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Organic Compounds Containing Oxygen

Those organic compounds which contain oxygen show great degree of diversification. These include alcohols, phenols, ethers, aldehydes, ketones, carboxylic acid and their derivatives. Although these are quite different from each other in structure and chemical properties. But still presence of oxygen in them serves as the common factor responsible for similar approach towards their reactions.

IN THIS CHAPTER ....

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

Alcohols

The hydroxy derivatives of aliphatic hydrocarbons are called alcohols. They are obtained by replacing one or more hydrogen atoms of a hydrocarbon by —OH group. The general formula for monohydric alcohol is $C_nH_{2n+2}O$ or $C_nH_{2n+1}OH$. The name of an alcohol is derived by replacing 'e' of the parent alkane by adding suffix 'ol'.

$$\text{Alkane} \xrightarrow{-\text{e} + \text{ol}} \text{Alkanol}$$

Classifications

Alcohols may be classified on the following basis

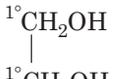
On the Basis of Number of —OH Group Present

Depending upon the number of —OH group present, the alcohols may be monohydric (i.e. have one —OH group), dihydric (have two —OH groups), trihydric (have three —OH groups) and polyhydric (have more than 3 —OH groups).

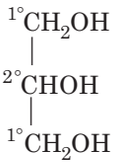
Some examples of monohydric, dihydric and trihydric alcohols are given below

CH_3OH
Methanol
(monohydric alcohol)

C_2H_5OH
Ethanol
(monohydric alcohol)

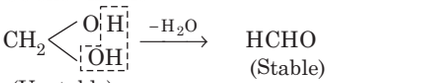


Ethylene glycol
(dihydric alcohol)



Glycerol
(trihydric alcohol)
Glucose is the best example of polyhydric alcohols.

Remember In dihydric alcohols, the two or more —OH groups must be present at different carbon atoms. Their presence at the same carbon atom, lead to the removal of water molecule as shown below

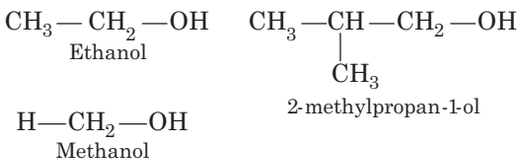


(Unstable) Formaldehyde (Stable)

On the Basis of Nature of Carbon Atom

Monohydric alcohols are classified as primary, secondary and tertiary depending upon the nature of carbon atom to which hydroxyl group is attached.

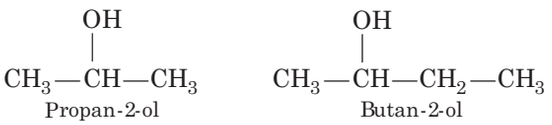
(i) **Primary alcohols** In primary (1°) alcohol, the carbon, which carries the —OH group, is attached with none or one C-atom. In particular they contain —CH_2OH group. e.g.



Ethanol — 2-methylpropan-1-ol — Methanol

(ii) **Secondary alcohols** In a secondary (2°) alcohol, the carbon carrying —OH group is joined directly to **two** C-atoms, which may or may not be same.

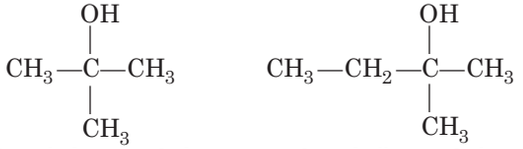
In other words, they have $>$CHOH group. e.g.



Propan-2-ol — Butan-2-ol

(iii) **Tertiary alcohols** In these alcohols (3°), the carbon atom holding the —OH group is attached directly to **three** C-atoms, which may or may not be same.

In other words, they have $\gtrless$C—OH group. e.g.



2-methylpropan-2-ol — 2-methylbutan-2-ol

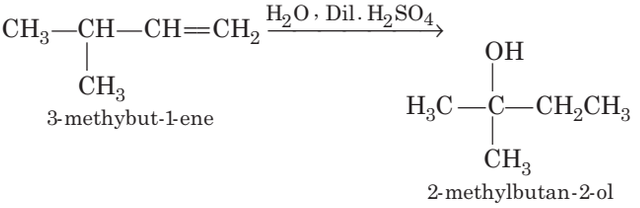
Preparation of Monohydric Alcohols

Important methods used to prepare alcohols are as follows

1. From Alkenes

Following methods are used to prepare alcohols from alkenes.

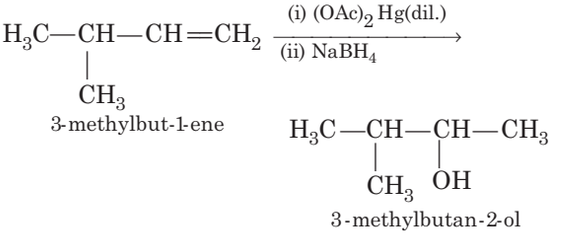
(a) **By acid catalysed hydration** Alkenes react with water in the presence of acid as catalyst to form alcohols.



3-methybut-1-ene — 2-methylbutan-2-ol

In case of unsymmetrical alkenes, the addition reaction takes place in accordance with *Markownikoff's* rule. In this reaction intermediate carbocation is formed and rearrange itself by 1, 2-hydride or methyl shift. Therefore, — OH group gets attached at the carbon atom of maximum degree.

(b) **By oxymercuration-demercuration reaction line**



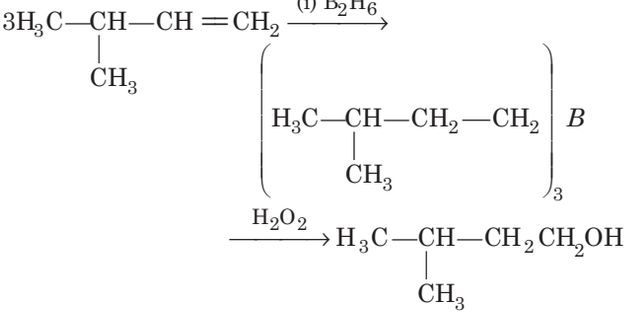
3-methylbut-1-ene — 3-methylbutan-2-ol

Intermediate carbocation does not form and alcohol is formed according to Markownikoff's rule.

Notify the formation of 3-methyl-butan-2-ol in this reaction and compare it with the product of reaction (a) given above. Although the reactant is same in both the cases but product differ due to carbocation formation in first case.

(c) **By hydroboration oxidation reaction**

Diborane reacts with alkenes to give trialkyl boranes as addition product. This is oxidised to alcohols by hydrogen peroxide in the presence of aqueous sodium hydroxide as shown below.



Intermediate carbocation does not form and alcohol formed is comperable with anti-Markownikoff addition product.

2. By Reduction of Carbonyl Compounds

Aldehydes on reduction give primary alcohols and ketones give secondary alcohols in the presence of weak reducing agents like $NaBH_4$.

$$\underset{\text{Aldehyde}}{R\text{CHO}} \xrightarrow{NaBH_4} \underset{1^\circ \text{ alcohol}}{R\text{CH}_2\text{OH}}$$

$$\underset{\text{Ketone}}{R\text{COR}'} \xrightarrow{NaBH_4} R\text{—}\underset{\underset{\text{OH}}{|}}{\text{CH}}\text{—}R' \quad (2^\circ \text{ alcohol})$$

3. By Reduction of Acids and Esters

Carboxylic acids and esters on reduction in the presence of strong reducing agents like $LiAlH_4$ give primary alcohols.

$$\underset{\text{Acid}}{R\text{COOH}} \xrightarrow{LiAlH_4} \underset{\text{Alcohol}}{R\text{CH}_2\text{—OH}}$$

$$\underset{\text{Ester}}{\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3} \xrightarrow{LiAlH_4} \underset{\text{Ethanol}}{\text{CH}_3\text{CH}_2\text{OH}} + \underset{\text{Propanol}}{\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}}$$

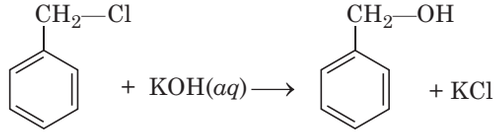
In another pathway, acids are reduced to alcohols by converting them to the esters followed by their reduction using hydrogen in the presence of catalyst.

$$R\text{COOH} \xrightarrow[H^+]{R'\text{OH}} R\text{COOR}' \xrightarrow[\text{catalyst}]{H_2} R\text{CH}_2\text{OH} + R'\text{OH}$$

4. By Hydrolysis of Alkyl Halides

Hydrolysis of alkyl halide is a nucleophilic substitution reaction. Here, a nucleophile OH^- reacts with haloalkane having a partial positive charge on the carbon atom bonded to halogen to produce alcohol as shown below.

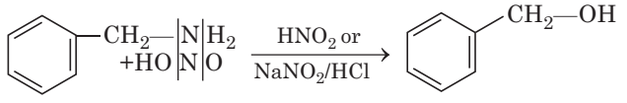
$$\underset{\text{Bromoethane}}{\text{CH}_3\text{—CH}_2\text{Br}} + \text{NaOH}(aq) \longrightarrow \underset{\text{Ethanol}}{\text{CH}_3\text{—CH}_2\text{—OH}} + \text{NaBr}$$



Benzyl chloride — Ethanol

5. From Primary Aliphatic Amines

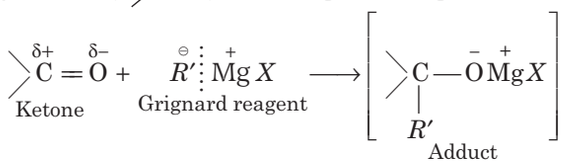
Primary amines react with nitrous acid to form diazomium salts which being unstable liberate nitrogen gas quantitatively and form alcohols. The reaction is known as **deamination** reaction.

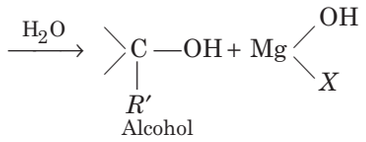


Benzyl amine — Benzyl alcohol

6. From Grignard Reagent

Grignard reagent ($R'MgX$) on reaction with aldehydes / ketones followed by hydrolysis gives alcohols.The nature of alcohol formed depends upon the aldehyde or ketone taken. For example, if in the reaction aldehyde is formaldehyde then primary alcohol (—CH_2OH) is obtained while other aldehydes give secondary alcohol ($\rangle CHOH$) with Grignard reagents. Ketones on the otherhand, give tertiary alcohol ($\rangle COH$) with Grignard reagents.





The outline of preparation of alcohol are as follows

1. Hydration of alkenes
   conc. H_2SO_4
2. Oxymercuration-demercuration of alkenes $(OAc)_2Hg$
   high temperature, high pressure
3. Hydroboration-oxidation of alkenes
   B_2H_6 in THF or DIGLYME/H_2O_2
4. Reduction of carbonyl compounds
   $NaBH_4$
5. Reduction of acids and esters
   $LiAlH_4$
6. Hydrolysis of alkyl halides
   aq. KOH or NaOH
7. Reaction with HNO_2 of primary amines
   $NaNO_2$/HCl
8. Grignard reagent
   Carbonyl compounds

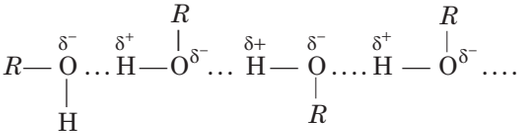
Alcohols

Physical Properties of Monohydric Alcohols

Some important physical properties of monohydric alcohol are as follows

(i) **Physical state** Their lower members are colourless, volatile liquids with a characteristic smell and burning taste. Higher members are odourless and tasteless. Alcohols with more than 12 carbon atoms are colourless crystalline solids or liquids.

(ii) **Boiling points** Alcohols have higher boiling point than hydrocarbons, ether, haloalkanes and haloarenes of comparable molecular mass because alcohols have intermolecular hydrogen bonding. The —OH group present in alcohol is involved in intermolecular hydrogen bonding as shown below.



Such a hydrogen bonding is not visible in haloalkanes.

As the number of carbon atoms increases, boiling point increases. The boiling point decreases with increase of branching in carbon chain.

(iii) **Solubility** Alcohols are soluble in water due to their ability to form hydrogen bonds with water. However, as the number of carbon atoms increases, solubility decreases.

Chemical Properties of Monohydric Alcohols

Order of reactivity of alcohols is as follows

$$1° \text{ alcohol} > 2° \text{ alcohol} > 3° \text{ alcohol}$$

The reaction of alcohols may be due to cleavage of O—H bond or C—H bond.

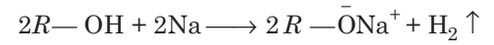
1. Reactions Involving Cleavage of O—H Bond

This cleavage of O—H bond simply indicates the acidic behaviour of alcohols. Electron releasing group decreases the polarity of — OH bond. Thus, decreases the acid strength. So, the acidity of alcohols in decreasing order is

primary alcohols > secondary alcohols > tertiary alcohols.

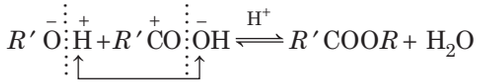
Important reactions of this category are given below

- **Reaction with metals**

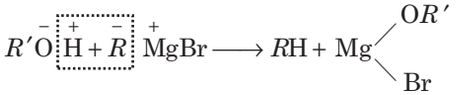


Release of hydrogen indicates the acidic nature of alcohol. The alkoxide formed above in a better base than NaOH.

- **Reaction with acid and acid derivatives** Alcohols react with carboxylic acids, acid chlorides and acid anhydrides to form esters. This reaction is called **esterification.**



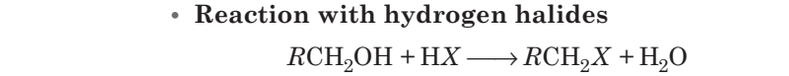
- **With Grignard reagent** Alcohols when react with Grignard reagents give alkanes.



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

The breakage between alkyl and —OH group is seen through following reactions

- **Reaction with hydrogen halides**

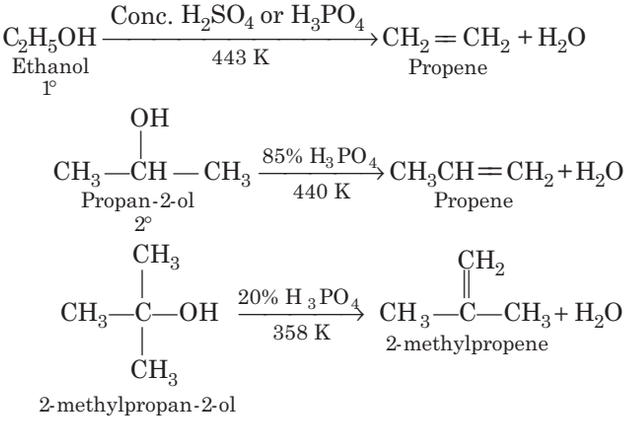


Reactivity of alcohol for this reaction follows the order

$$3° > 2° > 1°$$

- **Dehydration**

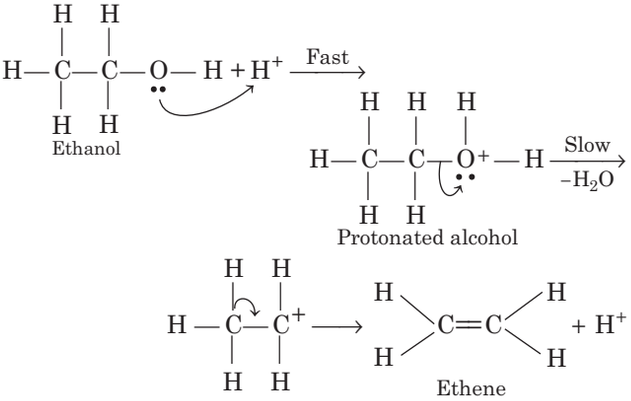
It is carried out in the presence of protic acids like conc. H_2SO_4 or H_3PO_4 or in presence of catalysts such as anhyd. $ZnCl_2$ or Al_2O_3.



Ease of dehydration of alcohols is as follows

$$3° > 2° > 1°$$

Mechanism of dehydration



3. Oxidation

Different reagents are used to oxidise alcohol. The oxidation products of monohydric alcohols are carbonyl compounds generally.

A summary of oxidation products is as follows

$$\underset{\text{Alcohol}}{R\text{CH}_2\text{OH}} \xrightarrow[\text{Acidified KMnO}_4]{[\text{O}]} \underset{\text{Aldehyde}}{R\text{CHO}} \xrightarrow{[\text{O}]} \underset{\text{Carboxylic acid}}{R\text{COOH}}$$

$$\underset{1^\circ \text{ alcohol}}{R\text{CH}_2\text{OH}} \xrightarrow{\text{CrO}_3} \underset{\text{Aldehyde}}{R\text{CHO}}$$

$$\underset{2^\circ \text{ alcohol}}{R\text{—}\underset{\displaystyle \underset{\displaystyle \text{OH}}{|}}{\text{CH}}\text{—}R'} \xrightarrow{\text{CrO}_3} \underset{\text{Ketone}}{R\text{—}\underset{\displaystyle \underset{\displaystyle \text{O}}{\|}}{\text{C}}\text{—}R'}$$

$$\underset{\text{But-2-en-1-ol}}{\text{CH}_3\text{—CH=CH—CH}_2\text{OH}} \xrightarrow{\text{PCC}} \underset{\text{But-2-en-1-al}}{\text{CH}_3\text{—CH=CH—CHO}}$$

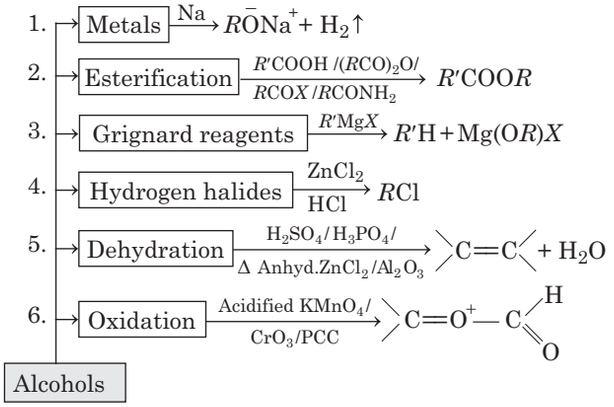
PCC is pyridinium chlorochromate. It is a very good oxidising agent.

Tertiary alcohols do not undergo oxidation reaction. In the 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.

$$\text{CH}_3\text{—}\underset{\displaystyle \underset{\displaystyle \text{CH}_3}{|}}{\overset{\displaystyle \overset{\displaystyle \text{CH}_3}{|}}{\text{C}}}\text{—OH} \xrightarrow[\text{KMnO}_4]{\text{Acidified}} \text{CH}_3\text{COOH}$$

Remember MnO_2 selectively oxidises —OH group of allylic and benzylic 1° and 2° alcohols to aldehydes and ketones respectively. N_2O_4 in $CHCl_3$ oxidises 1° and 2° benzyl alcohol.

Flow chart showing summary of reactions of alcohols



Identification of Primary, Secondary and Tertiary Alcohols

1°, 2° and 3° alcohols can be identified by following tests.

1. Victor-Meyer's Test

In this test, first the given alcohol is treated with P /I_2 and then with $AgNO_2$ and HNO_2. The final product obtained gives different (or no) colour with NaOH. By identifying the colour produced, the alcohols are identified as shown below.

(i) **Primary alcohols give blood red colour**

$$\underset{\text{Alcohol}}{R\text{CH}_2\text{OH}} \xrightarrow{\text{P/I}_2} \underset{\text{Alkyl iodide}}{R\text{CH}_2\text{I}} \xrightarrow[-\text{AgI}]{\text{AgNO}_2} \underset{\text{Nitroalkane}}{R\text{CH}_2\text{NO}_2} \xrightarrow{\text{O=N—OH}} \underset{\displaystyle \underset{\displaystyle \text{N—OH}}{\|}}{R\text{—C—NO}_2} \xrightarrow{\text{NaOH}} \text{blood red}$$

(ii) **Secondary alcohols give blue colour**

$$\underset{2^\circ \text{ alcohol}}{\begin{matrix} R \\ R \end{matrix}\!\!>\!\text{CHOH}} \xrightarrow{\text{P / I}_2} \begin{matrix} R \\ R \end{matrix}\!\!>\!\text{CH—I} \xrightarrow[-\text{AgI}]{\text{AgNO}_2} R_2\text{CHNO}_2 \xrightarrow{\text{O=N—OH}} \underset{\text{Pseudo nitrole}}{\underset{\displaystyle \underset{\displaystyle \text{N=O}}{|}}{R_2\text{C—NO}_2}} \xrightarrow{\text{NaOH}} \text{blue colour}$$

(iii) **Tertiary alcohols produce no colour**

$$\underset{3^\circ \text{ alcohol}}{R_3\text{C—OH}} \xrightarrow{\text{P/I}_2} R_3\text{C—I} \xrightarrow{\text{AgNO}_2} R_3\text{CNO}_2 \xrightarrow{\text{HNO}_2}$$

$$\text{No reaction} \xrightarrow{\text{NaOH}} \text{no colour}$$

2. Lucas Test

An equimolar mixture of anhydrous $ZnCl_2$ and concentrated HCl is called Lucas reagent. When alcohols are treated with it,

- tertiary alcohols produce turbidity or cloudiness immediately. This shows that these compounds react immediately with Lucas reagent.
- secondary alcohols produce turbidity after 5 min. So, these react with Lucas reagent after about 5 minutes.
- primary alcohols do not produce turbidity at room temperature. It means their reaction is slowest with Lucas reagent.

3. Dehydrogenation

Cu or Ag are used for this purpose. In this reaction

(i) Primary alcohols give aldehydes

$$\underset{1^\circ \text{ alcohol}}{R\text{CH}_2\text{OH}} \xrightarrow{\text{Cu/573K}} \underset{\text{Aldehyde}}{R\text{CHO}} + \text{H}_2\uparrow$$

(ii) Secondary alcohols give ketones

$$\underset{2^\circ \text{ alcohol}}{R_2\text{CHOH}} \xrightarrow{\text{Cu/573K}} \underset{\text{Ketones}}{R_2\text{C=O}}$$

(iii) Tertiary alcohols are not dehydrogenated. They are rather dehydrated

$$\underset{3^\circ \text{ alcohol}}{(\text{CH}_3)_3\text{C—OH}} \xrightarrow[-\text{H}_2\text{O}]{\text{Cu/573K}} \underset{\text{Alkene}}{(\text{CH}_3)_2\text{C=CH}_2}$$

4. Oxidation Method

Oxidation reaction is also used to distinguish between 1°, 2° and 3° alcohols.

1° alcohol ⟶ Aldehydes

2° alcohol ⟶ Ketones

3° alcohol ⟶ No oxidation

These reactions have been discussed in chemical properties of alcohols in detail.

Uses of Monohydric Alcohols

- Ethanol is usually sold as industrial methylated spirits which is ethanol with a small quantity of methanol added.
- Methanol is poisonous and so the industrial methylated spirits is unfit to drink.
- Ethanol burns to give carbon dioxide and water. Thus, can be used as a fuel in its own right or in mixtures with petrol (gasoline). "Gasohol" is a petrol/ethanol mixture containing about 10-20% ethanol.
- Methanol also burns to form carbon dioxide and water.

$$2CH_3OH + 3O_2 \longrightarrow 2CO_2 \uparrow + 4H_2O$$

Thus, it can be used as petrol additive to improve combustion.

- Ethanol is widely used as a solvent. It is relatively safe and can be used to dissolve many organic compounds which are insoluble in water.

Dihydric Alcohols

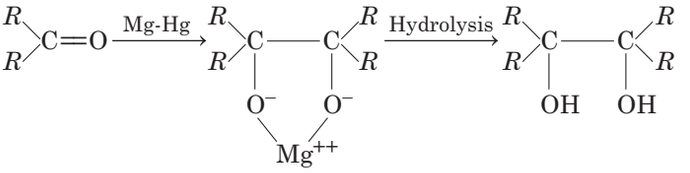
The compounds which contain two —OH groups attached to successive C-atoms are called glycols. Ethylene glycol $\begin{pmatrix} CH_2OH \\ | \\ CH_2OH \end{pmatrix}$ is the first member of this homologous series.

These compounds can be obtained by any of the following methods

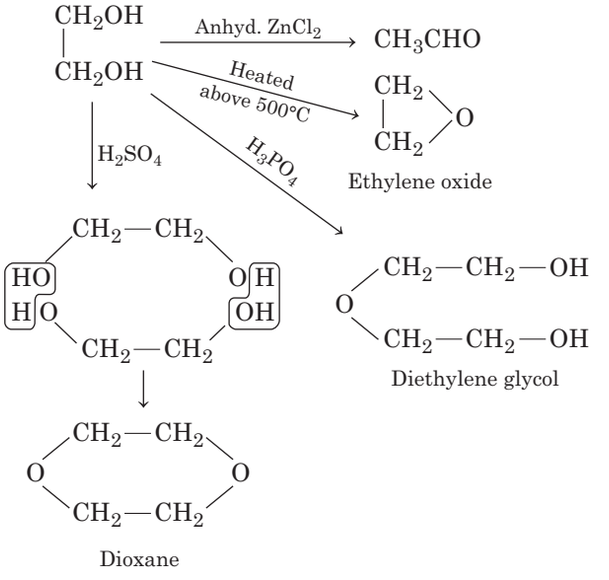
- By the oxidation of ethylene or other alkenes with Baeyer's reagent.
- By the hydrolysis of
  (a) *vicinal*-dihalides
  (b) halohydrins
  (c) epoxy compounds like ethylene oxide

  All these reactions are given in detail in previous chapters (hydrocarbons, haloalkanes and haloarenes).
- The higher members of glycols can be prepared by reducing ketones in the absence of proton donor with electropositive metals.

Ketones show dimerisation and equation of complete reaction is given below



Among the chemical propertein of ethylene glycol the dehydration reactions are important. An outline of these reactions is given below.

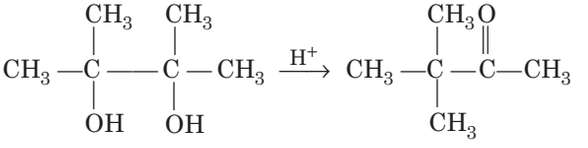


Completely substituted 1, 2-diols are called **pinacols**. These behave very differently in the presence of acids and this reaction is called **pinacol-pinacolone rearrangement**.

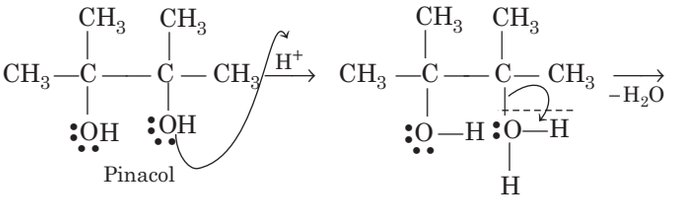
Pinacol-Pinacolone Rearrangement

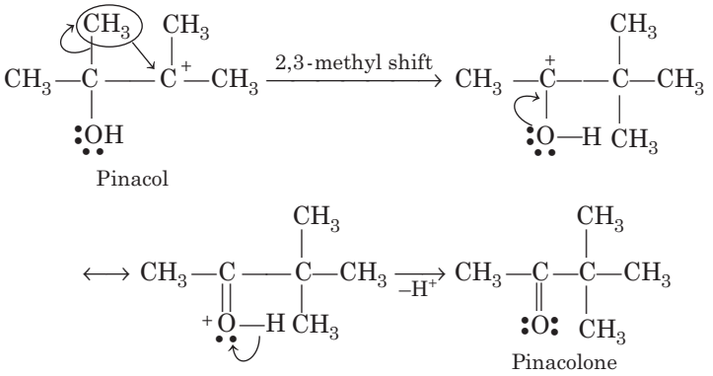
The acid catalysed 1, 2 migration of a diol to an oxo derivative is in this reaction.

The simplest representation and mechanism of it is given below



Mechanism

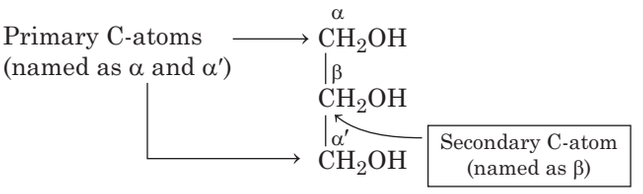




Glycerol or Propane -1, 2, 3-triol

Compounds containing three —OH groups at successive C-atoms are called **triols**. The introduction of third —OH group in a diol makes alcohol more sweet, raises the b.p. by about 100°C (due to enhancement in intermolecular H-bonding) and increases viscosity.

Glycerol is the first member of this series with following structural formula



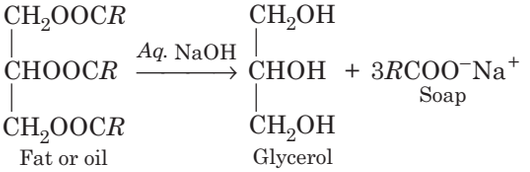
Methods of Preparation

Following methods are used to prepare glycerol.

1. From Fats and Oils

Fats and oils are triglycerides i.e. triesters of glycerol with long chain fatty acids or carboxylic acids.

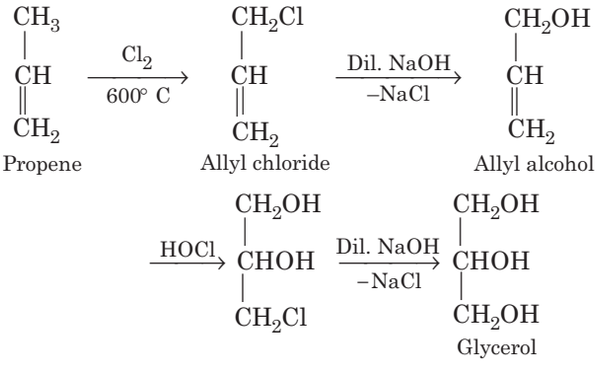
Their hydrolysis in alkaline medium produces Na salts of these long chain fatty acids (soap) and glycerol. This glycerol is present as **sweet lye** in mother liquor. This hydrolysis reaction is called **saponification**.



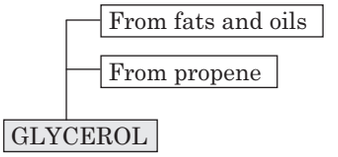
Thus, glycerol is the byproduct of saponification reaction.

2. From Propene

Propene on reaction with Cl_2 at 600°C in dil. alkaline medium gives allyl alcohol which further reacts with HOCl (in dil. alkaline medium) gives glycerol.



The outline of methods of preparation looks like



Physical Properties

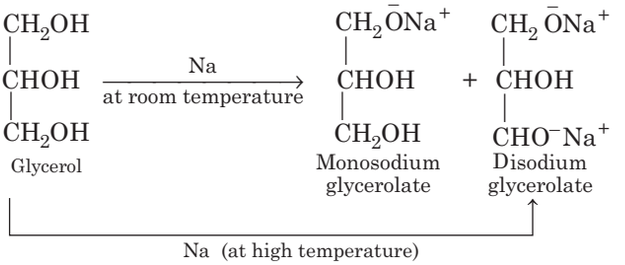
- It is a colourless, odourless, sweet tasting syrupy liquid with b.p. 290°C.
- It is non-toxic, miscible with water and ethanol but immiscible with ether.
- It is hygroscopic in nature.

Chemical Properties

Some important chemical properites of glycerol are as follows

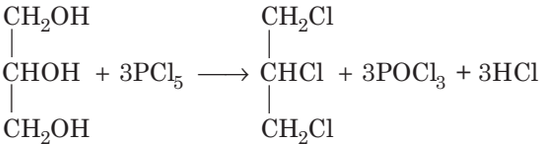
1. With Na

Disodium salt is obtained. It is seen that the secondary alcoholic group does not react at all.



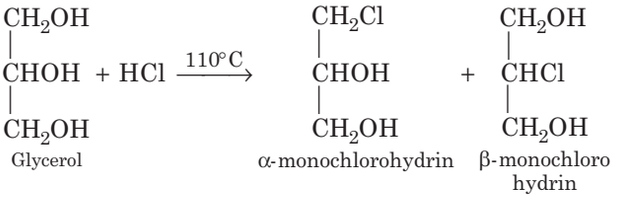
2. With PX_5

This reaction is majorly seen with pentachloride only (as the pentahalides as Br_2 and I_2 are not known and PF_5 is unstable).

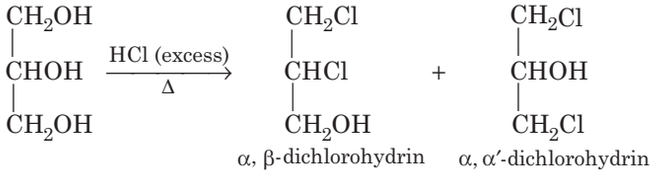


3. With HX

Glycerol on reaction with HCl at 110°C gives α-monochlorohydrin and β-monochlorohydrin.

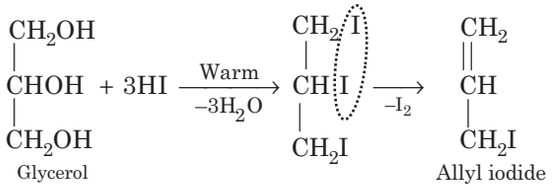


Long exposure to HCl at higher temperature on reaction with glycerol gives,

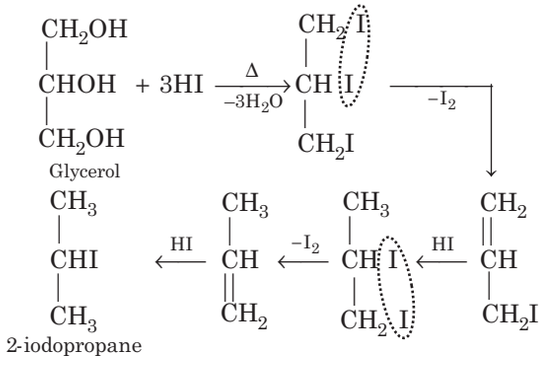


HBr behaves similarly but reaction with HI takes place differently. Equation of this reaction is given below in detail.

(a) With small amount of HI on warming gives,

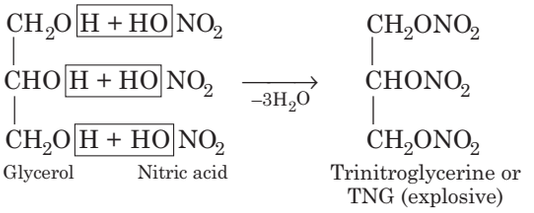


(b) With large amount of HI on heating gives,



4. With HNO_3

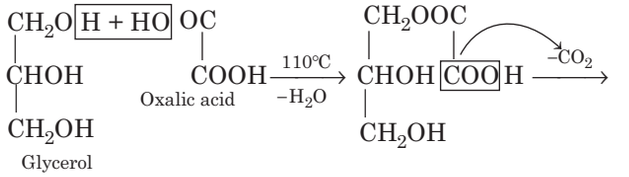
With nitric acid, it yields an explosive compound compound named as trinitroglycerine or TNG.

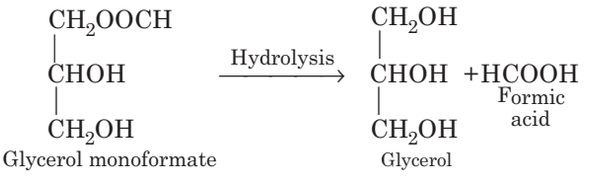


5. With Oxalic Acid

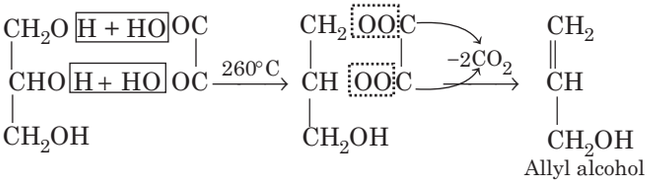
Both glycerol and oxalic acid react with each other at two different temperatures.

At 110°C



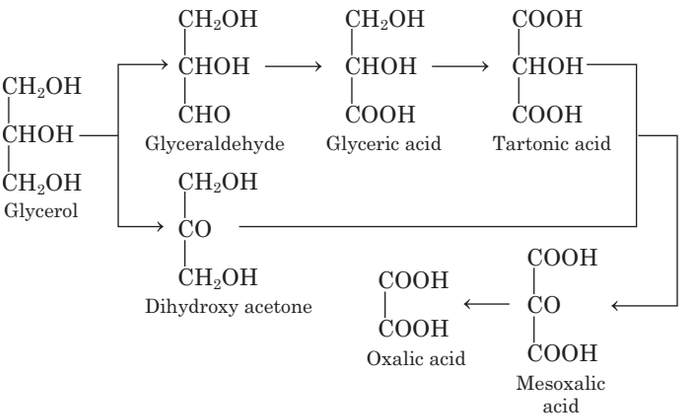


At 260°C



6. Oxidation

Glycerol can give rise to variety of oxidation products which are summarised as follows



The products given by differents reagents are given below

(i) With dil. HNO_3 ⟶ Glyceric acid + Tartonic acid

(ii) With conc. HNO_3 ⟶ Glyceric acid.

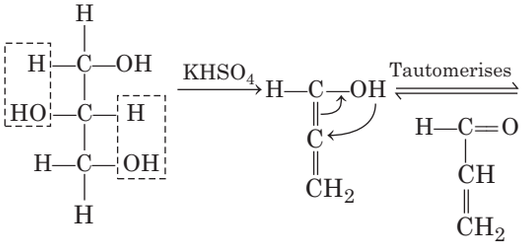
(iii) With bismuth nitrate ⟶ Mesoxalic acid.

(iv) With Br_2 water, sodium hypobromite or Fenton's reagent ($FeSO_4 + H_2O_2$) ⟶ A mixture of glyceraldehyde and dihydroxy acetone (glycerose).

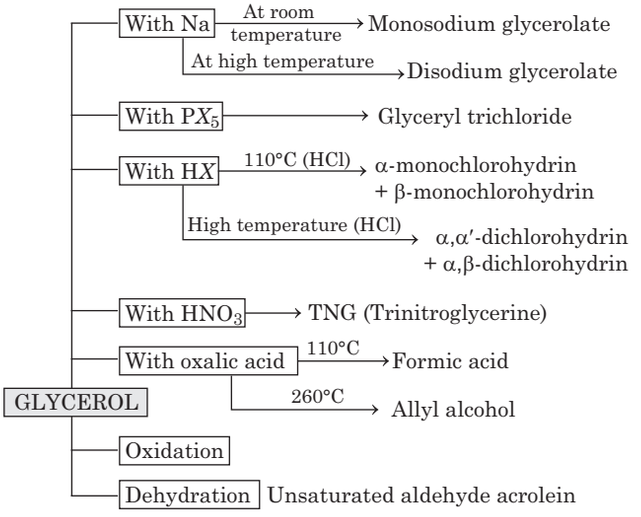
(v) With periodic acid ⟶ Formaldehyde + Formic acid.

7. Dehydration

Glycerol when heated in the presence of $KHSO_4$, unsaturated aldehyde acrolein is obtained.

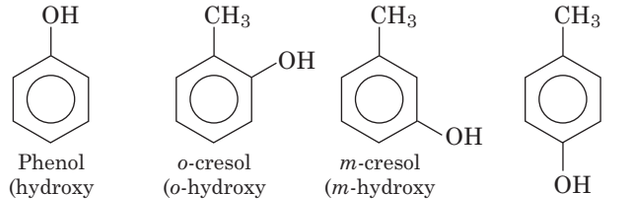


The outline of chemical properties of glycerol looks like



Phenols

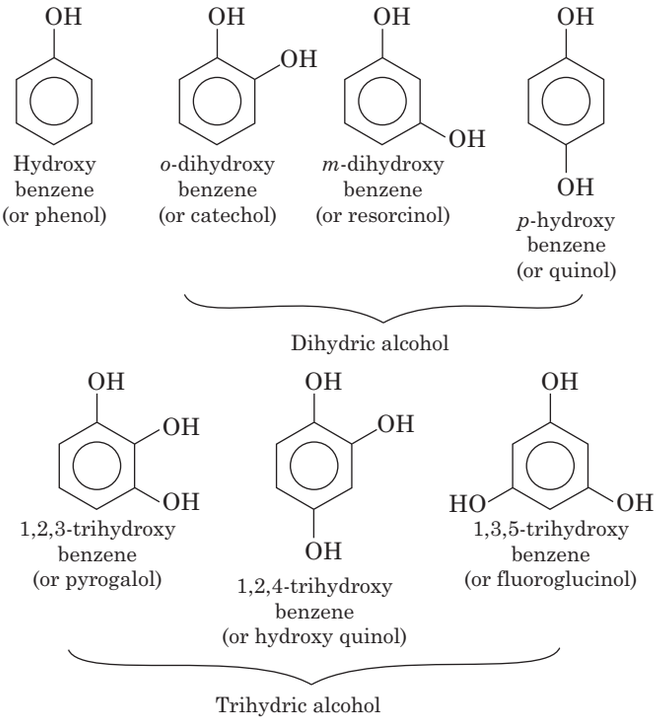
Aromatic compounds in which hydroxyl group (— OH) is directly attached with benzene nucleus are called phenols. Some of these are given below



Phenol (hydroxy benzene) | *o*-cresol (*o*-hydroxy toluene) | *m*-cresol (*m*-hydroxy toluene) | *p*-cresol (*p*-hydroxy toluene)

On the basis of number of —OH groups present, phenols are termed as monohydric, dihydric, trihydric phenols etc.

Complete equation of the reaction is given below

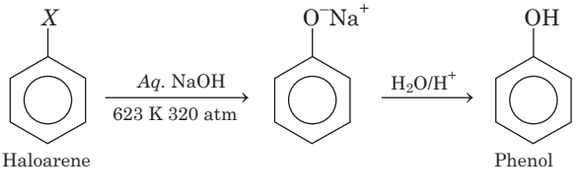


Preparation of Phenols

Some general and important methods of preparation of phenols are discussed below

1. By Hydrolysis of Halobenzene

When chlorobenzene in fluxed with *aq*. NaOH at 623 K and 320 atmospheric pressure. Sodium phenoxide is produced. Then phenol is obtained by acidification of this sodium phenoxide.



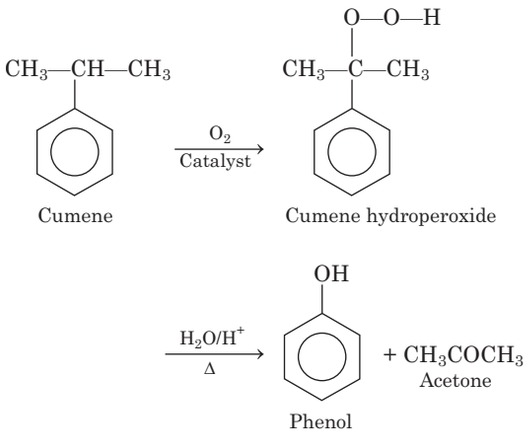
Haloarene | Phenol

The halobenzene used here is prepared by Dow process or Raschig's process.

2. Cumene Process

Phenol is manufactured from cumene or isopropyl benzene.

Cumene is oxidised in the presence of air to cumene hydroperoxide. It is then converted to phenol and acetone by treating it with dilute acid.

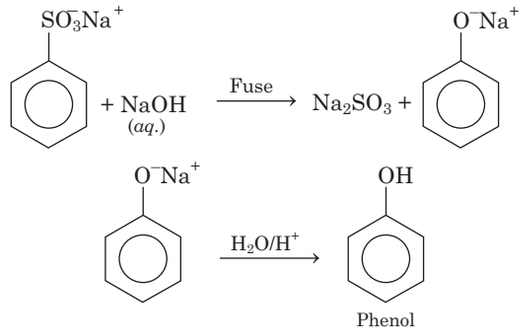


The reaction proceeds at 150°C in the presence of HBr as a catalyst. The reaction is also called **auto-oxidation.**

The major advantage of this reaction is that the by product, i.e. acetone is also an important reagent.

3. From Na or K Salts of Sulphonic Acid

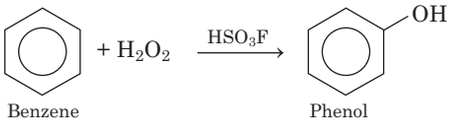
In this reaction, benzene sulphonic acid is converted to sodium phenoxide on heating with molten sodium hydroxide. Acidification of sodium salt gives phenol.



Fusion at high temperatures may leads to undesirable side products.

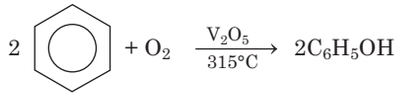
4. By Hydroxylation of Benzene

Direct hydroxylation is involved,



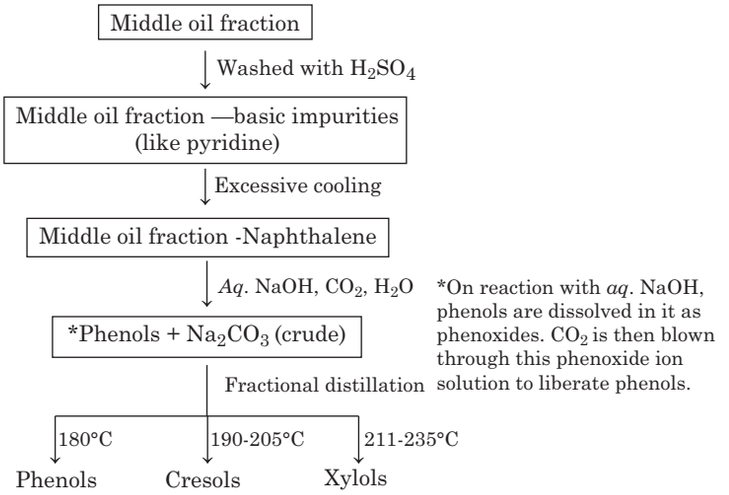
5. By Oxidation of Benzene

Benzene on air oxidation with V_2O_5 at 315°C give phenol. It is the latest method used to manufacture phenol.

