Course: Chemistry-III (6458)
Semester: Autumn, 2021

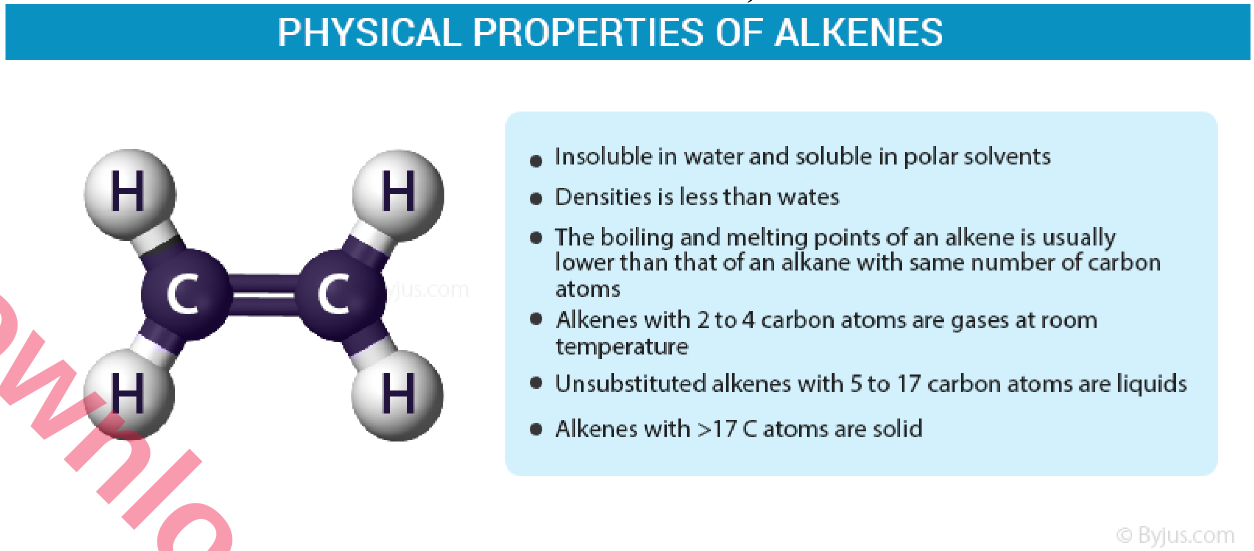
ASSIGNMENT No. 2

Q. 1 Describe the physical properties of alkenes. How these properties do are likened with those of the alkanes?

Alkenes contain a carbon-carbon double bond which changes the physical properties of alkenes. Alkenes are unsaturated carbon compounds which have a general formula of [latex]C_nH_{2n}[/latex]. These compounds are also known as olefins.

Alkenes are a family of compounds containing hydrogen and carbon only (hydrocarbons) with a carbon-carbon double bond. Ethene and Propene are the first two hydrocarbons.

1. Physical State
   - These double-bonded compounds are colourless and odourless in nature.
   - However, ethene is an exception because it is a colourless gas but has a faintly sweet odour.
   - The first three members of the alkene group are gaseous in nature, the next fourteen members are liquids and the remaining alkenes are solids.
2. Solubility
   - The alkenes are insoluble in water due to their nonpolar characteristics.
   - But are completely soluble in nonpolar solvents such as benzene, ligroin, etc.
3. Boiling Point
   - The boiling points of the compounds increase as the number of carbon atoms in the compound increases.
   - When alkenes are compared with alkanes, it is found that the boiling points of both are almost similar, as if the compounds are made up of the same carbon skeleton.
   - The boiling point of straight-chain alkenes is more that branched-chain alkenes just as in alkanes.
4. Melting Point
   - The melting points of these double-bonded compounds depend upon the positioning of the molecules.
   - The melting point of alkenes is similar to that of alkanes.
   - However, cis-isomer molecules have a lower melting point than trans- isomers as the molecules are packed in a U-bending shape.
5. Polarity
   - Alkenes are weakly polar just like alkanes but are slightly more reactive than alkanes due to the presence of double bonds.
   - The π electrons which make up the double bonds can easily be removed or added as they are weakly held.
   - Hence, the dipole moments exhibited by alkenes are more than alkanes.
   - The polarity depends upon the functional group attached to the compounds and the chemical structures.

