are oxidised only in the presence of strong oxidising agents and at elevated temperatures. Their oxidation involves carbon-carbon bond cleavage to give a mixture of carboxylic acids having lesser number of carbon atoms than the parent ketone. e.g.

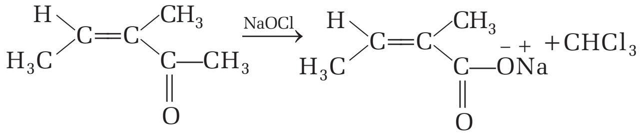


$$CH_3\underset{\underset{O}{\|}}{C}CH_2CH_2CH_3 \xrightarrow{\text{Alkaline }KMnO_4} CH_3COOH + CH_3CH_2COOH$$

- **Methyl ketones** ($-COCH_3$) are also oxidised by **haloform reaction** in which they are treated with halogen in the presence of alkali or hypohalite salt.



$$R-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[\text{or } NaOH+X_2]{NaOX} RCO\overset{-}{O}\overset{+}{Na} + CHX_3\ (X = Cl, Br, I)$$

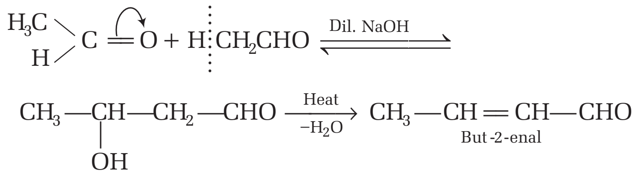


$$\underset{H_3C}{\overset{H}{>}}C=C\underset{\underset{\underset{O}{\|}}{C}-CH_3}{\overset{CH_3}{<}} \xrightarrow{NaOCl} \underset{H_3C}{\overset{H}{>}}C=C\underset{\underset{\underset{O}{\|}}{C}-\overset{-}{O}\overset{+}{Na}}{\overset{CH_3}{<}} + CHCl_3$$

CH_3 group of $COCH_3$ is converted into haloform as it contains acidic hydrogen atoms. Acid salt is obtained corresponding to total number of carbon atoms apart from $-CH_3$ of $RCOCH_3$.

Reactions due to Acidic α-Hydrogen

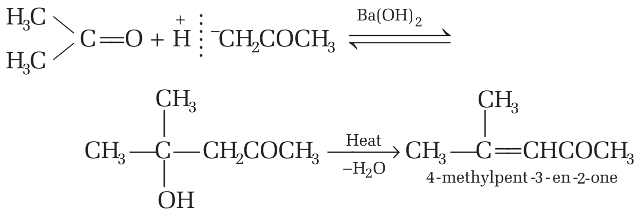
- Aldehydes or ketones having atleast one α-hydrogen atom undergo a reaction in the presence of dilute alkali as catalyst to form β–hydroxy aldehydes (aldol) or β-hydroxy ketones (ketol) respectively. This is known as **aldol condensation**.



$$\underset{H}{\overset{H_3C}{>}}C=O + H\vdots CH_2CHO \underset{}{\overset{\text{Dil. NaOH}}{\rightleftharpoons}} CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CHO \xrightarrow[-H_2O]{\text{Heat}} CH_3-CH=CH-CHO$$

3-hydroxybutanal (aldol)

But-2-enal

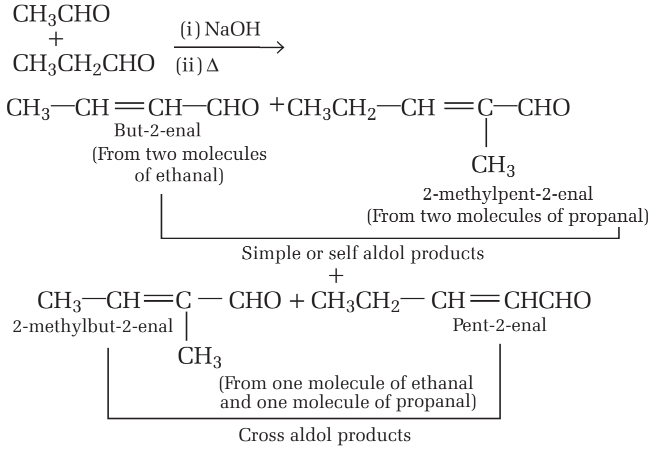


$$\underset{H_3C}{\overset{H_3C}{>}}C=O + \overset{+}{H}\vdots\,^{-}CH_2COCH_3 \overset{Ba(OH)_2}{\rightleftharpoons} CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2COCH_3 \xrightarrow[-H_2O]{\text{Heat}} CH_3-\overset{\overset{CH_3}{|}}{C}=CHCOCH_3$$

4-hydroxy-4-methyl pentan-2-one (ketol)

4-methylpent-3-en-2-one

- When aldol condensation is carried out between two different aldehydes and /or ketones containing α-hydrogen, it is called **cross aldol condensation**, e.g.



$$\begin{matrix}CH_3CHO\\+\\CH_3CH_2CHO\end{matrix}\xrightarrow[\text{(ii)}\ \Delta]{\text{(i) NaOH}}$$

$$\underset{\substack{\text{But-2-enal}\\\text{(From two molecules}\\\text{of ethanal)}}}{CH_3-CH=CH-CHO} + \underset{\substack{\text{2-methylpent-2-enal}\\\text{(From two molecules of propanal)}}}{CH_3CH_2-CH=\underset{CH_3}{\underset{|}{C}}-CHO}$$

Simple or self aldol products

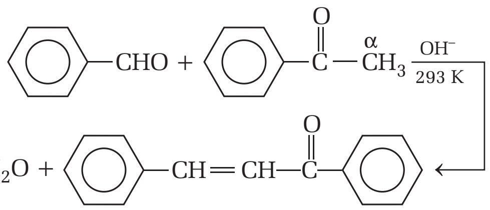
$+$

$$\underset{\text{2-methylbut-2-enal}}{CH_3-CH=\underset{CH_3}{\underset{|}{C}}-CHO} + \underset{\text{Pent-2-enal}}{CH_3CH_2-CH=CHCHO}$$

(From one molecule of ethanal and one molecule of propanal)

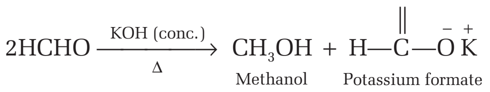
Cross aldol products

- This reaction is of great synthetic use even if one of the carbonyl group do not possess α-H atom.

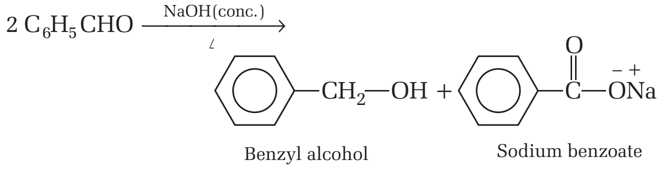


1,3-diphenylprop-2-en-1-one
(Benzalacetophenone)
major product

- Aldehydes which do not have α-hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali. This reaction is known as **Cannizzaro reaction**.



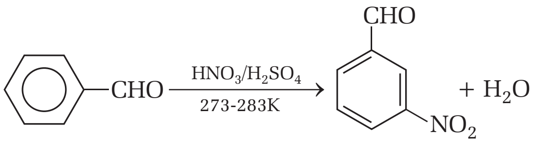
$$2HCHO \xrightarrow[\Delta]{\text{KOH (conc.)}} \underset{\text{Methanol}}{CH_3OH} + \underset{\text{Potassium formate}}{H-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{-}{O}\overset{+}{K}}$$



Benzyl alcohol Sodium benzoate

Electrophilic Substitution Reaction

Aromatic aldehydes and ketones undergo electrophilic substitution. Carbonyl group are electron withdrawing in nature, therefore acts as a deactivating and *meta* directing group.



m-nitrobenzaldehyde

Chemical Test to Distinguish Between Aldehydes and Ketones

Aldehydes and ketones can be distinguished by several tests which are tabulated below:

Dishtinguish between Aldehydes and Ketones

Name of test	Reagent	Aldehydes	Ketones
Tollen's test	Ammoniacal silver nitrate	Silver mirror (deposition of Ag on surface of test tube) formed	No change
Fehling's test	Alkaline solution of $CuSO_4$ containing Rochelle salt (sodium potassium tartarate.)	Red precipitate of Cu_2O. (only aliphatic aldehydes give this test)	No change
Benedict test	Alkaline solution of copper acetate and sodium citrate	Red precipitate of Cu_2O. (only aliphatic aldehydes give this test)	No change
Schiff's test	*p*-rosaniline hydrochloride	Pink colour	No change

Uses of Aldehydes and Ketones

- In chemical industry, aldehydes and ketones are used as solvents, starting materials and reagents for the synthesis of other products.
- Formaldehyde, under the name formalin, (40% solution) is used to preserve biological specimens.
- Formaldehyde is also used to prepare bakelite, urea-formaldehyde glues and other polymeric products.

Carboxylic Acids

Carbon compounds containing a carboxylic functional group, —COOH are called carboxylic acids. Some higher members of aliphatic carboxylic acids (C_{12}-C_{18}) are known as fatty acids, occur in natural fats as esters of glycerol.

Preparation

Preparation of carboxylic acids are as follows:

1. From Acid Derivatives

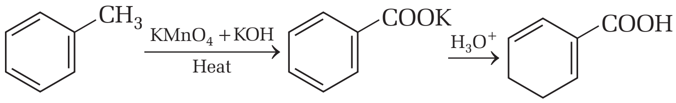
All acid derivatives like amides ($RCONH_2$), acid halides ($RCOCl$), esters ($RCOOR'$), acid anhydrides ($RCO-O-COR$) on hydrolysis give carboxylic acids.

$$RCOZ \xrightarrow[\text{Dil. NaOH}]{\text{Dil. HCl}\atop\text{or}} RCOOH$$

$$Z = -NH_2, -X\ (X = Cl, Br, I), OR', RCOO- \text{ etc.}$$

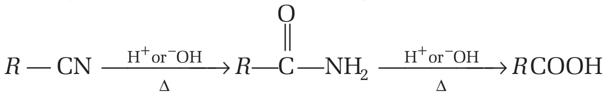
2. From Alkyl Benzene

Alkyl benzene when treated with strong oxidising agent like H_2CrO_4 (chromic acid), acidic or alkaline $KMnO_4$ gives benzoic acid.



3. From Nitriles

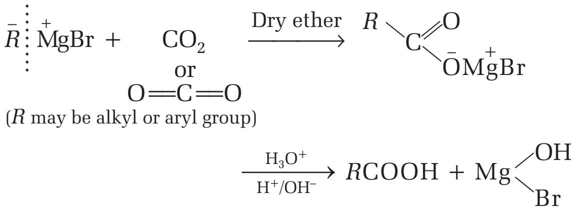
Nitriles are hydrolysed to amides and then to acids in the presence of H^+ or $\bar{O}H$ as catalyst. Mild reaction conditions are used to stop the reaction at milder stage.



$$R-CN \xrightarrow[\Delta]{H^+\text{ or }{}^-OH} R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[\Delta]{H^+\text{ or }{}^-OH} RCOOH$$

4. From Grignard Reagent

Grignard reagents react with carbon dioxide (dry ice) to form salts of carboxylic acid which give corresponding carboxylic acid after acidification with universal acid.



(R may be alkyl or aryl group)

Physical Properties

- Carboxylic acids exist in the form of dimer due to hydrogen bonding.
- As compared to aldehydes, ketones and hydrocarbons, carboxylic acids have higher boiling point due to intermolecular hydrogen bonding.

Chemical Properties

The reactions of carboxylic acids are classified as follows :

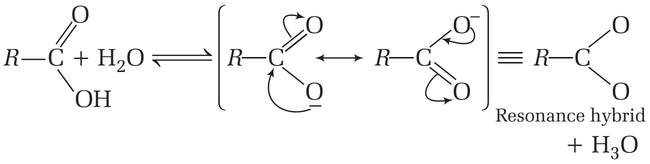
- Carboxylic acids evolve hydrogen gas with electropositive metals and form salts with alkalies.

$$2\,RCOOH + 2Na \longrightarrow 2RCO\overset{-}{O}\overset{+}{N}a + H_2$$

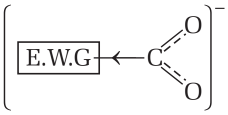
$$RCOOH + NaOH \longrightarrow RCO\overset{-}{O}\overset{+}{N}a + H_2O$$

$$RCOOH + NaHCO_3 \longrightarrow RCO\overset{-}{O}\overset{+}{N}a + H_2O + CO_2$$

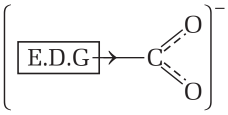
- Carboxylic acids dissociate in water to give resonance stabilised carboxylate anions and hydronium ion.



- Substituents may affect the stability of the conjugate base and also affect the acidity of carboxylic acids.
  - (a) Electron withdrawing group (E.W.G.) stabilises the carboxylate anion and strengthens the acid.



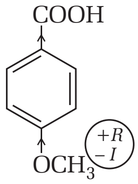
  - (b) Electron donating group (E.D.G.) destabilises the carboxylate anion and weakens the acid. Strong acids have higher value of K_a and hence lower value of pK_a.



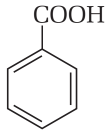
- Following acids are arranged in order of decreasing acidity.

$CF_3COOH > CCl_3COOH > CHCl_2COOH$
$NO_2CH_2COOH > NC-CH_2COOH$
$> FCH_2COOH > ClCH_2COOH > BrCH_2COOH >$
$HCOOH > ClCH_2CH_2COOH >$
$C_6H_5COOH > C_6H_5CH_2COOH > CH_3COOH > CH_3CH_2COOH$

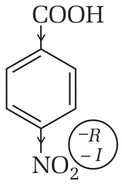
- In case of aromatic carboxylic acids, more the $-R$ effect, more is the acidic nature.