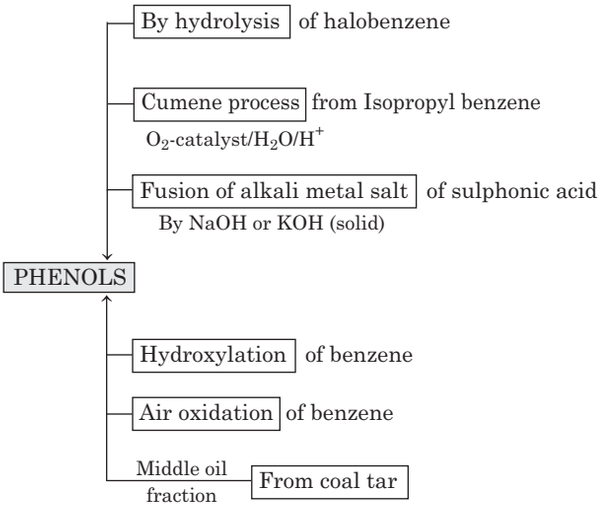


6. By Middle Oil Fraction of Coal tar

The middle oil fraction of coal tar distillation has naphthalene and phenolic compounds. From this fraction, phenolic compounds are isolated as,



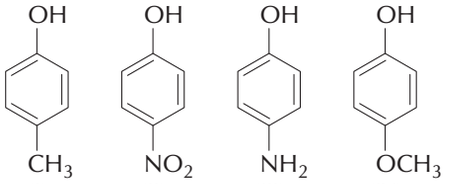
The methods of preparation of phenols in outline are summerised below



Physical Properties of Phenols

- These are colourless liquids or solids with red tint and have carbolic odour.
- Phenols are highly toxic. Due to stronger intermolecular H-bonding their boiling point are higher than corresponding alcohols.
- They are more miscible with water as compare to alcohols.
- They have high dipole moments and are acidic in nature.
- Phenols are found to be even more acidic than aliphatic alcohols.

Example 1. *The increasing order of boiling points of the following compounds is*



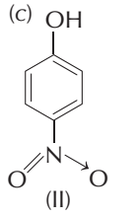
(I) (II) (III) (IV)

(JEE Main 2020)

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

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

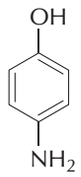
Sol. (c)



(II)

shows strongest hydrogen bonding from —OH group.

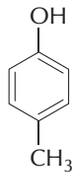
(Boiling point 279°C)



(III)

shows stronger hydrogen bonding from both side of —OH group as well as —NH_2 group.

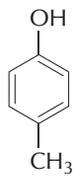
(Boiling point 284°C)



(I)

shows hydrogen bonding from —OH group only.

(Boiling point 202°C)



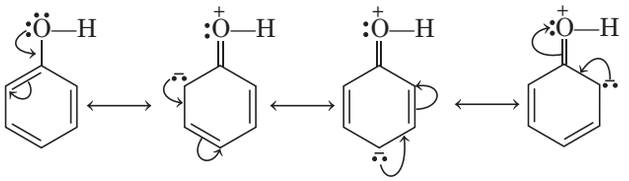
(I)

shows hydrogen bonding from —OH group only.

(Boiling point 202°C)

Acidic Nature of Phenols

Phenols are acidic in nature, even more acidic than aliphatic alcohols. The more acidic character of phenols is due to conjugation between lone pair of oxygen and benzene nucleus as shown below



The (+) ve charge on oxygen signifies the weakening of O—H bond.

Presence of *electron releasing group* like — CH_3, —C_2H_5 over benzene nucleus destabilises the phenoxide ion, thus, *decreases the acidity of phenol*.

On the otherhand *presence of electron withdrawing groups* like —NO_2, —CN, etc., stabilises the phenoxide ion and thus, *increases the acidity of phenol*.

Example 2. *Arrange the following compounds in increasing order of* C—OH *bond length : methanol, phenol, p-ethoxyphenol* ***(JEE Main 2020)***

(a) phenol < methanol < *p*-ethoxyphenol

(b) phenol < *p*-ethoxyphenol < methanol

(c) methanol < *p*-ethoxyphenol < phenol

(d) methanol < phenol < *p*-ethoxyphenol

Sol. (*b*) The increasing order of C—OH bond length in the given compounds is

phenol < *p*-ethoxy phenol < methanol.

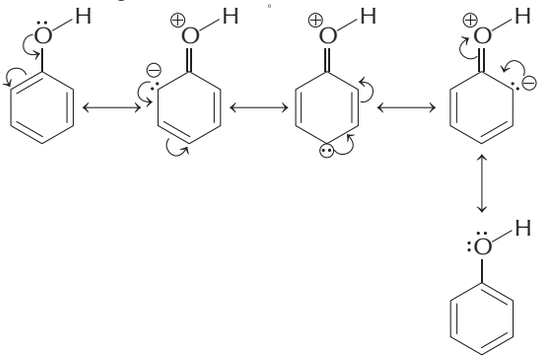
It is explained as follows

Methanol has no resonance and no partial double bond character in C—OH bond.

∴ It has maximum C—OH bond length.

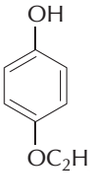
In both phenol and *p*-ethoxyphenol, resonance is involved.

∴ C—OH bond has partial double bond character and hence C—OH bond length is less than methanol.



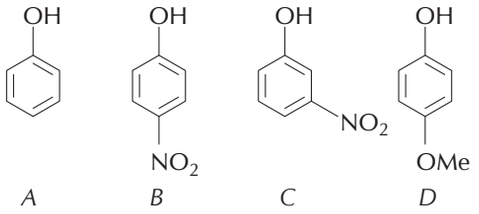
(*p*-ethoxyphenol also exhibits similar resonating structures).

But in *p*-ethoxyphenol, there is +*M*-effect of 'OC_2H_5' group also.



So in this case the ' C—OH' bond has less double bond character and slightly longer bond length than the C—OH' bond length in phenol.

Example 3. *The increasing order of the* pK_a *values of the following compounds is* **(JEE Main 2019)**



A *B* *C* *D*

(a) $D < A < C < B$ (b) $B < C < A < D$

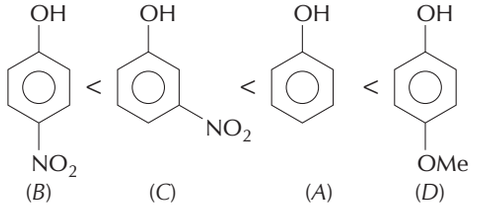
(c) $C < B < A < D$ (d) $B < C < D < A$

Sol. (*b*) Acidic strength is inversely proportional to pK_a value. The acidity of phenols is due to greater resonance stabilisation of phenoxide ion relative to phenol.

Therefore, any substituent which stabilises the phenoxide ion more by dispersal of negative charge will tend to increase the acidity of phenol.

Electron withdrawing groups (—NO_2) increases the acidic strength of phenol whereas electron donating group (—OCH_3) decreases the acidic strength of phenol. In case of —NO_2 group attached to phenol, the dispersal of negative charge is more pronounced at *o*-and *p*-position than at *m*-position.

Thus, order of acidic strength of nitrophenol is *p*-nitrophenol > *m*-nitrophenol and the correct order of the pK_a values of give option is



(*B*) (*C*) (*A*) (*D*)

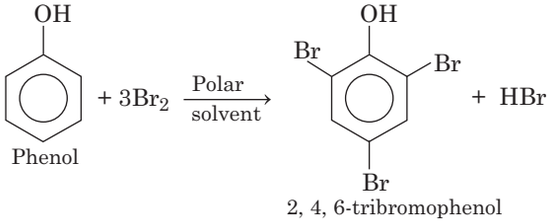
Chemical Properties of Phenols

Phenols exhibit following chemical properties

1. Electrophilic Substitution Reactions

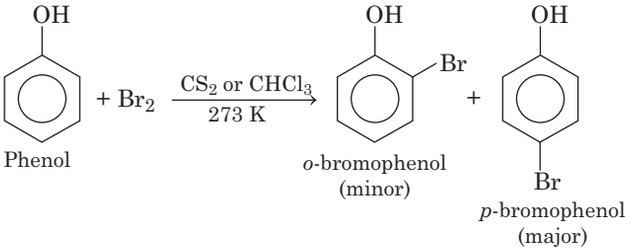
In phenol, the —OH group shows $+M$ and $-I$-effect and hence, highly activates the benzene ring towards electrophilic substitution reactions. It is an *ortho* and *para* directing group. The normal electrophilic substitution of phenol are given below

(i) **Halogenation** In polar solvent 2, 4, 6-trihalo phenol is the major product.

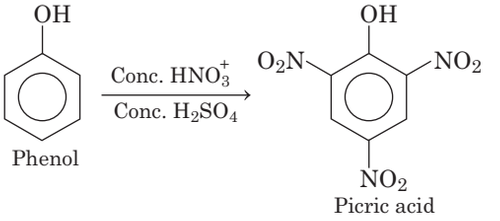


In polar solvent, phenol is in equilibrium with phenoxide ion which is the actual substrate.

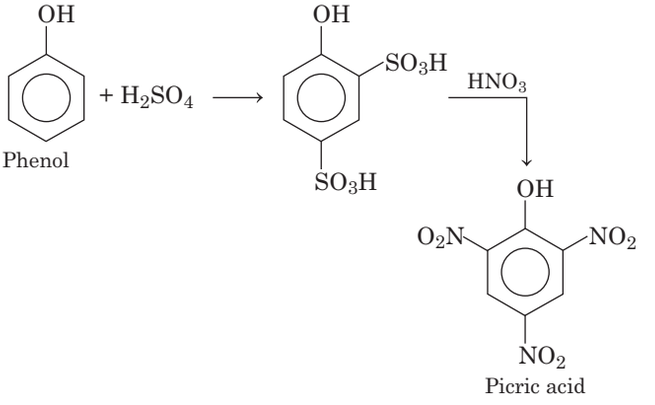
However, in the presence of CS_2 or $CHCl_3$, *ortho* and *para* halophenols are the main products.



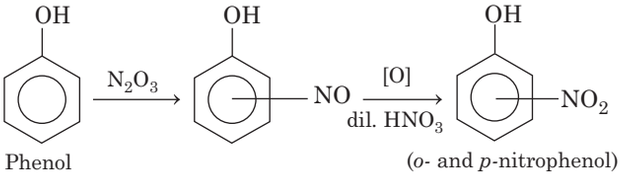
(ii) **Nitration** Picric acid is produced with nitrating mixture



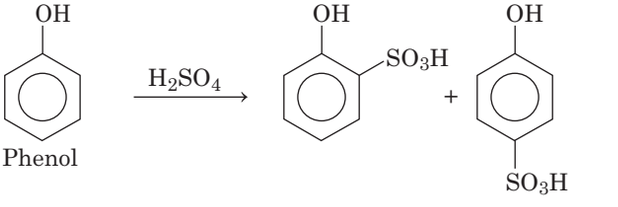
However, nitration after deactivating the ring by sulphonation, gives picric acid in better yield.



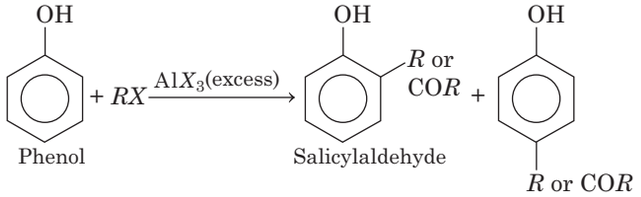
For preparing *o*- and *p*-nitrophenols, dil. HNO_3 is used. The reaction involves initial nitrosation of phenol with N_2O_3 which is then oxidised to nitrophenol as,



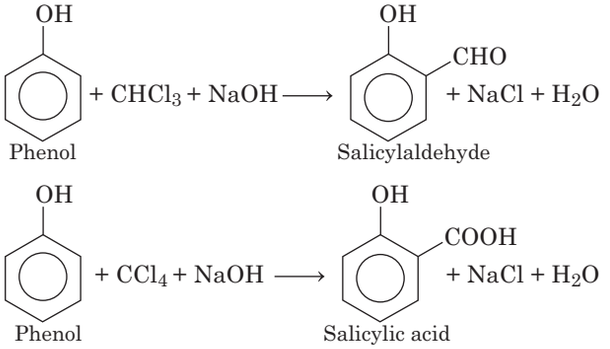
(iii) **Sulphonation**, *ortho* and *para* phenol sulphonic acids are produced.



(iv) **Friedel-Craft reactions**, i.e. alkylation and acylation occur in the excess of Lewis acid like AlX_3 as,

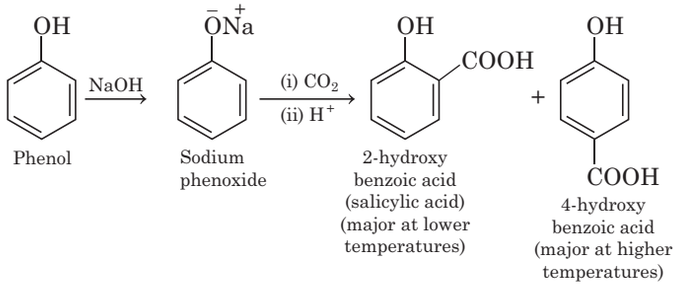


(v) **Reimer-Tiemann reaction** In this reaction, phenol reacts with trihalogen or tetrahalogen methane followed by hydrolysis with alkali. As the result *o/p* salicylaldehyde or salicylic acid are produced.



(vi) **Kolbe reaction** This reaction involves electrophilic attack of very weak electrophile (CO_2) on activated *ortho* or *para* position of phenoxide ion.

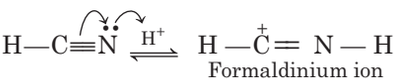
In this reaction, phenoxide ion generated by treating phenol with sodium hydroxide is even more reactive than phenol towards electrophilic substitution reaction. At lower temperatures *ortho* isomer predominates whereas *para* isomer obtained in excess of reagent, at higher temperatures.



Kolbe Schmidt reaction is infact a modification of Kolbe's reaction. Here, a pressure of 5-7 atmosphere is also applied because of which reaction occurs at comparatively lower temperatures.

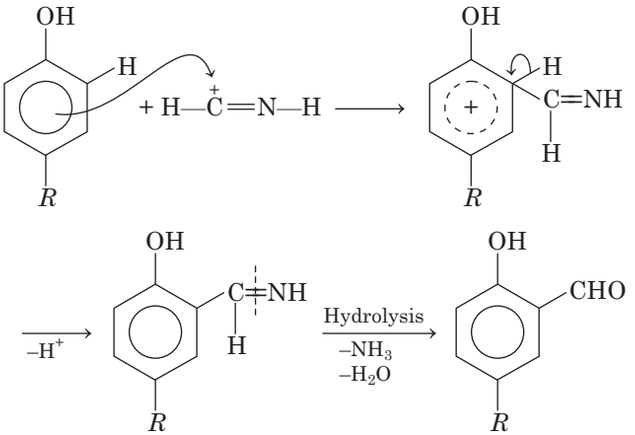
(vii) **Gattermann synthesis** This is an aromatic electrophilic substitution reaction, involving the attack of **formaldinium ion** formed by HCN and HCl with help of $AlCl_3$ giving rise to aldimine.

Aldimine on hydrolysis gives phenolic aldehyde as given below



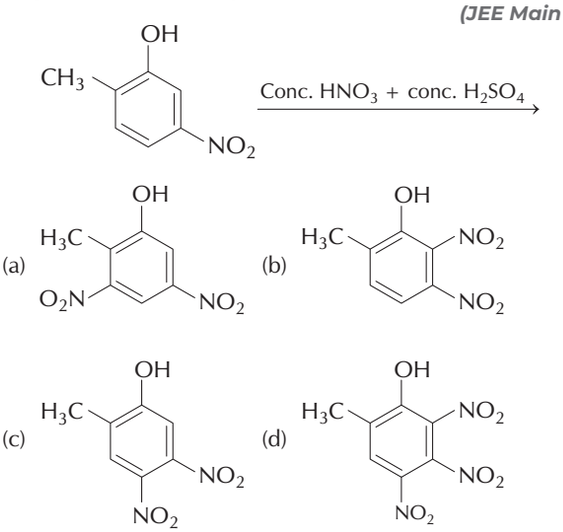
[The Cl^- of HCl is trapped by $AlCl_3$ as

$$HCl^- + AlCl_3 \longrightarrow AlCl_4^- + H^+]$$



The —CHO group prefers *para*-position and attacks on *ortho*-position only if *para*-position is blocked.

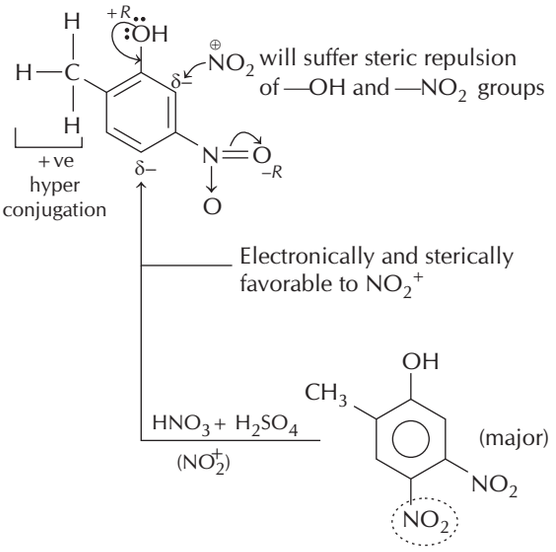
Example 4. *The major product of the following reaction is* ***(JEE Main 2020)***



Sol. (c) The substrate undergoes nitration reaction ($ArSE_2$). The electrophile (NO_2^+) will prefer to attack benzene nucleus which is rich with electron density (by +*R* or +*I*-effect of substituent, where + *R* > + *I*) as wall as sterically less crowded.

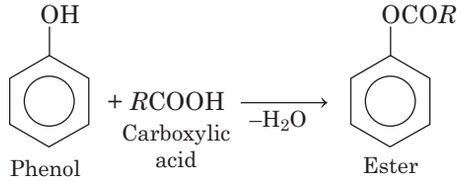
Out of three substituents, the —OH group will dominate the rate of initiation reaction, because —OH has strong ring activating property by its +*R* or + *M* effect.

The ring activating order is $\underset{(+R\text{-effect})}{-OH} > \underset{(+\text{ve hyper conjugation})}{-CH_3} > \underset{(-R\text{-effect})}{-NO_2}$



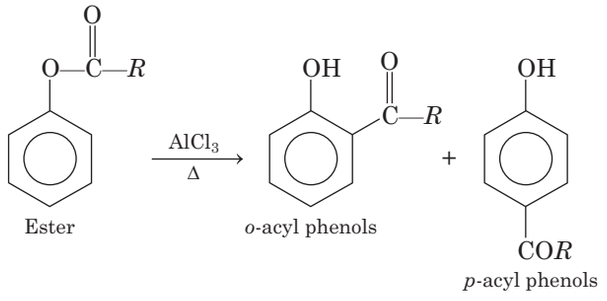
2. Esterification

Phenols react with carboxylic acids to form esters.

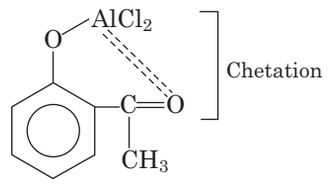


This reaction is already described completely in properties of aliphatic alcohols.

Phenolic esters on heating with $AlCl_3$ (Lewis acid) give *o*- and *p*-acyl phenols, the reaction is called **Fries migration**. e.g.



At low temperatures (below 100°C) *para* isomer is major product while at high temperature *ortho* isomer is major product. This is because intermediate of *ortho* isomer is stabilised by chelation as

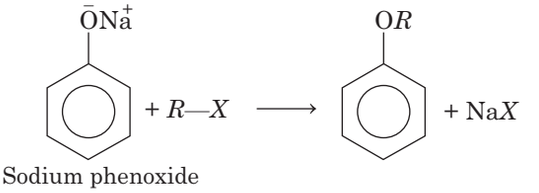


Presence of electron withdrawing group in the substrate favours retardation of reaction.

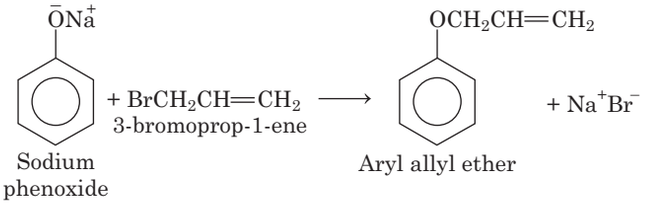
Solvent is generally not required for the reaction. Nitrobenzene may be used which reduces the reaction temperature.

3. Ether Formation

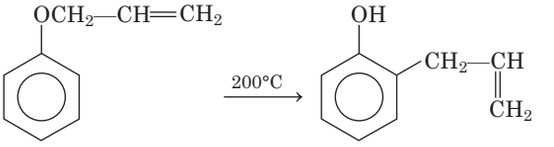
Sodium or potassium alkoxide on reaction with alkyl halide give aryl allyl ether.



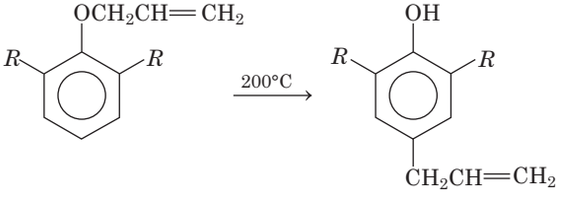
Similarly, sodium or potassium alkoxide on reaction with allyl bromide give aryl allyl ethers as,



These aryl allyl ethers when heated to 200°C show **Claisen rearrangement** which involves migration of allyl group from ethereal oxygen to ring C at *ortho* position and to *para* position when both the *ortho* position are blocked as,

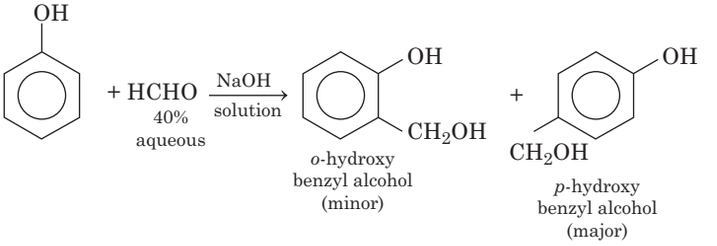


Similarly,

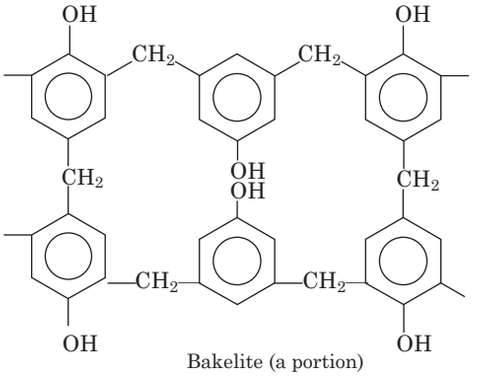


4. Lederer-Manasse Reaction

Hydroxymethylation with HCHO as the reagent of phenols using formaldehyde in presence of acid or base catalyst is called Lederer- Manasse reaction.



Intermolecular condensation of these hydroxy methyl phenols lead to the formation of **bakelite**.



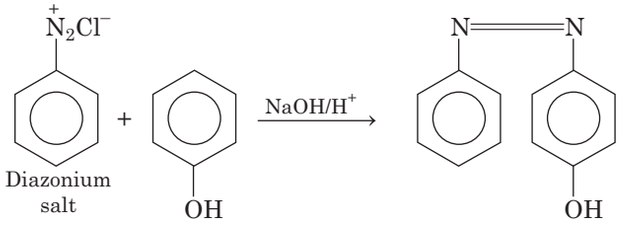
Bakelite (a portion)

5. Other Reactions of Phenols

Some other chemical reactions of phenols are as follows

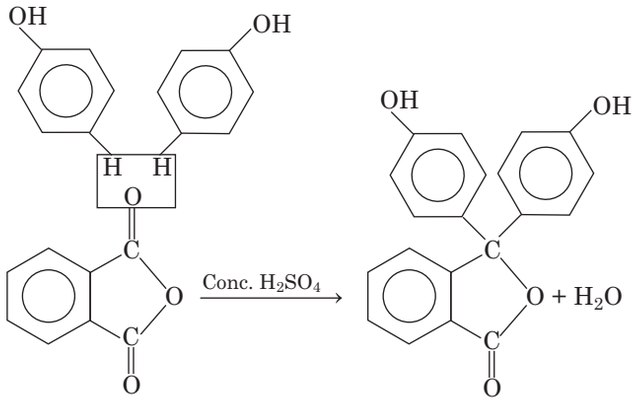
(i) **Coupling reaction** Phenols couple with benzene diazonium chloride in an alkaline solution to form *p*-hydroxyazobenzene (a dye).

The equation of reaction is shown below



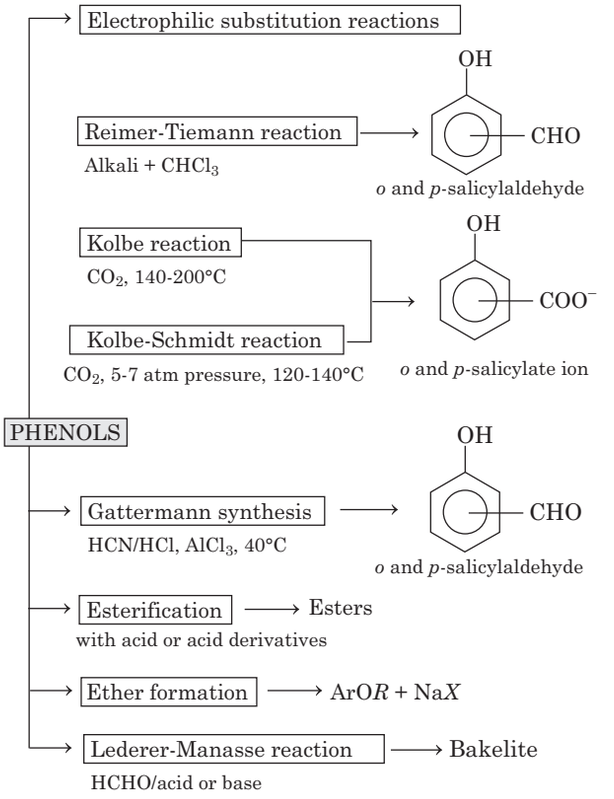
Diazonium salt — Phenol — *para*-hydroxyazobenzene

(ii) **Condensation with phthalic anhydride** In the presence of conc. H_2SO_4 , phenol combines with phthalic anhydride to form phenolphthalein as



Phenolphthalein

The outline of chemical properties of phenol is summerised below



Uses of Phenols

- Aqueous solution of phenol is sold in the market with the commercial name "**carbolic acid**".
- 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. Thus, ethers may look like, $R'—O—R''$.

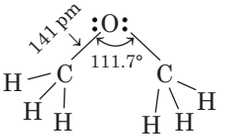
In other words, the substitution of a hydrogen atom in a hydrocarbon by an alkoxy or aryloxy group (R—O/Ar—O) yields ethers. When both the R groups (alkyl groups) are same, the ethers are called **simple** or **symmetrical ether** and when both the groups are different, the ethers are called **mixed** or **unsymmetrical ethers**.

e.g. $CH_3 — O — CH_3$ (Simple or symmetrical ethers)

$CH_3OC_2H_5$ (Mixed ether or unsymmetrical ethers)

Structure of Ethers

In ethers, the four electron pairs, i.e. the two bond pairs and two lone pairs of electrons on oxygen are arranged approximately in a tetrahedral arrangement. The C—O bond length (141 pm) is almost the same as in alcohols. The structure of methoxymethane is shown below



The bulkier R groups result in the greater forces of repulsion and thus the $\begin{matrix} R \\ \diagdown \\ \diagup \\ R \end{matrix}$O bond angle is 110°. It is somewhat greater than the normal tetrahedral bond angle 109.28″. Thus, ethers have a bent structure (like H_2O) and dipolar nature.

Preparation of Ethers

General methods used for the preparation of ethers are as follows

1. Williamson's Ether Synthesis

This method is used for the preparation of both symmetrical and unsymmetrical ethers. The reaction involves S_N2 attack of an alkoxide ion on primary alkyl halide.

$$R\bar{O}Na^+ + R'X \longrightarrow ROR' + Na^+X^-$$

Best yield of asymmetrical ethers are obtained when the alkyl halides are primary and alkoxides are tertiary. For detail, also see in the properties of alkyl halides in haloalkane and haloarene chapter.

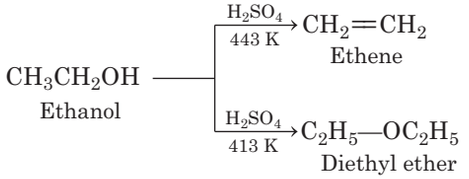
2. Reaction of RX with Dry Silver Oxide

It is already discussed in properties of alkyl halides. The reaction looks like as

$$2RX + Ag_2O \longrightarrow ROR + 2AgX$$

3. By Dehydration of Alcohols

Alcohols undergo dehydration in the presence of protic acids like H_2SO_4, H_3PO_4. The formation of the reaction product, alkene or ether depends on the reaction conditions especially temperature.



The order of ease of dehydration of alcohols follow the sequence, tertiary < secondary < primary.

The method is generally useless for the preparation of asymmetrical ethers, because if mixture of alcohols is taken then complex mixture of ether is obtained. e.g.

$$ROH + R'OH \xrightarrow[140°]{\text{Conc. } H_2SO_4} ROR + ROR' + R'OR'$$

$$\underset{\text{(Excess)}}{RCH_2OH} \xrightarrow[250°C]{Al_2O_3} RCH_2—O—CH_2R$$

In the second case, Al of Al_2O_3 works as Lewis acid.

Here, R and R' may be same or different alkyl or aryl groups.

4. By the Action of Diazomethane on Alcohols

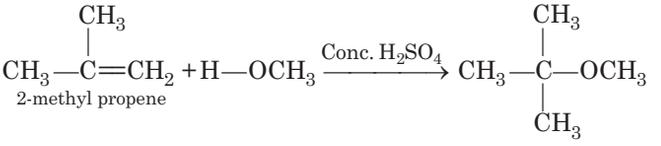
$$ROH + CH_2N_2 \xrightarrow{HBF_4} R—O—CH_3 + N_2\uparrow$$

The method is suitable for the preparation of methyl ethers only and remember, tetrafluoroboric acid (HBF_4) is used as the catalyst.

5. From Alkenes

Ethers can be prepared from alkenes in following ways

(i) **By adding alcohols** This reaction proceeds through the formation of a carbonium ion, thus a possibility always exists that the carbonium ion may rearranges itself to form a more stable carbonium ion to affect the result.

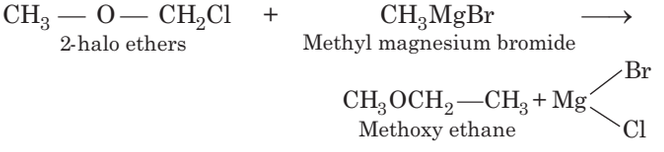


(ii) **Alkoxy mercuration-demercuration** This reaction does not involve carbonium ion formation thus no rearrangements are possible to affect the result of reaction.

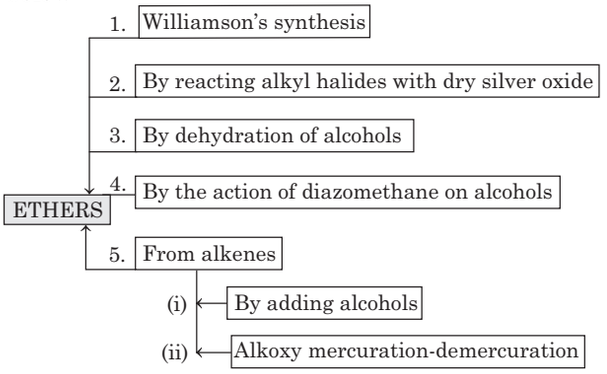
$$\text{Alkene + Alcohol} \xrightarrow[\text{(ii) } NaBH_4/OH^-]{\text{(i) } Hg(OOCCF_3)_2} \text{Ether}$$

6. Preparation of Higher Ethers

Higher ethers can be prepared by treating α-halo ethers with suitable Grignard's reagent as



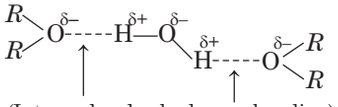
The outlines of the methods of preparation of ethers is shown below



Physical Properties

Dimethyl ether and ethyl methyl ether are gases at room temperature while other homologues are colourless liquids with characteristic ether smell. These have a dipole moment of 1.15 to 1.3D. Their **boiling points are found lower than their isomeric alcohols**.

It is due to lesser hydrogen bonding in them as compared to the corresponding alcohols. Ethers upto 3C-atoms are soluble in water due to the formation of intermolecular hydrogen bonds shown below



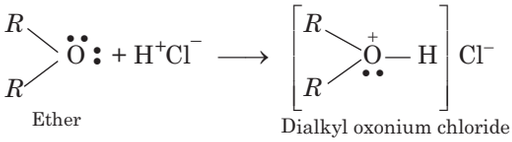
Chemical Properties

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

1. Reactions Due to Ethereal Oxygen

These **reactions are mainly due to the lone pair electrons of oxygen.** Here, ethers behave as base. Due to such electrons following reactions are shown by ethers.

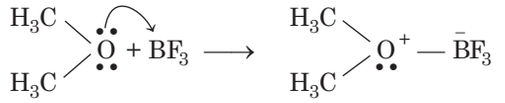
(i) **Action of concentrated acids** Oxonium salts are formed, i.e. such salts are formed when H^+ of acid accepts one of the lone pair of oxygen.



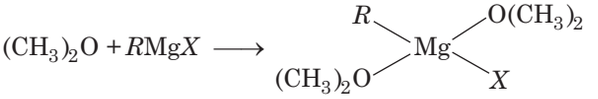
These salts are stabilised due to the presence of the anion of acids as shown below

$$\underset{\text{Dimethyl ether}}{(CH_3)_2O} + H_2SO_4 \longrightarrow \underset{\text{Diethyl oxonium hydrogen sulphate}}{[(CH_3)_2OH]^+HSO_4^-}$$

(ii) **Formation of coordination complexes** ethereal oxygen, being **Lewis base** form coordination complexes, called **etherates**, with Lewis acids such as BF_3, $AlCl_3$, $FeCl_3$, Grignard's reagent etc. The equation of these reactions is given below



Similarly,



[Due to this complex formation Grignard reagents show their dissolution in dry ether.]

2. Reactions Involving Cleavage of Carbon-Oxygen Bond

Cleavage of C— O bond results to following reactions of ethers.

(i) **With H*X*** The reaction of dialkyl ether with H—*X* gives two alkyl halide molecules.

$$\underset{\text{Ether}}{R—O—R} + HX \xrightarrow{100°C} \underset{\text{Alcohol}}{R—OH} + \underset{\text{Alkyl halide}}{RX}$$

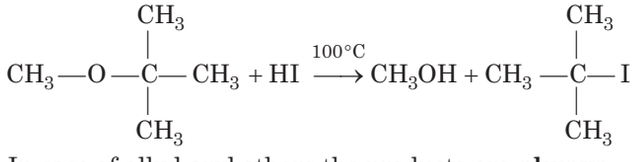
$$R—OH + HX \longrightarrow R—X + H_2O$$

- The order of reactivity of halogen acids follow the sequence

$$HI > HBr > HCl$$

- In case of asymmetrical ethers, the alkyl halide is always formed from the **smaller alkyl group** provided no tertiary (3°) alkyl group is present. If any 3° alkyl group is present, the halogen gets attached with it. e.g.

$$\underset{\text{Methoxy ethene}}{CH_3—O—C_2H_5} + HBr \xrightarrow{100°C} \underset{\text{Bromomethane}}{CH_3Br} + \underset{\text{ethanol}}{CH_3CH_2OH}$$



In case of alkyl aryl ethers the products are **always phenol and an alkyl halide**. e.g.

$$C_6H_5—O—CH_3 + HBr \xrightarrow{100°C} C_6H_5OH + CH_3Br$$

(ii) **With sulphuric acid** With dil H_2SO_4, under pressure, ethers are hydrolysed to alcohols as

$$\underset{\text{Ether}}{R—O—R} + H_2O / H^+ \xrightarrow[\text{under pressure}]{\text{Dil. } H_2SO_4, \Delta} \underset{\text{Alcohol}}{2R—OH}$$

With conc. H_2SO_4, alcohols and alkyl hydrogen sulphates are formed as

$$\underset{\text{(Primary ether)}}{R—O—R} + \text{Conc. } H_2SO_4 \xrightarrow{\Delta} R—OH + RHSO_4$$

Secondary and tertiary ethers however, form alkenes instead of alcohols.

(iii) **With PCl_5** The reaction looks like

$$CH_3—O—CH_3 + PCl_5 \longrightarrow 2CH_3—Cl + POCl_3$$

(iv) **With acid derivatives** Acid chlorides react with ethers in the presence of anhydrous $ZnCl_2$ or $AlCl_3$ to form alkyl halide and esters as

$$R\,OR + R'COCl \xrightarrow[\Delta]{AlCl_3 \text{ or Anhyd. } ZnCl_2} RCl + R'COOR$$

Acid anhydrides form only esters under similar conditions as

$$R—O—R + (CH_3CO)_2O \xrightarrow[\text{or } ZnCl_2/\Delta]{\text{Anhy. } AlCl_3} 2CH_3COOR$$

3. Reactions Involving Alkyl Group

(i) **Action of air and light** When exposed to air and light for a long time, ethers are oxidised to form hydroperoxides or simply peroxides as

$$\underset{\text{Diethyl ether}}{CH_3CH_2—O—CH_2CH_3} \xrightarrow[\text{Light}]{O_2} CH_3—\overset{\overset{OOH}{|}}{CH}—O—CH_2CH_3$$

The reaction is free radical and **oxidation occurs at the C-atom next to ethereal oxygen**.

These peroxides are very dangerous compounds as these decompose violently at high temperatures.

(ii) **Halogenation** With halogens, ethers give substitution products. The extent of halogenation, however, depends upon the reaction conditions.

Diethyl ether reacts in dark to form only monosubstituted products of alkyl group. e.g.

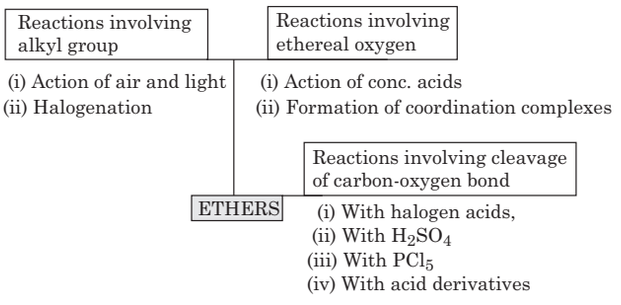
$$\underset{\text{Diethyl ether}}{CH_3—CH_2—O—CH_2—CH_3} \xrightarrow[-2HCl]{Cl_2,\ \text{dark}} CH_3—\underset{\underset{Cl}{|}}{CH}—O—\underset{\underset{Cl}{|}}{CH}—CH_3$$

α, α′-dichlorodiethyl ether

In the presence of light and excess of chlorine all hydrogen atoms are substituted as

$$CH_3—CH_2—O—CH_2—CH_3 + 10Cl_2 \xrightarrow{h\nu} C_2Cl_5—O—C_2Cl_5 + 10HCl$$

The outline of their chemical properties looks like



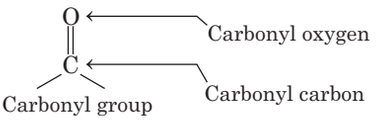
Uses of Ethers

- Ethers are used as a solvent for oils, fats and Grignard reagent etc.
- These are used as general anaesthetic.
- They provide inert and moisture free medium for various reactions.

Aldehydes and Ketones

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

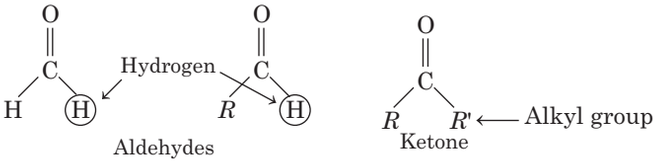
These compounds are widely spread both in plants and animal kingdom and they play an important role in biological processes.



$\rangle C{=}O$ group containing compounds can be divided into following two classes.

- First class includes those carbonyl compounds in which the carbonyl carbon is attached to either hydrogen atoms or alkyl or aryl groups. **Aldehydes** and **ketones** belong to this class.
- The other class includes those carbonyl compounds in which carbonyl carbon is attached to —OH, $—NH_2$ etc., functional groups along with H or alkyl groups. Carboxylic acids and their derivatives belongs to this class.
- This portion of our chapter is dedicated to aldehydes and ketones. In aldehydes, the carbonyl carbon is bonded to one or more hydrogens while in ketones, it is bonded to two alkyl groups.

This categorisation of aldehydes and ketones is shown below



where, R and R' may be similar or different alkyl or aryl group.

If R and R' represent the same group, the ketone is referred to as **simple ketone.** If the two R and R' groups are different, the ketone is called a **mixed ketone**.

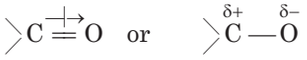
Structure and Nature of Carbonyl Group

The carbon atom of carbonyl group is sp^2-hybridised and forms three sigma (σ) bonds. The fourth valence electron of

carbon remains in its *p*-orbital and forms a π-bond with oxygen after overlapping with *p*-orbital of an oxygen.

In addition, the oxygen atom also has two non-bonding electron pairs. Thus, the carbonyl carbon and the three atoms attached to it lie in the same plane the the π-electron cloud is above and below this plane.

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

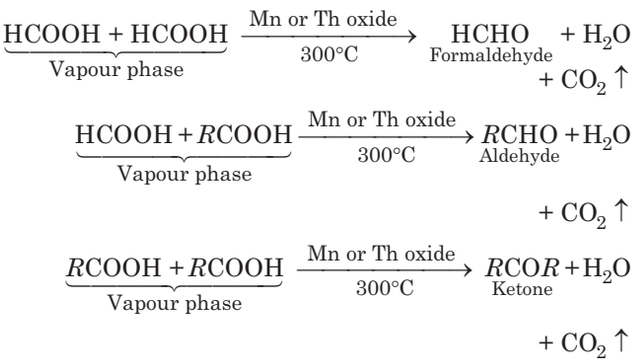


Methods of Preparation of Aldehydes and Ketones both

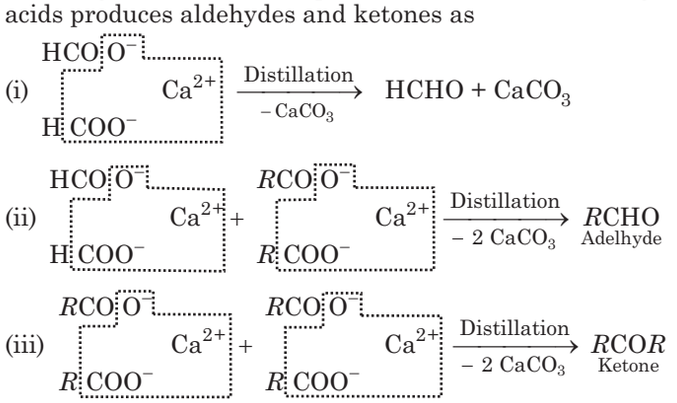
There are several methods from which both aldehydes as well as ketones can be synthesised.

1. Catalytic Decomposition of Acids and their Calcium Salts

Catalytic decomposition of acids is done with the help of oxides of manganese and thorium. The equations of complete reaction are shown below



Similarly, distillation of vapours of calcium salts of fatty acids produces aldehydes and ketones as

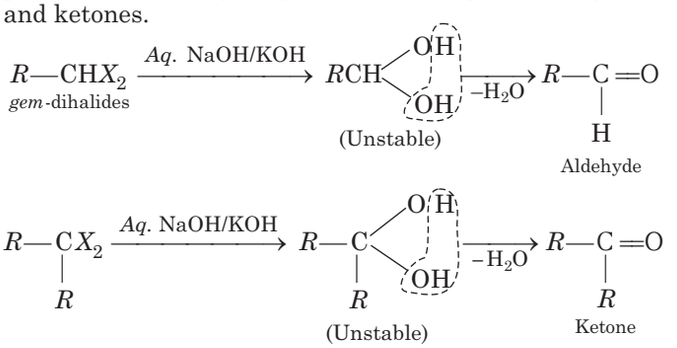


So from the above equations following conclusions can be made

- vapours of formic acid or its calcium salt always give HCHO.
- vapours of formic acid or its calcium salt with the vapours of any other acid/calcium salt always give RCHO (higher aldehyde).
- vapours of any acid other than HCOOH/calcium salt will always give *R*CO*R* (ketones).

2. Hydrolysis of *gem*-dihalides

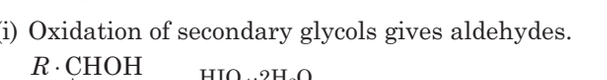
gem-dihalides on hydrolysis with alkali gives aldehydes and ketones.



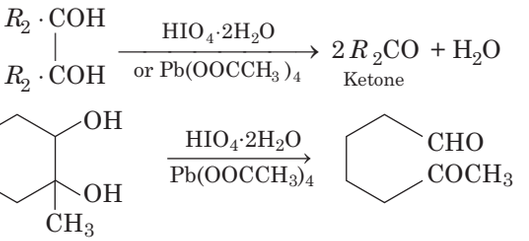
3. Cleavage of Glycol

The glycol cleavage using $HIO_4 \cdot 2H_2O$ (periodic acid) or $Pb(OOCCH_3)_4$ (lead tetra acetate) gives aldehydes and ketones, e.g.

(i) Oxidation of secondary glycols gives aldehydes.

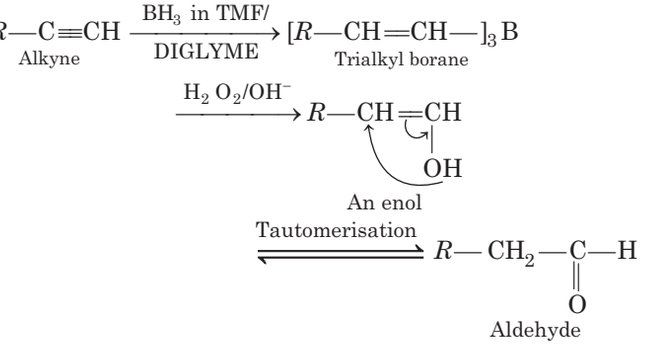


(ii) Tertiary glycols under similar conditions give ketones.

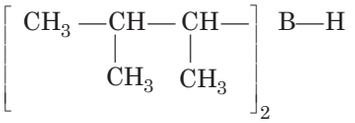


4. Hydroboration-Oxidation of Alkynes

The equation reaction is as follows

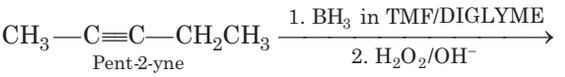


To avoid complications due to double addition of BH_3, bulky sterically hindered boranes such as *bis* (1, 2-dimethylpropyl) borane (common name-disiamyl borane) is used.

