

Major Concepts

- 16.1 Hydrocarbons
- 16.2 Alkanes and Cycloalkanes
- 16.3 Radical Substitution Reactions
- 16.4 Oxidation of Organic Compounds
- 16.5 Alkenes
- 16.6 Isomerism
- 16.7 Alkynes
- 16.8 Addition Reactions of Alkynes
- 16.9 Benzenes and Substituted Benzenes

Learning Outcomes:

Students will be able to:

- Classify hydrocarbons as aliphatic and aromatic. (**Understanding**)
- Describe nomenclature of alkanes and cycloalkanes. (**Understanding**)
- Explain the shapes of alkanes and cycloalkanes exemplified by ethane and cyclopropane. (**Applying**)
- Explain unreactive nature of alkanes towards polar reagents. (**Applying**)
- Define homolytic and heterolytic fission, free radical initiation, propagation and termination. (**Remembering**)
- Describe the mechanism of free radical substitution in alkanes exemplified by methane and ethane. (**Understanding**)
- Identify organic redox reactions. (**Understanding**)
- Explain what is meant by a chiral centre and show that such a centre gives rise to optical isomerism. (**Understanding**)
- Identify chiral centers in given structural formula of a molecule. (**Analyzing**)
- Explain the nomenclature of alkenes. (**Understanding**)
- Explain shape of ethene molecule in terms of sigma and pi C—C bonds. (**Understanding**)
- Describe the structure and reactivity of alkenes as exemplified by ethene. (**Applying**)
- Define and explain with suitable examples the terms isomerism, stereoisomerism and structural isomerism. (**Remembering**)
- Explain dehydration of alcohols and dehydrohalogenation of RX for the preparation of ethene. (**Understanding**)
- Describe the chemistry of alkenes by the following reactions of ethene: Hydrogenation, hydrohalogenation, hydration, halogenation, halohydration,

- epoxidation, ozonolysis, polymerization. (**Understanding**)
- Explain the concept of conjugation in alkenes having alternate double bonds. (**Understanding**)
 - Use the IUPAC naming system for alkenes. (**Applying**)
 - Explain the shape of benzene molecule (molecular orbital aspect). (**Understanding**)
 - Define resonance, resonance energy and relative stability. (**Understanding**)
 - Compare the reactivity of benzene with alkanes and alkenes. (**Applying**)
 - Describe what is meant by the term delocalized electrons in the context of the benzene ring. (**Understanding**)
 - Describe addition reactions of benzene and methyl benzene. (**Applying**)
 - Describe the mechanism of electrophilic substitution in benzene. (**Understanding**)
 - Discuss chemistry of benzene and methyl benzene by nitration, sulphonation, halogenation, Friedal Craft's alkylation and acylation. (**Applying**)
 - Apply the knowledge of positions of substituents in the electrophilic substitution of benzene. (**Applying**)
 - Use the IUPAC naming system for alkynes. (**Applying**)
 - Compare the reactivity of alkynes with alkanes, alkenes and arenes. (**Analyzing**)
 - Discuss the shape of alkynes in terms of sigma and pi C-C bonds. (**Applying**)
 - Describe the preparation of alkynes using elimination reactions. (**Applying**)
 - Describe acidity of alkynes. (**Understanding**)
 - Discuss chemistry of alkynes by hydrogenation, hydrohalogenation, hydration, bromination, ozonolysis, and reaction with metals. (**Understanding**)
 - Describe and differentiate between substitution and addition reactions. (**Understanding**)
 - Explain isomerism in alkanes, alkenes, alkynes and substituted benzene. (**Understanding**)

Introduction

Hydrocarbons are the simplest organic compounds composed of only carbon and hydrogen atoms. The carbon and hydrogen atoms are bonded to each other by covalent bonds. Examples are: methane (CH_4), ethylene (C_2H_4), acetylene (C_2H_2), benzene (C_6H_6) etc. Hydrocarbons are further classified as aliphatic or aromatic hydrocarbons depending on the presence of benzene ring.

16.1 Types of Hydrocarbons

There are two types of hydrocarbons:

- Aliphatic hydrocarbons and
- Aromatic hydrocarbons.

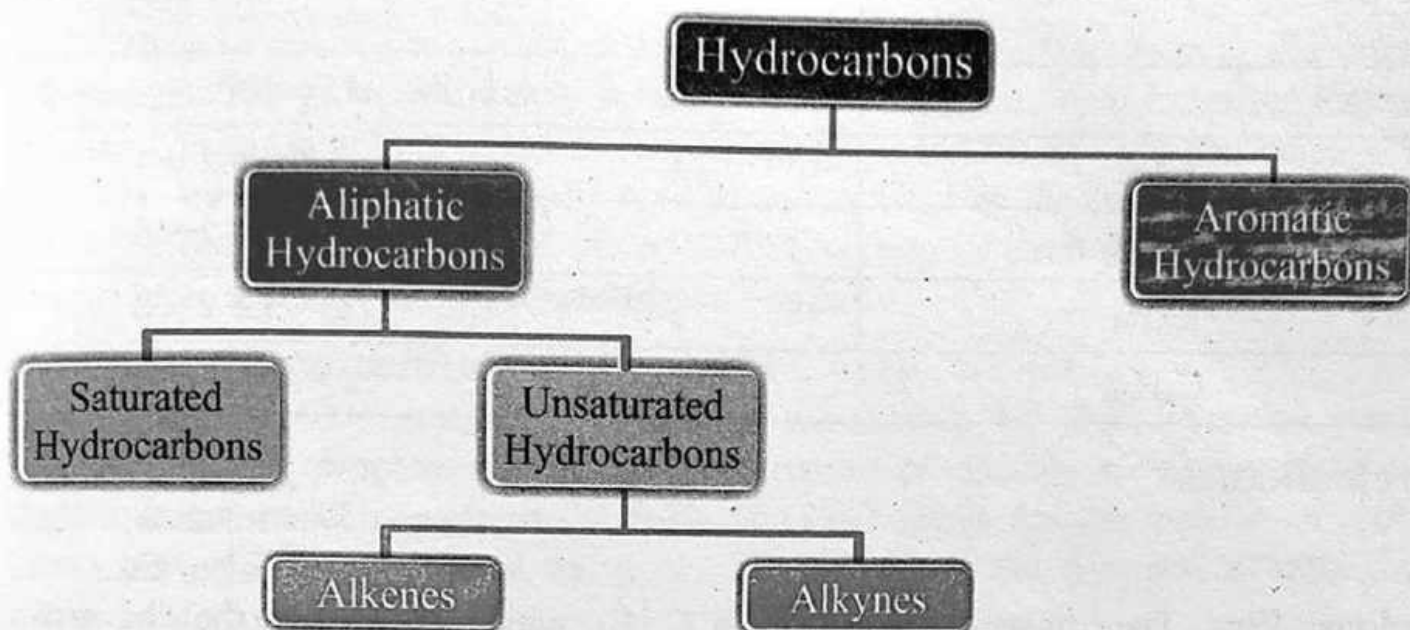


Figure 16.1: Classification of Hydrocarbons

Aliphatic Hydrocarbons

Hydrocarbons that are straight chained, branched or non-aromatic are called aliphatic hydrocarbons. They may also be linear or cyclic. Most of the aliphatic hydrocarbons are volatile and flammable. They may be classified as saturated or unsaturated.

Saturated hydrocarbons contain only single bonds between carbon atoms. These hydrocarbons include alkanes and cycloalkanes. **Unsaturated hydrocarbons** have at least one double or triple bond between two carbon atoms. These hydrocarbons include alkenes and alkynes.

Keep in Mind

In a straight chain compound, the carbon atom is never bonded to more than two carbon atoms. In branched compound, the carbon atom may be bonded to three or four carbon atoms at a time.

Aromatic Hydrocarbons

Hydrocarbons which have at least one benzene ring in their structures are called aromatic hydrocarbons.

16.2 Alkanes and Cycloalkanes

Alkanes

Hydrocarbons that contain only single bonds between carbon atoms are called alkanes. They are also known as paraffins. The word paraffin is derived from the Latin words "parum" meaning "little", and "affin", meaning "affinity". Thus the combination of words means "little affinity" or "the least reactive". Petroleum and natural gas are usually composed of alkanes. They have general formula C_nH_{2n+2} , where n is the number of carbon atoms for each molecule.

Table 16.1: The Calculation of Number of Carbon and Hydrogen Atoms

Molecular Formula of Alkanes	No. of C-atoms = n	No. of H-atoms = $2n + 2$
CH_4	1	$2 \times 1 + 2 = 4$
C_2H_6	2	$2 \times 2 + 2 = 6$
C_3H_8	3	$2 \times 3 + 2 = 8$
C_4H_{10}	4	$2 \times 4 + 2 = 10$

Cycloalkanes

The saturated hydrocarbons in which the carbon atoms are linked by single covalent bonds to form a ring are called cycloalkanes. They are also known as cycloparaffins. They have general formula C_nH_{2n} , which shows that they have two hydrogen atoms less than the corresponding alkanes due to ring structure.

16.2.1 Nomenclature

System of naming compounds is called nomenclature. There are two main systems for naming of organic compounds:

- (i) Common System
- (ii) IUPAC System

(i) Common System

In the early days, organic compounds were named according to their plant or animal sources or name of discoverer. These names are called common names. For example, methane is called marsh gas because it is found in marshy places. Acetic acid got its name from the Latin word *acetum*, which means vinegar because acetic acid is found in vinegar. The methyl alcohol is known as wood spirit because it is obtained by destructive distillation of wood. Other compounds were named by their discoverer for more personal reasons. For example, Adolf von Baeyer supposedly named barbituric acid after a woman named Barbara. Common name system does not follow rules of any formal system. Hence, it is impossible to give common names to millions of organic compounds and we cannot remember all of them by their common names. However, common names for compounds are still in wide use today.

(ii) IUPAC System

To avoid memorizing the names of millions of organic compounds, the commission of 34 chemists from nine countries met at Geneva (Switzerland) in

Keep in Mind

Common names are normally beneficial when the alternate IUPAC names are lengthy and complicated. For example, it is easy to say "tartaric acid" than its IUPAC name "2,3-Dihydroxybutanedioic acid".

1892. They developed a system called the Geneva system for naming the organic compounds. The group ultimately became known as International Union of Pure and Applied Chemistry (abbreviated as IUPAC and pronounced as "eye-you-pack"). The IUPAC rules have been continually revised and updated by the commission since that time. The fundamental principle of the IUPAC system is: **each different compound should have a different and unambiguous name.**

16.2.1.1 Nomenclature of Straight Chain Alkanes

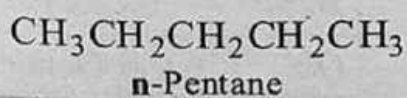
The first four members of alkanes are known by their common names: methane, ethane, propane and butane. The names of alkanes with more than four carbon atoms are derived from the Latin or Greek prefix for the number of carbon atoms per molecule followed by *-ane*. The names of the first ten straight-chain alkanes are given in the table below:

Table 16.2: The first 10 Straight-Chain Alkanes

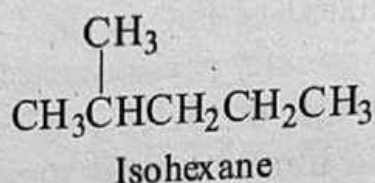
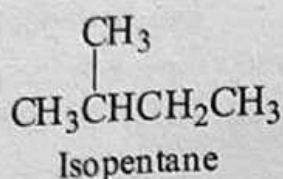
IUPAC Name	Number of C-atoms	Molecular Formula	Condensed Structural Formula	Line-Angle Formula
Methane	1	CH ₄	CH ₄	
Ethane	2	C ₂ H ₆	CH ₃ CH ₃	—
Propane	3	C ₃ H ₈	CH ₃ CH ₂ CH ₃	
Butane	4	C ₄ H ₁₀	CH ₃ (CH ₂) ₂ CH ₃	
Pentane	5	C ₅ H ₁₂	CH ₃ (CH ₂) ₃ CH ₃	
Hexane	6	C ₆ H ₁₄	CH ₃ (CH ₂) ₄ CH ₃	
Heptane	7	C ₇ H ₁₆	CH ₃ (CH ₂) ₅ CH ₃	
Octane	8	C ₈ H ₁₈	CH ₃ (CH ₂) ₆ CH ₃	
Nonane	9	C ₉ H ₂₀	CH ₃ (CH ₂) ₇ CH ₃	
Decane	10	C ₁₀ H ₂₂	CH ₃ (CH ₂) ₈ CH ₃	

In the common system, all the isomeric alkanes have the same parent name. For example, the parent names of three isomeric C₅H₁₀ alkanes are pentanes. The prefixes *n*, *iso* or *neo* are used to differentiate between the names of isomers.

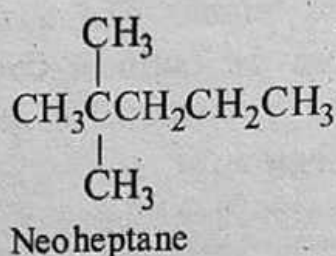
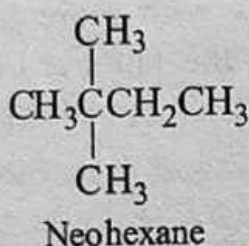
The prefix "**n**-" (or **normal**) is used for those alkane in which all carbon atoms form a continuous, unbranched chain.



The prefix "**iso-**" is used for those alkanes which have a methyl group bonded to the second carbon atom of the continuous chain.



The prefix "**neo-**" is used for those alkanes which have two methyl groups bonded to the second carbon atom of the continuous chain.



In the IUPAC system, the name of every organic compound has three parts: (i) root (ii) suffix and (iii) prefix. The **root** shows the number of carbon atoms in the longest continuous chain in the compound. The **suffix** shows the family of the organic compounds. The **prefix** shows the identity, position, and number of substituents attached to the carbon chain.

Table 16.3: Parts of the Name of Organic Compounds

1	2	3
Prefix	Base or Root	Suffix
What substituents?	How many carbon atoms?	Which family?

The names given in table 16.4 for the simple alkanes consist of the parent name, which shows the number of carbon atoms in the longest continuous chain, and the suffix '*-ane*' shows that the compounds are alkanes. The root name for one carbon is meth-, for two carbons is eth-, for three carbons is prop-, and so on.

Table 16.4: Parent Names for Alkanes

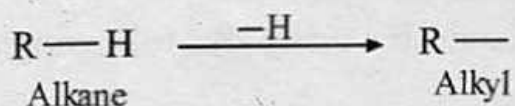
No. of C-atoms	Base or Root name	Parent Name	No. of C-atoms	Base or Root name	Parent Name
1	<i>Meth</i>	Methane	5	<i>Pent</i>	Pentane
2	<i>Eth</i>	Ethane	6	<i>Hex</i>	Hexane
3	<i>Prop</i>	Propane	7	<i>Hept</i>	Heptane
4	<i>But</i>	Butane	8	<i>Oct</i>	Octane

No. of C-atoms	Base or Root name	Parent Name
9	Non	Nonane
10	Dec	Decane
11	Undec	Undecane
12	Dodec	Dodecane
13	Tridec	Tridecane
14	Tetradec	Tetradecane

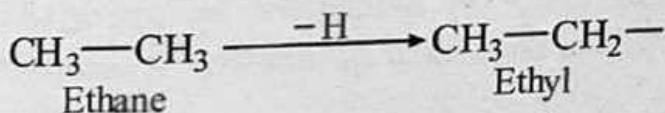
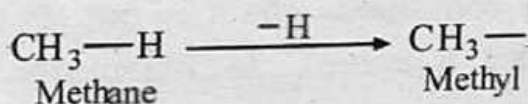
No. of C-atoms	Base or Root name	Parent Name
15	Pentadec	Pentadecane
16	Hexadec	Hexadecane
17	Heptadec	Heptadecane
18	Octadec	Octadecane
19	Nonadec	Nonadecane
20	Icos	Icosane

Naming an Alkyl Group

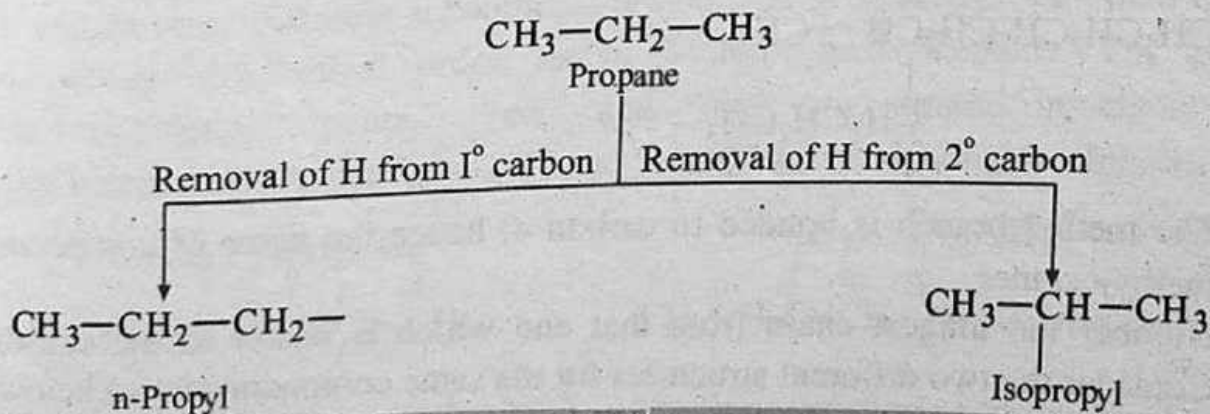
The group that is formed by the removal of one hydrogen atom from an alkane is called an alkyl group. The symbol R is used to indicate an alkyl group.



Alkyl groups are named by replacing the "ane" of the alkane with "yl".

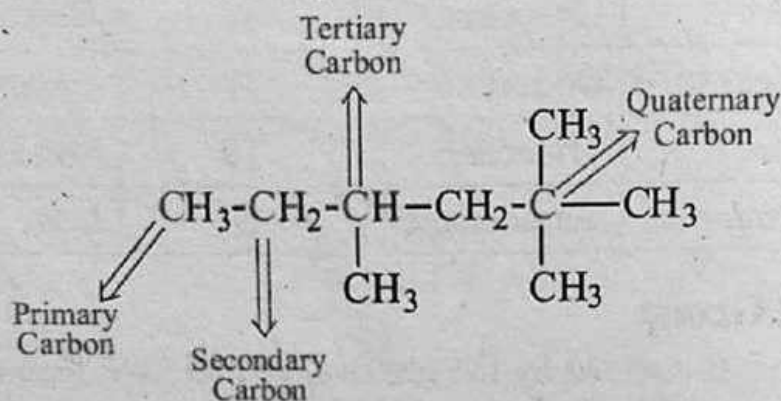


The naming of three carbon alkyl group is more difficult because the parent hydrocarbon has more than one kind of carbon atom. For example, propane has both primary and secondary carbon atoms, and removal of H-atoms from each of these carbon atoms gives a different alkyl group with a different name, n-propyl or isopropyl.



Keep in Mind

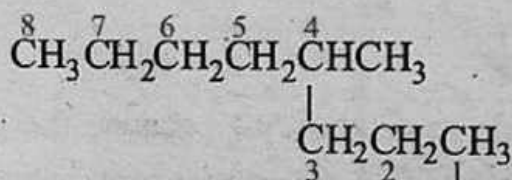
A **primary carbon** atom is directly bonded to only one other carbon atom.
 A **secondary carbon** atom is directly bonded to two other carbon atoms.
 A **tertiary carbon** atom is directly bonded to three other carbon atoms.
 A **quaternary carbon** atom is directly bonded to four other carbon atoms.



16.2.1.2 Nomenclature of Branched Chain Alkanes

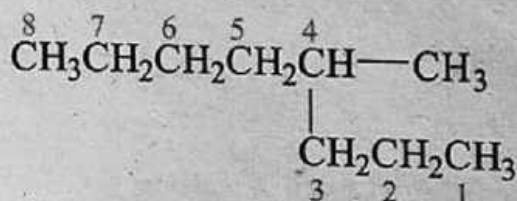
Names of branched chain alkanes are obtained by using the following IUPAC rules:

- i) Select the longest continuous chain of carbon atoms and name it. This is the stem name or parent name. The longest continuous chain is not always in a straight line; sometimes you must "turn a corner" to obtain the longest continuous chain.



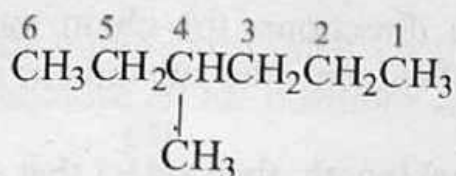
The parent name of the compound is octane because there are eight carbon atoms in the longest continuous chain.

- ii) Indicate the position of substituent (branch) by the number of carbon atom to which it is bonded.

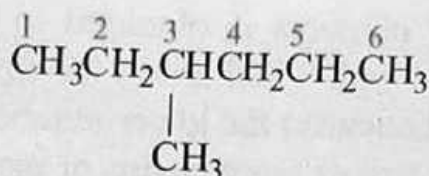


The methyl branch is bonded to carbon 4, hence the name of compound is 4-methyloctane.

- iii) Number the longest chain from that end which is nearer to the substituents. Consider the two different structures for the same compound shown below:



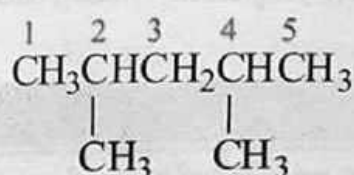
Incorrect



Correct

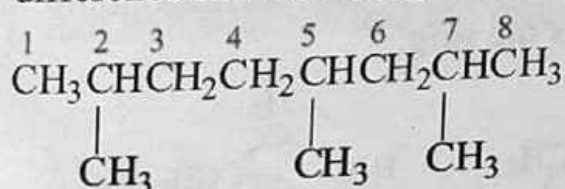
The compound on the right is numbered correctly because the methyl group is located at carbon 3 of the hexane chain; in the compound on the left, the methyl group is located at carbon 4. Thus, the name of the compound is 3-methylhexane, and not 4-methylhexane.

- iv) If two or more identical substituents are bonded to the parent hydrocarbon, then the prefixes "di", "tri", "tetra", "penta" etc. are used to indicate how many identical substituent the compound has.

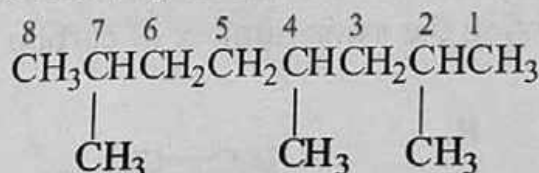


The hydrocarbon has two identical methyl groups. One methyl is bonded to carbon 2 and the other one is bonded to carbon 4. The name of compound is 2,4-dimethylpentane.