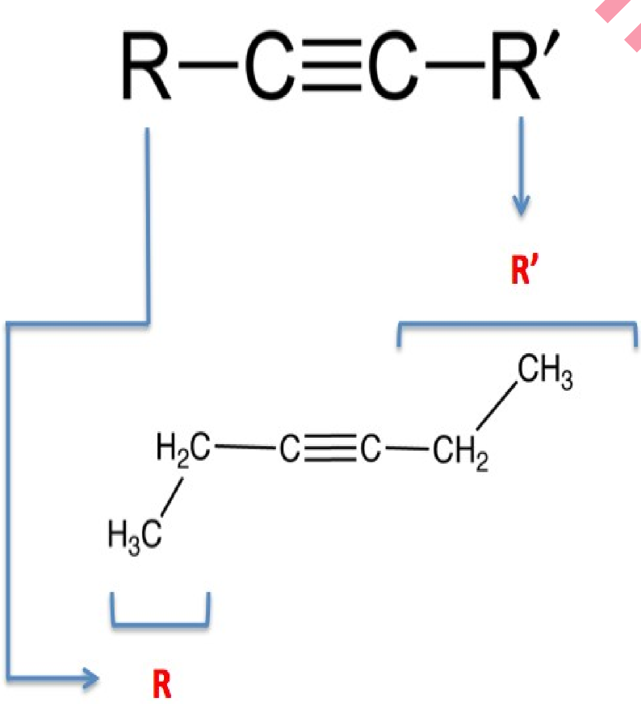


Q. 2 Define alkynes. Discuss the application of alkynes in pharmaceuticals industry and drug formation.

Alkynes are hydrocarbons, which are organic chemical compounds containing carbon (C) and hydrogen (H) atoms, and the feature that makes them recognized as alkynes is the presence of triple bonds.

Chemical compounds that have triple and double bonds in their chemical structures are referred to as **unsaturated**. Because alkynes have triple bonds in their chemical structure and consist of carbon and hydrogen atoms, they are **unsaturated hydrocarbons**.

Here we can see the general chemical structure of alkynes (RCCR'):



General Formula of Alkynes and Example

The carbon (C) atoms shown below are bonded together by a triple bond. We can also see two side groups, R and R', which are bonded to the carbon (C) atoms. The side groups R and R' could be any group that consist of hydrogen and/or carbon atoms. In this example of an alkyne, there is a triple bond between two carbon (C) atoms and the side groups R and R' are both -CH sub 2CH sub 3.

Properties of Alkynes

What do alkynes physically look like? Are they usually solids, liquids, or gases? In general, alkynes are in gaseous form and they are soluble in organic solvents, like benzene and acetone. They are, however, insoluble in water. Another property of an alkyne is that, if you try to burn it, the flame results will turn out to be a sooty flame.

Let's compare the acidity and boiling point of alkynes to the other hydrocarbons, alkenes (hydrocarbons that have double bonds) and alkanes (hydrocarbons that are only made of single bonds). In general, alkynes are more acidic than alkenes and alkanes, and the boiling point of alkynes also tends to be slightly higher than alkenes and alkanes.

Alkynes have various industrial applications. Let's take a look at a few examples of common alkynes and what they are used for.

Acetylene, also referred to as ethyne, is one of the most well-known and widely used alkynes. Acetylene is very useful because it can undergo several chemical reactions that are needed in manufacturing products in different industries.

Let's think about plastic. We use plastic products for so many things, and plastic is made using a compound called polyethylene. Acetylene is an important raw material in the chemical industry to produce polyethyelene. Have you ever heard of an acetylene torch? This type of torch is used to cut and weld steel, and it uses acetylene as fuel.

Another alkyne is propyne, also known as methylacetylene, which is commonly used as a substitute for acetylene as fuel for welding torches. It is also being investigated as possible fuel for rockets in spacecraft.