4-methoxy benzoic acid
(pK_a = 4.46)



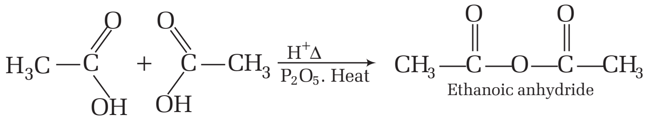
Benzoic acid
(pK_a = 4.19)



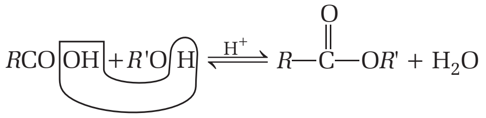
4-nitrobenzoic acid
(pK_a = 3.41)

Reactions involving cleavage of C—OH bond

1. Formation of Anhydride



2. Esterification

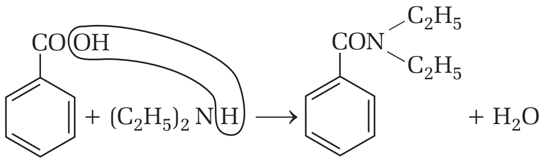


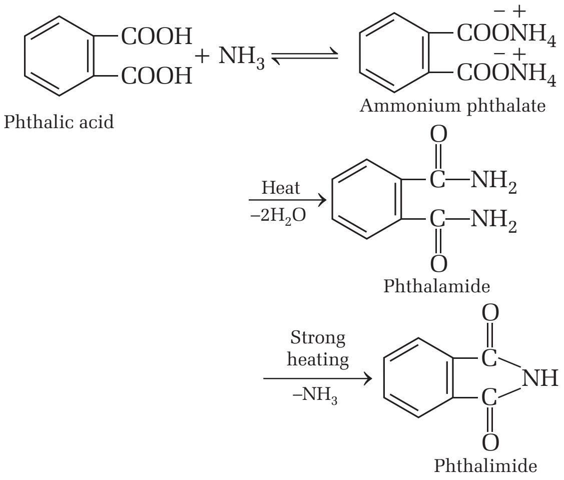
3. Reaction with PCl_5, PCl_3 and $SOCl_2$

- $RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$
- $3RCOOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3$
- $RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2\uparrow + HCl\uparrow$

4. Reaction with ammonia and its derivatives

- $\mathrm{CH_3COOH + NH_3 \rightleftharpoons \underset{\text{Ammonium acetate}}{CH_3COO^-NH_4^+} \xrightarrow{\text{Heat}} \underset{\text{Acetamide}}{CH_3CONH_2}}$

- 

- 

Reactions Involving —COOH Group

1. **Reduction** Carboxylic acids are reduced to primary alcohols by $LiAlH_4$ or better with B_2H_6. B_2H_6 does not easily reduce functional groups such as ester, nitro, halo, etc. $NaBH_4$ does not reduce the carboxyl group.

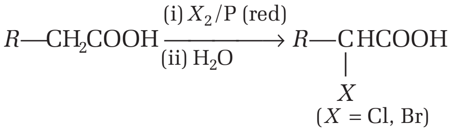
$$R\mathrm{COOH} \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } LiAlH_4/\text{Ether or } B_2H_6} R\mathrm{CH_2OH + H_2O}$$

2. **Decarboxylation** Carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with sodalime.

$$R\mathrm{CO\overset{-}{O}\overset{+}{N}a + NaOH \xrightarrow[\text{Heat}]{\text{CaO}}} R\mathrm{H + Na_2CO_3}$$

Substitution Reactions

1. **Halogenation** Carboxylic acids having an $\alpha-H$ are halogenated at the $\alpha-$ position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give α-halo carboxylic acids.

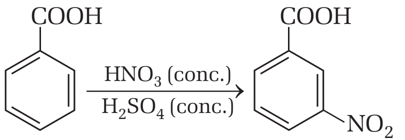


$$R\text{—}\mathrm{CH_2COOH} \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2/\text{P (red)}} R\text{—}\underset{\underset{X}{|}}{\mathrm{C}}\mathrm{HCOOH}$$

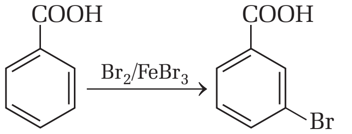
$(X = \mathrm{Cl, Br})$

The reaction is known as **Hell Volhard-Zelinsky** reaction.

2. **Ring Substitution** Aromatic carboxylic acids undergo **electrophilic substitution reaction.** —COOH group shows $-R$-effect, therefore acts as a deactivating and *meta*-directing group. Carboxylic acids do not undergo Friedel-Crafts' reaction because the carboxylic group is deactivating and the catalyst $AlCl_3$ (anhyd.) gets bonded to the carboxylic group.



m-nitrobenzoic acid



m-bromobenzoic acid

Uses of Carboxylic Acid

- Formic acid is used in leather tanning, textile, dyeing and finishing.
- Acetic acid is used in the manufacture of rayon and in plastics, rubber and silk industries and in cooking.
- Benzoic acid and its salts are used as urinary antiseptics.

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

1 Arrange the following compounds in increasing order of boiling point. Propan-1-ol, butan-1-ol, butan-2-ol, pentan-1-ol

(a) Propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol
(b) Propan-1-ol, butan-1-ol, butan-2-ol, pentan-1-ol
(c) Pentan-1-ol, butan-2-ol, butan-1-ol, propan-1-ol
(d) Pentan-1-ol, butan-1-ol, butan-2-ol, propan-1-ol

2 From amongst the following alcohols, the one that would react fastest with conc. HCl and anhydrous $ZnCl_2$, is → AIEEE 2010

(a) 2-butanol
(b) 2-methylpropan-2-ol
(c) 2-methylpropanol
(d) 1-butanol

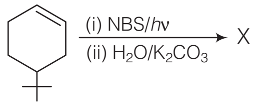
3 Amongst the following alcohols which would react fastest with conc. HCl and $ZnCl_2$? → JEE Main (Online) 2013

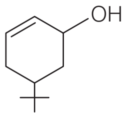
(a) Pentanol
(b) 2-methylbutanol
(c) 2-pentanol
(d) 2-methylbutan-2-ol

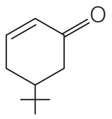
4 An unknown alcohol is treated with the "Lucas reagent" to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism? → JEE Main (Online) 2013

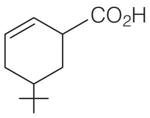
(a) Secondary alcohol by S_N1
(b) Tertiary alcohol by S_N1
(c) Secondary alcohol by S_N2
(d) Tertiary alcohol by S_N2

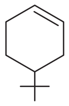
5 The product of the reaction given below is → JEE Main 2016



(a) 

(b) 

(c) 

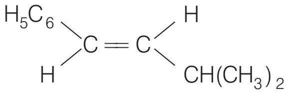
(d) 

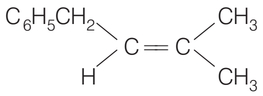
6 Rate of dehydration of alcohols follows the order → JEE Main (Online) 2013

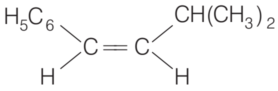
(a) 2°>1°<CH_3OH>3°
(b) 3°>2°>1°>CH_3OH
(c) 2°>3°>1°>CH_3OH
(d) CH_3OH>1°>2°>3°

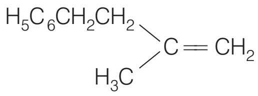
7 The main product of the following reaction is

$C_6H_5CH_2CH(OH)CH(CH_3)_2 \xrightarrow{\text{Conc. } H_2SO_4} ?$ → AIEEE 2010

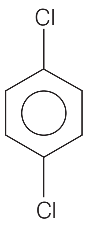
(a) 

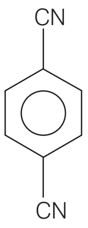
(b) 

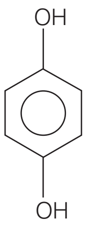
(c) 

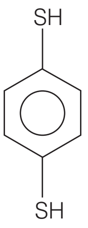
(d) 

8 For which of the following molecule, significantly $\mu \neq 0$? → JEE Main 2014


I

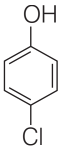

II

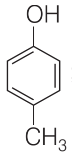

III

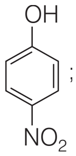

IV

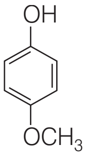
(a) Only I
(b) I and II
(c) Only III
(d) III and IV

9 Arrange the following compounds in the order of decreasing acidity → JEE Main (Online) 2013


I


II


III


IV

(a) II > IV > I > III
(b) I > II > III > IV
(c) III > I > II > IV
(d) IV > III > I > II

10 The major product obtained on interaction of phenol with sodium hydroxide and carbon dioxide is

(a) benzoic acid
(b) salicylaldehyde
(c) salicylic acid
(d) phthalic acid

11 Sodium phenoxide reacts with CO_2 at 400K and 4.7 atm pressure to give

(a) catechol
(b) salicylaldehyde
(c) sodium salicylate
(d) benzoic acid

12 Phenol on heating with $CHCl_3$ and NaOH gives salicylaldehyde. The reaction is called

→ JEE Main (Online) 2013

(a) Reimer-Tiemann reaction
(b) Claisen reaction
(c) Cannizzaro's reaction
(d) Hell-Volhard-Zelinsky reaction

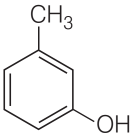
13 Phenol is heated with a solution of mixture of KBr and $KBrO_3$. The major product obtained in the above reaction is → AIEEE 2011

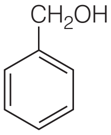
(a) 2-bromophenol (b) 3-bromophenol
(c) 4-bromophenol (d) 2, 4, 6-tribromophenol

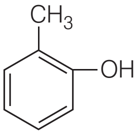
14 Phenol is heated with phthalic anhydride in presence of conc. H_2SO_4, the product gives pink colour with alkali. The product is

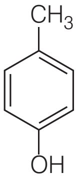
(a) phenolphthalein (b) bakelite
(c) salicylic acid (d) fluorescein

15 The structure of the compound that gives a tribromo derivative on treatment with bromine water is

(a)


(b)


(c)


(d)


16 When benzene sulphonic acid and *p*-nitrophenol are treated with $NaHCO_3$, the gases released respectively, are

(a) SO_2, NO_2 (b) SO_2, NO
(c) SO_2, CO_2 (d) CO_2, CO_2

17 The reaction of phenol with benzoyl chloride to give phenyl benzoate is known as → JEE Main (Online) 2013

(a) Claisen reaction (b) Schotten-Baumann reaction
(c) Reimer-Tiemann reaction (d) Gattermann-Koch reaction

18 Match the following and choose the correct option.

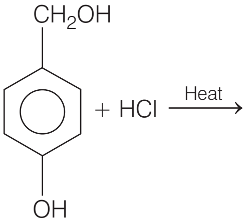
	Column I		Column II
A.	Kolbe's reaction	1.	Conversion of phenol to *o*-hydroxysalicylic acid
B.	Reimer-Tiemann reaction	2.	Conversion of phenol to salicyaldehyde
C.	Conversion of 2°alcohol to ketone	3.	Heated copper at 573 K
D.	Williamson's synthesis	4.	Reaction of alkyl halide with sodium alkoxide

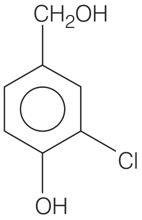
Codes

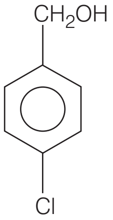
	A	B	C	D		A	B	C	D
(a)	1	2	3	4	(b)	1	4	3	2
(c)	4	3	2	1	(d)	3	4	1	2

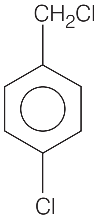
19 The major product in the following reaction.

→ JEE Main (Online) 2013



(a)


(b)


(c)


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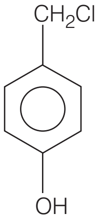
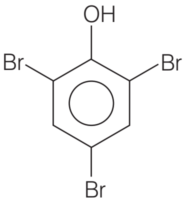
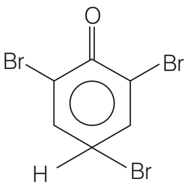


20 What is the structure of the major product when phenol is treated with bromine water?

→ JEE Main (Online) 2013

(a)


(b)


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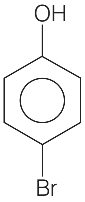

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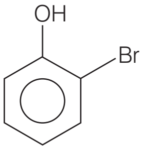
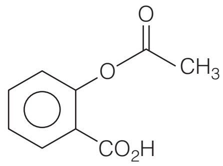
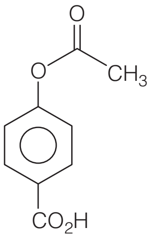


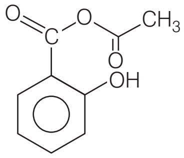
21 An ether (*A*), $C_5H_{12}O$ when heated with excess of hot concentrated HI produced two alkyl halides which when treated with NaOH yielded compounds (*B*) and (*C*). Oxidation of (*B*) and (*C*) gave a propanone and an ethanoic acid respectively. The IUPAC name of the ether (*A*) is → JEE Main (Online) 2013

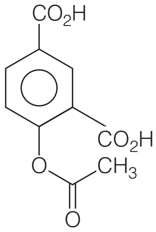
(a) 2-ethoxypropane (b) ethoxypropane
(c) methoxybutane (d) 2-methoxybutane

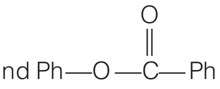
22 Phenol on treatment with CO_2 in the presence of NaOH followed by acidification produces compound *X* as the major product. *X* on treatment with $(CH_3CO)_2O$ in the presence of catalytic amount of H_2SO_4 produces:
→ JEE Main 2018

(a) 

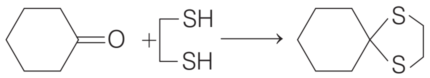
(b) 

(c) 

(d) 

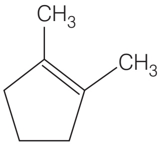
23 Compound  $Ph—O—\overset{\overset{O}{\|}}{C}—Ph$ can be prepared by the reaction of
(a) phenol and benzoic acid in the presence of NaOH
(b) phenol and benzoyl chloride in the presence of pyridine
(c) phenol and benzoyl chloride in the presence of $ZnCl_2$
(d) phenol and benzaldehyde in the presence of palladium

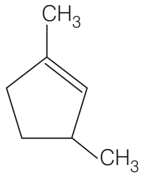
24 Which is the suitable catalyst for bringing out the transformation given below.