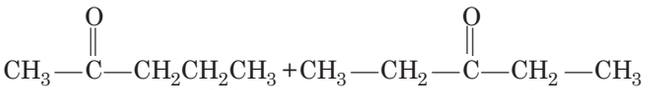


Disiamylborane

- Aldehydes can be prepared from terminal alkynes while other alkynes give ketones. Symmetrical non-terminal alkynes give a single ketone and unsymmetrical non-terminal alkynes gives a mixture of two ketones in which methyl ketone predominates.



Pent-2-yne

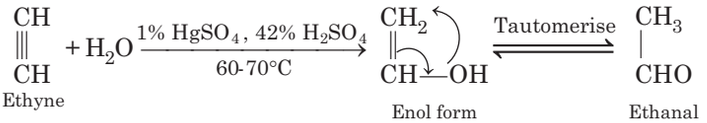


2- pentanone (major) 3 - pentanone (minor)

- Formaldehyde cannot be prepared by this method.

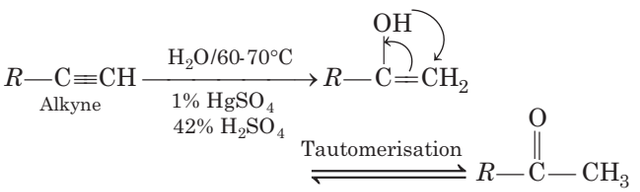
5. Hydration of Alkynes

When acetylene is passed in 42% H_2SO_4 solution, containing 1% $HgSO_4$ at 60-70°C, acetaldehyde is formed.



Ethyne Enol form Ethanal

- Hydration of other alkynes gives ketones. The addition of water follows Markownikoff's rule.



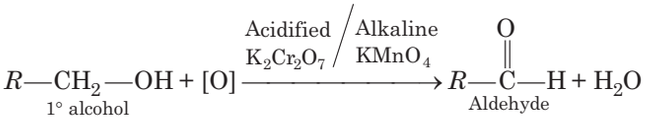
Alkyne

- Formaldehyde cannot be prepared by this reaction.

6. Oxidation of Alcohols

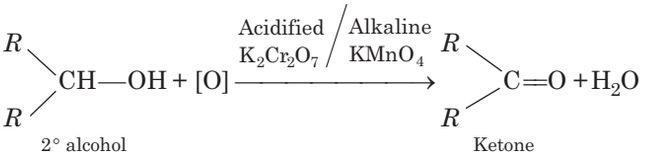
Different alcohols give different products on oxidation, e.g.

(i) Primary alcohols are oxidised to give aldehydes.



1° alcohol Aldehyde

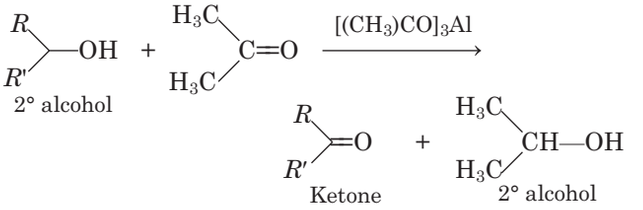
(ii) Secondary alcohols are oxidised to give ketones.



2° alcohol Ketone

- To prevent the further oxidation to acids some another reagents are also used. These are
  (a) Sarett reagent – $CrO_3 \cdot 2C_5H_5N$ in pyridine
  (b) Collin's reagent – $CrO_3 \cdot 2C_5H_5N$ in CH_2Cl_2
  (c) Corey's reagent (PCC – pyridinium chloro chromate) – $C_5H_5NH^+CrO_3Cl^-$
  (d) Pyridinium dichromate (PDC) – $(C_5H_5NH^+)_2Cr_2O_7^{2-}$
- As these reagents are very selective, hence used to oxidise allylic and benzylic alcohols as well.

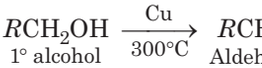
Oxidation of secondary alcohols with tertiary butoxide of aluminium in the presence of *iso*-propyl alcohol is called **Oppenauer oxidation.**



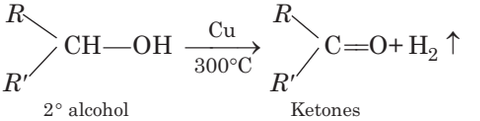
2° alcohol Ketone 2° alcohol

7. Catalytic Dehydrogenation of Alcohols

1° and 2° alcohols when heated with Cu or Ag to 300°C yield aldehydes and ketones respectively.



1° alcohol Aldehyde

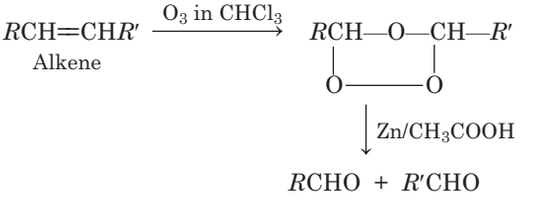


2° alcohol Ketones

This method gives good yield and described in the tests of monohydric alcohols.

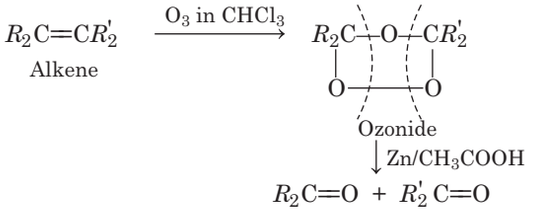
8. Ozonolysis of Alkenes

The alkenes upon treatment with O_3 (in $CHCl_3$) gives ozonide, which on subsequent treatment with Zn / CH_3COOH gives aldehydes and ketone depending on the structure of alkene.

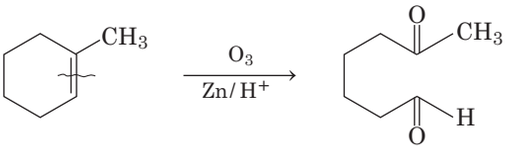


Alkene

With dialkyl substituted alkenes, ketones are obtained.

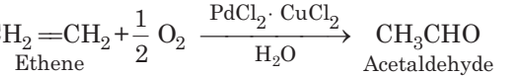


Similarly,



9. Wacker's Process

The alkene is oxidised as

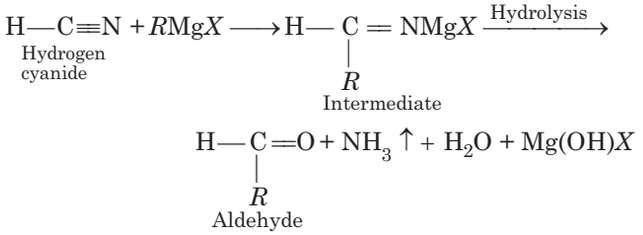


The oxidation is mainly done by $PdCl_2$.

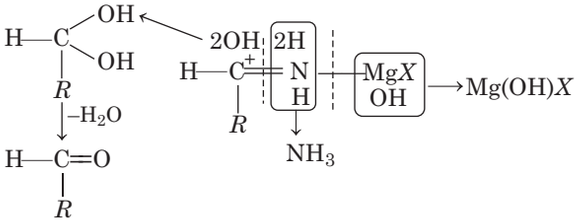
As $PdCl_2$ is an expensive reagent, hence, cooxidant $CuCl_2$ reoxidise Pd to $PdCl_2$ and itself reoxidise by air. Thus, the atmospheric oxygen is the only oxidising agent used. The process is discussed in detail within chapter. Hydrocarbons; Alkene.

10. From Grignard Reagent and Cyanides

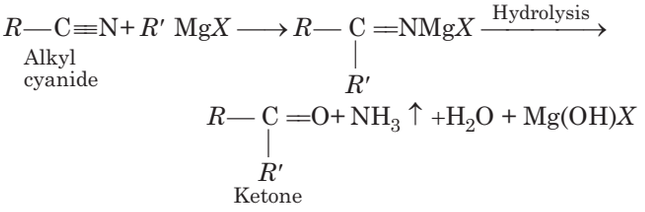
(i) Reaction of Grignard's reagent with HCN gives aldehydes other than HCHO. In fact HCHO cannot be prepared by this reaction.



The breakage outline of intermediate is shown below

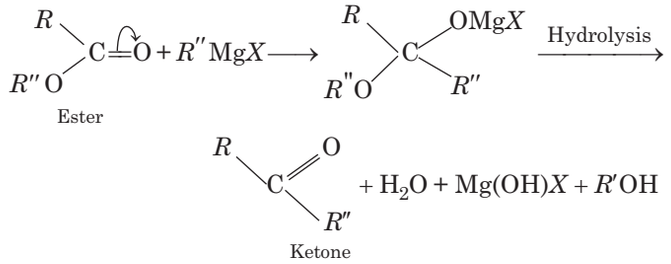


(ii) Ketones are produced by the reaction of RCN with R'MgX as



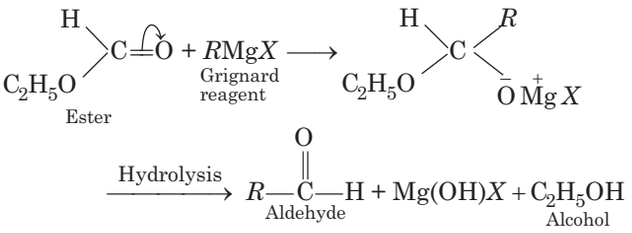
11. From Grignard Reagent and Esters

- Grignard reagent give ketones on treatment with acid derivatives like esters as



But the yield here is very less as the ketone formed further reacts with R''MgX.

- Aldehydes are formed by reaction of ethyl formate with Grignard reagent.

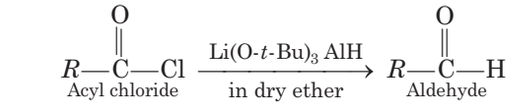


Methods of Preparation for Aldehydes

Following methods are employed for the synthesis of aldehydes only.

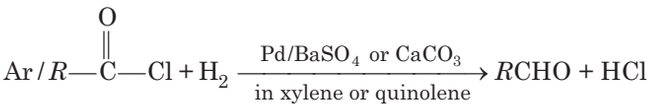
1. Reduction of Acids and Acid Derivatives

Reduction of acids and acid derivatives under normal conditions with strong reducing agents like $LiAlH_4$ results to alcohols. The procedure routes through carbonyl compound formation. Thus, mild reducing agents like DIBAL-H (di *iso*-butyl aluminium hydride), lithium *tri*-(tertiary) butoxy aluminium hydride [$Li(O\text{-}t\text{-}C_4H_9)_3AlH$] and *tri n*-butyl tinhydride are used for the purpose. $NaAlH_4$ also shows same results.



Rosenmund Reaction

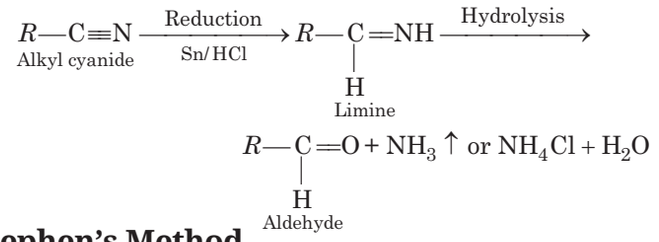
In particular hydrogenation of RCOCl with H_2 in the presence of Lindlar's catalyst to produce aldehydes is called Rosenmund reaction, i.e.



Reduction of acids normally produces very less yield that's why acyl halides and esters are preferred over them. Formyl chloride cannot be reduced to give formaldehyde because of being unstable.

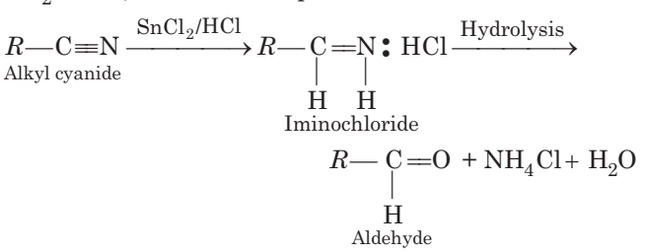
2. Reductive Hydrolysis of Alkyl Cyanides

The generalised reaction looks like



Stephen's Method

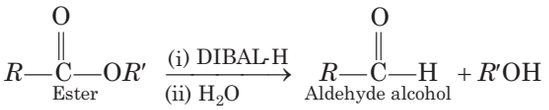
- Specifically when reduction is carried out with $SnCl_2$ / HCl, it is called Stephen's method.



- Reduction can also be seen with the help of DIBAL-H (di *iso*-butyl aluminium hydride). It does not reduce double or triple bond directly but have the ability to reduce π-bond of nitrile group.

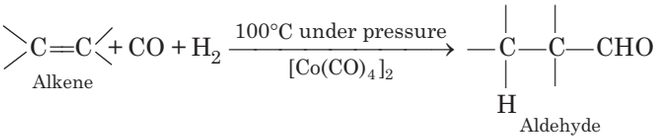
3. Reduction of Esters

Esters are reduced to aldehydes by DIBAL-H or $NaAlH_4$.

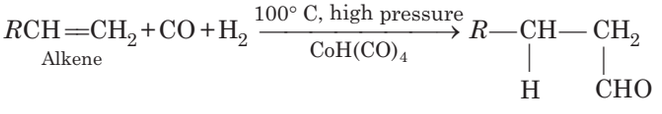


4. Oxo Process

The process is also called **carboformylation** or **hydroformylation**.



- $CoH(CO)_4$ can also be used as catalyst.
- The reaction appears to be an anti-Markownikoff addition of formaldehyde to the alkene.

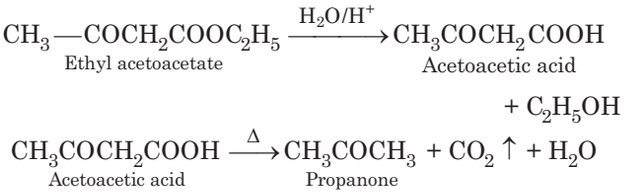


Methods of Preparation for Ketones

Following methods are used for the synthesis of ketones only.

1. Hydrolysis of Ethyl Acetoacetate

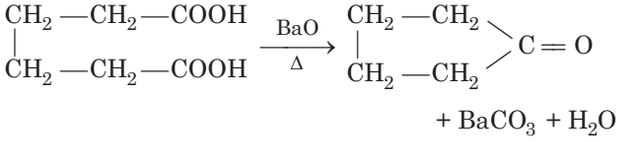
When ethyl acetoacetate (EAA) is hydrolysed with dil. HCl, acetoacetic acid is formed which on heating undergoes decarboxylation. The equation of complete reaction is shown below



This hydrolysis is called *ketonic hydrolysis of EAA*. The reaction is specifically used for the preparation of acetone.

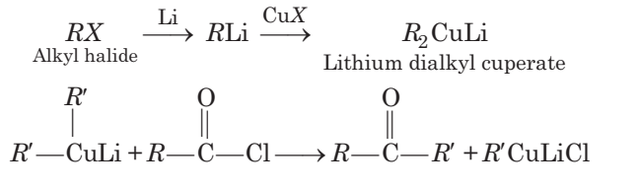
2. From Dicarboxylic Acids

Dicarboxylic acids are heated with BaO or CaO to give cyclic ketones.

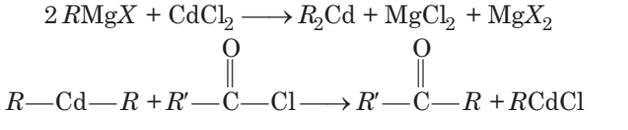


3. By Organometallic Compounds

Lithium organocuprate reacts rapidly with acid chlorides to yield ketones.

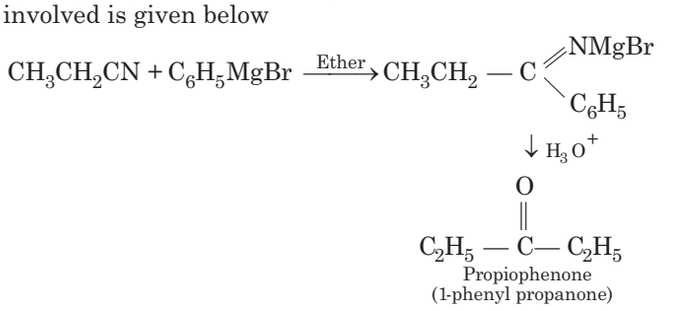


- Cadmium salts may also be used.



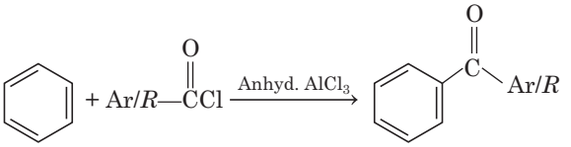
4. From Nitriles

Treatment of a nitrile with Grignard reagent followed by hydrolysis yield a ketone. Equation of the reaction involved is given below

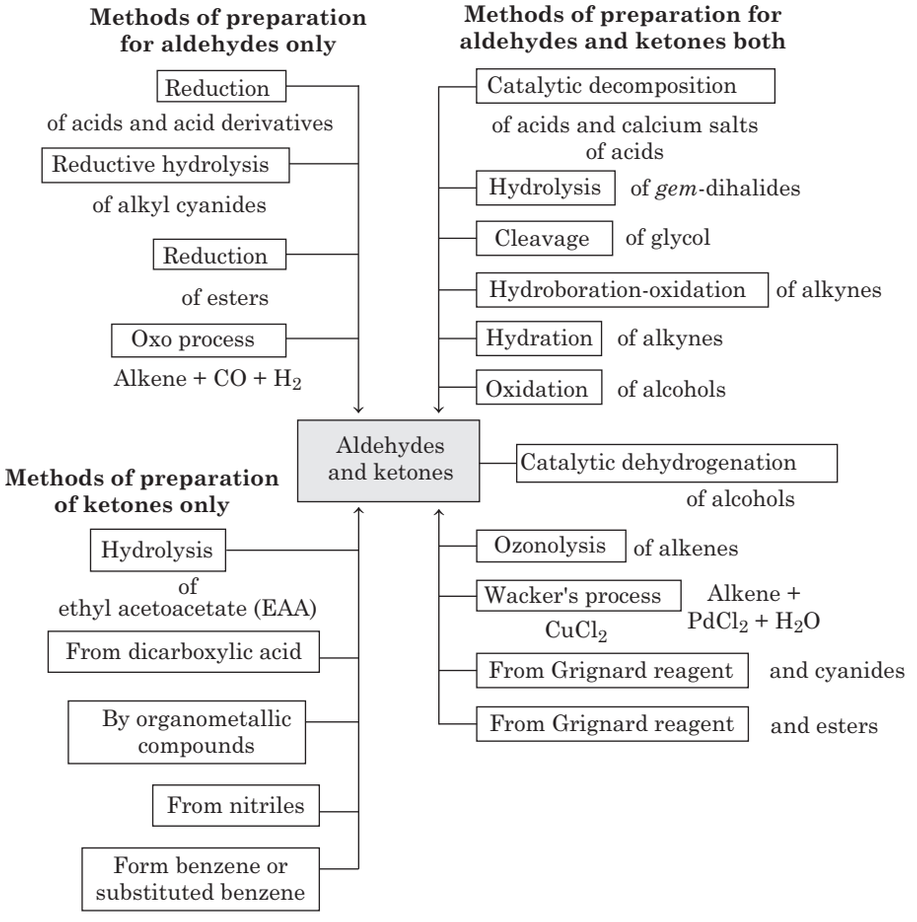


5. From Benzene or Substituted Benzene

When benzene or substituted benzene is treated with acid chloride in presence of anhyd. $AlCl_3$, it gives ketone. This reaction is known as Friedel-Craft acylation reaction.



The outline of methods of preparation of these carbonyl compounds looks like



Physical Properties

(i) **Physical state** HCHO is a pungent smelling gas, CH_3CHO is a volatile liquid.

Other aldehydes and ketones (upto 11C-atoms) are colourless liquids which still higher members are solids.

(ii) **Smell** Generally pleasent smelling, however, lower members have unpleasent pungent smell.

(iii) **Boiling points** of aldehydes and ketones are higher than those of hydrocarbons and ethers of comparable molecular masses. The reason behind this fact is to dipole-dipole interactions between the opposite ends of the $\rangle C{=}O$ dipoles.

(iv) **Solubility** decreases with increase in molecular mass. Lower aldehydes and ketones containing upto four carbon atoms are soluble in water.

Chemical Reactions of Aldehydes and Ketones

Aldehydes and ketones because of the presence of polar carbonyl group exhibit the following characteristics.

1. Nucleophilic Addition Reactions

Carbonyl compounds show nucleophilic addition reactions. A nucleophile attacks at the positively charged carbon atom of the polar carbonyl group.

$$\rangle \overset{\delta+}{C}{=}\overset{\delta-}{O}$$

sp^2, carbonyl group

As the number of carbon atoms/number of alkyl groups increases, reactivity decreases due to steric hindrance. Hence, their order of reactivity is

$$HCHO > CH_3CHO > CH_3COCH_3 > C_2H_5COC_2H_5$$

Among the aldehydes and ketones, the size of alkyl group is inversely proportional to their reactivity.

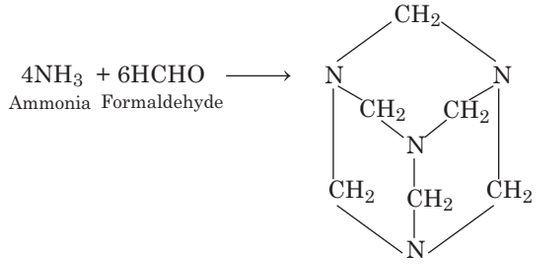
Among the ketones their less reactivity is due to $+I$ effect of alkyl groups present due to which the partial (+) ve charge on carbon atom of carbonyl group decreases, thus, decreasing the possibility of nucleophilic attack.

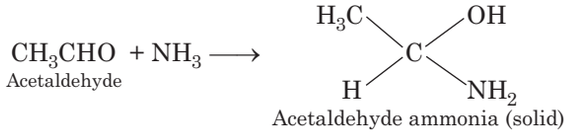
I. **Addition of hydrogen cyanide** The reaction proceeds as

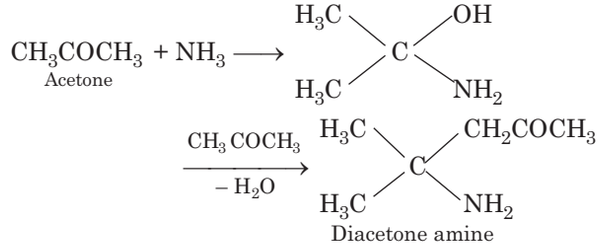
- HCN in itself is not a powerful nucleophile that attacks on $>C=O$ therefore, the reaction requires base catalysis in order to convert HCN into a strong nucleophile CN^-.
- Ketones give *d* and *l* cyanohydrin only if both the alkyl groups attached to carbonyl carbon are differentm i.e. ketone is unsymmetrical.
- Cyanohydrins are useful synthetic substances since they can be readily hydrolysed to give α-hydroxy acids by Strecker synthesis.

II. **Addition of ammonia and its derivatives**

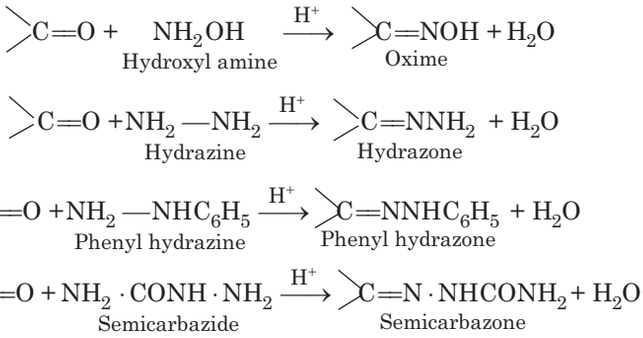
The reaction of aldehydes and ketones with ammonia are illustrated below



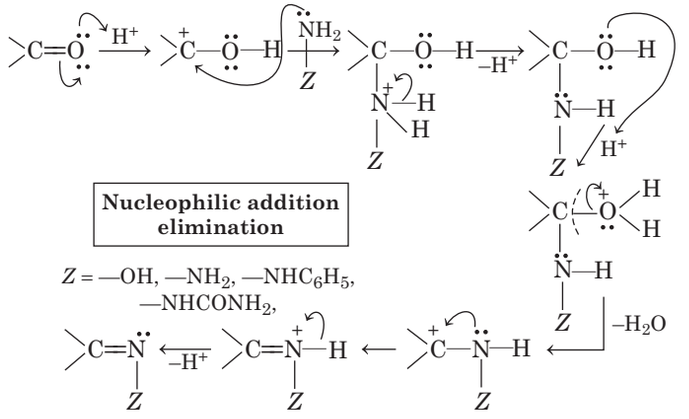




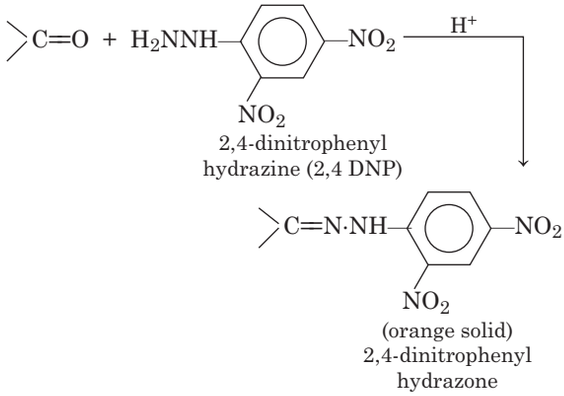
With Ammonia Derivatives



Mechanism of the reactions is summarised as

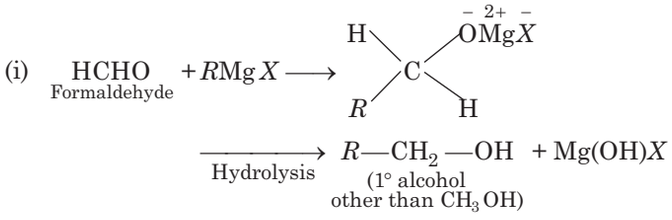


2, 4-DNP is used to distinguish carbonyl compounds from the mixture as we get solid orange precipitate of 2,4-dinitrophenyl hydrazone.

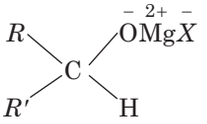


In these reactions, pH of medium must be controlled to about 3.5, i.e. the medium must be weakly acidic in order to protonate the carbonyl group.

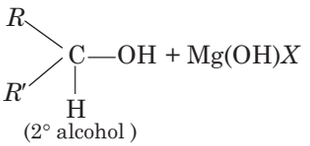
III. **Addition of Grignard reagent** The reactions are as



(ii) $R\text{CHO} + R'\,\text{Mg}X \longrightarrow$ (Aldehyde)

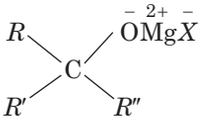


$\xrightarrow[\text{Hydrolysis}]{}$

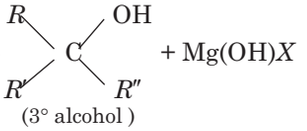


(2° alcohol)

(iii) $R\text{—CO}R' + R''\,\text{Mg}X \longrightarrow$ (Ketone)



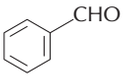
$\xrightarrow[\text{Hydrolysis}]{}$

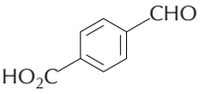


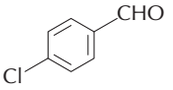
$+ \text{Mg(OH)}X$

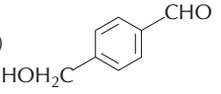
(3° alcohol)

Example 5. *The aldehydes which will not form Grignard product with one equivalent Grignard reagents are*

(A) 

(B) 

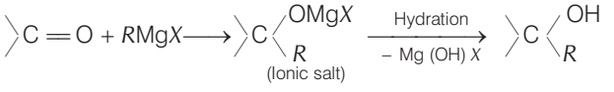
(C) 

(D) 

(a) (C), (D) (b) (B), (D) (c) (B), (C), (D) (d) (B), (C)

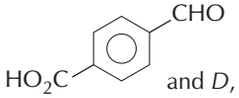
(JEE Main 2019)

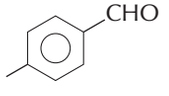
Sol. (b) Grignard reagent usually attacks on $\rangle C{=}O$ group as



The question is related to above reaction only with the condition that the consumption of $R\text{Mg}X$ will be more than 1 equivalent in some of the given cases.

Among the given compounds *B*, i.e.



and *D*, i.e. 

contain additional groups which can give active hydrogens.

Grignard reagents produce alkanes whenever come in contact with any group or compound which can give active hydrogen as

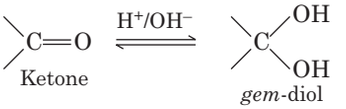
$$R\text{OH} + R'\text{Mg}X \xrightarrow[\text{ether}]{\text{Dry}} R'\text{H} + \text{Mg}\langle^{OR}_{X}$$

These reactions are equivalent to acid-base reactions. So, in both of these compounds more than one equivalent will be required to form Grignard products. Remember these compounds will give 2 type of products as:

(i) from the $\rangle C{=}O$ group

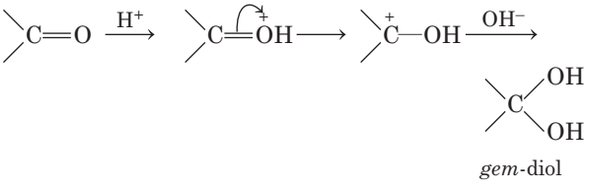
(ii) from the group which release active hydrogen

IV. **Addition of water** In aqueous solution, carbonyl compounds are in equilibrium with its hydrate– *gem*-diol, which is unstable and loses water molecule to form original compound again.

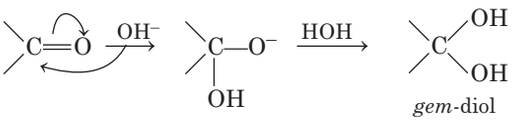


Mechanism of the reaction is summarised as,

(i) **Acid catalysed path**

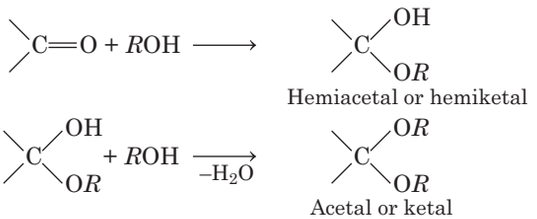


(ii) Base **catalysed path**



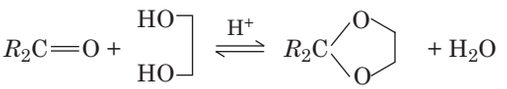
Aldehydes form more stable hydrates as compared to ketones.

V. **Addition of alcohols** Acetals (from aldehydes) and ketals (from ketones) are produced as given below



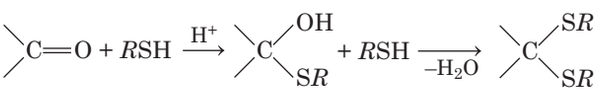
The reaction follows nucleophilic addition-elimination mechanism.

Carbonyl compounds react with glycol to produce cyclic acetals or ketals.



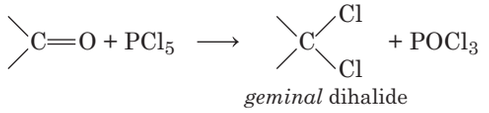
Acetals (or ketals) are stable in the presence of alkali, thus used to protect carbonyl group against alkaline oxidising agents.

VI. **Addition of thioalcohols** Mercptals thioacetals and mercaptols or thioketals are produced as,



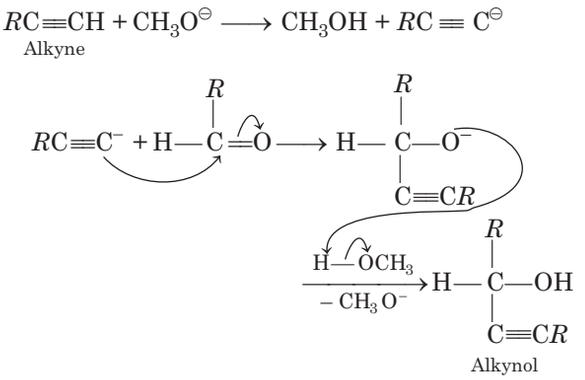
In acidic solutions, aldehyde (and ketone) groups can be protected by mercaptal and mercaptol formation respectively.

VII. **Addition of PX_5** *Geminal* dihalides (alkylidene dihalides) are produced as,



geminal dihalide

VIII. **Addition of alkynes, i.e. ethinylation** Terminal alkynes ($RC{\equiv}CH$) can add on to carbonyl group in the presence of a base (RO^-) forming alkynol (alkynediol with $CH{\equiv}CH$). This reaction is called **ethinylation.**



Alkynol

Example 6. *The increasing order of the reactivity of the following compounds in nucleophilic addition reaction is*

Propanal, Benzaldehyde, Propanone, Butanone

(JEE Main 2020)

(a) Benzaldehyde < Butanone < Propanone < Propanal
(b) Butanone < Propanone < Benzaldehyde < Propanal
(c) Propanal < Propanone < Butanone < Benzaldehyde
(d) Benzaldehyde < Propanal < Propanone < Butanone

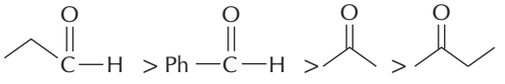
Sol. (*b*) Reactivity order toward nucleophilic addition reaction is aldehydes > ketones.

Due to the following reasons aldehydes are more reactive than ketones.

(i) **Inductive effect** An alkyl group has electron donating (+*I*) inductive effect. Hence, greater the number of alkyle group attached to carbonyl group, greater the electron density on carbonyl carbon. Thus, it lowers the attack of nucleophile and hence, reactivity decreases.

(ii) **Steric effect** Increase in the number of alkyl group attached to carbon results in the attack of nucleophile on carbonyl group becomes more and more difficult due to steric hinderance. Therefore, due to two bulky *R* groups, ketones are less reactive than aldehydes.

So, the correct reactivity order is



2. Oxidation

Aldehydes ($RCHO$) can be easily oxidised to $RCOOH$ by weak oxidising agents like

- **Tollen's reagent**, i.e. ammoniacal $AgNO_3$.
- **Fehling's solution** ammoniacal Cu^{2+} solution complexes with tartarate ion.
- **Benedict's solution** alkaline Cu^{2+} ion complex with citrate ion etc.

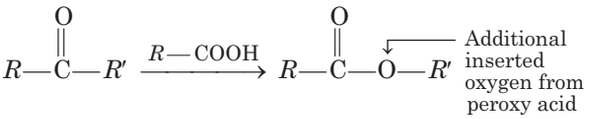
(i) $R{-}CHO + \underset{\text{Tollen's reagent}}{2Ag(NH_3)_2^+} + 3\,OH^- \longrightarrow R{-}COO^- + 2H_2O + 4NH_3\uparrow + \underset{\text{Silver mirror}}{2Ag\downarrow}$

(ii) $R{-}CHO + \underset{\text{Fehling's solution}}{2Cu(OH)_2} + NaOH \longrightarrow RCOONa + \underset{\text{Red ppt.}}{Cu_2O\downarrow} + H_2O$

- Aldehydes and ketones with a methyl or methylene group adjacent to carbonyl group are oxidised with SeO_2 as,

$$\underset{\text{Ethanal}}{CH_3CHO} + SeO_2 \longrightarrow \begin{matrix}CHO\\|\\CHO\end{matrix} + H_2O + Se$$

- Both aldehydes and ketones are oxidised by peroxy acids to esters and the reaction is called **Baeyer-Villiger oxidation** This reaction is especially useful for ketones.



- Aldehydes and ketones are oxidised by strong oxidising agents like $KMnO_4/H^+$, $K_2Cr_2O_7/H^+$, hot conc. HNO_3 etc.

$$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{KMnO_4/H^+} \underset{\text{Ethanoic acid}}{CH_3COOH}$$

$$\underset{\text{Acetone}}{CH_3{-}\overset{\overset{O}{\|}}{C}{-}CH_3} \xrightarrow{KMnO_4/H^+} \underset{\text{Ethanoic acid}}{2CH_3COOH}$$

3. Haloform Reaction

Acetaldehyde and methylketones react rapidly with halogens (Cl_2, Br_2 or I_2) in the presence of alkali to form haloform and acid salt.

$$R{-}\overset{\overset{O}{\|}}{C}{-}CH_3 + 3Br_2 + 4NaOH \xrightarrow{\Delta} CHBr_3 + R{-}\overset{\overset{O}{\|}}{C}{-}\overset{-}{O}\overset{+}{Na} + 3H_2O + 3NaBr$$

This reaction is used to diagnose the presence of $CH_3{-}\overset{\overset{O}{\|}}{C}{-}$ group and also to distinguish methyl ketones from others.

4. Reduction

Reducing reaction as shown with the help of different reducing agents are listed below

- Reducing agents like $LiAlH_4$ reduces $>C=O$ group to $>C(H)-OH$ group generally. $NaBH_4$ can also show same capability but it is unable to reduce $>C=O$ group of ester and acid chlorides. Zn-Hg/HCl reduces $>C=O$ group to $>CH_2$ **(Clemmensen reduction)**.
- Similarly, hydrazine ($NH_2—NH_2$) followed by heating with strong base like alkali or alkaline glycol also reduces $>C=O$ group to $>CH_2$. Here, N_2 is also liberated and the reaction is called **Wolff-Kishner reduction. It is the specific method for the reduction of $>C=O$ group.**
- Aluminium isopropoxide ($Al[OCH(Me)_2]_3$) in the presence of excess of isopropyl alcohol reduces $>C=O$ group to $>C(H)-OH$ group and the reaction is called **Meerwein-Ponndrof-Verley's** (MPV) **reduction.**

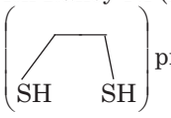
$$R_2CO + [Al[OHC(Me)_2]_3 \rightleftharpoons R_2CHOAl[OHCMe_2]_2$$

$$+MeCOMe \xrightarrow{\text{Dil. } H_2SO_4} R_2CHOH$$

- Mg in the presence of benzene reduces carbonyl compounds to pinacols as,

$$2\,RCOR \xrightarrow{Mg/Benzene} R-\underset{O}{\overset{R}{C}}-\underset{O}{\overset{R}{C}}-R \xrightarrow{\text{Hydrolysis}} R-\underset{OH}{\overset{R}{C}}-\underset{OH}{\overset{R}{C}}-R$$

(Mg bridges the two O atoms; Pinacols)

- Reduction with Raney Ni (Ni : Al = 1 : 1) along with dimercaptal  produces hydrocarbon with same number of carbon atoms.
- HI/Red P can also be used effectively at high temperature to reduce $>C=O$ to $>CH_2$.

5. Halogenation

In aliphatic aldehydes and ketones, one or more α-hydrogen atoms are replaced by the halogen atoms in the presence of acid or base.

$$CH_3CHO + Cl_2 \xrightarrow{H^+/OH^-} \underset{\alpha\text{-chloroacetaldehyde}}{CH_2ClCHO} + HCl$$

$$CH_3COCH_3 + Br_2 \xrightarrow{H^+/OH^-} \underset{\alpha\text{- bromoacetone}}{CH_2BrCOCH_3} + HBr$$

Aldol Condensation

Aldehydes and ketones having at least one α-hydrogen undergo a reaction in the presence of dil. alkali as catalyst to form β-hydroxy aldehydes (aldol) or β-hydroxy ketones (ketols). This is known as aldol condensation.

Enolisation property (ability to convert into enol form on tautomerisation) **is responsible for this reaction.** As tautomerisation (keto-enol) is possible with acid or base both that's why this reaction can also occur in the presence of dil acid as well as dil base.

The reaction can occur between

(i) two identical or different aldehydes,

(ii) two identical or different ketones,

(iii) one aldehyde and one ketone.

Presence of α-hydrogen in atleast one type of molecules is the necessity of this reaction.

The outline equation of complete reaction is shown below

$$CH_3-\underset{H}{\overset{}{C}}(=O) + HCH_2CO \xrightarrow[\text{or } K_2CO_3]{\text{Dil. alkali}} CH_3-\underset{H}{\overset{OH}{C}}-CH_2C=O \quad (H,\ \text{Aldol})$$

Self condensation of CH_3CHO

$$\xrightarrow{\text{Dil. acid}} \xrightarrow[-H_2O]{\Delta} CH_3-CH=CH-C=O \quad (H)$$

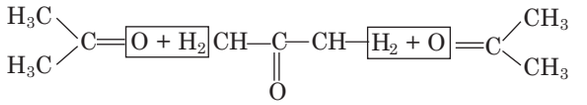
Crotonaldehyde
α, β-unsaturated aldehyde.
Directly produced in the presence of dil. acid like dil. HCl.

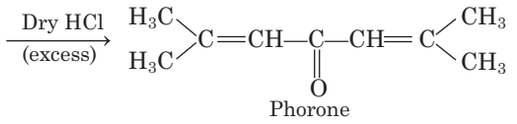
When the condensation is between two different carbonyl compounds, it is called **'cross aldol condensation'.** In brief, the products (self as well as different) of HCHO, CH_3CHO and CH_3COCH_3 condensation under different conditions are,

I. **Aldol condensation in acetone**

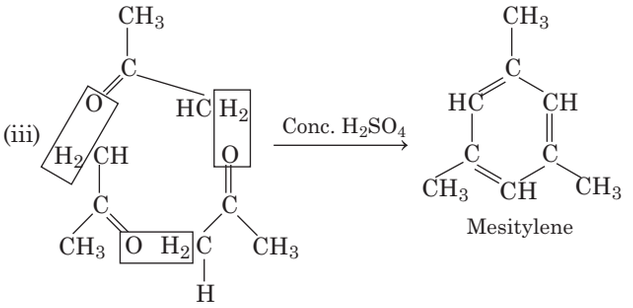
(i) $$(H_3C)_2C=O + H_2CHCOCH_3 \xrightarrow{\text{Dry HCl}} (H_3C)_2C=CHCOCH_3$$

Mesityl oxide

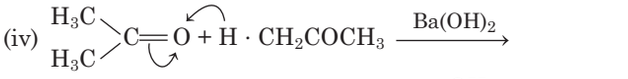
(ii) 

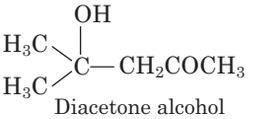


Phorone

(iii) 

Mesitylene

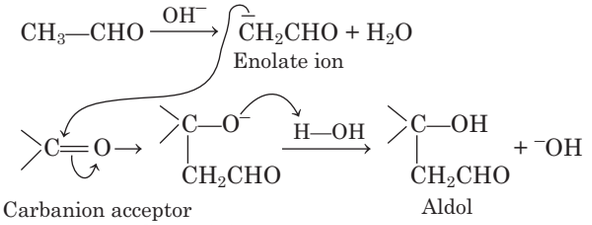
(iv) 



Diacetone alcohol

Mechanism

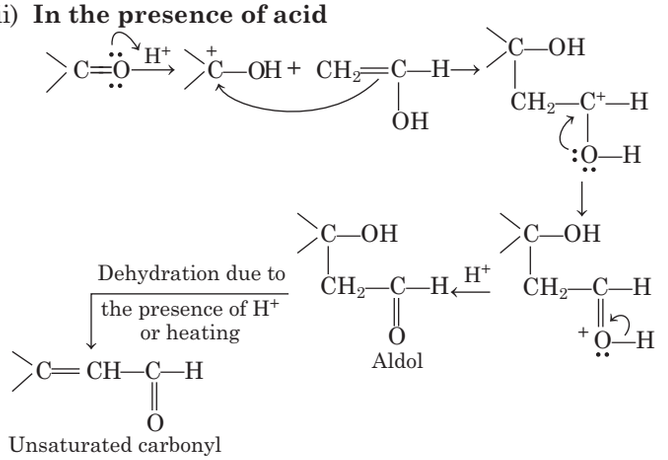
(i) **In the presence of base**



Carbanion acceptor (any compound containing carbonyl group)

Aldol

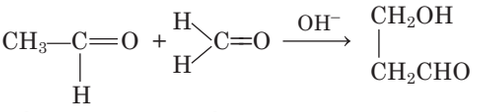
(ii) **In the presence of acid**



Unsaturated carbonyl compound

Aldol

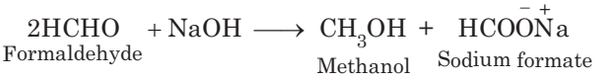
II. **Cross aldol condensation**



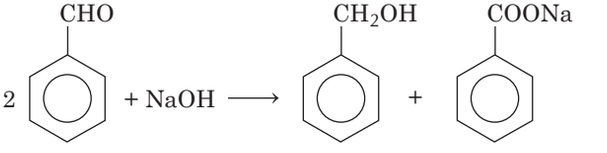
6. Cannizzaro Reaction

This reaction is given by those aldehydes which do not have α-hydrogen atom. It is a disproportionation or self oxidation-reduction reaction in which half of the molecules of aldehyde are oxidised and other half are reduced.

The equation of Cannizzaro reaction shown by HCHO is given below

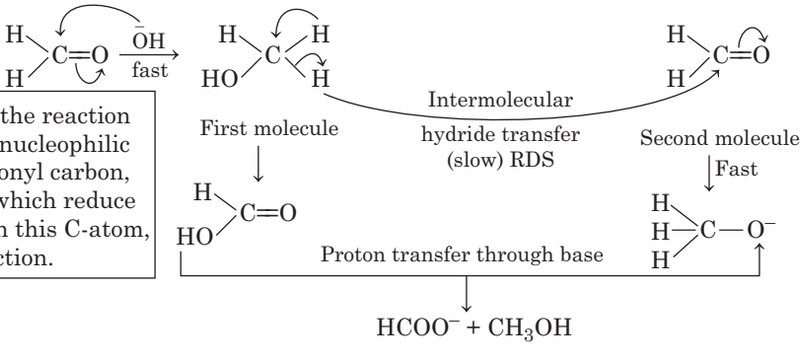


Formaldehyde — Methanol — Sodium formate



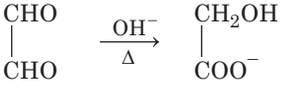
Benzaldehyde — Benzyl alcohol — Sodium benzoate

Mechanism

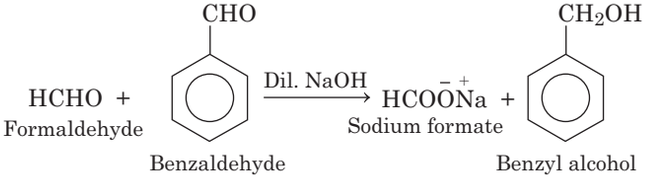


It is seen that the reaction depends upon nucleophilic attack on carbonyl carbon, hence factors which reduce (+)ve charge on this C-atom, retard the reaction.