Uses of Alkynes

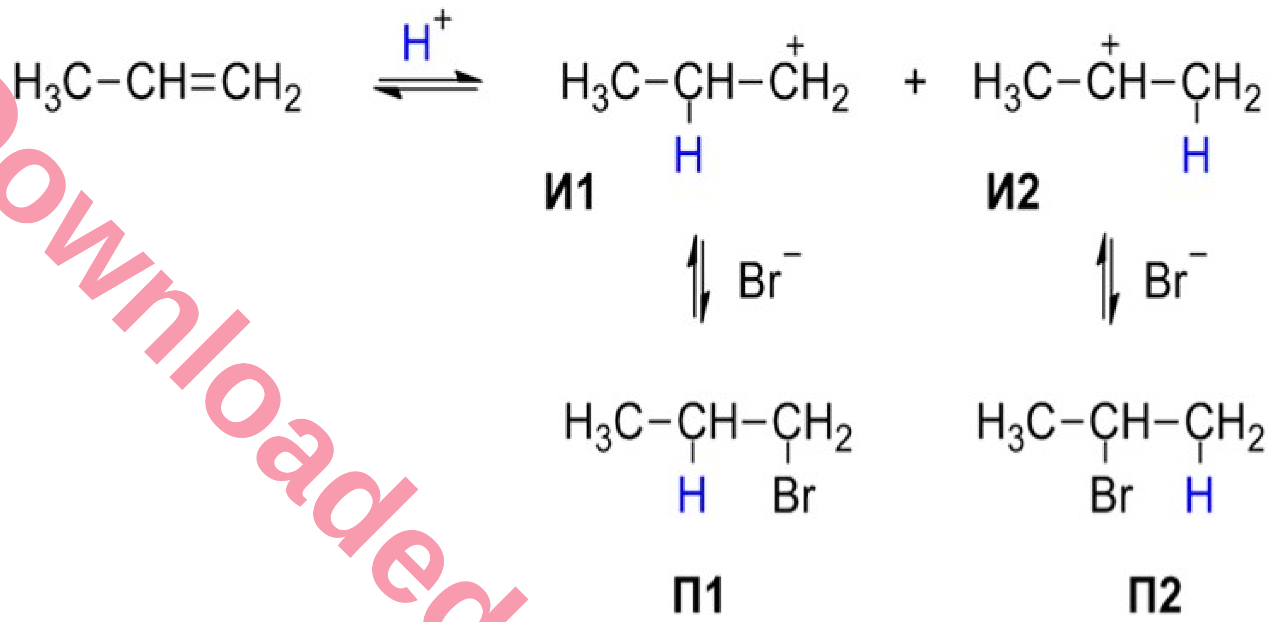
The most common form of alkynes Ethyne is used in preparing many other compounds. Some of these uses are as follows:

- The most common use of Ethyne is for making organic compounds like ethanol, ethanoic acid, acrylic acid, etc.
- It is also used for making polymers and its beginning materials. For instance, vinyl chloride is used as the starting material for PVC and chloroprene is used for synthetic rubber neoprene.
- Ethyne is used for preparing many organic solvents.
- Alkynes are commonly used to artificially ripe fruits.

Q. 3 Discuss elimination mechanism, orientation of double bond and reactivity with reference to alkyl halides.

Preparation of Alkyl Halides

1. Preparation of Alkyl Halides from Alkenes



Preparation of alkyl halides from alkenes

The addition of hydrogen halides to alkenes follows either Markovnikov's rule or exhibit Kharash effect. All the electrophilic addition reactions of alkenes following Markovnikov rule are known as Markovnikov addition reactions. A general example of such reaction is given below:

2. Preparation of Alkyl Halides from Alcohols

Alkyl halides can easily be prepared from alcohols upon the addition of halides. In this reaction the hydroxyl group of alcohol is replaced with the halogen atom attached to the other compound involved. This reaction requires a catalyst for primary and secondary alcohols whereas it doesn't require any catalyst for tertiary alcohols.

$$CH_3CH_2OH + SOCl_2 \xrightarrow{\Delta} CH_3CH_2Cl + SO_2 + HCl$$

$$CH_3CH_2OH + PCl_3 \xrightarrow{\Delta} CH_3CH_2Cl + P(OH)_3 + HCl$$

$$CH_3CH_2OH + PCl_5 \xrightarrow{\Delta} CH_3CH_2Cl + POCl_3 + HCl$$

$$CH_3CH_2OH + PBr_3 \xrightarrow{\Delta} CH_3CH_2Br + P(OH)_3 + HBr$$

Preparation of alkyl halides from alcohols

3. Preparation of Alkyl Halides by Free Radical Halogenation

A complex mixture of isomeric mono- and polyhaloalkanes upon free radical chlorination or bromination of alkanes.