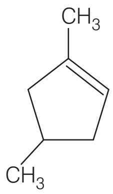


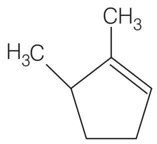
(a) BF_3, Et_2O
(b) NaOEt
(c) Tungsten lamp
(d) dibenzoyl peroxide

25 Which compound would give 5-keto-2-methyl hexanal upon ozonolysis?
→ JEE Main 2015

(a) 

(b) 

(c) 

(d) 

26 The most suitable reagent for the conversion of $R—CH_2—OH \Rightarrow R—CHO$ is
→ JEE Main 2014
(a) $KMnO_4$
(b) $K_2Cr_2O_7$
(c) CrO_3
(d) PCC (pyridinium chlorochromate)

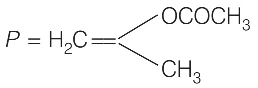
27 In Rosenmund reaction,

$$RCOCl + H_2 \xrightarrow{Pd/BaSO_4} RCHO + HCl$$

$BaSO_4$ here,
(a) promotes catalytic activity of Pd
(b) removes the HCl formed in the reaction
(c) deactivates palladium
(d) activates palladium

28 The formation of aldehyde from alkyl cyanide is related with the name
(a) Stephen reaction
(b) Rosenmund reaction
(c) Wurtz reaction
(d) HVZ reaction

29 The product of acid hydrolysis of *P* and *Q* can be distinguished by



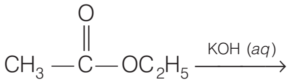
$P = H_2C{=}C\begin{matrix}OCOCH_3\\ CH_3\end{matrix}$, $Q = CH_3CH{=}CHOCOCH_3$

(a) Lucas reagent
(b) 2, 4-DNP
(c) Fehling's solution
(d) $NaHSO_3$

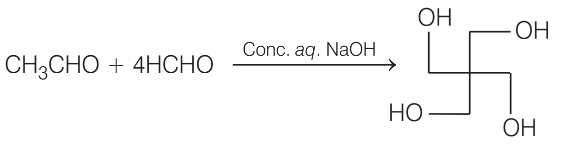
30 Silver mirror test is given by which one of the following compounds?
→ AIEEE 2011
(a) Acetaldehyde
(b) Acetone
(c) Formaldehyde
(d) Benzophenone

31 Clemmensen reduction of a ketone is carried out in the presence of
→ JEE Main (Online) 2013
(a) $LiAlH_4$
(b) Zn-Hg with HCl
(c) glycol with KOH
(d) H_2 with Pt as catalyst

32 Which of the following carbonyl compounds on condensation gives an aromatic compound?
(a) CH_3CHO
(b) HCHO
(c) CH_3COCH_3
(d) CH_3CH_2CHO

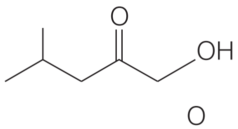
33 α,β-unsaturated aldehyde is formed in the sequence
(a) $HCHO \xrightarrow{KOH(aq)}$
(b) $CH_3CHO \xrightarrow{\text{Dil. KOH}} A \xrightarrow{\Delta} B$
(c) $CCl_3CHO \xrightarrow{KOH\ (aq)}$
(d)  $CH_3—\overset{\overset{O}{\|}}{C}—OC_2H_5 \xrightarrow{KOH\ (aq)}$

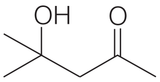
34 The number of aldol reactions that occurs in the given transformation is
→ IIT JEE 2012

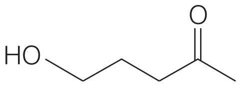


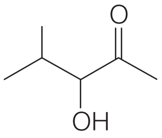
(a) 1
(b) 2
(c) 3
(d) 4

35 Which of the following is the product of aldol condensation? → JEE Main (Online) 2013

(a) 

(b) 

(c) 

(d) 

36 In Cannizzaro reaction given below:

$$2PhCHO \xrightarrow{OH^{\ominus}} PhCH_2OH + PhCO_2^{\ominus}$$

The slowest step is

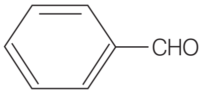
(a) the attack of $OH^{\ominus}$

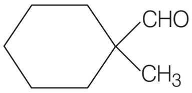
(b) the transfer of hydride to the carbonyl group

(c) the abstraction of proton from the carboxylic group

(d) the deprotonation of $PhCH_2OH$

37 Cannizzaro's reaction is not given by → JEE Main (Online) 2013

(a) 

(b) 

(c) CH_3CHO

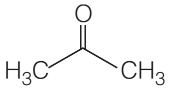
(d) $HCHO$

38 Dry distillation of calcium formate and subsequent treatment with conc. KOH gives the mixture of

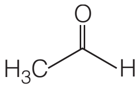
(a) CH_3OH, HCOOK (b) CH_3CHO, HCOOK

(c) HCHO, HCOOK (d) None of the above

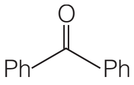
39 The order of reactivity of phenyl magnesium bromide with the following compounds is



(I)



(II)



(III)

(a) II > III > I (b) I > III > II

(c) II > I > III (d) All react with the same rate

40 Iodoform can be prepared from all except → AIEEE 2012

(a) ethyl methyl ketone (b) isopropyl alcohol

(c) 3-methyl-2-butanone (d) isobutyl alcohol

41 Both HCHO and CH_3CHO give similar reactions with all the reagents except

(a) Schiff's reagent (b) Fehling solution

(c) ammoniacal $AgNO_3$ (d) ammonia

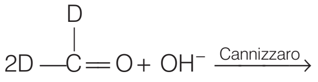
42 The reagent which does not react with both, acetone and benzaldehyde.

(a) Sodium hydrogen sulphite

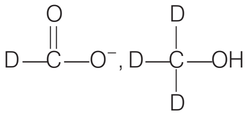
(b) Phenyl hydrazine

(c) Fehling's solution

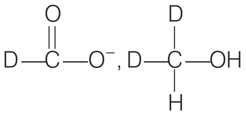
(d) Grignard reagent

43 

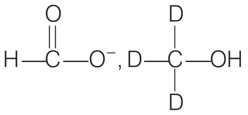
$2D-\overset{D}{\overset{|}{C}}=O + OH^- \xrightarrow{\text{Cannizzaro}}$ X and Y (Y is alcohol, D is deuterium). X and Y will have structure

(a) 

$D-\overset{O}{\overset{||}{C}}-O^-, D-\underset{D}{\overset{D}{C}}-OH$

(b) 

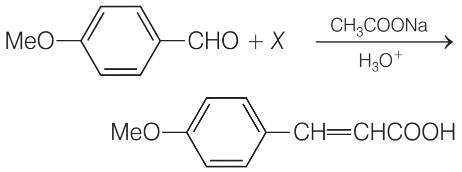
$D-\overset{O}{\overset{||}{C}}-O^-, D-\underset{H}{\overset{D}{C}}-OH$

(c) 

$H-\overset{O}{\overset{||}{C}}-O^-, D-\underset{D}{\overset{D}{C}}-OH$

(d) None of these

44



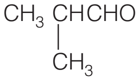
The compound X is

(a) CH_3COOH (b) $BrCH_2-COOH$

(c) $(CH_3CO)_2O$ (d) $CHO-COOH$

45 Which of the following compounds neither forms semicarbazone nor oxime?

(a) HCHO (b) $CH_3CONHCH_3$

(c) CH_3COCH_2Cl (d) 

$CH_3\underset{CH_3}{\underset{|}{CH}}CHO$

46 In the reaction,

$$C_6H_5CHO + (CH_3CO)_2O \xrightarrow{CH_3COONa} A,$$

product A is

(a) acetaldehyde (b) cinnammic acid

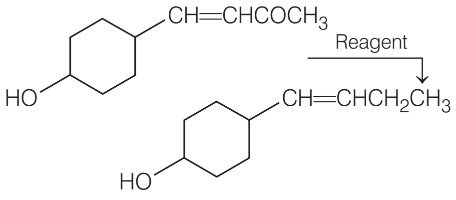
(c) β-naphthol (d) phenol

47 Formaldehyde can be distinguished from acetaldehyde by the use of → JEE Main (Online) 2013

(a) Schiff's reagent (b) Tollen's reagent

(c) I_2, alkali (d) Fehling's solution

48 In the given transformation, which of the following is the most appropriate reagent? → AIEEE 2012



(a) NH_2NH_2, OH^- (b) Zn-Hg /HCl

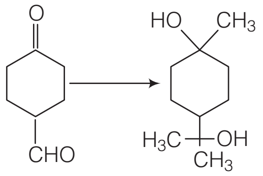
(c) Na, liq. NH_3 (d) $NaBH_4$

49 Trichloroacetaldehyde was subjected to Cannizzaro's reaction by using NaOH. The mixture of the products contains sodium trichloroacetate ion and another compound. The other compound is → AIEEE 2011

(a) 2, 2, 2-trichloroethanol (b) trichloromethanol

(c) 2, 2, 2-trichloropropanol (d) chloroform

50 The correct sequence of reagents for following conversion will be ➞ JEE Main 2017



(a) $[Ag(NH_3)_2]^+OH^- H^+/CH_3OH, CH_3MgBr$
(b) $CH_3MgBr, H^+/CH_3OH, [Ag(NH_3)]^+OH^-$
(c) $CH_3MgBr, [Ag(NH_3)^2]^+OH^-, H^+/CH_3OH$
(d) $[Ag(NH_3)_2]^+OH^-, CH_3MgBr, H^+/CH_3OH$

51 Identify the correct order of boiling points of the following compounds

$CH_3CH_2CH_2CH_2OH$, $CH_3CH_2CH_2CHO$, $CH_3CH_2CH_2COOH$
A B C

(a) $A > B > C$ (b) $C > A > B$
(c) $A > C > B$ (d) $C > B > A$

52 Monocarboxylic acids are functional isomers of ➞ JEE Main (Online) 2013

(a) ethers (b) amines
(c) esters (d) alcohols

53 A liquid was mixed with ethanol and a drop of concentrated H_2SO_4 was added. A compound with a fruity smell was formed. The liquid was

(a) CH_3OH (b) HCHO
(c) CH_3COCH_3 (d) CH_3COOH

54 $C_8H_6O_4 \xrightarrow{\Delta} X \xrightarrow{NH_3} Y$

The compound X is

(a) o-xylene (b) phthalic acid
(c) phthalic anhydride (d) salicylic acid

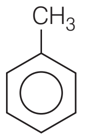
55 In the following sequence of reaction,

Toluene $\xrightarrow{KMnO_4} A \xrightarrow{SOCl_2} B \xrightarrow[BaSO_4]{H_2/Pd} C$

The product C is ➞ JEE Main 2015

(a) C_6H_5COOH (b) $C_6H_5CH_3$
(c) $C_6H_5CH_2OH$ (d) C_6H_5CHO

56

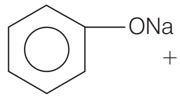


$\xrightarrow{[O]} A \xrightarrow{SOCl_2} B \xrightarrow{NaN_3} C \xrightarrow{Heat} D$

What is D in the above sequence?

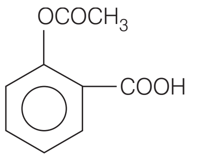
(a) An amide
(b) Primary amine
(c) Phenyl isocyanate
(d) None of the above

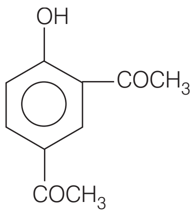
57 Sodium phenoxide when heated with CO_2 under pressure at 125°C yields a product which on acetylation produces C.



$+CO_2 \xrightarrow[5\text{ atm}]{125°} B \xrightarrow[Ac_2O]{H^+} C$

The major product C would be ➞ JEE Main 2014

(a)


(b)


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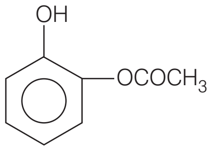

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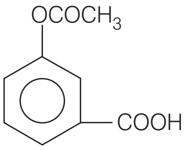


58 In the reaction,

$CH_3COOH \xrightarrow{LiAlH_4} A \xrightarrow{PCl_5} B \xrightarrow{Alc.KOH} C$

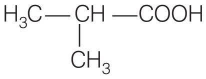
The product C is ➞ JEE Main 2014

(a) acetaldehyde (b) acetylene
(c) ethylene (d) acetyl chloride

59 Sodium ethoxide has reacted with ethanoyl chloride. The compound that is produced in the above reaction is ➞ AIEEE 2011

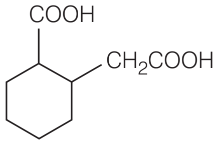
(a) diethyl ether (b) 2-butanone
(c) ethyl chloride (d) ethyl ethanoate

60 An organic compound A upon reacting with NH_3 gives B. On heating B, gives C. C in presence of KOH reacts with Br_2 to give $CH_3CH_2NH_2$. A is ➞ IIT JEE Main 2013

(a) $CH_3CH_2CH_2COOH$ (b)

$H_3C-\underset{CH_3}{\underset{|}{CH}}-COOH$

(c) CH_3CH_2COOH (d) CH_3COOH

61 The compound that undergoes decarboxylation most readily under mild condition is [IIT JEE 2012]

(a)


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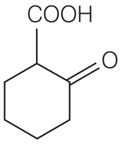

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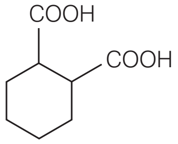

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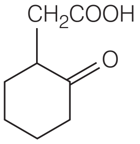
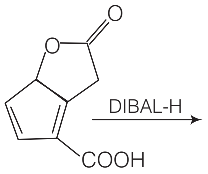
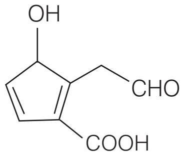
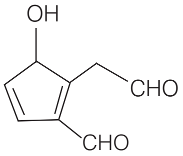


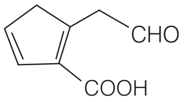
62 The major product obtained in the following reaction is

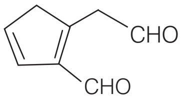


➞ JEE Main 2017

(a) 

(b) 

(c) 

(d) 

63. Which of the following reagents may be used to distinguish between phenol and benzoic acid?

(a) Aqueous NaOH (b) Tollen's reagent
(c) Molisch reagent (d) Neutral $FeCl_3$

Direction (Q. Nos. 64-69) *In the following questions, Assertion* (A) *followed by a Reason* (R) *is given. Choose the correct answer out of the following choices.*

(a) Both A and R are true and R is correct explanation of A
(b) Both A and R are true but R is not correct explanation of A
(c) A is false but R is true
(d) Both A and R are false

64 **Assertion** (A) Formaldehyde is a planar molecule.

Reason (R) It contains sp^2-hybridised carbon atom.