- The reaction may be intramolecular also, i.e.



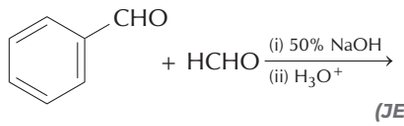
- **In cross Cannizzaro reaction** two different aldehydes which don't have alpha hydrogen atoms undergo Cannizzaro reaction.



HCHO being smaller molecule having lesser steric hindrance is easily oxidised and other aldehyde is reduced. So, always under such conditions in crossed Cannizzaro reaction formaldehyde forms sodium formate.

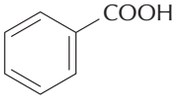
- **2-methylpropanal** although has α-hydrogen atom but undergoes both aldol condensation and Cannizzaro reaction. Actually it is difficult for the base to eliminate α-hydrogen from sterically crowded carbon atom.

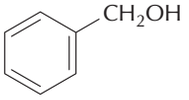
Example 7. *Major products of the following reaction are*

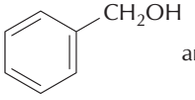


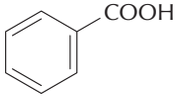
(JEE Main 2019)

(a) CH_3OH and HCO_2H

(b) CH_3OH and 

(c) HCOOH and 

(d) 

and 

Sol. (c) The given reaction is a crossed Cannizzaro reaction which is a redox reaction too. Oxidation number of carbon atom of the — CHO groups of Ph— CHO and H— CHO are +1 and zero respectively.

So, HCHO is the stronger reducing agent than PhCHO. As a result, HCHO is oxidised to HCOONa (by donation of hydride, H^-) and PhCHO (H^- acceptor) is reduced to $PhCH_2OH$.

$$Ph\overset{+1}{C}HO + H\overset{0}{C}HO \xrightarrow{50\%\ NaOH} Ph\overset{-1}{C}H_2OH + H\overset{+2}{C}OO^-Na^+$$

$$\downarrow H_3O^+$$

$$PhCH_2OH + HCOOH$$

(Major products)

7. Tischenko Reaction

In this reaction, aldehydes (with or without α-H) in presence of aluminium or magnesium alkoxide undergo auto-oxidation and redcution to form carboxylic acid and alcohol which results in the formation of ester as the final products.

The reaction looks like

$$2CH_3CHO \xrightarrow{Al(OEt)_3} \underbrace{CH_3COOH + CH_3CH_2OH}_{\text{Combine to give}}$$

$$\downarrow$$

$$CH_3COOC_2H_5 + H_2O$$

8. Action of Schiff's Reagent

Aldehydes restore the pink colour of Schiff's reagent. Chemically this reagent is magenta or rosaniline hydrochloride dissolved in water and its red or pink colour decolourises by passing SO_2. while ketones do not respond to this test.

$$\underset{\text{(colourless)}}{\text{Aldehyde + Schiff's reagent}} \longrightarrow \text{Pink colour}$$

9. Polymerisation

Some important reactions of HCHO and *R*CHO are as follows

(i) Formalin evaporated to dryness $\longrightarrow$

$$HOCH_2(CH_2O)_n CH_2OH$$

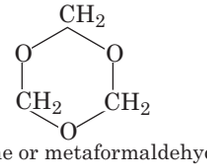
Paraformaldehyde ($n = 5 - 60$)

(ii) HCHO on treatment with conc. H_2SO_4 $\longrightarrow$

$$(CH_2O)_n\ 2H_2O$$

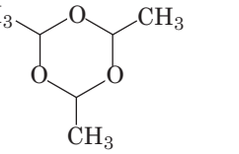
Polyoxymethylene ($n > 100$)

(iii) HCHO gas at room temperature slowly polymerises to $\longrightarrow$



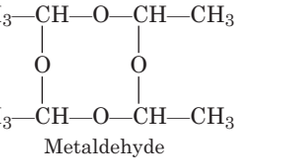
Trioxane or metaformaldehyde

(iv) CH_3CHO + small amount of conc. $H_2SO_4 \xrightarrow[\text{temperature}]{\text{Room}}$



Paraldehyde

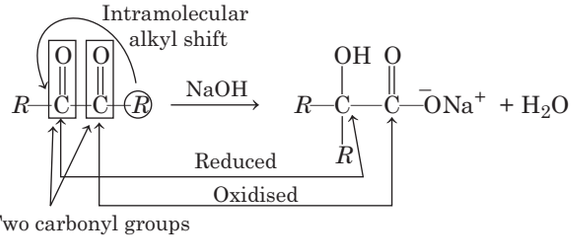
(v) CH_3CHO + Conc. H_2SO_4 (small amount) $\xrightarrow{0°C}$



Metaldehyde

10. Benzilic Acid Rearrangement

This intramolecular Cannizzaro reaction type procedure is seen in the case of diketones. The reaction looks like

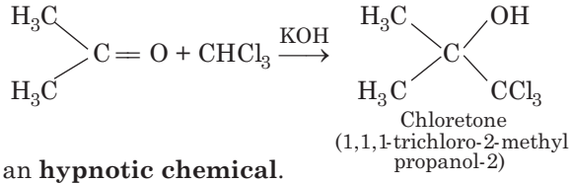


Here, the oxidation and reduction of carbonyl groups is associated with an intramolecular alkyl shift from the carbonyl group to be oxidised to the carbonyl group to be reduced as seen above.

It is seen that barium and thallous hydroxides are more effective than NaOH or KOH.

11. Addition of Chloroform

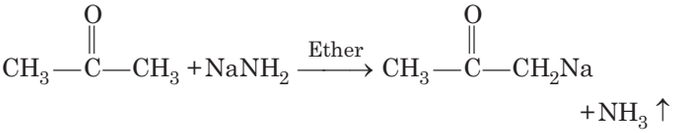
Chloroform reacts with ketones in the presence of KOH to form chlorohydroxy condensation compounds.



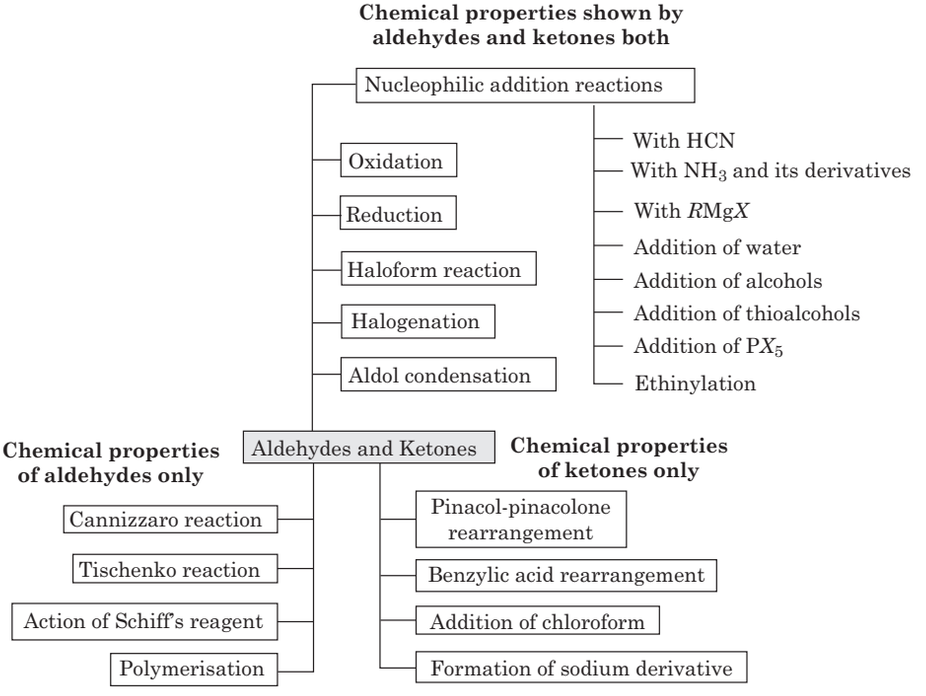
It is an **hypnotic chemical**.

12. Formation of Sodium Derivative

Ketones when treated with sodamide in ethereal solution, give their sodium derivatives.



Flow chart showing the reactions of aldehydes and ketones is given below



Chemical Test to Distinguish Aldehydes and Ketones

These compounds be distinguished by several tests which are tabulated below

Distinguish between Aldehydes and Ketones

Name of test	Reagent	Aldehydes	Ketones
Tollen's test	Ammoniacal silver nitrate	Silver mirror formation, i.e. deposition of Ag on surface of test tube formed	No change
Fehling's test	Alkaline solution of $CuSO_4$ containing Rochelle salt, i.e., 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

Remember Aromatic aldehydes do not reduce Fehling solution and Benedict solution because they are weak reagents.

Carboxylic Acids

Organic compounds which contain carboxyl group (—COOH) are called **carboxylic acids.** The name carboxyl is derived from carbonyl and hydroxyl as —C(=O)—OH contain both the group in it.

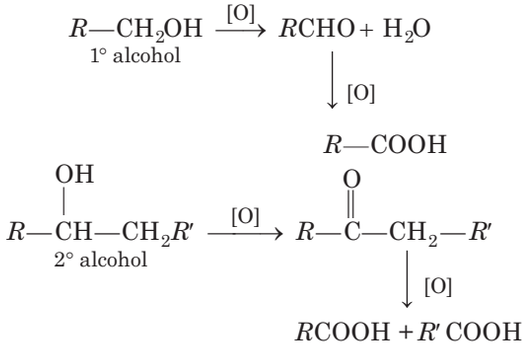
In other words, these are the carbonyl compounds in which acyl group is attached to —OH group which can be easily replaced by another group. Acid derivatives also belongs to this class.

Preparation of Carboxylic Acids

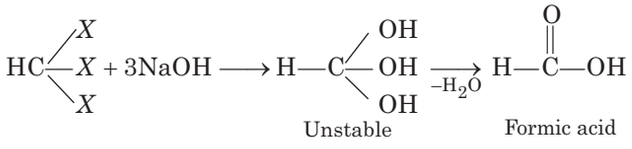
Following methods are used for the prepare carboxylic acids

(i) **Oxidation of alcohols, aldehydes and ketones**

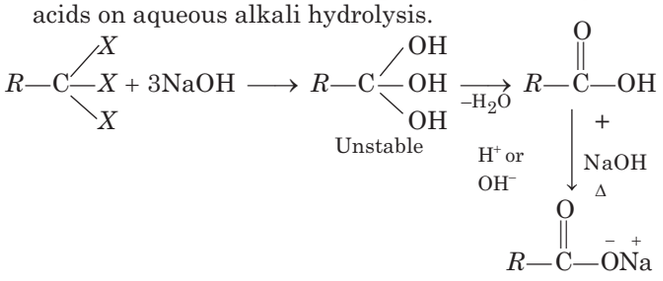
- Primary alcohols are oxidised to carboxylic acids with common oxidising agents such as potassium permanganate in neutral, acidic or alkaline media or by potassium dichromate and chromium trioxide in acidic media.
- Aldehydes on treatment with even mild oxidising agents give carboxylic acids whereas ketones oxidised under vigorous conditions, i.e. with strong oxidising agents.



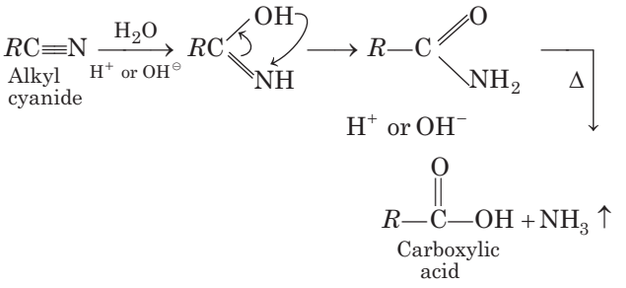
(ii) **From haloforms** Haloforms on aqueous alkali hydrolysis gives formic acid as shown below



Trihaloderivatives of alkanes give, other carboxylic acids on aqueous alkali hydrolysis.



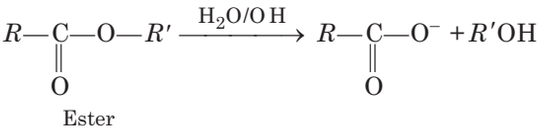
(iii) **From cyanides** Hydrolysis of cyanides with acid or alkali is a good synthetic method. Cyanides are first hydrolysed to amides and then to acids in the presence of H^+ or $\overset{\ominus}{O}H$ as catalyst.



(iv) **By hydrolysis of acid derivatives**

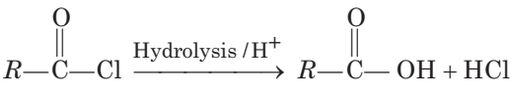
It is achieved through following reactions.

(a) **Hydrolysis of ester**

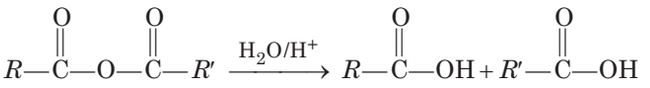


The alkaline hydrolysis is preferred for good yield as in the case of acidic hydrolysis the reaction is reversible.

(b) **Hydrolysis of acid chloride**



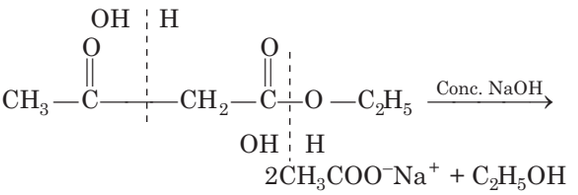
(c) **Hydrolysis of anhydride**



- Relative reactivity of acyl compounds toward hydrolysis is,

$$RCOCl > RCO — O — COR > RCOOR' > RCONH_2$$

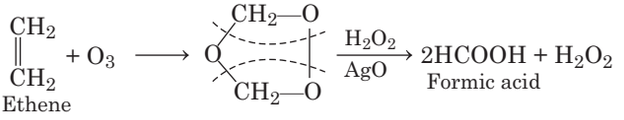
(v) **By the hydrolysis of acetoacetic ester or EAA.**



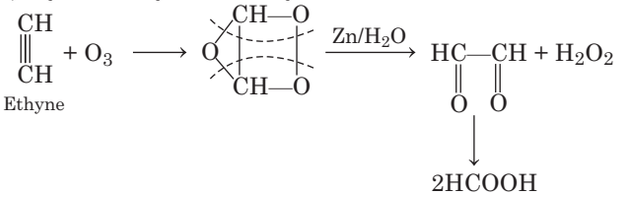
As reaction gives acid as its product that's why it is called acidic hydrolysis.

(vi) **From alkenes**

(a) **By ozonolysis of alkenes**



(b) **By ozonolysis of alkynes**



Ethyne

(c) The recent industrial method of making carboxylic acids is as follows

$$\underset{\text{Ethene}}{CH_2{=}CH_2} + CO + H_2O \xrightarrow[300\text{-}400^\circ C]{H_3PO_4} \underset{\text{Propanoic acid}}{CH_3CH_2COOH}$$

This reaction involves the electrophilic addition of H^+ ion on the alkene to produce more stable carbocation followed by the attack of CO as nucleophile.

$$\underset{\text{Propanoic}}{CH_3CH{=}CH_2} + CO + H_2O \xrightarrow[300\text{-}400^\circ C]{H_3PO_4} \underset{\text{2-methyl propanoic acid}}{CH_3-\overset{\overset{CH_3}{|}}{CH}-COOH}$$

Formic acid cannot be prepared by this reaction.

(vii) **From phenoxide ion** When phenoxide ion is refluxed with CO, so respective carboxylic acids are produced.

$$\underset{\text{Under pressure}}{\bar{R}O\overset{+}{Na} + CO \xrightarrow{\Delta}} R-\overset{O}{\overset{\|}{C}}-\bar{O}\overset{+}{Na} \xrightarrow{H_2O/H^+} R-\overset{O}{\overset{\|}{C}}-OH$$

(viii) **From Grignard's reagent** Grignard reagents on reaction with CO_2 followed by hydrolysis give acids.

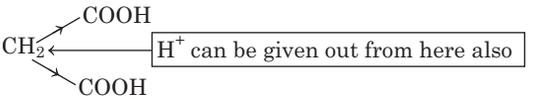
$$R\overset{\delta-}{-}\overset{2+}{Mg}\overset{\delta-}{-}X + C(=O)=O \longrightarrow R-\overset{O}{\overset{\|}{C}}-O\overset{\delta-}{-}\overset{2+}{Mg}\overset{\delta-}{-}X \xrightarrow{\text{Hydrolysis}} R-\overset{O}{\overset{\|}{C}}-OH + Mg(OH)X$$

(ix) **From dicarboxylic acid** Malonic acid is a β-acid. It is very useful in the preparation of different carboxylic acids due to its two main properties.

(a) It is decarboxylated very easily on heating as,

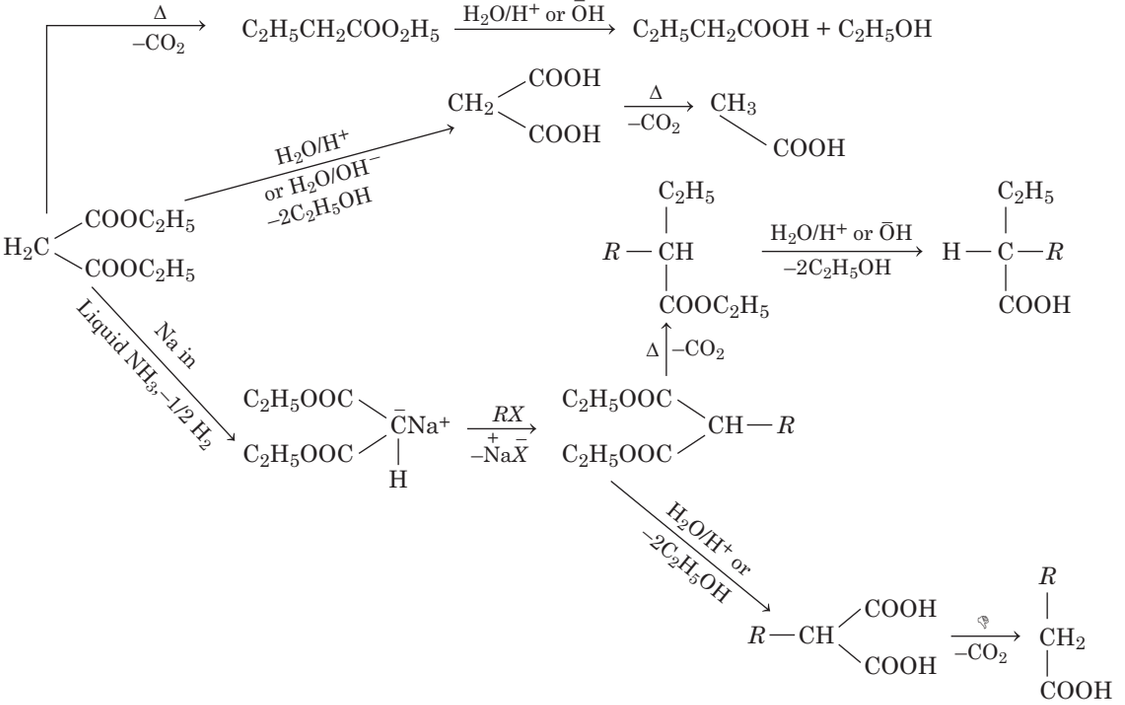
$$CH_2(COOH)_2 \xrightarrow{\Delta} CH_3COOH + CO_2$$

(b) Due to $-I$-effect of —COOH group, H^+ can also be eliminated from $—CH_2$ group, i.e.



From dicarboxylic acids and their derivatives we can synthesis almost all kinds of carboxylic acids. The most famous synthesising patter of this sort is given below as

Malonic Ester Synthesis



(x) **Vigorous oxidation of alkenes and alkynes** oxidative cleavage of alkenes and alkynes also gives carboxylic acid.

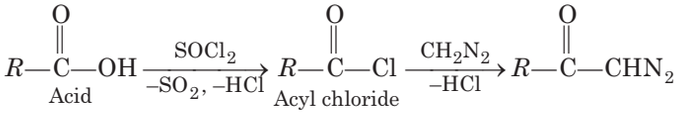
$$\underset{\text{Alkene}}{R\text{—CH=CH—}R'} \xrightarrow[\text{(hot, conc.)}]{KMnO_4} RCOOH + R'COOH$$

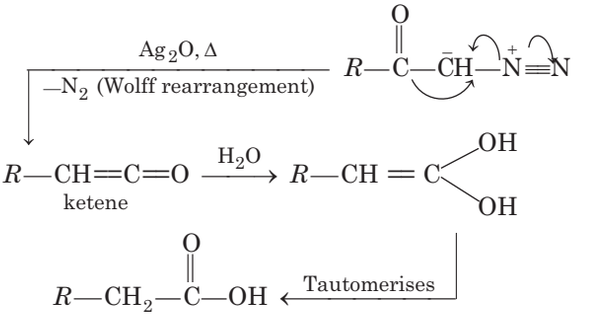
$$\underset{\text{Alkyne}}{CH_3\text{—C}\equiv\text{CH}} \xrightarrow[\text{(hot, conc.)}]{KMnO_4} CH_3COOH + HCOOH$$

(xi) **From long chain hydrocarbon** Long chain hydrocarbons are oxidised by air at 120°C in the presence of manganous sterate as catalyst.

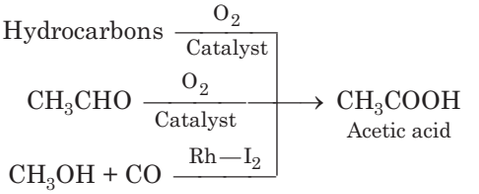
$$\underset{\text{Higher alkanes}}{2RCH_3} + 3O_2 \xrightarrow[\text{Manganous stearate}]{120°C/} \underset{\text{Fatty acid}}{2RCOOH} + 2H_2O$$

(xii) **Arndt-Eistert reaction** The conversion of an acid ($RCOOH$) into its next higher homologue (RCH_2COOH) is called homologation of that acid it is also called as Arndt-Eistert reaction (named after Fritz Arndt and Bernd Eistert).



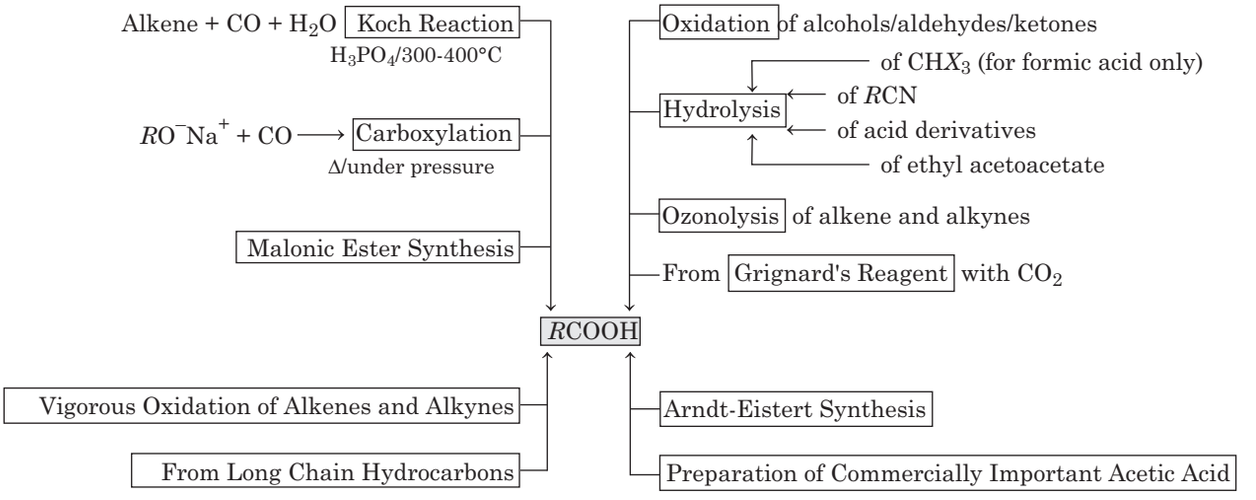


(xiii) **Preparation of acetic acid** Acetic acid is the most important carboxylic acid, prepared by the following methods



Remember Large amounts of acetic acid are produced from oxidation of ethyl alcohol in the presence of aceto-bacter bacteria. This dilute aqueous solution is known as **vinegar**.

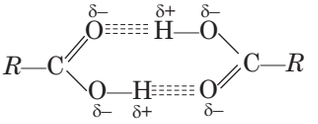
The outline of their methods of preparation of carboxylic acids looks like



Physical Properties

Physical properties of carboxylic acids are as follows

- First three members of this series are colourless, pungent smelling liquids. C_4—C_9 are oily liquids.
- Carboxylic acids usually exist in the form of dimer due to hydrogen bonding.
- **Solubility** of carboxylic acids in water decreases due to increase in size of hydrophobic hydrocarbon part. Lower carboxylic acids having upto four carbon atoms are miscible with water due to the formation of hydrogen bonds with water.
- **Boiling point** of carboxylic acids is higher than those of hydrocarbons, aldehydes, ketones and alcohols of comparable molecular masses due to intermolecular H-bonding as shown in the figure below



- **Melting points** of carboxylic acids increase with increase in their molecular mass.

The melting point of an acid with even number of carbon atom is higher than the next lower and next higher homologue containing odd number of carbon atoms.

Acidic Strength or Acidity of Carboxylic Acid

Carboxylic acids are acidic in nature but they are weaker acids than mineral acids. Still they are stronger acids than phenols. It is because the carboxylate ion is more stabilised with resonance as compared to phenoxide ion.

The carboxylic acids liberate hydrogen on reaction with electropositive metals like sodium. They form salts with alkalies.

Effect of Substituents on the Acidity of Carboxylic Acid

- Electron withdrawing groups increase the acidity of carboxylic acids by stabilising the conjugate base. It is done through delocalisation of the negative charge by inductive or resonance effects.
- Similarly, electron donating groups decrease the acidity by destabilising the conjugate base.

Stabilise the carboxylate ion Destabilise the carboxylation

- Strength of acid is indicated by its pK_a value. Higher the value of K_a or lower the value of pK_a, stronger is the acid.

Usually aromatic acids are more acidic than aliphatic acids but HCOOH is more acidic than benzoic acid.

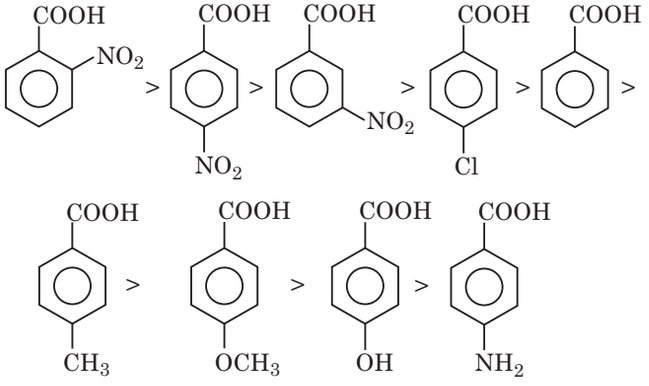
The order of acidic strength of some important aliphatic acids is given below

- $HCOOH > CH_3COOH > (CH_3)_2CHCOOH > (CH_3)_3COOH$

  $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH > CH_3COOH$
- $CH_3CH_2CHClCOOH > CH_3CHClCH_2COOH > ClCH_2CH_2CH_2COOH$
- $CF_3COOH > CCl_3COOH > CHCl_2COOH > NO_2CH_2COOH$

  $FCH_2COOH > ClCH_2COOH > BrCH_2COOH > HCOOH$

Among substituted aromatic acids the strength decreases as follows



- ***ortho* effect** In aromatic acids the effect of a group is maximum at *ortho* position due to nearness. It is basically related with the change in plane and thus reduced conjugation between the ring and C ═ O bond of —COOH.

  At some places intramolecular H-bonding is also associated with it. All these factors increase the acidic strength of substituted benzoic acid concerned.

  As all these changes occur due to *ortho* position of substituent hence, this effect is called *ortho* effect.

Example 8. *The correct decreasing order for acid strength is* ***(JEE Main 2019)***

(a) $FCH_2COOH > NCCH_2COOH > NO_2CH_2COOH > ClCH_2COOH$

(b) $CNCH_2COOH > O_2NCH_2COOH > FCH_2COOH > ClCH_2COOH$

(c) $NO_2CH_2COOH > NCCH_2COOH > FCH_2COOH > ClCH_2COOH$

(d) $NO_2CH_2COOH > FCH_2COOH > CNCH_2COOH > ClCH_2COOH$

Sol. (c) All the given compounds are α-monosubstituted acetic acid derivatives and the α-substitutions have been made by strong *–I* groups/atoms.

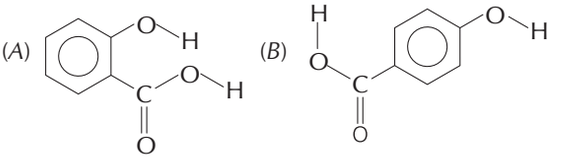
More powerful the *– I* group, stronger will be the acid.
–I power of different groups is as follows

$$—NO_2 > —CN > —F > —Cl$$

Thus, the correct decreasing order for acid strength is

$$NO_2CH_2COOH > NCCH_2COOH > FCH_2COOH > ClCH_2COOH$$

Example 9. *Consider the following molecules and statements related to them*

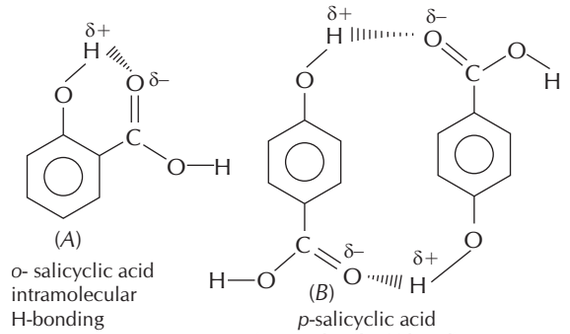


(I) (*B*) is more likely to be crystalline than (*A*).
(II) (*B*) has higher boiling point than (*A*).
(III) (*B*) dissolves more readily than (*A*) in water.

Identify the correct option from below ***(JEE Main 2020)***

(a) (I) and (III) are true
(b) Only (I) is true
(c) (II) and (III) are true
(d) (I) and (II) are true

Sol. (c) Given, molecules (*A*) and (*B*) undergoes intramolecular H-bonding and intermolecular H-bonding respectively. It is shown as follows



(*A*)
o- salicyclic acid
intramolecular
H-bonding

(*B*)
p-salicyclic acid
intermolecular H-bonding

Among the given statements, II and III are true whereas I is false. Corrected statement I, (*A*) is more likely to crystalline than (*B*).

Chemical Properties

Carboxylic acids exhibit following characteristic chemical properties.

I. Reactions of Replacable —H

Some of the chemical reactions which involve the replace —H are as follows

(i) **With alkalies and carbonates** Carboxylic acids react with bases to form ionic salts with pronounced ionic characters and are soluble in water.

$$2R\text{COOH} + \text{NaHCO}_3 \longrightarrow R\text{COO}^-\text{Na}^+ + \text{CO}_2\uparrow + \text{H}_2\text{O}$$

$$2R\text{COOH} + \text{Na}_2\text{CO}_3 \longrightarrow 2R\text{COO}^-\text{Na}^+ + \text{CO}_2\uparrow + \text{H}_2\text{O}$$

$$R\text{COOH} + \text{NaOH} \longrightarrow R\text{COO}^-\text{Na}^+ + \text{H}_2\text{O}$$

$$2R\text{COOH} + \text{CaO} \longrightarrow (R\text{COO})_2\text{Ca} + \text{H}_2\text{O}$$

$$R\text{COOH} + \text{AgOH} \longrightarrow R\text{COO}^-\text{Ag}^+ + \text{H}_2\text{O}$$

(ii) **With metals** The reaction looks like,

$$2R\text{COOH} + 2\text{Na} \longrightarrow 2R\text{COO}^-\text{Na}^+ + \text{H}_2\uparrow$$

$$2R\text{COOH} + \text{Zn} \longrightarrow (R\text{COO})_2\text{Zn} + \text{H}_2\uparrow$$

II. Reactions of —OH Group

Some of the chemical reactions which involve the replacement of —OH group are as follows

(i) **Esterification** Carboxylic acids react with alcohols in the presence of conc. H_2SO_4 to form ester.

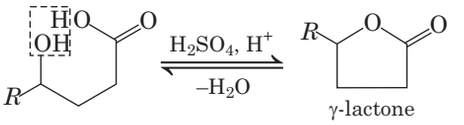
$$R\text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—OH} + \text{H—O}R' \underset{}{\overset{\text{H}_2\text{SO}_4}{\rightleftharpoons}} R\text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—O}R' + \text{H}_2\text{O}$$

- The order of reactivity follows below given sequence,

$$\text{HCOOH} > \text{CH}_3\text{COOH} > (\text{CH}_3)_2\text{COOH} > (\text{CH}_3)_3\text{CCOOH}$$

$$\text{CH}_3\text{OH} > \text{CH}_3\text{CH}_2\text{OH} > (\text{CH}_3)_2\text{CHOH} > (\text{CH}_3)_3\text{COH}$$

- γ or δ hydroxy carboxylic acids undergo an intramolecular esterification to give cyclic ester-lactones.



γ-lactone

(ii) **With $SOCl_2$, PCl_3 and PCl_5** Acyl halides are formed.

$$R\text{—COOH} \xrightarrow{\text{SOCl}_2} R\text{COCl} + \text{SO}_2\uparrow + \text{HCl}\uparrow$$

$$R\text{—COOH} \xrightarrow{\text{PCl}_3} R\text{COCl} + \text{H}_3\text{PO}_3$$

$$R\text{—COOH} \xrightarrow{\text{PCl}_5} R\text{COCl} + \text{POCl}_3 + \text{HCl}\uparrow$$

Carboxylic acid

$SOCl_2$ is preferred over other two reagents, because SO_2 and HCl escape the reaction mixture (as these are gases) and make the purification of product easier.

(iii) **With NH_3** The reaction looks like,

$$R\text{COOH} + \text{NH}_3 \longrightarrow R\text{COO}^-\text{NH}_4^+ \xrightarrow{\text{Heat}} R\text{CONH}_2 + \text{H}_2\text{O}$$

(iv) **Dehydration** The reaction proceeds as,

$$R\text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—OH} + \text{H O—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—}R \xrightarrow[-\text{H}_2\text{O}]{\text{P}_2\text{O}_5,\,\Delta} R\text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—O—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—}R$$

III. Reactions due to —COOH group

Reaction involve due to —COOH group are as follows

(i) **Decarboxylation** Salts of carboxylic acid on heating with sodalime (NaOH and CaO) undergo decarboxylation to produce alkanes.

(ii) **Kolbe's electrolysis** The aqueous solution of sodium or potassium salts of carboxylic acids on electrolysis gives alkanes.

(iii) **Dry distillation** The Ca salts of carboxylic acids gives carbonyl compounds on dry distillation.

(iv) **Borodine-Hunsdiecker reaction** The silver salts of carboxylic acids upon treatment with Br_2/ CCl_4 give alkyl bromide.

$$R\text{COO}^-\text{Ag}^+ + \text{Br}_2 \xrightarrow{\text{CCl}_4} R\text{Br} + \text{CO}_2\uparrow + \text{AgBr}\downarrow$$

The silver salts of carboxylic acids on treatment with I_2/ether form esters. The reaction is called **Birnbaum-Simonini reaction**.

$$2R\text{COOAg} + \text{I}_2 \xrightarrow{\text{Ether}} \underset{\text{Ester}}{R\text{COO}R} + \text{CO}_2\uparrow + 2\text{AgI}\downarrow$$

(v) **Reductions** Carboxylic acids give following reduction reactions.

(a) **Reduction to alkanes**

$$R\text{COOH} + 6\text{HI} \xrightarrow[\Delta]{\text{Red P}} R\text{—CH}_3 + 2\text{H}_2\text{O} + 3\text{I}_2$$

(b) **Reduction to alcohols**

$$R\text{COOH} \xrightarrow[\text{(ii) } \text{H}_3\text{O}^+,\ \text{H}^+]{\text{(i) } \text{LiAlH}_4/\text{ether}} R\text{CH}_2\text{OH}$$

(c) **Reduction to aldehydes and ketones**

$$\underbrace{HCO\boxed{OH + HCOO}H}_{\text{vapour phase}} \xrightarrow[\Delta]{MnO} HCHO + CO_2\uparrow + H_2O$$

$$\underbrace{CH_3CO\boxed{OH + HOOC}CH_3}_{\text{vapour phase}} \xrightarrow[\Delta]{MnO} CH_3COCH_3 + CO_2\uparrow + H_2O$$

(vi) **Schmidt reaction** Reaction proceeds as,

$$RCOOH + N_3H \xrightarrow[\Delta]{H_2SO_4} RNH_2 + N_2\uparrow + CO_2\uparrow$$

IV. Reaction of Alkyl group

Following are the reaction of alkyl group present in carboxylic acid compounds are as follows

(i) **Halogenation** In monocarboxylic acid bromination takes place only at the α-position, but chlorination may also takes place further in the chain.

$$CH_3CH_2COOH \xrightarrow{Cl_2} CH_3\underset{Cl}{\underset{|}{CH}}\,COOH + CH_2\underset{Cl}{\underset{|}{}}\,CH_2COOH$$

(ii) **Oxidation** Carboxylic acids gives following oxidation reactions.

(a) All acids, except formic acid are resistance to oxidation. On prolonged heating, with powerful oxidising agent ($KMnO_4$) they results in CO_2 and H_2O.

$$HCOOH \xrightarrow{SeO_2} CO_2\uparrow + H_2O$$

$$R{-}CH_2COOH \xrightarrow{SeO_2} R{-}\overset{\overset{O}{\|}}{C}{-}COOH$$

$$CH_3{-}\underset{CH_3}{\underset{|}{CH}}{-}COOH \xrightarrow{SeO_2} CH_3{-}\underset{CH_3}{\overset{OH}{\overset{|}{C}}}{-}COOH$$

(b) With mild oxidising agent such as H_2O_2, they are oxidised to β-hydroxy acids.

$$CH_3CH_2CH_2COOH \xrightarrow{H_2O_2} CH_3\overset{OH}{\overset{|}{C}}H\,CH_2COOH$$

(iii) **Hell-Volhard Zelinsky reaction** α-hydrogen of a carboxylic acid can be replaced by halogen using red phosphorus.

$$R{-}CH_2COOH + X_2 \xrightarrow{\text{Red P}} R{-}\overset{X}{\overset{|}{C}}H{-}COOH$$

α-halogenated acids are infact good starting material for preparing other α-substituted acids as

$$\underset{\alpha\text{-halo acid}}{R{-}\overset{X}{\overset{|}{C}}H{-}COOH} \xrightarrow{NaOH} R{-}\overset{OH}{\overset{|}{C}}H{-}COOH + NaX$$

$$R{-}\overset{X}{\overset{|}{C}}H{-}COOH \xrightarrow{NaCN} R{-}\overset{CN}{\overset{|}{C}}H{-}COOH + NaX$$

$$R{-}\overset{X}{\overset{|}{C}}H{-}COOH \xrightarrow{2NH_3} R{-}\overset{NH_2}{\overset{|}{C}}H{-}COOH + NH_4Br$$

Special Facts about HCOOH

The first member of series, i.e. HCOOH is unique and different from rest in many aspects. These are as follows

(i) It decolourises $KMnO_4$,

(ii) It gives positive tests with Tollen's reagent (silver mirror) and Fehling's solution,

(iii) Reduces mercuric chloride to mercurous chloride which is further converted to grey precipitate of mercury as shown below.

$$HCOOH + 2HgCl_2 \longrightarrow CO_2 + Hg_2Cl_2\downarrow + 2HCl$$

$$HCOOH + Hg_2Cl_2 \longrightarrow CO_2 + 2Hg\downarrow + 2HCl$$

Thus, it is only monocarboxylic acid with can oxidise easily.

The main reason behind this is complete absence of alkyl group from this compound.

- Its boiling point is 373.5 K which is very near to that of H_2O, i.e. 373K.

Action of heat

$$\underset{\text{Formic acid}}{HCOOH} \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} H_2O + CO_2\uparrow$$

$$HCOOH \xrightarrow{\Delta} CO_2\uparrow + H_2\uparrow$$

- Its Na or K salt on heating under pressure at about 400°C produces sodium or potassium salt of oxalic acid. H_2 is liberated in the process as

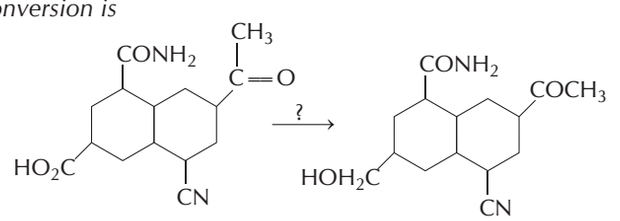
$$\begin{matrix} HCO\bar{O}\ Na^+ \\ + \\ HCO\bar{O}\ Na^+ \end{matrix} \xrightarrow[\text{under pressure}]{400^\circ C} \begin{matrix} CO\bar{O}Na^+ \\ | \\ COONa^+ \end{matrix} + H_2\uparrow$$

—COOH group shows $-M$ effect, therefore acts as a **deactivating and *meta*-directing group**.

Benzoic acid give all the normal electrophilic substitutions but with a bit difficulty.

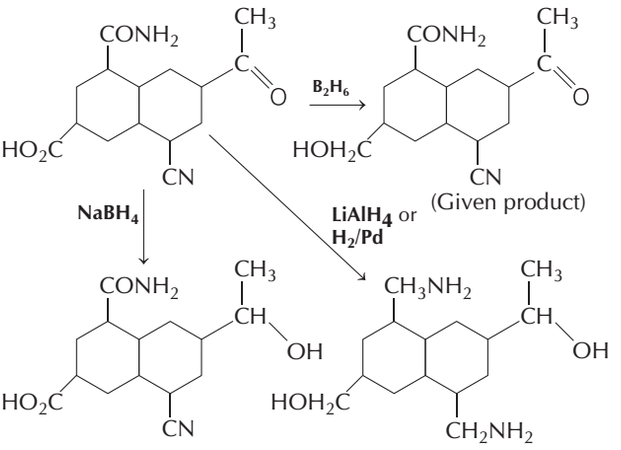
It does not undergo Friedel-Crafts reaction because the **carboxylic group is deactivating and the catalyst $AlCl_3$ (anhyd) gets bonded to the carboxylic group**.

Example 10. *The most suitable reagent for the given conversion is*



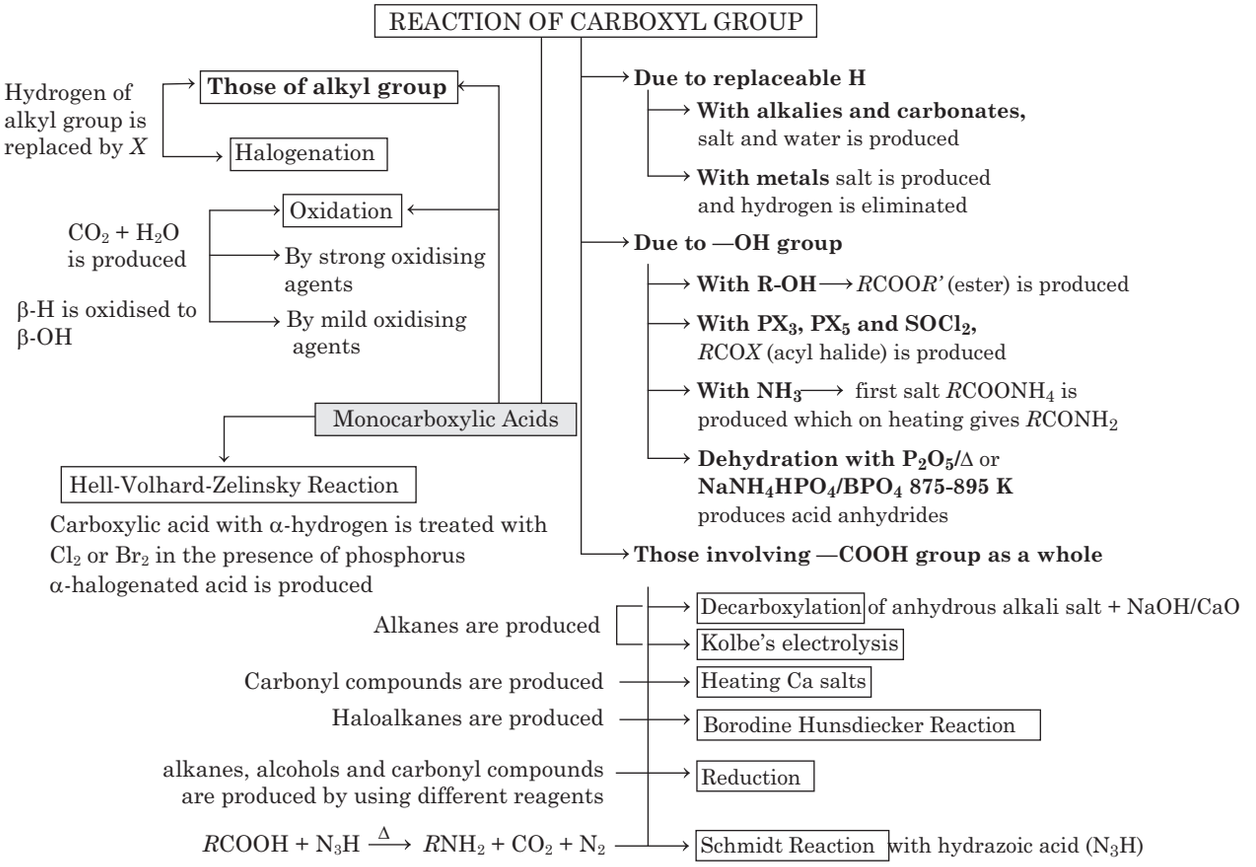
(a) B_2H_6
(b) $LiAlH_4$
(c) $NaBH_4$
(d) H_2 / Pd

(JEE Main 2020)



Sol. *(a)* The most suitable reagent for the given conversion is B_2H_6.

The outline of the chemical properties of carboxylic acids looks like



Uses of Carboxylic acids

- 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.

