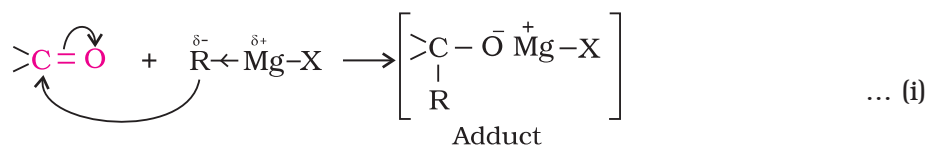


### 3. From Grignard reagents

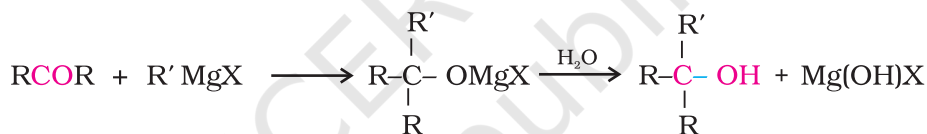
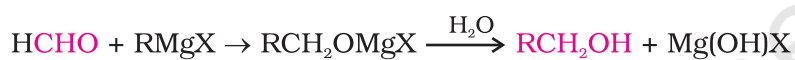
Alcohols are produced by the reaction of Grignard reagents (Unit 10, Class XII) with aldehydes and ketones.

The first step of the reaction is the nucleophilic addition of Grignard reagent to the carbonyl group to form an adduct. Hydrolysis of the adduct yields an alcohol.



The reaction of Grignard reagents with methanal produces a primary alcohol, with other aldehydes, secondary alcohols and with ketones, tertiary alcohols.

The overall reactions using different aldehydes and ketones are as follows:

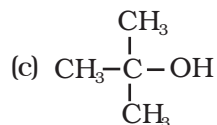
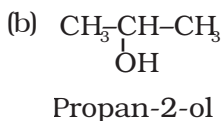
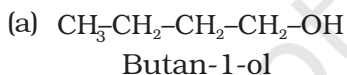


You will notice that the reaction produces a primary alcohol with methanal, a secondary alcohol with other aldehydes and tertiary alcohol with ketones.

Give the structures and IUPAC names of the products expected from the following reactions:

#### Example 11.2

- Catalytic reduction of butanal.
- Hydration of propene in the presence of dilute sulphuric acid.
- Reaction of propanone with methylmagnesium bromide followed by hydrolysis.



2-Methylpropan-2-ol

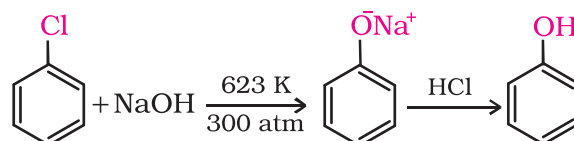
#### Solution

#### 11.4.2 Preparation of Phenols

Phenol, also known as carboic acid, was first isolated in the early nineteenth century from coal tar. Nowadays, phenol is commercially produced synthetically. In the laboratory, phenols are prepared from benzene derivatives by any of the following methods:

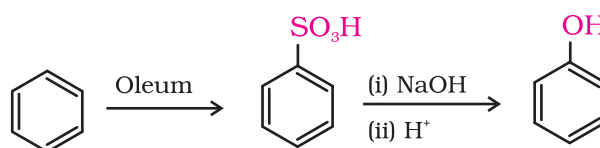
### 1. From haloarenes

Chlorobenzene is fused with NaOH at 623K and 320 atmospheric pressure. Phenol is obtained by acidification of sodium phenoxide so produced (Unit 10, Class XII).



