

22

HYDROXY
COMPOUNDS

Student Learning Outcomes

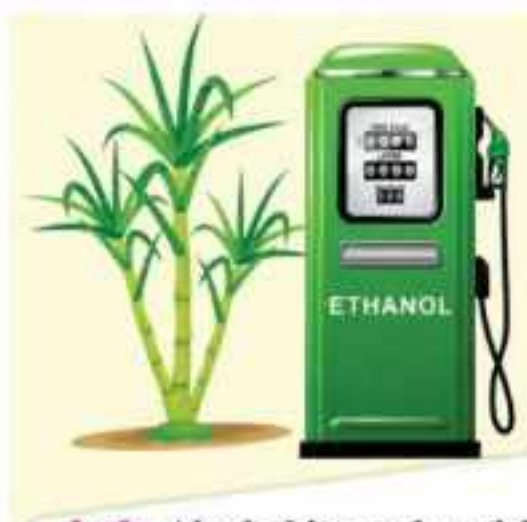
[C-12-D-41 to C-12-D-58]

- ⊙ State the reactions (reagents and conditions) by which alcohols can be produced:
 - a. electrophilic addition of steam to an alkene, $\text{H}_2\text{O}_{(\text{g})}$ and H_3PO_4 catalyst.
 - b. reaction of alkenes with cold dilute acidified potassium manganate (VII) to form a diol.
 - c. substitution of a halogenoalkane using $\text{NaOH}_{(\text{aq})}$ and heat.
 - d. reduction of an aldehyde or ketone using NaBH_4 or LiAlH_4 .
 - e. reduction of carboxylic acid using LiAlH_4 .
 - f. hydrolysis of an ester using dilute acid or dilute alkali and heat, describe the reaction with oxygen (combustion) of organic hydroxy compounds.
- ⊙ Describe substitution to halogenoalkanes, e.g. by reaction with HX or KBr with H_2SO_4 or H_3PO_4 ; or with SOCl_2 .
- ⊙ Describe the reaction of hydroxy organic compounds with $\text{Na}_{(\text{s})}$.
- ⊙ Describe the oxidation with acidified $\text{K}_2\text{Cr}_2\text{O}_7$ or acidified KMnO_4 to: carbonyl compounds by distillation, carboxylic acids by refluxing (primary alcohols give aldehydes which can be further oxidized to carboxylic acids, secondary alcohols give ketones, tertiary alcohols cannot be oxidized).
- ⊙ Describe the dehydration of alcohols to alkenes by using a heated catalyst, e.g., Al_2O_3 or a concentrated acid.
- ⊙ Describe the formation of esters by reaction with carboxylic acids and concentrated H_2SO_4 or H_3PO_4 as catalyst as exemplified by ethanol.
- ⊙ Classify alcohols as primary, secondary and tertiary alcohols, to include examples with more than one alcohol group.
- ⊙ State characteristic distinguishing reactions, e.g., mild oxidation with acidified $\text{K}_2\text{Cr}_2\text{O}_7$, color change from orange to green.
- ⊙ Deduce the presence of a $\text{CH}_3\text{CH}(\text{OH}) -$ group in an alcohol, $\text{CH}_3\text{CH}(\text{OH}) - \text{R}$, from its reaction with I_2 to form a yellow precipitate of tri-iodomethane and an ion, RCO_2^- .
- ⊙ Explain the acidity of alcohols compared with water.
- ⊙ Describe the reaction with acyl chlorides to form esters using ethyl ethanoate.
- ⊙ Recall the reactions (reagents and conditions) by which phenol can be produced: Reaction of phenylamine with HNO_2 or NaNO_2 and dilute acid below 1°C to produce the diazonium salt; further warming of the diazonium salt with H_2O to give phenol.
- ⊙ Recall the chemistry of phenol, as exemplified by the following reactions: with bases, for example $\text{NaOH}_{(\text{aq})}$ to produce sodium phenoxide with $\text{Na}_{(\text{s})}$ to produce sodium phenoxide and $\text{H}_{2(\text{g})}$ in $\text{NaOH}_{(\text{aq})}$ with diazonium salts, to give azo compounds nitration of the aromatic ring with dilute $\text{HNO}_{3(\text{aq})}$ at room temperature to give a mixture of 2-nitrophenol and 4-nitrophenol bromination of the aromatic ring with $\text{Br}_{2(\text{aq})}$ to form 2,4,6-tribromophenol.



- ⊙ Explain, the acidity of phenol.
- ⊙ Describe the relative acidities of water, phenol and ethanol.
- ⊙ Explain, why the reagents and conditions for the nitration and bromination of phenol are different from those for benzene.
- ⊙ Recall that the hydroxyl group of phenol directs to the 2-, 4- and 6- positions.
- ⊙ Apply knowledge of the reactions of phenol to those of other phenolic compounds, e.g. naphthol.

Alcohols and phenols are hydroxy organic compounds with at least one hydroxyl group attached to an aliphatic or an aryl carbon, respectively. The study of alcohols and phenols holds a significant place due to their widespread occurrence and diverse applications. Almost everyone is aware of ethanol, also known as ethyl alcohol or grain alcohol. It is commonly known that alcohols can be used as fuels.



Left: Alcohol is produced from bio-based materials and is used as a biofuel.



Right: Phenol is an ingredient in disinfectants, such as soaps, hospitals disinfectant liquids, etc.

After Louis Pasteur's research revealed the existence of bacteria, scientists started cleaning surgical instruments and wounds with phenol solutions in 1867. A patient's chances of surviving surgery significantly increased due to the phenol solution's potent antiseptic properties. Since phenol burns healthy tissues, it was too potent for this use, and alternatives were eventually discovered.

22.1 ALCOHOLS

Hydroxyl group (-OH) is the functional group of all alcohols. Alcohols are represented by the general formula ROH, where R is an alkyl or aryl group. The family also includes familiar substances as cholesterol and the carbohydrates. Methanol (CH₃OH) and ethanol (CH₃CH₂OH) are the first two members of the homologous series of monohydric alcohols.

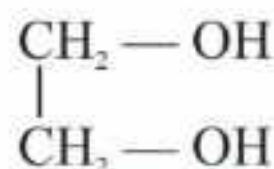
Depending on the number of hydroxyl groups attached, alcohols can be classified into monohydric and polyhydric alcohols.



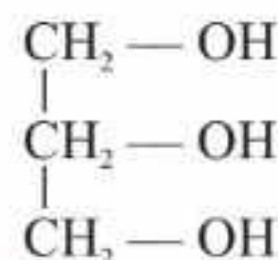
ethanol



propan-1-ol



1,2-ethandiol (glycol)



1,2,3-propantriol (glycerol)

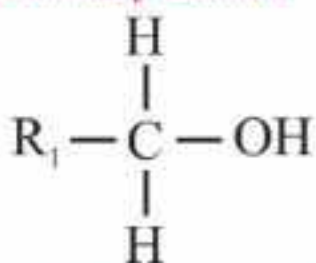
Depending on the number of carbon atoms which are directly attached to the carbon that is bonded with the -OH group, alcohols can be classified into three types.

 **A primary (1°) alcohol** is one in which the OH group is attached a primary carbon atom. Its general formula is R₁CH₂OH.

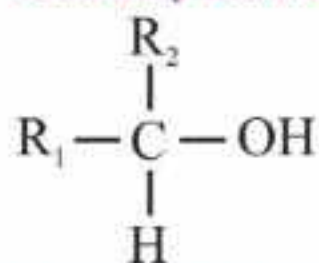
 **A secondary (2°) alcohol** is one in which the OH group is attached to a secondary carbon atom. Its general formula is R₂CHOH.

 A **tertiary (3°) alcohol** is one in which the OH group is attached to a tertiary carbon atom. Its general formula is R_3COH .