- v) If the first substituent has the same distance from both ends, number the chain to give the second substituent the lower number. Always look for the first point of difference in numbering from each end of the longest chain.



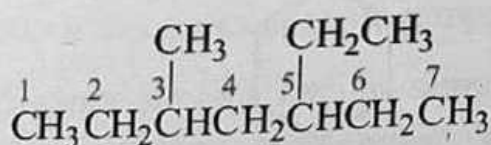
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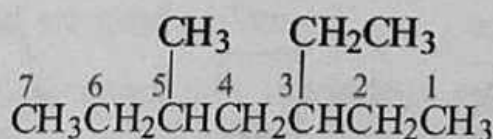
Correct

The correct name of compound is 2,4,7-trimethyloctane and not 2,5,7-trimethyloctane.

- vi) If two or more different substituents are bonded to a parent chain, then they are named in alphabetical order, as in 3-ethyl-5-methylheptane. The prefixes "di", "tri", "tetra", "penta", "sec," and "tert" are ignored in alphabetizing substituents, but the prefixes "iso" and "cyclo" are not ignored in alphabetizing.



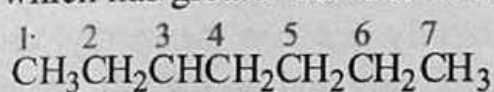
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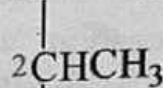
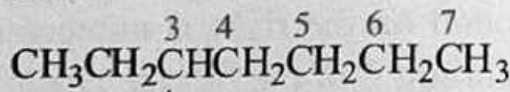
Correct

If the same set of numbers is obtained in both directions, the chain must be numbered from that end, which gives the first substituent (the substituent which is listed first alphabetically) the lower number.

- vii) If a compound has two or more chains of the equal length, then select that chain which has greater number of substituents.



Incorrect



Correct

The name of this compound is 3-ethyl-2-methylheptane but not 3-isopropylheptane.

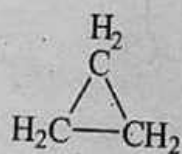
Keep in Mind

- Note that the branch name and the parent name are written as a single word, and a hyphen follows the number.
- The numbers that show the positions of the identical substituents are separated from each other by commas while the number and the word are separated by a hyphen.

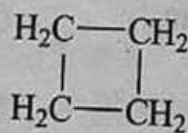
16.2.1.3 Nomenclature of Cycloalkanes

The IUPAC rules for naming cycloalkanes are as follows:

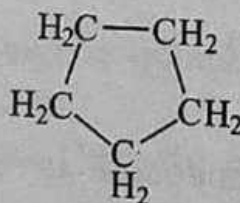
- i) They are named by prefixing cyclo to the name of the corresponding alkane having the same number of carbon atoms as the ring.



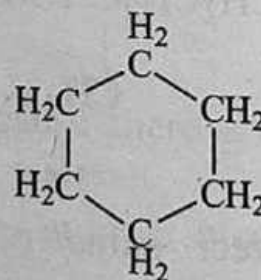
Cyclopropane



Cyclobutane



Cyclopentane



Cyclohexane

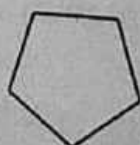
They are often shown by simple geometric figures. Cyclopropane is shown by a triangle, cyclobutane is shown by a square, cyclopentane is shown by a pentagon and cyclohexane is shown by a hexagon. In their figures each corner shows one carbon and two hydrogen atoms.



Cyclopropane



Cyclobutane



Cyclopentane



Cyclohexane

- iii) Alkanes having 18 or more carbon atoms are colourless waxy solids at room temperature. They are used as lubricants. Vaseline is a semisolid, made up of mixture of alkanes with more than 25 carbon atoms.
- iv) They are mostly non-polar in nature and are insoluble in polar solvents like water. They are soluble in non-polar solvents like benzene, ether, carbon tetrachloride, acetone etc.
- v) The boiling points and melting points of alkanes increase with the increase in the number of carbon atoms but the increase in melting point is not very regular. The boiling point increases by 20 to 30°C for addition of each methylene group ($-\text{CH}_2-$) to the molecule.
- vi) The boiling points of straight chain alkanes are higher than branched chain alkanes. For example, the boiling point of n-butane (55°C) is higher than isobutane (-10.2°C).

Keep in Mind

Straight chain alkanes have higher boiling points than their corresponding branched chain alkanes. This is because straight chain alkanes have the larger surface area of contact between the molecules as compared to branched chain alkanes. With increasing surface area, the van der Waals forces between molecules increase; therefore, more energy is required to remove such molecules. As a result straight chain alkanes have higher boiling point than branched chain alkanes.

- vii) The densities of alkanes increase gradually with increase in the number of carbon atoms. They have densities from 0.62g/mL to about 0.79g/mL. They are less dense than water (1.0g/mL) and therefore, float on the surface of water.
- viii) The viscosity of alkanes increases with increasing molecular mass.

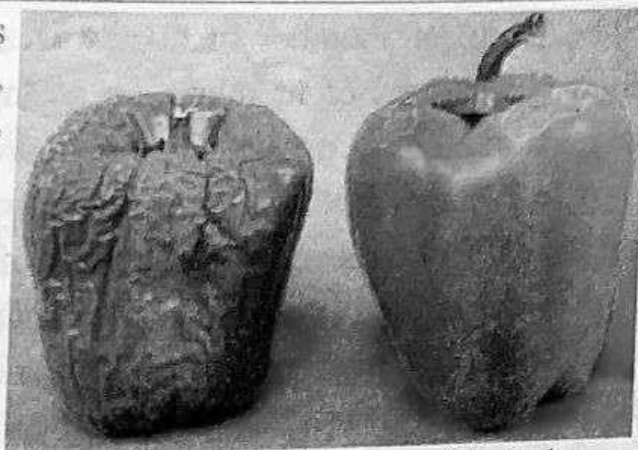
Table 16.5: Physical Properties of Normal Chain Alkanes

No. of Carbon Atoms	Name	Melting Point (°C)	Boiling Point (°C)	Density (g/mL)
1	Methane	-182.5	-161.7	—
2	Ethane	-183.5	-88.6	—
3	Propane	-187.7	-42.1	—
4	Butane	-138.3	-0.5	0.5787
5	Pentane	-129.8	36.1	0.5572
6	Hexane	-95.3	68.7	0.6603
7	Heptane	-90.6	98.4	0.6837
8	Octane	-56.8	125.7	0.7026
9	Nonane	-53.5	150.8	0.7177
10	Decane	-29.7	174.0	0.7299

Interesting Information

The solid alkanes are used in waxy coatings added to fruits (apples, plums, oranges, pears, etc.) and vegetables (cucumber, turnips, green tomatoes etc.) to:

- Prevent loss of water that helps to maintain firmness and juiciness
- Improve appearance and increase visual freshness
- Slow down the natural degradation by microbes



Uncoated

Coated

16.2.2.2 Physical Properties of Cycloalkanes

- Cyclopropane and cyclobutane are gases at room temperature.
- Cycloalkanes having five or more carbon atoms are liquids at room temperature.
- Cycloalkanes are soluble in non-polar solvents like benzene, ether etc. and are insoluble in polar solvents.
- The melting and boiling points of cycloalkanes show gradual increase with the increase in molecular mass.
- They have low densities like alkanes. Alkanes and cycloalkanes are the least dense of all groups of organic compounds.
- Liquid cycloalkanes are soluble in one another.

Table 16.6: Physical Properties of Cycloalkanes

No. of Carbon Atoms	Name	Melting Point ($^{\circ}\text{C}$)	Boiling Point ($^{\circ}\text{C}$)	Density (g/mL)
3	Cyclopropane	-126.6	-33	—
4	Cyclobutane	-90	13	—
5	Cyclopentane	-94	49	0.751
6	Cyclohexane	6.5	81	0.779
7	Cycloheptane	-12	118.5	0.811
8	Cyclooctane	13.5	149	0.834

- i) The carbon-hydrogen bond is the least polar.
- ii) The carbon-carbon bond is completely non-polar.
- iii) There is no unshared pair of electrons.
- iv) There is no unsaturation point.
- v) There is no electrophilic and nucleophilic centre.

16.2.5 Reactivity of Alkanes and Cycloalkanes

Alkanes have only strong sigma bonds. Furthermore, the electrons in the C—H and C—C sigma bonds are shared equally by the bonding atoms, so none of the bonding atoms in an alkane has significant charge. This means that they neither act as electrophile nor nucleophile. Because of this they are the least reactive organic compounds and they do not react with acids, bases, strong oxidizing agents or with some other reagents at room temperature. Most useful reactions of alkanes occur under drastic conditions. However alkanes show two types of reactions: (i) substitution reactions (ii) thermal and catalytic reactions. The properties of cycloalkanes are similar to those of alkanes except cyclopropane and cyclobutane. The reactivity of cyclopropane and cyclobutane is due to the largest ring strain.

16.3 Radical Substitution Reactions

A radical (free radical) is a highly reactive specie containing an atom with an unpaired electron, formed by homolysis of a covalent bond.



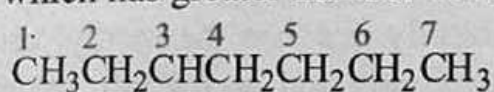
The products A and B are called free radicals. They are electrically neutral. They are very reactive and unstable due to incomplete octet. Radical process involves single electron, so half-headed arrows are used to show the movement of electrons. One half-headed arrow is used for each electron.

16.3.1 Overview

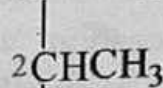
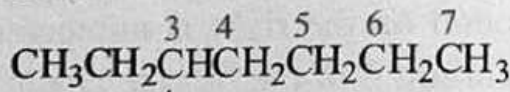
- i) The reactions in which an atom or group of atoms in a molecule is replaced by another atom or group of atoms are called substitution reactions.
- ii) Alkanes react with chlorine (Cl_2) or bromine (Br_2) to form alkyl chlorides and alkyl bromides.
- iii) The reactivity order for alkanes is: tertiary > secondary > primary > methyl
- iv) The reactivity order for halogens is: $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$
- v) Chlorination gives the less stable and bromination gives the most stable radical.
- vi) Reaction proceeds via radical chain mechanism which involves radical intermediates.
- vii) The termination steps are of low probability due to the low concentration of the radical species meaning that the chances of collisions are very low.

If the same set of numbers is obtained in both directions, the chain must be numbered from that end, which gives the first substituent (the substituent which is listed first alphabetically) the lower number.

- vii) If a compound has two or more chains of the equal length, then select that chain which has greater number of substituents.



Incorrect



Correct

The name of this compound is 3-ethyl-2-methylheptane but not 3-isopropylheptane.

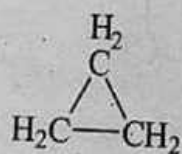
Keep in Mind

- Note that the branch name and the parent name are written as a single word, and a hyphen follows the number.
- The numbers that show the positions of the identical substituents are separated from each other by commas while the number and the word are separated by a hyphen.

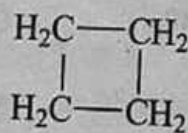
16.2.1.3 Nomenclature of Cycloalkanes

The IUPAC rules for naming cycloalkanes are as follows:

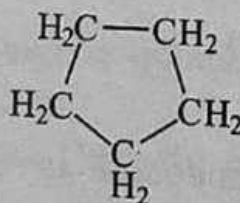
- i) They are named by prefixing cyclo to the name of the corresponding alkane having the same number of carbon atoms as the ring.



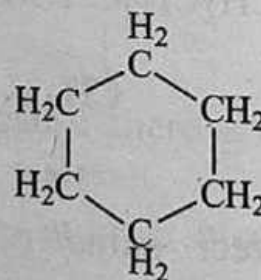
Cyclopropane



Cyclobutane



Cyclopentane



Cyclohexane

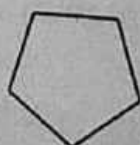
They are often shown by simple geometric figures. Cyclopropane is shown by a triangle, cyclobutane is shown by a square, cyclopentane is shown by a pentagon and cyclohexane is shown by a hexagon. In their figures each corner shows one carbon and two hydrogen atoms.



Cyclopropane



Cyclobutane



Cyclopentane



Cyclohexane

16.2.3 Structure of Alkanes and Cycloalkanes

16.2.3.1 Structure of Alkanes

The simplest member of alkane is methane (CH_4). The hydrogen atoms of methane are arranged around the central carbon atom in order that each hydrogen atom is as far apart from other hydrogen atoms as possible. Methane gives tetrahedral geometry with an angle of 109.5° .

Although the three dimensional shapes of higher alkanes are more complex than that of methane, the four bonds about each carbon are still arranged in a tetrahedral manner, and all the bond angles are nearly 109.5° .

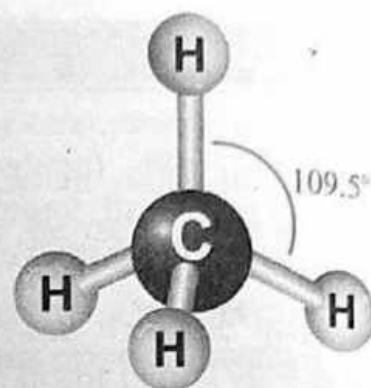
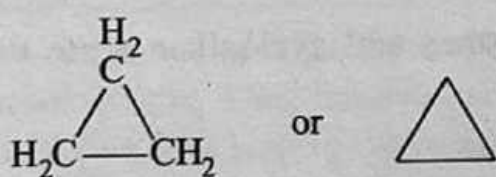


Figure 16.2: Methane Molecule

16.2.3.2 Structure of Cycloalkanes

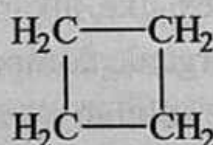
The simplest member of cycloalkane is cyclopropane. When writing structural formulas for cycloalkanes, chemists use line-angle formula to represent cycloalkane ring. Each ring is represented by a regular polygon that has the same number of sides as there are carbon atoms in the ring. For example, chemists represent cyclopropane by a triangle, cyclobutane by a square, cyclopentane by a pentagon, and cyclohexane by a hexagon.



or



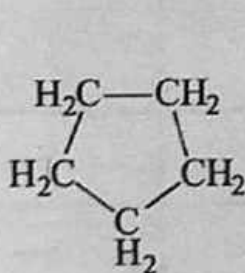
Cyclopropane



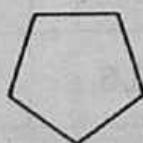
or



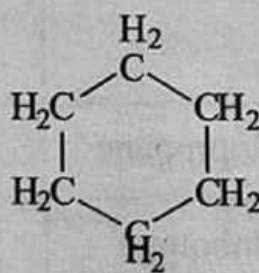
Cyclobutane



or



Cyclopentane



or



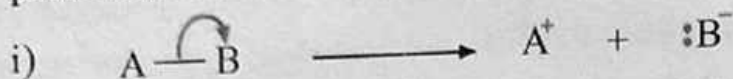
Cyclohexane

16.2.4 Relative Stability of Alkanes and Cycloalkanes

Alkanes are relatively stable. Branched chain alkanes are more stable than straight chain (linear), unbranched alkanes. For example, 2-methylpropane is more stable than n-butane. On the other hand, the cycloalkanes are stable except cyclopropane and cyclobutane. The inertness of alkanes is due to the following reasons:

Keep in Mind

When a bond breaks so that both of its electrons stay with one of the atoms, the process is called **heterolytic bond cleavage** or **heterolysis**.



When a bond breaks so that each of the atoms retains one of the bonding electrons, the process is called **homolytic bond cleavage**, or **homolysis**.

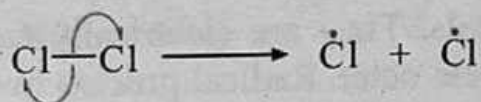


16.3.2 Reaction Mechanism

The halogenation of alkanes occurs through the formation of free radical and is called free radical mechanism. It takes place in three steps:

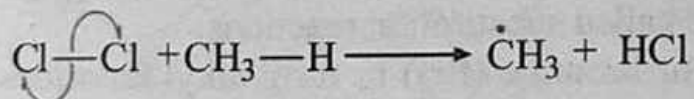
Initiation Step

In this step, the chlorine free radicals are formed by homolytic fission of Cl_2 molecule in the presence of heat or light. Each atom takes one of the bonding electrons and two highly reactive chlorine atoms are produced. This is called initiation step because it produces radicals.



Propagation Step

- i) The chlorine radical produced in the initiation step abstracts a hydrogen atom from the methane, forming a molecule of HCl and a methyl radical.



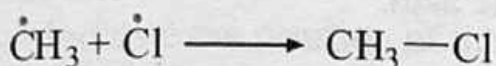
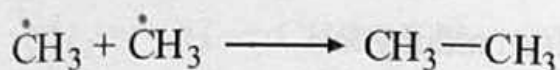
- ii) The methyl radical abstracts a chlorine atom from a chlorine molecule (Cl_2), forming a molecule of methyl chloride and another chlorine radical, which can then abstract a hydrogen atom from another molecule of methane.



These two steps (i) and (ii) are repeated again and again and a chain reaction starts. These steps are called propagation steps because they propagate the reaction.

Termination Step

Free radicals of similar and dissimilar types combine together to give neutral molecules.



The combination of these radicals is called a termination step because it helps to carry the reaction to an end by decreasing the number of radicals available to propagate the reaction.

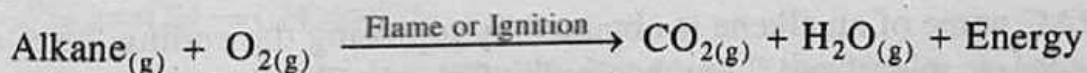
The reaction of methane with chlorine also produces the highly halogenated products such as CH_2Cl_2 , CHCl_3 and CCl_4 as well as additional HCl .

16.4 Oxidation of Organic Compounds

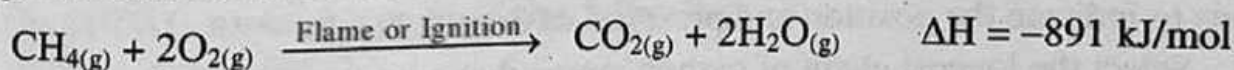
16.4.1 Complete Oxidation

Oxidation of organic molecule generally corresponds to increasing its oxygen content and to decreasing its hydrogen content. The reverse of oxidation is reduction. Oxidation and reduction take place simultaneously, therefore they are redox reactions.

Alkanes such as natural gas, gasoline, and diesel burn readily in the presence of oxygen to produce carbon dioxide, water vapours, and energy.



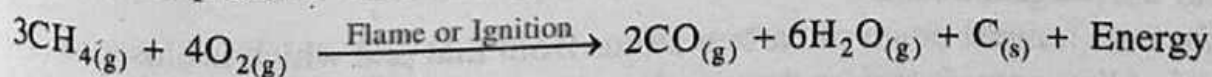
The burning of organic compounds in the presence of oxygen is called combustion. Methane gas is found in natural gas and is used for cooking and heating. The equation for the combustion of methane is written as:



The amount of heat evolved when one mole of hydrocarbon is completely burnt to give CO_2 and H_2O is called heat of combustion.

16.4.2 Incomplete Oxidation

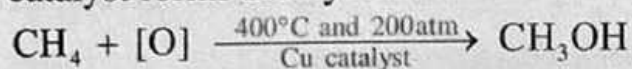
When there is an insufficient supply of oxygen or air, then hydrocarbons on combustion produce carbon monoxide, water vapours and carbon black.



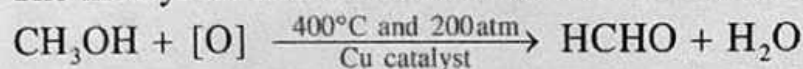
16.4.3 Catalytic Oxidation

When lower alkanes are burnt in the presence of metallic catalyst at high temperature and pressure, then they form many useful products.

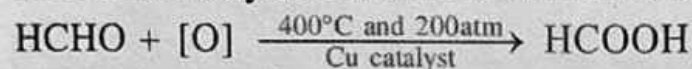
- i) The oxidation of methane at 400°C and 200atm in the presence of copper catalyst forms methyl alcohol.



- ii) The methyl alcohol is further oxidized to formaldehyde.



- iii) The formaldehyde is further oxidized to formic acid.



16.5 Alkenes

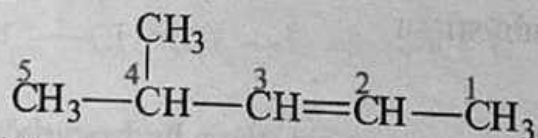
The unsaturated hydrocarbons that contain one or more carbon-carbon double bonds ($\text{C}=\text{C}$) are called alkenes. They are also known as olefins. The word olefin is derived from French word "olefiant" which means oil forming because the lower members of alkenes give oily products on treatment with chlorine or bromine. Alkenes are present in natural gas, coal gas and gasoline in small amounts. They are produced in large amounts by cracking of petroleum. Alkenes (monoenes) have general formula C_nH_{2n} , where n is the number of carbon atoms. Ethylene is the first member of the series.

16.5.1 Nomenclature

Alkenes are normally named using the IUPAC system, but many older names are still in common use. Ethene is often called ethylene and propene is called propylene.

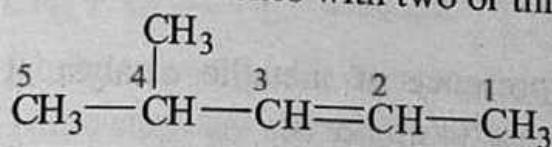
The IUPAC name of an alkene is obtained by replacing the ending "ane" of the corresponding alkane with "ene." For example, $\text{CH}_2=\text{CH}_2$ is called ethene and $\text{CH}_3\text{CH}=\text{CH}_2$ is called propene. When there are two or more possible locations for the double bond in a molecule, its position is shown by a number. The IUPAC rules for naming of alkenes are similar to those used for naming alkanes, with a few additions to indicate the position and presence of double bonds.

Step 1. Select the longest chain of carbon atoms that contains the double bond and name it.

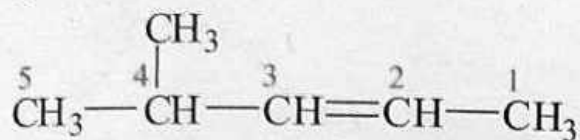


The parent name of the compound is pentene. It means that there are five carbon atoms in the longest chain.

Step 2. Number the longest chain of carbon atoms from that end which is closer to the double bond. Alkenes with two or three carbon atoms do not need numbers.