Practice Exercise

ROUND I Topically Divided Problems

Introduction and Methods of Preparation of Alcohols

1. *Iso*-propyl alcohol is *(NCERT)*

(a) $CH_2—CH(CH_3)—CH_2—OH$ (b) $(CH_3)_2C(H)—OH$

(c) $CH_3—CH(CH_3)—OH$ (d) $CH_3—CH(OH)—CH_2—CH_3$

2. Which of the following structure is represented by 3-cyclohexylpentan-3-ol? *(NCERT)*

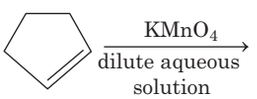
(a) $CH_3CH_2C(OH)(CH_2CH_2CH_3)$(cyclohexyl)

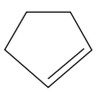
(b) $CH_2CH_2CH(CH_2CH_3)$(cyclohexyl)$(OH)CH_2CH_3$

(c) $CH_3CH_2C(OH)(CH_2CH_2CH_3)$(cyclohexyl)

(d) None of these

3. By which of the following reactions can *trans*-cyclopentane-1,2- diol be obtained?

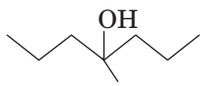
(a)  $\xrightarrow[\text{dilute aqueous solution}]{KMnO_4}$

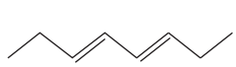
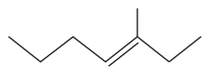
(b)  $\xrightarrow[\text{(ii) } H^+]{\text{(i) } OsO_4}$

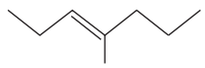
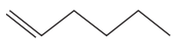
(c)  $\xrightarrow{H^+}$

(d) None of these

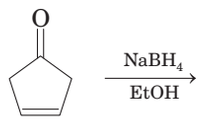
4. Which of the following alkene will give the following alcohol? *(NCERT)*



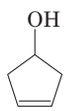
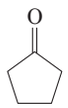
(a)  (b) 

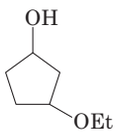
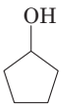
(c)  (d) 

5. The major product of the following reaction is



(JEE Main 2019)

(a)  (b) 

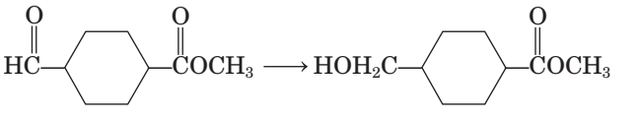
(c)  (d) 

6. The major product of the following reaction is

$CH_3CH{=}CHCO_2CH_3 \xrightarrow{LiAlH_4}$ *(JEE Main 2019)*

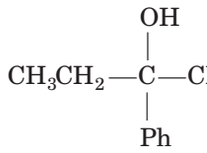
(a) $CH_3CH{=}CHCH_2OH$
(b) $CH_3CH_2CH_2CH_2OH$
(c) $CH_3CH_2CH_2CO_2CH_3$
(d) $CH_3CH_2CH_2CHO$

7. The reduction,



can be achieved by using

(a) $NaBH_4$ (b) $LiAlH_4$
(c) $CuO{\cdot}CuCN_2O_4$ (d) None of these

8.  cannot be prepared by

(JEE Main 2019)

(a) $CH_3CH_2COCH_3 + PhMgX$
(b) $PhCOCH_3 + CH_3CH_2MgX$
(c) $PhCOCH_2CH_3 + CH_3MgX$
(d) $HCHO + PhCH(CH_3)CH_2MgX$

9. In the following reaction, identify *X*.
Methyl magnesium bromide + $X \longrightarrow$ 2-methyl propan-2-ol *(NCERT)*

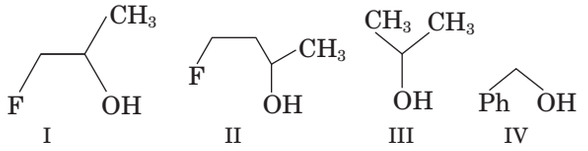
(a) propanol (b) ethanone
(c) propanone (d) butane

Physical and Chemical Properties of Alcohols

10. Arrange the following compounds in increasing order of boiling point. Propan-1-ol, butan-1-ol, butan-2-ol, pentan-1-ol. *(NCERT Exemplar)*

(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

11. The order of reactivity of the following alcohols is



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

12. The acidic character of 1°, 2°, 3° alcohols, H_2O and $RC{\equiv}CH$ is of the order

(a) $H_2O > 1° > 2° > 3° > RC{\equiv}CH$
(b) $RC{\equiv}CH > 3° > 2° > 1° > H_2O$
(c) $1° > 2° > 3° > H_2O > RC{\equiv}CH$
(d) $3° > 2° > 1° > H_2O > RC{\equiv}CH$

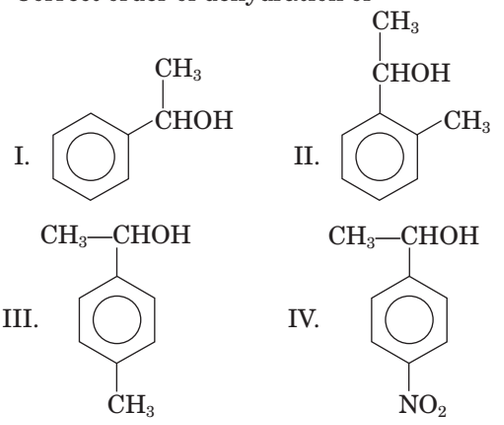
13. What is the correct order of reactivity of alcohols in the following reaction?

$$R\text{—OH} + HCl \xrightarrow{ZnCl_2} R\text{—Cl} + H_2O$$

(NCERT Exemplar)

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

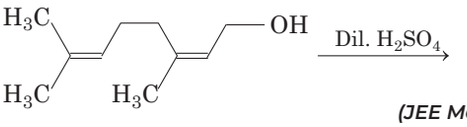
14. Correct order of dehydration of



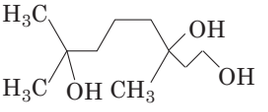
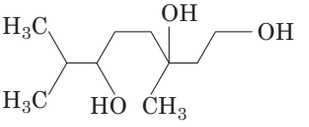
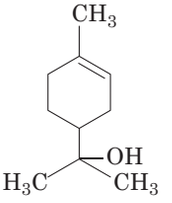
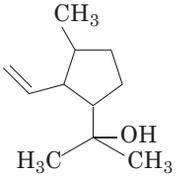
is

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

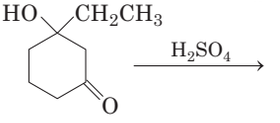
15. The major product of the following reaction is



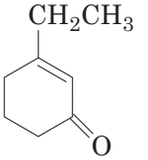
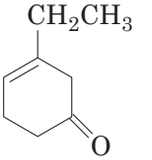
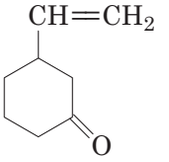
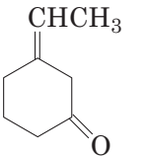
(JEE Main 2020)

(a) 
(b) 
(c) 
(d) 

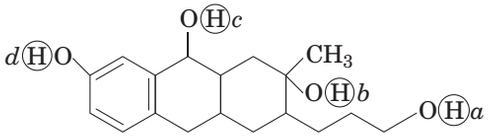
16. The major product of the following reaction is



(JEE Main 2020)

(a) 
(b) 
(c) 
(d) 

17. Consider the following reaction :



$\xrightarrow[\text{anhydride}]{\text{Chromic}}$ '*P*' The product '*P*' gives positive ceric ammonium nitrate test. This is because of the presence of which of these —OH group(s)?

(a) (b) and (d) ***(JEE Main 2020)***
(b) (d) only
(c) (b) only
(d) (c) and (d)

18. Reaction of tertiary butyl alcohol with hot Cu at 350°C produces

(a) butanol
(b) butanal
(c) 2-butene
(d) 2-methylpropene

19. Which is the most suitable reagent for the following transformation ?

$$CH_3-CH=CH-CH_2-\underset{\displaystyle OH}{\underset{|}{C}}H-CH_3 \longrightarrow CH_3-CH=CH-CH_2CO_2H$$

(JEE Main 2019)

(a) Tollen's reagent (b) I_2/NaOH
(c) Alkaline $KMnO_4$ (d) CrO_2Cl_2 / CS_2

20. Reagent used for the oxidation of allyl alcohol to acrolein is

(a) $KMnO_4$
(b) H_2O_2
(c) active MnO_2
(d) OsO_4

21. A compound '*A*' having the molecular formula $C_5H_{12}O$, on oxidation gives a compound '*B*' with molecular formula $C_5H_{10}O$. Compound '*B*' gave a 2,4-dinitrophenylhydrazine derivative but did not answer haloform test or silver mirror test. The structure of compound '*A*' is

(a) $CH_3CH_2CH_2CH_2CH_2OH$
(b) $CH_3-CH_2-CH_2-\underset{\displaystyle OH}{\underset{|}{C}}H-CH_3$
(c) $CH_3-CH_2-\underset{\displaystyle OH}{\underset{|}{C}}H-CH_2-CH_3$
(d) $CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}H-CH_2-OH$

22. Consider the following reaction,

$$C_2H_5OH + H_2SO_4 \longrightarrow \text{Product}$$

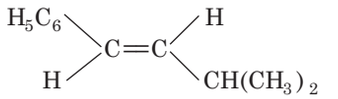
Among the following, which one cannot be formed as a product under any conditions?

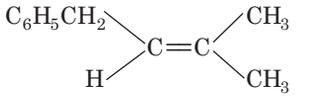
(a) Ethyl hydrogen sulphate
(b) Ethylene
(c) Acetylene
(d) Diethyl ether

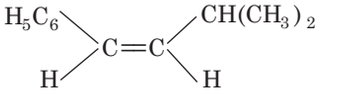
23. The main product of the following reaction is

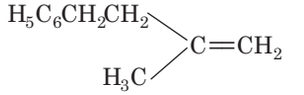
$$C_6H_5CH_2CH(OH)CH(CH_3)_2 \xrightarrow{\text{Conc. } H_2SO_4} ?$$

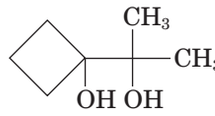
(AIEEE 2010)

(a) 

(b) 

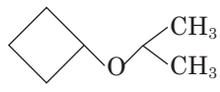
(c) 

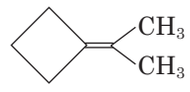
(d) 

24. 

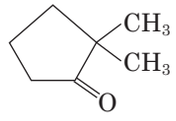
$\xrightarrow{\text{Conc. } H_2SO_4}$ *A*,

The product *A* is

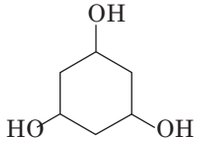
(a) 

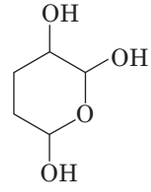
(b) 

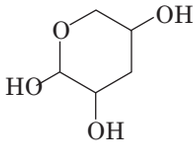
(c) 

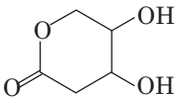
(d) 

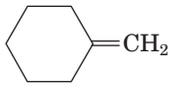
25. In which molecule, cleavage by HIO_4 is not observed?

(a) 

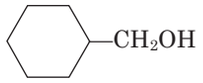
(b) 

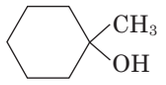
(c) 

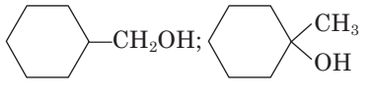
(d) 

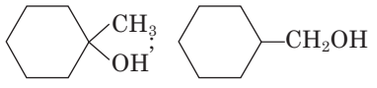
26. $B \xleftarrow[\text{(ii) } H_2O_2/OH^-]{\text{(i) } B_2H_6/THF}$  $\xrightarrow{H_3O^+} A$

A and B respectively are

(a) Both 

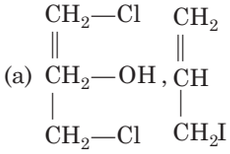
(b) Both 

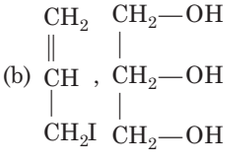
(c) 

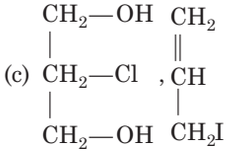
(d) 

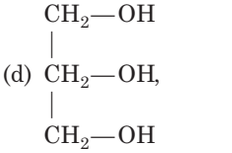
27. $A + HI \xrightarrow{\text{Warm}} \underset{\displaystyle CH_2—I}{\overset{\displaystyle CH_2—I}{\overset{|}{\underset{|}{CHI}}}} \longrightarrow B$

Compound 'A' and 'B' respectively are

(a) 

(b) 

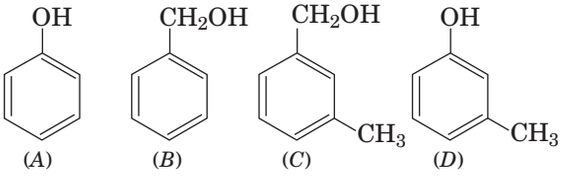
(c) 

(d) 

$CH_2=CH—CH_2I$

Introduction and Methods of Preparation of Phenols

28. Which of the following compounds is aromatic alcohol?



(*A*) (*B*) (*C*) (*D*)

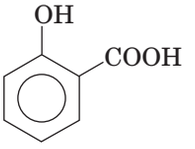
(NCERT Exemplar)

(a) *A, B, C, D* (b) *A, D*
(c) *B, C* (d) *A*

29. IUPAC name of *m*-cresol is *(NCERT Exemplar)*

(a) 3-methylphenol
(b) 3-chlorophenol
(c) 3-methoxyphenol
(d) benzene-1,3-diol

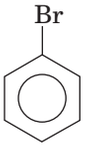
30. IUPAC name of *m*-cresol is



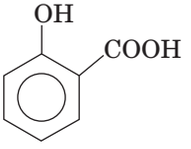
(a) 0-hydroxybenzoic acid
(b) 2-hydroxybenzoic acid
(c) Phenol-2-carboxylic acid
(d) 6-hydroxybenzoic acid

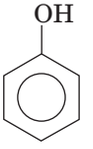
31. Among the following, which contains phenolic group

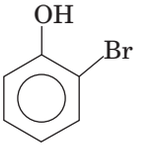
(a) picric acid (b) phenyl acetic acid
(c) phthalic acid (d) tetrephthalic acid

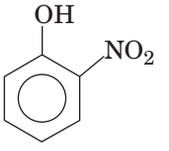
32.  $\xrightarrow[\text{(ii) } O_2 \text{ (iii) } H_3O^+]{\text{(i) Mg/Dry ether}} A$

Compound 'A' is

(a) 

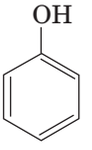
(b) 

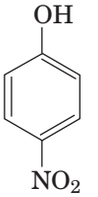
(c) 

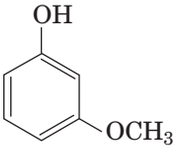
(d) 

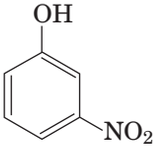
Physical and Chemical Properties of Phenol

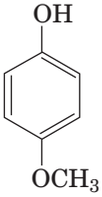
33. Mark the correct order of decreasing acid strength of the following compounds.

I. 

II. 

III. 

IV. 

V. 

(NCERT Exemplar)

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

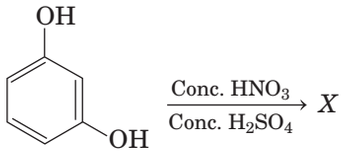
34. Phenol is heated with a solution of mixture of KBr and $KBrO_3$. The major product obtained in the above reaction is *(AIEEE 2011)*

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

35. Phenol on reaction with Br_2 in non-polar aprotic solvent furnishes

(a) *p*-bromophenol (b) *m*-bromophenol
(c) *o*/*p*-bromophenol (d) 2,4,6-tribromophenol

36. Consider the following reaction,



Product *X* is

(a) picric acid (b) styphnic acid
(c) salicylic acid (d) benzoic acid

37. On Friedel-Crafts acetylation, anisole yields *(NCERT)*

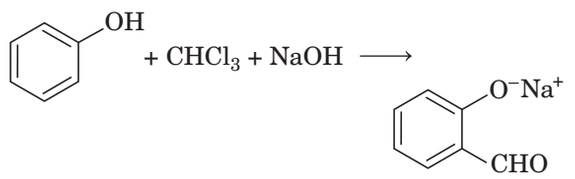
(a) 2-methoxyacetophenone
(b) 4-methoxyacetophenone
(c) Both (a) and (b)
(d) None of the above

38. Compound  can be prepared by the reaction of *(NCERT Exemplar)*

(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

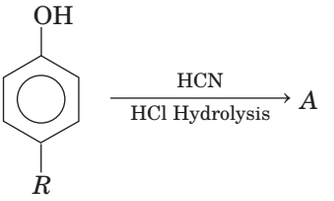
39. The major product obtained on interaction of phenol with sodium hydroxide and carbon dioxide is *(AIEEE 2009)*

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

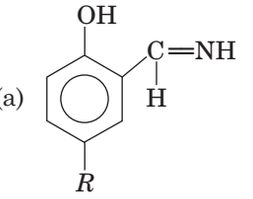
40. 

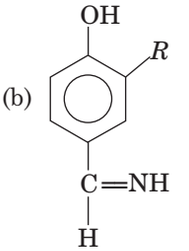
The electrophile involved in the above reaction is *(AIEEE 2006)*

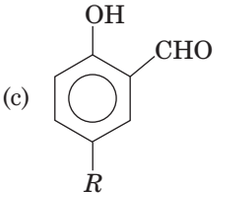
(a) dichloromethyl cation ($\overset{\oplus}{C}HCl_2$)
(b) dichlorocarbene ($:CCl_2$)
(c) trichloromethyl anion ($\overline{C}Cl_3$)
(d) formyl cation ($\overset{\oplus}{C}HO$)

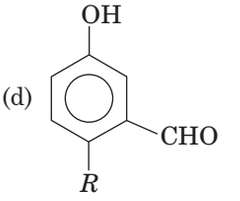
41. 

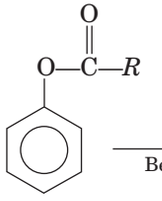
Compound '*A*' is

(a) 

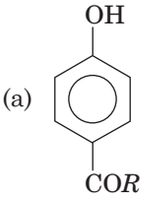
(b) 

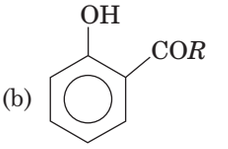
(c) 

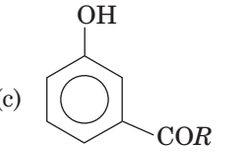
(d) 

42. 

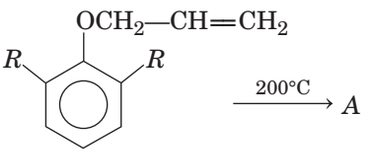
Major product will be

(a) 

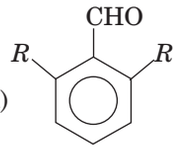
(b) 

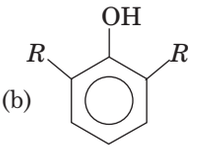
(c) 

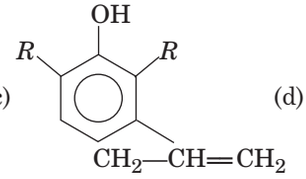
(d) Both (a) and (b) in equal ratio

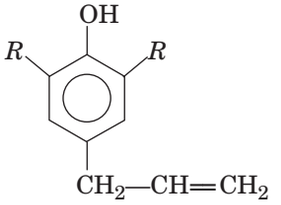
43. 

Compound '*A*' will be

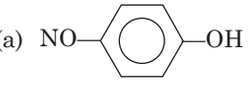
(a) 

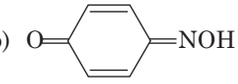
(b) 

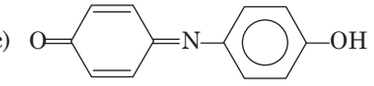
(c) 

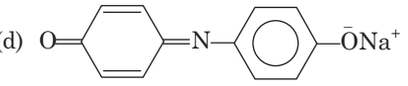
(d) 

44. In the Liebermann test for phenols, the blue or green colour produced is due to the formation of

(a) 

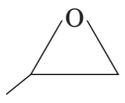
(b) 

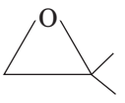
(c) 

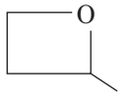
(d) 

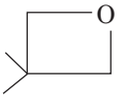
Introduction and Methods of Preparation of Ethers

45. Structure of the compound which is named as 2, 2-dimethyl oxirane.

(a) 

(b) 

(c) 

(d) 

46. C—O—C angle would be maximum in

(a) $CH_3—O—CH_3$

(b) $CH_3—O—C_2H_5$

(c) $C_2H_5—O—C_2H_5$

(d) $(CH_3)_2CH—O—CH(CH_3)_2$

47. To prepare an ether by Williamson's synthesis, the reactants needed are

(a) ethyl alcohol and *tert* butyl alcohol

(b) sodium ethoxide and *tert* butyl bromide

(c) sodium *tert* butoxide and ethyl bromide

(d) sodium ethoxide and sodium *tert* butoxide

48. Which of the following is the best method for making *iso*-propylmethyl ether?

(a) $CH_3I + (CH_3)_2CHOH \longrightarrow$

(b) $CH_3I + (CH_3)_2CHO^- \longrightarrow$

(c) $(CH_3)_2CHI + CH_3O^- \longrightarrow$

(d) $(CH_3)_2CHCl + CH_3OH \longrightarrow$

49. Ethyl bromide reacts with sodium methoxide to form ethyl methyl ether. It is an example of

(a) S_N2 reaction (b) S_N1 reaction

(c) S_N1 reaction (d) elimination reaction

50. 2-methoxybutane is obtained by reacting diazomethane with

(a) 2-butanol (b) 1-butanol

(c) 2-butanone (d) butanal

51. Which of the following reactions does not yield an ether?

(a) Sodium methoxide reacts with dimethyl sulphate

(b) Sodium ethoxide reacts with ethyl bromide

(c) Sodium ethoxide reacts with bromocyclopropane

(d) Ethanol reacts with CH_2N_2 in presence of HBF_4

52. The reaction,

$$2CH_3CH_2OH \xrightarrow[413\ K]{H^+} CH_3CH_2OCH_2CH_3$$

is believed to occur through the formation of

(a) $CH_3\overset{+}{C}H_2$

(b) $CH_3CH_2—\overset{+}{\underset{\displaystyle H}{\underset{|}{O}}}—CH_2CH_3$

(c) Both (a) and (b)

(d) None of them

Physical and Chemical Properties of Ethers

53. An ether is more volatile than an alcohol having the same molecular formula. This is due to

(a) intermolecular hydrogen bonding in alcohols

(b) dipolar character of ethers

(c) alcohols having resonance structures

(d) intermolecular hydrogen bonding in ether

54. Some time explosion occurs while distilling ethers. It is due to the presence of

(a) oxide (b) ketones (c) aldehyde (d) peroxides

55. On boiling with concentrated hydrobromic acid, phenyl ethyl ether yields

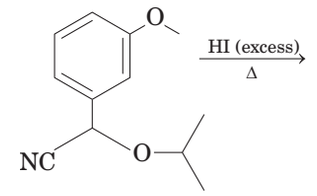
(a) phenol and ethane

(b) phenol and ethyl bromide

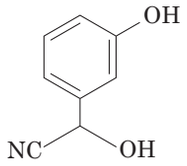
(c) bromobenzene and ethanol

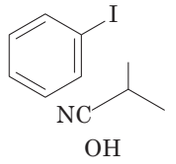
(d) bromobenzene and ethane

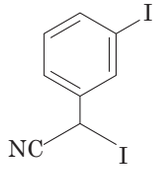
56. The major product of the following reaction is

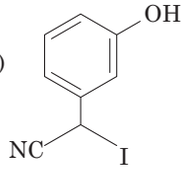


(JEE Main 2019)

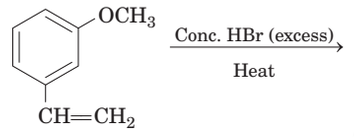
(a) 

(b) 

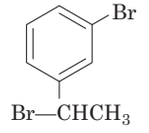
(c) 

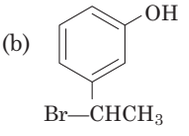
(d) 

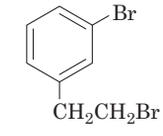
57. The major product of the following reaction is

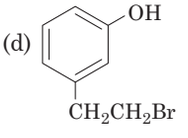


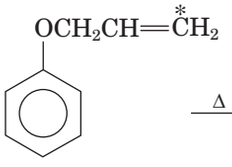
(JEE Main 2019)

(a) 

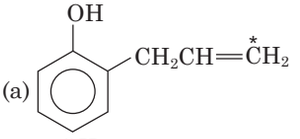
(b) 

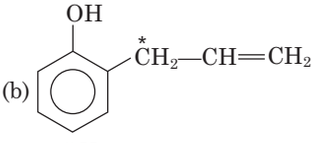
(c) 

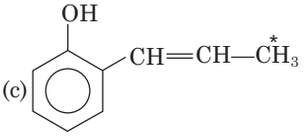
(d) 

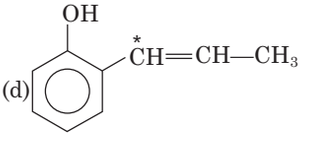
58. 

$\xrightarrow{\Delta}$? Product is

(a) 

(b) 

(c) 

(d) 

Introduction and Methods of Preparation and Ketones

59. $A \xrightarrow{Aq.\,NaOH} B$

Compound '*A*' and '*B*' respectively are

(a) $RCHX_2$ and $RCHO$ (b) $RCHO$ and $RC(R)X_2$

(c) $RC(R)X_2$ and $RCHX_2$ (d) $RCH(OH)_2$ and $RC(R)X_2$

60. Which of the following on heating with aqueous KOH, produces acetaldehyde?

(a) CH_3COCl (b) CH_3CH_2Cl

(c) CH_2ClCH_2Cl (d) CH_3CHCl_2

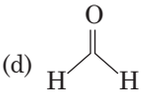
61. $CH_3—C\equiv C—CH_2CH_3 \xrightarrow[(ii)\,H_2O_2/OH^-]{(i)\,BH_3\text{ in TMF}}$ Major product + Minor product

Major product will be

(a) $CH_3—CH_2—C(=O)—CH_2—CH_3$

(b) $CH_3—C(=O)—CH_2—CH_2—CH_3$

(c) $CH_3—CH_2CH_2CH_2—C(=O)—H$

(d) 

62. $CH_3—C\equiv CH \xrightarrow[1\%\ HgSO_4]{40\%\ H_2SO_4} A \xrightarrow{\text{Isomerisation}} CH_3—C(=O)—CH_3$

Structure of '*A*' and type of isomerism in the above reaction are respectively. *(NCERT Exemplar)*

(a) Prop-1-en-2-ol, metamerism

(b) Pro-1-en-1-ol, tautomerism

(c) Prop-2-en-2-ol, geometrical isomerism

(d) Prop-1-en-2-ol, tautomerism

63. Which of the following compounds will give butanone on oxidation with alkaline $KMnO_4$ solution? *(NCERT Exemplar)*

(a) Butan-1-ol (b) Butan-2-ol

(c) Both (a)and (b) (d) None of these

64. Collin's reagent is used to convert

(a) $>C=O \longrightarrow >CHOH$ (b) $—CH_2OH \longrightarrow —CHO$

(c) $—CHO \longrightarrow —COOH$ (d) $—CHO \longrightarrow —CH_2OH$

65. The best reagent to convert pent-3-en-2-ol into pent-3-en-2-one is *(AIEEE 2005)*

(a) pyridinium chloro-chromate
(b) chromic anhydride in glacial acetic acid
(c) acidic dichromate
(d) acidic permanganate

66. In the Rosenmund's 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

67. Etard's reaction involves the preparation of benzaldehyde from

(a) toluene (b) ethyl benzene
(c) benzoyl chloride (d) sodium benzoate

68. The correct match between Column I (starting material) and Column II (reagent) for the preparation of benzaldehyde is

Column I	Column II
I. Benzene	(P) HCl and $SnCl_2$, H_3O^+
II. Benzonitrile	(Q) H_2, Pd-$BaSO_4$, S and quinoline
III. Benzoyl chloride	(R) CO, HCl and $AlCl_3$

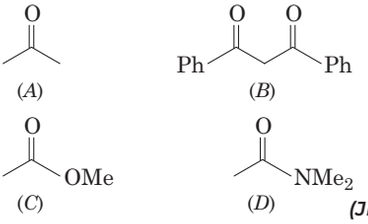
(a) (I) - (Q), (II) - (R) and (III) - (P) *(JEE Main 2020)*
(b) (I) - (P), (II) - (Q) and (III) - (R)
(c) (I) - (R), (II) - (P) and (III) - (Q)
(d) (I) - (R), (II) - (Q) and (III) - (P)

Physical and Chemical Properties of Aldehydes and Ketones

69. Arrange the following compounds in increasing order of their boiling points. CH_3CHO, CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$ *(NCERT)*

(a) $CH_3CH_2CH_3 < CH_3CH_2OH < CH_3OCH_3 < CH_3CHO$
(b) $CH_3OCH_3 < CH_3CH_2CH_3 < CH_3CH_2OH < CH_3CHO$
(c) $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$
(d) $CH_3CH_2OH < CH_3CHO < CH_3OCH_3 < CH_3CH_2OH$

70. The increasing order of the acidity of the α-hydrogen of the following compounds is



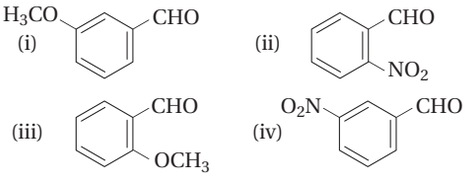
(JEE Main 2020)

(a) (*D*) < (*C*) < (*A*) < (*B*) (b) (*C*) < (*A*) < (*B*) < (*D*)
(c) (*A*) < (*C*) < (*D*) < (*B*) (d) (*B*) < (*C*) < (*A*) < (*D*)

71. Which of the following has the most acidic hydrogen?

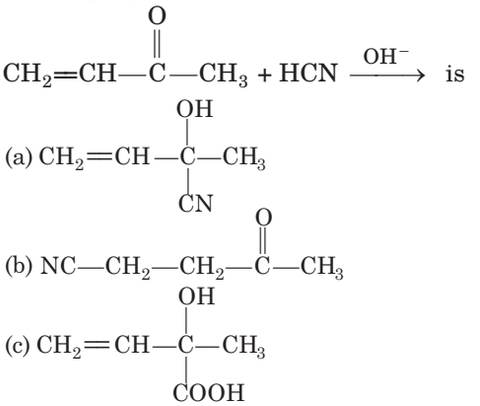
(a) 3-hexanone (b) 2,4-hexanedione
(c) 2,5-hexanedione (d) 2,3-hexanedione

72. The increasing order of the following compounds towards HCN addition is *(JEE Main 2020)*



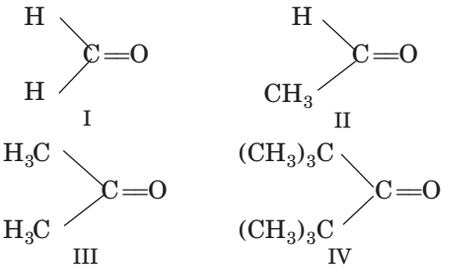
(a) (i) < (iii) < (iv) < (ii) (b) (iii) < (iv) < (i) < (ii)
(c) (iii) < (iv) < (ii) < (i) (d) (iii) < (i) < (iv) < (ii)

73. The major product obtained in the reaction,



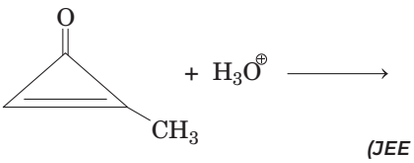
(d) None of the above

74. What will be the order of reactivity of the following carbonyl compounds with Grignard's reagent?

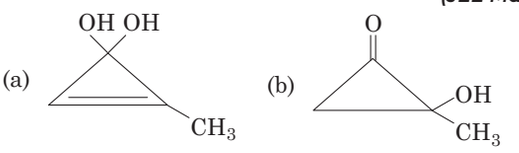


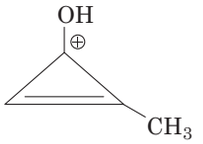
(a) I > II > III > IV (b) IV > III > II > I
(c) II > I > IV > III (d) III > II > I > IV

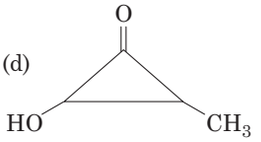
75. The major product in the following reaction is



(JEE Main 2020)



(c) 

(d) 

76. In the following reaction,

Aldehyde + Alcohol $\xrightarrow{HCl}$ Acetal

Aldehyde	Alcohol
HCHO	^{t}BuOH
CH_3CHO	MeOH

The best combination is *(JEE Main 2019)*

(a) CH_3CHO and MeOH (b) CH_3CHO and ^{t}BuOH

(c) HCHO and MeOH (d) HCHO and ^{t}BuOH

77. The reagent which does not react with both, acetone and benzaldehyde is *(NCERT Exemplar)*

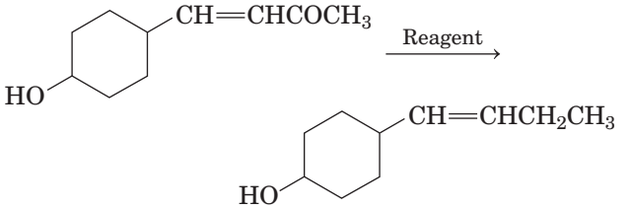
(a) sodium hydrogen sulphite

(b) phenyl hydrazine

(c) Fehling's solution

(d) Grignard reagent

78. In the given transformation, which of the following is the most appropriate reagent? *(AIEEE 2012)*



(a) $NH_2NH_2, \overset{\ominus}{O}H$ (b) Zn—Hg / HCl

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

79. Which one of the following undergoes reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid ? *(AIEEE 2004)*

(a) Phenol (b) Benzaldehyde

(c) Butanal (d) Benzoic acid

80. A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives

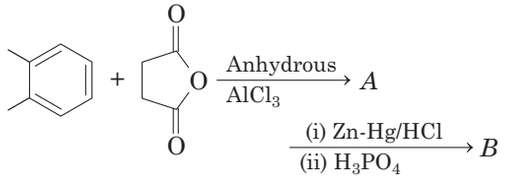
(a) benzyl alcohol and sodium formate

(b) sodium benzoate and methyl alcohol

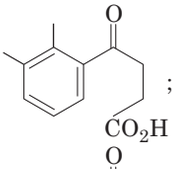
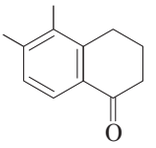
(c) sodium benzoate and sodium formate

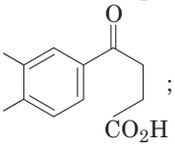
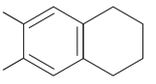
(d) benzyl alcohol and methyl alcohol

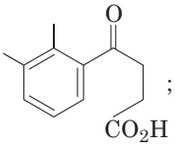
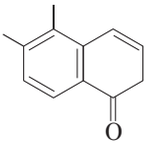
81. In the following reaction sequence the major products A and B are

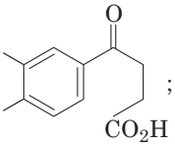
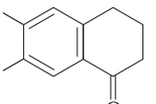


(JEE Main 2020)

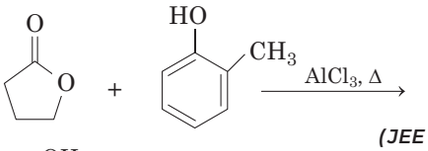
(a) A =  ; B = 

(b) A =  ; B = 

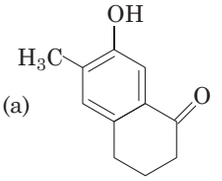
(c) A =  ; B = 

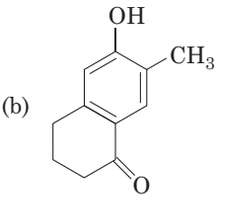
(d) A =  ; B = 

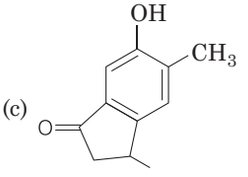
82. The major product of the following reaction is

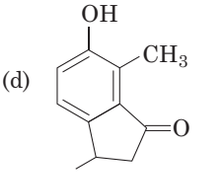


(JEE Main 2019)

(a) 

(b) 

(c) 

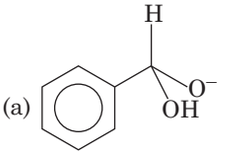
(d) 

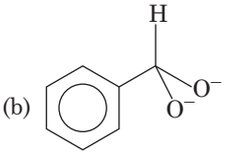
83. Hydride ion transfer takes place in

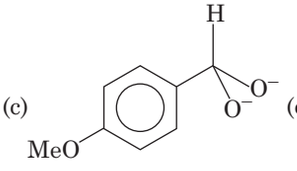
(a) Frankland method (b) Wurtz reaction

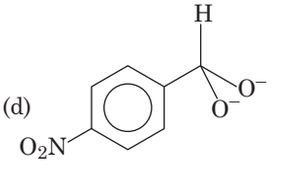
(c) Cannizzaro's reaction (d) Wolff-Kishner reduction

84. In a Cannizzaro reaction, the intermediate that will be best hydride donor is

(a) 

(b) 

(c) 

(d) 

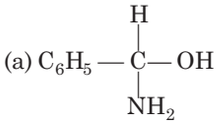
85. In Cannizzaro reaction given below

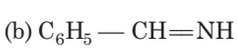
$$2PhCHO \xrightarrow{OH^{\ominus}} PhCH_2OH + PhCO_2^{\ominus}$$

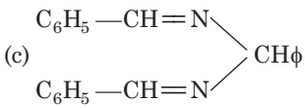
the slowest step is *(AIEEE 2009)*

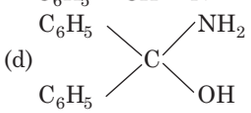
(a) the attack of : : $OH^{\ominus}$ at the carboxyl group
(b) the transfer of hydride to the carbonyl group
(c) the abstraction of proton from the carboxylic group
(d) the deprotonation of $PhCH_2OH$

86. $C_6H_5^- CHO + NH_3 \longrightarrow$? Product is

(a) 

(b) 

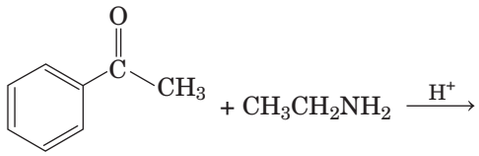
(c) 

(d) 

87. Which of the following does not undergo benzoin condensation?

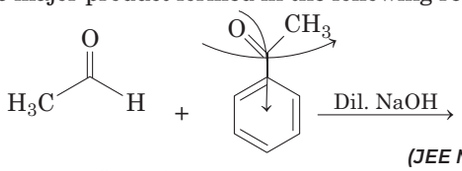
(a) Benzene carbaldehyde
(b) *p*-toluene carbaldehyde
(c) Phenylethanal
(d) 4-methoxybenzaldehyde

88. Predict the product of the following reaction. *(NCERT)*

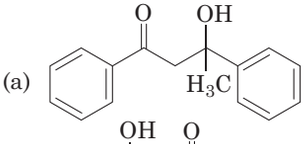


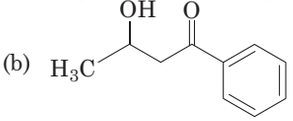
(a) Schiff's base (b) Tollen's reagent
(c) Bendict solution (d) Molisch's reagent

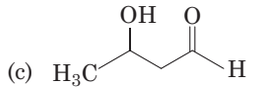
89. The major product formed in the following reaction is

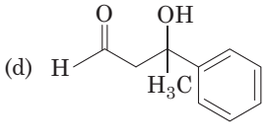


(JEE Main 2019)

(a) 

(b) 

(c) 

(d) 

90. Match the following.

I. $C_6H_5COCH_3 \longrightarrow C_6H_5CH_2CH_3$ (A) $SnCl_2$
II. $C_6H_5COCH_3 \longrightarrow C_6H_5CH(OH)CH_3$ (B) Zn-Hg/HCl
III. $C_6H_5NO_2 \longrightarrow C_6H_5NHOH$ (C) $NaBH_4$
IV. $C_6H_5CH_2—OTs \longrightarrow C_6H_5CH_3$ (D) Zn/NH_4Cl

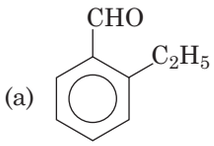
Codes

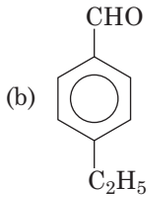
(a) (I)-B, (II)-C, (III)-D, (IV)-A
(b) (I)-B, (II)-A, (III)-D, (IV)-C
(c) (I)-B, (II)-A, (III)-C, (IV)-D
(d) (I)-A, (II)-B, (III)-D, (IV)-C

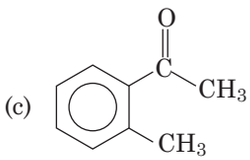
91. An aromatic compound '*X*' with molecular formula $C_9H_{10}O$ gives the following chemical tests. It

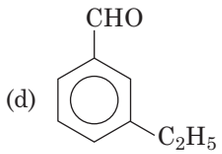
I. forms 2, 4-DNP derivative
II. reduces Tollen's reagent
III. undergoes Cannizzaro reaction and
IV. on vigorous oxidation 1,2-benzenedicarboxylic acid is obtained.

X is *(NCERT)*

(a) 

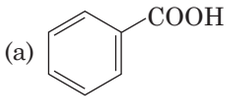
(b) 

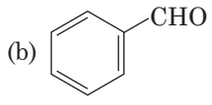
(c) 

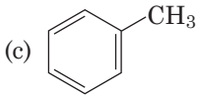
(d) 

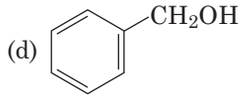
92. The reactant (*X*) in the reaction

$$(X) \xrightarrow[(CH_3CO)_2O]{CH_3COONa} \text{cinnamic acid, is}$$

(a) 

(b) 

(c) 

(d) 

93. C_6H_5CHO undergoes Claisen condensation with another aldehyde to give cinnamaldehyde. The aldehyde is

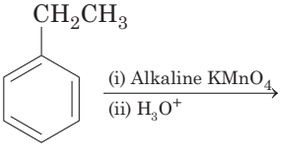
(a) formaldehyde
(b) acetaldehyde
(c) crotonaldehyde
(d) propanaldehyde

Intrduction and Methods of Preparation of Carboxylic Acids

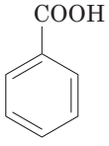
94. Tamarind contains

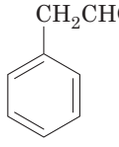
(a) (+) tartaric acid (b) (–) tartaric acid
(c) ± tartaric acid (d) None of these

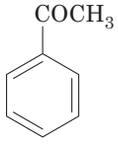
95. The major product of the following reaction is

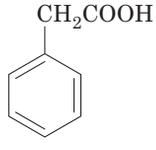


(JEE Main 2019)

(a) 

(b) 

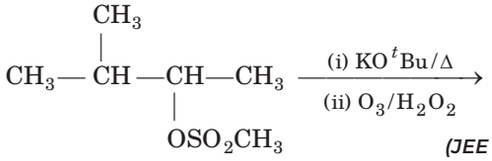
(c) 

(d) 

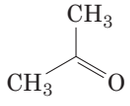
96. $CH_2{=}CH_2 + CO + H_2O \xrightarrow[573\text{-}673K]{H_3PO_4} A$

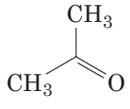
(a) CH_3COOH
(b) CH_3CH_2COOH
(c) $CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}COOH$
(d) HCOOH

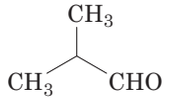
97. The major products of the following reaction are

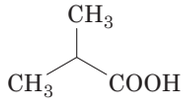


(JEE Main 2020)

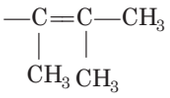
(a)  + CH_3CHO

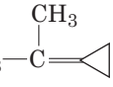
(b)  + CH_3COOH

(c)  + HCHO

(d)  + HCOOH

98. An unsaturated hydrocarbon *X* on ozonolysis gives *A*. Compound *A* when warmed with ammonical silver nitrate forms a bright silver mirror along the sides of the test tube. The unsaturated hydrocarbon *X* is *(JEE Main 2021)*

(a) 

(b) 

(c) $HC{\equiv}C{-}CH_2{-}CH_3$
(d) $CH_3{-}C{\equiv}C{-}CH_3$

Physical and Chemical Properties of Carboxylic Acids

99. Which of the following order represent acidic strength of (I) benzoic acid, (II) 4-nitrobenzoic acids, (III) 3,4-dinitro benzoic acid and (IV) 4-methoxy benzoic acid? *(NCERT)*

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

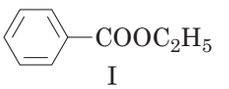
100. Consider the the following compounds.

I. PhCOOH II. *o*-$NO_2C_6H_4COOH$
III. *p*-$NO_2C_6H_4COOH$ IV. *m*-$NO_2C_6H_4COOH$

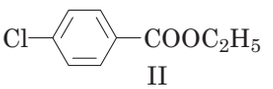
The correct acidic order of given carboxylic acids are as follows

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

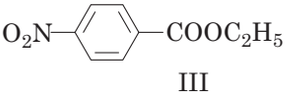
101. The decreasing order of ease of alkaline hydrolysis for the following esters is *(JEE Main 2019)*



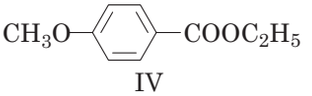
I



II



III



IV

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

102. An organic compound [*A*], molecular formula $C_{10}H_{20}O_2$ was hydrolysed with dilute sulphuric acid to give a carboxylic acid [*B*] and an alcohol [*C*]. Oxidation of [*C*] with CrO_3—H_2SO_4 produced [*B*]. Which of the following structures are not possible for [*A*]? *(JEE Main 2020)*

(a) CH_3CH_2—CH(CH$_3$)—OCOCH$_2$CH(CH$_3$)—CH$_2$CH$_3$

(b) CH_3CH_2—CH(CH$_3$)—COOCH$_2$CH(CH$_3$)—CH$_2$CH$_3$

(c) $CH_3CH_2CH_2COOCH_2CH_2CH_2CH_2CH_2CH_3$

(d) $(CH_3)_3$—C—$COOCH_2C(CH_3)_3$

103. Which of the following carboxylic acids undergoes decarboxylation easily ?

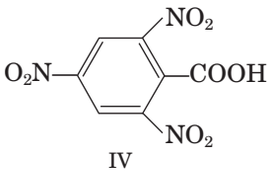
(a) $C_6H_5COCH_2COOH$ (b) $C_6H_5COCOOH$

(c) C_6H_5CH(OH)—COOH (d) C_6H_5CH(NH$_2$)C OOH

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

$\underset{I}{CH_3COOH}$; $CH_2=CH-\underset{II}{CH_2COOH}$;

$\underset{III}{CH_2(COOH)_2}$

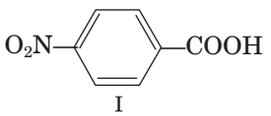


IV

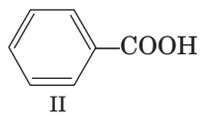
(a) I > II > III > IV (b) III > IV > II > I

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

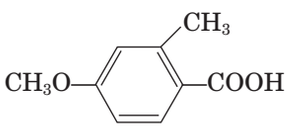
105. Give the order of ease of the esterification of the following acids and accordingly choose the correct code that are given below.