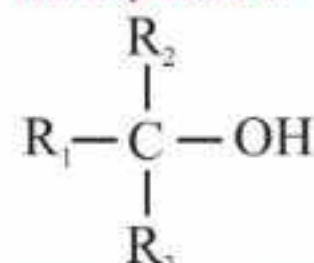
Primary alcohol



Secondary alcohol



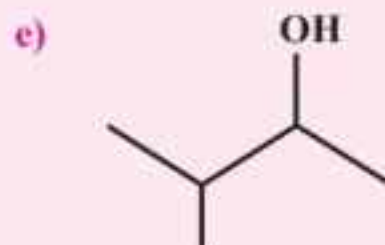
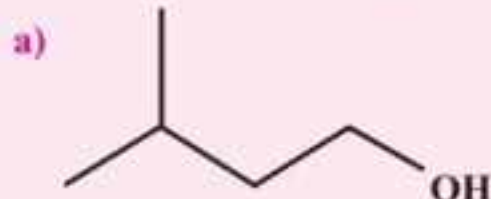
Tertiary alcohol



Quick Check 22.1



1. Which ones of these are 1°, 2° and 3° alcohols?

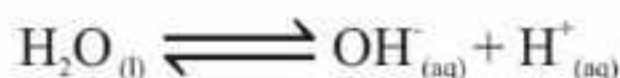


22.2 ACIDITY OF ALCOHOLS AND PHENOLS

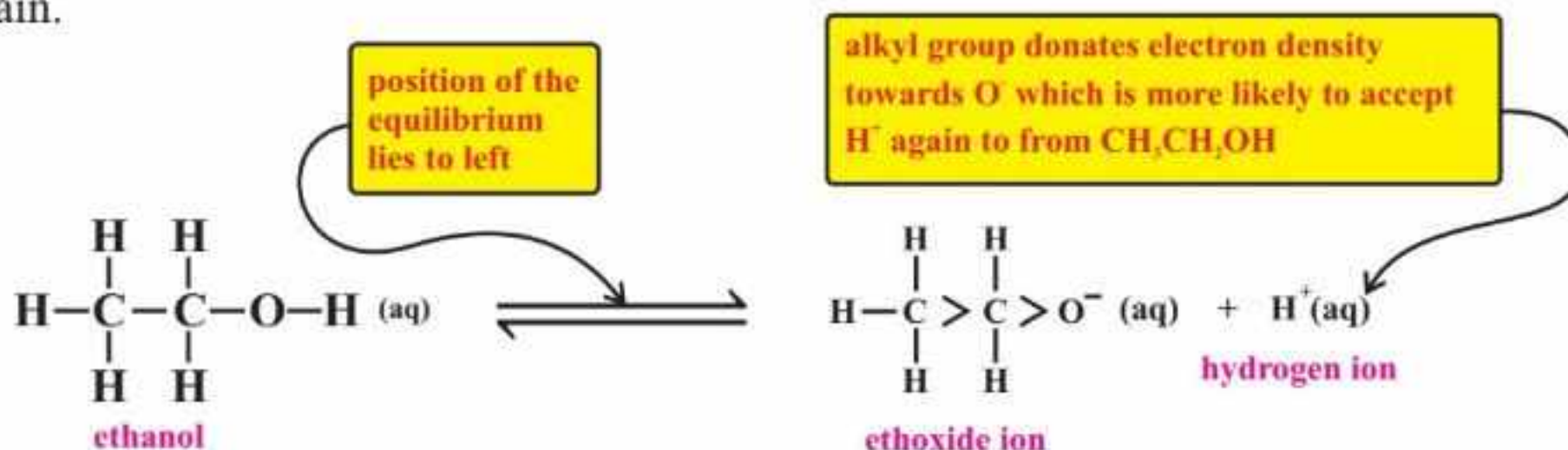
Alcohols have a low degree of dissociation. This means that when dissolved in water, alcohol molecules do not dissociate (split up) to a great extent. The position of the equilibrium lies to the left, meaning that there are far more alcohol molecules than $RO^-_{(aq)}$ and $H^+_{(aq)}$ ions.



When water dissociates, the position of the equilibrium still lies to the left, but there are more H^+ ions compared to the dissociation of alcohols. As alcohols have a lower $[H^+_{(aq)}]$ in solution compared to water, alcohols are weaker acids than water.

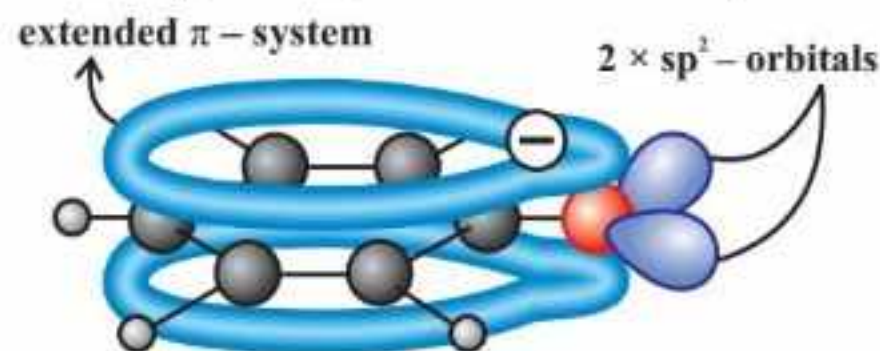
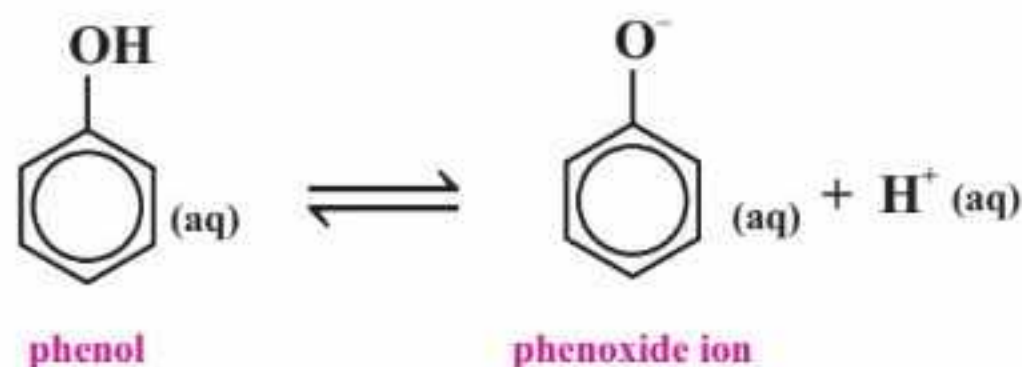


The reason for alcohols being less acidic than water is the presence of alkyl groups. Alkyl groups are electron donating groups. Electron-donating species push electrons into a covalent bond and are said to have a positive inductive effect. The alkyl groups destabilize the alkoxide ion, which is formed by removing one proton (H^+) from the alcohol molecule. The oxygen atom in the alkoxide ion is bonded to an electron-donating alkyl group. This means that there is more electron density on the O atom. The alkoxide ion is, therefore, more likely to accept an H^+ ion and form the alcohol again.



Although phenol compounds contain an alcohol (-OH) group, they are weakly acidic and this is due to the delocalisation of one of the lone pairs from the oxygen atom into the aromatic ring. The delocalisation stabilises the phenoxide ion, the conjugate base of phenol.

This is possible as one of the lone pairs on the oxygen atom overlaps with the delocalised π system of the ring. Because of this delocalisation, there is less charge density on the oxygen atom. The H^+ ions are, therefore, not strongly attracted to the phenoxide ion and are less likely to reform the phenol molecule. This means that phenol is more likely to lose a proton (and act as an acid) rather than to gain a proton (and act as a base).