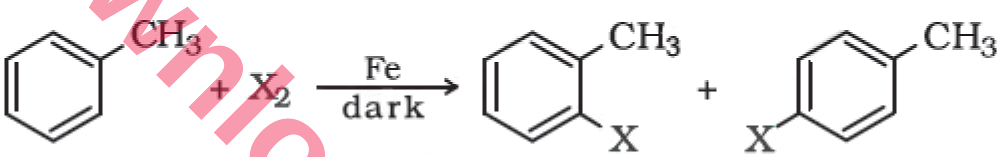
$$CH_3CH_2CH_2CH_3 \xrightarrow{Cl_2/UVlight} CH_3CH_2CHCl\,CH_3 + CH_3CH_2CH_2CH_2Cl$$

Preparation of Alkyl Halides via Free Radical Halogenation

Preparation of Aryl Halides

1. Preparation of Aryl Halides via Electrophilic Substitution Reactions

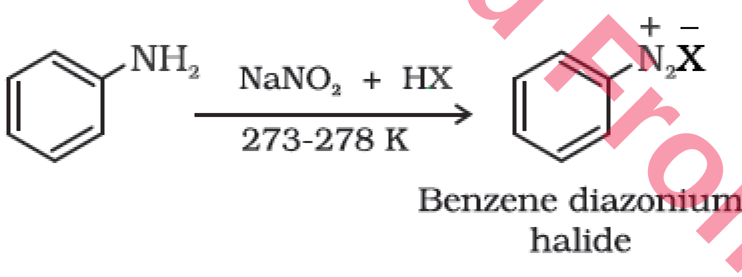
Aryl halides can be prepared by electrophilic aromatic substitution of arenes with halogens in the presence of a Lewis acid.

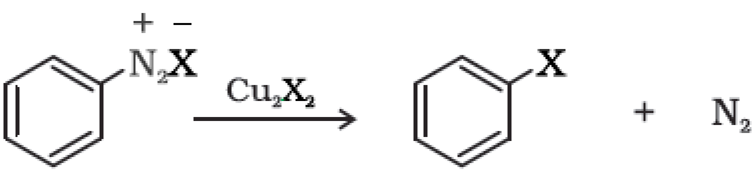


Preparation of aryl halides via electrophilic substitution reactions

2. Preparation of Aryl Halides through Sandmeyer's Reaction

Aryl halides can also be prepared by mixing the solution of freshly prepared diazonium salt from the primary aromatic amine with cuprous chloride or cuprous bromide.





Preparation of aryl halides through Sandmeyer's reaction

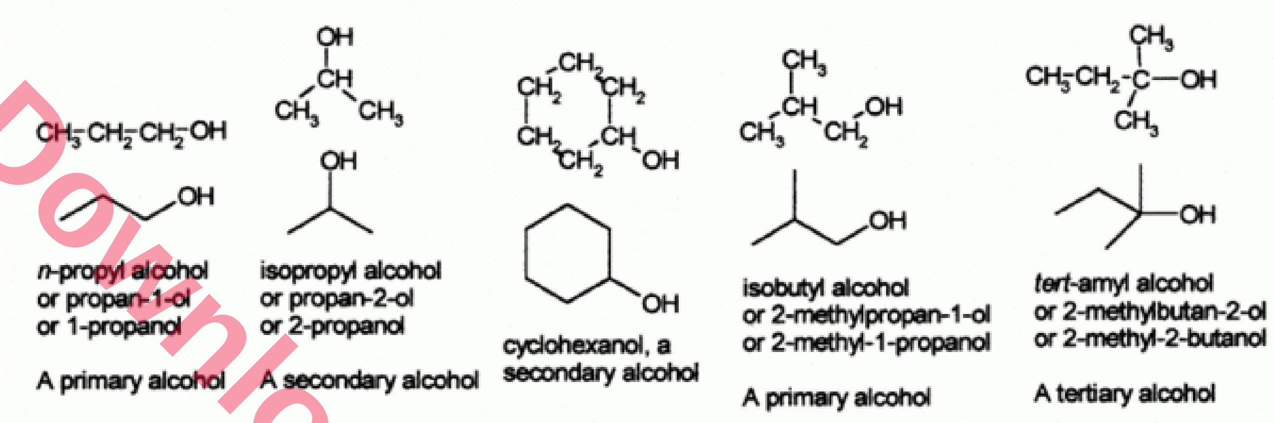
Q. 4 discuss the concept of the physical nature of Aromatic Hydrocarbon.

Functional groups refer to specific atoms bonded in a certain arrangement that give a compound certain physical and chemical properties.

In organic chemistry, a functional group is a specific group of atoms or bonds within a compound that is responsible for the characteristic chemical reactions of that compound. The same functional group will behave in a similar fashion, by undergoing similar reactions, regardless of the compound of which it is a part. Functional groups also play an important part in organic compound nomenclature; combining the names of the functional groups with the names of the parent alkanes provides a way to distinguish compounds.

The atoms of a functional group are linked together and to the rest of the compound by covalent bonds. The first carbon atom that attaches to the functional group is referred to as the alpha carbon; the second, the beta carbon;

the third, the gamma carbon, etc. Similarly, a functional group can be referred to as primary, secondary, or tertiary, depending on if it is attached to one, two, or three carbon atoms.