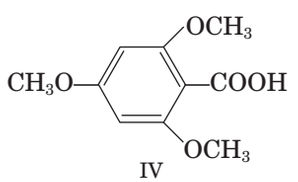
I



II



III



IV

Codes

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

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

106. Which can reduce $RCOOH \longrightarrow RCH_2OH$?

(a) $NaBH_4$ (b) Na /C_2H_5OH

(c) BH_3 / THF / H_3O^+ (d) H_2 / catalyst

107. When $CH_2=CH-COOH$ is reduced with $LiAlH_4$, the compound obtained will be *(AIEEE 2003)*

(a) CH_3-CH_2-COOH

(b) $CH_2=CH-CH_2OH$

(d) $CH_2=CH-CH_2OH$

(c) CH_3-CH_2-CHO

108. Formic acid and acetic acid are distinguished by

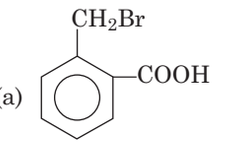
(a) $NaHCO_3$

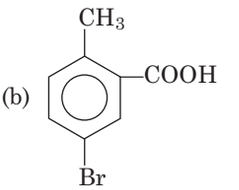
(b) $FeCl_3$

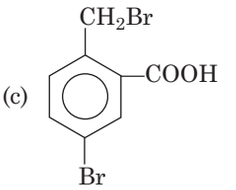
(c) Victor Meyer test

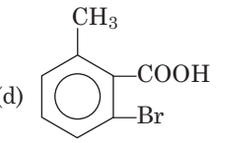
(d) Tollen's reagent

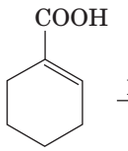
109. *o*-toluic acid on reaction with Br_2 + Fe gives

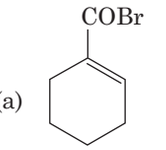
(a) 

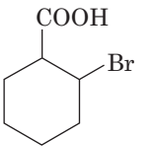
(b) 

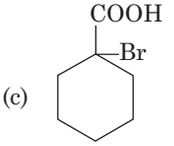
(c) 

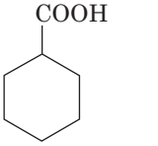
(d) 

110.  $\xrightarrow{HBr}$? Product is

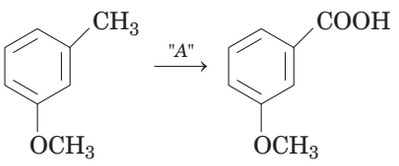
(a) 

(b) 

(c) 

(d) 

ROUND II Mixed Bag

1. 

In the above reaction, the reagent "*A*" is

(JEE Main 2021)

(a) $NaBH_4$, H_3O^+ (b) $LiAlH_4$
(c) Alkaline $KMnO_4$, H^+ (d) HCl, Zn-Hg

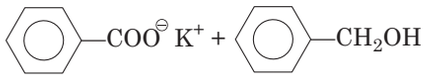
2. Which of the following steps will be required for the conversion of ethanal into butane-1,3-diol?

(a) Acylation, reduction *(NCERT)*
(b) Cross aldol condensation, dehydration
(c) Aldol condensation, oxidation
(d) Aldol condensation, reduction

3. The compound, *A* in the following :

$$A \xrightarrow[\text{(ii) Conc. } H_2SO_4/\Delta]{\text{(i) } CH_3MgBr/H_2O} B \xrightarrow[\text{(ii) } Zn/H_2O]{\text{(i) } O_3} C + D$$

$$C \xrightarrow[\text{(ii) } \Delta]{\text{(i) Conc. KOH}}$$



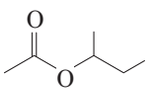
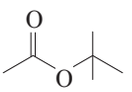
$$D \xrightarrow[\Delta]{Ba(OH)_2} H_3C-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$$

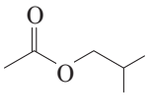
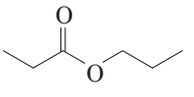
(JEE Main 2020)

(a) $C_6H_5-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$ (b) $C_6H_5-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$

(c) $C_6H_5-\overset{\displaystyle O}{\overset{\|}{C}}-CH_2CH_3$ (d) $C_6H_5-\overset{\displaystyle O}{\overset{\|}{C}}-CH\begin{matrix}CH_3\\CH_3\end{matrix}$

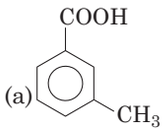
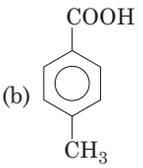
4. An organic compound (*A*) (molecular formula $C_6H_{12}O_2$) was hydrolysed with dil. H_2SO_4 to give a carboxylic acid (*B*) and an alcohol (*C*). '*C*' gives white turbidity immediately when treated with anhydrous $ZnCl_2$ and conc. HCl. The organic compound (*A*) is *(JEE Main 2020)*

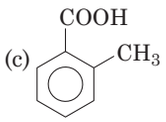
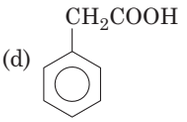
(a)  (b) 

(c)  (d) 

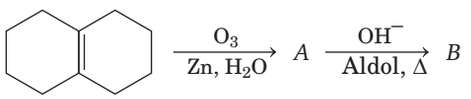
5. [*P*] on treatment with $Br_2/FeBr_3$ in CCl_4 produced a single isomer $C_8H_7O_2Br$ while heating [*P*] with sodalime gave toluene. The compound [*P*] is

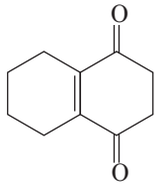
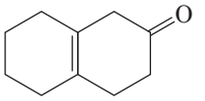
(JEE Main 2020)

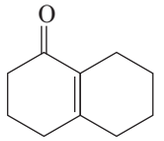
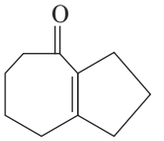
(a)  (b) 

(c)  (d) 

6. Identify the final product of the reaction.



(a)  (b) 

(c)  (d) 

7. In the following sequence of reactions,

$$CH_3CH_2OH \xrightarrow{P+I_2} A \xrightarrow[\text{ether}]{Mg} B \xrightarrow{HCHO} C \xrightarrow{H_2O} D$$

the compound '*D*' is *(AIEEE 2007)*

(a) butanal
(b) *n*-butyl alcohol
(c) *n*-propyl alcohol
(d) propanal

8.

$$CH_3OH \xrightarrow{CH_2=C=O} A \xrightarrow{\text{Rearrangement}} CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-OCH_3$$

In the above reaction, *A* is

(a) $CH_3-\underset{\displaystyle OH}{\underset{|}{C}}=CH_2$ (b) $CH_2=\underset{\displaystyle OH}{\underset{|}{C}}-OCH_3$

(c) $CH_2=CHOH$ (d) None of these

9. 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

10. Two compounds *A* and *B* with same molecular formula (C_3H_6O) undergo Grignard's reaction with methylmagnesium bromide to give products *C* and *D*. Products *C* and *D* show following chemical tests.

Test	*C*	*D*
Ceric ammonium nitrate test	Positive	Positive
Lucas test	Turbidity obtained after five minutes	Turbidity obtained immediately
Iodoform test	Positive	Negative

C and *D* respectively are *(JEE Main 2020)*

(a) *C* = $H_3C—CH_2—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3$;
D = $H_3C—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}—OH$

(b) *C* = $H_3C—CH_2—CH_2—CH_2—OH$;
D = $H_3C—CH_2—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3$

(c) *C* = $H_3C—CH_2—CH_2—CH_2—OH$;
D = $H_3C—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}—OH$

(d) *C* = $H_3C—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}—OH$; *D* = $H_3CCH_2—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3$

11. Phthalic acid

$$A \xrightarrow{NH_3} B \xrightarrow[H_2O]{NaOH} C \xrightarrow{Br_2/KOH} D \xrightarrow{HCl} E$$

In this reaction, the product *E* is

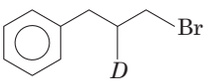
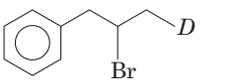
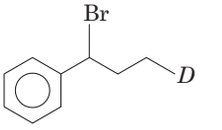
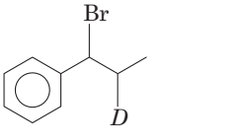
(a) *o*-nitrobenzoic acid
(b) salicylic acid
(c) anthranilic acid
(d) crotonic acid

12. The major product [*C*] of the following reaction sequence will be

$$CH_2=CH—CHO \xrightarrow[(ii)\ SOCl_2]{(i)NaBH_4} [A]$$

$$\xrightarrow[\text{Anhyd. } AlCl_3]{} [B] \xrightarrow{DBr} [C]$$

(JEE Main 2020)

(a) 
(b) 
(c) 
(d) 

13. Phenol

$$\xrightarrow[(ii)\ CO_2/140°C]{(i)\ NaOH} A \xrightarrow{(iii)\ H^+/H_2O} B \xrightarrow{(iv)\ Ac_2O} C$$

In this reaction, the end product *C* is *(NCERT)*

(a) salicylaldehyde (b) salicylic acid
(c) phenyl acetate (d) aspirin

14. Consider the following reactions :

(A) $(CH_3)_3CCH(OH)CH_3 \xrightarrow{Conc.\ H_2SO_4}$

(B) $(CH_3)_2CHCH(Br)CH_3 \xrightarrow{Alc.\ KOH}$

(C) $(CH_3)_2CHCH(Br)CH_3 \xrightarrow{(CH_3)_3\ O^{\ominus}K^{\oplus}}$

(D) $(CH_3)_2\underset{\displaystyle OH}{\underset{|}{C}}—CH_2—CHO \xrightarrow{\Delta}$

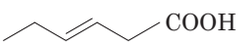
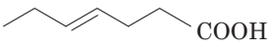
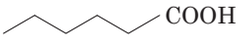
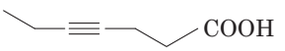
Which of these reaction(s) will not produce Saytzeff product? *(JEE Main 2020)*

(a) (A), (C) and (D)
(b) (B) and (D)
(c) (C) Only
(d) (D) Only

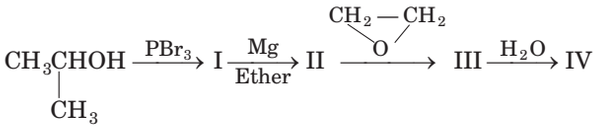
15. What is the product of following reaction?

Hex - 3 - ynal $\xrightarrow[(ii)\ PBr_3\ (iii)\ Mg/ether\ (iv)\ CO_2/H_3O^+]{(i)\ NaBH_4}$?

(JEE Main 2020)

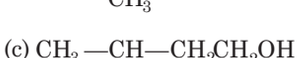
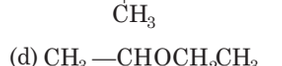
(a) 
(b) 
(c) 
(d) 

16. The final product (IV) in the sequence of reactions

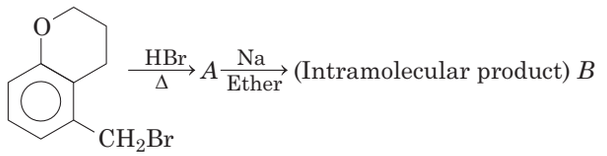


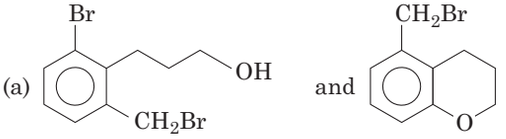
is

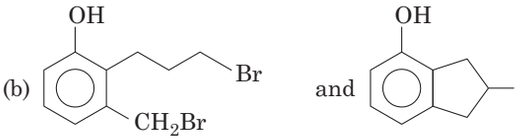
(a) 
(b) 

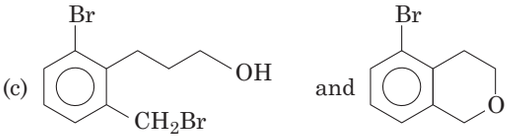
(c) 
(d) 

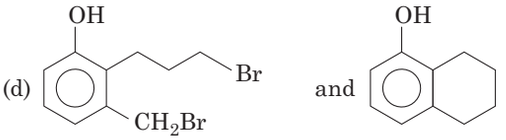
17. In the following reaction sequence, structures of A and B, respectively will be *(JEE Main 2020)*



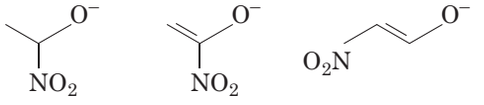
(a) 

(b) 

(c) 

(d) 

18. The correct order of stability for the following alkoxides is *(JEE Main 2020)*



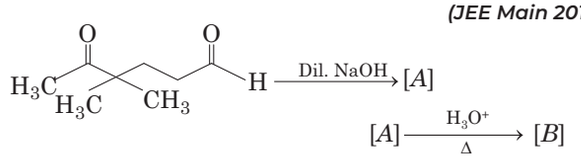
(A) (B) (C)

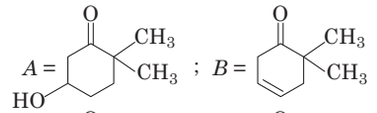
(a) (C) > (B) > (A)
(b) (B) > (C) > (A)
(c) (B) > (A) > (C)
(d) (C) > (A) > (B)

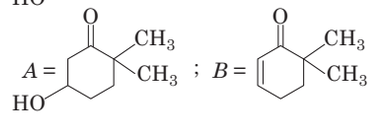
19. A colourless water soluble organic liquid decomposes sodium carbonate and liberates CO_2. It produces black precipitate with Tollen's reagent. The liquid is

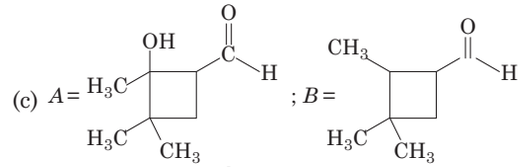
(a) acetaldehyde
(b) acetamide
(c) formic acid
(d) acetone

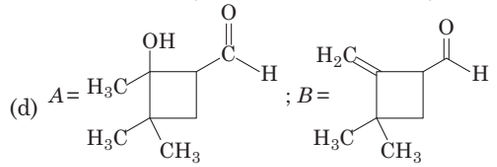
20. In the following reactions, products A and B are *(JEE Main 2019)*



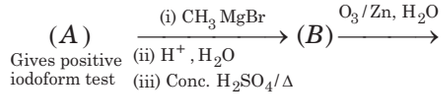
(a) 

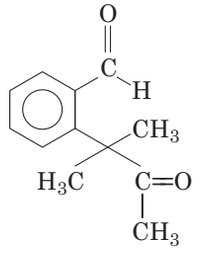
(b) 

(c) 

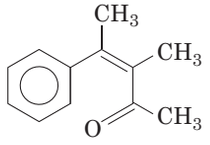
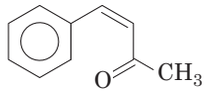
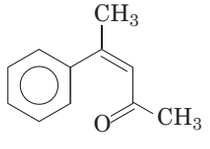
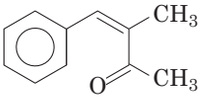
(d) 

21. Identify (A) in the following reaction sequence

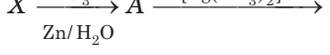




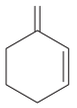
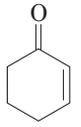
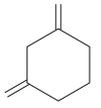
(JEE Main 2020)

(a) 
(b) 
(c) 
(d) 

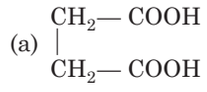
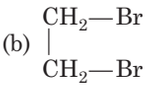
22. An unsaturated hydrocarbon X absorbs two hydrogen molecules on catalytic hydrogenation, and also gives following reaction

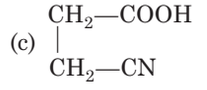
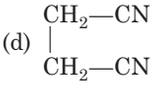


B (3-oxo-hexanedicarboxylic acid) X will be *(JEE Main 2020)*

(a)  (b)  (c)  (d) 

23. The final product of the following sequence of reaction is

(a)  (b) 

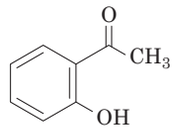
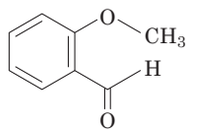
(c)  (d) 

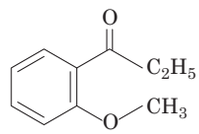
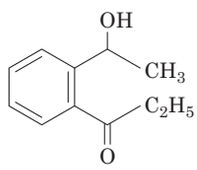
24. Compound A when treated with ethyl magnesium iodide in dry ether forms an addition compound which on hydrolysis forms compound B. The compound B on oxidation form 3-pentanone. Hence, the compound A and B are

(a) propanal, 3-pentanol (b) pentanol, 3-pentanol

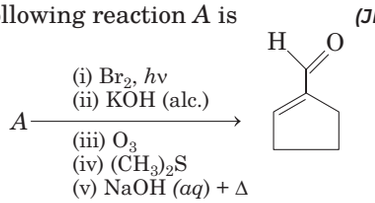
(c) ethanal, pentanal (d) acetone, 3-pentanol

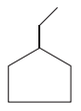
25. An organic compound neither reacts with neutral ferric chloride solution nor with Fehling solution. It however, reacts with Grignard reagent and gives positive iodoform test. The compound is *[JEE Main 2019]*

(a)  (b) 

(c)  (d) 

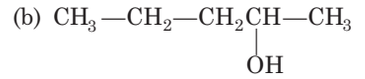
26. In the following reaction A is *(JEE Main 2020)*

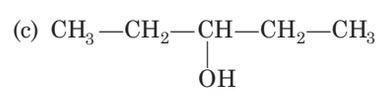


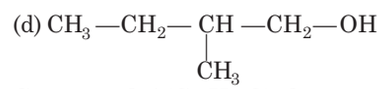
(a)  (b)  (c)  (d) 

27. A compound 'A' having the molecular formula $C_5H_{12}O$, on oxidation gives a compound 'B' with molecular formula $C_5H_{10}O$. Compound 'B' gave a 2,4-dinitrophenylhydrazine derivative but did not answer haloform test or silver mirror test. The structure of compound 'A' is

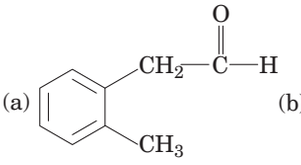
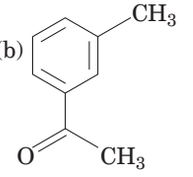
(a) $CH_3CH_2CH_2CH_2CH_2OH$

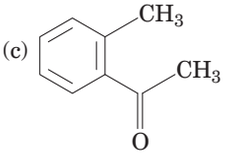
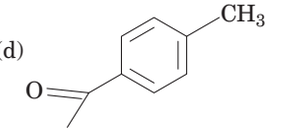
(b) 

(c) 

(d) 

28. Compound $A(C_9H_{10}O)$ shows positive iodoform test. Oxidation of A with $KMnO_4$ / KOH gives acid B ($C_8H_6O_4$). Anhydride of B is used for the preparation of phenolphthalein. Compound A is *(JEE Main 2019)*

(a)  (b) 

(c)  (d) 

29. An organic compound 'X' with molecular formula, C_7H_8O is insoluble in aqueous $NaHCO_3$ but dissolves in NaOH. When treated with bromine water, 'X' rapidly gives 'Y', $C_7H_5OBr_3$. The compounds 'X' and 'Y' respectively, are

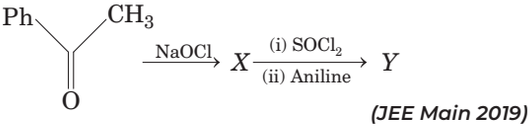
(a) benzyl alcohol and 2,4,6-tribromo-3-methoxybenzene

(b) benzyl alcohol and 2,4,6-tribromo-3-methylphenol

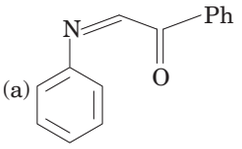
(c) *o*-cresol and 3,4,5-tribromo-2-methylphenol

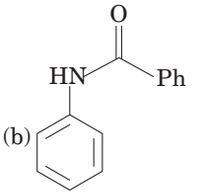
(d) *m*-cresol and 2,4,6-tribromo-3-methylphenol

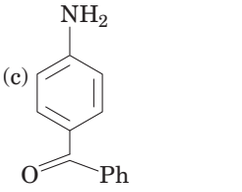
30. The major product Y in the following reaction is

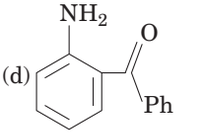


(JEE Main 2019)

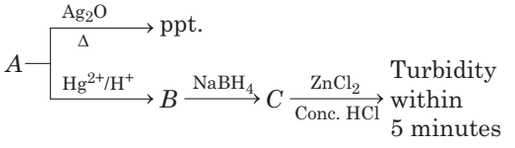
(a) 

(b) 

(c) 

(d) 

31. Consider the following reactions,

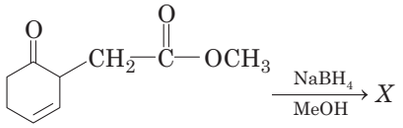


A is *(JEE Main 2019)*

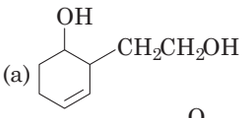
(a) $CH \equiv CH$ (b) $CH_3C \equiv CCH_3$

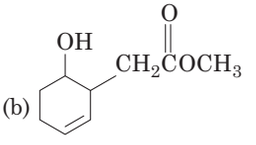
(c) $CH_3—C \equiv CH$ (d) $CH_2 = CH_2$

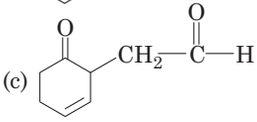
32. The major product 'X' formed in the following reaction is

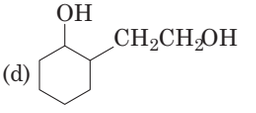


(JEE Main 2019)

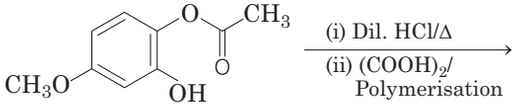
(a) 

(b) 

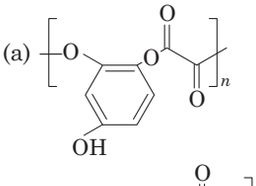
(c) 

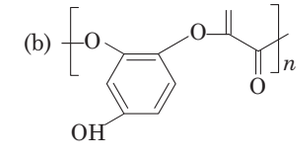
(d) 

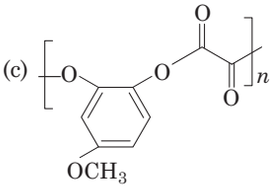
33. The major product of the following reaction is

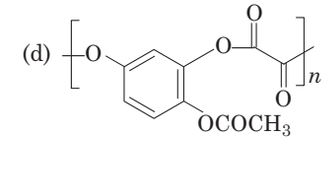


(JEE Main 2019)

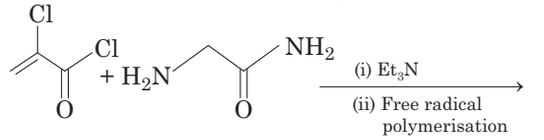
(a) 

(b) 

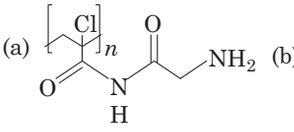
(c) 

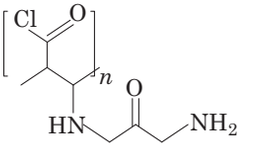
(d) 

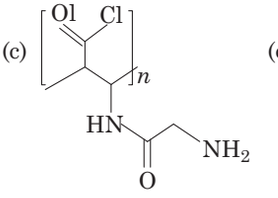
34. Major product of the following reaction is

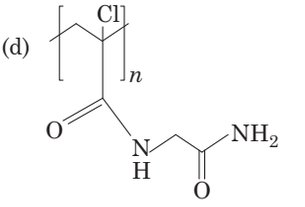


(JEE Main 2019)

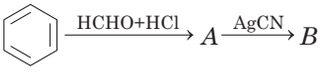
(a) 

(b) 

(c) 

(d) 

35. The compounds A and B in the following reaction are, respectively



(JEE Main 2019)

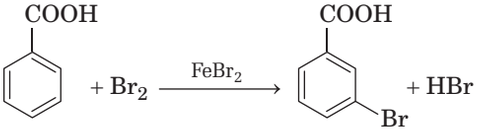
(a) A = Benzyl alcohol, B = Benzyl isocyanide

(b) A = Benzyl alcohol, B = Benzyl cyanide

(c) A = Benzyl chloride, B = Benzyl isocyanide

(d) A = Benzyl chloride, B = Benzyl cyanide

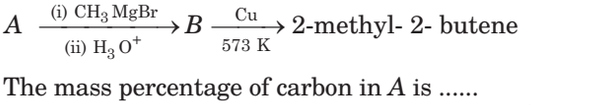
Numeric Value Questions

36. 

Consider the above reaction where 6.1 g of benzoic acid is used to get 7.8 g of *m*-bromo benzoic acid. The percentage yield of the product is …… .
(Round off to the Nearest Integer)

[Given : Atomic masses : C = 12.0 u, H : 1.0 u, O : 16.0 u, Br = 80.0 u] *[JEE Main 2021]*

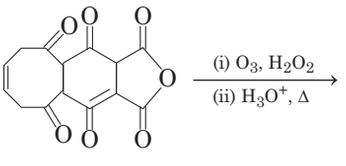
37. Consider the following reactions



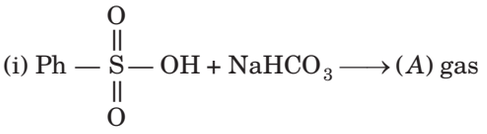
The mass percentage of carbon in A is .....

(JEE Main 2020)

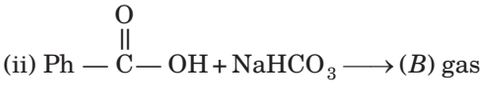
38. Numebr of carbonyl groups present in the final product of the following reaction sequence is



39. Consider the following reactions



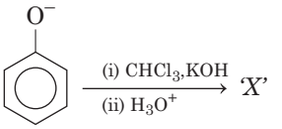
(i) $Ph-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH + NaHCO_3 \longrightarrow (A)$ gas



(ii) $Ph-\overset{\overset{O}{\|}}{C}-OH + NaHCO_3 \longrightarrow (B)$ gas

Sum of molecular mass of $A + B = ?$

40. Consider the following reactions



Identify the molecular weight of the product '*X*' give your answer in this way if molecular weight is 121 and on adding 1 + 2 + 1 the total will be 4. So in similar the sum of the numeric value of molecular weight of *x* will be …….

Answers

Round I

1. *(c)*	***2.*** *(a)*	***3.*** *(c)*	***4.*** *(c)*	***5.*** *(a)*	***6.*** *(a)*	***7.*** *(a)*	***8.*** *(d)*	***9.*** *(c)*	***10.*** *(a)*
11. *(c)*	***12.*** *(a)*	***13.*** *(c)*	***14.*** *(b)*	***15.*** *(c)*	***16.*** *(a)*	***17.*** *(c)*	***18.*** *(d)*	***19.*** *(b)*	***20.*** *(c)*
21. *(c)*	***22.*** *(c)*	***23.*** *(a)*	***24.*** *(d)*	***25.*** *(a)*	***26.*** *(d)*	***27.*** *(d)*	***28.*** *(c)*	***29.*** *(a)*	***30.*** *(b)*
31. *(a)*	***32.*** *(b)*	***33.*** *(b)*	***34.*** *(d)*	***35.*** *(c)*	***36.*** *(b)*	***37.*** *(c)*	***38.*** *(b)*	***39.*** *(c)*	***40.*** *(b)*
41. *(c)*	***42.*** *(a)*	***43.*** *(d)*	***44.*** *(d)*	***45.*** *(b)*	***46.*** *(d)*	***47.*** *(c)*	***48.*** *(b)*	***49.*** *(a)*	***50.*** *(a)*
51. *(c)*	***52.*** *(d)*	***53.*** *(a)*	***54.*** *(d)*	***55.*** *(b)*	***56.*** *(d)*	***57.*** *(b)*	***58.*** *(b)*	***59.*** *(a)*	***60.*** *(d)*
61. *(b)*	***62.*** *(d)*	***63.*** *(b)*	***64.*** *(b)*	***65.*** *(b)*	***66.*** *(c)*	***67.*** *(a)*	***68.*** *(c)*	***69.*** *(c)*	***70.*** *(a)*
71. *(b)*	***72.*** *(d)*	***73.*** *(b)*	***74.*** *(a)*	***75.*** *(c)*	***76.*** *(c)*	***77.*** *(c)*	***78.*** *(a)*	***79.*** *(b)*	***80.*** *(a)*
81. *(d)*	***82.*** *(c)*	***83.*** *(c)*	***84.*** *(d)*	***85.*** *(b)*	***86.*** *(c)*	***87.*** *(c)*	***88.*** *(a)*	***89.*** *(c)*	***90.*** *(a)*
91. *(a)*	***92.*** *(b)*	***93.*** *(b)*	***94.*** *(a)*	***95.*** *(a)*	***96.*** *(b)*	***97.*** *(d)*	***98.*** *(c)*	***99.*** *(b)*	***100.*** *(d)*
101. *(b)*	***102.*** *(a)*	***103.*** *(a)*	***104.*** *(c)*	***105.*** *(a)*	***106.*** *(c)*	***107.*** *(b)*	***108.*** *(d)*	***109.*** *(b)*	***110.*** *(b)*

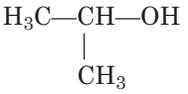
Round II

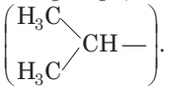
1. *(c)*	***2.*** *(d)*	***3.*** *(a)*	***4.*** *(b)*	***5.*** *(b)*	***6.*** *(d)*	***7.*** *(c)*	***8.*** *(b)*	***9.*** *(a)*	***10.*** *(a)*
11. *(c)*	***12.*** *(c)*	***13.*** *(d)*	***14.*** *(c)*	***15.*** *(d)*	***16.*** *(c)*	***17.*** *(d)*	***18.*** *(a)*	***19.*** *(c)*	***20.*** *(b)*
21. *(d)*	***22.*** *(b)*	***23.*** *(a)*	***24.*** *(a)*	***25.*** *(d)*	***26.*** *(c)*	***27.*** *(c)*	***28.*** *(c)*	***29.*** *(d)*	***30.*** *(b)*
31. *(c)*	***32.*** *(b)*	***33.*** *(c)*	***34.*** *(d)*	***35.*** *(c)*	***36.*** *(78)*	***37.*** *(66.67)*	***38.*** *(4)*	***39.*** *(88)*	***40.*** *(5)*

Solutions

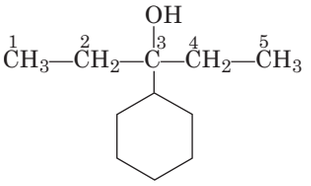
Round I

1. *Iso*-propyl alcohol is

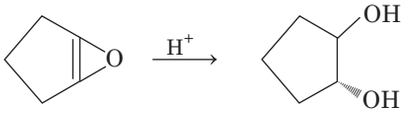


because, here alcohol group (—OH) attached with *iso*-propyl group  .

2. The correct structure of 3-cyclohexylpentan-3-ol is

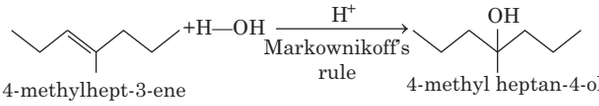


3.



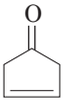
(*trans*-cyclopentane-1, 2-diol)

4.



4-methylhept-3-ene — Markownikoff's rule — 4-methyl heptan-4-ol

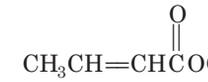
5. Reducing agents like $LiAlH_4$, $NaBH_4$, i.e. complex hydrides usually does not affect olifenic or π-bonds.

Thus, if $NaBH_4$ is applied to a compound like  then its $\rangle C{=}O$ bond will be reduced only and we get  as the final product.

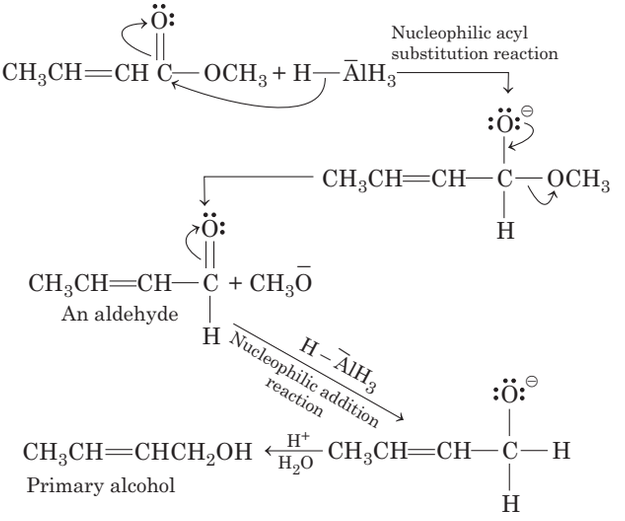
6. $LiAlH_4$ reagent is used for the reduction of —CHO,  . It does not reduce double bonds.

The reaction of an ester with $LiAlH_4$ produces two alcohols, one corresponding to the acyl portion of the ester and one corresponding to the alkyl portion.

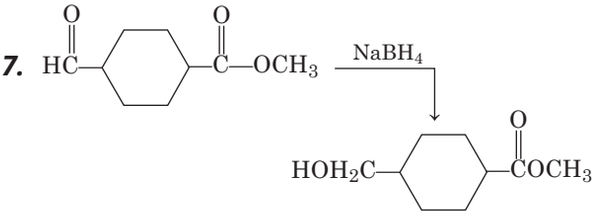
But-2- en-1- ol — Methanol

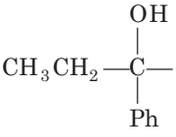
Thus, the major product of the given reactant  in presence of $LiAlH_4$ is $CH_3CH{=}CHCH_2OH$ and CH_3OH. The reaction proceeds through following mechanism.

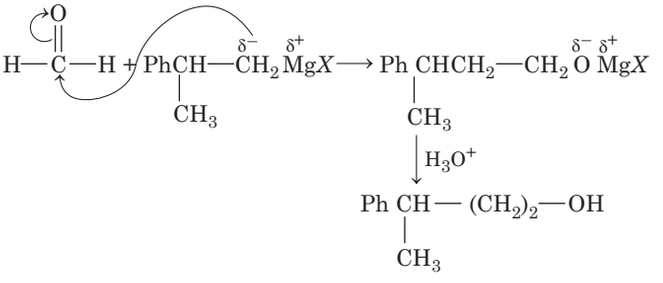
Mechanism



7.

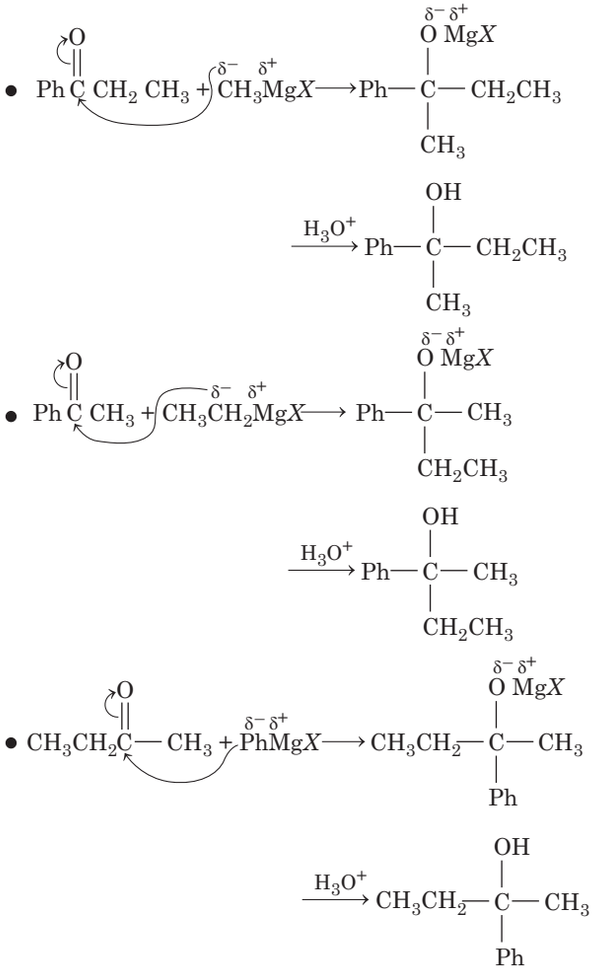


8.  cannot be prepared by HCHO and $PhCH(CH_3)CH_2MgX$. This can be easily illustrated by following reaction.



The obtained product is not the required substance. While option (a), (b) and (c) can readily prepare the required substance.

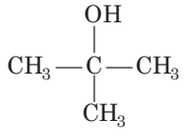
The reactions are as follows



9. Since, carbonyl compounds give alcohols with Grignard regent, so we take a general carbonyl compound $R_2C{=}O$.

$$CH_3MgBr + \begin{matrix} R \\ R' \end{matrix}\!\!>\!C{=}O \longrightarrow \begin{matrix} R \\ R' \end{matrix}\!\!>\!C(CH_3)\text{—}OMgBr \xrightarrow{H_2O} \begin{matrix} R \\ R' \\ H_3C \end{matrix}\!\!>\!C\text{—}OH$$

The structure of 2-methyl propan-2-ol is



Thus, R and R' must be CH_3.

Therefore, X is $\begin{matrix} H_3C \\ H_3C \end{matrix}\!\!>\!C{=}O$ (propanone)

10. Boiling points of alcohols increases with molecular weight. Alcohols with same molecular weight are expected to have almost same boiling point however, two more factor other than molecular weight are important, they are namely H-bonding and surface area. Both these factors are least in 3° alcohols and maximum in 1° alcohols.

Therefore, the correct order of boiling points of alcohols will be

$$\underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH} < \underset{\text{Butan-2-ol}}{CH_3CH_2CH(OH)CH_3} < \underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2OH} < \underset{\text{Pentan-1-ol}}{CH_3CH_2CH_2CH_2CH_2OH}$$

11. The order of reactivity depends upon the stability of the carbocation formed, i.e. $FCH_2\overset{+}{C}HCH_3$, $FCH_2CH_2\overset{+}{C}HCH_3$, $CH_3\overset{+}{C}HCH_3$ and $Ph\overset{+}{C}H_2$. The stability order of carbocations is

$Ph\overset{+}{C}H_2 > CH_3\overset{+}{C}HCH_3 > FCH_2CH_2\overset{+}{C}HCH_3 > FCH_2\overset{+}{C}HCH_3$. Thus, the order of reactivity follows the order IV > III > II > I.

12. Alcohols are more acidic than alkynes but less acidic than water thus, the correct order of acidity is

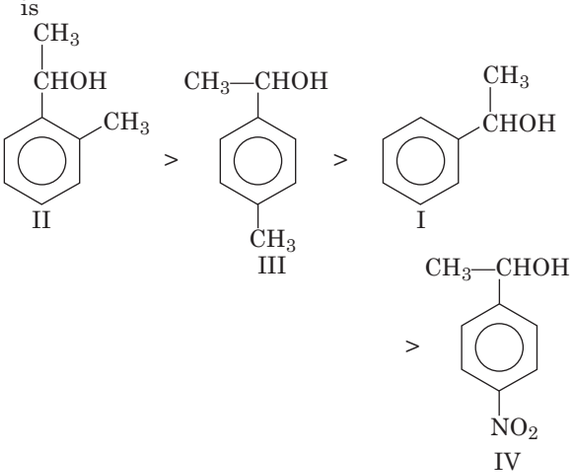
$$H_2O > 1° > 2° > 3° > RC{\equiv}CH$$

13. Lucas test is used to distinguish between primary, secondary and tertiary alcohols. A mixture of conc. HCl + anhy. $ZnCl_2$ is called Lucas reagent.

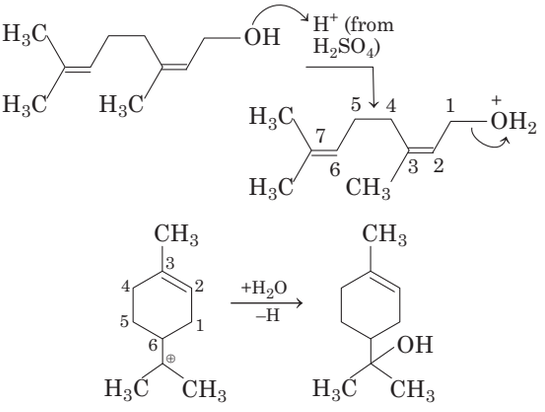
In Lucas test, tertiary alcohols immediately give turbidity while secondary alcohols give turbidity after 5 min. Primary alcohols give no reaction with Lucas reagent at room temperature.

Thus, order of reactivity of alcohols is 3°>2°>1.

14. In the given compounds, correct order of dehydration is

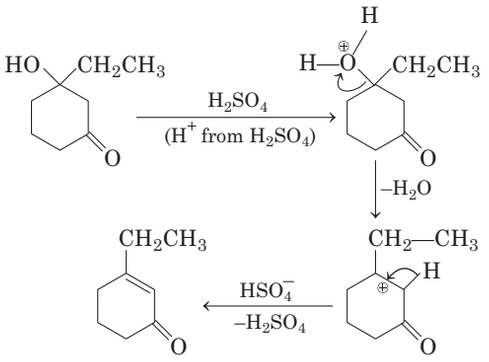


15. The reaction proceeds as follows

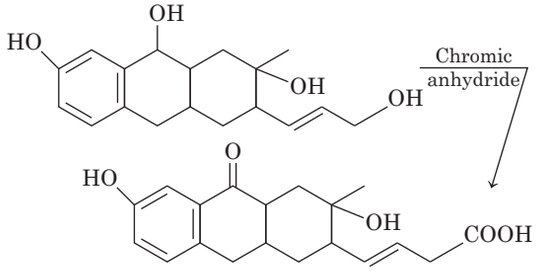


(Torpineol)

16.



17. Only 3° alcohol give positive ceric ammonium nitrate test.



Product '*P*'
(3° alcohol gives red colour with ceric ammonium nitrate)

18. $H_3C-\underset{\underset{CH_3}{|}}{\overset{CH_3}{|}}{C}-OH \xrightarrow[350°C]{Cu\ (Hot)} CH_3-\underset{CH_3}{\overset{|}{C}}=CH_2 + H_2O$

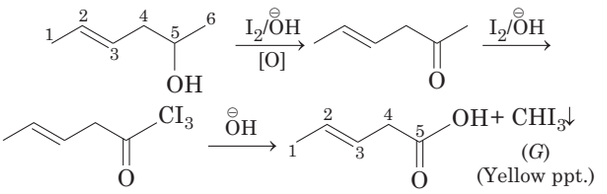
(*tert*-butyl alcohol) (2-methylpropene)

19. The most suitable reagent to carry out given transformation is I_2/NaOH.

$$\overset{6}{C}H_3-\overset{5}{C}H=\overset{4}{C}H-\overset{3}{C}H_2-\overset{2}{\underset{OH}{\underset{|}{C}}}H-\overset{1}{C}H_3 \xrightarrow[\text{(Oxidative cleavage)}]{\text{Strong oxidation, [O]}}$$

$$\overset{6}{C}H_3-\overset{5}{C}H=\overset{4}{C}H-\overset{3}{C}H_2-\overset{2}{\overset{O}{\overset{\|}{C}}}-OH + CHI_3\downarrow + CO_2\uparrow$$

Here, the haloform reaction will give following reaction:



(*G*)
(Yellow ppt.)

(i) Tollen's reagent ($AgNO_3$ + NH_4OH) is a mild oxidising agent. It does not react with $-\underset{OH}{\underset{|}{CH}}-CH_3$ group (2° alcohol).

(ii) Alkaline $KMnO_4$ cannot perform the oxidative cleavage, rather it will hydroxylate the C=C.

$$\overset{6}{C}H_3-\overset{5}{C}H=\overset{4}{C}H-\overset{3}{C}H_2-\overset{2}{\underset{OH}{\underset{|}{C}}}H-\overset{1}{C}H_3 \xrightarrow[OH^-]{KMnO_4} \overset{6}{C}H_3-\overset{5}{\underset{OH}{\underset{|}{C}}}H-\overset{4}{\underset{OH}{\underset{|}{C}}}H-\overset{3}{C}H_2-\overset{2}{\underset{OH}{\underset{|}{C}}}H-\overset{1}{C}H_3$$

(iv) CrO_2Cl_2/CS_2 will not react here.

20. Active MnO_2 is a mild oxidising agent and is used for oxidation of allylic alcohol to the corresponding aldehydes.

$$\underset{\text{Allyl alcohol}}{CH_2=CH-CH_2OH} \xrightarrow[MnO_2]{\text{Active}} \underset{\text{Acrolein}}{CH_2=CH-CHO}$$

21. Since, the compound '*B*' gave a 2,4-dinitrophenylhydrazine derivative but did not answer haloform test or silver mirror test, it must contain a $>C=O$ group, but it is neither a methyl ketone nor an aldehyde.