The negative charge on the oxygen is delocalised and spread on the aromatic ring making it a stable ion

The relative acidities are as follows: **phenol > water > ethanol**



Quick Check 22.2

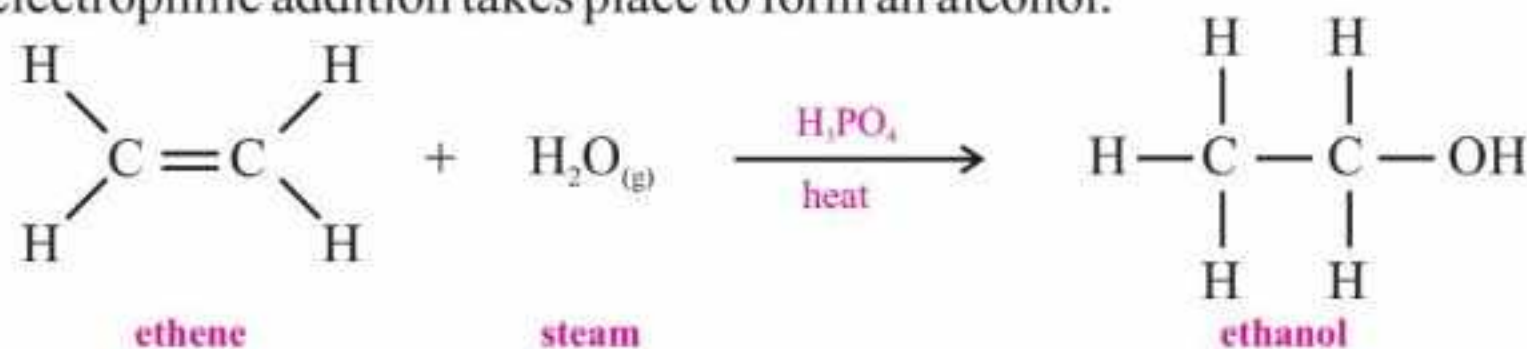


- Compare the relative acidic strength of methanol and ethanol.
- Showing the electron delocalisation explain why the phenoxide (PhO^-) is more stable than the ethoxide ion ($\text{C}_2\text{H}_5\text{O}^-$).
- Alkali metals react with stronger acids to produce the hydrogen gas. A piece of sodium is added to two beakers; one containing ethanol and the other phenol.
 - Predict in which beaker the hydrogen gas will be evolved earlier and more rapidly.
 - If the phenolphthalein indicator is already present before adding sodium to the above solutions, which solution will turn pink earlier?

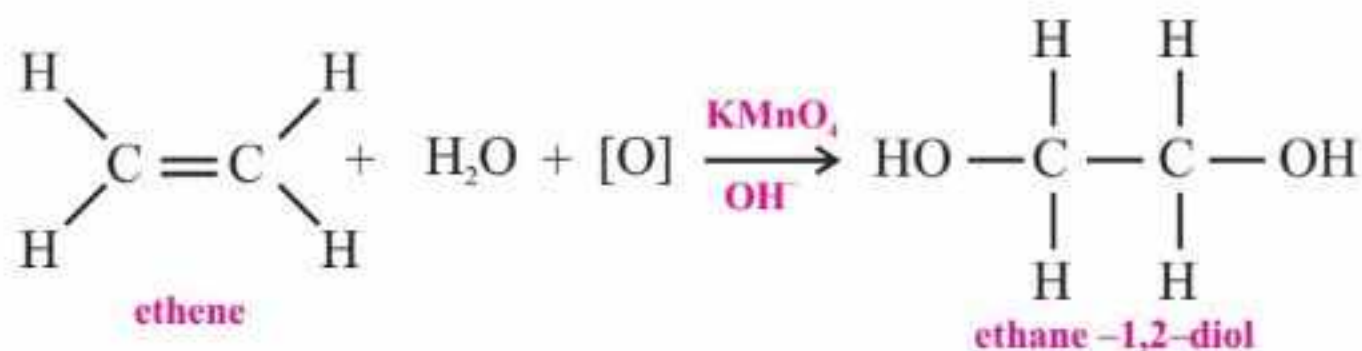
22.3 SYNTHESIS OF ALCOHOLS

Alcohols can be prepared from alkenes, halogenoalkanes, carbonyl compounds, carboxylic acids, and esters.

- I)** When hot steam is reacted with an alkene, using concentrated phosphoric acid (H_3PO_4) as a catalyst, electrophilic addition takes place to form an alcohol.

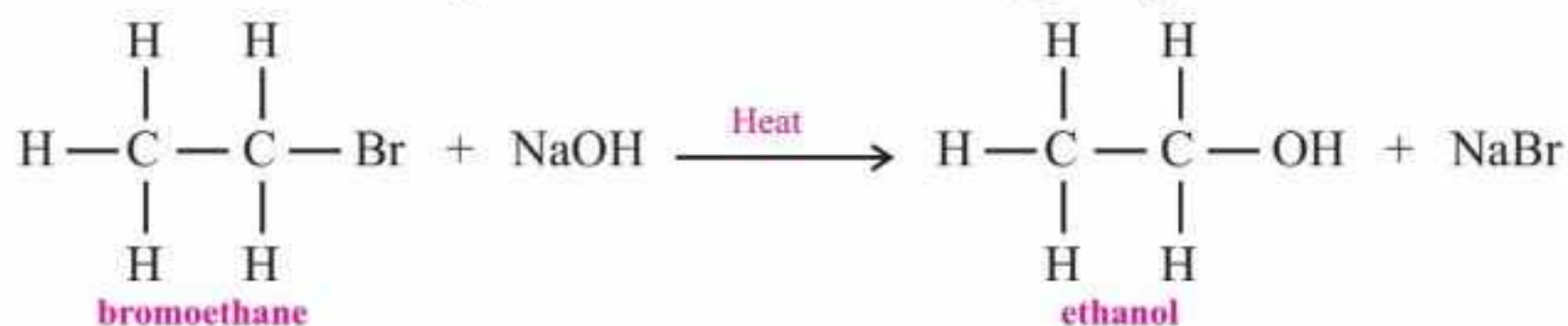


- ii.** Alcohols are obtained by the oxidation of alkenes with cold, dilute KMnO_4 , a mild oxidising agent.

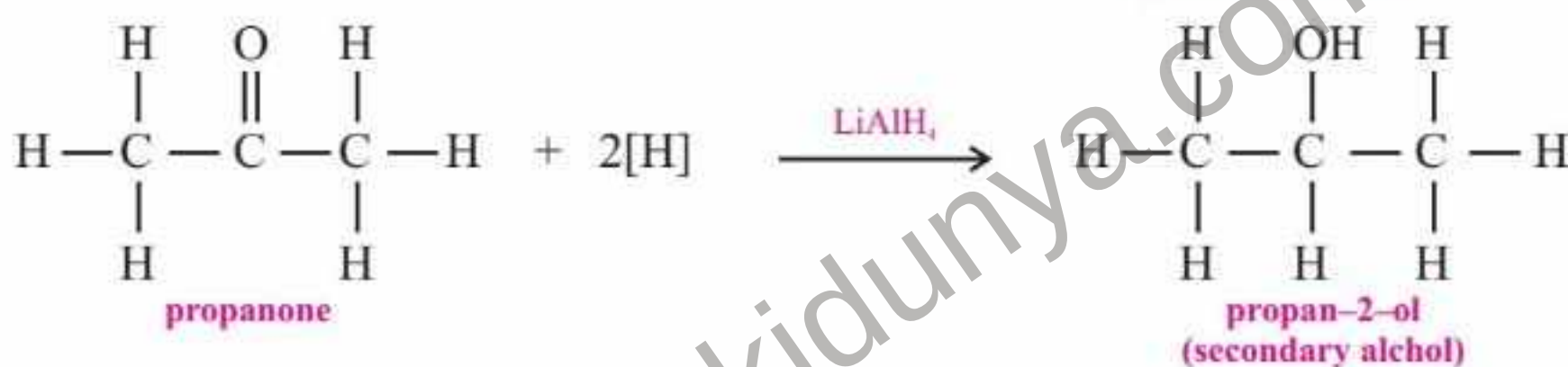
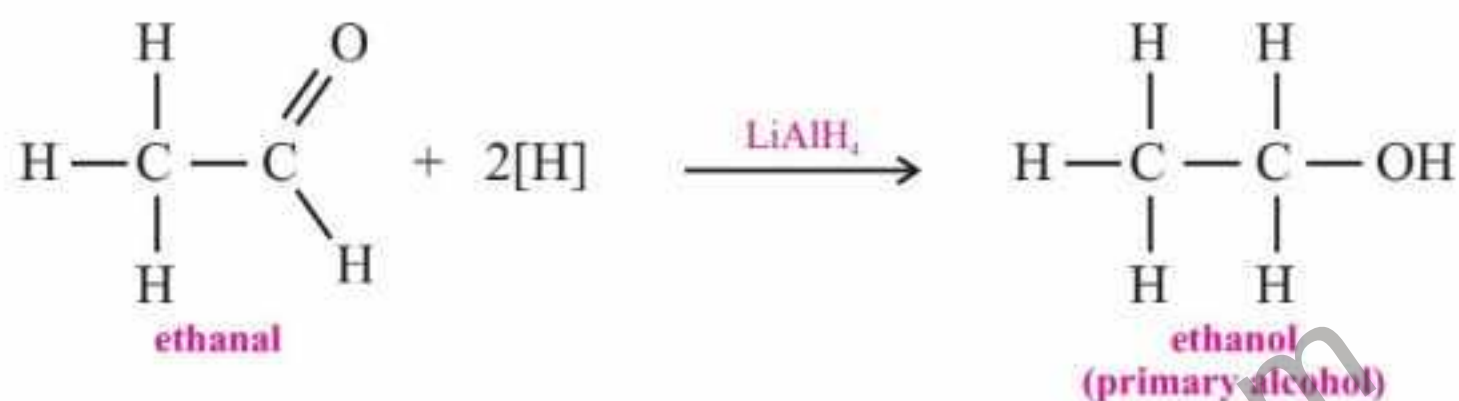