Classification of alcohols: Alcohols are a common functional group (-OH). They can be classified as primary, secondary, or tertiary, depending on how many carbon atoms the central carbon is attached to.

Functional Groups and Reactivity

Functional groups play a significant role in directing and controlling organic reactions. Alkyl chains are often nonreactive, and the direction of site-specific reactions is difficult; unsaturated alkyl chains with the presence of functional groups allow for higher reactivity and specificity. Often, compounds are functionalized with specific groups for a specific chemical reaction. Functionalization refers to the addition of functional groups to a compound by chemical synthesis. Through routine synthesis methods, any kind of organic compound can be attached to the surface. In materials science, functionalization is employed to achieve desired surface properties; functional groups can also be used to covalently link functional molecules to the surfaces of chemical devices.

In organic chemistry, the most common functional groups are carbonyls (C=O), alcohols (-OH), carboxylic acids (CO_2H), esters (CO_2R), and amines (NH_2). It is important to be able to recognize the functional groups and the physical and chemical properties that they afford compounds.

Organic chemistry functional groups lesson: This video provides a great overview of the various functional groups in organic chemistry.

Alcohols

Alcohols are functional groups characterized by the presence of an -OH group.

Alcohols are organic compounds in which the hydroxyl functional group (-OH) is bound to a carbon atom. Alcohols are an important class of molecules with many scientific, medical, and industrial uses.

Nomenclature of Alcohols

According to the IUPAC nomenclature system, an alcohol is named by dropping the terminal "-e" of the parent carbon chain (alkane, alkene, or alkyne in most cases) and the addition of "-ol" as the ending. If the location of the hydroxyl group must be specified, a number is inserted between the parent alkane name and the "-ol" (propan-1-ol) or before the IUPAC name (1-propanol). If a higher priority group is present, such as an aldehyde, ketone or carboxylic acid, then it is necessary to use the prefix "hydroxy-" instead of the ending "-ol."

Alcohols are classified as primary, secondary, or tertiary, based upon the number of carbon atoms connected to the carbon atom that bears the hydroxyl group.

Structure and Physical Properties of Alcohols

The structure of an alcohol is similar to that of water, as it has a bent shape. This geometrical arrangement reflects the effect of electron repulsion and the increasing steric bulk of the substituents on the central oxygen atom. Like water, alcohols are polar, containing an unsymmetrical distribution of charge between the oxygen and hydrogen atoms. The high electronegativity of the oxygen compared to carbon leads to the shortening and strengthening of the -OH bond. The presence of the -OH groups allows for hydrogen bonding with other -OH groups, hydrogen atoms, and other molecules. Since alcohols are able to hydrogen bond, their boiling points are higher than those of their parent molecules.

Alcohols are able to participate in many chemical reactions. They often undergo deprotonation in the presence of a strong base. This weak acid behavior results in the formation in an alkoxide salt and a water molecule. Hydroxyl groups alone are not considered good leaving groups. Often, their participation in nucleophilic substitution reactions is instigated by the protonation of the oxygen atom, leading to the formation a water moiety—a better leaving group. Alcohols can react with carboxylic acids to form an ester, and they can be oxidized to aldehydes or carboxylic acids.

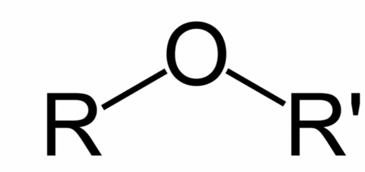
Alcohols have many uses in our everyday world. They are found in beverages, antifreeze, antiseptics, and fuels. They can be used as preservatives for specimens in science, and they can be used in industry as reagents and solvents because they display an ability to dissolve both polar and non-polar substances.

Ethers

Ethers are a class of organic compounds characterized by an oxygen atom connected to two alkyl or aryl groups.

Structure of Ethers

Ethers are a class of organic compounds that contain an ether group. An ether group is an oxygen atom connected to two alkyl or aryl groups. They follow the general formula R-O-R'. The C-O-C linkage is characterized by bond angles of 104.5 degrees, with the C-O distances being about 140 pm. The oxygen of the ether is more electronegative than the carbons. Thus, the alpha hydrogens are more acidic than in regular hydrocarbon chains.