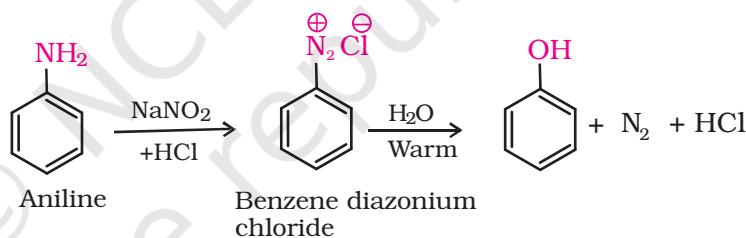
### 2. From benzenesulphonic acid

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



### 3. From diazonium salts

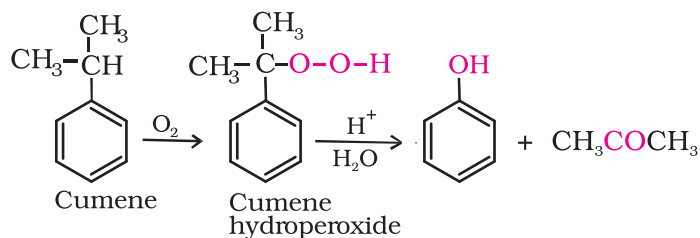
A diazonium salt is formed by treating an aromatic primary amine with nitrous acid ( $\text{NaNO}_2 + \text{HCl}$ ) at 273-278 K. Diazonium salts are hydrolysed to phenols by warming with water or by treating with dilute acids (Unit 13, Class XII).



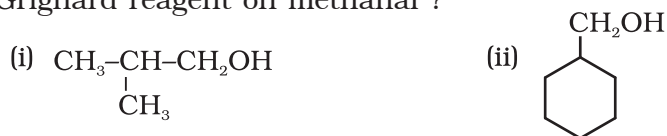
Most of the worldwide production of phenol is from cumene.

### 4. From cumene

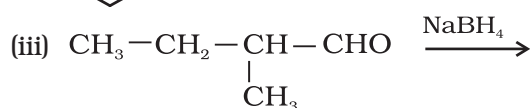
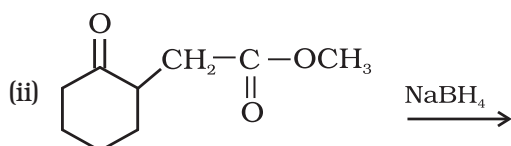
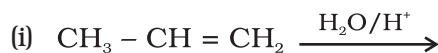
Phenol is manufactured from the hydrocarbon, cumene. Cumene (isopropylbenzene) is oxidised in the presence of air to cumene hydroperoxide. It is converted to phenol and acetone by treating it with dilute acid. Acetone, a by-product of this reaction, is also obtained in large quantities by this method.



11.4 Show how are the following alcohols prepared by the reaction of a suitable Grignard reagent on methanal ?



11.5 Write structures of the products of the following reactions:



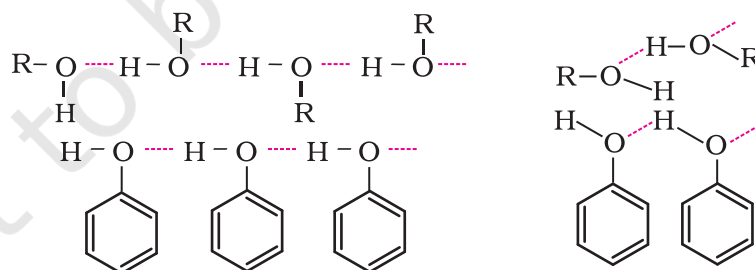
### 11.4.3 Physical Properties

Alcohols and phenols consist of two parts, an alkyl/aryl group and a hydroxyl group. The properties of alcohols and phenols are chiefly due to the hydroxyl group. The nature of alkyl and aryl groups simply modify these properties.

#### Boiling Points

The boiling points of alcohols and phenols increase with increase in the number of carbon atoms (increase in van der Waals forces). In alcohols, the boiling points decrease with increase of branching in carbon chain (because of decrease in van der Waals forces with decrease in surface area).

The -OH group in alcohols and phenols is involved in intermolecular hydrogen bonding as shown below:

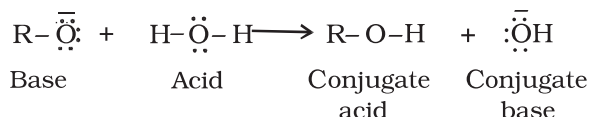


It is interesting to note that boiling points of alcohols and phenols are higher in comparison to other classes of compounds, namely hydrocarbons, ethers, haloalkanes and haloarenes of comparable molecular masses. For example, ethanol and propane have comparable molecular masses but their boiling points differ widely. The boiling point of methoxymethane is intermediate of the two boiling points.