65 **Assertion** (A) Like bromination of benzene, bromination of phenol is also carried out in the presence of Lewis acid.

Reason (R) Lewis acid polarises the bromine molecule.

66 **Assertion** (A) Solubility of *n*-alcohol in water decreases with increase in molecular weight.

Reason (R) The reactive proportion of the hydrocarbon part in alcohols increases with increasing molecular weight which permits enhanced hydrogen bonding with water.

67 **Assertion** (A) *p*-nitrophenol is a stronger acid than *o*-nitrophenol.

Reason (R) Intramolecular hydrogen bonding makes the *o*-isomer weaker than the *p*-isomer.

68 **Assertion** (A) Acetic acid does not undergo haloform reaction.

Reason (R) Acetic acid has no alpha hydrogen.

69 **Assertion** (A) *p*-hydroxy benzoic acid has lower boiling point than *o*-hydroxy benzoic acid.

Reason (R) *o*-hydroxy benzoic acid has intramolecular hydrogen bonding.

DAY PRACTICE SESSION 2

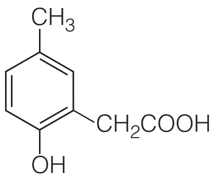
PROGRESSIVE QUESTIONS EXERCISE

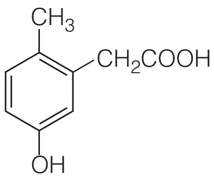
1 I. 1, 2– dihydroxy benzene
II. 1, 3– dihydroxy benzene
III. 1, 4 – dihydroxy benzene
IV. Hydroxy benzene

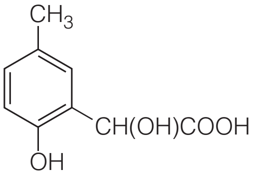
The increasing order of boiling points of above mentioned alcohols is

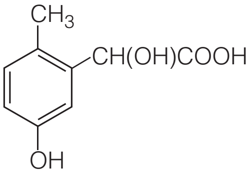
(a) I < II < III < IV
(b) I < II < IV < III
(c) IV < I < II < III
(d) IV < II < I <III

2 *p*-cresol reacts with chloroform in alkaline medium to give the compound *A* which adds hydrogen cyanide to form the compound *B*. The latter, on acidic hydrolysis gives chiral carboxylic acid. The structure of the carboxylic acid is

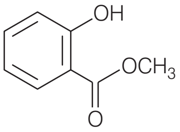
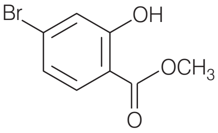
(a) 

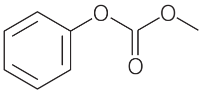
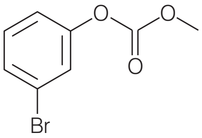
(b) 

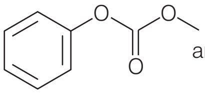
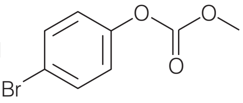
(c) 

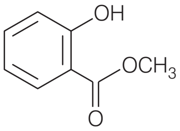
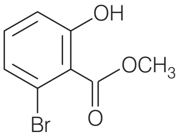
(d) 

3 Phenol reacts with methyl chloroformate in the presence of NaOH to form product *A*. *A* reacts with Br_2 to form product *B*. *A* and *B* are respectively → JEE Main 2018

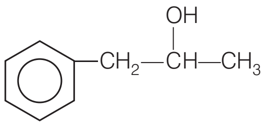
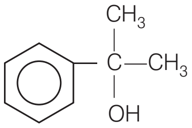
(a)  and 

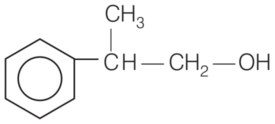
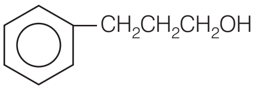
(b)  and 

(c)  and 

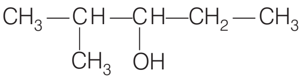
(d)  and 

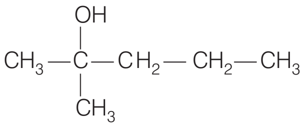
4 An unknown compound (*A*), $C_9H_{12}O$ have four isomeric structures. All the compounds react with sodium to give odourless and colourless gas except one. The three out of the four pre oxidised by hot $KMnO_4$ / OH^- to produce benzoic acid. One another isomer does not respond iodoform test. But one isomer out of these four fulfills all the conditions. The isomer is

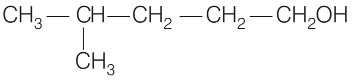
(a)  (b) 

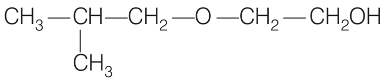
(c)  (d) 

5 An alcohol ‘*A*’ when heated with copper gives a product ‘ *B*’ not having oxygen atom. ‘*B*’ on ozonolysis gives two isomeric product ‘*C*’ and ‘*D*’. ‘*C*’on oxidation gives a monobasic acid ‘*E*’, silver salt of which contains 59.6% Ag. The structure of ‘*A*’ is

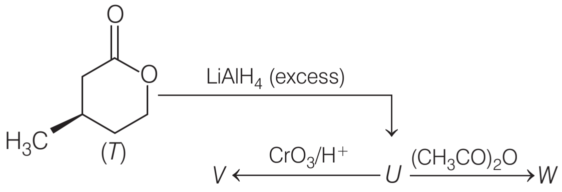
(a) 
$CH_3-\underset{CH_3}{CH}-\underset{OH}{CH}-CH_2-CH_3$

(b) 
$CH_3-\overset{OH}{\underset{CH_3}{C}}-CH_2-CH_2-CH_3$

(c) 
$CH_3-\underset{CH_3}{CH}-CH_2-CH_2-CH_2OH$

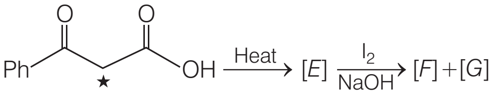
(d) 
$CH_3-\underset{CH_3}{CH}-CH_2-O-CH_2-CH_2OH$

6 With reference to the scheme given, which of the given statement about *T*, *U*, *V* and *W* is incorrect?

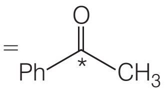
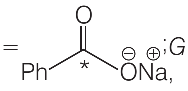


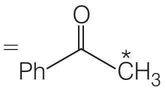
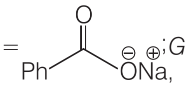
(a) *T* is soluble in hot aqueous NaOH
(b) *V* is optically active
(c) Molecular formula of *W* is $C_{10}H_{18}O_4$
(d) *V* gives effervescence on treatment with aqueous $NaHCO_3$

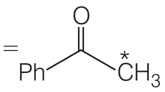
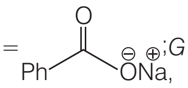
7 In the following reaction sequence, the correct structures of *E*, *F* and *G* are,

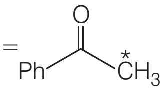
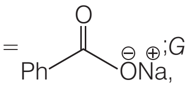


(* implies ^{13}C labelled carbon)

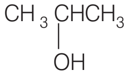
(a) E =  F =  ;$G = CHI_3$

(b) E =  F =  ;$G = CHI_3$

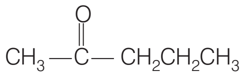
(c) E =  F =  ;$G = \overset{*}{C}HI_3$

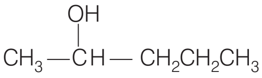
(d) E =  F =  ;$G = \overset{*}{C}H_3I$

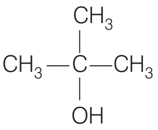
8 An organic compound containing C,H and O gives red colouration with sodium nitroprusside solution but does not reduce Tollen’s reagent and yields chloroform on treating with NaOH and Cl_2. The compound is

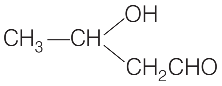
(a) CH_3CH_2OH
(b) 
$CH_3\underset{OH}{CH}CH_3$
(c) CH_3COCH_3
(d) $(CH_3)_3CH-CHO$

9 An organic compound (*A*), $C_4H_8O_2$, on treatment with an equivalent of C_2H_5MgBr gives (*B*), which do not respond to iodoform test. (*B*) on treatment with $LiAlH_4$ gives (*C*) which respond to Lucas test in 5-10 minutes. (*C*) upon treatment with H^+/ HCl gives (*D*), which on reaction with KOH (*aq*) gave (*E*) which is oxidised with CrO_3 to form (*F*). (*E*) and (*F*) can respond positively to iodoform test. (*F*) can also be obtained by treating butyl methanoate with one equivalent of *n*-prMgBr, H_2O / H^+. Based on this information, (*F*) is

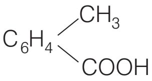
(a) 
$CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_2CH_3$

(b) 
$CH_3-\overset{\overset{OH}{|}}{C}H-CH_2CH_2CH_3$

(c) 
$CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

(d) 
$CH_3-CH\begin{matrix}OH\\CH_2CHO\end{matrix}$

10 The freezing point constant of C_6H_6 is 4.90 K mol^{-1} and its melting point 5.51°C. A solution of 0.816 g of compound '*A*' when dissolved in 7.5 g of benzene, freezes at 1.59°C. The compound '*A*' has C = 70.58%, H = 5.88% and the rest is oxygen. Compound '*A*' on heating with sodalime gives another compound '*B*' which on oxidation and subsequent acidification gives an acid '*C*' of equivalent weight 122. '*C*' on heating with sodalime gives benzene. The compound '*A*' is

(a) 
$C_6H_4\begin{matrix}CH_3\\COOH\end{matrix}$

(b) $C_6H_5CH_2COOH$

(c) Both (a) and (b)

(d) None of these

11 The major product formed in the following reaction is

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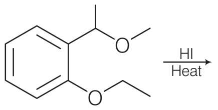
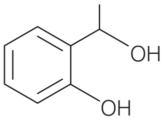
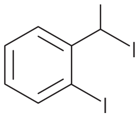
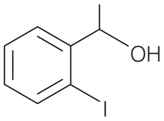
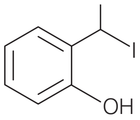


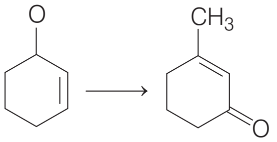
(a) 

(b) 

(c) 

(d) 

12 Which is the correct combination of reagent which can carry out following conversions?



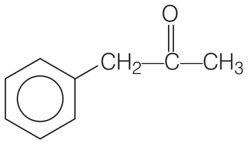
(a) (i) CH_3—MgBr then H^+ (ii) H_2SO_4 / Δ (iii) NH_2—NH_2/KOH

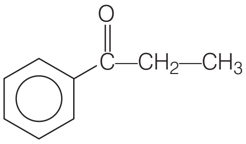
(b) (i) $(CH_3)_2$ CuLi then H^+ (ii) $NaBH_4$/EtOH (iii) H_2SO_4 / Δ

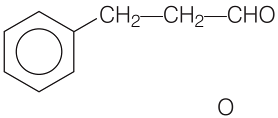
(c) CH_3—Li then H^+ (ii) PCC/Δ

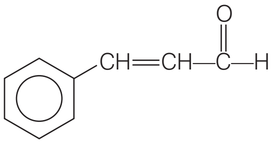
(d) $NaBH_4$. $CeCl_3$ then H^+ (ii) MnO_2 (iii) CH_3—Li

13 An organic compound (*A*) with molecular formula $C_9H_{10}O$ forms an orange-red precipitate with 2,4-DNP reagent and gives yellow precipitate on heating with iodine and NaOH. It does not reduce Tollen's reagent or Fehling's solution nor it decolourises bromine water as Baeyer's reagent. On drastic oxidation with chromic acid, it gives a carboxylic acid having molecular formula $C_7H_6O_2$. Identify the compound (*A*).

(a) 

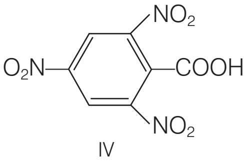
(b) 

(c) 

(d) 

14 Give the order of ease of decarboxylation of the following acids.

$\underset{I}{CH_3COOH}$; $\underset{II}{CH_2=CH-CH_2COOH}$; $\underset{III}{CH_2(COOH)_2}$



IV

(a) I > II > III > IV

(b) III > IV > II > I

(c) IV > III > II > I

(d) I > III > II > IV

15 Reaction of cyclohexanone with dimethylamine in the presence of catalytic amount of an acid forms a compound. Water during the reaction is continuously removed. The compound formed is generally known as

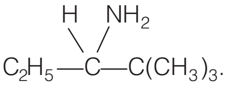
(a) an amine

(b) an imine

(c) an enamine

(d) a Schiff's base `

16 A product obtained by the reaction of *X* with hydroxylamine and on further reduction gives


$C_2H_5-\overset{H\ \ NH_2}{\overset{\backslash\ /}{C}}-C(CH_3)_3$. Hence, the compound *X* can be

(a) 2,2-dimethyl-3-pentanone

(b) 3,3-dimethyl-3-butanone

(c) 1-methyl-3-pentanone

(d) diethyl ketone

17 An ester (*A*) with molecular formula $C_9H_{10}O_2$ was treated with excess of CH_3MgBr and the complex so formed was treated with H_2SO_4 to give an olefin (*B*). Ozonolysis of (*B*) gave a ketone with molecular formula C_8H_8O which shows positive iodoform test. The structure of (*A*) is

(a) $C_6H_5COOC_2H_5$

(b) $C_6H_5COOC_6H_5$

(c) $C_6H_5COOCH_3$

(d) *p*-$H_3CO-C_6H_4COCH_3$

ANSWERS

SESSION 1	**1** (a)	**2** (b)	**3** (d)	**4** (b)	**5** (a)	**6** (b)	**7** (a)	**8** (d)	**9** (c)	**10** (c)
	11 (c)	**12** (a)	**13** (d)	**14** (a)	**15** (a)	**16** (d)	**17** (b)	**18** (a)	**19** (d)	**20** (a)
	21 (a)	**22** (a)	**23** (b)	**24** (a)	**25** (b)	**26** (d)	**27** (c)	**28** (a)	**29** (c)	**30** (a)
	31 (b)	**32** (c)	**33** (b)	**34** (d)	**35** (b)	**36** (b)	**37** (c)	**38** (a)	**39** (c)	**40** (d)
	41 (d)	**42** (c)	**43** (a)	**44** (c)	**45** (b)	**46** (b)	**47** (c)	**48** (a)	**49** (a)	**50** (a)
	51 (b)	**52** (c)	**53** (d)	**54** (c)	**55** (d)	**56** (c)	**57** (a)	**58** (c)	**59** (d)	**60** (c)
	61 (b)	**62** (a)	**63** (d)	**64** (a)	**65** (d)	**66** (c)	**67** (a)	**68** (c)	**69** (d)	
SESSION 2	**1** (c)	**2** (c)	**3** (c)	**4** (a)	**5** (b)	**6** (b)	**7** (c)	**8** (c)	**9** (a)	**10** (c)
	11 (d)	**12** (c)	**13** (a)	**14** (c)	**15** (c)	**16** (a)	**17** (a)			

Hints and Explanations

SESSION 1

1 With the increase in molecular mass, the boiling points also increases. Amongst isomeric alcohols, the boiling points decrease with branching due to decrease in surface area. Thus, the correct increasing order of boiling point is

propan-1-ol < butan-2-ol < butan-1-ol < pentan-1-ol

2 The reaction of alcohol with conc. HCl and anhydrous $ZnCl_2$ follows S_N1 pathway, so greater the stability of carbocation formed, faster is the reaction. 2-methylpropan-2-ol forms 3° carbocation.