Oxidation of alkenes using cold, dilute KMnO_4 to form a diol

- iii) The halogen atom in halogenoalkanes can be substituted by $-\text{OH}$ group when heated with aqueous NaOH in a nucleophilic substitution reaction, giving an alcohol.



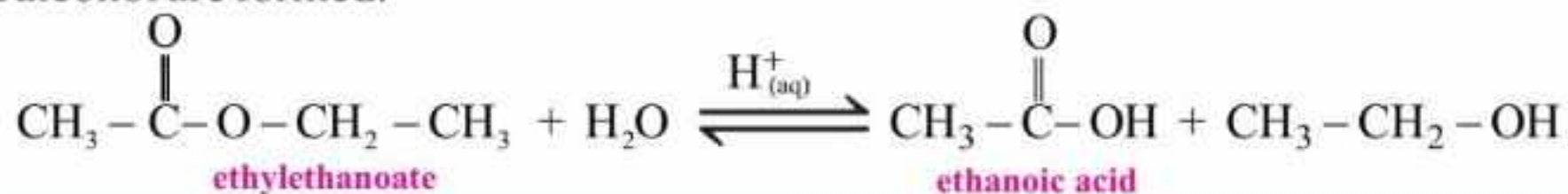
- iv) Aldehydes and ketones can be reduced by reducing agents such as NaBH_4 or LiAlH_4 to obtain alcohols. Aldehydes are reduced to primary alcohols. Ketones are reduced to secondary alcohols.



- v) Similarly, carboxylic acids are reduced by LiAlH_4 to primary alcohols.



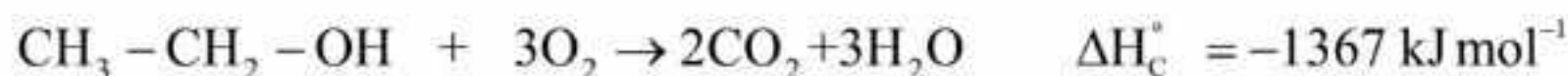
- vi) When an ester is heated with dilute acid or alkali, hydrolysis takes place and a carboxylic acid and alcohol are formed.



22.4 REACTIONS OF ALCOHOLS

1. Combustion of alcohols

Alcohols when ignited, undergo complete combustion to form carbon dioxide and water.

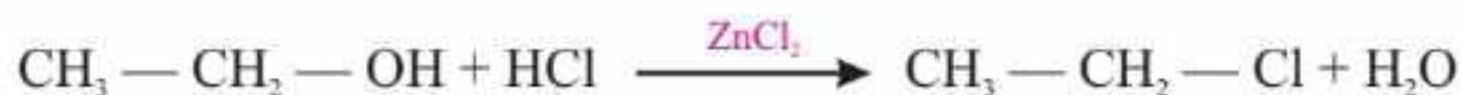


- i) The above reaction is highly exothermic; this is why the alcohol is used as an alternate to petrol in some countries.



ii. Substitution reaction

In the substitution of alcohols, a hydroxy group (-OH) is replaced by another substituent (e.g. halogens) to form a new product (e.g., halogenoalkanes). The substitution of different halogens with the -OH group is given in the following reactions.



Quick Check 22.3



- Write chemical reaction of propan-1-ol with SOCl_2 .
- Differentiate the reaction of PCl_3 and PCl_5 with propan-1-ol with the help of the chemical equations.
- How ethanol reacts with KBr ? give reaction equation.

iii. Reaction with sodium metal

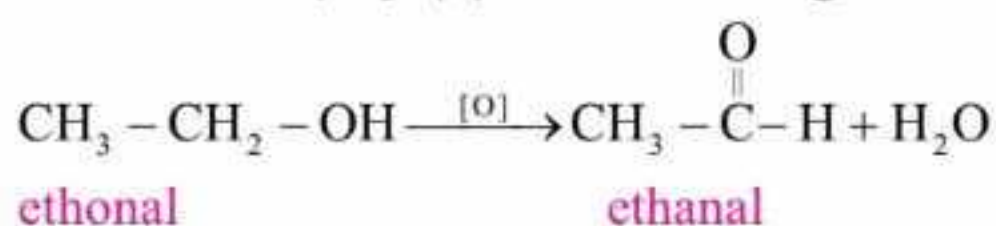
When an alcohol reacts with a reactive metal such as sodium (Na), the oxygen-hydrogen bond in the hydroxyl group breaks. Though the reaction is less vigorous than sodium reacting with water, hydrogen gas is given off and a base (alkoxide) is formed. This reaction can be used as a test for hydroxy (-OH) group. Bubbles of hydrogen gas are released if a hydroxy group is present. If the excess ethanol is evaporated off after the reaction, a white crystalline solid of sodium alkoxide is left. The longer the hydrocarbon chain in the alcohol, the less vigorous the reaction becomes.

When sodium metal is added to a solution of phenolphthalein and ethanol, pink colour is formed slowly. With water, the pink colour appears immediately. It shows that reaction of Na with ethanol is slower than with water.



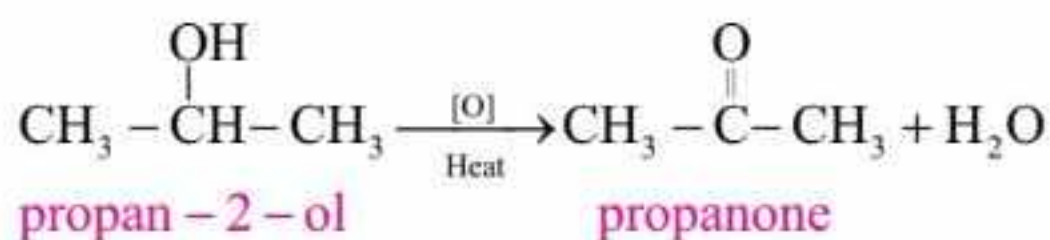
iv. Oxidation of alcohols

Primary alcohols can be oxidised to form aldehydes and the secondary alcohols can be oxidised to form only ketones using oxidizing agents. Tertiary alcohols do not undergo oxidation. The oxidising agents for alcohols include acidified $\text{K}_2\text{Cr}_2\text{O}_7$ and acidified KMnO_4 . Acidified potassium chromate(VI), $\text{K}_2\text{Cr}_2\text{O}_7$, is an orange oxidising agent. When alcohols are oxidised the orange dichromate ions ($\text{Cr}_2\text{O}_7^{2-}$) are reduced to green Cr^{3+} ions.