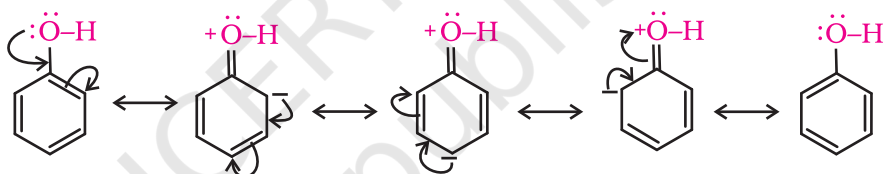
Alcohols are, however, weaker acids than water. This can be illustrated by the reaction of water with an alkoxide.



This reaction shows that water is a better proton donor (i.e., stronger acid) than alcohol. Also, in the above reaction, we note that an alkoxide ion is a better proton acceptor than hydroxide ion, which suggests that alkoxides are stronger bases (sodium ethoxide is a stronger base than sodium hydroxide).

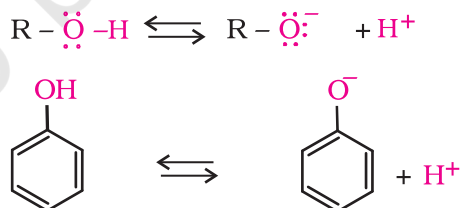
Alcohols act as Bronsted bases as well. It is due to the presence of unshared electron pairs on oxygen, which makes them proton acceptors.

(iii) *Acidity of phenols:* The reactions of phenol with metals (e.g., sodium, aluminium) and sodium hydroxide indicate its acidic nature. The hydroxyl group, in phenol is directly attached to the  $sp^2$  hybridised carbon of benzene ring which acts as an electron withdrawing group. Due to this, the charge distribution in phenol molecule, as depicted in its resonance structures, causes the oxygen of -OH group to be positive.



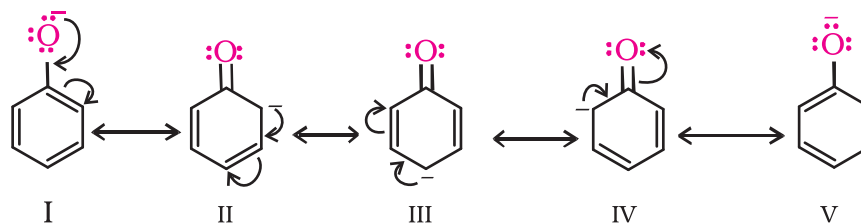
The reaction of phenol with aqueous sodium hydroxide indicates that phenols are stronger acids than alcohols and water. Let us examine how a compound in which hydroxyl group attached to an aromatic ring is more acidic than the one in which hydroxyl group is attached to an alkyl group.

The ionisation of an alcohol and a phenol takes place as follows:



Due to the higher electronegativity of  $sp^2$  hybridised carbon of phenol to which -OH is attached, electron density decreases on oxygen. This increases the polarity of O-H bond and results in an increase in ionisation of phenols than that of alcohols. Now let us examine the stabilities of alkoxide and phenoxide ions. In alkoxide ion, the negative charge is localised on oxygen while in phenoxide ion, the charge is delocalised. The delocalisation of negative charge (structures I-V) makes

phenoxide ion more stable and favours the ionisation of phenol. Although there is also charge delocalisation in phenol, its resonance structures have charge separation due to which the phenol molecule is less stable than phenoxide ion.



In substituted phenols, the presence of electron withdrawing groups such as nitro group, enhances the acidic strength of phenol. This effect is more pronounced when such a group is present at *ortho* and *para* positions. It is due to the effective delocalisation of negative charge in phenoxide ion. On the other hand, electron releasing groups, such as alkyl groups, in general, do not favour the formation of phenoxide ion resulting in decrease in acid strength. Cresols, for example, are less acidic than phenol.