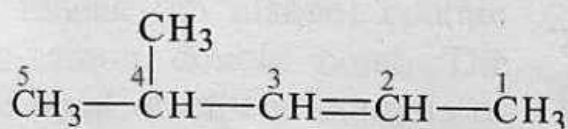


Step 3. Indicate the position of the double bond by the lower numbered carbon atom bound by the double bond.



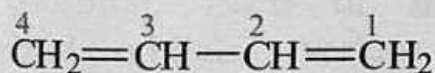
The double bond is present between carbon 2 and 3, so the name of compound is 2-pentene.

Step 4. Indicate the position of the substituent by the number of that carbon to which it is attached and name it in a manner similar to alkanes. The name of substituent is stated before the name of the longest continuous chain of carbon atoms that contains the double bond, together with a number to designate the carbon to which the substituent is bonded. Note that if a compound's name contains both a double bond suffix and a substituent, the double bond suffix gets the lowest possible number.



The methyl group is located at carbon 4 and the name of compound is 4-methyl-2-pentene or 4-methylpent-2-ene.

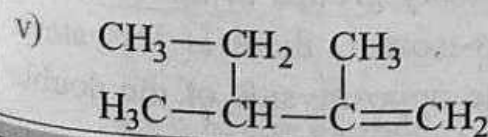
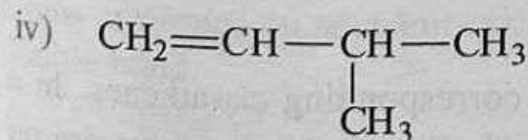
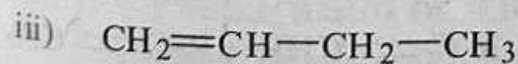
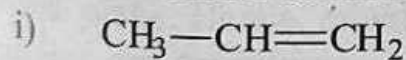
Step 5. If an alkene has two or more double bonds, the “ne” of the corresponding alkane is replaced with “diene,” “triene,” “tetraene,” and so on depending upon the number of double bonds present in the parent alkene.

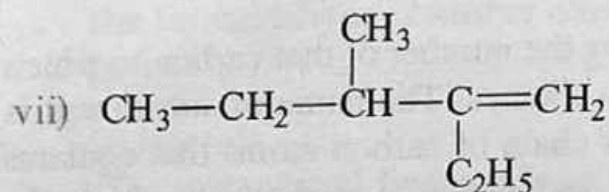
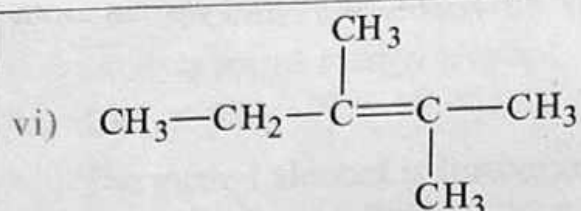


The compound has two double bonds and the name of compound is 1,3-butadiene or buta-1,3-diene.

Practice Exercise - 1

Give the IUPAC name for each of the following:





Practice Exercise - 2

Draw the structure for each of the following:

- 2-Butene
- 2-Methyl-1-butene
- 3,4-Dimethyl-2-pentene
- 1,3-Butadiene
- 3-Ethyl-2-pentene
- 3-Ethyl-4-methylhex-3-ene
- 1,3,5-Hexatriene
- 2,3-dimethyl-1,3,5-hexatriene

16.5.2 Relative Stability

There are three factors that influence the relative stability of alkene:

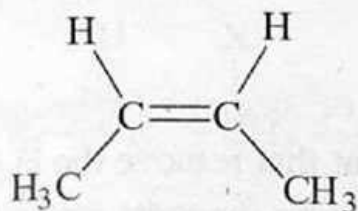
i) Degree of Substitution

The stability of alkene increases as the number of R (alkyl) groups on the $\text{C}=\text{C}$ increases. The increasing order of stability of alkenes is as:

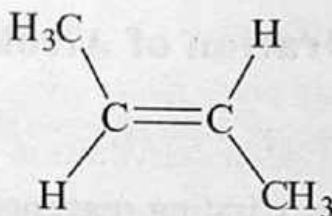


ii) Stereochemistry

Trans-alkenes are usually more stable than the corresponding *cis*-alkenes. In a *cis*-isomer, there is more steric hindrance, because the bulky groups or atoms are on the same side of the double bond whereas in a *trans*-isomer, there is less steric hindrance, because the bulky groups or atoms are on the opposite side of the double bond.



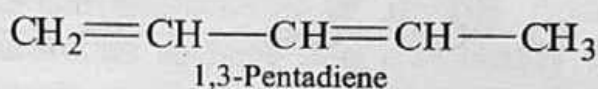
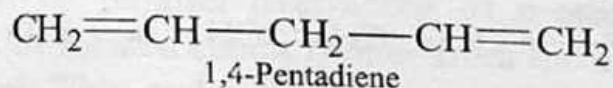
Cis-2-butene (Less Stable)



Trans-2-butene (More Stable)

iii) Conjugation

Conjugated alkenes are more stable than isolated alkenes. For example, 1,3-pentadiene is more stable than 1,4-pentadiene.



16.5.3 Structure

Ethene (an alkene) contains carbon-carbon double bond. The double bond of ethene consists of one sigma bond and one pi bond. The carbon atoms attached through pi bond are sp^2 hybridized. Hence, each doubly bonded carbon has three sp^2 hybrid orbitals and one pure p-orbital. Each of these sp^2 hybrid orbitals overlaps an orbital of another atom to form a sigma bond. The remaining p-orbital of one of the sp^2 carbon atoms overlaps with the remaining p-orbital of the other sp^2 carbon atom to form a pi bond. Sigma bonds are formed by head-to-head overlap of hybrid orbitals and pi bond is formed by side-to-side overlap of pure p-orbitals. All six atoms of the double-bond system are in the same plane. Hence, ethene has trigonal planar structure in which $\text{H}\hat{\text{C}}\text{H}$ and $\text{H}\hat{\text{C}}\text{C}$ bond angles are approximately equal to 120° . The carbon-carbon double bond length is 134 pm and carbon-hydrogen bond lengths are 109 pm.

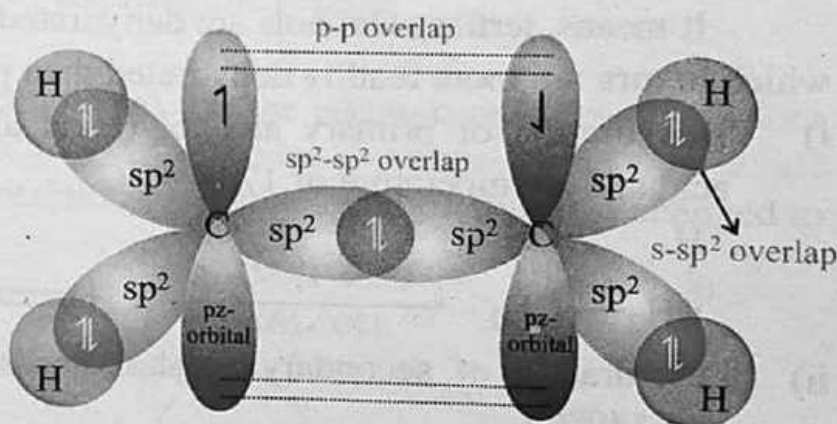
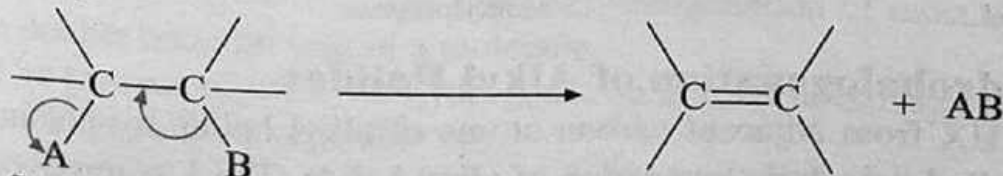


Figure 16.2: C_2H_4 Molecules

16.5.4 Preparation of Alkenes

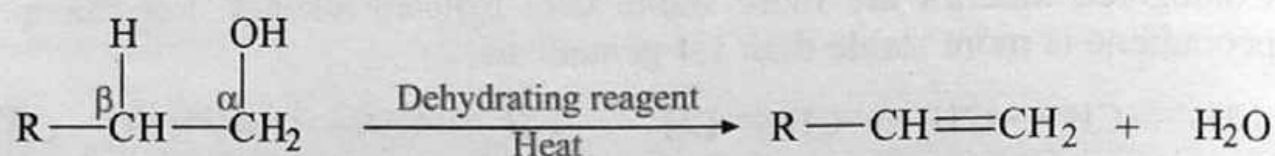
Alkenes are generally prepared through β -elimination reactions, in which two atoms or groups on adjacent carbon atoms are removed, resulting in the formation of a double bond.



Some of the methods of preparation of alkenes are given:

16.5.4.1 Dehydration of Alcohols

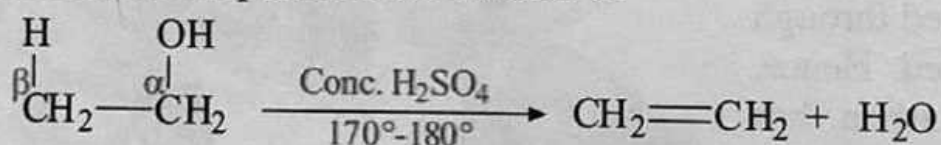
The removal of H_2O from adjacent carbon atoms of alcohols by heating with dehydrating agent is called dehydration of alcohol. Reagent that remove the H_2O from alcohols are called dehydrating reagents. The best dehydrating reagents are: (i) Conc. H_2SO_4 (ii) Al_2O_3 (iii) P_2O_5 . All the dehydrating reagents work at high temperature. The OH is removed from α -carbon and H is removed from β -carbon.



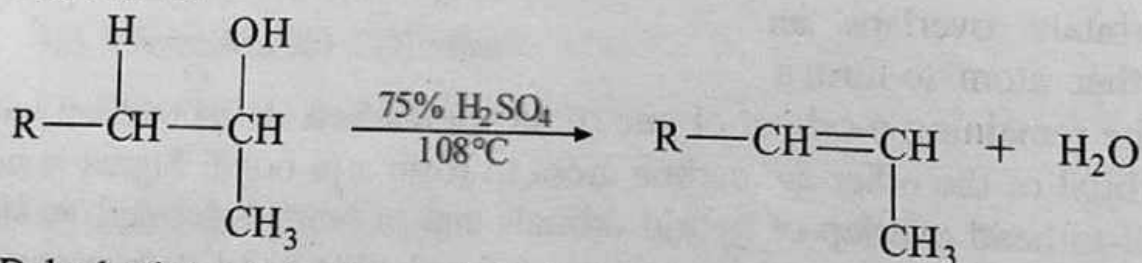
The ease of dehydration of alcohols is: $3^\circ \text{ alcohol} > 2^\circ \text{ alcohol} > 1^\circ \text{ alcohol}$.

It means, tertiary alcohols are dehydrated more readily than secondary alcohols which in turn are more readily dehydrated than primary alcohols.

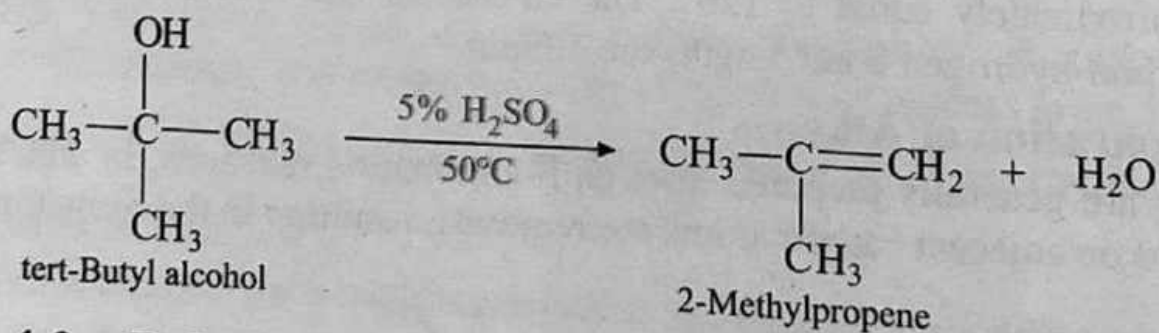
- i) Dehydration of primary alcohol (ethyl alcohol) needs concentrated sulphuric acid and a temperature of $170-180^\circ\text{C}$.



- ii) Dehydration of secondary alcohol needs 75% H_2SO_4 and a temperature of $100-140^\circ\text{C}$.

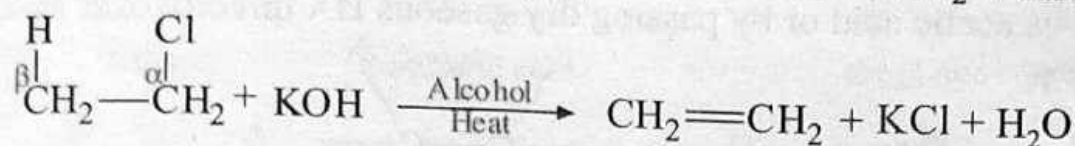
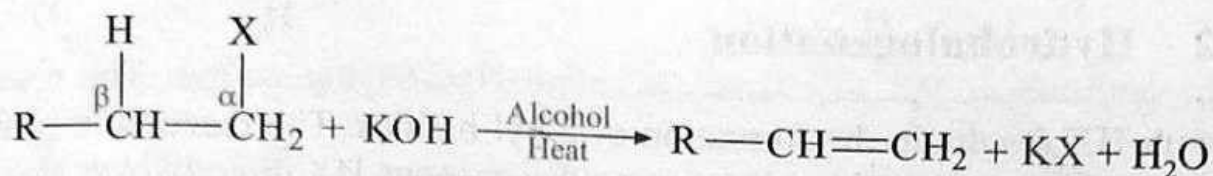


- iii) Dehydration of tertiary alcohol (tert-butyl alcohol) needs 5% H_2SO_4 and a temperature of 50°C .



16.5.4.2 Dehydrohalogenation of Alkyl Halides

Removal of HX from adjacent carbon atoms of alkyl halide by heating with alcoholic KOH is called dehydrohalogenation of alkyl halide. The X is removed from α -carbon and H is removed from β -carbon.

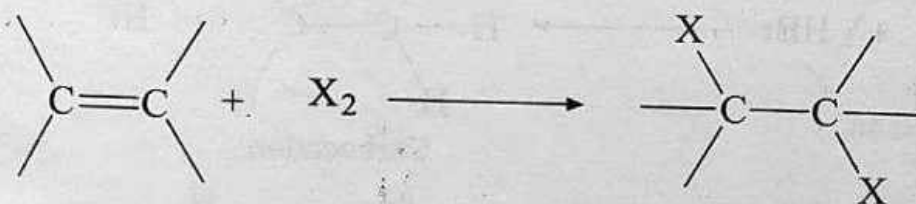


16.5.5 Reactivity of Alkenes

Alkenes are more reactive than alkanes due to presence of π -bond. A π -bond is formed by parallel overlapping of p-orbitals. The π -electrons of double bond are therefore located much farther from the carbon nuclei and are thus less firmly bound to them. This makes π -bond a weak bond as compared to sigma bond. Therefore it breaks much more easily by the attack of electrophilic reagent.

16.5.6 Reactions of Alkenes

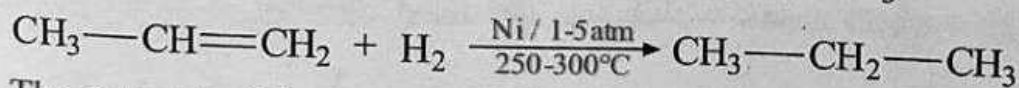
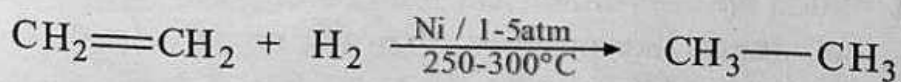
The most important reactions of alkenes are the addition reactions. Addition reactions are those reactions in which two molecules combine to form a single molecule of product. During addition reactions, a double bond of alkene is changed to a single bond.



The common addition reactions of alkenes are given below:

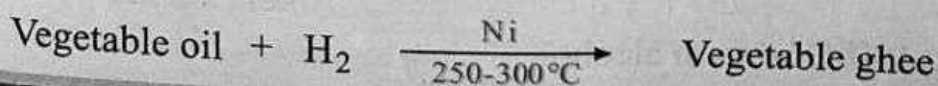
16.5.6.1 Catalytic Hydrogenation

The reaction in which hydrogen is added to an alkene in the presence of catalyst such as platinum, nickel, or palladium and at moderate pressure of 1 to 5 atmosphere to give a saturated hydrocarbon (alkane) is known as catalytic hydrogenation of alkene.



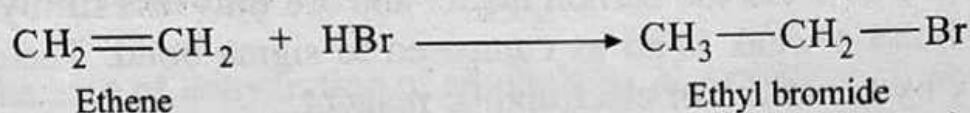
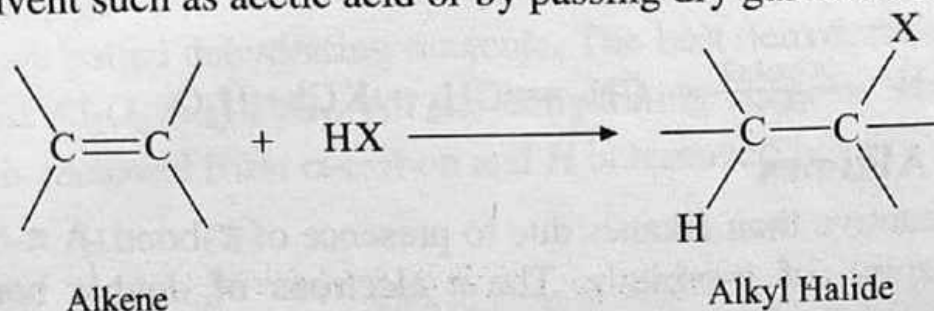
The amount of heat evolved when one mole of an alkene is hydrogenated is called heat of hydrogenation. The heat of hydrogenation of most alkene is 120kJ/mol for each double bond present in a molecule.

The process of catalytic hydrogenation is used in industry for the manufacture of vegetable ghee from vegetable oil.



16.5.6.2 Hydrohalogenation

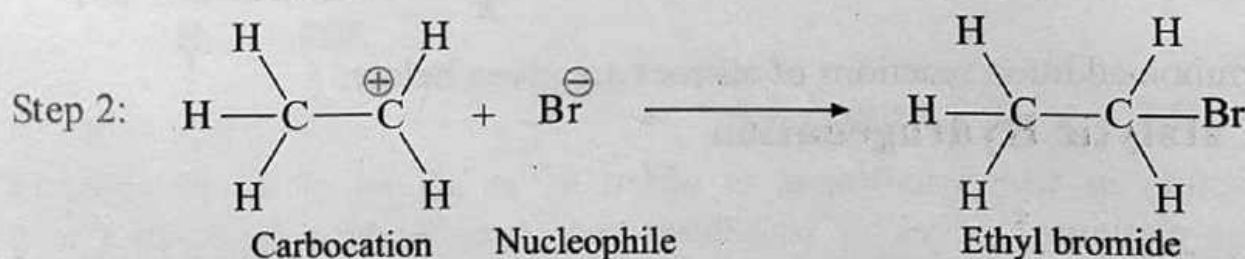
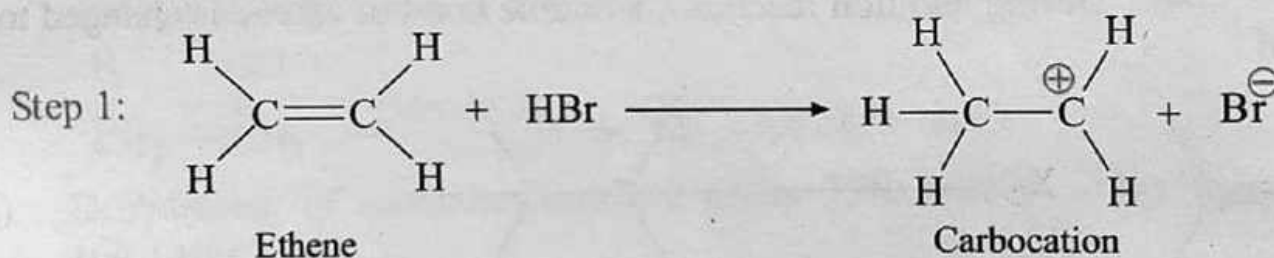
The addition of HX to alkenes is called Hydrohalogenation. The reaction of alkenes with HX results in the formation of alkyl halides. The reaction is carried out in a solvent such as acetic acid or by passing dry gaseous HX directly over an alkene.