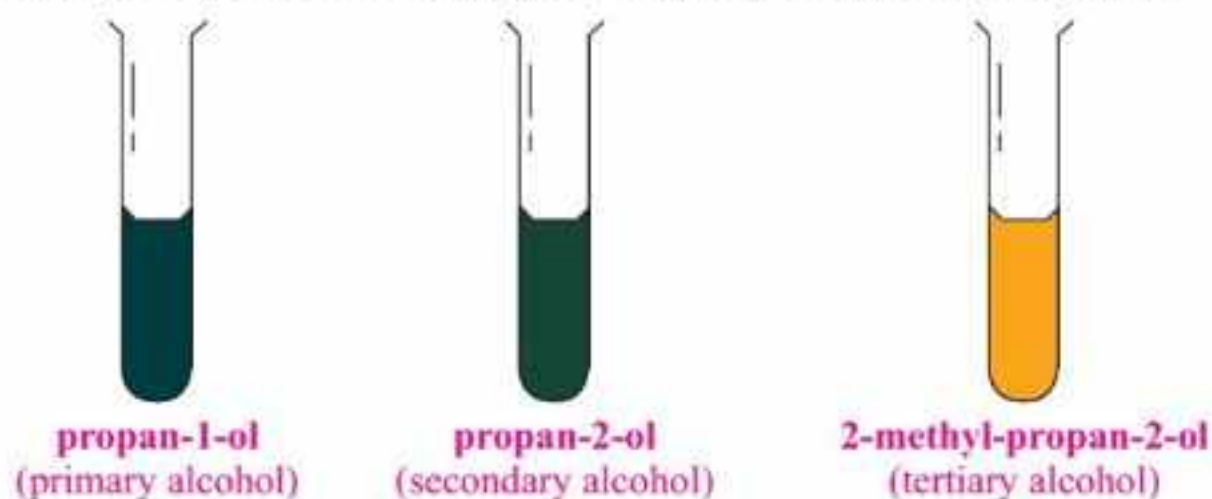


Keep in Mind

For potassium dichromate(VI) to act as an oxidising agent, it must first be reduced. This reduction requires hydrogen (H^+) ions which are provided by the acidic medium.



Therefore, only the oxidation of primary and secondary alcohols will change the colour of acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution as the **orange** $\text{Cr}_2\text{O}_7^{2-}$ ions are reduced to **green** Cr^{3+} ions, which is used to check the presence of primary or secondary alcohol.



Only propan-1-ol and propan-2-ol, which are primary and secondary alcohols respectively, can get oxidised, turning the orange solution green; no colour change is observed with 2-methyl-propan-2-ol, which is a tertiary alcohol.



Interesting Information

Driving after consuming alcohol is very dangerous. A breathalyser is a device that is used by the traffic officers to check if a driver is drunk or not. This device uses the oxidation of ethanol, which requires electrons. The amount of current used is proportional to the amount of alcohol consumed.



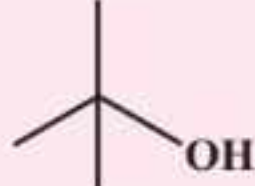
Quick Check 22.4



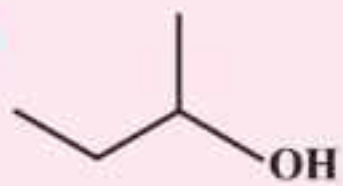
- a) Three alcohols A, B and C are structural isomers of $\text{C}_4\text{H}_{10}\text{O}$. Each alcohol is refluxed with acidified dichromate(VI), $\text{H}^+/\text{Cr}_2\text{O}_7^{2-}$.
- i)



ii)

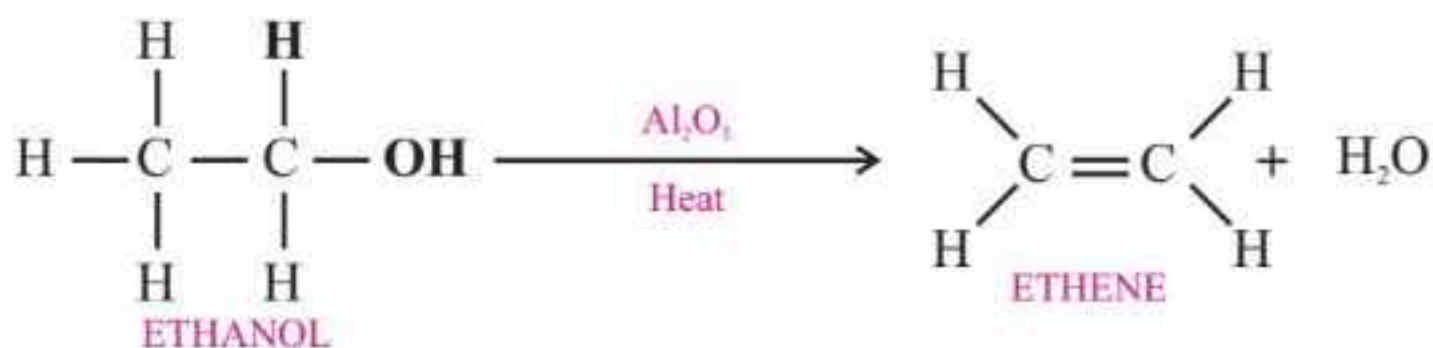


iii)


- Write the systematic name for alcohol C.
 - Write the equation for the complete combustion of alcohol A.
- b) Acidified potassium manganate(VII), KMnO_4 , is a purple oxidising agent. What colour change would you observe when alcohols are oxidised with manganate ions (MnO_4^-).
- c) Draw the structures for the organic products of the oxidation of the following. If there is no reaction, write 'NONE'.

v. Dehydration of alcohols

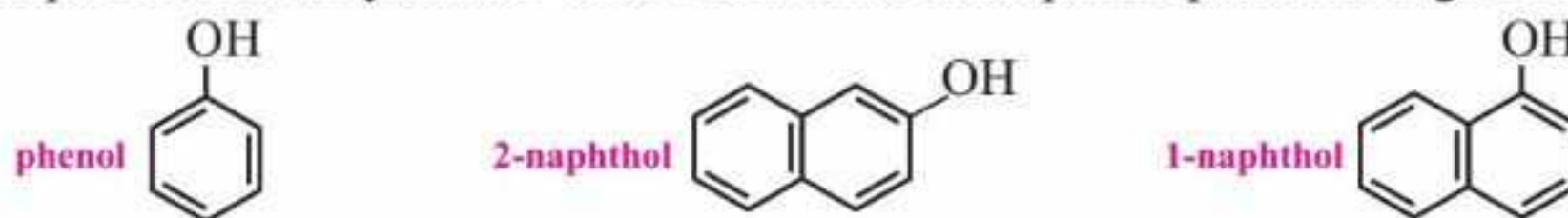
Alcohols can also undergo dehydration to form alkenes. Dehydration is the type of the elimination reaction in which a water molecule is removed.



Dehydrating agents may be aluminium oxide, conc. sulphuric acid, conc phosphoric acid, etc.