The greater the  $pK_a$  value, the weaker the acid.

**Table 11.3:  $pK_a$  Values of some Phenols and Ethanol**

Compound	Formula	$pK_a$
<i>o</i> -Nitrophenol	<i>o</i> -O <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub> -OH	7.2
<i>m</i> -Nitrophenol	<i>m</i> -O <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub> -OH	8.3
<i>p</i> -Nitrophenol	<i>p</i> -O <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub> -OH	7.1
Phenol	C <sub>6</sub> H <sub>5</sub> -OH	10.0
<i>o</i> -Cresol	<i>o</i> -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -OH	10.2
<i>m</i> -Cresol	<i>m</i> -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -OH	10.1
<i>p</i> -Cresol	<i>p</i> -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -OH	10.2
Ethanol	C <sub>2</sub> H <sub>5</sub> OH	15.9

From the above data, you will note that phenol is million times more acidic than ethanol.

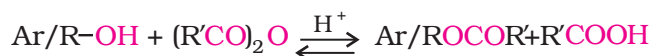
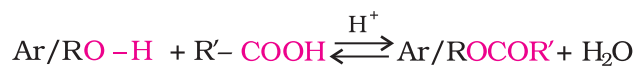
Arrange the following compounds in increasing order of their acid strength: [Example 11.4](#)

Propan-1-ol, 2,4,6-trinitrophenol, 3-nitrophenol, 3,5-dinitrophenol, phenol, 4-methylphenol.

Propan-1-ol, 4-methylphenol, phenol, 3-nitrophenol, 3,5-dinitrophenol, 2,4,6-trinitrophenol. [Solution](#)

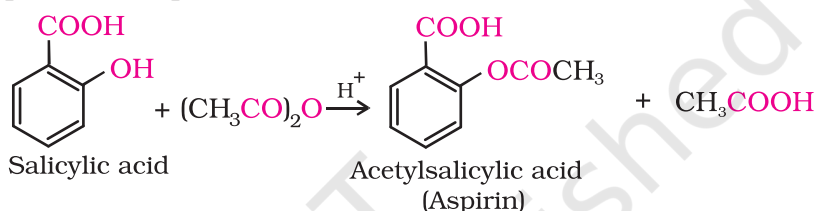
## 2. Esterification

Alcohols and phenols react with carboxylic acids, acid chlorides and acid anhydrides to form esters.



Aspirin possesses analgesic, anti-inflammatory and antipyretic properties.

The reaction with carboxylic acid and acid anhydride is carried out in the presence of a small amount of concentrated sulphuric acid. The reaction is reversible, and therefore, water is removed as soon as it is formed. The reaction with acid chloride is carried out in the presence of a base (pyridine) so as to neutralise HCl which is formed during the reaction. It shifts the equilibrium to the right hand side. The introduction of acetyl ( $\text{CH}_3\text{CO}$ ) group in alcohols or phenols is known as acetylation. Acetylation of salicylic acid produces aspirin.



### (b) Reactions involving cleavage of carbon - oxygen (C-O) bond in alcohols

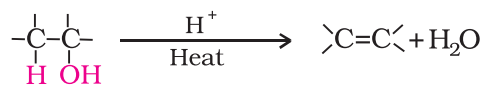
The reactions involving cleavage of C-O bond take place only in alcohols. Phenols show this type of reaction only with zinc.

- 1. Reaction with hydrogen halides:** Alcohols react with hydrogen halides to form alkyl halides (Refer Unit 10, Class XII).

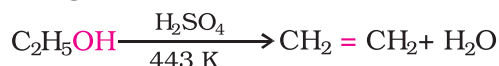


The difference in reactivity of three classes of alcohols with HCl distinguishes them from one another (**Lucas test**). Alcohols are soluble in Lucas reagent (conc. HCl and  $\text{ZnCl}_2$ ) while their halides are immiscible and produce turbidity in solution. In case of tertiary alcohols, turbidity is produced immediately as they form the halides easily. Primary alcohols do not produce turbidity at room temperature.