The order of reactivity of HX is: $\text{HI} > \text{HBr} > \text{HCl}$

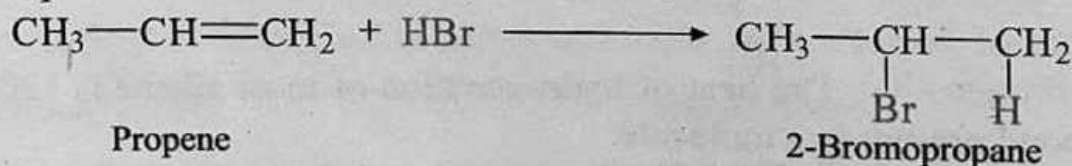
Mechanism of Reaction

Consider the addition of HBr to ethene. It involves two steps:



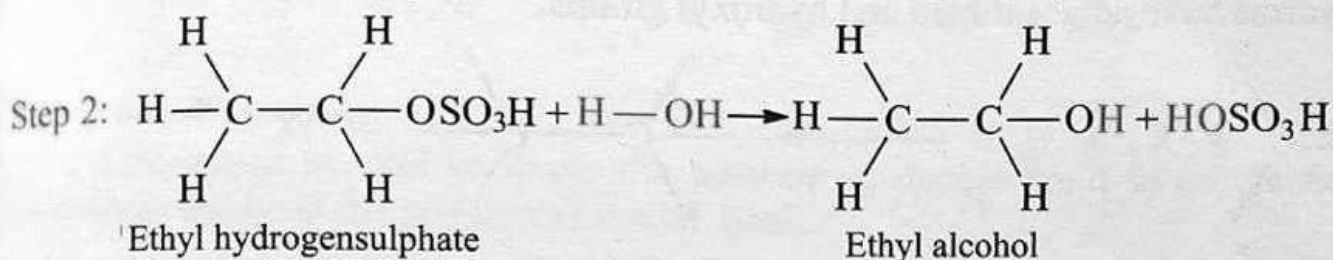
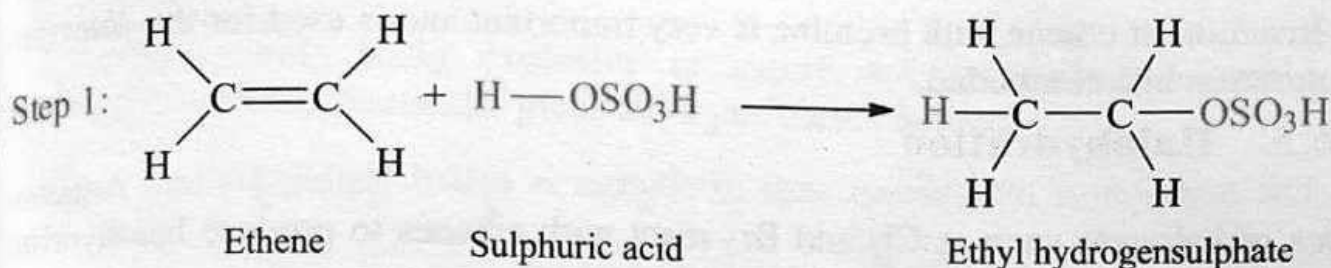
Markovnikov's Rule

This rule states that "when an unsymmetrical molecule (polar reagent) such as HX is added to unsymmetrical alkene like propene, then the negative part of adding molecule goes to that carbon atom, which has the least number of hydrogen atoms." For example:



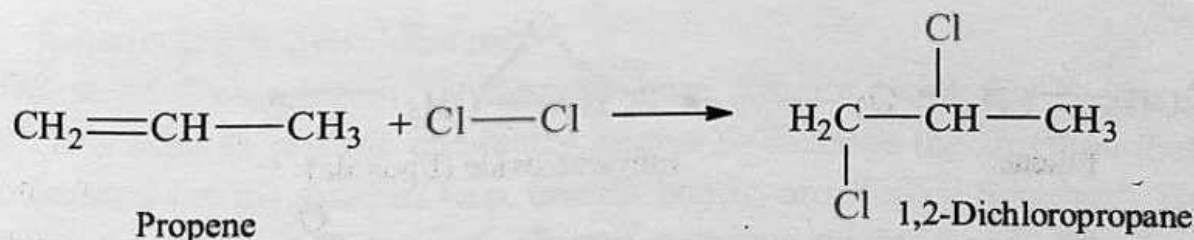
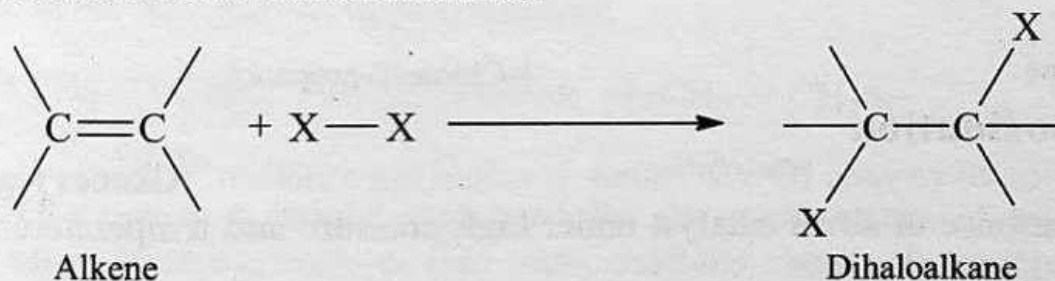
16.5.6.3 Hydration

The addition of water molecule is called hydration. Alkenes react with H_2O in the presence of H_2SO_4 at 100°C to form alcohol.



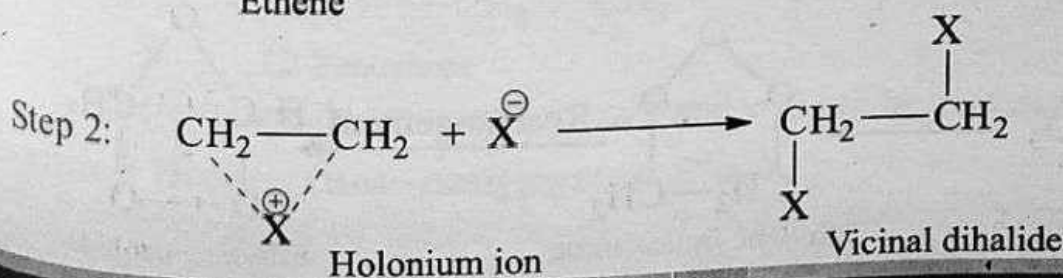
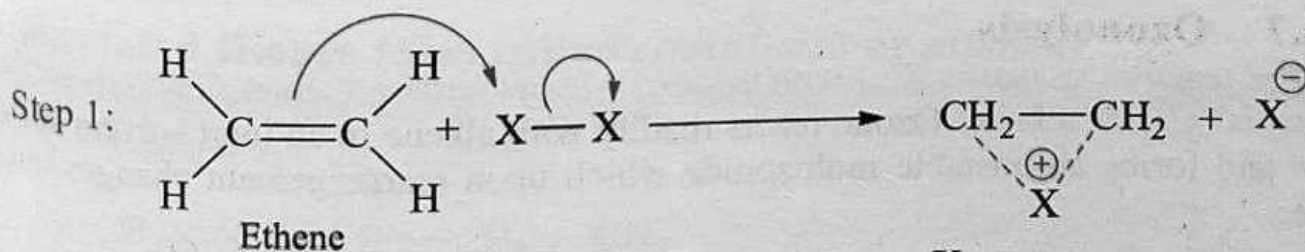
16.5.6.4 Halogenation

The addition of halogens such as chlorine (Cl_2) and bromine (Br_2) to alkenes is called halogenation. Alkenes react readily with Cl_2 or Br_2 , in an inert solvent such as CCl_4 , in dark to form vicinal dihalides.



Mechanism of Reaction

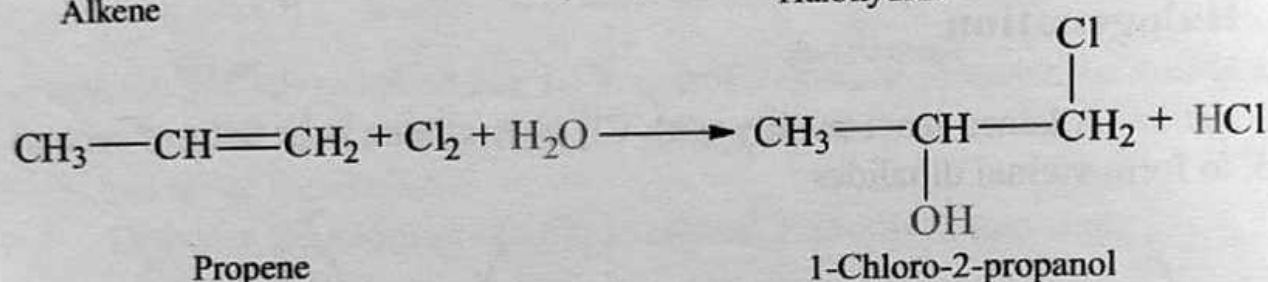
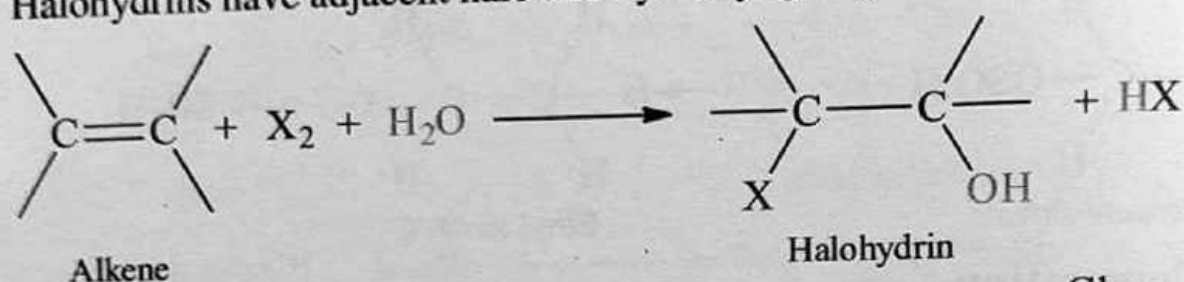
The addition of X_2 to ethene occurs in two steps:



Reaction of ethene with bromine is very important and is used for the detection of unsaturation in a compound.

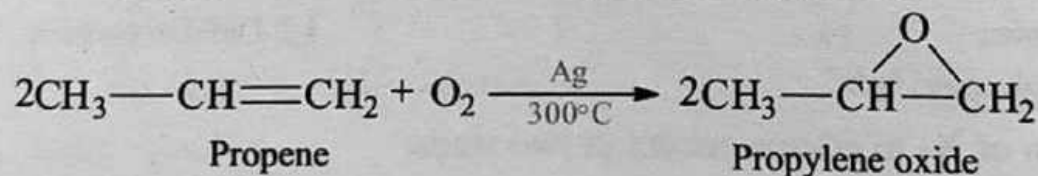
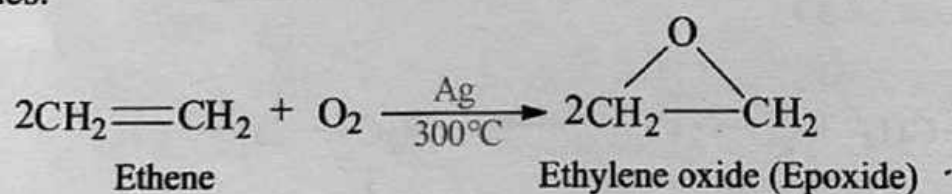
16.5.6.5 Halohydration

The addition of hypohalous acid to alkenes is called Halohydration. Aqueous solutions of halogens such as Cl_2 and Br_2 react with alkenes to produce halohydrins. Halohydrins have adjacent halo and hydroxyl groups.



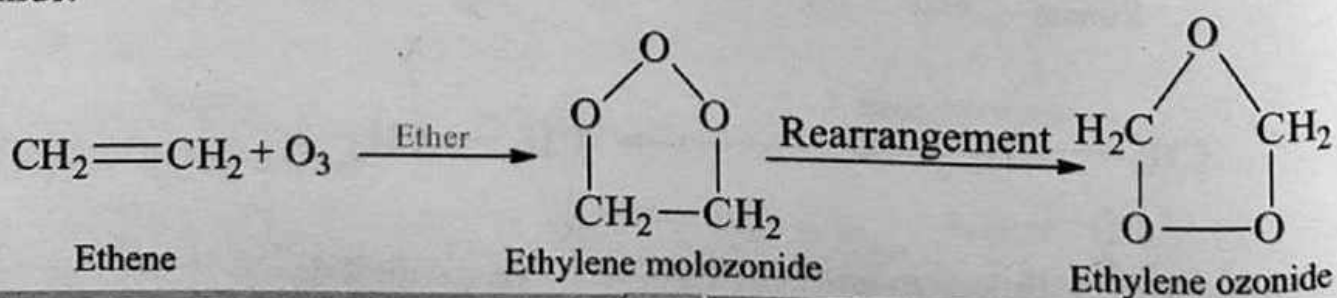
16.5.6.6 Epoxidation

The addition of oxygen (O_2) to alkene is called epoxidation. Alkenes react with oxygen in the presence of silver catalyst under high pressure and temperature to give epoxides.

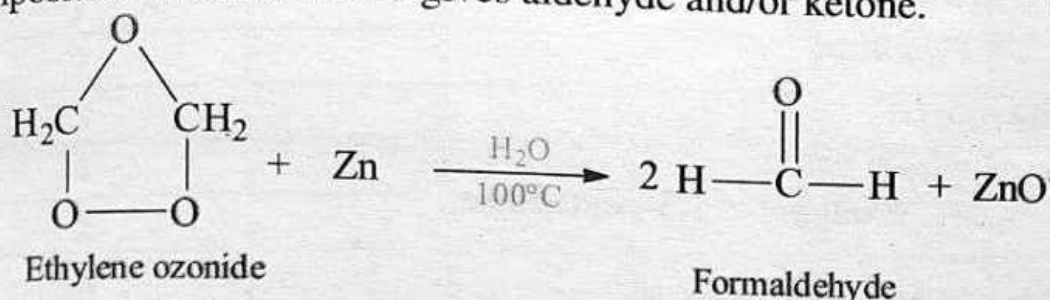


16.5.6.7 Ozonolysis

The reaction of ozone (O_3) with alkene to break carbon-carbon double bond is called ozonolysis of alkene. Ozone reacts readily with alkene in an inert solvent such as ether and forms an unstable molozonide which upon rearrangement changes into ozonide.



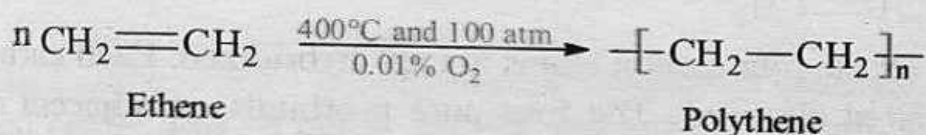
The ozonide being explosive in nature are not isolated. Ozonide upon decomposition with zinc/water gives aldehyde and/or ketone.



Ozonolysis is used to locate the position of double bond in an alkene. The molecule cleaves at the position of double bond.

16.5.6.8 Polymerization

The process by which small molecules (called monomers) combine together to form large molecules (called polymers) is known as polymerization. Ethylene (an alkene) undergoes polymerization in the presence of catalyst at high temperature and pressure to form polythene or polyethylene.



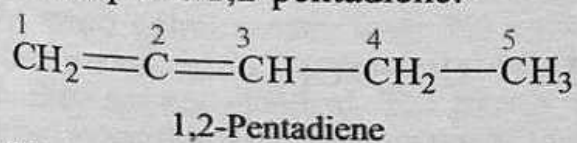
Polythene is a plastic and used for the manufacture of toys, bags, boxes, purses, carpet backing, buckets, rain coats, dustbins, shoes soles and pipe.

16.5.7 Conjugation in Alkenes

The word "*conjugation*" is derived from a Latin word that means "to link together". It is used in organic chemistry system to describe the situation that occurs when conjugated (or pi) systems (e.g. double bonds) are "linked together". The focus of this topic is on dienes. Dienes are alkenes with two double bonds. There are three different classes of dienes that depends on closeness of the pi bonds. They are cumulated, conjugated, or isolated.

Cumulated Dienes (also called *cumulenes* or *allenes*)

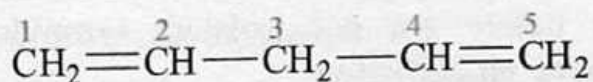
The dienes in which the two double bonds are adjacent are called cumulated dienes. Example is 1,2-pentadiene.



The compounds are relatively rare and will not be discussed here in this topic.

Isolated Dienes (non-conjugated dienes)

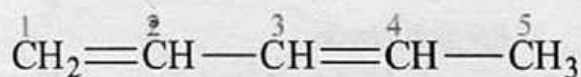
The dienes in which the double bonds are separated by more than one single bond are called isolated dienes. Example is 1,4-pentadiene.



1,4-Pentadiene

Conjugated Dienes

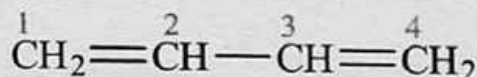
The dienes in which the double bonds are separated by one single bond are called conjugated dienes. Example is 1,3-pentadiene.



1,3-Pentadiene

Conjugation

Conjugation takes place whenever p-orbitals overlap on three or more adjacent atoms. The common conjugated system is 1,3-diene. The simplest example of conjugated diene is 1,3-butadiene.



In 1,3-butadiene, all the four carbon atoms are sp^2 hybridized. Each carbon has pure p-orbital with unpaired electrons. The four pure p-orbitals on adjacent carbon atoms make 1,3-butadiene a conjugated system.

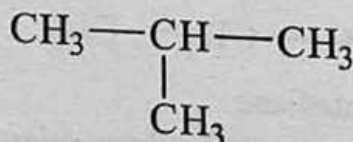
A molecule which has three or more pure p-orbitals on adjacent atoms allows p-orbitals to overlap and electrons to delocalize over the whole molecule. When p-orbitals overlap, the electron density in each of the pi bonds is spread out over all the four atoms of the molecule, thus lowering the energy of the molecule and making it more stable. Conjugation makes 1,3-butadiene (conjugated diene) different from 1,4-pentadiene (an isolated diene). The pi bonds in 1,4-pentadiene are separated by more than one sigma bond and are too far apart to be conjugated.

16.6 Isomerism

The compounds having same molecular formula but different structural formulas are called isomers and the phenomenon is called isomerism. For example, n-butane and isobutane are isomers; they have same molecular formula (C_4H_{10}) but different structures.



n-Butane



Isobutane

Isomers have different physical, chemical and biological properties.

Number of Isomers depend upon the number of carbon atoms. The number of isomers increases with the increase of carbon atoms.

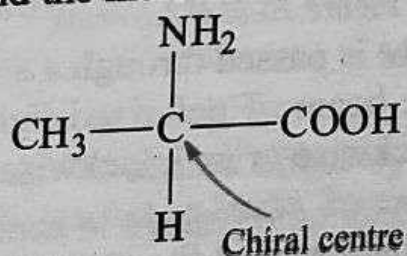
Table 16.7 : Number of Isomers of Alkanes

No. of C-atoms	No. of Isomers	No. of C-atoms	No. of Isomers
1	1	11	159
2	1	12	355
3	1	13	802
4	2	14	1858
5	3	15	4347
6	4	16	10359
7	9	17	24894
8	18	18	60523
9	35	19	148284
10	75	20	366319

There are two main types of isomerism: *constitutional isomerism* and *stereoisomerism*.

16.6.1 Chiral Centres and Carbon based Chiral Centres

Tetrahedral atoms usually carbon atoms that have four different substituents are called chiral centres (or sometimes stereogenic centres). A molecule that contains a chiral centre will be chiral and the molecules that does not contain a chiral centre will be achiral. Molecules with a single chiral centre are always chiral and the molecules with two or more chiral centres, may or may not be chiral. For example, alanine (an amino acid) contains a carbon atom with four different substituents; this carbon atom is chiral centre, and the molecule itself is chiral.



The four different groups bonded to chiral centre are: CH_3 , H , COOH and NH_2 .

Keep in Mind

The word chiral comes from the Greek word *cheir*, which means "hand." Your left and right hands are chiral i.e. they are not identical. The mirror image of chiral object is not the same as an image of the object itself. A hand is chiral because when you look at your right hand in a mirror, you see not a right hand but a left hand. Left and right hands are mirror images that do not superimpose on each other.



16.6.2 Optical Activity

Ordinary light consists of waves vibrating in many different planes. When it is passed through polarizer (Nicol prism or Polaroid lens), the light vibrates in one plane only. This light which vibrates in one plane only is called plane polarized light.

The compounds having the ability to rotate the plane of polarized light in either clockwise or anticlockwise direction are called optically active and the property of rotating the plane of polarized light of compounds is called optical activity.

Optical activity in a compound is measured by means of Polarimeter.

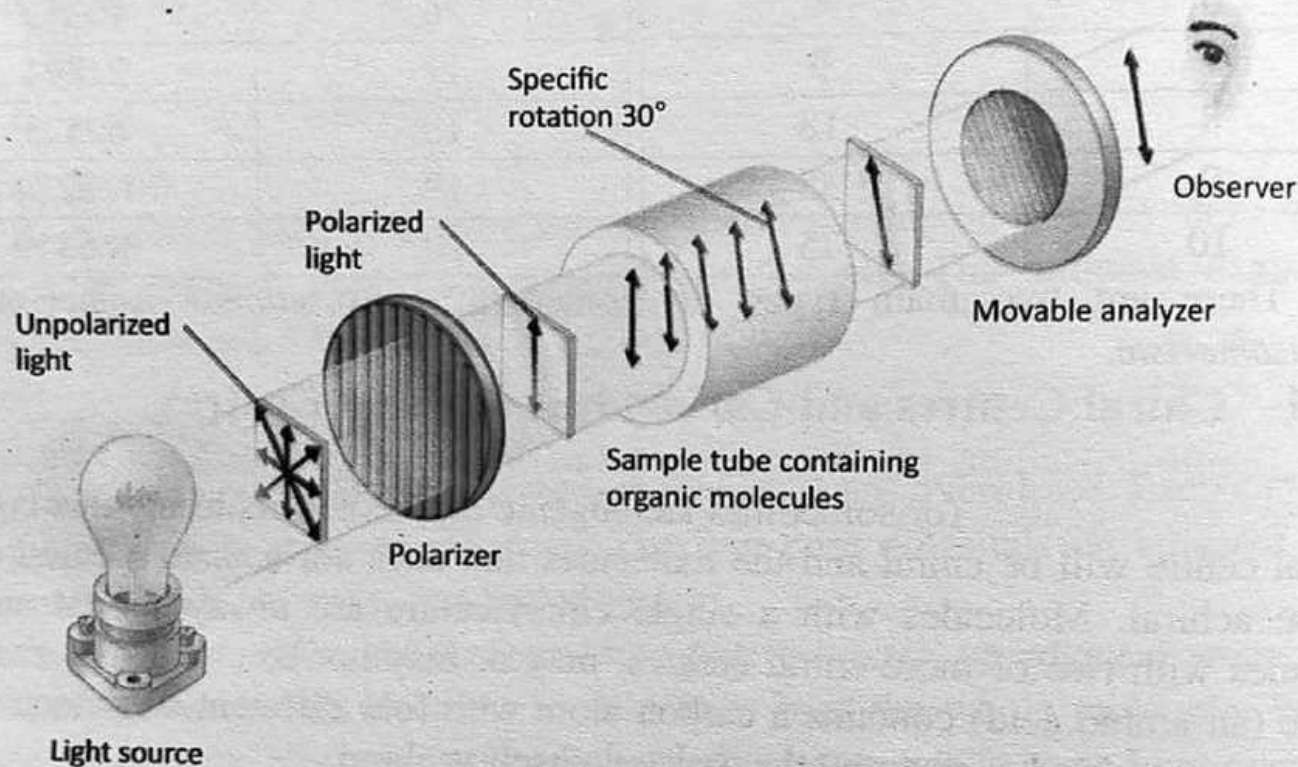


Figure 16.3: Polarimeter

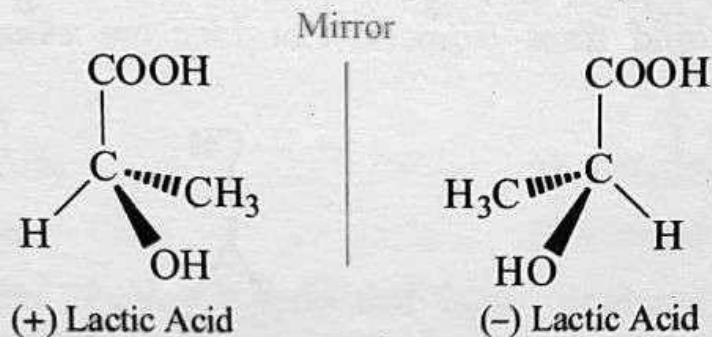
When plane polarized light is passed through a solution of chiral compound (an optically active compound), the beam of polarized light is rotated through a certain number of degrees, either in clockwise or anticlockwise direction. The compound that rotates the plane of polarization of plane-polarized light in clockwise direction is called dextrorotatory. It can be indicated in the compound's name by the prefix lower case *d* or (+). The compound that rotates the plane of polarization of plane-polarized light in anticlockwise direction is called levorotatory. It can be indicated in the compound's name by the prefix lowercase *l* or (-). *Dextro* and *levo* are Latin prefixes. The word "Dextro" means "to the right" and the word "levo" means "to the left." Sometimes lowercase *d* and *l* are used rather than (+) and (-).