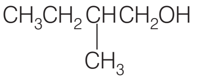
Hence, it reacts rapidly with conc. HCl and anhyd. $ZnCl_2$ (Lucas reagent).

3 Conc. HCl and $ZnCl_2$ is Lucas reagent and 3° alcohols (alcohols having —C—OH group) react fastest with it.

The structures of the given alcohols are as

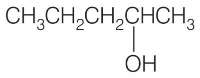
$CH_3CH_2CH_2CH_2CH_2OH$

Pentanol (1° alcohol)



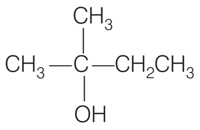
$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2OH$

2-methylbutanol
(1° alcohol)



$CH_3CH_2CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$

2-pentanol
(2° alcohol)



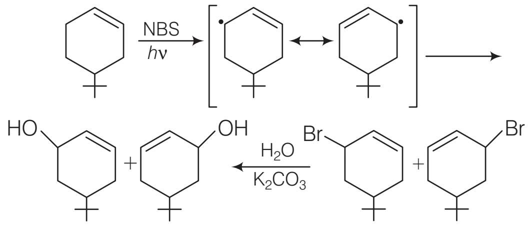
$CH_3—\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}—CH_2CH_3$

2-methylbutan-2-ol
(3° alcohol)

Hence, 2-methylbutan-2-ol reacts fastest with the given reagent.

4 The reaction of alcohol with Lucas reagent occur through S_N1 mechanism and the rate of reaction is directly proportional to the stability of carbocation formed in the reaction. Since, 3° alcohol forms 3° carbocation (most stable) hence, it will react fastest.

5

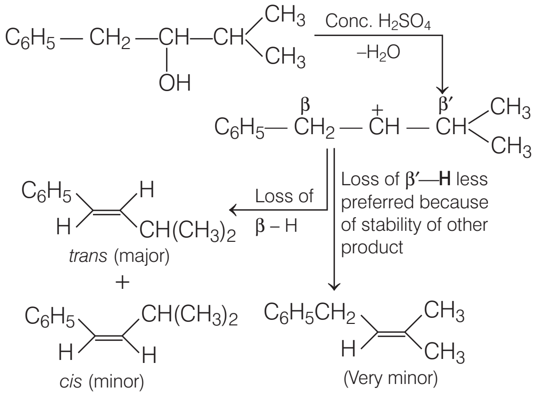


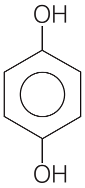
6 Dehydration of alcohols takes place according to Saytzeff rule. In acid catalysed dehydration, formation of most stable carbocation takes place.

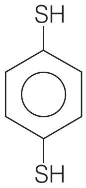
Thus, the order of dehydration of alcohols is

$$3° > 2° > 1° > CH_3OH.$$

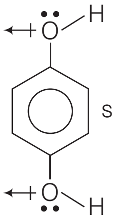
7



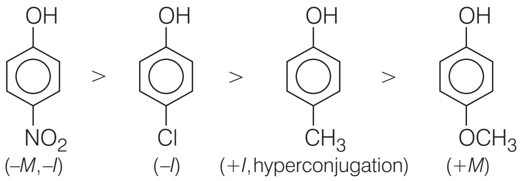
8 In the quinol 

and thioquinol 

—OH groups and —SH groups do not cancel their dipole moment as they exist in different confirmation.

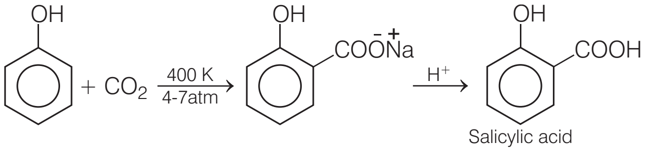


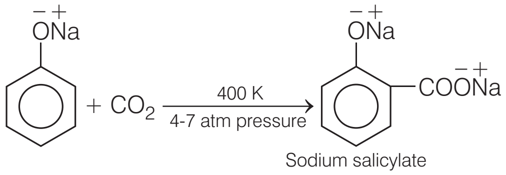
same as in thioquinol.

9 

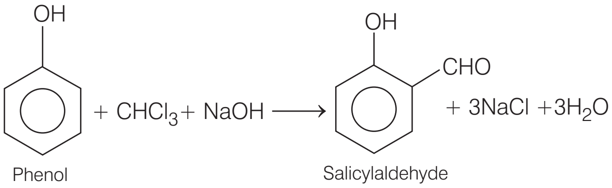
Electron releasing group decreases while electron withdrawing group increases acidic strength by destabilising and stabilising the phenoxide ion formed respectively.

10 Salicylic acid is obtained as a major product by the interaction of phenol with NaOH and CO_2 at 400 K and 4-7 atm. This reaction is called Kolbe's reaction.



11 

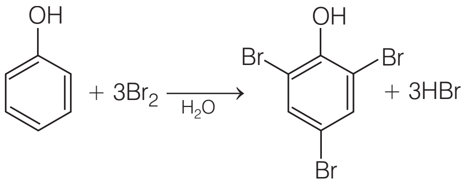
12 This reaction is known as Reimer-Tiemann reaction.



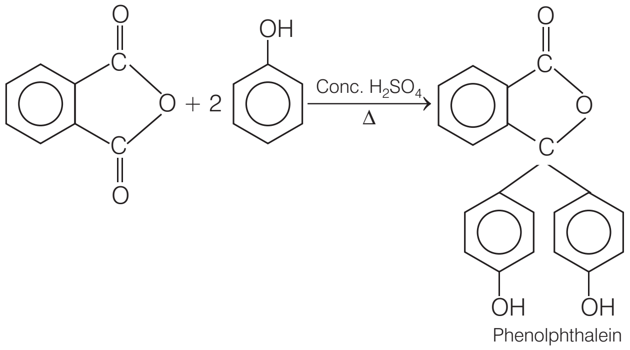
13 Br_2 is formed by a redox reaction,

$$5Br^- + BrO_3^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$$

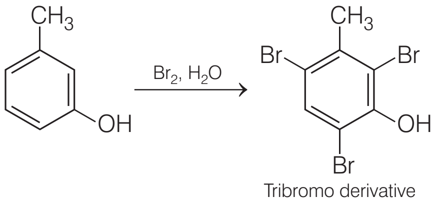
—OH group is the activating group and there is S_E at *o*-and *p*-positions giving yellowish white precipitate of 2, 4, 6-tribromophenol.

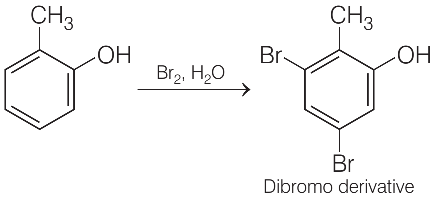


14 Phenol is heated with phthalic anhydride in presence of conc. H_2SO_4 to give phenolphthalein which gives pink colour with alkali.



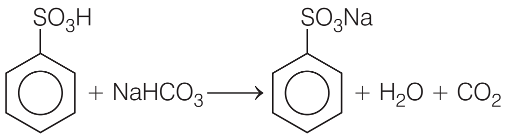
15 *m*-cresol, due to phenoxide ion in H_2O solvent, gives tribromo derivative at all *ortho*-and *para*-positions.

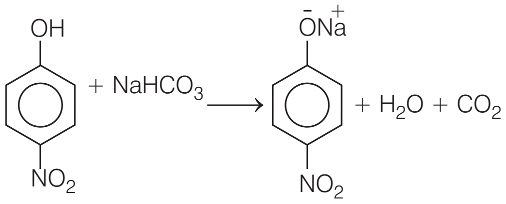




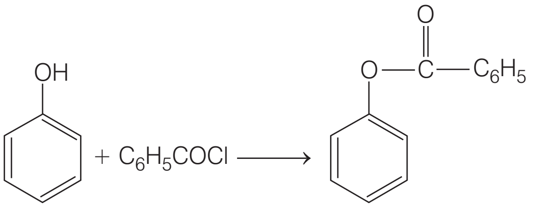
16 Benzene sulphonic acid and *p*-nitrophenol both are stronger acids than $H_2CO_3 (H_2O + CO_2)$, so they are capable to evolve CO_2 when reacts with $NaHCO_3$.

$$HCO_3^- + \underset{\text{Acid}}{H^+} \longrightarrow H_2O + CO_2 \uparrow$$





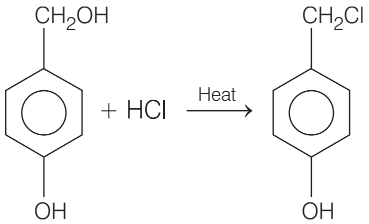
17 The reaction of phenol with benzoyl chloride to give phenyl benzoate is also known as Schotten-Baumann reaction.



Phenyl benzoate

18 $A \longrightarrow 1, B \longrightarrow 2, C \longrightarrow 3, D \longrightarrow 4$

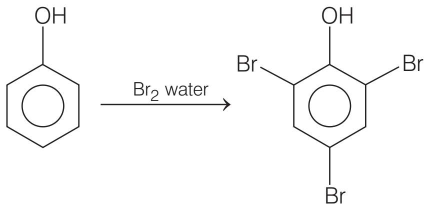
19



Major product

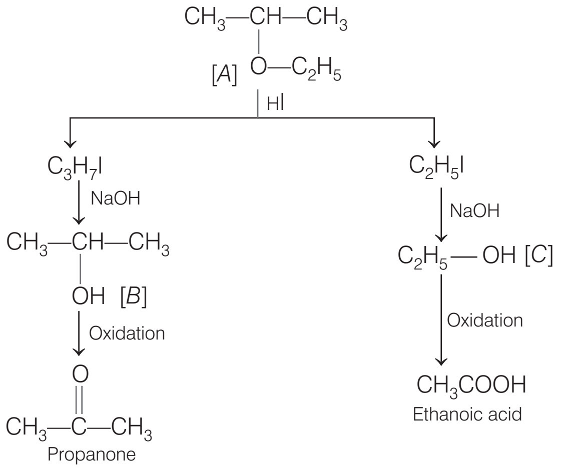
Only aliphatic —OH is substituted by Cl^-. This is because in phenol the C—O bond is stabilised by resonance.

20

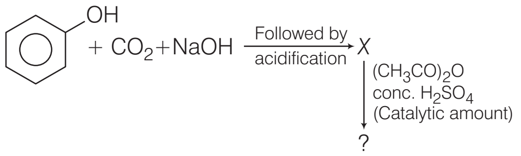


2, 4, 6-tribromophenol

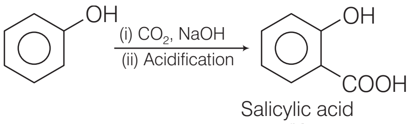
21 Ether (*A*) is 2-ethoxypropane



22

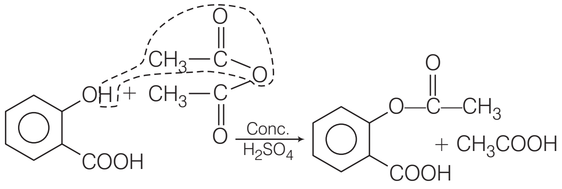


The very first reaction in the above road map looks like Kolbe's reaction which results to salicylic acid as :



Salicylic acid
(*X*)

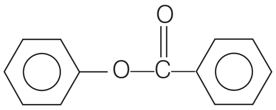
The salicylic acid with acetic anhydride $[(CH_3CO)_2O]$ in the presence of catalytic amount of conc. H_2SO_4 undergoes acylation to produce aspirin as :



Acetyl salicylic acid (Aspirin)

Aspirin is a non-narcotic analgesic (Cpain killer).

23 For the reaction of

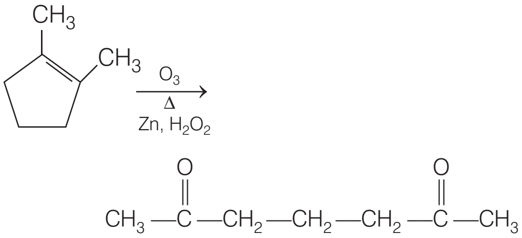


following reaction takes place.

24 BF_3 increases the electrophilicity of carbonyl carbon due to which sulphur attacks on carbonyl carbon.

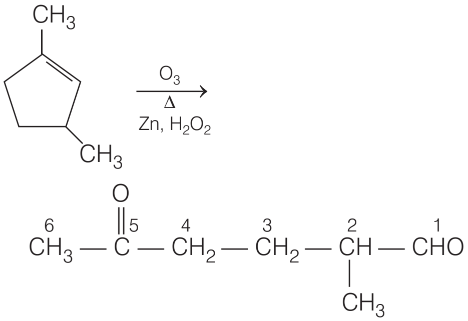
25

(a)



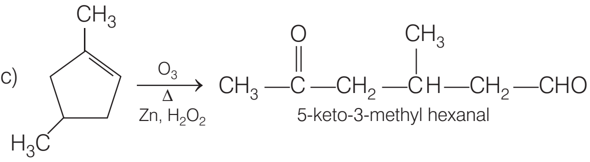
Heptane-2,6-diketone

(b)



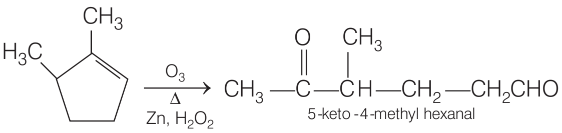
5-keto-2-methylhexanal

(c)



5-keto-3-methyl hexanal

(d)



5-keto -4-methyl hexanal

26 $R-CH_2OH \xrightarrow{PCC} R-CH=O$

Pyridinium chlorochromate is the mild oxidising agent which causes conversion of alcohol to aldehyde stage. While others causes conversion of alcohol to acid.