- 2. Reaction with phosphorus trihalides:** Alcohols are converted to alkyl bromides by reaction with phosphorus tribromide (Refer Unit 10, Class XII).
- 3. Dehydration:** Alcohols undergo dehydration (removal of a molecule of water) to form alkenes on treating with a protic acid e.g., concentrated  $\text{H}_2\text{SO}_4$  or  $\text{H}_3\text{PO}_4$ , or catalysts such as anhydrous zinc chloride or alumina (Unit 13, Class XI).

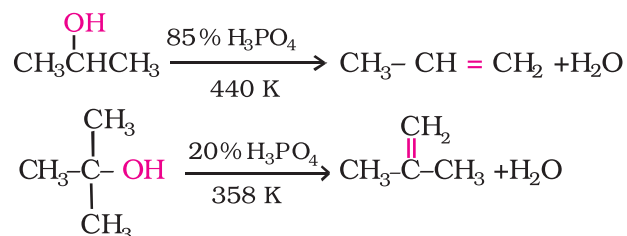


Ethanol undergoes dehydration by heating it with concentrated  $\text{H}_2\text{SO}_4$  at 443 K.





Secondary and tertiary alcohols are dehydrated under milder conditions. For example



Thus, the relative ease of dehydration of alcohols follows the following order:

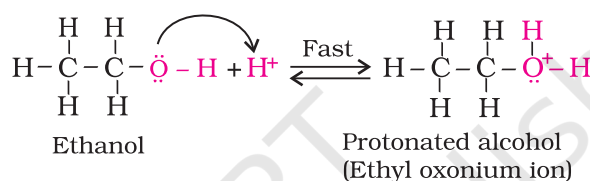


The mechanism of dehydration of ethanol involves the following steps:

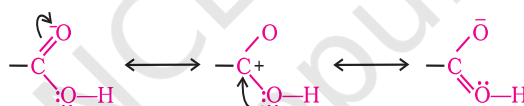
*Tertiary carbocations are more stable and therefore are easier to form than secondary and primary carbocations; tertiary alcohols are the easiest to dehydrate.*

### Mechanism

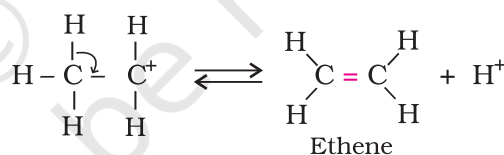
**Step 1:** Formation of protonated alcohol.



**Step 2:** Formation of carbocation: It is the slowest step and hence, the rate determining step of the reaction.

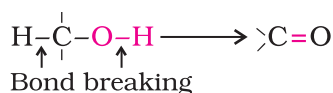


**Step 3:** Formation of ethene by elimination of a proton.

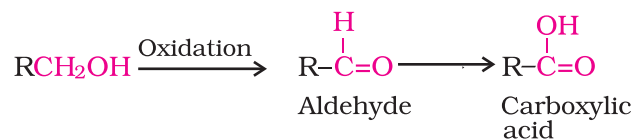


The acid used in step 1 is released in step 3. To drive the equilibrium to the right, ethene is removed as it is formed.

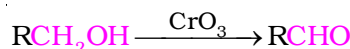
**4. Oxidation:** Oxidation of alcohols involves the formation of a carbon-oxygen double bond with cleavage of an O-H and C-H bonds.



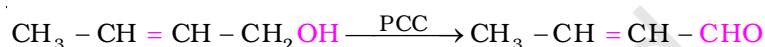
Such a cleavage and formation of bonds occur in oxidation reactions. These are also known as **dehydrogenation** reactions as these involve loss of dihydrogen from an alcohol molecule. Depending on the oxidising agent used, a primary alcohol is oxidised to an aldehyde which in turn is oxidised to a carboxylic acid.