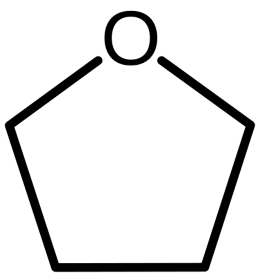
Ethers: The general structure of an ether. An ether is characterized by an oxygen bonded to two alkyl or aryl groups, represented here by R and R'. The substituents can be, but do not need to be, the same.

Nomenclature of Ethers

There are two ways to name ethers. The most common way is to identify the alkyl groups on either side of the oxygen atom in alphabetical order, then write "ether." For example, ethyl methyl ether is the ether that has an ethyl group and a methyl group on either side of the oxygen atom. If the two alkyl groups are identical, the ether is called di[alkyl] ether. For example, diethyl ether is the ether with an ethyl group on each side of the oxygen atom.

The other way of naming ethers is the formal, IUPAC method. This way, the form is: [short alkyl chain][oxy] [long alkyl chain]. For example, the IUPAC name for ethyl methyl ether would be methoxyethane.

In cyclic ethers, the stem of the compound is known as a oxacycloalkane. The "oxa" is an indicator of the replacement of the carbon by an oxygen in the ring. An example is oxacyclopentane, a five-membered ring in which there are four carbon atoms and one oxygen atom.



Tetrahydrofuran (THF): The common name of the cyclic ether "oxacyclopentane" is tetrahydrofuran, or THF. It is a common organic solvent that is miscible with water.

Properties of Ethers

Ethers are rather nonpolar due to the presence of an alkyl group on either side of the central oxygen. The presence of the bulky alkyl groups that are adjacent to it means that the oxygen atom is largely unable to participate in hydrogen bonding. Ethers, therefore, have lower boiling points compared to alcohols of similar molecular weight. However, as the alkyl chain of the ethers becomes longer, the difference in boiling points becomes smaller. This is due to the effect of increased Van der Waals interactions as the number of carbons increases, and therefore the number of electrons increases as well. The two lone pairs of electrons present on the oxygen atoms make it possible for ethers to form hydrogen bonds with water. Ethers are more polar than alkenes, but not as polar as esters, alcohols or amides of comparable structures.

Reactions

Ethers have relatively low chemical reactivity, but they are still more reactive than alkanes. Although they resist undergoing hydrolysis, they are often cleaved by acids, which results in the formation of an alkyl halide and an alcohol. Ethers tend to form peroxides in the presence of oxygen or air. The general formula is R-O-O-R'. Ethers can serve as Lewis and Bronsted bases, serving to donate electrons in reactions, or accept protons. Ethers can be formed in the laboratory through the dehydration of alcohols (2R-OH → R-O-R + H_2O at high temperature), nucleophilic displacement of alkyl halides by alkoxides (R-ONa + R'-X → R-O-R' + NaX), or electrophilic addition of alcohols to alkenes ($R_2C=CR_2$ + R-OH → $R_2CH-C(-O-R)-R_2$).

Q. 5 Explain the halogenation, alkylation, acylation and sulphonation reaction in phenol.

Electrophilic aromatic substitution reactions are the reactions where an electrophile replaces one or more hydrogen atoms attached to the aromatic ring. Phenols are highly prone to electrophilic substitution reactions due to rich electron density.

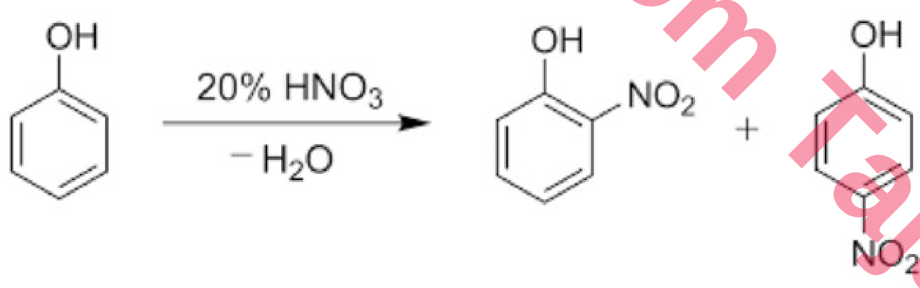
The hydroxyl group attached to the aromatic ring in phenol facilitates the effective delocalization of the charge in the aromatic ring. Thus, it stabilizes the arenium ion through resonance. The **hydroxyl group also acts as ortho para directors.** Hence, we acknowledge most of these substitutions at ortho and para positions only.