22.5 PHENOLS

Compounds in which a hydroxyl group is bonded to an arene called phenols. The chemical formula of the simplest phenol is C_6H_5OH . Phenol is also known as carbolic acid and was used as carbolic soap. Phenol is a crystalline white solid. Some examples of phenols are given below:

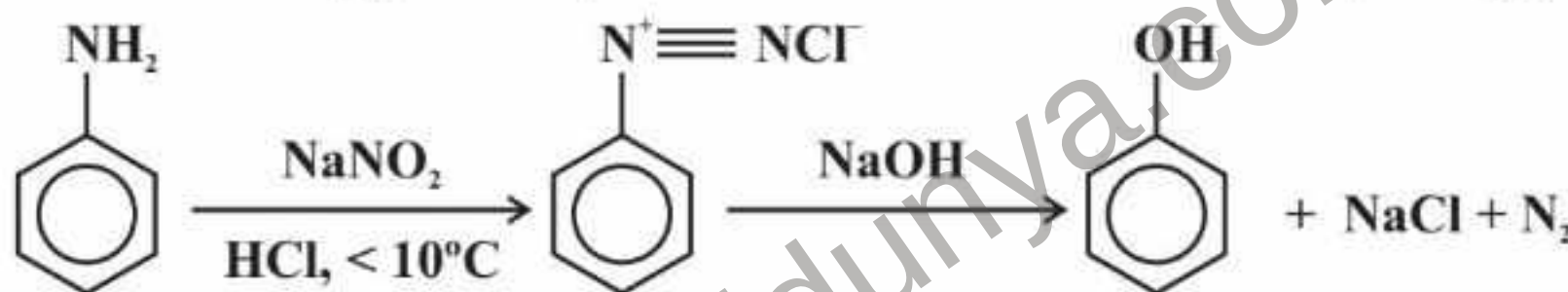


Phenols can be produced by the reaction of phenylamine with nitrous acid (HNO_2). The nitrous acid used here is produced *in situ*. The reaction occurs in three steps.

Step 1 - The HNO_2 is so unstable that it needs to be prepared in a test-tube by reacting sodium nitrite ($NaNO_2$) and dilute hydrochloric acid (HCl) while keeping the temperature below $10^\circ C$ using ice.

Step 2 - Phenylamine is then reacted with the HNO_2 to form an unstable diazonium salt

Step 3 - On further warming, phenol is produced as diazonium salt is decomposed (hydrolysed).



22.6 REACTIONS OF PHENOL

Phenols can undergo many types of reactions as both the electron-rich benzene ring and the polar OH group can participate in chemical reactions. Some of the reactions of phenols are given below.

22.6.1 Reactions of the -OH Group in Phenols

The -OH group in phenols has a slightly acidic character. It can therefore act as an acid and take part in acid-base reactions.

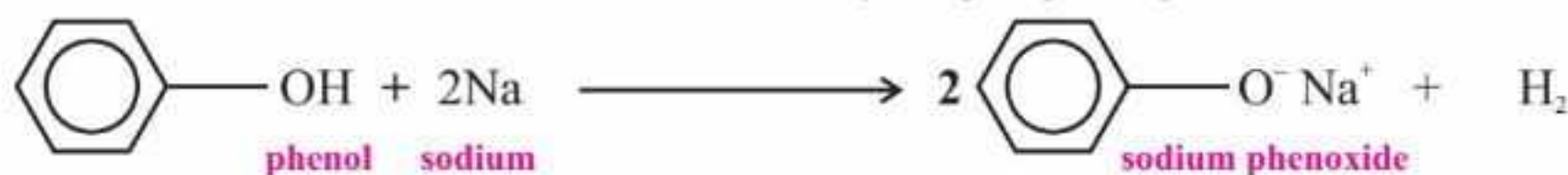
i. Reaction with bases

Phenols are only slightly soluble in water due to the large non-polar benzene ring. However, they do dissolve in alkaline solutions and undergo acid-base reactions with bases to form a soluble salt and water.



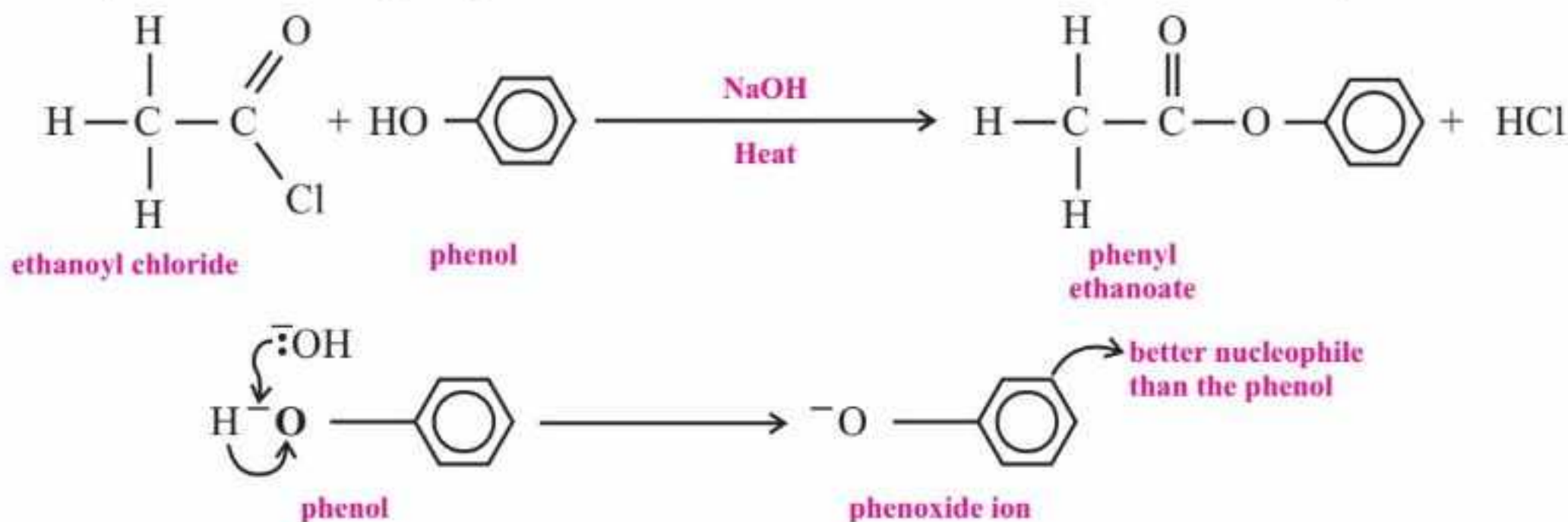
ii. Reaction with reactive metals

Molten phenols react vigorously with reactive metals such as sodium (Na). This is also an acid-base reaction. Now, a soluble salt is formed and hydrogen gas is given off.



iii. Reaction with acyl chloride

When phenol is heated with acyl chloride in the presence of a base, an ether is produced. The base is needed to deprotonate the phenol and form a phenoxide ion. The phenoxide ion is a better nucleophile than the original phenol molecule and will be able to attack the carbonyl carbon.