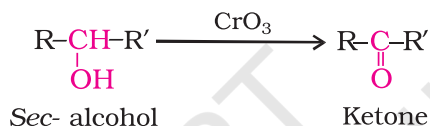
Strong oxidising agents such as acidified potassium permanganate are used for getting carboxylic acids from alcohols directly.  $\text{CrO}_3$  in anhydrous medium is used as the oxidising agent for the isolation of aldehydes.



A better reagent for oxidation of primary alcohols to aldehydes in good yield is pyridinium chlorochromate (PCC), a complex of chromium trioxide with pyridine and HCl.

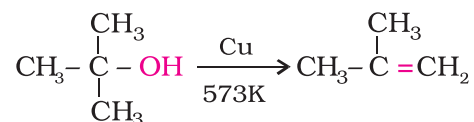
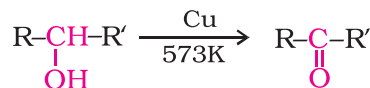
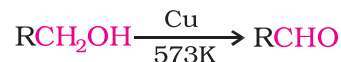


Secondary alcohols are oxidised to ketones by chromic anhydride ( $\text{CrO}_3$ ).



Tertiary alcohols do not undergo oxidation reaction. Under strong reaction conditions such as strong oxidising agents ( $\text{KMnO}_4$ ) and elevated temperatures, cleavage of various C-C bonds takes place and a mixture of carboxylic acids containing lesser number of carbon atoms is formed.

When the vapours of a primary or a secondary alcohol are passed over heated copper at 573 K, dehydrogenation takes place and an aldehyde or a ketone is formed while tertiary alcohols undergo dehydration.



Biological oxidation of methanol and ethanol in the body produces the corresponding aldehyde followed by the acid. At times the alcoholics, by mistake, drink ethanol, mixed with methanol also called denatured alcohol. In the body, methanol is oxidised first to methanal and then to methanoic acid, which may cause blindness and death. A methanol poisoned patient is treated by giving intravenous infusions of diluted ethanol. The enzyme responsible for oxidation of aldehyde ( $\text{HCHO}$ ) to acid is swamped allowing time for kidneys to excrete methanol.

### (c) Reactions of phenols

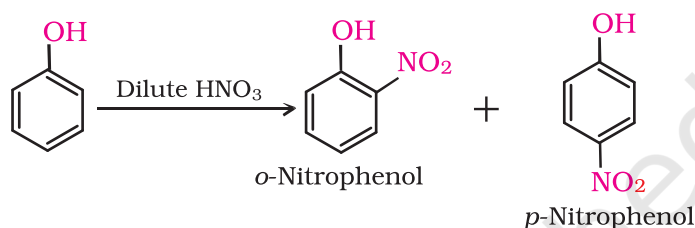
Following reactions are shown by phenols only.

## 1. Electrophilic aromatic substitution

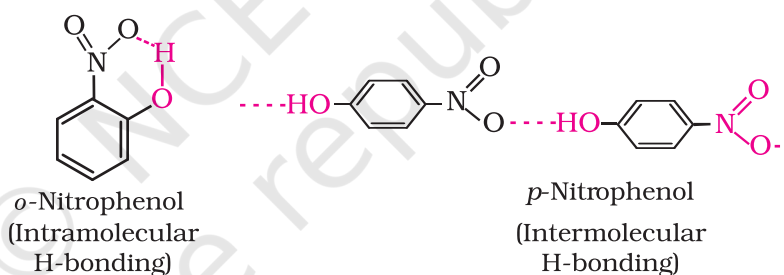
In phenols, the reactions that take place on the aromatic ring are electrophilic substitution reactions (Unit 13, Class XI). The  $-OH$  group attached to the benzene ring activates it towards electrophilic substitution. Also, it directs the incoming group to *ortho* and *para* positions in the ring as these positions become electron rich due to the resonance effect caused by  $-OH$  group. The resonance structures are shown under acidity of phenols.

Common electrophilic aromatic substitution reactions taking place in phenol are as follows:

(i) *Nitration*: With dilute nitric acid at low temperature (298 K), phenol yields a mixture of *ortho* and *para* nitrophenols.