27 $BaSO_4$ decreases the activity of Pd.

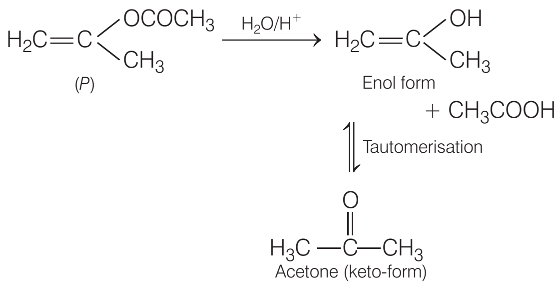
$$RCOCl + H_2 \xrightarrow{Pd/BaSO_4} RCHO + HCl$$

28 Formation of aldehyde from alkyl cyanide takes place by Stephen's reaction.

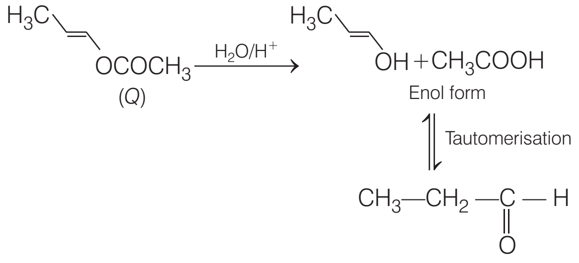
$$\underset{\text{Alkyl cyanide}}{RCN} + 2H \xrightarrow{SnCl_2+HCl} \underset{\text{Iminochloride}}{R\,CH=NH\cdot HCl}$$

$$\xrightarrow{H_2O} \underset{\text{Aldehyde}}{RCHO} + NH_4Cl + H_2O$$

29



Fehling's solution is not reduced with acetone.



Fehling solution is reduced with aldehyde, i.e. CH_3CH_2CHO. Hence, the product of acid hydrolysis of *P* (ketone) and *Q* (aldehyde) can be distinguished by Fehling's solution.

30 All aldehydes including reducing sugar (as glucose, fructose) give silver-mirror test (with Tollen's reagent).

$$RCHO + 2[Ag(NH_3)_2]^+ + 3OH^- \xrightarrow{\Delta}$$

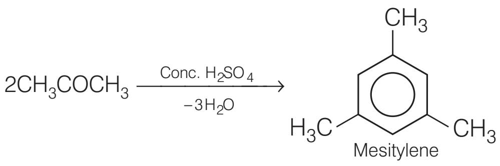
$$RCOO^- + \underset{\text{Silver mirror}}{2Ag\downarrow} + 4NH_3 + 2H_2O\ (R = H, CH_3)$$

Thus, (a) acetaldehyde and (c) formaldehyde give silver-mirror test.

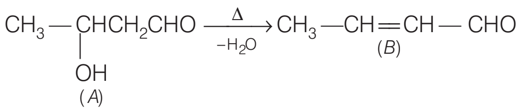
31 Zn - Hg with HCl is called Clemmensen reagent. It reduces the $>C=O$ group of a ketone into $>CH_2$ group. Thus, the reaction is called Clemmensen reduction.

$$>C=O \xrightarrow[\text{Conc. HCl}]{\text{Zn-Hg}} >CH_2$$

32

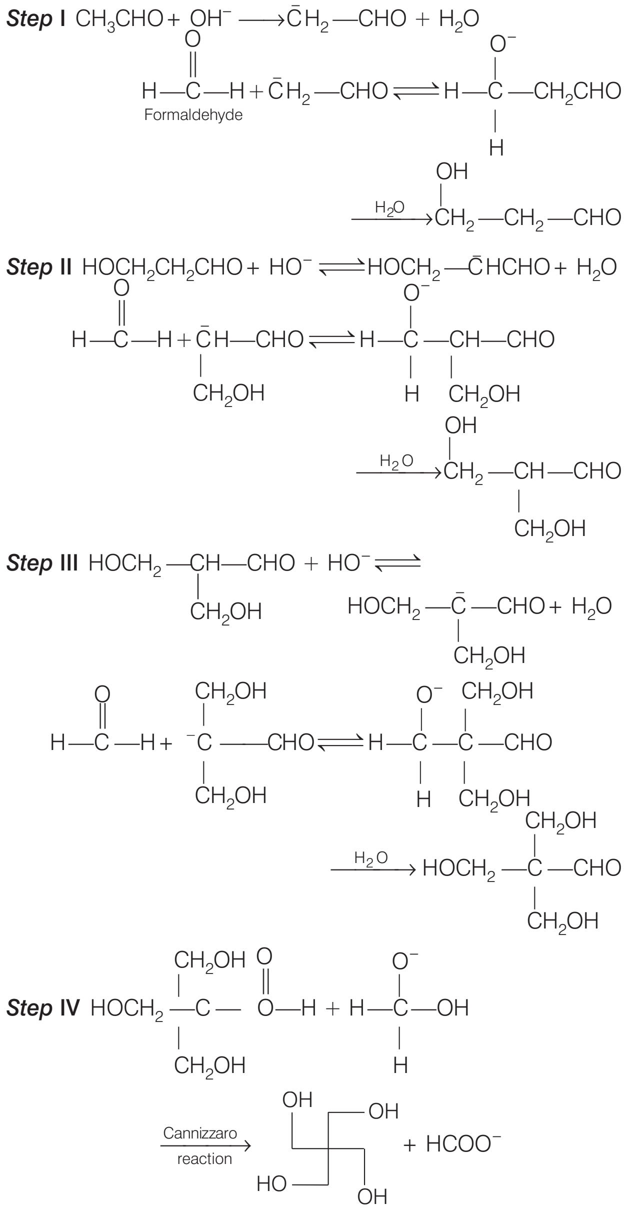


33 $2CH_3CHO \xrightarrow[\text{Aldol condensation}]{\text{Dil. NaOH}}$



$$\underset{(A)}{CH_3-\underset{OH}{\underset{|}{C}H}CH_2CHO} \xrightarrow[-H_2O]{\Delta} \underset{(B)}{CH_3-CH=CH-CHO}$$

34 The given reaction is an example of repeated aldol condensation followed by Cannizzaro reaction.



Step I $CH_3CHO + OH^- \longrightarrow \bar{C}H_2-CHO + H_2O$

$$\underset{\text{Formaldehyde}}{H-\overset{O}{\overset{\|}{C}}-H} + \bar{C}H_2-CHO \rightleftharpoons H-\overset{O^-}{\overset{|}{\underset{H}{\underset{|}{C}}}}-CH_2CHO$$

$$\xrightarrow{H_2O} \overset{OH}{\overset{|}{C}}H_2-CH_2-CHO$$

Step II $HOCH_2CH_2CHO + HO^- \rightleftharpoons HOCH_2-\bar{C}HCHO + H_2O$

$$H-\overset{O}{\overset{\|}{C}}-H + \underset{CH_2OH}{\underset{|}{\bar{C}H}}-CHO \rightleftharpoons H-\overset{O^-}{\overset{|}{\underset{H}{\underset{|}{C}}}}-\underset{CH_2OH}{\underset{|}{CH}}-CHO$$

$$\xrightarrow{H_2O} \overset{OH}{\overset{|}{C}}H_2-\underset{CH_2OH}{\underset{|}{CH}}-CHO$$

Step III $HOCH_2-\underset{CH_2OH}{\underset{|}{CH}}-CHO + HO^- \rightleftharpoons$

$$HOCH_2-\underset{CH_2OH}{\underset{|}{\bar{C}}}-CHO + H_2O$$

$$H-\overset{O}{\overset{\|}{C}}-H + {}^-\overset{CH_2OH}{\overset{|}{\underset{CH_2OH}{\underset{|}{C}}}}-CHO \rightleftharpoons H-\overset{O^-}{\overset{|}{\underset{H}{\underset{|}{C}}}}-\overset{CH_2OH}{\overset{|}{\underset{CH_2OH}{\underset{|}{C}}}}-CHO$$

$$\xrightarrow{H_2O} HOCH_2-\overset{CH_2OH}{\overset{|}{\underset{CH_2OH}{\underset{|}{C}}}}-CHO$$

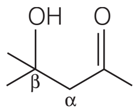
Step IV $HOCH_2-\overset{CH_2OH}{\overset{|}{\underset{CH_2OH}{\underset{|}{C}}}}-\overset{O}{\overset{\|}{O}}-H + H-\overset{O^-}{\overset{|}{\underset{H}{\underset{|}{C}}}}-OH$

$$\xrightarrow[\text{reaction}]{\text{Cannizzaro}}$$

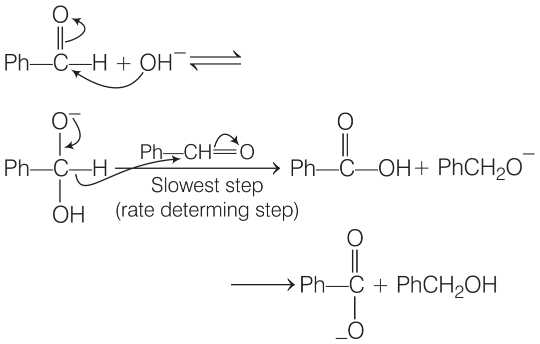
$+ HCOO^-$

In the last step, formaldehyde is oxidised and the other aldehyde is reduced giving the desired product.

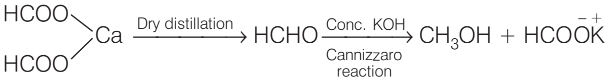
35 When two aldehydes or ketones (or carbonyl compounds) having α-hydrogen atoms react in the presence of a base, they result in the formation of β -hydroxy aldehyde or ketone called the aldol or ketol and the reaction is called aldol condensation.

Thus,  is the product of aldol condensation.

36 In Cannizzaro reaction, the transfer of H^- to another carbonyl group is difficult.

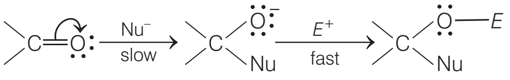


37 Only those aldehydes undergo Cannizzaro reaction in the presence of concentrated base, which have lack of α-H atom. CH_3CHO contains three α-H atoms, that's why it does not undergo Cannizzaro's reaction, rather it undergoes aldol condensation.

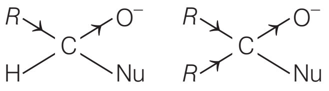
38 

$$(HCOO)_2Ca \xrightarrow{\text{Dry distillation}} HCHO \xrightarrow[\text{Cannizzaro reaction}]{\text{Conc. KOH}} CH_3OH + HCO\overset{-}{O}\overset{+}{K}$$

39 In phenyl magnesium bromide, phenyl is attached with that C-atom of carbonyl group which has low electron density (higher electropositive charge). In carbonyl compounds, aldehydes are more reactive, towards nucleophile in nucleophilic addition reactions because in ketones alkyl groups is present on both sides (due to $+I$ effect) which decreases the electropositive charge of carbon of carbonyl group.



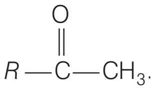
Hence, attraction of nucleophile decreases. Moreover in the tetrahedral intermediate, aldehydes have less steric repulsion than ketones and also the aldehyde increases the negative charge on oxygen less in comparison of ketones.

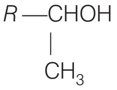


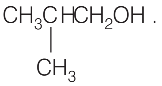
Therefore, the order of reactivity of acetone (I), acetaldehyde (II) and benzophenone (III) with PhMgBr is (II) > (I) > (III).

40 Iodoform reaction shown by the following compounds.

(i) CH_3CH_2OH (ii) CH_3CHO

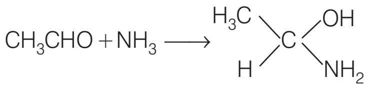
(iii) All carbonyl compounds of the type  $R—\overset{O}{\overset{\|}{C}}—CH_3$.

(iv) 2° alcohol  $R—\underset{CH_3}{\underset{|}{C}}HOH$

Therefore, iodoform is not prepared from  $CH_3\underset{CH_3}{\underset{|}{C}}HCH_2OH$.

41 HCHO and CH_3CHO give different reactions with NH_3.

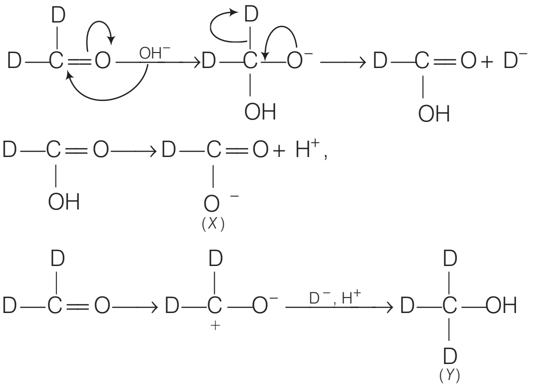
$$6HCHO + 4NH_3 \longrightarrow \underset{\text{Urotropine}}{(CH_2)_6N_4} + 6H_2O$$

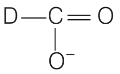


$$CH_3CHO + NH_3 \longrightarrow (H_3C)(H)C(OH)(NH_2)$$

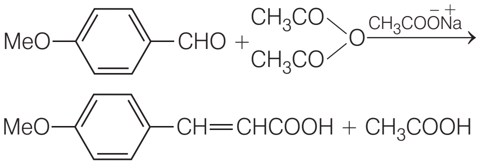
Acetaldehyde ammonia

42 With Fehling's solution, both acetone and benzaldehyde do not react. Only aliphatic aldehydes react with Fehling solution.

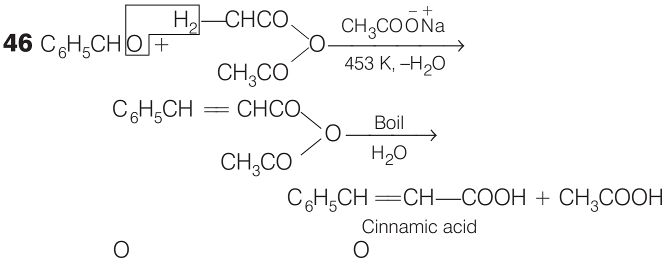
43 

Thus, products are  $D—\underset{O^-}{\underset{|}{C}}=O$ and CD_3OH.