iv. Reaction with diazonium ions

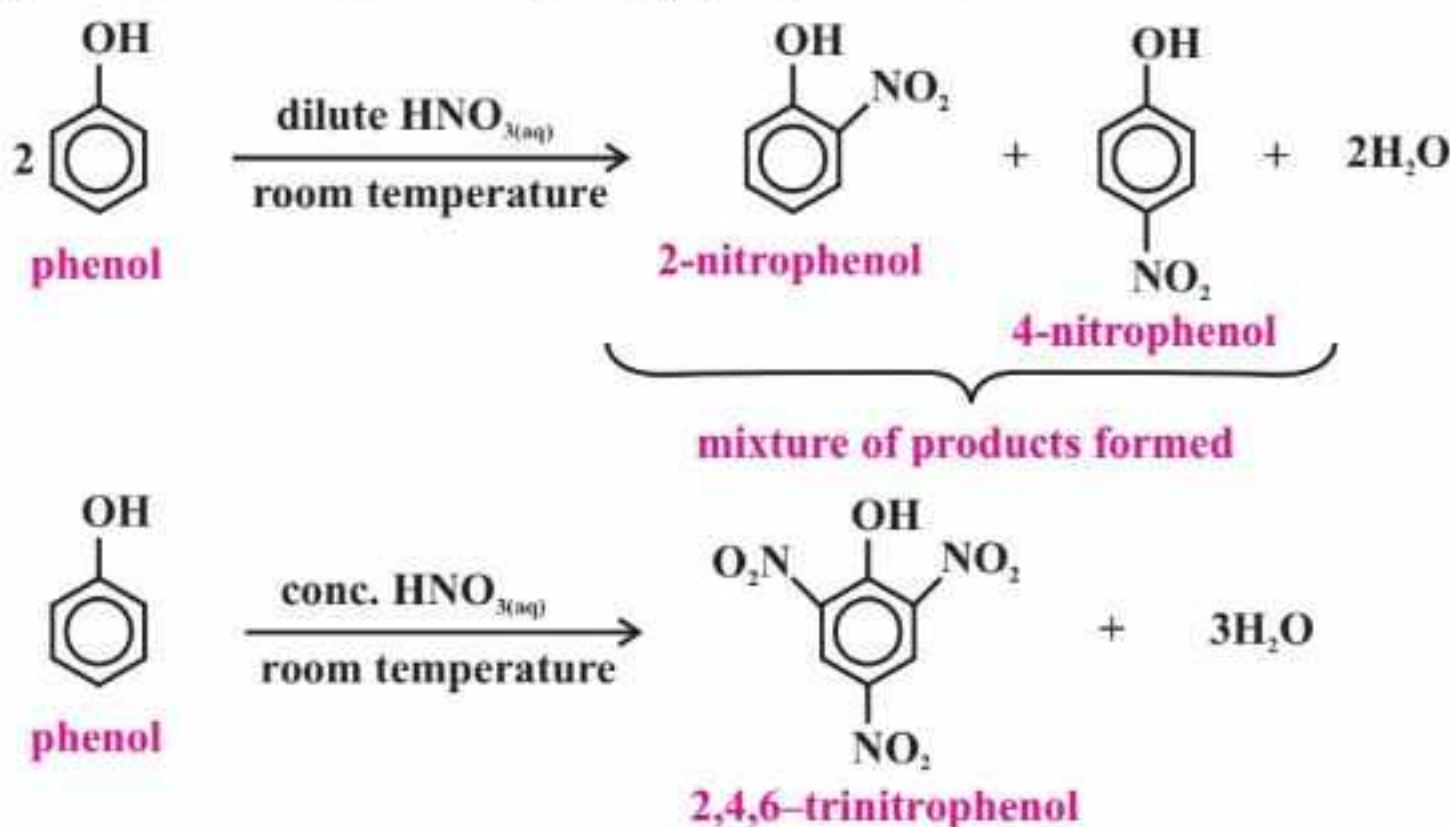
This reaction of phenol will be discussed in Chapter 24 (Organic Nitrogen Compounds).

22.6.2 Reactions of the Aromatic Ring in Phenols

Phenols consist of a hydroxyl (-OH) group attached to a benzene ring. The oxygen atom in this hydroxyl group donates electron density into the ring. One of the lone pairs of the oxygen atom overlaps with the π system of the benzene ring and becomes delocalised, causing an increased electron density in the aromatic ring. Due to the increased electron density, the benzene ring is more likely to undergo electrophilic attack and becomes activated. The incoming electrophiles are directed by the hydroxyl group of phenol to the 2, 4, and 6 positions.

i. Nitration

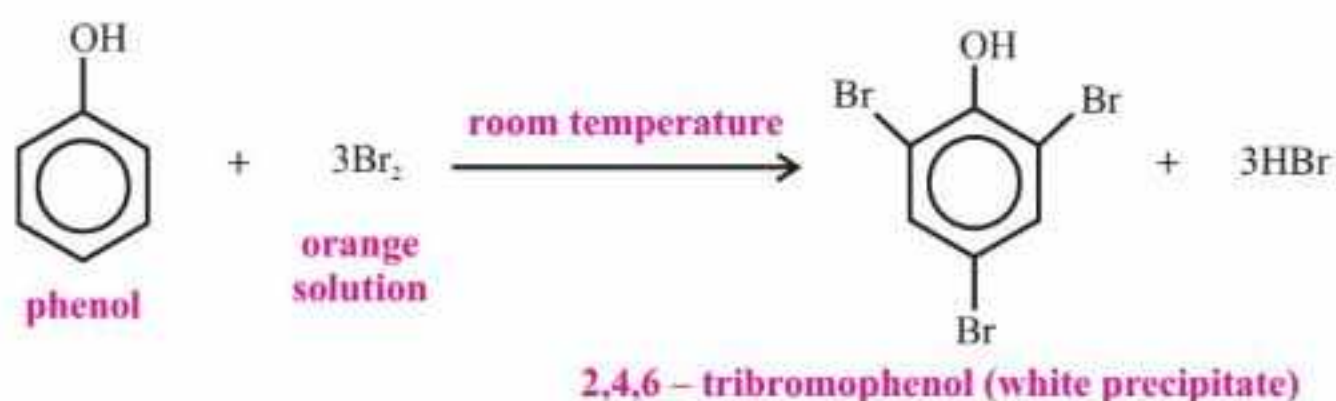
Phenols can undergo electrophilic substitution reactions when reacted with dilute nitric acid (HNO_3) at room temperature to give a mixture of 2-nitrophenol and 4-nitrophenol. When concentrated HNO_3 is used, the product will be 2,4,6-trinitrophenol instead. A hydrogen atom in the benzene ring is substituted by a nitro ($-\text{NO}_2$) group. This is known as the nitration of phenol.



The nitration of benzene requires a mixture of concentrated nitric acid (HNO_3) and sulfuric acid (H_2SO_4) refluxed with benzene between 25°C and 60°C . Since phenol is more reactive, nitration can occur under milder conditions by reacting it with dilute nitric acid at room temperature. If concentrated nitric acid is used, 2,4,6-trinitrophenol is formed.

ii. Bromination

Phenols also undergo electrophilic substitution reactions when reacted with bromine water at room temperature. Phenol decolourises the orange bromine solution to form a white precipitate of 2,4,6-tribromophenol. This is also known as the bromination of phenol.



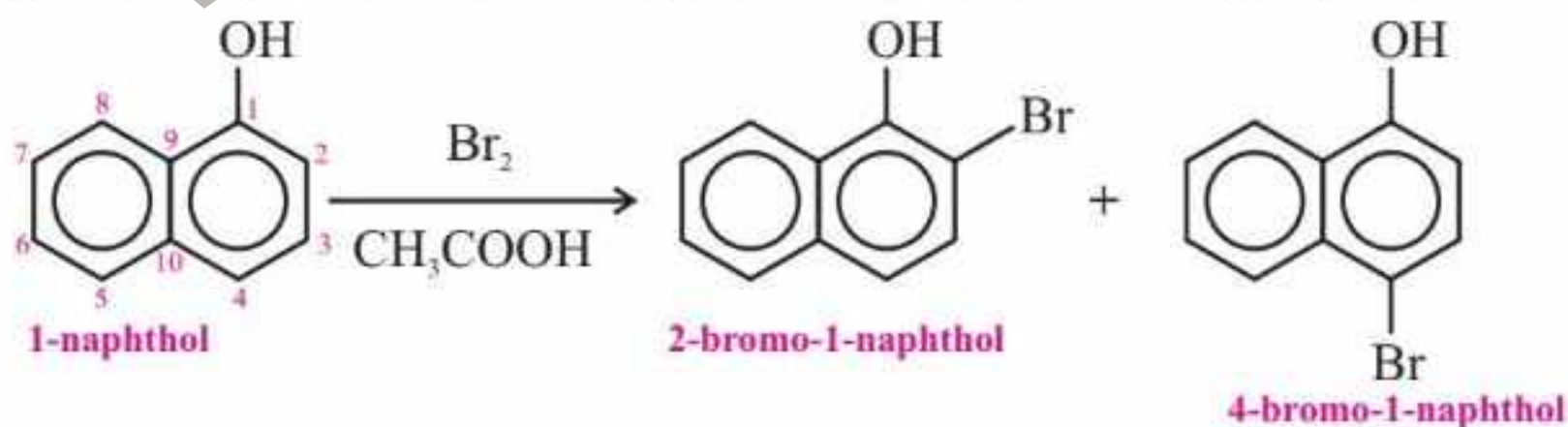
Benzene will undergo bromination only when reacted with pure bromine (not a solution) and in the presence of anhydrous aluminium bromide (AlBr_3) catalyst at room temperature. Phenol on the other hand readily reacts with bromine water in the absence of a catalyst.