16.6.3 Optical Isomers

The optically active compounds having same molecular formulas, structural formulas but differing in their interaction towards plane polarized light are called optical isomers and the phenomenon is known as optical isomerism. Optical isomers have same physical and chemical properties.

Optical Isomers of Lactic Acid

The two optically active forms of lactic acid (+) and (-) are similar in physical and chemical properties but differ only in their behaviour toward plane polarized light. The (+) lactic acid is dextrorotatory whereas (-) lactic acid is levorotatory. The (+) lactic acid is the mirror image of the (-) lactic acid.



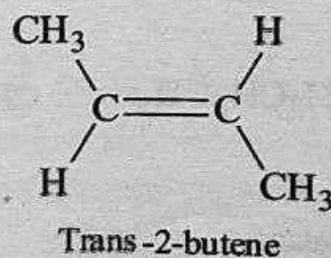
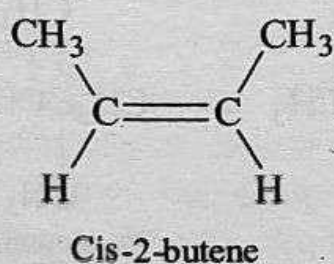
The mixture of equal amounts of (+) lactic acid and (-) lactic acid i.e. ($\pm$) lactic acid (called racemic mixture or racemate) rotate plane-polarized light to an equal extent but in opposite directions, the rotations cancel, and no rotation is observed.

16.6.4 Stereoisomers (Configurational Isomers)

The compounds having same molecular and structural formulas but differ in the arrangement of atoms or groups in space are called stereoisomers and the phenomenon is called stereoisomerism. There are two types of stereoisomers: geometric isomers and optical isomers.

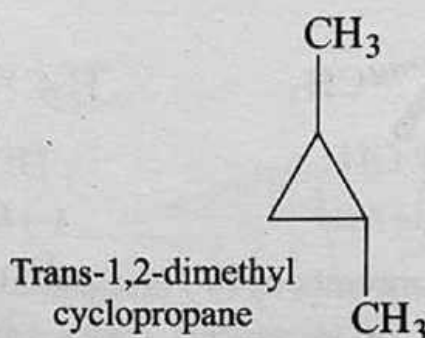
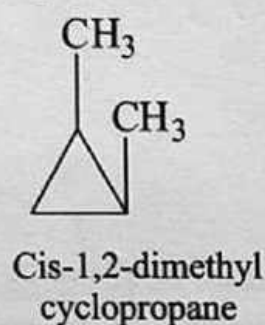
16.6.4.1 Geometrical Isomers (Cis-Trans Isomers)

Compounds having same molecular and structural formulas but restricted rotation are called geometric isomers and the phenomenon is called geometric isomerism. Restricted rotation can be caused either by a carbon-carbon double bonds or by a carbon-carbon single bonds in cyclic compounds. The cis isomer (Latin, cisoid = same side) has similar groups on the same side of carbon-carbon double bond and the trans isomer (Latin, transoid = opposite side) has the similar groups on opposite sides of the carbon-carbon double bond. For example, the cis isomer of 2-butene has hydrogen atoms on the same side of the double bond whereas the trans isomer has the hydrogen atoms on opposite sides of the double bond.



Cis and trans isomers are two different compounds and have different physical and chemical properties. It is found that *trans* isomers are more stable than the corresponding *cis* isomers. This is because, in the *cis* isomer, the bulky (big) groups are on the same side of the double bond. The repulsion of bulky groups makes the *cis* isomer less stable than *trans* isomer.

Cyclic compounds that have two substituents bonded to two different carbon atoms also have *cis* and *trans* isomers. Consider the example of 1,2-dimethylcyclopropane.



The *cis* isomer has its methyl groups on the same side of the ring, whereas the *trans* isomer has its methyl groups on opposite sides of the ring.

Conditions for Geometric Isomers

- The geometric isomers must have a double bond.
- There must be two different atoms or groups bonded to each carbon atom of the double bond.

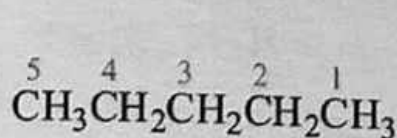
16.6.5 Constitutional isomers (Structural Isomers)

The compounds having same molecular formula but different structural formulas are called constitutional isomers and the phenomenon is called constitutional isomerism. Structural isomers differ in the arrangement of atoms within the molecule.

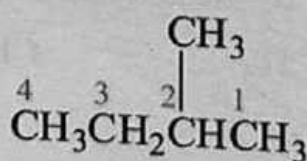
Constitutional isomers are further divided into five types namely, chain isomers, position isomers, functional group isomers, metamers and tautomers.

16.6.5.1 Chain Isomers (Skeleton Isomers)

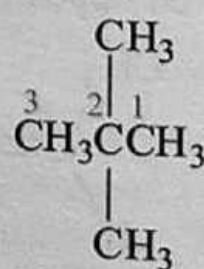
The compounds having same molecular formula but different carbon chains (or skeletons) are called chain isomers and the phenomenon is called chain isomerism. For example, the chain isomers of pentane has the same molecular formula (C_5H_{12}) but they have different chains of carbon atoms.



n-Pentane



Isopentane

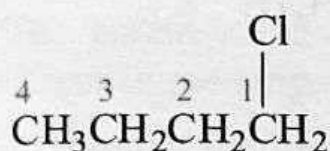


Neopentane

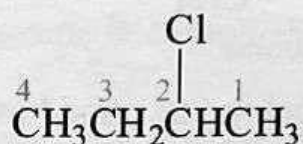
The compound n-pentane has five carbon chain, isopentane has four carbon chain and neopentane has three carbon chain.

16.6.5.2 Position Isomers

The compounds having same molecular formula but different positions of the same functional group are called position isomers and the phenomenon is called position isomerism. Examples of position isomers are the following:

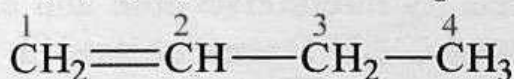


1-Chlorobutane

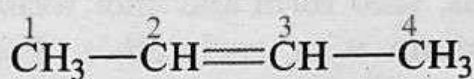


2-Chlorobutane

The compounds, 1-chlorobutane and 2-chlorobutane, have same molecular formula ($\text{C}_4\text{H}_9\text{Cl}$) but different positions of chlorine atoms (functional groups).



1-Butene



2-Butene

The compounds, 1-butene and 2-butene, have same molecular formula (C_4H_8) but different positions of double bonds (functional group).

16.6.5.3 Functional Group Isomers (Functional Isomers)

The compounds having same molecular formula but differ in the nature of functional groups are called functional group isomers and the phenomenon is known as functional group isomerism. For example, ethyl alcohol and dimethyl ether have same molecular formula ($\text{C}_2\text{H}_6\text{O}$) but different functional groups.

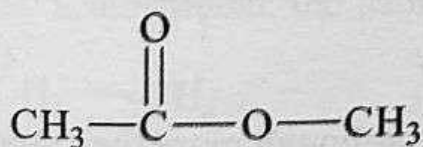


Ethyl alcohol

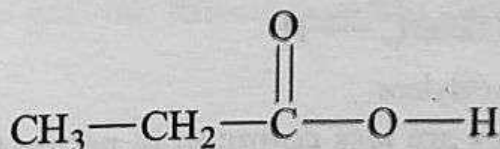


Dimethyl ether

Similarly, methyl acetate and propionic acid have same molecular formula ($\text{C}_3\text{H}_6\text{O}_2$) but different functional groups.



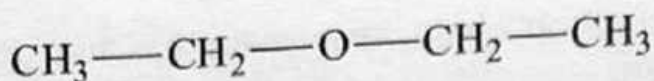
Methyl acetate



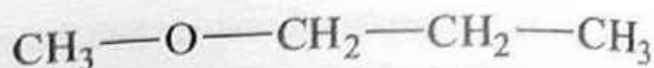
Propionic acid

16.6.5.4 Metamers

The compounds having same molecular formula and functional group but differ in the distribution of carbon atoms on either side of the functional group are called metamers and the phenomenon is called metamerism. For example, diethyl ether and methyl-n-propyl ether are metamers.

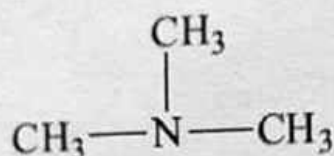


Diethyl ether

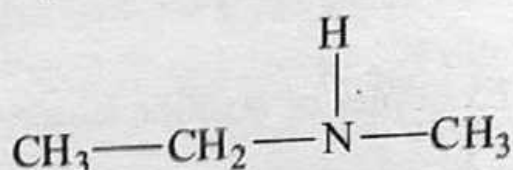


Methyl-n-propyl ether

Similarly, trimethylamine and ethylmethylaniline are metamers.



Trimethylamine

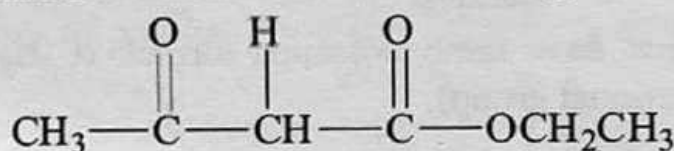


Ethylmethylaniline

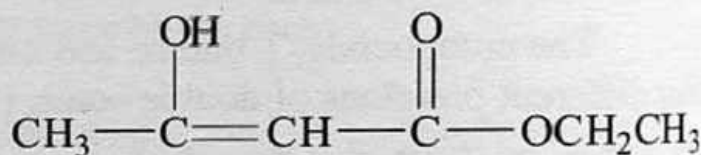
Metamers belong to same homologous series.

16.6.5.5 Tautomers

The two forms of same compound, which differ in the position of the protons and electrons are called tautomers and the phenomenon is called tautomerism. The two forms, that is, keto form and enol form are readily interconvertible and exist in dynamic equilibrium with each other. For example, ethyl acetoacetate is in an equilibrium mixture of the following two forms:



Keto-Form (93% at 25°C)



Enol-Form (7% at 25°C)

Usually the 'keto' form of the compound is more stable, but in some cases the 'enol' form can be more stable.

16.7 Alkynes

Alkynes are unsaturated hydrocarbons which contain one or more carbon-carbon triple bonds in their structures. The simplest member of the alkyne series is ethyne, commonly called acetylene. The common name of alkynes is acetylenes, after the simplest member, acetylene. They have the general formula $\text{C}_n\text{H}_{2n-2}$, where $n = 2, 3, 4, 5, \dots$. The structure for acetylene is:



Acetylene

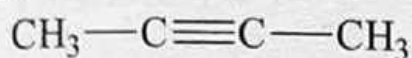
Alkynes are less common in nature than alkenes, although more than thousand different alkynes have been isolated from natural sources. They are produced during cracking of petroleum.

16.7.1 Nomenclature

Alkynes are named in the same way as alkenes. The IUPAC name of an alkyne is obtained by replacing the ending "ane" of the corresponding alkane with "yne." For example, $\text{CH}\equiv\text{CH}$ is called ethyne and $\text{CH}_3\text{C}\equiv\text{CH}$ is called propyne. When there

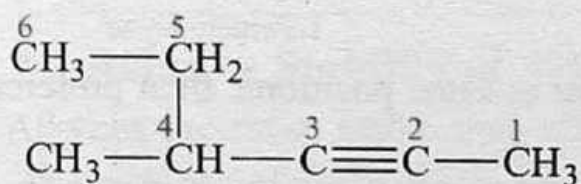
are two or more possible location for the triple bond in a molecule, its position is shown by a number. The IUPAC rules for naming alkynes are similar to those used for naming alkenes.

Step 1. Select the longest chain of carbon atoms that contains the triple bond and name it.

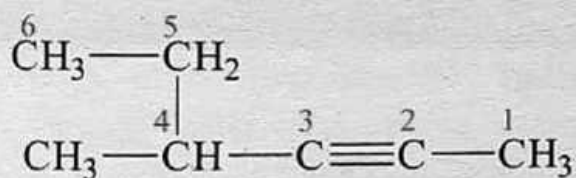


The parent name of the compound is butyne. It means that there are four carbon atoms in the longest chain.

Step 2. Number the longest chain of carbon atoms from that end which is closer to the triple bond. Alkynes with two or three carbon atoms do not need numbers.

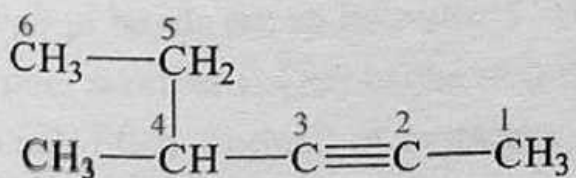


Step 3. Indicate the position of the triple bond by the lower numbered carbon atom bound by the triple bond.



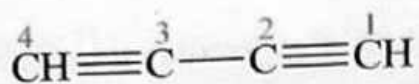
The triple bond is present between carbon 2 and 3, so the name of compound is 2-hexyne.

Step 4. Indicate the position of the substituent by the number of that carbon to which it is attached and name it in a manner similar to alkanes. The name of substituent is stated before the name of the longest continuous chain of carbon atoms that contains the triple bond, together with a number to designate the carbon to which the substituent is attached. Note that if a compound's name contains both a triple bond suffix and a substituent, the triple bond suffix gets the lowest possible number.



The methyl group is located at carbon 4 and the name of compound is 4-methyl-2-hexyne.

Step 5. If an alkyne has two or more triple bonds, the "ne" of the corresponding alkane is replaced with "diyne," "triyne," "tetrayne," and so on depending upon the number of triple bonds present in the parent alkyne.



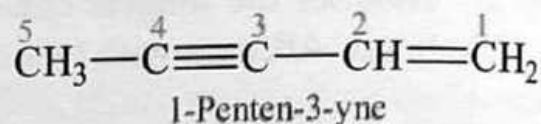
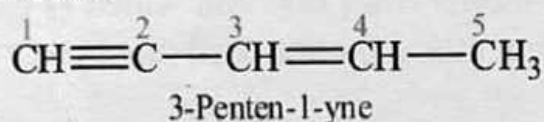
The compound has two triple bonds and the name of compound is 1,3-butadiyne or buta-1,3-diyne.

Alkenyne

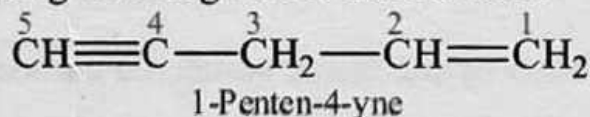
Alkynes are hydrocarbons which have both double and triple bonds.

Nomenclature

Step 1. If double and triple bonds are present at different positions from respective ends, then preference in numbering will be given to that end which is closer to double or triple bond.

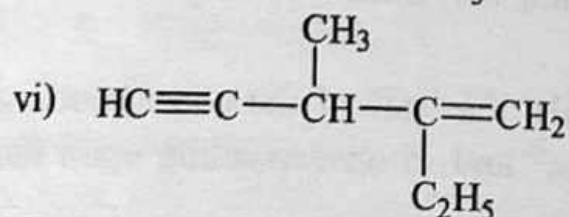
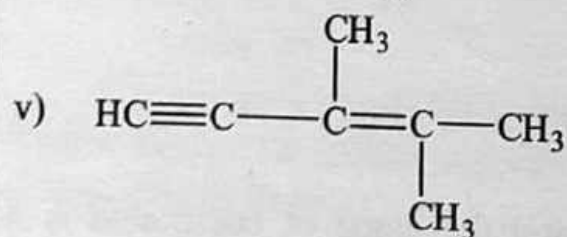
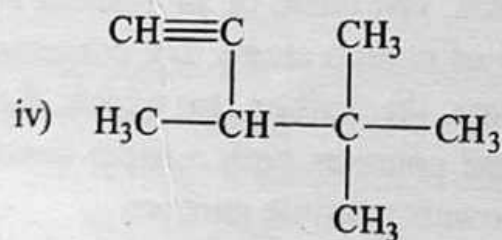
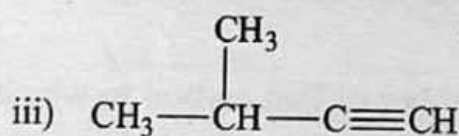


Step 2. If double and triple bonds are present at same positions, then preference in numbering will be given to double bond.



Practice Exercise - 1

Give the IUPAC name for each of the following:



Practice Exercise - 2

Draw the structure for each of the following:

- | | |
|-----------------------|-------------------------|
| i) 2-Butyne | ii) Pent-2-yne |
| iii) 1,3-Butadiyne | iv) 3-Methyl-1-butyne |
| v) 4-Methyl-2-pentyne | vi) Penta-1,3-diyne |
| vii) Hexa-2,4-diyne | viii) Octa-2,4,6-triyne |
| ix) 3-Hexen-1-yne | x) 1-Hexen-4-yne |

16.7.2 Relative Stability of Alkynes

Alkynes are more stable than alkenes because of smaller bond length of triple bond. The stability of alkynes also depend upon:

i) The Position of Triple Bond

The internal alkynes (alkynes with triple bond located elsewhere along the chain, other than the end of the chain) are more stable than terminal alkynes (alkynes with triple bond located at the end of the chain). For example, 2-pentyne is more stable than 1-pentyne.

ii) The Number of Substituents

Branched alkynes are more stable than unbranched alkynes. For example, 2,5-dimethyl-3-hexyne is more stable than 3-hexyne.

16.7.3 Structure of Alkynes

Acetylene (an alkyne) has carbon-carbon triple bond. The triple bond of acetylene consists of one sigma bond and two pi bonds. The two carbon atoms linked through pi bonds are sp hybridized. Thus, each carbon has two sp hybrid orbitals and two pure p -orbitals. One of the two sp hybrid orbitals of each carbon atom overlaps with half-filled s orbital of hydrogen atom to form C—H sigma bonds. The other sp hybrid orbital of one carbon atom overlaps with sp hybrid orbital of the other carbon atom to form C—C sigma bond. The remaining two pure p -orbitals form two pi bonds between two carbon atoms through sidewise overlapping. Acetylene has linear shape with bond angles of 180° . The carbon-carbon triple bond length is 120pm and carbon-hydrogen bond lengths are 106pm.

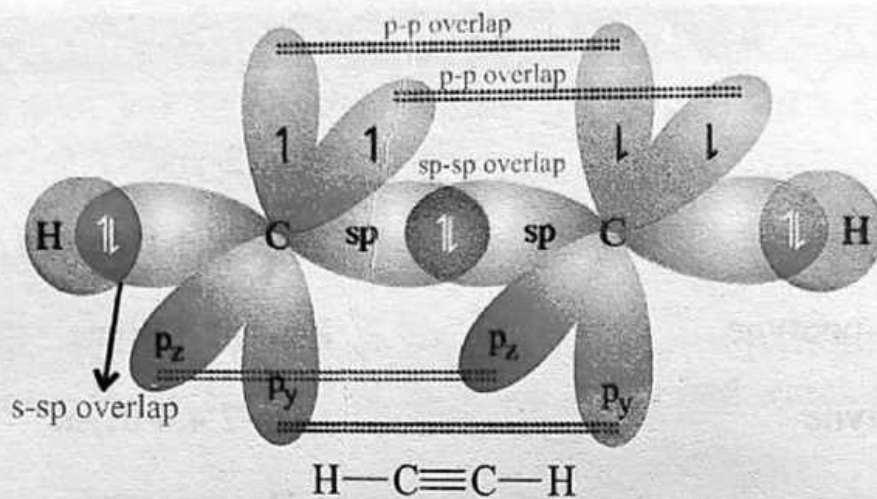


Figure 16.4: Acetylene (C_2H_2) Molecule

16.7.4 Physical Properties

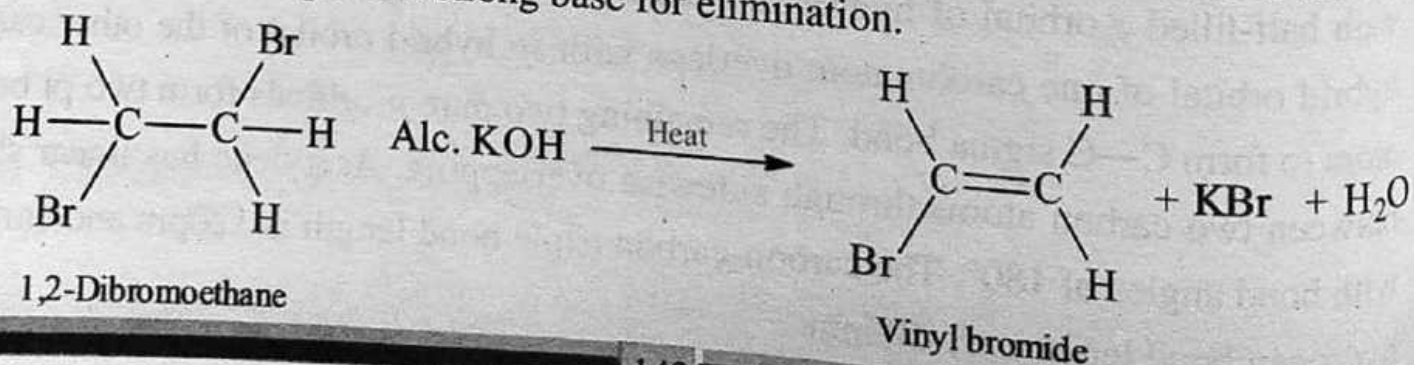
- The first three members of alkynes are gases, next eight members are liquids and higher members are solids.
- Alkynes are colourless and odourless except acetylene which has a garlic like smell.
- They are generally non-polar and are soluble in non-polar solvents like ether, benzene, CCl_4 , etc.
- Their melting points, boiling points and densities increase gradually with the increase in molecular masses.