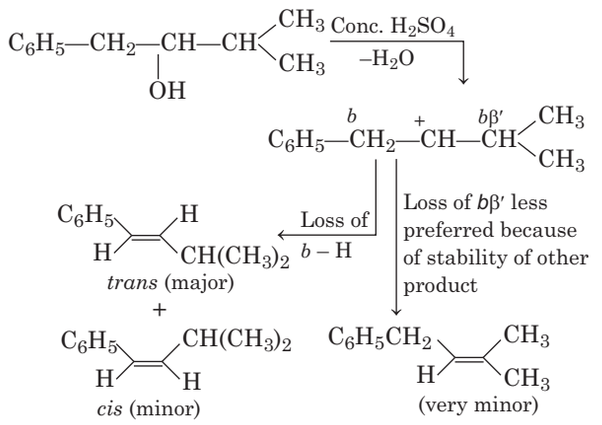
Moreover, compound '*B*' is obtained by the oxidation of compound *A*, having molecular formula $C_5H_{12}O$, so the compound *A* must be a secondary alcohol.

$$\underset{\substack{\text{2° alcohol}\\\text{(compound 'A')}}}{CH_3CH_2-\underset{OH}{\underset{|}{CH}}-CH_2CH_3} \xrightarrow[-H_2O]{[O]} \underset{\substack{\text{Ketone}\\\text{(compound '}B\text{')}}}{CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_2CH_3}$$

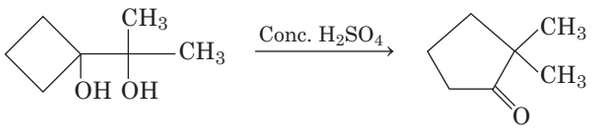
22. $C_2H_5OH + H_2SO_4 \xrightarrow{\text{Room temp.}} \underset{\text{Ethyl hydrogen sulphate}}{C_2H_5HSO_4}$

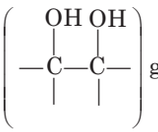
$$C_2H_5HSO_4 \xrightarrow[C_2H_5OH]{140°} \underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} \qquad C_2H_5HSO_4 \xrightarrow[-H_2SO_4]{170°} \underset{\text{Ethylene}}{CH_2=CH_2}$$

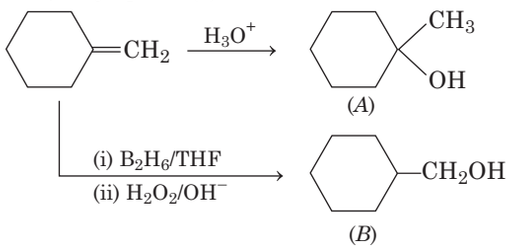
(a), (b), (d) may be formed but (c) is never formed.

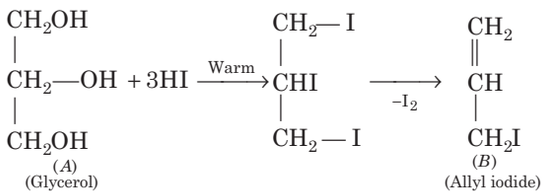
23. 

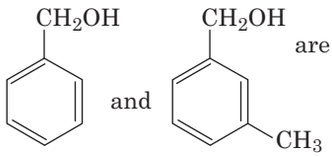
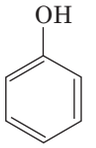
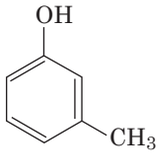
24. The pinacol-pinacolone rearrangement involves dehydration of diols through the formation of carbocation intermediate which rearranges to more stable compound.

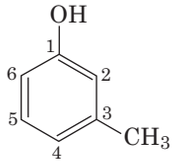


25. All those compounds which have  groups are oxidised by periodic acid (HIO_4).
Thus, only option (a) is not oxidised.

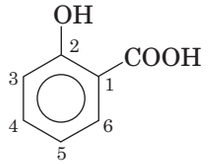
26. 

30. 

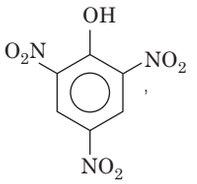
28.  and are aromatic alcohols due to presence of benzene ring and — OH group is attached with aliphatic carbon.  and  are phenols.

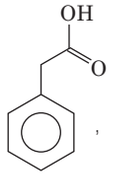
29. 

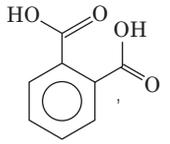
IUPAC name is 3-methylphenol.

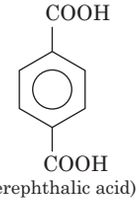
30. 

IUPAC name is 2-hydroxybenzoic acid.

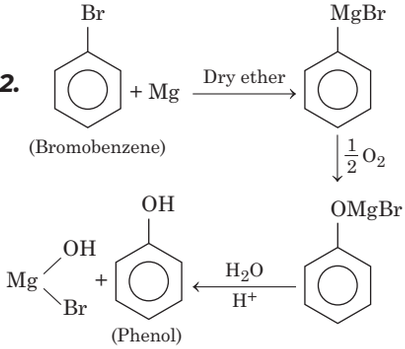
31. 







Only **picric acid** contains phenolic gorup.

32. 

33. Phenols are acidic in nature due to resonance stabilisation of phenoxide ion. Presence of electron withdrawing groups (such as —NO_2, —*X*, —NR_3^+, —CHO, —CO*X*,—COO*R*, —CN) in the ring stabilise phenoxide ion and increases the acidic nature of phenols. On the other hand, presence of electron releasing groups (such as —CH_3,—O*R*) in the ring

destabilises the phenoxide ion and decreases the acidic nature of phenols.

Furthermore *meta*-isomer is less acidic than *p*-and *o*-isomers because it is stabilised by inductive effect only.

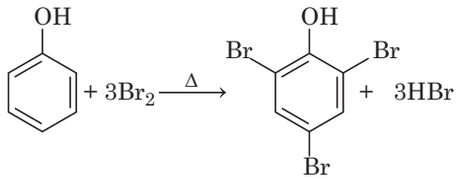
Thus, correct order of acidic strength is

$$II > IV > I > III > V$$

34. Br_2 is formed by a redox reaction

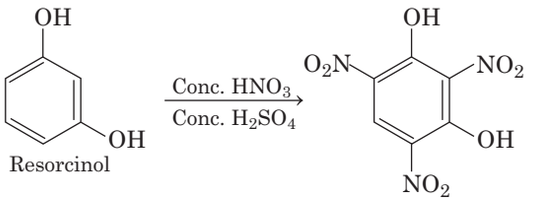
$$5Br^- + BrO_3^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$$

— 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.

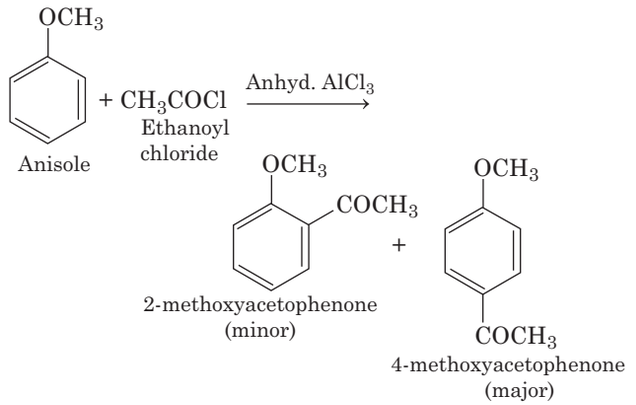


35. In the presence of non-polar aprotic solvents such as $CHCl_3$, CCl_4 etc., Br_2 reacts with phenol to give a mixture of *o*-and *p*-bromophenol.

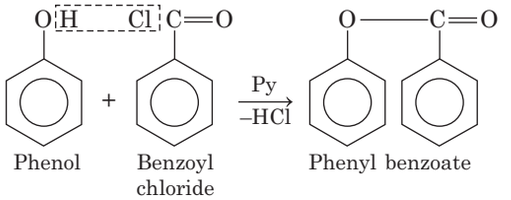
36.



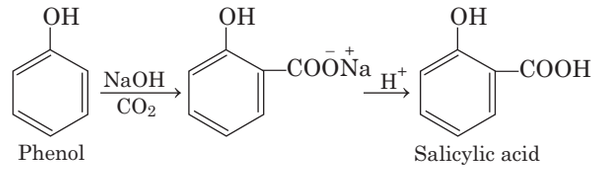
37. Friedel-Crafts' acetylation of anisole



38.



39.



40. $CHCl_3 + OH^{\ominus} \longrightarrow \underset{\text{(Unstable)}}{{}^{\ominus}CCl_3} + H_2O$

$${}^{\ominus}CCl_3 \longrightarrow \underset{\text{Dichlorocarbene}}{:CCl_2} + Cl^-$$

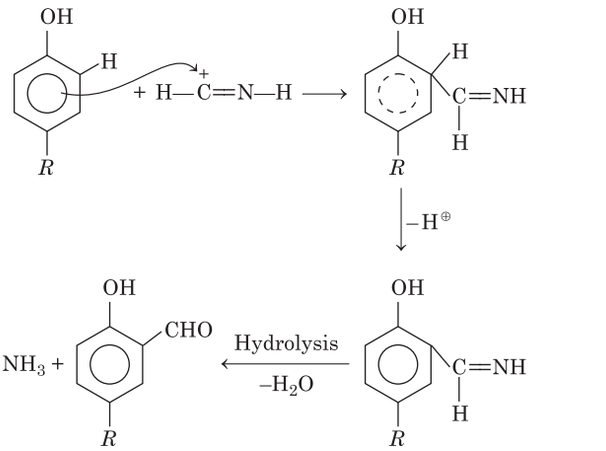
41. In Gattermann synthesis,

$$HCl \longrightarrow H^+ + Cl^{\ominus}$$

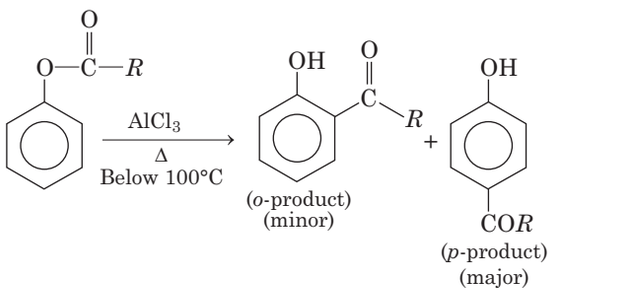
$$H-C\equiv N \overset{H^+}{\rightleftharpoons} H-\overset{+}{C}=N-H$$

(Formaldinium ion)

[Cl^- of HCl is trapped by $AlCl_3$ as $Cl^- + AlCl_3 \longrightarrow AlCl_4^-$]

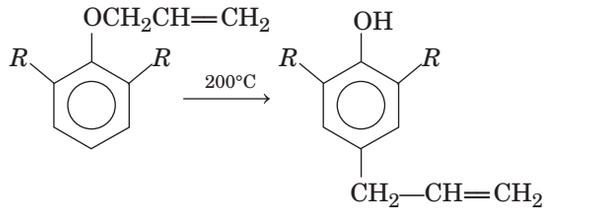


42.



Below 100°C *para* isomer is major product,while at high temperature *ortho* isomer is major product this is because intermediate of *ortho* isomer is stabilised by chelation.

43.



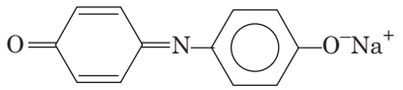
This is Claisen rearrangement.

44. Phenol gives Libermann's nitroso reaction.

Phenol in conc. $H_2SO_4 \xrightarrow[\text{excess of water}]{NaNO_2}$ Red colour

$\xrightarrow[\text{(Excess)}]{NaOH}$ Blue colour

This blue colour is formed due to the formation of



46. Bulkier the alkyl groups in the ether, greater is the C—O—C bond angle due to steric factor.

47. 1° alkyl halides on treatment with an alkoxide ion tend to undergo substitution to form ethers. So, sodium *tert* butoxide and ethyl bromide reagent is used.

48. $CH_3I + (CH_3)_2CHO^- \longrightarrow CH_3—\underset{\underset{CH_3}{|}}{CH}—O—CH_3$

Iso- propyl ether

49. $CH_3CH_2Br + CH_3ONa \longrightarrow CH_3CH_2OCH_3$ is an example of S_N2 reaction.

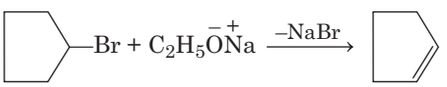
50. $CH_3CH_2—\underset{\underset{OH}{|}}{CH}—CH_3$ + CH_2N_2 $\longrightarrow$

2- butanol Diazomethane

$CH_3CH_2—\underset{\underset{CH_3}{|}}{CH}—OCH_3 + N_2\uparrow$

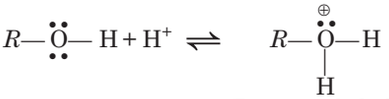
2-methoxybutane

51. 2° cyclic alkyl halides tend to undergo elimination. Thus, bromocyclopentane on treatment with sodium ethoxide (a strong base) gives cyclopentane rather than cyclophentyl ethyl ether.

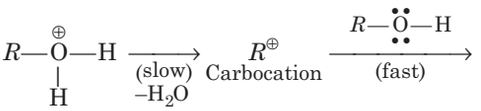


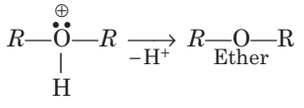
Cyclopentene

52. Alcohol is initially protonated by the acid to form protonated alcohol or oxonium ion. It is then attacked by a second molecule of alcohol which acts as nucleophile.



(Protonated alcohol)

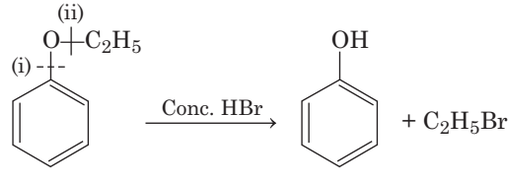




53. Ether is more volatile than an alcohol having the same molecular formula due to intermolecular hydrogen bonding in alcohols.

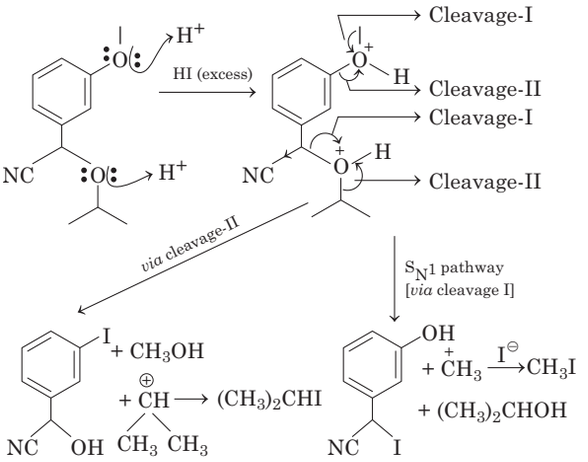
54. In the presence of air and light, ether form peroxides which cause explosion during distillation.

55.



Breaking of bond (i) is difficult as this bond has a partial double bond character due to resonance. Thus, bond (ii) break and form phenol and ethyl bromide.

56. The given reaction takes place as follows

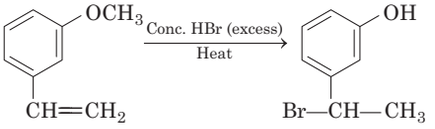


Product-1 Product-2

Product-2 is formed.

57. Ethers are least reactive functional groups. The cleavage of C—O bond in ethers take place under drastic conditions with excess of H*X*.

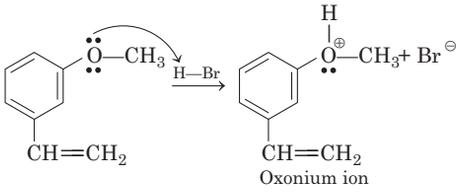
The major product obtained in the reaction is as follows



As conc. HBr is in excess. So, reaction will take place at both the substituents.

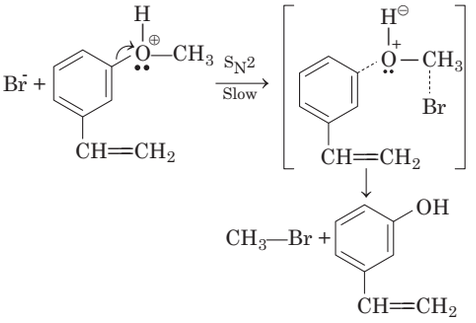
Mechanism

***Step* I** Protonation of ether to form oxonium ion.

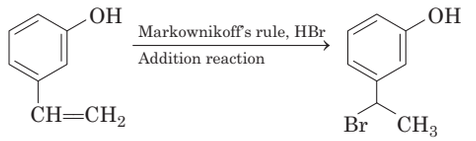


Oxonium ion

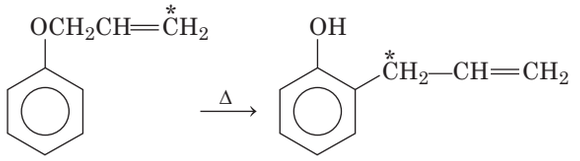
***Step* II** Attack of nucleophile at the protonated ether.



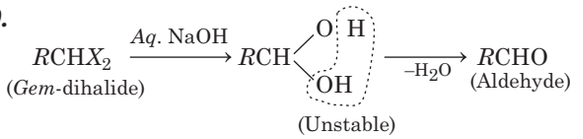
***Step* III** As HBr is in excess, so, reaction will also take place at alkene.



58.



59.



This reaction is hydrolysis of *gem*-dihalides.

60. (a) $CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{Aq,\ KOH/\Delta} CH_3-\overset{O}{\overset{\|}{C}}-O^-$

(b) $CH_3CH_2Cl \xrightarrow{Aq,\ KOH/\Delta} CH_3CH_2OH$

(c) $ClCH_2-CH_2Cl \xrightarrow{Aq,\ KOH/\Delta} HOCH_2-CH_2OH$

(d) $CH_3CHCl_2 \xrightarrow{Aq,\ KOH/\Delta} \underset{\text{Intermediate}}{CH_3-CH(OH)_2} \longrightarrow \underset{\text{Acetaldehyde}}{CH_3-CH=O}$

61. Unsymmetrical non-terminal alkynes gives a mixture of two ketones in which methyl ketone predominates.

$$H_3C-C\equiv C-CH_2CH_3 \xrightarrow[(ii)\ H_2O_2/\bar{O}H]{(i)\ BH_3\text{ in TMF}}$$

$$\underset{\substack{\text{(2-pentanone)}\\\text{(major)}}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_3} + \underset{\substack{\text{(3-pentanone)}\\\text{(minor)}}}{CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2CH_3}$$

62. $\underset{\text{Prop-1-yne}}{CH_3-C\equiv CH} + H_2O \xrightarrow[1\%\ HgSO_4]{40\%\ H_2SO_4} \underset{\substack{\text{Prop-1-en-2-ol}\\(A)}}{CH_3-\overset{OH}{\overset{|}{C}}=CH_2} \xleftrightarrow{\text{Tautomerism}} \underset{\text{Acetone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3}$

63. Alkaline $KMnO_4$ is a strong oxidising agent. It oxidises primary alcohols into aldehydes and secondary alcohols into ketones.

$$\underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[\text{Alk. } KMnO_4]{[O]} \underset{\text{Butanal}}{CH_3CH_2CH_2CHO}$$

$$\underset{\text{Butan-2-ol}}{CH_3CH_2-\overset{OH}{\overset{|}{C}}H-CH_3} \xrightarrow[\text{Alk. } KMnO_4]{[O]} \underset{\text{Butanone}}{CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_3}$$

64. Collin's reagent is used to convert $-CH_2OH \rightarrow -CHO$

Collin's reagent $\rightarrow CrO_3\cdot 2C_5H_5N$ in CH_2Cl_2.

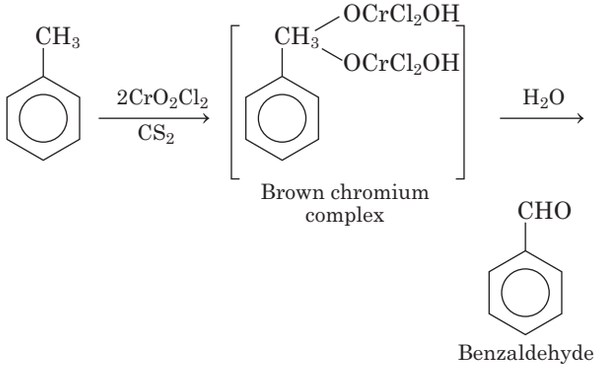
65. $CH_3-\overset{2^\circ}{\underset{OH}{CH}}-CH=CHCH_3 \longrightarrow CH_3-\underset{O}{\overset{\|}{C}}-CH=CHCH_3$

Only suitable reagent is chromic anhydride in glacial acetic acid. Other will also affect (C═C) bond.

66. In the Rosenmund's reaction, acid chlorides are converted to corresponding aldehydes by catalytic reduction. The reaction is carried out by passing through a hot solution of the acid chloride in the presence of Pd deposited over $BaSO_4$. Here, barium sulphate decrease the activity of palladium.

$$R\text{COCl} + H_2 \xrightarrow{Pd/BaSO_4} R\text{CHO} + HCl$$

67. Toluene can be oxidised to benzaldehyde with a solution of chromyl chloride (CrO_2Cl_2) in CS_2 or CCl_4. This is known as Etard's reaction.

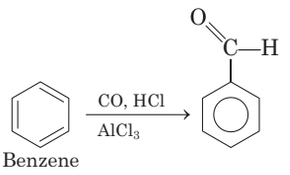


Brown chromium complex

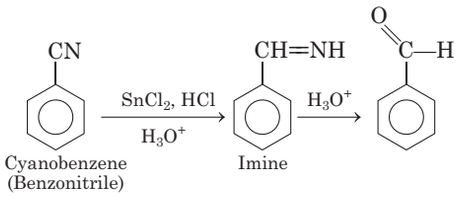
Benzaldehyde

Further oxidation of benzaldehyde to benzoic acid is avoided by protection of carbonyl group.

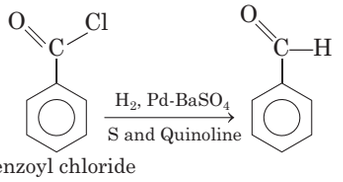
68. I.



II.



III.



Correct match of Column I and Column II will be

(I) - (R), (II) - (P) and (III) - (Q)

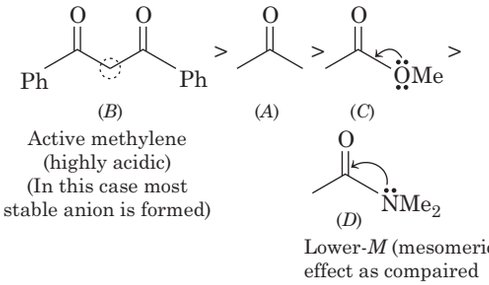
69. Boiling point is related to attractive forces. Stronger the attractive forces, higher is the boiling point. Hydrocarbons are non-polar having weakest attractive forces; Ethers are polar (dipolar forces); Aldehydes have stronger dipolar interactions;

Alcohols have maximum inter molecular forces due to hydrogen bonding.

Thus the order of boiling point is

$CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$.

70.



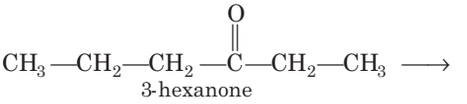
Compound (*B*) is a active methylene compound is highly resonance stabilised. This compound possessing a methylene bridge located between two strong electron withdrawing groups (such as carbonyl group). So, it is highly acidic in nature.

Compounds (*C*) and (*D*) having electron donating group. Which decreases the acidity and compound (*A*) is more acidic than (*C*) and (*D*) because it does not contain any electron releasing group.

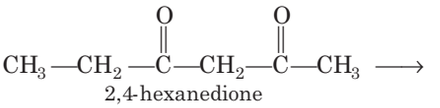
Hence, option (a) is correct.

(*D*) < (*C*) < (*A*) < (*B*)

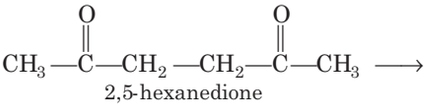
71. A compound that contains a —CH_2— or —CH— group flanked by two electron-withdrawing group such as $\rangle C{=}O$ group, becomes acidic compound and hydrogen atoms are called acidic hydrogen.



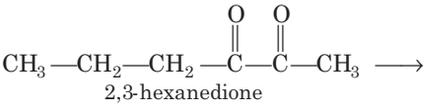
(contains no acidic hydrogen)



(contains 2 acidic hydrogen)



(contains no acidic hydrogen)



(contains no acidic hydrogen)

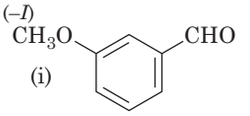
72. Addition of HCN to $\rangle C{=}O$ group of a carbonyl compound follows nucleophilic addition mechanism.

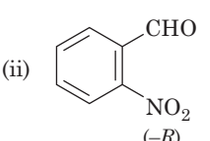
Rate of nucleophilic addition $\propto$ Polarity of the $\rangle C^{\delta+}{=}O^{\delta-}$ group $\propto$ Attachment of electron withdrawing group (EWG), i.e. $-R$ and $-I$ groups, where $-R > -I$

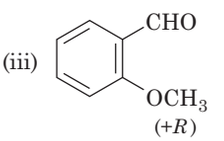
$$\propto \frac{1}{\text{Attachment of electron donating group (EDG), i.e. } +R \text{ and } +I \text{ groups}}$$

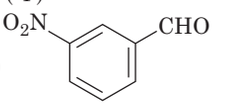
In substituted benzaldehyde, —NO_2 (EWG) shows $-R$ effect from *ortho*-and *para*-positions and $-I$ effect (only) from *meta*-positions. The group —OCH_3 (EDG) shows $+R$ effect from *ortho*-and *para*-position but $-I$ effect from *meta*-positions.

EWG ($-R > -I$) increases 'δ^+' character of sp^2 carbon of the $\rangle C{=}O$ group and hence attack of the nucleophile (CN^-) will be easier.









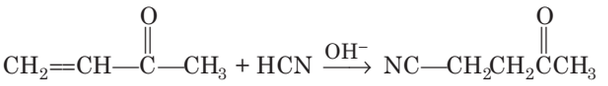
So, the increasing order of HCN addition is

(iii) < (i) < (iv) < (ii)

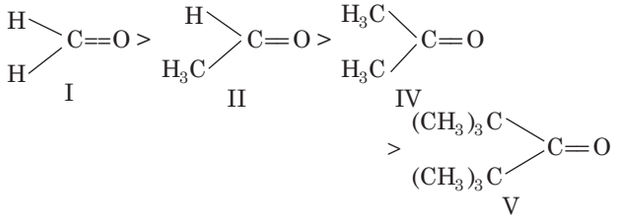
(+R) (−I) (−I) (−R)

$-I$ effect : $NO_2 > OCH_3$

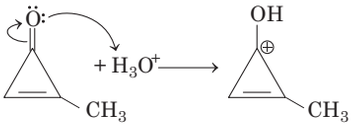
73. When addition of HCN takes place at α, β-unsaturated carbonyl compounds, it gives β-cyano compounds.



74. As the number and the size of the alkyl groups increases, reactivity decreases. Hence, the reactivity order is



75. Option (c) is the major product formed.



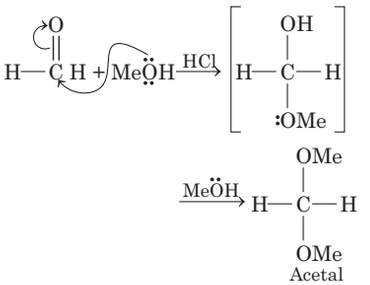
Aromatic product

76. Acetal formation is nucleophilic addition reaction due to the addition of alcohols on aldehydes.

The reactivity of nucleophilic addition depends on following two factors.

- **Inductive effect** Greater the number of alkyl group attached to carbonyl group, greater is the electron density on carbonyl carbon. Thus, lowers the attack of nucleophile. Hence, reactivity decreases.
- **Steric effect** As the number of alkyl group attached to carbonyl carbon increases, the attack of nucleophile on carbonyl group becomes more difficult due to steric hinderance.

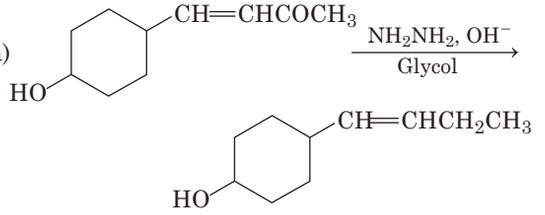
Thus, the best combination is HCHO and MeOH. The reaction is as follows



Acetal

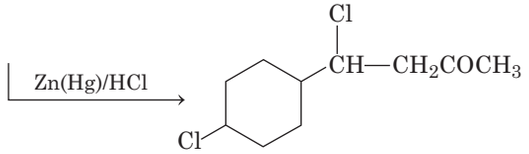
77. Acetone (ketone) and benzaldehyde (aromatic aldehyde) both do not react with Fehling solution. With aliphatic aldehydes, Fehling solution give red precipitate of cuprous oxide.

78. (a)



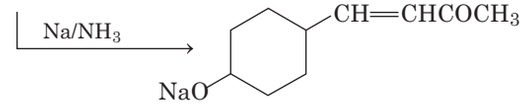
(Wolff-Kishner)

(b)



HCl attacks 2° alcohol as well as (C=C) bond.

(c)



(d) $\xrightarrow{NaBH_4}$ low yield

79. A + NaOH ⟶ alcohol + acid

Thus, it is Cannizzaro reaction.

A is thus aldehyde without H at α-carbon.

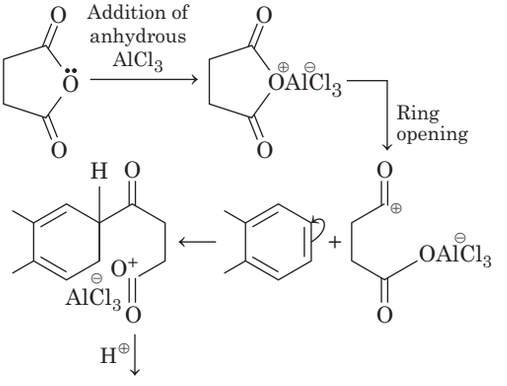
(as C_6H_5CHO, HCHO)

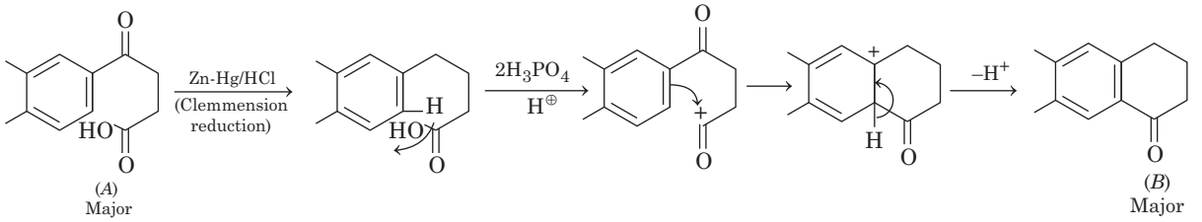
$2C_6H_5CHO + Aq.\,NaOH \longrightarrow C_6H_5CH_2OH + C_6H_5CO\overset{-}{O}\overset{+}{N}a$

80. In Cannizzaro reaction when formaldehyde reacts with other aldehydes lacking α-hydrogen, it is always oxidised and other aldehyde is reduced.

$$HCHO + C_6H_5CHO \xrightarrow[\Delta]{Aq.\ NaOH} HCOO^-Na^+ + C_6H_5CH_2OH$$

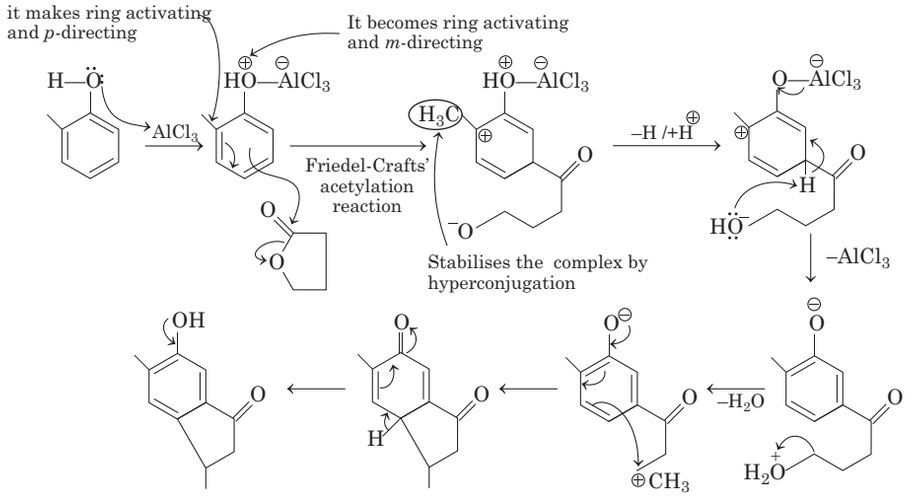
81.





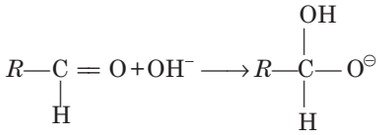
82. It is an aromatic electrophilic substitution reaction ($Ar S_E2$).

The reaction follows ArS_E2 (Aromatic electrophlic substitution pathway) as shown below

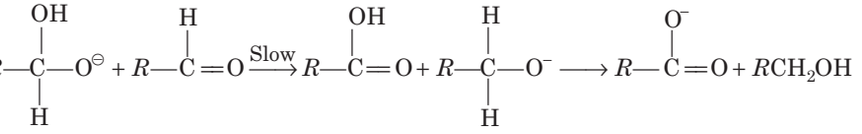


83. Cannizzaro reaction involves oxidation as well as reduction of aldehydes having lack of α-H atom. The mechanism of this reaction is as

(i) Attack of OH^- on carbonyl carbon

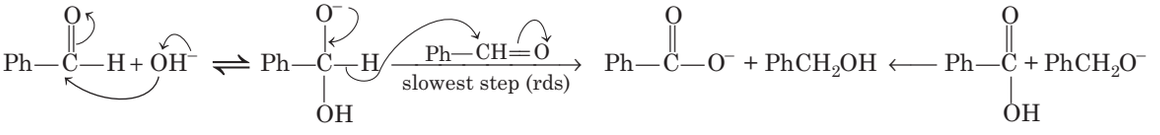


(ii) Transfer of hydride ion

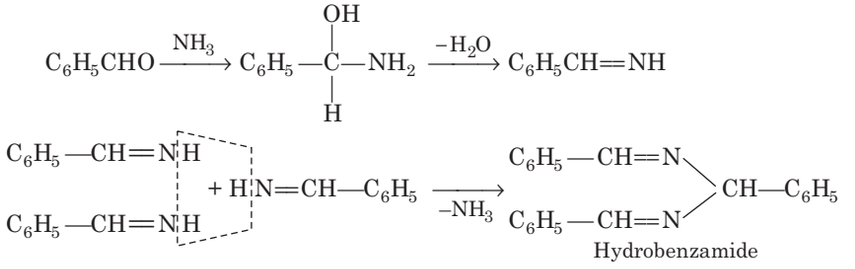


84. The effect of electron-withdrawing substituent in the benzene ring fastens the Cannizzaro reaction.

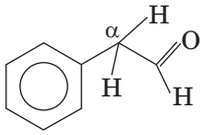
85. In Cannizzaro reaction, the transfer of H^- to another carbonyl group is difficult and the slowest step.



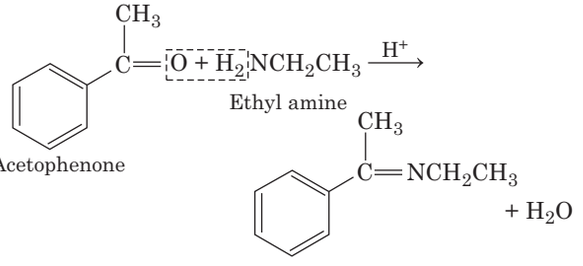
86. Benzaldehyde does not yield a simple addition product with ammonia, but forms a complex product, hydrobenzamide (90%).



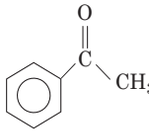
87. Benzoin condensation is a self condensation reaction of aromatic aldehyde (with no α-H) in presence of CN^- ion as a catalyst to α-hydroxy ketone. In this question, only phenyl ethanal have 2α-H so, phenyl ethanal does not undergo benzoin condensation.



88.

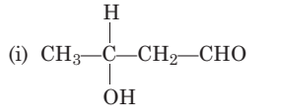


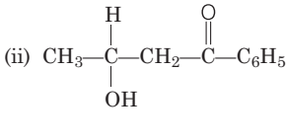
89. In aldol condensation, generally aldehydes react at a faster rate than ketones towards base. In the given case, CH_3CHO will lose

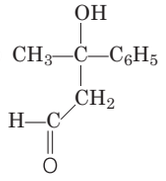
α-hydrogen faster than  due

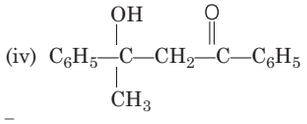
to one more reason, i.e. conjugation between benzene ring and $\rangle C=O$ group. Along with sterically less hindered nucleophile of CH_3CHO will also add to the major product formation.

Following four products are possible in the reaction:


(i) (Self aldol condensation of CH_3CHO)

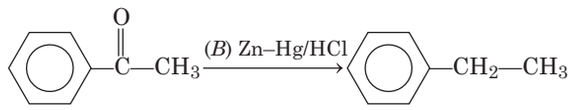

(ii) (Cross aldol condensation of CH_3CHO and $CH_3COC_6H_5$ in which $\rangle C=O$ group of CH_3CHO is carbanion acceptor).

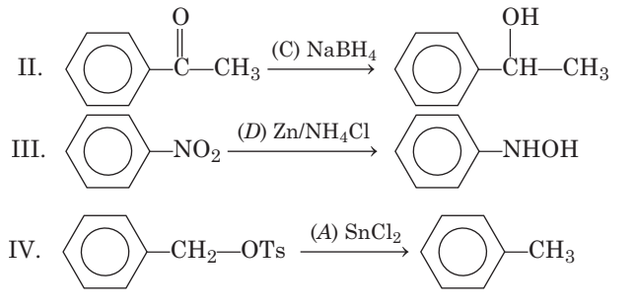

(iii) (Cross aldol condensation of CH_3CHO and $CH_3COC_6H_5$ in which $\rangle C=O$ group of $C_6H_5COCH_3$ is carbanion acceptor).


(iv) (Self Aldol condensation product of $C_6H_5COCH_3$)

$\bar{O}H$ of base will prefer to attack on $—CH_3$ group of CH_3CHO for the formation of carbanion and as among the $\rangle C=O$ groups available, the $\rangle C=O$ group of CH_3CHO is the best carbanion acceptor. Hence, self condensation product of CH_3CHO will be the major product.

90. I.

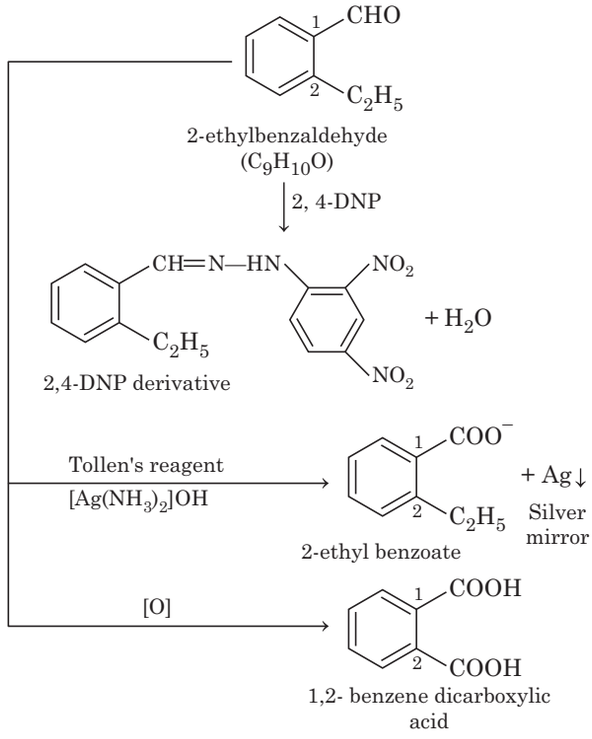




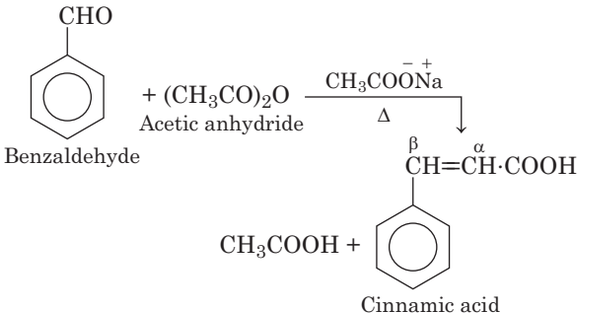
91. (I) and (II)The compound with molecular formula $C_9H_{10}O$ forms a 2,4-DNP derivative and reduces Tollen's reagent, so it is an aldehyde.

(III) It undergoes Cannizzaro reaction, so the aldehyde group should be directly attached to the benzene ring.

(IV) On vigorous oxidation, it gives 1,2-benzene dicarboxylic acid, so it should be an *ortho* substituted benzaldehyde. For molecular formula $C_9H_{10}O$, the possibility is only *o*-ethyl benzaldehyde.



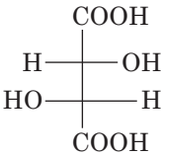
92. Perkin reaction is the condensation reaction in which aromatic aldehyde is heated with an anhydride of an aliphatic acid in the presence of sodium salt of the same acid to form α, β-unsaturated acid.



93. Cinnamaldehyde is prepared by the Claisen reaction between benzaldehyde and acetaldehyde.

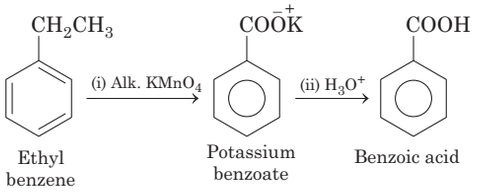
$$C_6H_5CHO + CH_3CHO \xrightarrow{NaOH} \underset{\text{Cinnamaldehyde}}{C_6H_5CH{=}CHCHO} + H_2O$$

94. Tamarind contains (+) tartaric acid.

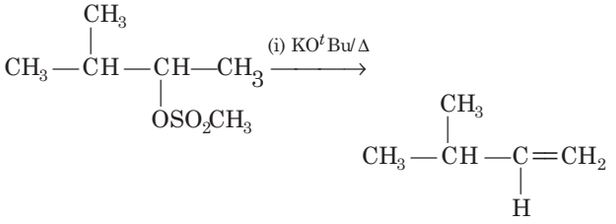


[(+) tartaric acid]

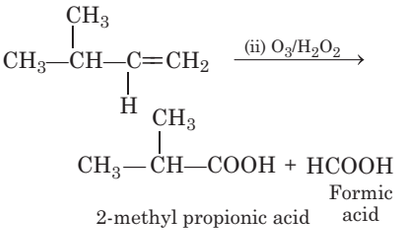
95. The major product of the given reaction is benzoic acid (C_6H_5COOH). On vigorous oxidation of alkyl benzene with acidic or alkaline $KMnO_4$, aromatic acids are obtained. During oxidation of alkyl benzene, the aromatic nucleus remains intact and the entire chain is oxidised to —COOH group irrespective of the length of carbon chain.



97. Tertiary butoxide is a bulky base, which favour elimination to form less substituted alkenes (Hofmann-product).



Now, alkene in presence of O_3/H_2O_2 undergoes oxidative ozonloysis to produce 2-methyl propionic acid and formic acid.



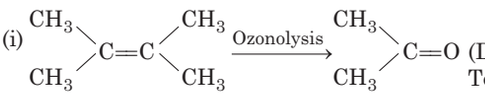
98. $\underset{\text{Unsaturated hydrocarbon}}{(X)} \xrightarrow{\text{Ozonolysis}} (A) \xrightarrow[\text{(Tollen's reagent)}]{\text{Ammonical } AgNO_3} \underset{\text{Silver mirror}}{Ag\downarrow}$

As (*A*) compound given positive tollen's test hence it may consist —CHO (aldehyde group) or it can be HCOOH.

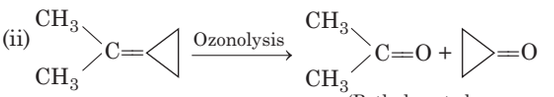
So. for the given option

(iii) $CH_3—CH_2—C{\equiv}CH \xrightarrow{\text{Ozonolysis}} CH_3CH_3COOH + \underset{\substack{(A)\\ \text{+ve Tollen's test}}}{HCOOH}$

and for other compounds (options)

(i) 

(Does not show Tollen's test)

(ii) 

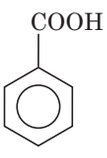
(Both do not show Tollen's test)

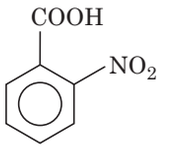
(iii) $CH_3—C{\equiv}C—CH_3 \xrightarrow{\text{Ozonolysis}} \underset{\substack{\text{(Does not show}\\ \text{Tollen's test)}}}{2CH_2—COOH}$

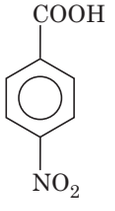
99. Presence of electron withdrawing group (EWG) makes an acid more acidic. As the distance between EWG and —COOH increases, acidity decreases.

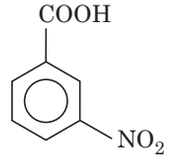
Electron donating group (— OCH_3) decreases the acidic strength. Therefore, increasing order of acidic strength is

4-methoxy benzoic acid <benzoic acid <4-nitrobenzoic acid <3,4-dinitrobenzoic acid.

100. I. 

II. 

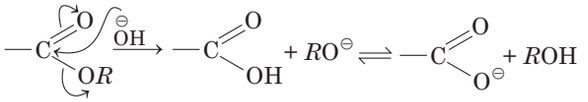
III. 

IV. 

—NO_2 group at any position shows electron withdrawing effect, thus acid strength is increased. But *o* -nitro benzoate ion is stabilised by intramolecular H-bonding like forces, hence its acid strength is maximum. Thus, the order of acid strength is II > III > IV > I.

The effect is more at *para* position than *meta*.

101. Alkaline hydrolysis of an ester (carboxylic acid derivative) follows acyl S_N2 mechanism.

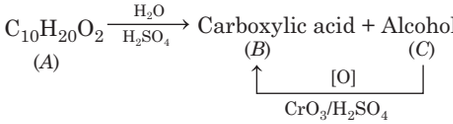


Rate of S_N2 mechanism depends on the polarity of group of —COO*R* group. Electron withdrawing group (– *R* > – *I*) increases the rate of S_N2 reaction whereas electron donating group (+ *R* > + *I*) decreases the rate of S_N2 reaction.