There exist many phenolic compounds other than phenol ($\text{C}_6\text{H}_5\text{OH}$). An example of a phenolic compound is 1-naphthol.



1-naphthol is a phenolic compound

1-naphthol contains a hydroxy group attached to position of 1 of naphthalene. Just like with phenol, the $-\text{OH}$ group in 1-naphthol is also electron-donating and activates the naphthalene ring to electrophilic substitution reactions. The electrophiles are directed to the 2 and/or 4 positions. Substitution at the 9 and 10 positions is not possible as there is no hydrogen atom on these carbons. 1-naphthol and other phenolic compounds react in a similar way as phenol.



Quick Check

22.5



- The reaction of phenol with bromine water is used for the identification of phenol. What will be the visual change during the reaction, also give the systematic name of the compound formed.
- Nitration is an example of aromatic electrophilic substitution and its rate depends upon the group already present in the benzene ring. Out of benzene and phenol, which one is more easily nitrated and why?
- Write the reaction equation for nitration of 1-naphthol.

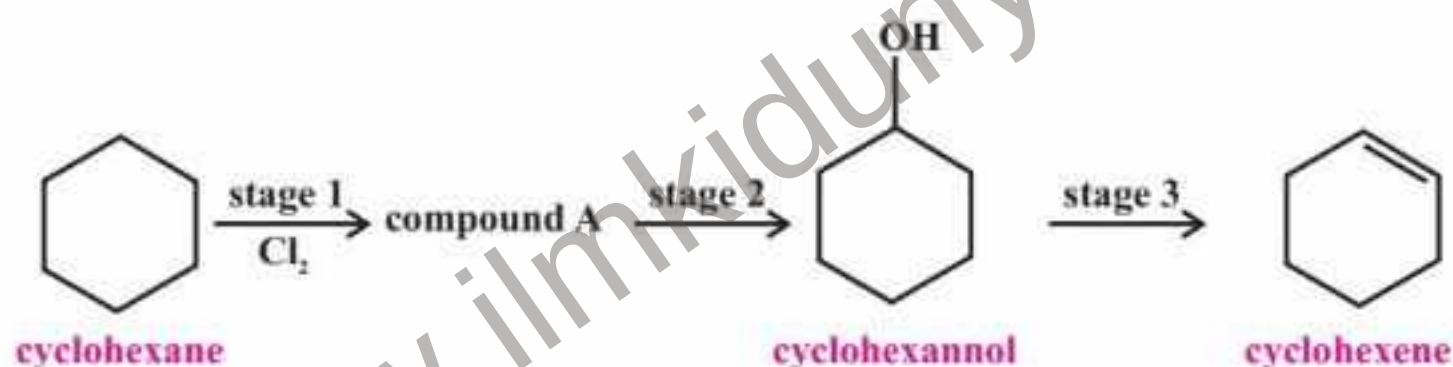
a) Br₂ and NaOH b) SOCl₂

c) Acidified $K_2Cr_2O_7$

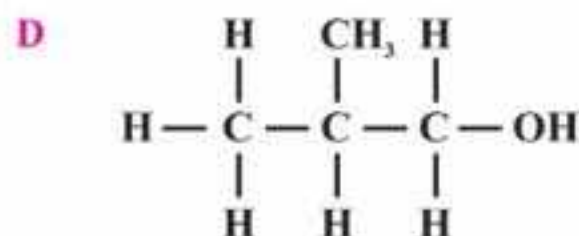
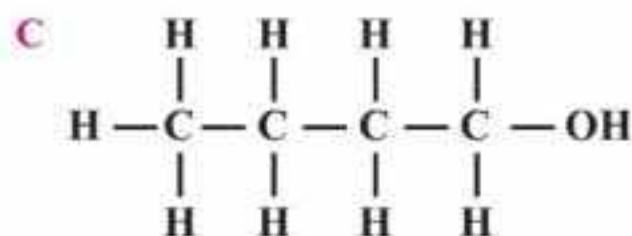
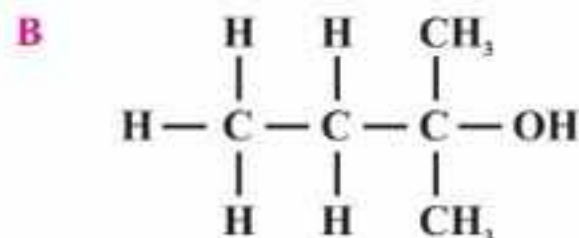
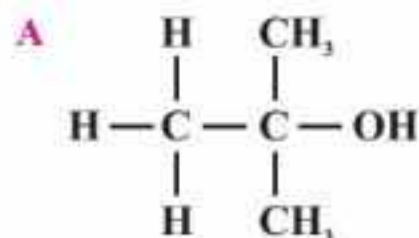
d) $\text{NaOH}_{(\text{aq})}$

Q2. SHORT ANSWER QUESTIONS

- a) Six alcohols are given below:
- | | |
|--------------------------|-------------------------|
| i. butan-2-ol | ii. ethane-1,2-diol |
| iii. 2-methylpentan-3-ol | iv. 2-methylpropan-2-ol |
| v. propan-1-ol | vi. propan-2-ol |
- i) Which alcohol is an example of a tertiary alcohol?
- ii) Which alcohol is an example of an alcohol that can be oxidized to carboxylic acid?.
- iii) Which alcohol is an example of an alcohol that can be oxidized to a ketone?
- v) Which alcohol can't change color of acidified potassium dichromate?
- b) Phenylamine reacts with $\text{HNO}_2(\text{aq})$ at 4°C to form compound P. Compound P reacts with phenol under alkaline conditions at 4°C . The product of this reaction is acidified, forming azo compound Q.
- i) Draw the structure of compound P and Q.
- ii) Circle the azo group on your structure.
- iii) State one use of an azo compound such as Q.
- c) Cyclohexane can be converted into cyclohexene via a three stage synthesis.



- i) In stage 1, cyclohexane reacts with chlorine to form the organic product, compound A.
Show the structure of compound A.
- ii) Stage 3 involves the dehydration of an alcohol. State a suitable reagent for dehydrating an alcohol.
- iii) Write a balanced equation for the dehydration of cyclohexanol, $C_6H_{11}OH$.
- d) There are four structurally isomeric alcohols of molecular formula $C_4H_{10}O$. Graphical formulae of these isomers, labelled A, B, C and D, are shown below.



- i) Identify the type of alcohol represented by A and by B.
 - ii) Give the name of alcohol A.
 - iii) Select one of the alcohols A, B, C or D which will, on oxidation, produce an aldehyde. Give the structural formula of the aldehyde produced by this reaction.
 - iv) All the alcohols A, B, C and D may be readily dehydrated. Explain what is meant by the term dehydration. State the type of compound formed by dehydration of alcohols.
 - v) Suggest suitable reagent(s) and condition(s) for the dehydration of alcohols.
- e) Select one of the alcohols A, B, C or D which, on dehydration, would give a single product. Draw the structural formula of this product.

Q3. CONSTRUCTED RESPONSE QUESTIONS

- I. Why nitration of phenol is easier than benzene. Which product is formed when phenol is nitrated with conc. HNO_3 at room temperature?
- ii. Sodium hydroxide reacts with phenol but not with ethanol. Give reason.
- iii. Give reactions of methanol with SOCl_2 , and PCl_5 .
- iv. How propanol can be converted into propanal?
- v. Write down the reaction for the substitution of each of Cl, Br, and I with $-\text{OH}$ in 2-propanol.
- vi. Construct a reaction for the preparation of nitro-substituted naphthol. Is there produced a single product? Explain.

DESCRIPTIVE QUESTIONS

- Q4. Explain the acidity of phenol.
- Q5. Explain why the reagents and conditions for the nitration and bromination of phenol are different from those for benzene.
- Q6. Describe how phenylamine can be converted into phenol, including reagents and conditions.
- Q7. Explain why ethanol is less acidic than water, but water is less acidic than phenol.