Some of the electrophilic substitution reactions of phenols are explained below:

1. Nitration of Phenols

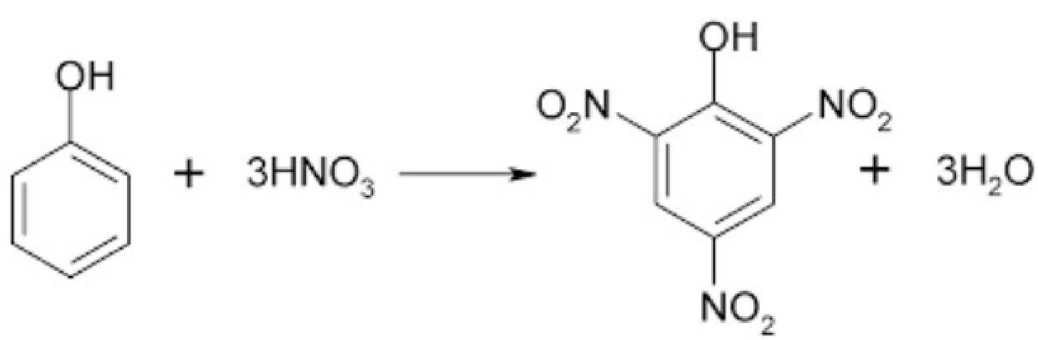
Phenols upon treatment with dilute nitric acid undergo nitration at low temperature (298 K) to give a mixture of ortho and para nitrophenols. The mixture formed is further separated into ortho and para nitrophenols by steam distillation on the basis of their volatility.

Due to intramolecular and intermolecular hydrogen bonding, ortho nitrophenols are lesser volatile in comparison to para nitrophenols which involves only intermolecular hydrogen bonding.



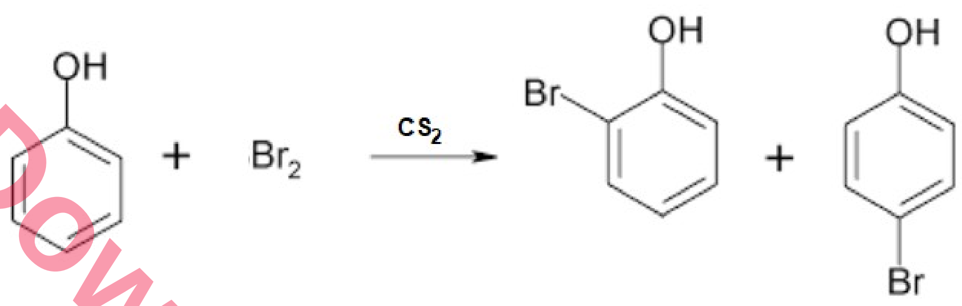
Nitration of Phenols

When phenol is treated with concentrated nitric acid, the nitration results in the formation of 2, 4, 6-trinitrophenol (commonly called picric acid).



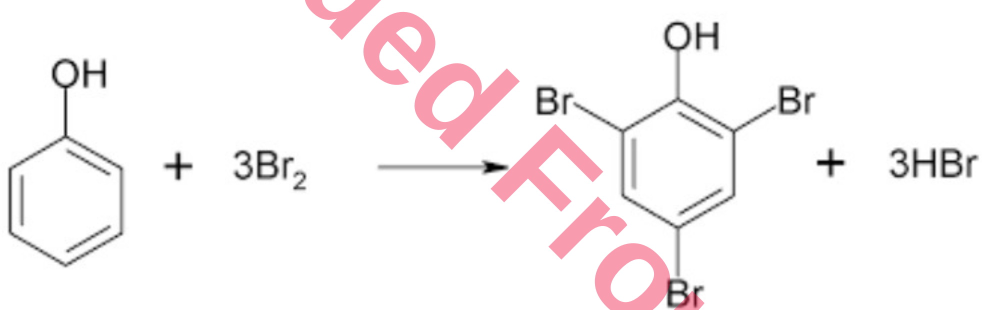
Formation of 2, 4, 6-trinitrophenol

2. Halogenation of Phenols



Due to a highly activating effect of the hydroxyl group in phenols, they undergo halogenation even in the absence of Lewis acids. When phenols are treated with bromine in the presence of a solvent of low polarity like $CHCl_3$ at low temperatures, monobromophenols are formed.