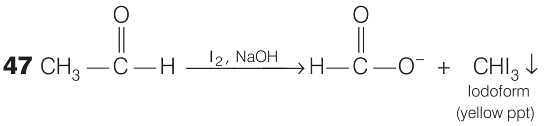
44 This reaction is an example of Perkin's reaction because in it, α,β-unsaturated acid is obtained from aromatic aldehydes. Therefore, X is acetic anhydride, i.e.$(CH_3CO)_2O$.



45 $CH_3CONHCH_3$ neither forms semicarbazone nor oxime because it is a substituted amide. While other compounds have carbonyl group, hence they form semicarbazone or oxime.

46 

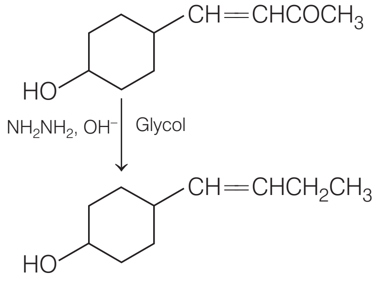
Cinnamic acid

47 

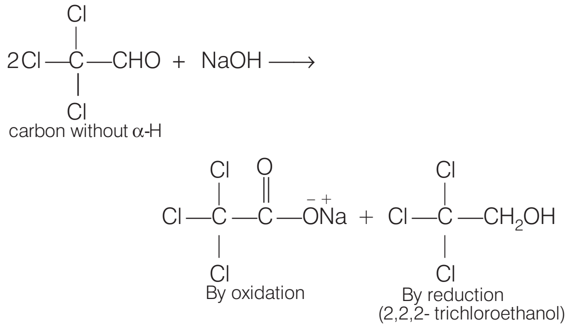
$$CH_3—\overset{O}{\overset{\|}{C}}—H \xrightarrow{I_2,\ NaOH} H—\overset{O}{\overset{\|}{C}}—O^- + \underset{\substack{\text{Iodoform}\\ \text{(yellow ppt)}}}{CHI_3\downarrow}$$

Formaldehyde does not form iodoform.

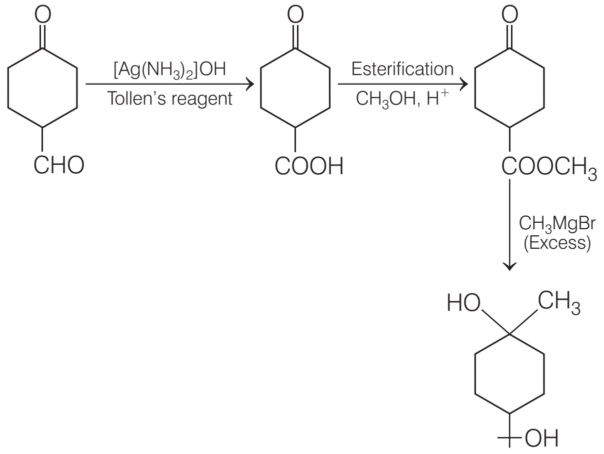
48



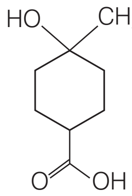
49 Cannizzaro's reaction is given by aldehydes (RCHO) lacking H at α-carbon or lacking α-carbon (as in HCHO). With NaOH, there is formation of acid salt ($R\text{COO}^-$) by oxidation and alcohol ($R\text{CH}_2\text{OH}$) by reduction.



50



Before final product is formed, intermediate is

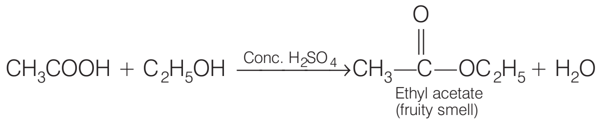


51 Compound C forms dimer due to hydrogen bonding and compound A also forms hydrogen bonds. Hence, in these, stronger hydrogen bonds are present which are more in compound C than compound A. Compound B does not form hydrogen bond. Hence, they follow the following order of molecular weight $C > A > B$. So, they have same order, in their boiling points.

52 Monocarboxylic acids and esters have the same general formula but different functional groups, so these are called functional isomers. e.g. $C_3H_6O_2$ can be CH_3CH_2COOH or CH_3COOCH_3.

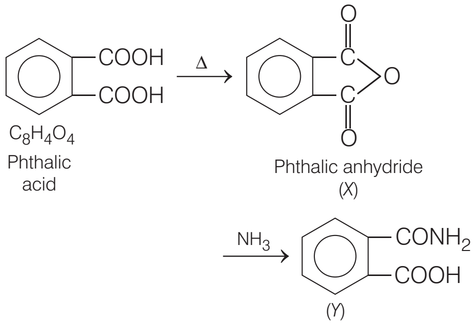
53 A liquid + $C_2H_5OH \xrightarrow{\text{Conc. } H_2SO_4} \underset{\text{(Fruity smell)}}{\text{Compound}}$

Fruity smell is the characteristic property of ester, thus reaction can be considered as follows :

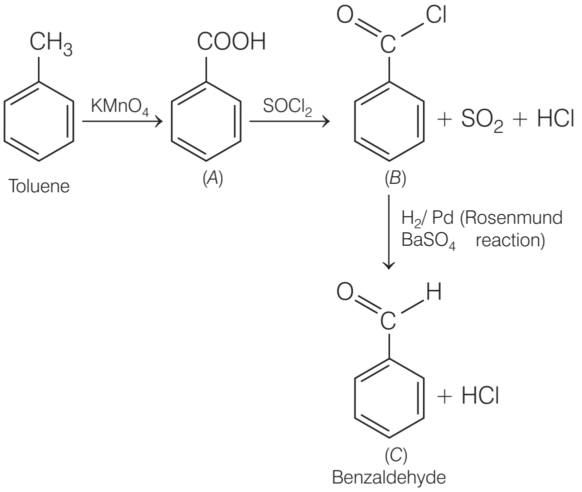


$$CH_3COOH + C_2H_5OH \xrightarrow{\text{Conc. } H_2SO_4} \underset{\substack{\text{Ethyl acetate}\\ \text{(fruity smell)}}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OC_2H_5} + H_2O$$

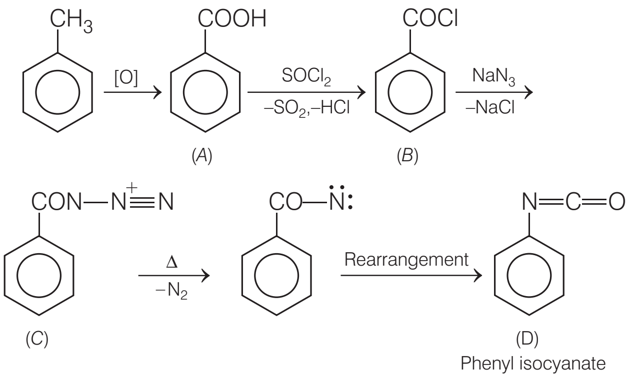
54



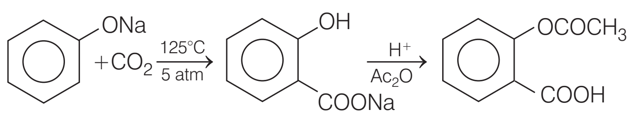
55 The reaction takes place as follows:



56



57

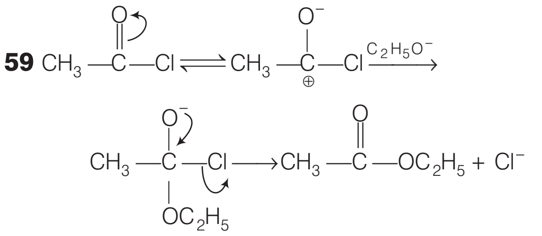


This reaction is known as Kolbe's synthesis.

58 $CH_3COOH \xrightarrow{LiAlH_4} \underset{(A)}{CH_3CH_2OH}$

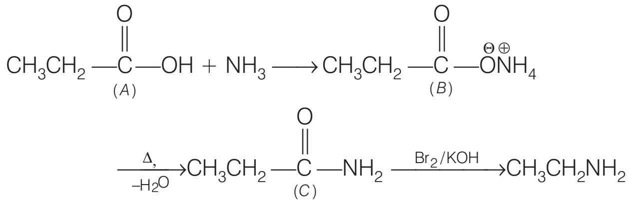
$$\xrightarrow{PCl_5} \underset{(B)}{CH_3CH_2Cl} \xrightarrow[-HCl]{Alc.\,KOH} \underset{\substack{(C)\\ \text{Ethylene}}}{CH_2 = CH_2}$$

59



This is by S_N reaction. Cl^- is a better leaving group than $C_2H_5O^-$ and the ethyl ethanoate is formed.

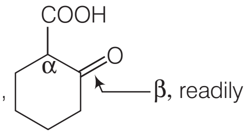
60



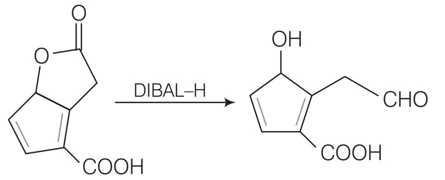
$$\underset{(A)}{CH_3CH_2-\overset{\overset{O}{\|}}{C}-OH} + NH_3 \longrightarrow \underset{(B)}{CH_3CH_2-\overset{\overset{O}{\|}}{C}-\overset{\ominus\oplus}{O}NH_4}$$

$$\xrightarrow[-H_2O]{\Delta,} \underset{(C)}{CH_3CH_2-\overset{\overset{O}{\|}}{C}-NH_2} \xrightarrow{Br_2/KOH} CH_3CH_2NH_2$$

61 It is a β-keto acid which undergoes decarboxylation in very mild condition, i.e. on simple heating. Ordinary carboxylic acid requires sodalime catalyst for decarboxylation (for decarboxylation β-keto acid must contain an α-H atom). Thus, β, readily undergoes decarboxylation.



62 DIBAL-H (Di-isobutyl aluminium hydride) is a reducing agent with formula. This is generally used for the preparation of aldehydes. Using DIBAL —H, lactones are reduced directly to aldehydes.



63

	Reagent	Phenol	Benzoic acid	Conclusion
(a)	Aqueous NaOH	Salt formation	Salt formation	No specific colour change
(b)	Tollen's reagent	No effect	No effect	
(c)	Molisch reagent	No effect	No effect	
(d)	Neutral $FeCl_3$	Violet colour	Buff-coloured precipitate	Thus, $FeCl_3$ can be used to make distinction.

64 Formaldehyde is a planar molecule as it contains sp^2 hybrid molecule.

65 Correct Assertion Bromination of benzene but not of phenol is carried out in presence of a Lewis acid.

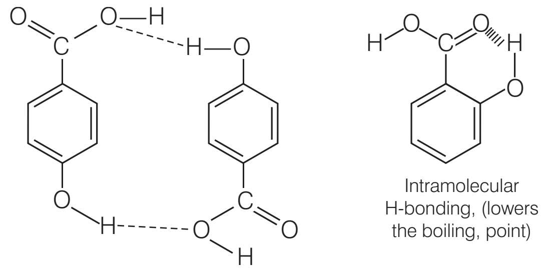
66 Solubility of alcohols $\propto \dfrac{1}{\text{molecular weight}}$

As the molecular weight increases, the hydrophobic part (alkyl part) of alcohol increases. This reduces the solubility of alcohols.

67 The compound which loses a proton more readily is more acidic. *o*-nitrophenol due to intramolecular hydrogen bonding becomes more stable and does not lose a proton, so it is weaker acid than *p*-isomer.

68 Compounds having $CH_3CO—$ or $CH_3-\underset{\underset{OH}{|}}{C}H—$ group undergo haloform reaction (*aq.* NaOH + I_2) but haloform reaction is given by only aldehydes, ketones and alcohols, so acetic acid does not undergo haloform reaction. In acetic acid α-hydrogen atoms are present.

69

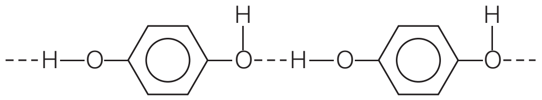


Intermolecular H-bonding, (higher boiling point)

Intramolecular H-bonding, (lowers the boiling, point)

SESSION 2

1 1, 4-dihydroxy benzene shows the highest boiling point among the given compounds because it forms strong intermolecular hydrogen bond



Intermolecular H-bonding

Order of H-bonding in *o*, *m* and *p*-isomers of a compound is given below

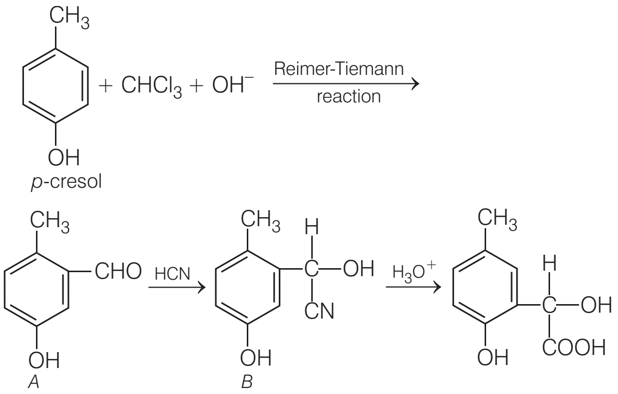
Intermolecular H-bonding $o < m < p$-isomers

Intramolecular H-bonding $o > m > p$-isomers

Hydroxy benzene do not form a chain of H-bonding. As the intermolecular H-bond is stronger than intramolecular H-bond, so the stability of 1, 4-dihydroxy benzene is highest. Hence, its boiling point is highest. The increasing order of the boiling points of the given compounds is

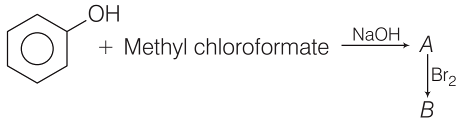
IV < I < II < III.

2



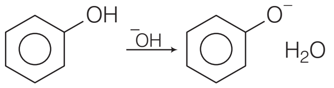
(—OH is more activating than —CH_3 in *o*, *p*-position, thus —CHO goes to *ortho* with respect to —OH.)