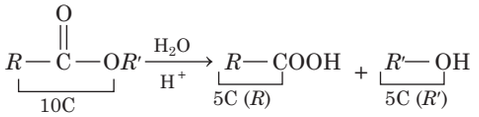
Here, the nature of functional groups attached *para* to the benzene ring are: $\underset{(-R)}{-NO_2} > \underset{(-I)}{-Cl} > \underset{(+R)}{-OCH_3}$

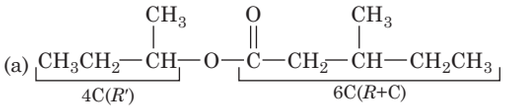
So, the order of hydrolysis will be, $\underset{(-R)}{III} > \underset{(-I)}{II} > I > \underset{(+R)}{IV}$

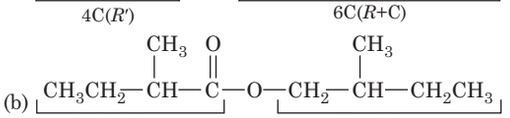
102. A can be written as : $[(CH_3)_3C—COOCH_2C(CH_3)_3]$

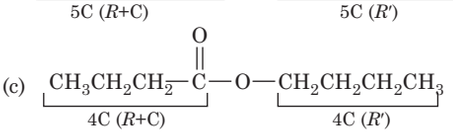


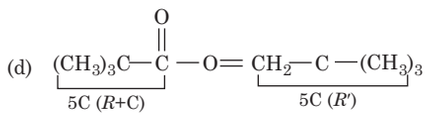
From the informations given, it is clear that *A* is an ester which contain 10 carbon atoms. Again, *C* on oxidation gives *B*. It indicates *B* and *C* contains equal number of carbon atom, i.e. each of *B* and *C* contains 5 carbon atom.



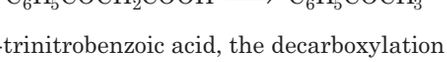








103. β-keto acids are the carboxylic acids that undergo decarboxylation easily.



104. 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

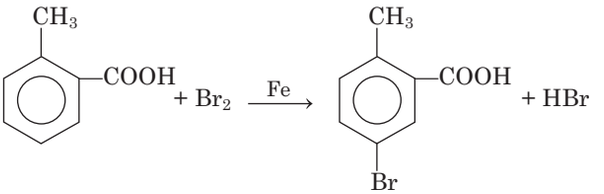
104. As —CH_3 group has a strong +*I*-effect and —OCH_3 group has a weak –*I*-effect but strong +*R*-effect, hence they increase the electron density on oxygen atom and O—H bond becomes stronger. On the other hand, —NO_2 group has a strong –*I* and –*R*-effect. It withdraws electrons from benzene ring as well as oxygen atom of —OH group and proton is easily removed. Thus, order of esterification is I > II > III > IV.

106. The reduction of carboxylic acids to alcohols is carried out by $LiAlH_4$ and boranes (BH_3 or B_2H_6) in THF.

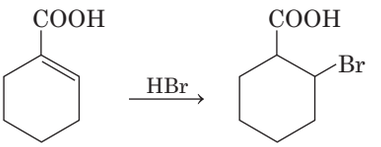
107. $LiAlH_4$ reduces —COOH to —CH_2OH without affecting C═C bond.

108. Formic acid has $-\overset{\overset{O}{\|}}{C}-H$ (aldehyde) group. It reduces Tollen's reagent to silver mirror like other aldehydes.

109. —COOH is *meta*-directing group.

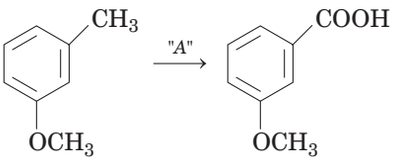


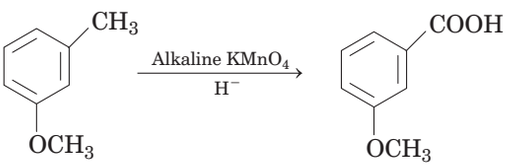
110. α, β-unsaturated acids add on halogen acids. The mode of addition is contrary to Markownikoff's rule and may be described to the inductive effect of the carboxyl group.



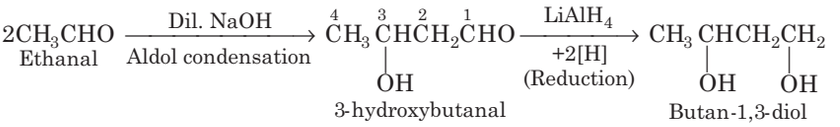
Round II

1.

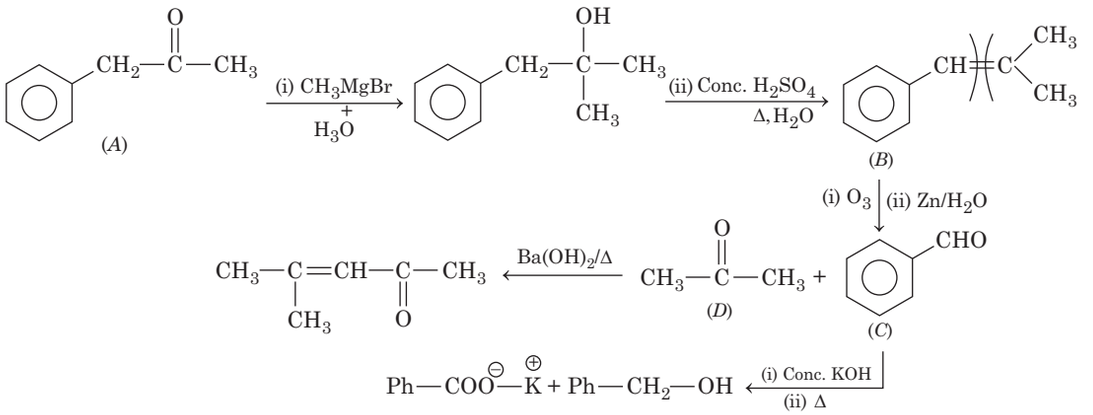




2. Ethanal to butane-1,3-diol



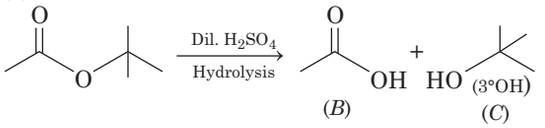
3. Complete the reaction is as follows



4. $ZnCl_2 + HCl \longrightarrow$ Lucas reagent

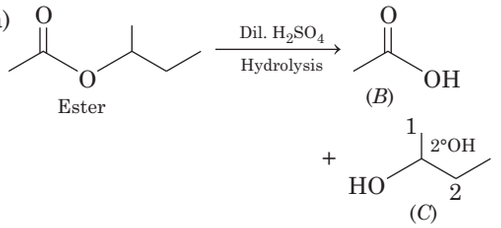
(*C*) give precipitate with Lucas reagent (immediately ppt.). It mean *C* will be 3° alcohol so, according to the given hints, option (b) fits the category.

(b)



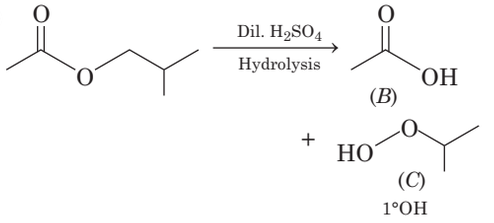
In 3°OH, it gives immediate ppt. then this is correct option. Explanation of other options are as follows

(a)



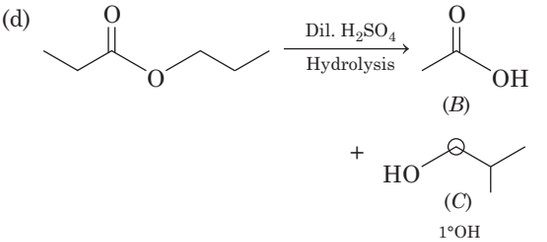
C is 2° alcohol, we want 3° alcohol therefore, this is a incorrect option.

(c)



C is 1°OH, it does not give ppt. immediately therefore, this is also a incorrect option.

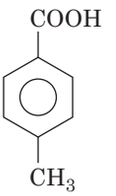
(d)



C is 1°OH that does not give test immdiately.

According to the question, compound (*A*) gives carboxylic acid and alcohol on hydrolysis. So, *A* must be an ester.

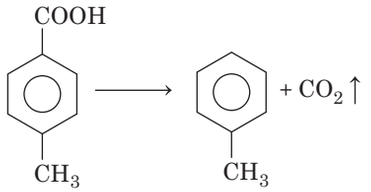
5. The compound [*P*] is option (b)



The compound [*P*] is 4-methyl benzoic acid.

Here, —CH_3 group is *o*-and *p*-directing but *p*-position is already acquired by — COOH group. So, only one single product is formed.

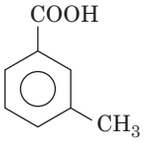
On treatment of option (b) with sodalime, CO_2 gas is released COOH.



Toluene

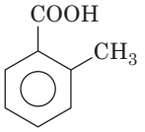
Other given options does not satisfy the condition.

Option (a)



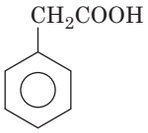
On promination 2 possible isomers will form.

Option (c)



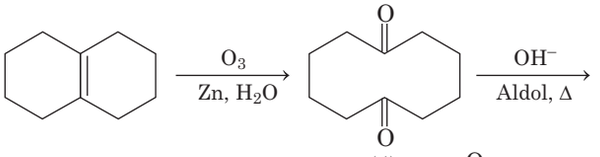
In respect of COOH, bromination occurs at *ortho* but in *ortho* is blocked by CH_3 and in respect of CH_3 bromination not possible.

Option (d)

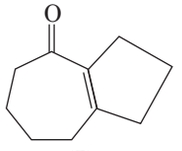


In respect of CH_2COOH bromination is done at *ortho* and *para*, then single isomer not possible.

6.



(*A*)



(*B*)

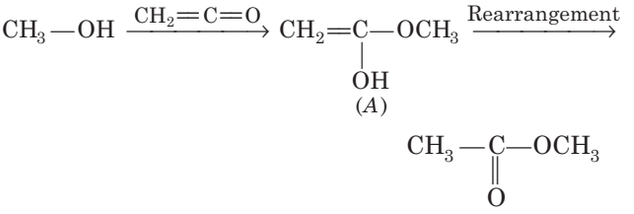
7. $CH_3CH_2OH \xrightarrow{P + I_2} \underset{'A'}{CH_3CH_2-I} \xrightarrow{Mg,\ ether}$

$\underset{'B'}{CH_3CH_2MgI} \xrightarrow{H-\overset{O}{\overset{\|}{C}}-H} CH_3\underset{'C'}{CH_2(OMgI)CH_2}$

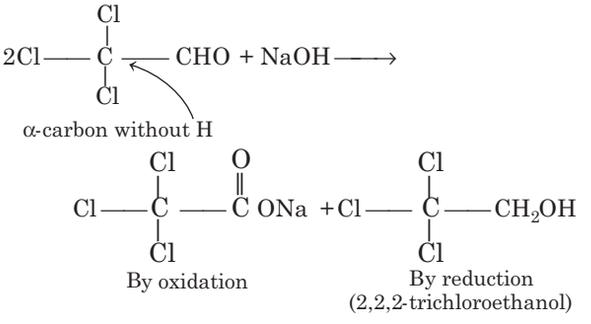
$\xrightarrow{H_2O} \underset{'D'}{CH_3CH_2(OH)CH_2} + Mg(OH)I$

n-propyl alcohol

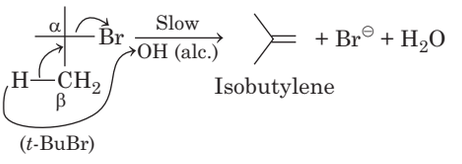
8.

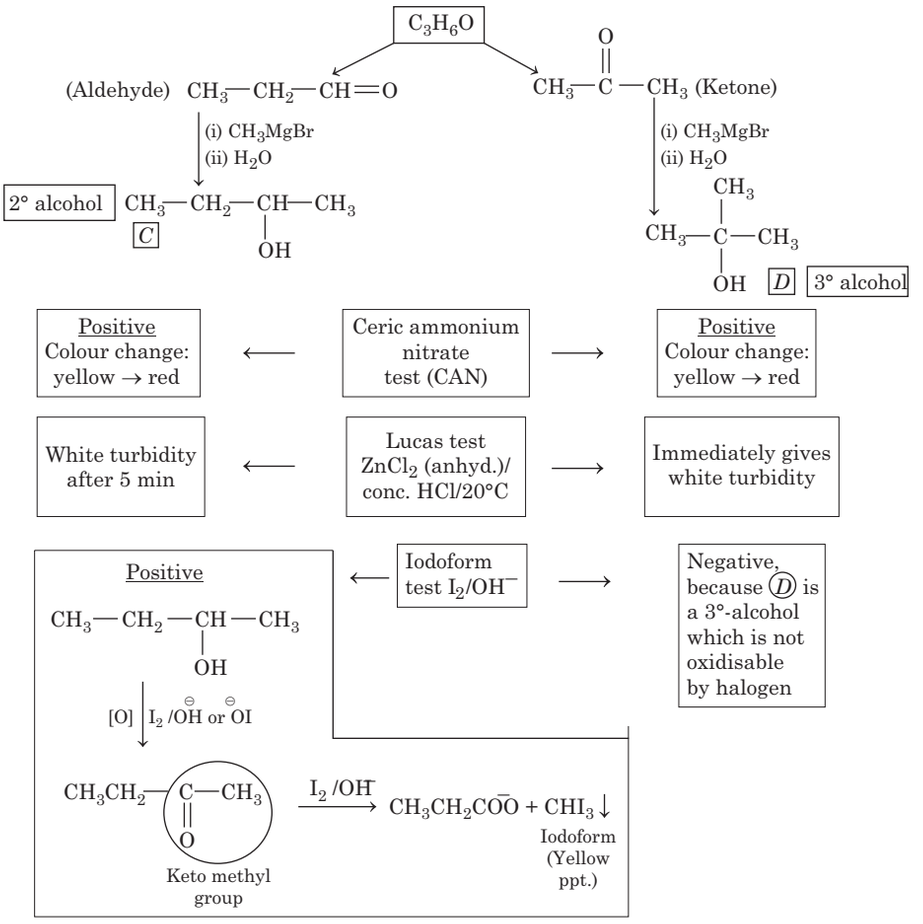


9. Cannizzaro's reaction is given by aldehydes (*R*CHO) lacking H at α-carbon or lacking α-carbon (as in HCHO). With NaOH, there is formation of acid salt ($RCOO^-$) by oxidation and alcohol (RCH_2OH) by reduction.

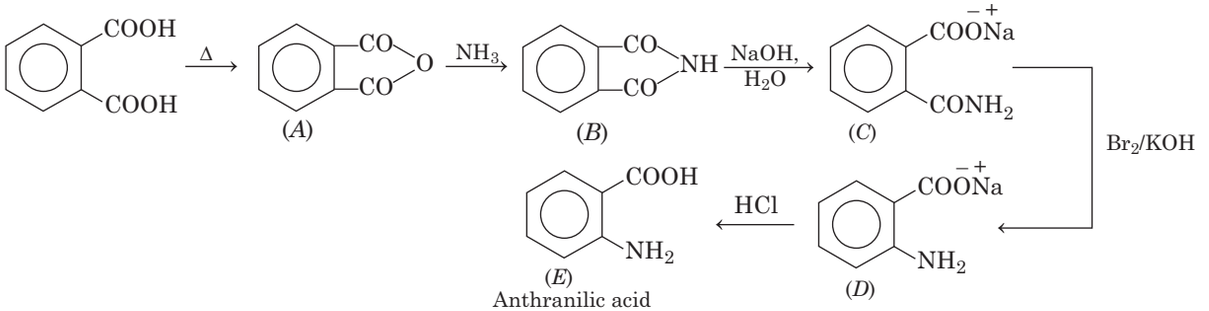


10.

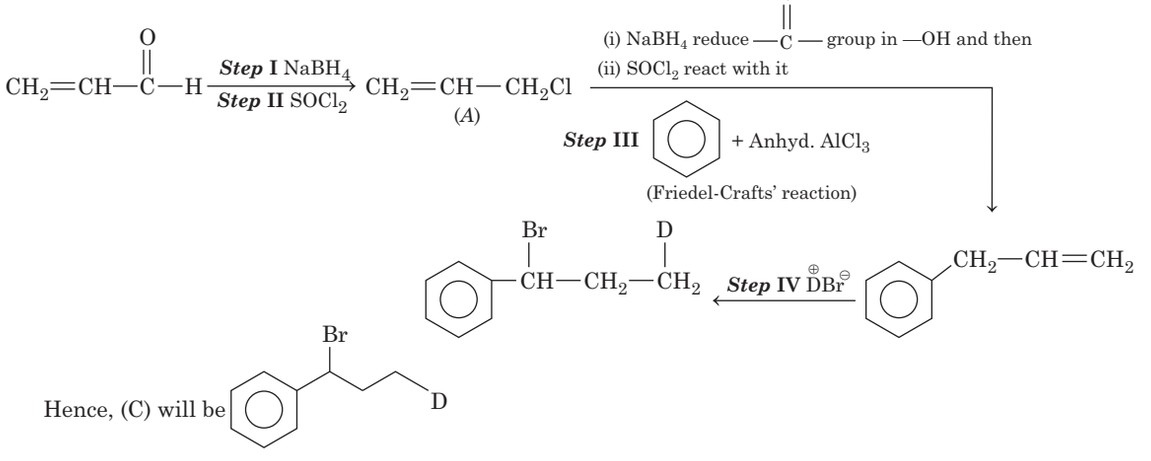



C3H6O
(Aldehyde) CH3—CH2—CH=O
CH3—C(=O)—CH3 (Ketone)
(i) CH3MgBr
(ii) H2O
2° alcohol
C
(i) CH3MgBr
(ii) H2O
D
3° alcohol
Positive
Colour change: yellow → red
Ceric ammonium nitrate test (CAN)
Positive
Colour change: yellow → red
White turbidity after 5 min
Lucas test ZnCl2 (anhyd.)/ conc. HCl/20°C
Immediately gives white turbidity
Positive
Iodoform test I2/OH−
Negative, because (D) is a 3°-alcohol which is not oxidisable by halogen
[O] I2 /OH or OI
Keto methyl group
I2 /OH
Iodoform (Yellow ppt.)

11.


COOH
COOH
Δ
(A)
NH3
(B)
NaOH, H2O
(C)
Br2/KOH
HCl
(D)
(E)
Anthranilic acid

12.


CH2=CH—C(=O)—H
Step I NaBH4
Step II SOCl2
CH2=CH—CH2Cl
(A)
(i) NaBH4 reduce —C(=O)— group in —OH and then
(ii) SOCl2 react with it
Step III
+ Anhyd. AlCl3
(Friedel-Crafts' reaction)
Step IV DBr
Hence, (C) will be

In the above reaction,

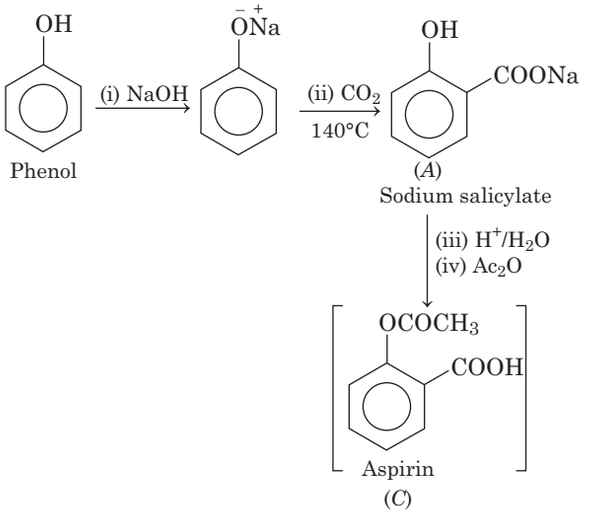
***Step* I** $NaBH_4$ reduce $-\overset{\overset{O}{\|}}{C}-H$ group into alcohol.

***Step* II** $SOCl_2$ react with this alcohol and form $R - X$.

***Step* III** This $R - X$ react with benzene in the presence of anhydrous $AlCl_3$ *via* Friedel-Crafts' reaction and form product.

***Step* IV** DBr react with this product and form rearranged product.

13.

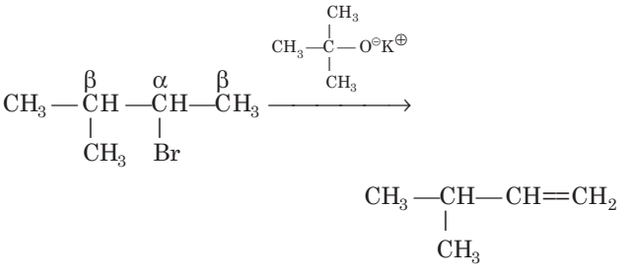


14. In a β-elimination reaction, a leaving group (like Cl^-) leaves along with a hydrogen (as H^+) from a β-position. Among available β-positions, H^+ removal is preferred to take place from the β-position having least H atoms according to Saytzeff's rule.

But in reaction (c), the major product is not Saytzeff 's product

because the given base, $CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-O^-$ is bulky and due to steric hinderance removes H^+ from—CH_3 group.

In this case reaction occurs as :

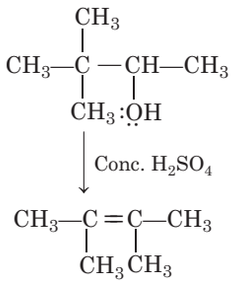


$$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH=CH_2$$

The major product is called Hofmann product.

The rest of the given reactions produce Saytzeff products as follows

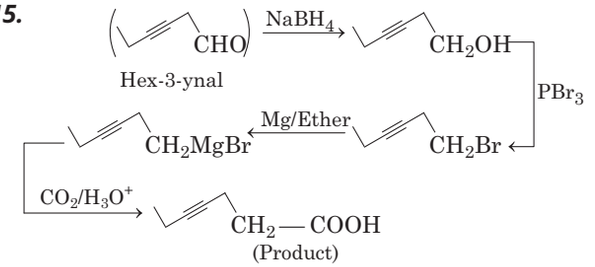
(a)



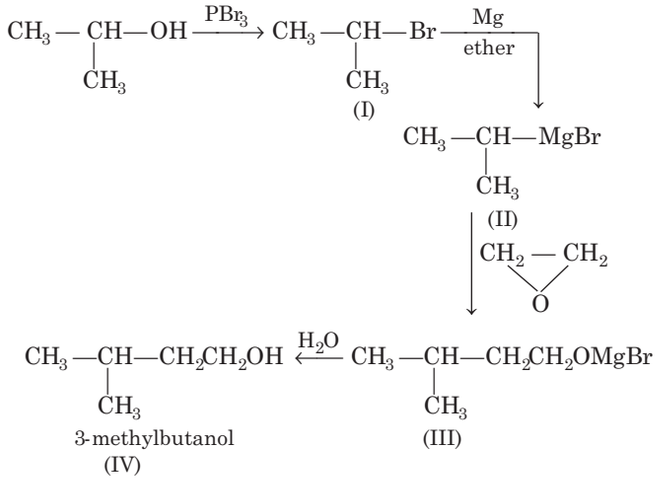
(b) $CH_3-\overset{\beta}{C}H-\overset{\alpha}{C}H-\overset{\beta}{C}H_3 \xrightarrow{\text{Alc. KOH}} CH_3-C(CH_3)=CH-CH_3$

(d) $\overset{\beta}{C}H_3-\overset{\alpha}{C}(OH)(\overset{\beta}{C}H_3)-CH_2-CHO \xrightarrow{\Delta} CH_3-C(CH_3)=C(H)-CHO$

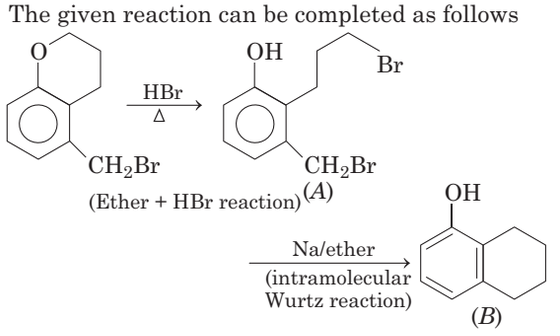
15.



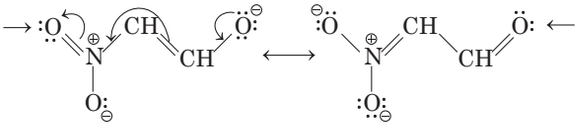
16.



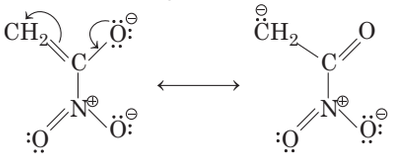
17. The given reaction can be completed as follows



18. (*C*) is most stable due to strong $-I$-effect as well as $-R$ (or $-M$) effect of '$—NO_2$' group. The negative charge is delocalised as represented by the following resonance structure



In (*A*), there is no resonance delocalisation of negative charge, and hence it is least stable. In (*B*), negative charge is delocalised by resonance as shown :

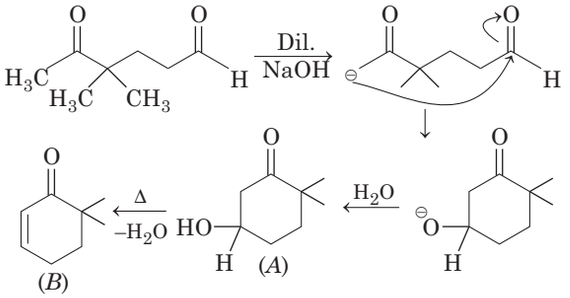


But the contribution of structure on RHS is relatively less, so stability of (*B*) is more than (*A*) but less than (*C*).

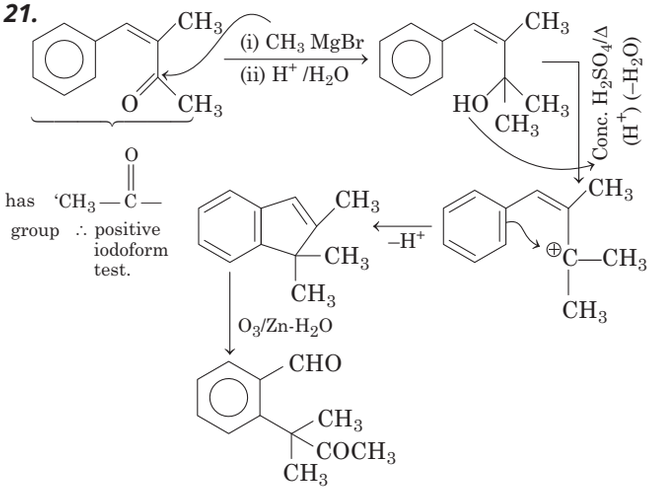
19. $\underset{\text{Formic acid}}{2HCOOH} + \underset{\substack{\text{Sodium}\\\text{carbonate}}}{Na_2CO_3} \longrightarrow 2HCO\overset{-}{O}\overset{+}{Na} + CO_2\uparrow + H_2O$

$HCOOH + \underset{\substack{\text{Tollen's}\\\text{reagent}}}{Ag_2O} \longrightarrow H_2O + CO_2\uparrow + \underset{\substack{\text{Black ppt.}\\\text{(silver mirror)}}}{2Ag}$

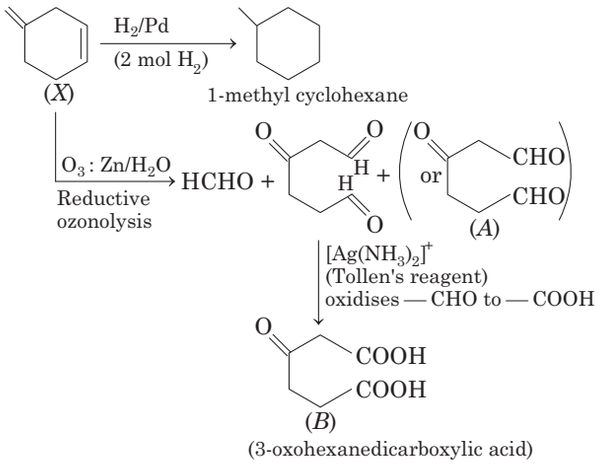
20. The reactant in presence of Dil. NaOH undergoes intramolecular aldol condensation reaction. As a result of this, β-hydroxyketone (*A*) is obtained which on hydrolysis followed by heating produces α, β-unsaturated ketone (*B*)



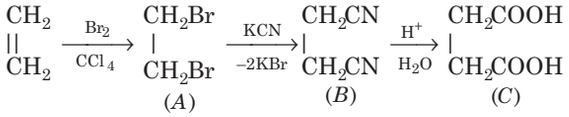
21.



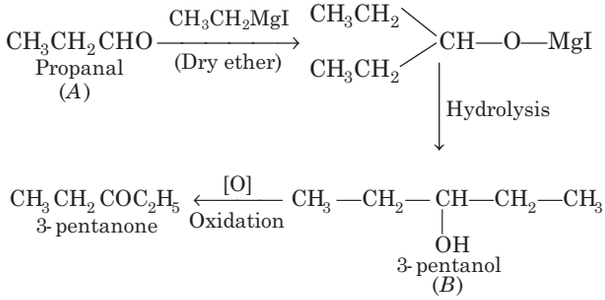
22.



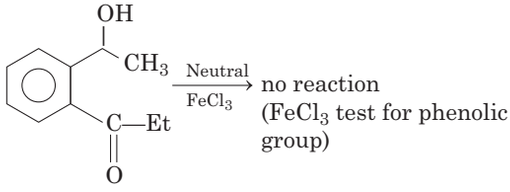
23.



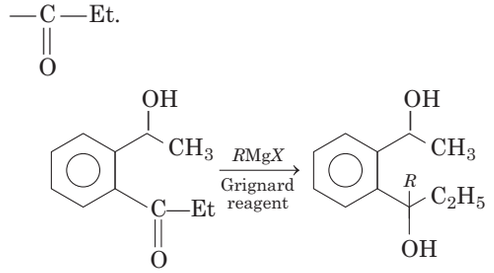
24.



25. According to the given conditions, compound (d) neither reacts with neutral ferric chloride solution nor with Fehling solution. It however reacts with Grignard reagent and gives positive iodoform test. As the compound does not contain any phenolic —OH group. Hence, it gives negative neutral $FeCl_3$ test.

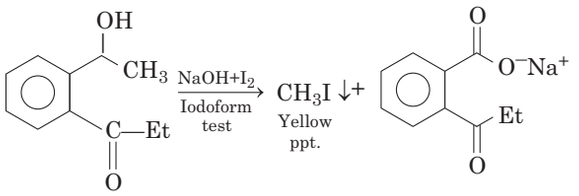


Compound gives reaction with *R*Mg*X* as it contains

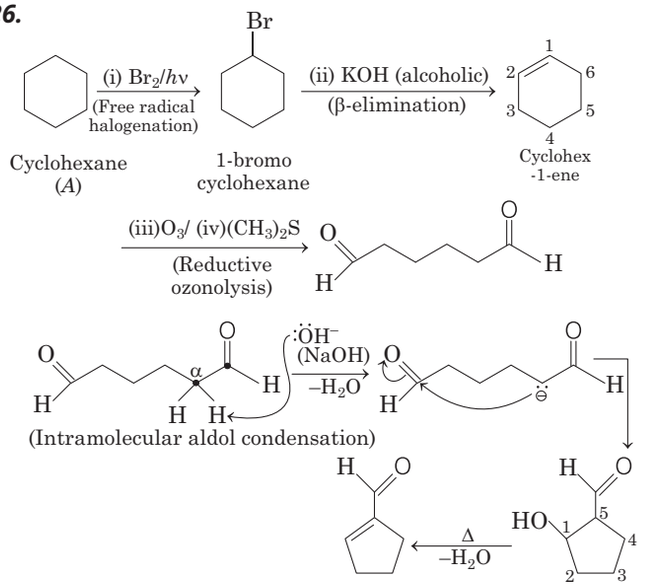


Compound with group undergoes iodoform

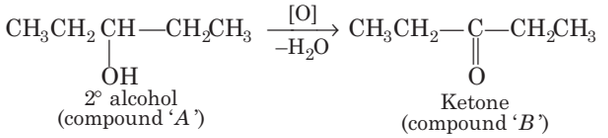
test in presence of NaOH and I_2.



26.



27. Since, the compound '*B*' gave a 2,4-dinitrophenylhydrazine derivative but did not answer haloform test or silver mirror test, it must contain a $\diagdown C{=}O$ group, but it is neither a methyl ketone nor an aldehyde. Moreover compound '*B*' is obtained by the oxidation of compound *A,* having molecular formula $C_5H_{12}O$, so the compound *A* must be a secondary alcohol.

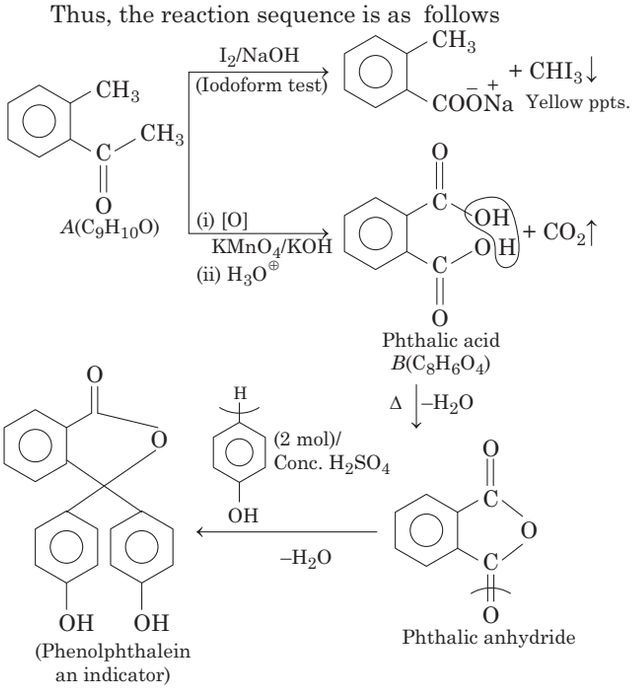


28. (i) $C_9H_{10}O$ shows positive iodoform test thus, $-\overset{\overset{O}{\|}}{C}-CH_3$ group is present.

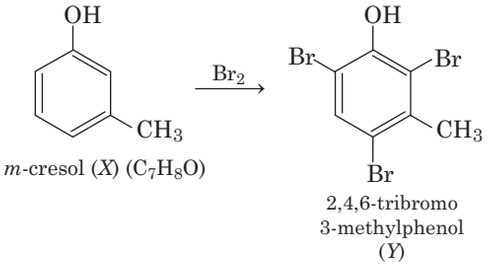
(ii) $C_9H_{10}O$ on strong oxidation ($KMnO_4$ /KOH), gives acid ($C_8H_6O_4$), indicating it can be a dicarboxylic acid. So, '*A*' contains $-COCH_3$ and one $-CH_3$ group which get oxidised into —COOH and —COOH respectively.

(iii) In the preparation of phenolphthalein from phenol, phthalic anhydride is used. So, '*B*' can be phthalic acid (benzene-1,2- dicarboxylic acid) which readily forms anhydride.

Thus, the reaction sequence is as follows



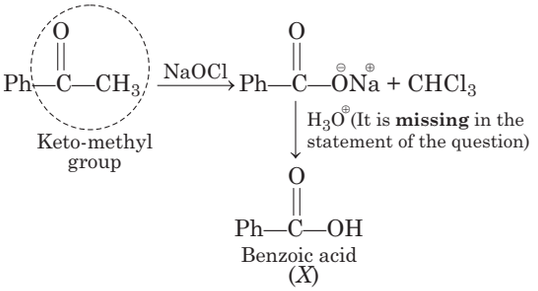
29. Compound '*X*' (C_7H_8O) is insoluble in aqueous $NaHCO_3$ but soluble in NaOH, so it is a phenol. Since, the number of carbon atoms remains the same after bromination, the compound must be *meta* cresol and reactions takes place as follows

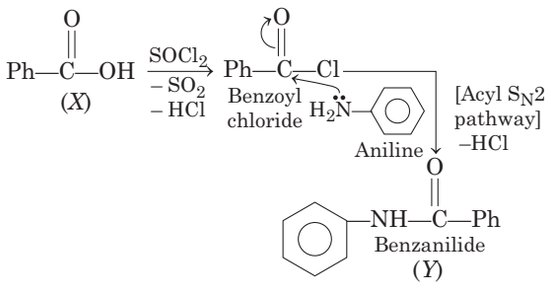


30. NaOCl (sodium hypochlorite) is the reagent of haloform (chloroform formation) reaction.

$$2NaOH + Cl_2 \longrightarrow NaOCl + NaCl + H_2O$$

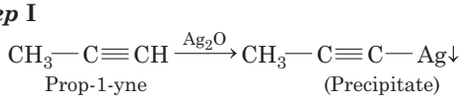
The given reaction takes place as follows



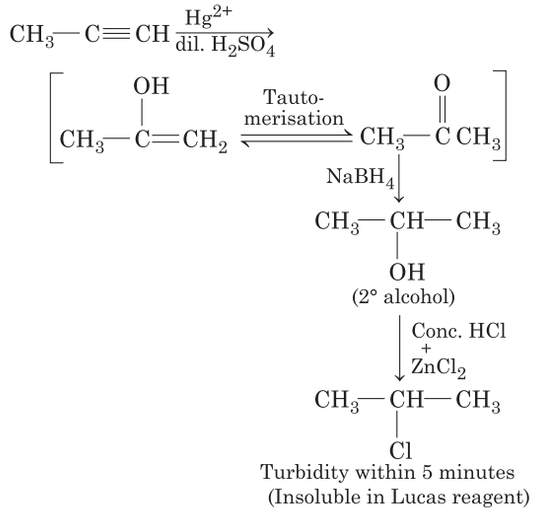


31. According to the given conditions, the compound should be alkyne with triple bond present at the terminal. The chemical reactions involved are as follows:

***Step* I**



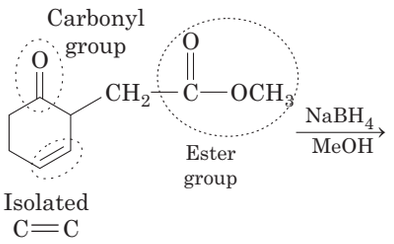
***Step* II**

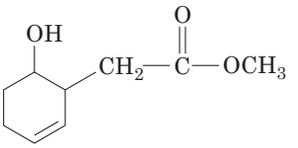


In **step I**, prop-1-yne reacts with Ag_2O to form $CH_3—C\equiv C—Ag$, that forms white precipitates.

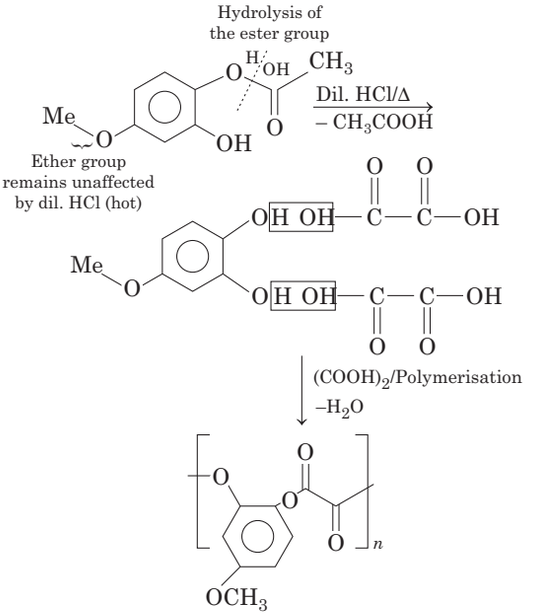
In **step II**, prop-1-yne in presence of mercuric sulphate and dil. H_2SO_4 produces carbonyl compound $(CH_3)_2C=O$ which produces $(CH_3)_2CH—OH$ in presence of $NaBH_4$. 2°alcohol on reaction with Lucas reagent produces turbidity in about 5 min.

32. $NaBH_4$ is a selective reducing agent. It reduces carbonyl $\left(\rangle C=O\right)$ group into an alcohol but cannot reduce an isolated $C=C$ and an ester group too.

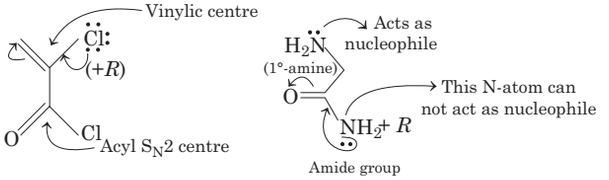




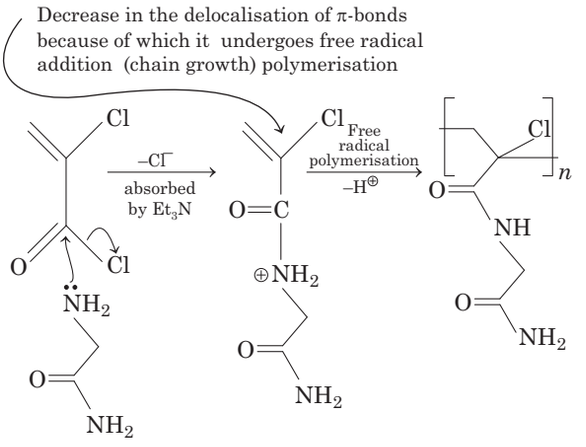
33. In the given reaction, ester get cleaved in presence of dil. HCl and readily forms alcohol. This alcohol on reaction with oxalic acid undergoes polymerisation reaction.



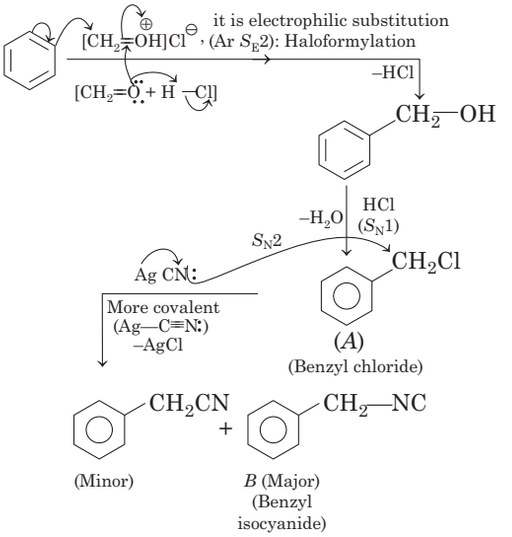
34. The analysis of both the substrates :



So, the reaction can take place as follows



35. The mechanism of the given reaction is as follows



Thus, both benzyl cyanide and benzyl isocyanide are the products of reaction but benzyl isocyanide being the major product gives the correct option as (c).

36. Moles of benzoic acid $= \frac{6.1}{122}$

= moles of *m*-bromobenzoic acid

So, weight of *m*-bromobenzoic acid

$$= \frac{6.1}{122} \times 201 \text{ g} = 10.05 \text{ g}$$

$$\% \text{ yield} = \frac{\text{Actual weight}}{\text{Theoretical weight}} \times 100$$

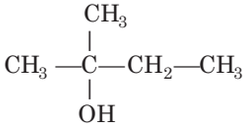
$$= \frac{7.8}{10.05} \times 100$$

$$= 77.61\%$$

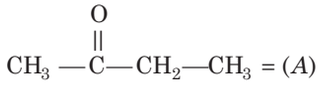
37. $B \xrightarrow[573\text{ K}]{\text{Cu}} CH_3-\underset{\text{2 methyl-2 -butene}}{\overset{CH_3}{\overset{|}{C}}=CH-CH_3}$

$\therefore$ *B* must be a 3° alcohol that, on oxidation produces alkene.

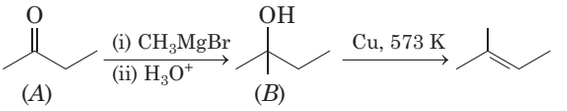
So, the structure of *B* is



To get *B* (alcohol) CH_3MgBr must react with a ketone.



Complete reaction is as follows

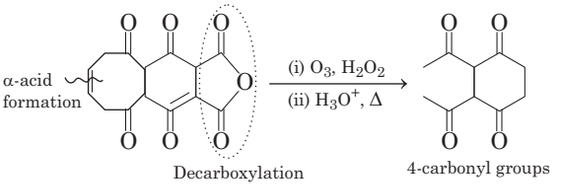


% *C* by mass

$$= \frac{\text{mass of C } (= 4 \times 12) \times 100}{\text{total molar mass } [= 4 \times 12 + (16) + (8 \times 1)]}$$

$$= \frac{48 \times 100}{72} = 66.67\%$$

38.



In the above reaction, there is breakage of double bond and formation of two α-acid takes place. This breakage of double bond is due to presence of O_3 and H_2O_2. After that, due to thermal condition, the ring gets open followed by decarboxylation led to the formation of product. Hence, the number of carbonyl group present in the final product is 4.

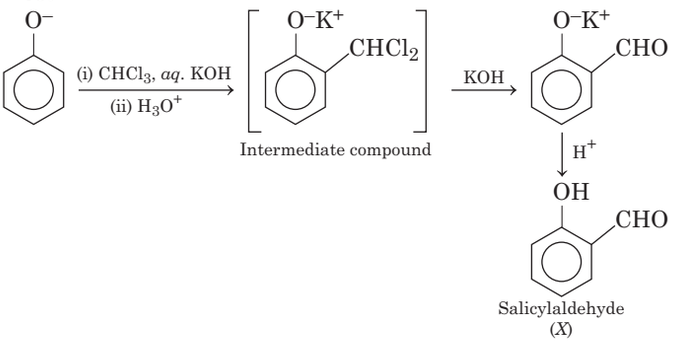
39. (i) $Ph-\underset{\underset{O}{\|}}{\overset{O}{\|}}{S}-OH + NaHCO_3 \longrightarrow Ph-\underset{\underset{O}{\|}}{\overset{O}{\|}}{S}-O^-Na^+ + \underset{(A)}{CO_2}\uparrow + H_2O$

(ii) $Ph-\underset{O}{\overset{O}{\|}}{C}-OH + NaHCO_3 \longrightarrow Ph-\underset{O}{\overset{O}{\|}}{C}-O^-Na^+ + \underset{(B)}{CO_2}\uparrow + H_2O$

So, we see that Gas '*A*' and Gas '*B*' is CO_2 and molecular mass of CO_2 is 44.

So, sum of molecular mass of $A + B$ is 88.

40.



Compound '*X*' is salicylaldehyde. Molecular weight of salicylaldehyde is 122, so possible answer is 1 + 2 + 2 = 5.