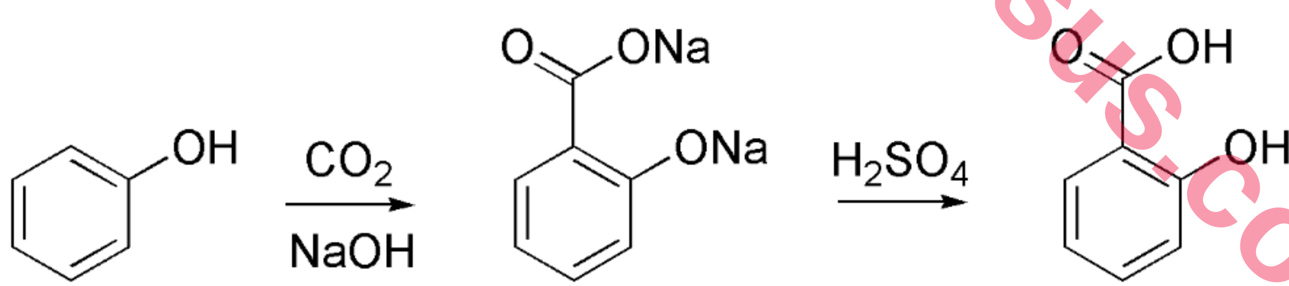
When phenol is treated with bromine water, a white precipitate of 2, 4, 6-tribromophenol is formed.



Formation of 2, 4, 6-tribromophenol

3. Kolbe's Reaction

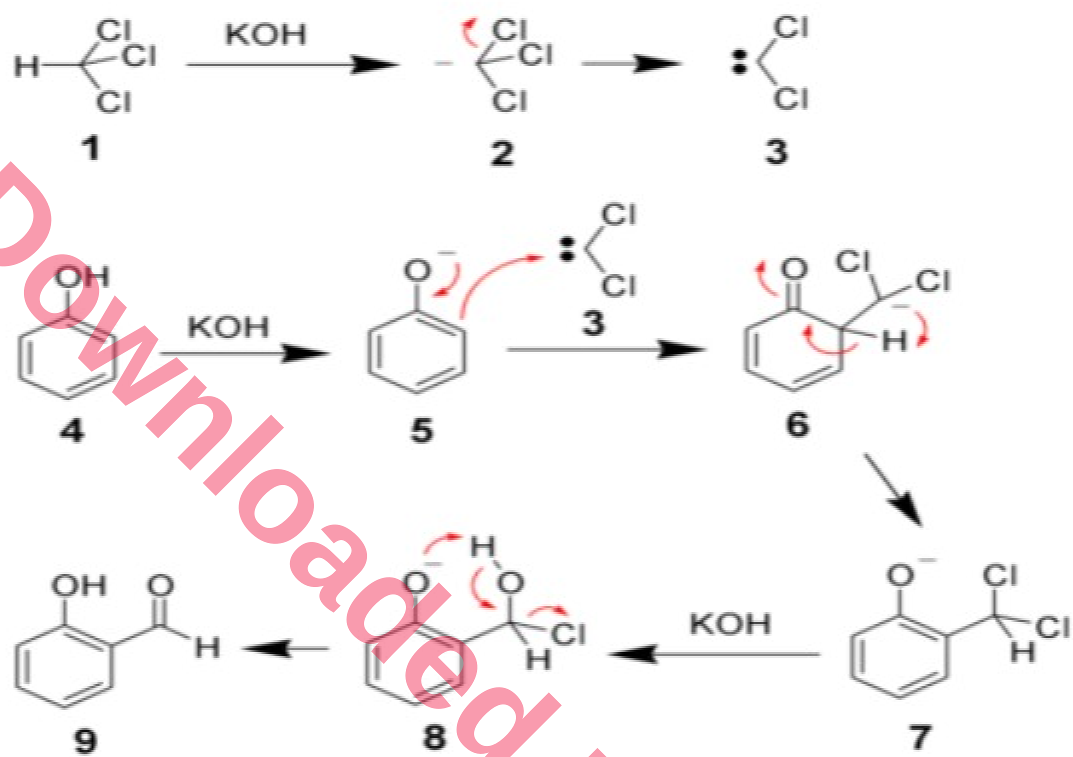
When phenol is treated with sodium hydroxide, phenoxide ion is formed. This phenoxide ion formed is highly reactive towards electrophilic substitution reactions. Upon treatment with a weak electrophile (carbon dioxide), it undergoes electrophilic substitution reaction to form Ortho-hydroxybenzoic acid. This reaction is popularly known as Kolbe's reaction.



Kolbe's Reaction

4. Reimer-Tiemann Reaction

When phenol is treated with chloroform in the presence of sodium hydroxide, an aldehyde group is formed at the ortho position of the benzene ring. This reaction is popularly known as the Reimer-Tiemann reaction.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