3 Given,

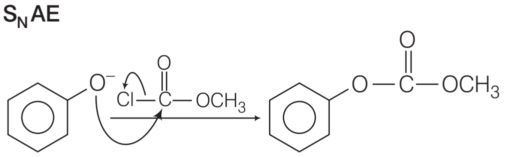


In the above road map, first reaction appears as acid base reaction followed by S_NAE (Nucleophilic substitution through Addition and Elimination). Both the steps are shown below

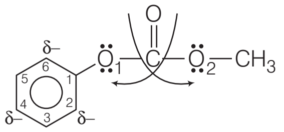
(i) Acid base reaction



(ii) **S_NAE**

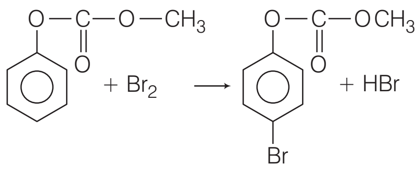


In the product of S_NAE, the attached group is *ortho* and *para*-directing due to following cross conjugation.

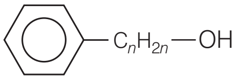


Cross conjugation due to which lone pair of oxygen 1 will be easily available to ring resulting to higher electron density at 2, 4, 6-position with respect to group. However from the stability point of view *ortho* positions are not preferred by substituents as group $-O-\underset{\underset{O}{\|}}{C}-O-CH_3$ is bulky.

Hence, on further bromination of S_NAE product *para* bromo derivative will be the preferred product, i.e.

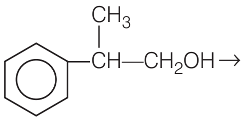


4 Molecular formula ($C_9H_{11}2O$) shows that it is a benzyl alcohol.



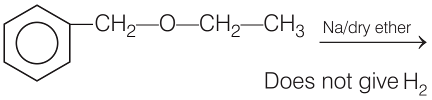
Hence, 4 isomers are

(i)



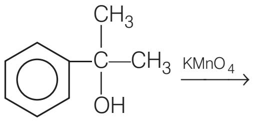
→ Does not respond to iodoform test

(ii)



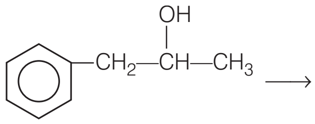
Does not give H_2

(iii)



Does not give iodoform test

(iv)



⟶ Fulfills all the conditions

Thus, the correct option is 'a'.

5 Molecular mass of silver salt of $E = \frac{108}{59.6} \times 100 = 181$

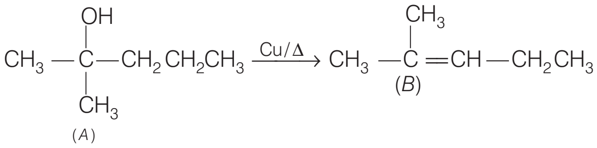
$RCOOAg = 181$

$R = 181 - (108 + 12 + 32) = 181 - 152 = 29$

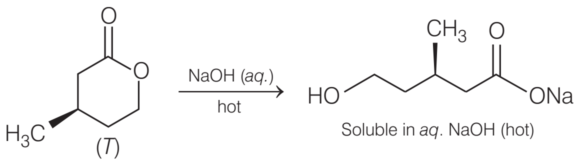
Thus, $R = -CH_2-CH_3$ and hence, acid salt is $CH_3-CH_2-COOAg$.

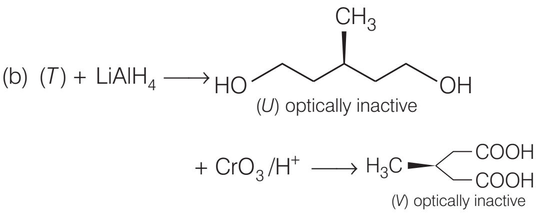
Corresponding to this salt, acid is CH_3-CH_2-COOH, which is obtained by oxidation of (*C*), an ozonolysis product. Thus, (*C*) is $CH_3-CH_2-CH{=}O$. Since, (*C*) and (*D*) are isomers, *D* is

$CH_3-\overset{\overset{CH_3}{|}}{C}{=}O$. On the basis of (*C*) and (*D*), we can get product (*B*) and finally (*A*).

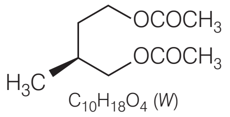


6 (a) *T* is an ester, so get hydrolysed.



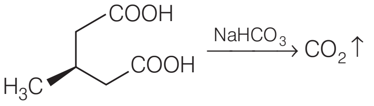


(c) (U) + $(CH_3CO)_2O \longrightarrow$



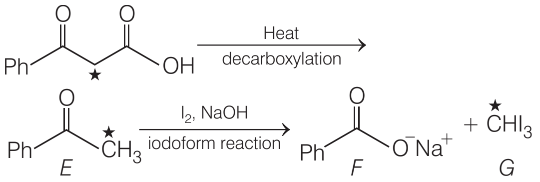
(U) On treatment with excess $(CH_3CO)_2O$ forms a diester (W).

(d) (U) + $CrO_3 \xrightarrow{H^+}$



(V) Dicarboxylic acid

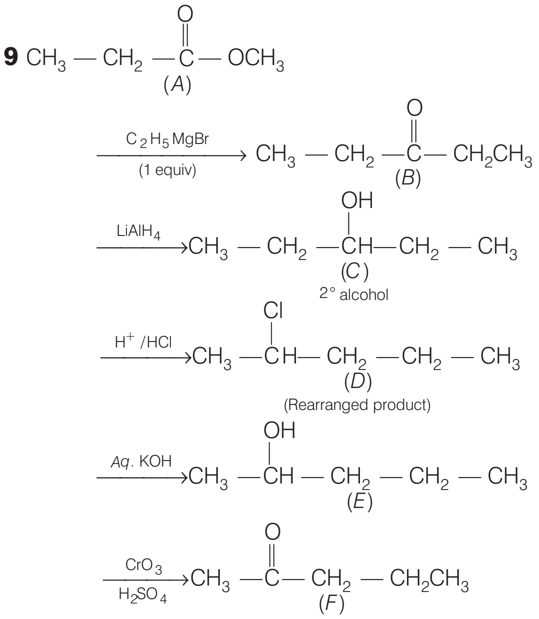
7



8 CH_3COCH_3 gives red colour with sodium nitroprusside solution but does not reduce Tollen's reagent. Acetone yields chloroform with $NaOH/Cl_2$. The chemical reaction followed as :

$$\underset{\text{Acetone}}{CH_3COCH_3} + Cl_2 \longrightarrow Cl_3C-COCH_3 \xrightarrow{NaOH} \underset{\text{Chloroform}}{CHCl_3}$$

9



$$\underset{(A)}{CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OCH_3}$$

$$\xrightarrow[\text{(1 equiv)}]{C_2H_5MgBr} \underset{(B)}{CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2CH_3}$$

$$\xrightarrow{LiAlH_4} \underset{\underset{2^\circ\text{ alcohol}}{(C)}}{CH_3-CH_2-\overset{\overset{OH}{|}}{CH}-CH_2-CH_3}$$

$$\xrightarrow{H^+/HCl} \underset{\underset{\text{(Rearranged product)}}{(D)}}{CH_3-\overset{\overset{Cl}{|}}{CH}-CH_2-CH_2-CH_3}$$

$$\xrightarrow{Aq.\ KOH} \underset{(E)}{CH_3-\overset{\overset{OH}{|}}{CH}-CH_2-CH_2-CH_3}$$

$$\xrightarrow[H_2SO_4]{CrO_3} \underset{(F)}{CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2CH_3}$$

10 (i) Molecular weight of (A), $M = \dfrac{1000\,K_f \times w}{\Delta T_f \times W}$

$\because$ $w = 0.816$ g, $W = 7.5$ g, $\Delta T_f = 5.51 - 1.59 = 3.92$,

$\therefore$ $M = \dfrac{1000 \times 4.9 \times 0.816}{3.92 \times 7.5} = 136$

(ii) For 'A'

Element	%	Relative number of atoms	Simplest ratio
C	70.58	5.88	4
H	5.88	5.88	4
O	23.54	1.47	1

$\therefore$ Empirical formula of (A) = C_4H_4O

Empirical formula weight = 68

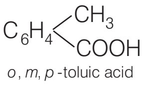
$\therefore$ Molecular formula of (A) is $(C_4H_4O)_2 = C_8H_8O_2$

(iii) Also given,

$$\underset{(A)}{C_8H_8O_2} \xrightarrow[-CO_2]{\text{Sodalime}} \underset{(B)}{C_7H_8} \xrightarrow[H^+]{[O]} \underset{(C)}{R-COOH} \xrightarrow{\text{Sodalime}} \underset{(D)}{\text{Benzene}}$$

(equiv. wt = 122)

Thus, (A) should be

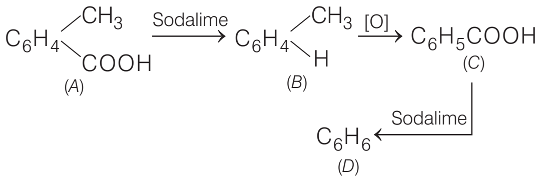


o, m, p-toluic acid

or $C_6H_5CH_2COOH$

Phenyl acetic acid

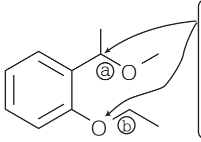
$\therefore$ Reactions are as follows:



$$\underset{(A)}{C_6H_5CH_2COOH} \xrightarrow{\text{Sodalime}} \underset{(B)}{C_6H_5CH_2CH_3} \xrightarrow{[O]} \underset{(C)}{C_6H_5CH_2COOH}$$

$$\xrightarrow{\text{Sodalime}} \underset{(D)}{C_6H_6}$$

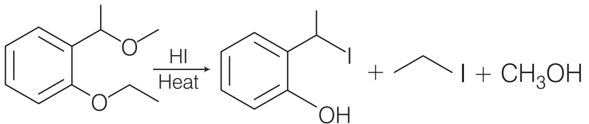
11 The reaction given is a nucleophilic substitution reaction in which cleavage at C—O bond is visible. The product formation can be visualised with the help of following analysis.



These two atoms are directly attached to benzene ring. Hence, development of any charge on these atoms is stabilised by the ring itself due to conjugation (Resonance).

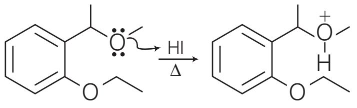
If any one properly visualise the fact written with figure above, than a conclusion can be made that C—O bonds marked (a) and (b) in the figure will undergo heterolysis during the reaction.

The reaction can be represented as :



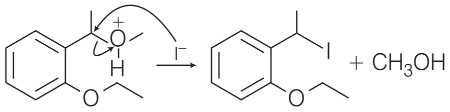
Mechanism

***Step* I** The reaction begins with the attack of H^+ of HI on oxygen to form oxonium ion as:

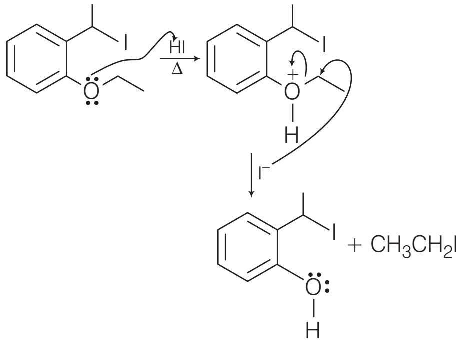


Oxonium ion

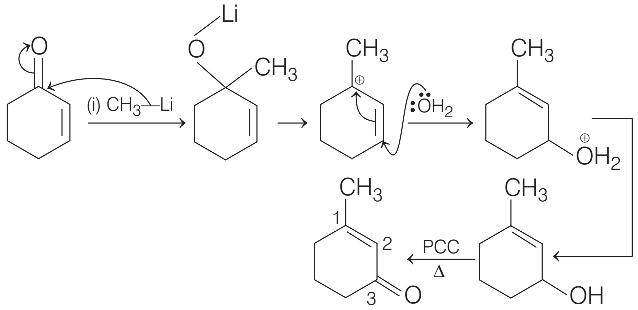
***Step* II** This oxonium ion undergoes lysis and addition of I^- to form two products as:



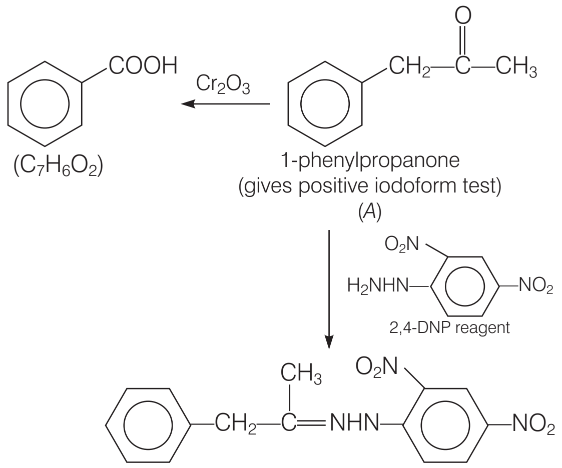
Step **III** Similar pathway is followed at the other oxygen atom, which can be visualised as:



12. Here CH_3 will attack at $C = O$ and dehydration will take place and again water attack at meta position as a nuleophile at the ring. PCC will convert —OH into =O.



13.



Red-orange precipitate

14. In 2,4,6-trinitrobenzoic acid, the decarboxylation takes place most easily, because of –*I* effect of nitro group, whereas in the dicarboxylic acid with one carbon atom having two carboxylic group it is also easier to remove CO_2. Hence, the order of ease of decarboxylation is

IV > III > II > I.

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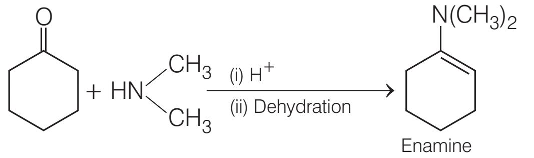

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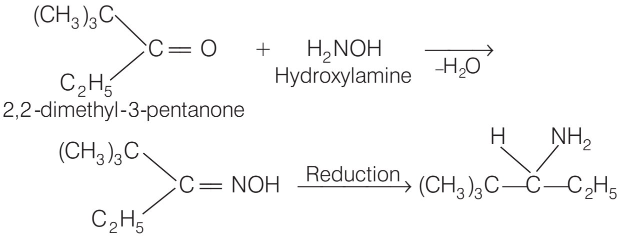

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