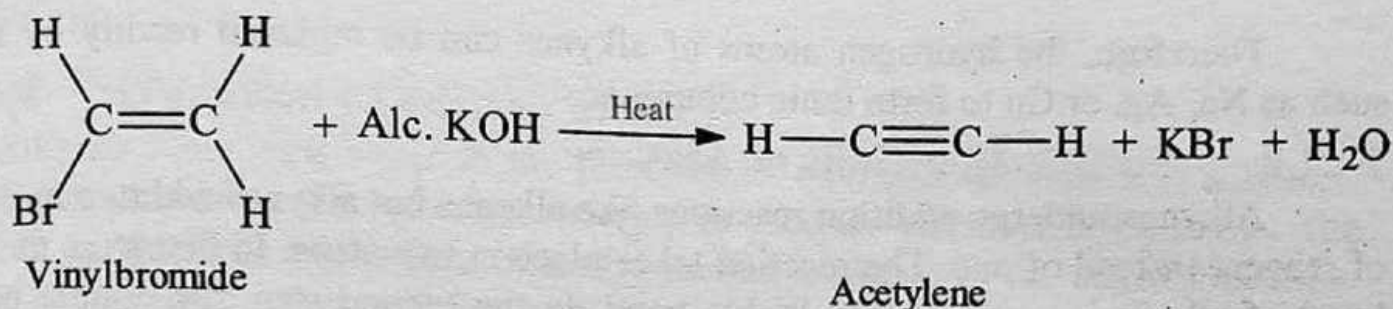
16.7.5 Preparation of Alkynes

Alkynes are prepared by the elimination of atoms (or group of atoms) from the adjacent carbon atoms.

16.7.5.1 Dehydrohalogenation of Dihalides (Removal of HX)

Alkynes are prepared by heating vicinal dihalide with alcoholic KOH. It is a two-step reaction. The removal of first HX results in the formation of vinyl halide and the removal of second HX result in the formation of alkyne. The removal of second HX is difficult and requires a strong base for elimination.

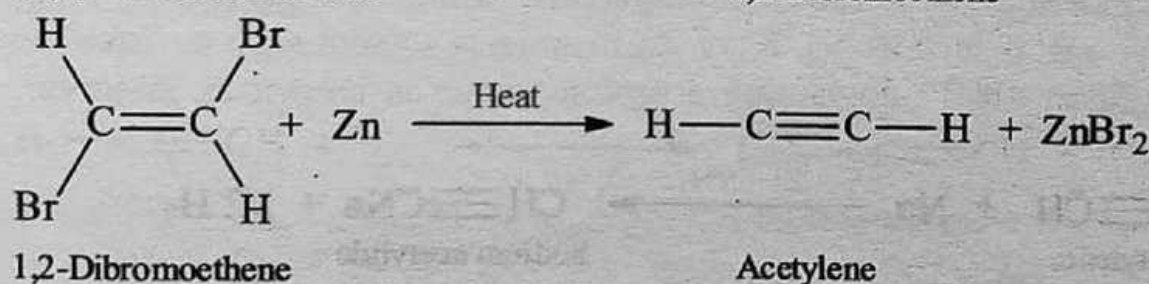
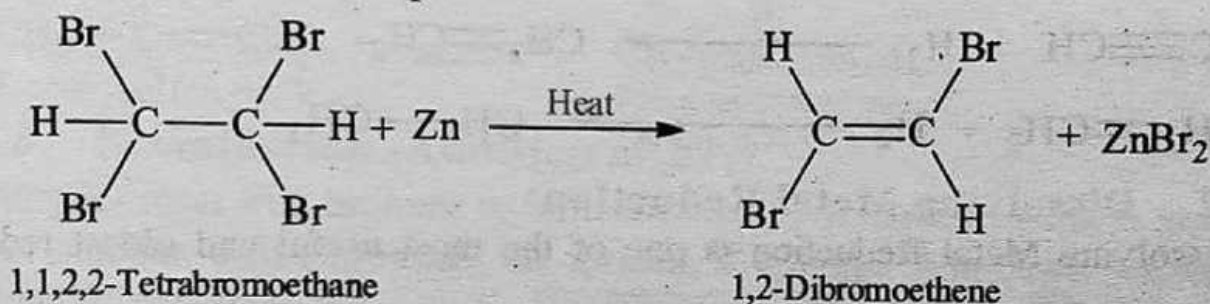




This method is useful for the preparation of alkynes because the vicinal dihalides are readily prepared from alkenes by the addition of halogens.

16.7.5.2 Dehalogenation of Tetrahalides

Alkynes are prepared by heating vicinal tetrahalides with zinc dust in ethanol. The reaction occurs in two steps.



This method is not used for the preparation of alkynes because the tetrahalides are themselves prepared by the halogenation of alkynes.

16.7.6 Reactivity of Alkynes

Alkynes contain a carbon-carbon triple bond. One of them is a sigma bond and the other two are pi bonds. The electron density between the carbon atoms is very high which draws atoms very close to each other. Hence, the electrons of the triple bond are less exposed than the electrons of the double bond. Thus alkynes are less reactive towards electrophilic reagents as compared to alkenes.

16.7.7 Acidity of Terminal Alkynes

In alkynes, the triply bonded carbon atom is sp hybridized. In terminal alkynes, the sp hybridized carbon is highly electronegative and so it is strongly electron withdrawing. This makes the attached hydrogen atom slightly acidic.



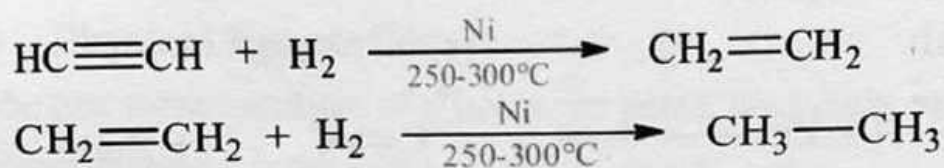
Therefore, the hydrogen atoms of alkynes can be replaced readily by metals such as Na, Ag, or Cu to form ionic compounds.

16.7.8 Addition Reactions of Alkynes

Alkynes undergo addition reactions like alkenes but alkynes add two molecules of reagent instead of one. The reaction takes place in two steps. In first step, the triple bond of alkyne is converted to double bond. In the second step, the double bond is converted to single bond.

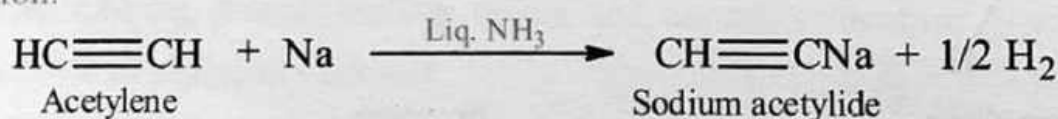
16.7.8.1 Hydrogenation (Addition of H₂)

Alkynes react with hydrogen gas in the presence of finely divided metal catalyst such as Ni, Pt or Pd at or above room temperature. The reaction occurs in two steps. The initial product is an alkene and the final product is an alkane.

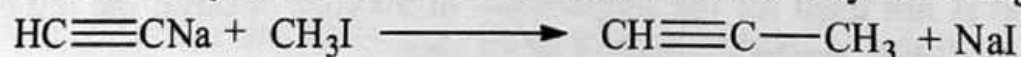


16.7.8.2 Dissolving Metal Reduction

Dissolving Metal Reduction is one of the most useful and oldest reduction methods. Reduction of organic compounds using the solution of strongly electropositive metal such as Na, K, or Zn in an inert solvent such as liquid ammonia or tetrahydrofuran (THF) containing a proton source is known as dissolving metal reduction.



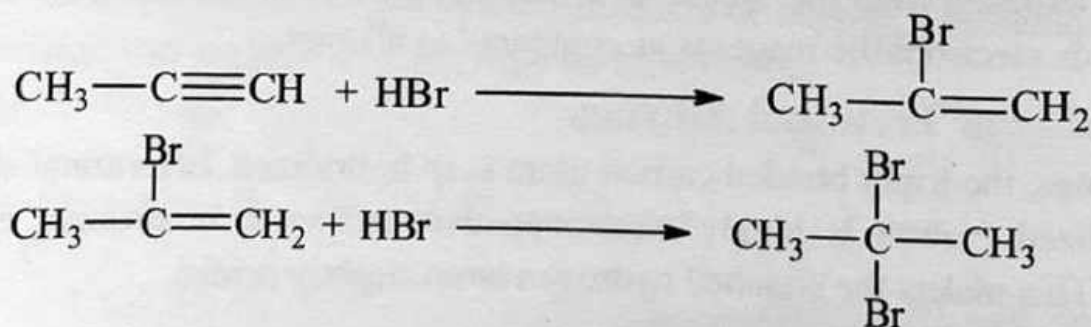
Sodium acetylides can be used to convert lower alkynes to higher alkynes.



In the above two reactions, the 'H₂' is added as 2e⁻ and 2H⁺.

16.7.8.3 Hydrohalogenation

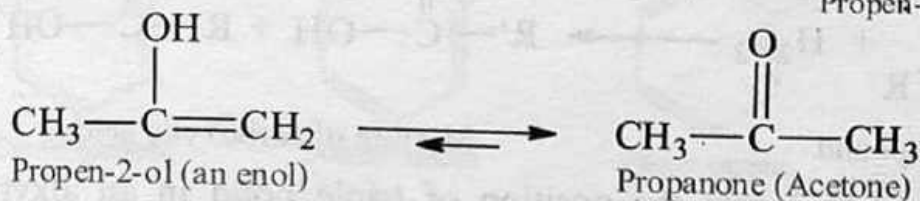
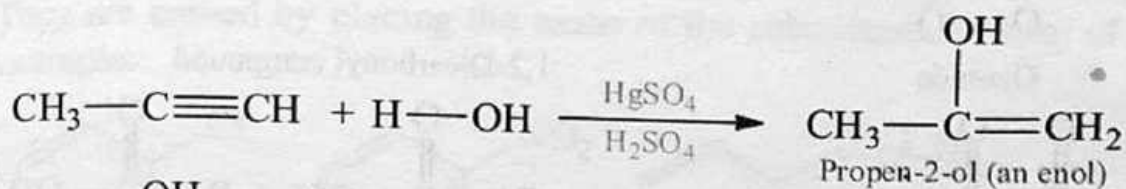
Alkynes react with halogen acids (HX) to produce dihaloalkanes. Addition of halogen acids follows Markovnikov's rule. Halogen atom adds to the carbon that has the lesser number of hydrogen atoms. The addition of HX occurs in two steps.



The order of reactivity for HX is: HI > HBr > HCl > HF

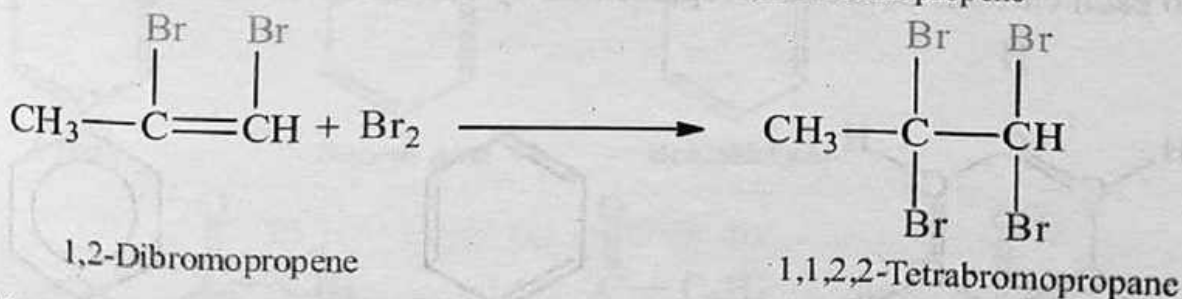
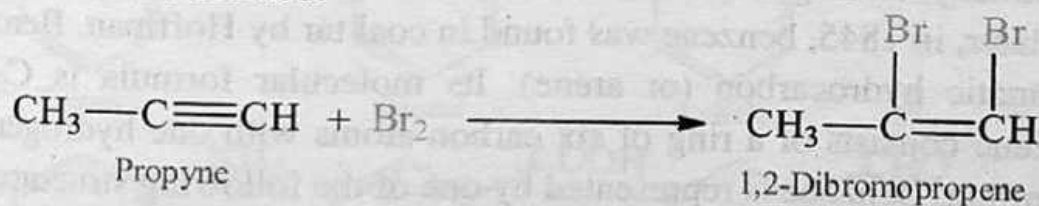
16.7.8.4 Hydration (Addition of H₂O)

Alkynes react with water in the presence of mercuric sulphate and sulphuric acid to form unstable enols which rearranges to produce carbonyl compounds. The product is an aldehyde in the case of acetylene and a ketone in the case of all other alkynes. The addition of water follows Markovnikov's rule.



16.7.8.5 Bromination (Addition of Br₂)

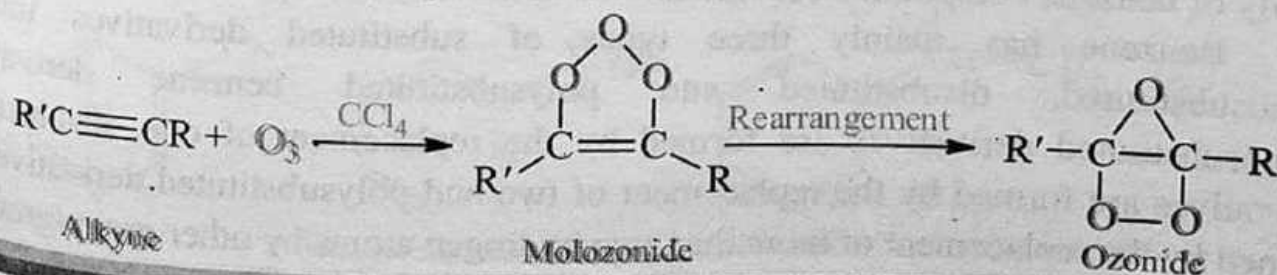
Alkynes react with bromine to form dibromides or tetrabromides. If bromine is in smaller amount, then dibromides are formed. If bromine is in larger amount, then tetrabromides are formed.



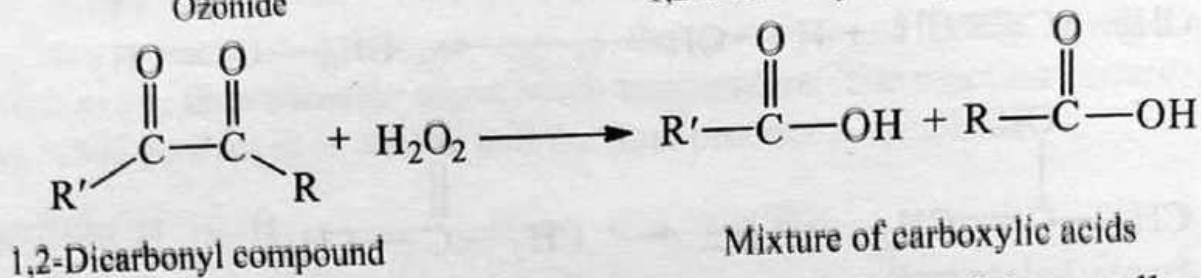
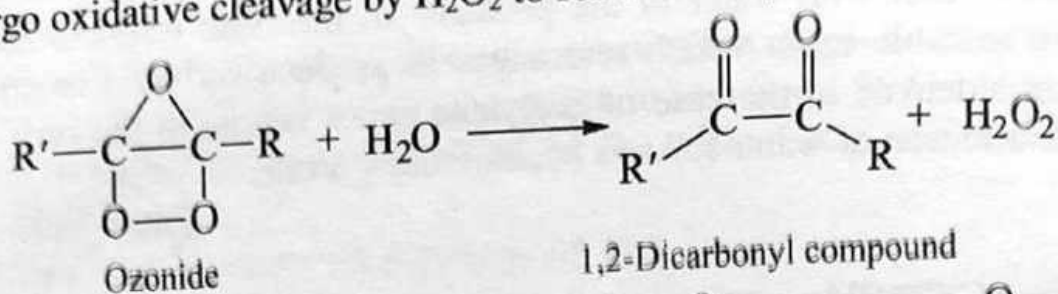
16.7.8.6 Ozonolysis (Addition of O₃)

The reaction of ozone (O₃) with alkynes to break carbon-carbon triple bond is called ozonolysis of alkynes. The reaction of ozone with alkynes occurs in two steps:

- i) Ozone adds to alkynes across the carbon-carbon π -bond to form molozonides. The molozonides rearrange to form ozonides.



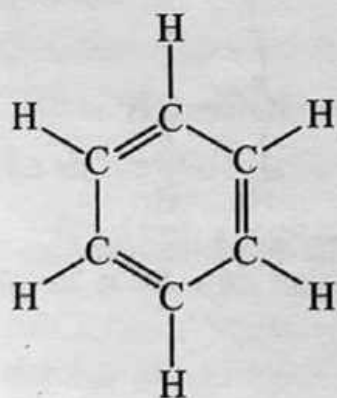
- ii) The ozonides are hydrolysed by water to form 1,2-dicarbonyl compounds which undergo oxidative cleavage by H_2O_2 to form carboxylic acid mixture.



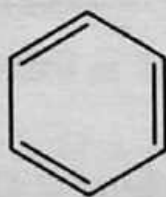
Ozonolysis is used to locate the position of triple bond in an alkyne. The molecules cleaves at the position of triple bond.

16.8 Benzene and Substituted Benzenes

Michael Faraday, an English scientist, in 1825 isolated benzene from the whale oil. Twenty year later, in 1845, benzene was found in coal tar by Hoffman. Benzene is the simplest aromatic hydrocarbon (or arene). Its molecular formula is C_6H_6 . A molecule of benzene consists of a ring of six carbon atoms with one hydrogen atom bonded to each carbon. Benzene is represented by one of the following structures:



OR



Benzene

OR



The organic compounds that contain benzene ring are called aromatic compounds. Because many compounds containing benzene had fragrant odours, the family of benzene compounds became known as aromatic compounds.

Benzene has mainly three types of substituted derivatives that is monosubstituted, disubstituted and polysubstituted benzene derivatives. Monosubstituted derivatives are formed by the replacement of one, disubstituted derivatives are formed by the replacement of two and polysubstituted derivatives are formed by the replacement of more than two hydrogen atoms by other group/groups.

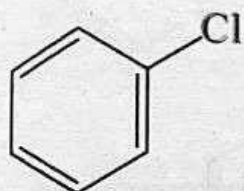
16.8.1 Nomenclature

The nomenclature of aromatic hydrocarbons is complex than aliphatic hydrocarbons.

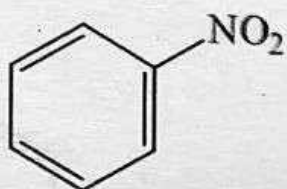
16.8.1.1 Monosubstituted Benzene Derivatives

The IUPAC rules for naming monosubstituted benzene derivatives are:

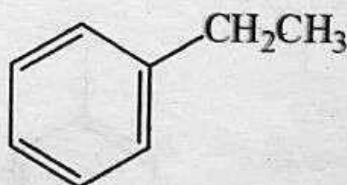
- i) They are named by placing the name of the substituent in front of benzene. For example:



Chlorobenzene

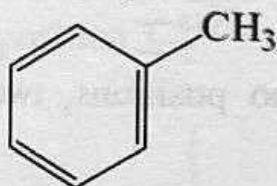


Nitrobenzene

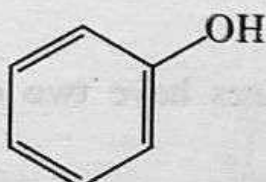


Ethylbenzene

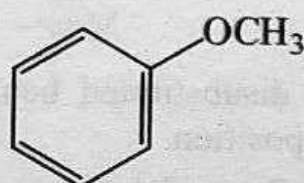
- ii) Some monosubstituted benzene derivatives have common names that are accepted by IUPAC. Such names have to be memorized.