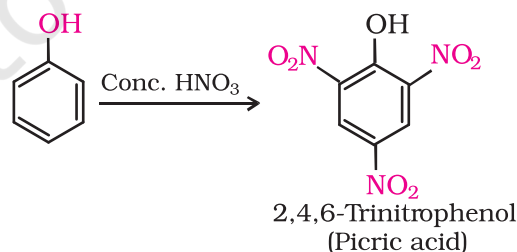


The *ortho* and *para* isomers can be separated by steam distillation. *o*-Nitrophenol is steam volatile due to intramolecular hydrogen bonding while *p*-nitrophenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules.



2, 4, 6 - Trinitrophenol is a strong acid due to the presence of three electron withdrawing  $-NO_2$  groups which facilitate the release of hydrogen ion.

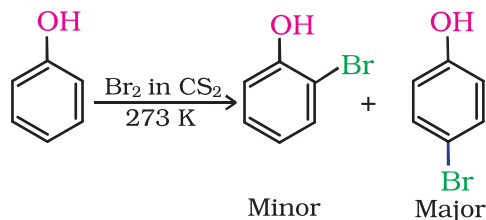
With concentrated nitric acid, phenol is converted to 2,4,6-trinitrophenol. The product is commonly known as picric acid. The yield of the reaction product is poor.



Nowadays picric acid is prepared by treating phenol first with concentrated sulphuric acid which converts it to phenol-2,4-disulphonic acid, and then with concentrated nitric acid to get 2,4,6-trinitrophenol. Can you write the equations of the reactions involved?

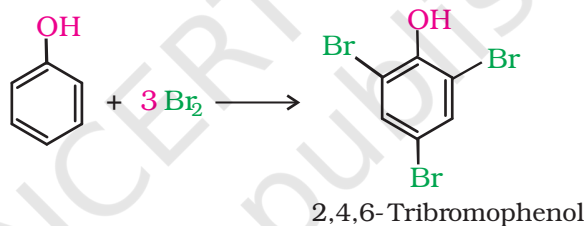
(ii) **Halogenation:** On treating phenol with bromine, different reaction products are formed under different experimental conditions.

(a) When the reaction is carried out in solvents of low polarity such as  $\text{CHCl}_3$  or  $\text{CS}_2$  and at low temperature, monobromophenols are formed.



The usual halogenation of benzene takes place in the presence of a Lewis acid, such as  $\text{FeBr}_3$  (Unit 10, Class XII), which polarises the halogen molecule. In case of phenol, the polarisation of bromine molecule takes place even in the absence of Lewis acid. It is due to the highly activating effect of  $-\text{OH}$  group attached to the benzene ring.

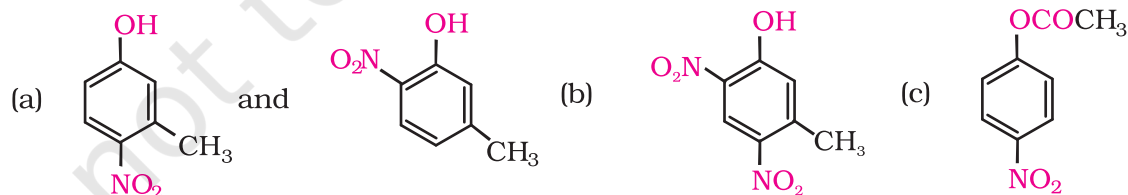
(b) When phenol is treated with bromine water, 2,4,6-tribromophenol is formed as white precipitate.



**Example 11.5** Write the structures of the major products expected from the following reactions:

- Mononitration of 3-methylphenol
- Dinitration of 3-methylphenol
- Mononitration of phenyl methanoate.

**Solution** The combined influence of  $-\text{OH}$  and  $-\text{CH}_3$  groups determine the position of the incoming group.



## 2. Kolbe's reaction

Phenoxide ion generated by treating phenol with sodium hydroxide is even more reactive than phenol towards electrophilic aromatic substitution. Hence, it undergoes electrophilic substitution with carbon dioxide, a weak electrophile. *Ortho* hydroxybenzoic acid is formed as the main reaction product.