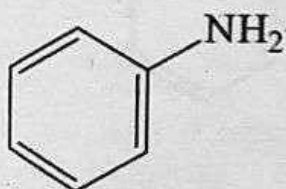
Toluene



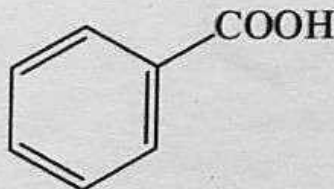
Phenol



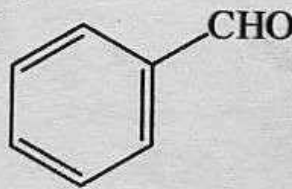
Anisole



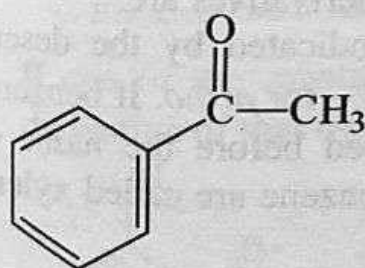
Aniline



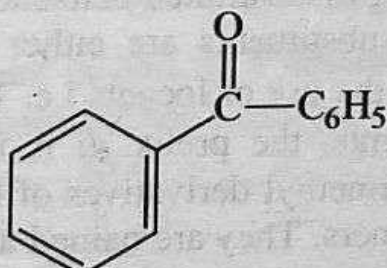
Benzoic Acid



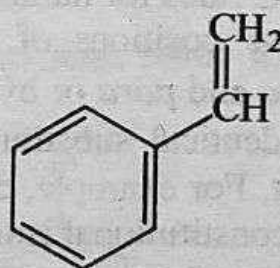
Benzaldehyde



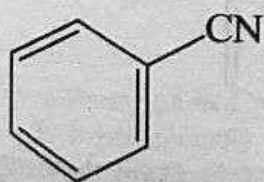
Acetophenone



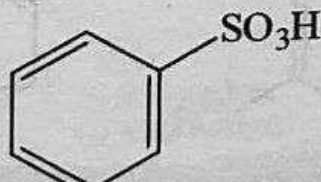
Benzophenone



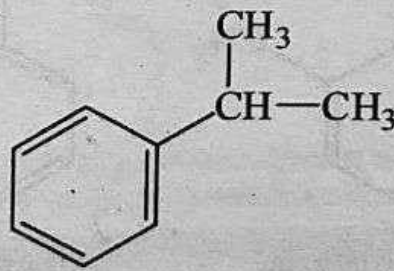
Styrene



Benzonitrile



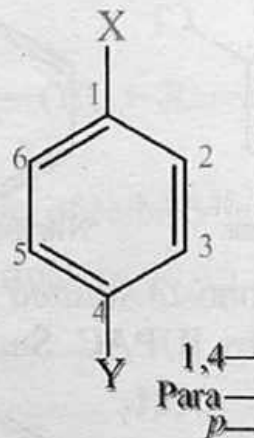
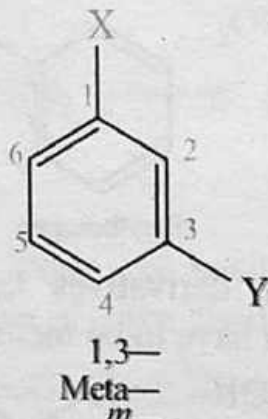
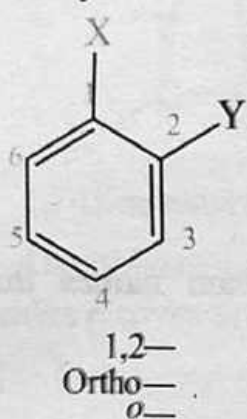
Benzenesulphonic acid



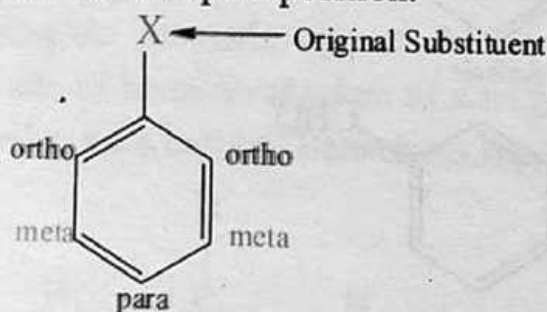
Cumene

16.8.1.2 Disubstituted Benzene Derivatives

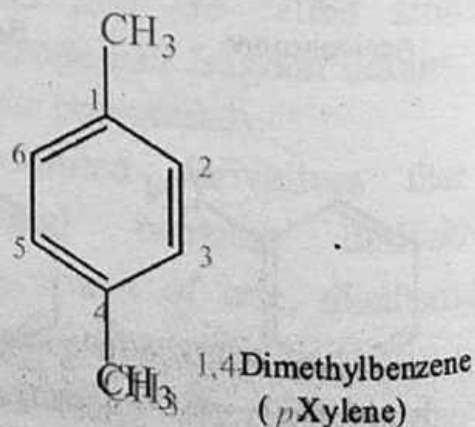
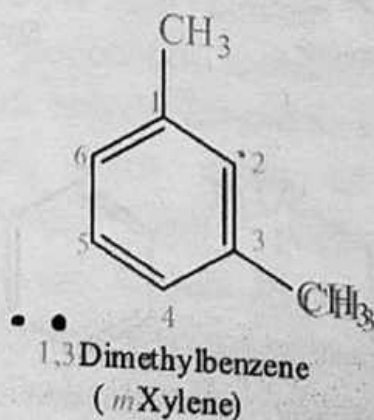
There are three different isomers for disubstituted benzene derivatives. Their structures have substitution at 1,2-; 1,3-; and 1,4- positions. They are designated by prefixes *ortho*, *meta* and *para*. 1,2- is equivalent to *ortho* (Greek, correct or straight), 1,3- is equivalent to *meta* (Greek, between, in the middle), and 1,4- is equivalent to *para* (Greek, beyond). *Ortho*, *meta* and *para* are also abbreviated as *o*-, *m*- and *p*- respectively.



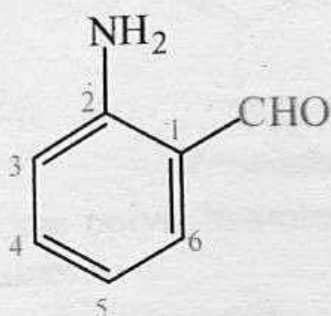
Notice that the disubstituted benzenes have two *ortho* positions, two *meta* positions and one *para* position.



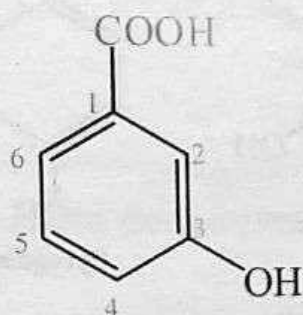
- i) The IUPAC rules for naming disubstituted benzene derivatives are:
- The relative positions of substituents are either indicated by the descriptors *ortho*, *meta* and *para* or by the use of locants i.e. 1,2- for *ortho*. If benzene ring has two identical substituents, the prefix *di* is used before the name of the substituent. For example, dimethyl derivatives of benzene are called xylene and has three constitutional isomers. They are named as:



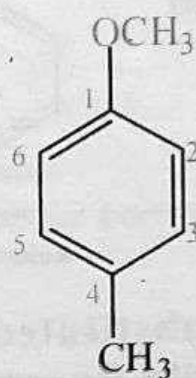
- ii) If benzene ring contains two different substituents, the position one is given to the group of high priority. The order of the priority of the groups is as: $-\text{COOH}$, $-\text{CN}$, $-\text{CHO}$, $-\text{COCH}_3$, $-\text{OH}$, $-\text{NH}_2$, $-\text{OR}$, $-\text{R}$
Examples are:



2-Aminobenzaldehyde
(*o*-Aminobenzaldehyde)

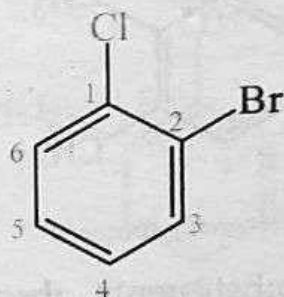


3-Hydroxybenzoic acid
(*m*-Hydroxybenzoic acid)

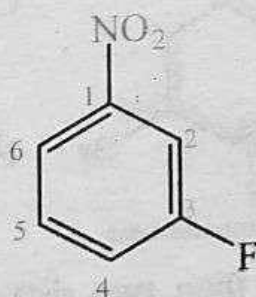


4-Methylanisole
(*p*-Methylanisole)

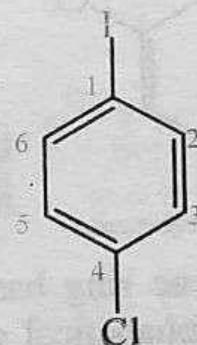
- iii) If benzene has two different substituents without priority order, then they are named in alphabetical order. The last name substituent is assumed to be in position 1.



2-Bromo chlorobenzene
(*o*-Bromo chlorobenzene)

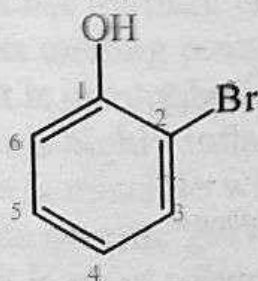


3-Fluoronitrobenzene
(*m*-Fluoronitrobenzene)

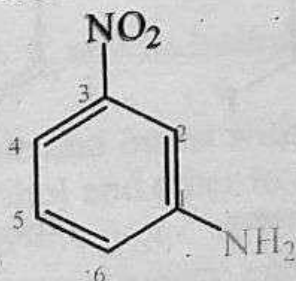


4-Chloro iodobenzene
(*p*-Chloro iodobenzene)

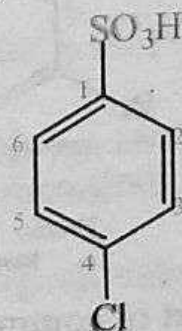
- iv) If one of the substituent is part of a common root, name the compound as a derivative of that monosubstituted benzene.



2-Bromophenol
(*o*-Bromophenol)

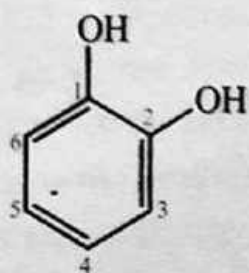


3-Nitroaniline
(*m*-Nitro aniline)

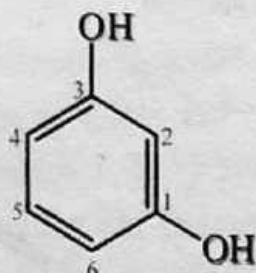


4-Chlorobenzenesulphonic acid
(*p*-Chlorobenzenesulphonic acid)

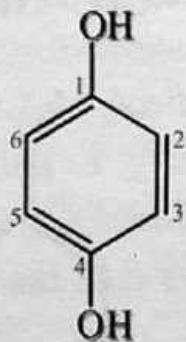
- v) Some disubstituted benzene derivatives are better known by their common names.



Catechol



Resorcinol

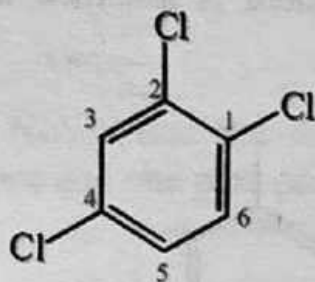


Hydroquinone

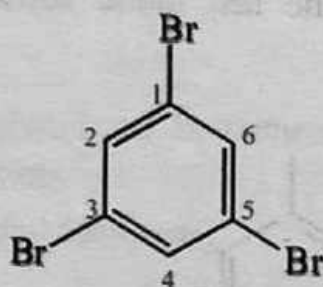
16.8.1.3 Polysubstituted Benzene Derivatives

The IUPAC rules for naming polysubstituted benzene derivatives are:

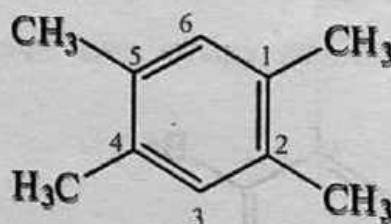
- i) When benzene ring has more than two identical substituents, the prefix *tri* is used for three, *tetra* for four, *penta* for five and *hexa* for six before the name of the substituents. Assign the lowest possible numbers to the substituents.



1,2,4-Trichlorobenzene

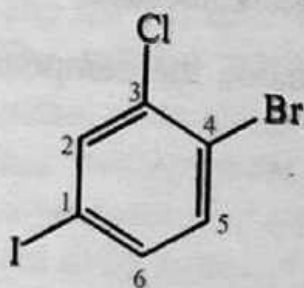


1,3,5-Tribromobenzene

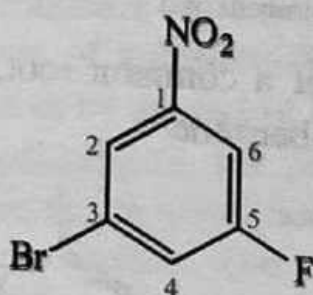


1,2,4,5-Tetramethylbenzene

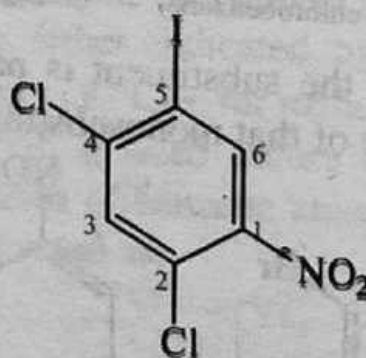
- ii) When benzene ring has more than two different substituents, then they are named in alphabetical order. The last name substituent is assumed to be in position 1.



4-Bromo-3-chloroiodobenzene

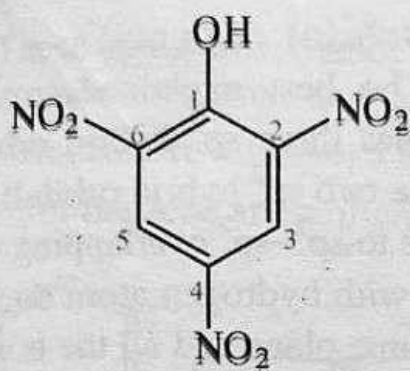


3-Bromo-5-fluoronitrobenzene

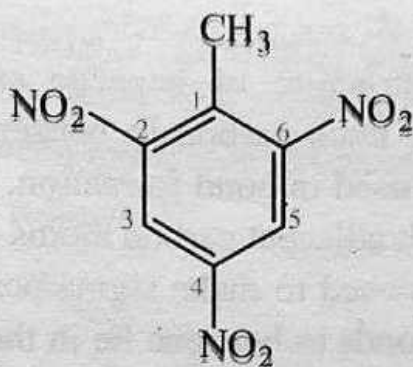


2,4-Dichloro-5-iodonitrobenzene

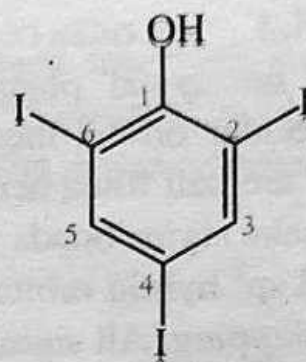
- iii) If substituents are part of common roots, name the compound as a derivative of that monosubstituted benzene. The substituent that includes the common root is assumed to be in position 1.



2,4,6-Trinitrophenol

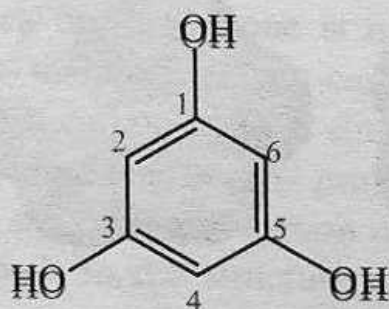


2,4,6-Trinitrotoluene

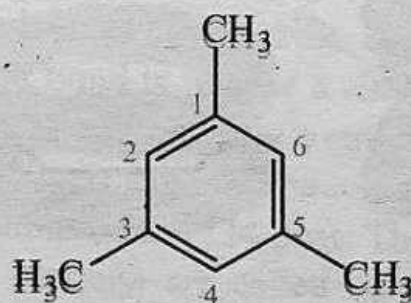


2,4,6-Triiodophenol

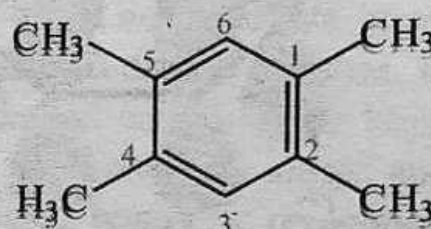
- iv) Some polysubstituted benzene derivatives are better known by their common names.



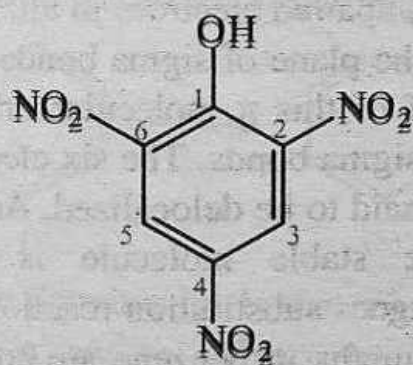
Phloroglucinol



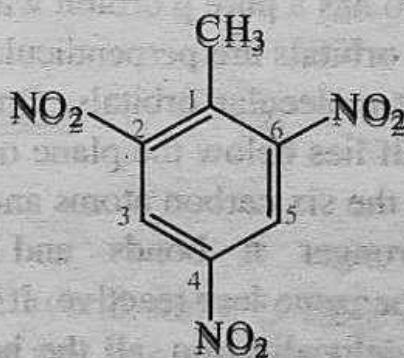
Mesitylene



Durene



Picric acid



TNT

16.8.2 Physical Properties of Benzene

- i) Benzene is a colourless liquid and has peculiar smell.
- ii) It has burning taste.
- iii) Its melting point is 5.5°C and its boiling point is 80.1°C .
- iv) It is insoluble in water.
- v) It is highly inflammable and burns with luminous and smoky flame.
- vi) It is miscible with alcohol and ether in all proportions.
- vii) Its specific gravity is 0.884 g/cm^3 at 15°C .
- viii) It is good solvent for many organic and inorganic substances such as fats, resins, sulphur, phosphorus, and iodine.
- ix) Its vapours are highly toxic which on inhalation produce loss of consciousness. In long run, its vapours destroy the red and white blood cells.

16.8.3 Structure of Benzene (Molecular Orbital Aspects)

The hexagonal planar structure of benzene can be best explained in terms of molecular orbital theory. Each carbon in benzene has three sp^2 hybrid orbitals and they are half filled hence used in bond formation. The two sp^2 hybrid orbitals are used to make sigma bonds with adjacent carbon atoms due to sp^2-sp^2 overlapping while the third sp^2 hybrid orbital is used to make sigma bond with hydrogen atom due to sp^2-s overlapping. All sigma bonds in benzene lie in the same plane and all the bond angles are of 120° . This confirms the regular hexagonal structure of benzene.

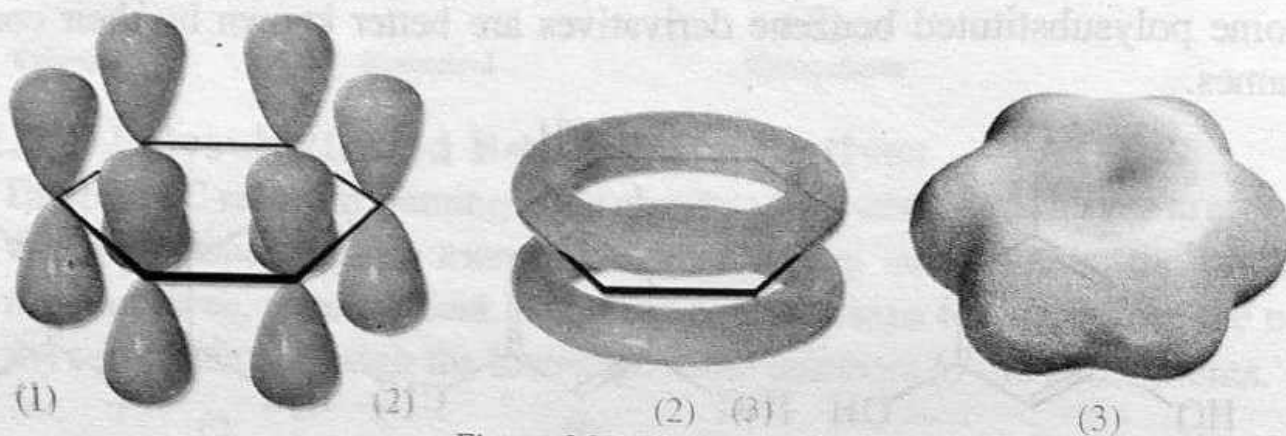


Figure 16.5: Structure of Benzene

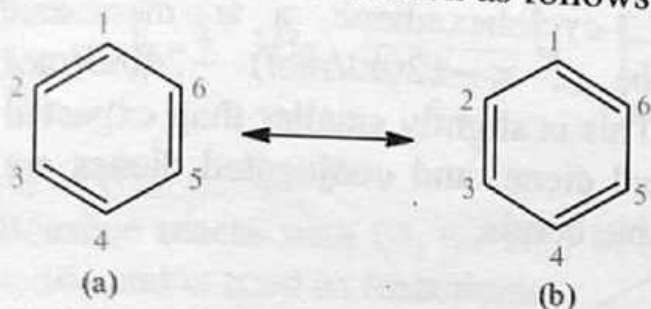
Each carbon also has a pure p orbital with an unpaired electron. In all, there are six p orbitals. These p orbitals are perpendicular to the plane of sigma bonds. The six pure p orbitals form π -molecular orbitals. One half of this π molecular orbital lies above and the other half lies below the plane of the sigma bonds. The six electrons of the p orbitals cover all the six carbon atoms and are said to be delocalized. As a result of delocalization, stronger π bonds and more stable molecule is formed. Delocalization makes benzene less reactive. It undergoes substitution reactions rather than addition. Due to delocalization, all the bond lengths in benzene are equal. The delocalization of six π electrons is shown by a circle in the ring.

16.8.4 Resonance, Resonance Energy and Stabilization

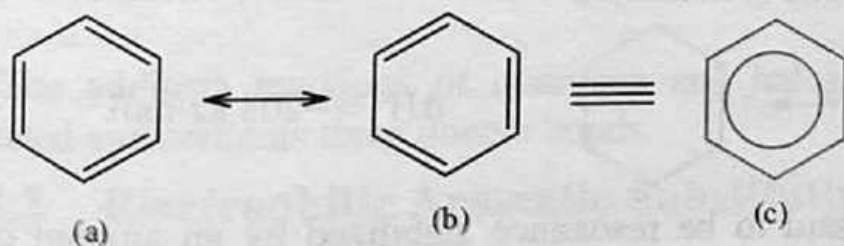
16.8.4.1 Resonance

The resonance is another term that is used for delocalization. The process in which two or more structures are written for a compound which differ only in the arrangement of electrons is called resonance. The different structures obtained are called resonance structures. They are also known as contributing structures or canonical structures. The resonance theory gave the correct description for the structure of benzene. It states that whenever a molecule is represented by two or more structures any one of the structure alone is not able to explain the characteristics of the molecule on the whole. The actual structure in such cases is a hybrid of all the resonance structures. These resonance structures are hypothetical and exist only in

theory. These structures cannot be isolated. In writing resonance structures we are allowed to move electrons and not the atoms. The resonance is represented by placing a double headed arrow ($\longleftrightarrow$) between resonance structures. The major contributing structures for benzene are written as follows:



Each drawing alone is inadequate to describe the structure of benzene. The problem is that each carbon-carbon bond is neither a single bond nor a double bond. Each carbon-carbon bond is single in one resonance structure and double in other, so the actual bond length (139 pm) is intermediate between a carbon-carbon single bond (153 pm) and a carbon-carbon double bond (134 pm). The three alternate single and double bonds in the structure of benzene are called conjugate bonds or resonating bonds. The actual structure of benzene may be represented as a hybrid of the above two (a and b) resonance structures.

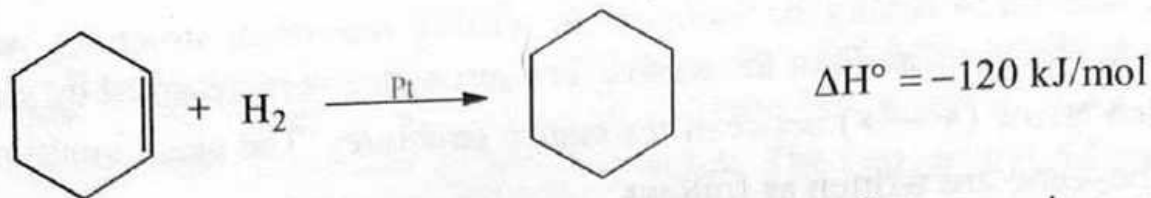


The drawing 'c' is the resonance hybrid and it is more stable than resonance structures 'a' and 'b'. This is because in any one canonical form the π -electrons are localized while in the hybrid the π -electrons are delocalized over six atoms of the benzene ring.

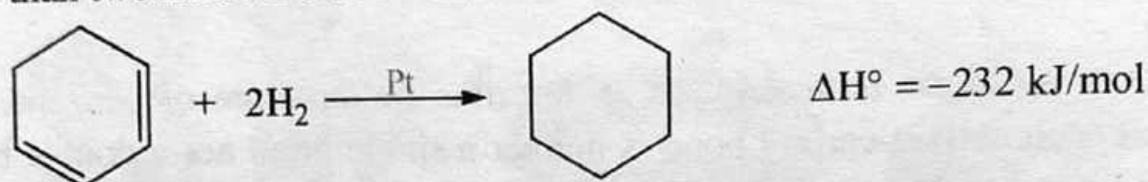
16.8.4.2 Resonance Energy and Stability of Benzene

The difference between the energy of the actual molecule (a resonance hybrid) and the most stable resonance structure is called resonance energy. It is also known as delocalization energy. Resonance energy can be used to explain unusual stability and lack of reactivity toward addition of benzene. Resonance energy can be determined by the difference between the calculated and experimental heats of hydrogenation of the compound. Consider the following thermochemical results to see the unusual stability of benzene.

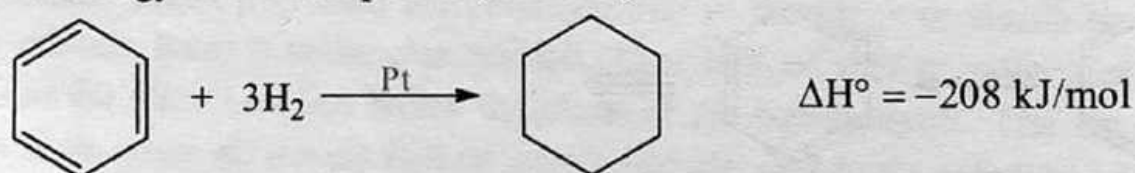
The heat of hydrogenation for cyclohexene, a six-membered ring containing one double bond, is found to be -120kJ/mol .



The heat of hydrogenation for 1,3-cyclohexadiene, a six-membered ring containing two double bonds, should be $(2 \times -120 \text{ kJ/mol}) -240 \text{ kJ/mol}$. The observed value, however, is -232 kJ/mol . This is slightly smaller than expected value because 1,3-cyclohexadiene is a conjugated diene, and conjugated dienes are more stable than two isolated carbon-carbon double bonds.



The heat of hydrogenation of 1,3,5-cyclohexatriene (benzene), a six-membered ring containing three double bonds, should be $(3 \times -120 \text{ kJ/mol}) -360 \text{ kJ/mol}$. The observed heat of hydrogenation, however, is only -208 kJ/mol . The observed value is 152 kJ/mol less than expected value. This difference between the amount of observed heat of hydrogenation and that of calculated heat of hydrogenation is called the resonance energy of the compound (benzene).



Benzene is, therefore, said to be resonance stabilized by an amount of 152 kJ/mol , which is known as resonance energy. Now it becomes clear that the process of resonance makes benzene more stable than the other unsaturated hydrocarbons.

16.8.5 Reactivity and Reactions of Benzene

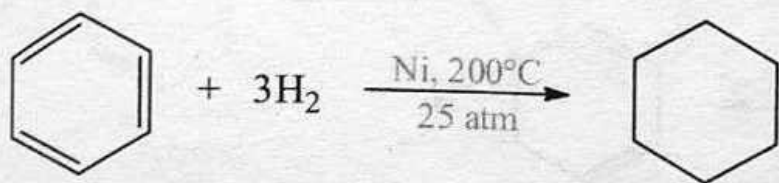
Benzene is highly unsaturated and has six π -electrons delocalized in six p orbitals. But it does not undergo addition reactions as happily as other unsaturated hydrocarbons such as alkenes and alkynes. This is because the loosely π -electrons in alkenes and alkynes are localized but in benzene are delocalized. In alkenes and alkynes the π -electrons are easily available for different addition reactions while, in benzene, the π -electrons are not easily available. Therefore, benzene is less reactive than alkenes and alkynes towards electrophilic addition reactions. The most common reactions of benzene are electrophilic substitution reactions.

16.8.5.1 Addition Reactions

There are two types of addition reactions: addition of hydrogen and addition of halogens.

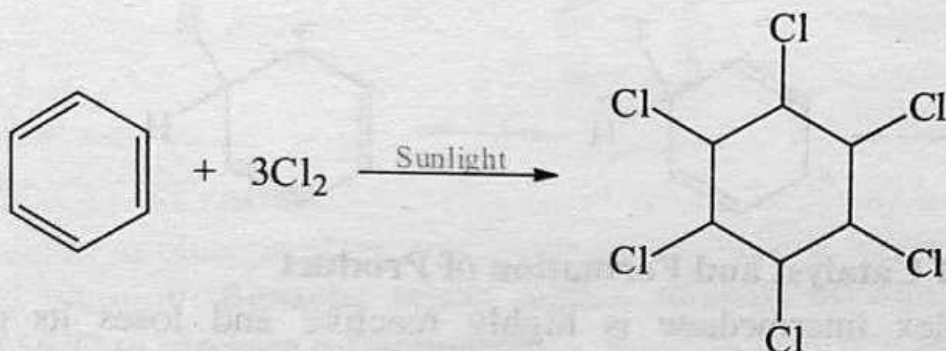
Reaction of Hydrogen (Catalytic Hydrogenation)

Benzene reacts with hydrogen in the presence of catalyst like Pt, Pd and Ni at temperature and pressure to produce cyclohexane.



Reaction of Halogens

Benzene reacts with Cl_2 (or Br_2) in the presence of sunlight to form benzene chloride and is used as insecticide.



Reaction of F_2 with benzene is vigorous and reaction of I_2 with benzene is very slow.

The addition reactions of hydrogen and halogens indicate that benzene is unsaturated and contains three double bonds.

5.2 Electrophilic Aromatic Substitution Reactions

5.2.1 General Introduction

The most important reactions of benzene are electrophilic substitution reactions. In these reactions, one of the hydrogen atom (proton) of the benzene ring is replaced by an electrophile. The electrophilic substitution reactions carried out in the presence of Lewis acid catalyst such as FeX_3 or AlX_3 that help in generation of electrophile. The electrophile will either be a positive ion, or the slightly positive end of a polar molecule.

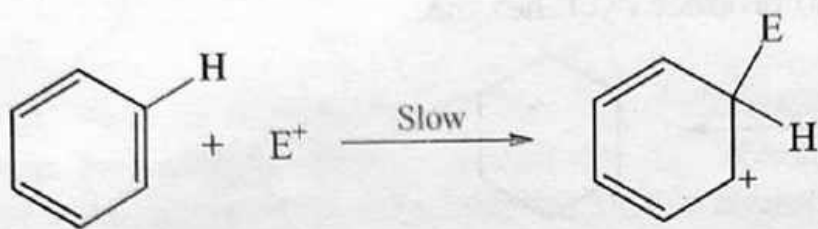
General Mechanism

The electrophilic aromatic substitution reaction generally involves two-steps:

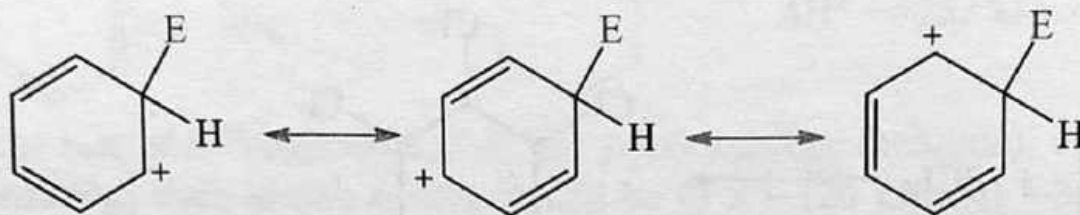
1: Formation of Arenium Ion

The electrophile attacks the π -electrons of the benzene ring to form a σ -bond with one of the carbon atoms of the benzene ring, generating a positively charged intermediate (cyclohexadienyl carbocation) known as Arenium ion or sigma complex. The sigma complex is not aromatic because the carbon that forms a bond to the electrophile becomes sp^3 hybridized and it has no p -orbital. Now only five carbon

atoms of the ring are sp^2 hybridized and has p -orbitals. Hence, the sigma complex does not possess a continuous system of overlapping p -orbitals.

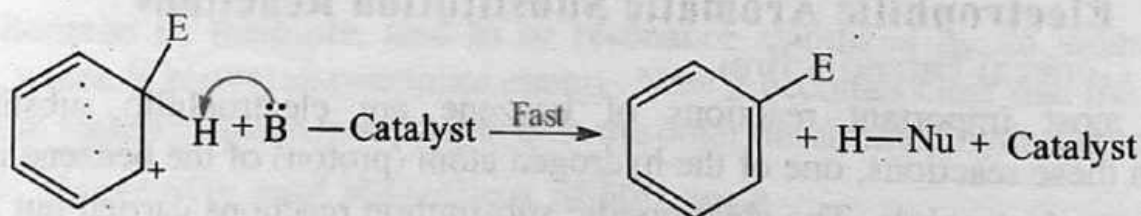


The positive charge is effectively distributed over three carbon atoms by resonance which makes it partially stable.



Step 2: Regeneration of Catalyst and Formation of Product

The sigma complex intermediate is highly reactive and loses its proton from sp^3 hybridized carbon to a Lewis base. The electrons that held the proton (hydrogen) move into the ring to restore its aromaticity. Remember that the proton is always removed from the carbon that has formed the new bond with the electrophile.

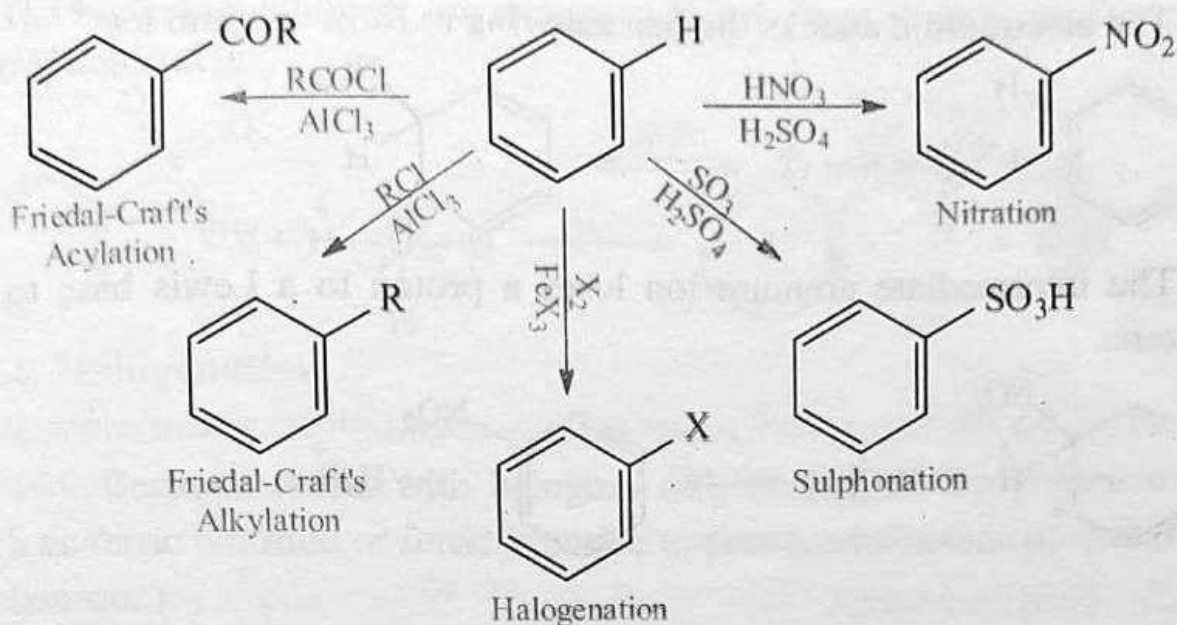


Keep in Mind

The first step is rate determining step and is relatively slow. This step consumes energy because an aromatic compound is being converted into a much less stable non-aromatic intermediate.

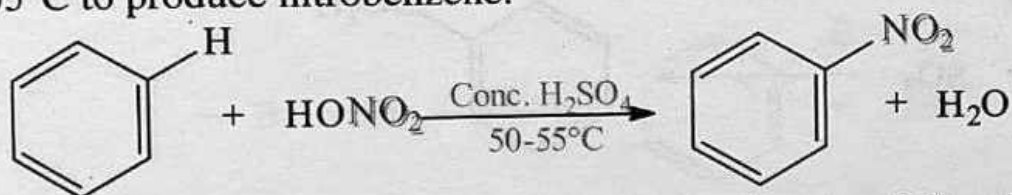
The second step is fast because the aromaticity of the benzene ring is restored.

The five most useful electrophilic aromatic substitution reactions are nitration, sulphonation, halogenation, Friedel-Craft's alkylation and Friedel-Craft's acylation.



16.8.5.2.2 Nitration

The replacement of hydrogen of an organic compound by a nitro group is called nitration. Benzene reacts with a mixture of conc. HNO_3 and conc. H_2SO_4 at $50-55^\circ\text{C}$ to produce nitrobenzene.

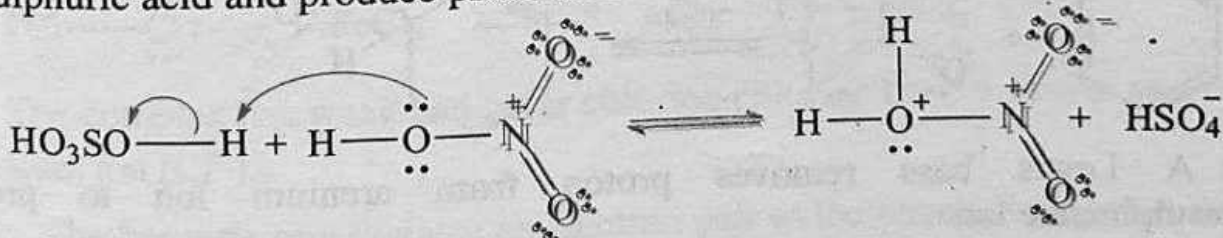


Conc. H_2SO_4 acts as a catalyst and increases the rate of chemical reaction by increasing the concentration of the electrophile, NO_2^+ (the nitronium ion).

Mechanism

The electrophile (NO_2^+) is produced from the acid-base reaction that occurs between HNO_3 and H_2SO_4 .

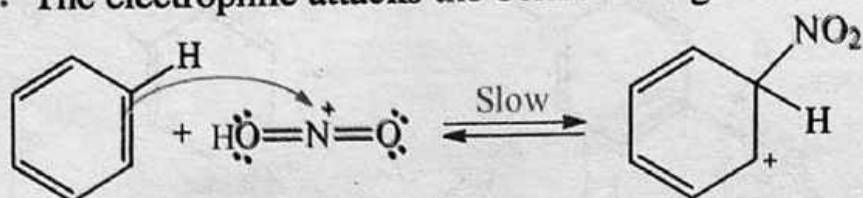
Step 1: Nitric acid acts as a base to accept a proton (hydrogen ion) from the stronger acid, sulphuric acid and produce protonated nitric acid.



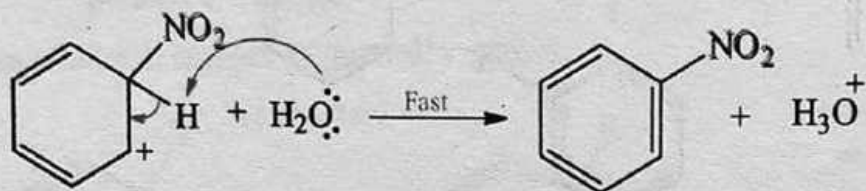
Step 2: Now protonated nitric acid dissociate to form a nitronium ion.



Step 3: The electrophile attacks the benzene ring to form arenium ion.

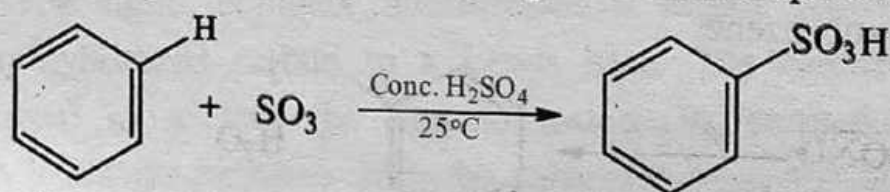


Step 4: The intermediate arenium ion loses a proton to a Lewis base to produce nitrobenzene.



16.8.5.2.3 Sulphonation

The replacement of hydrogen of an organic compound by a sulphonic acid ($-\text{SO}_3\text{H}$) group is called sulphonation. Benzene reacts with fuming sulphuric acid ($\text{H}_2\text{SO}_4 + \text{SO}_3$) at room temperature to give benzenesulphonic acid.

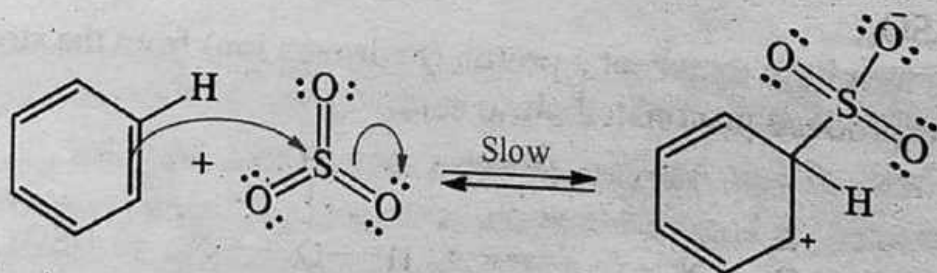


Mechanism

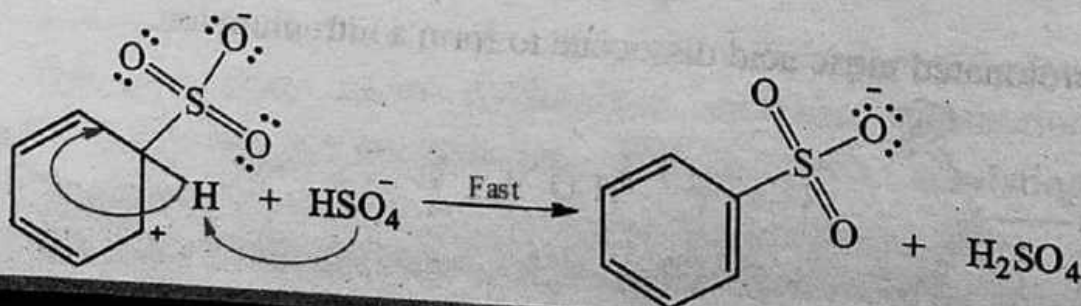
Step 1: The sulphuric acid ionizes in water to produce hydrogen sulphate and hydronium ions.



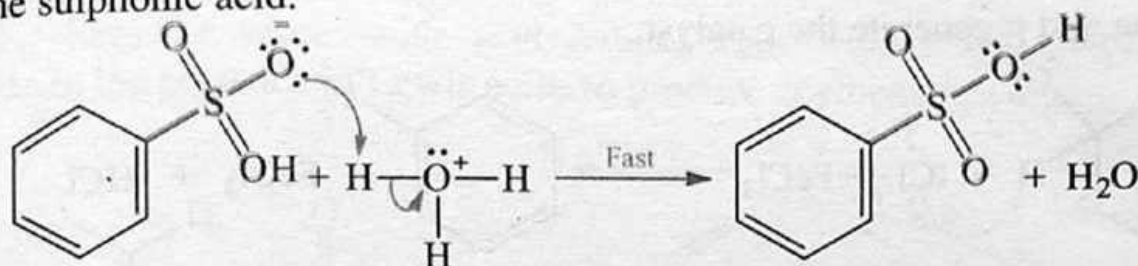
Step 2: The electrophile attacks the benzene ring to form arenium ion.



Step 3: A Lewis base removes proton from arenium ion to produce benzenesulphonate ion.

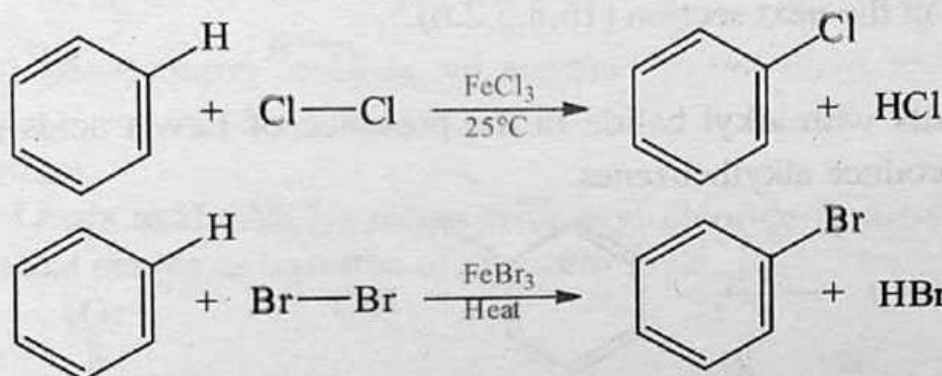


Step 4: The benzenesulphonate ion accepts a proton from hydronium ion to produce benzene sulphonic acid.



16.8.5.2.4 Halogenation

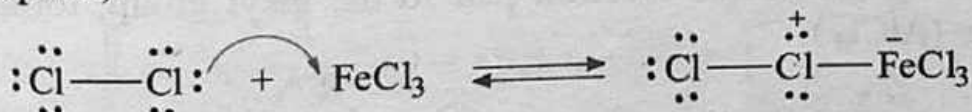
The replacement of hydrogen of an organic compound by a halogen is called halogenation. Benzene reacts with halogens (Cl_2 or Br_2) in the presence of Lewis acids such as ferric chloride or ferric bromide to produce halobenzene (chlorobenzene or bromobenzene).



The reactions of iodine and fluorine are not synthetically useful because the reaction of iodine with benzene is too slow and that of fluorine is too fast.

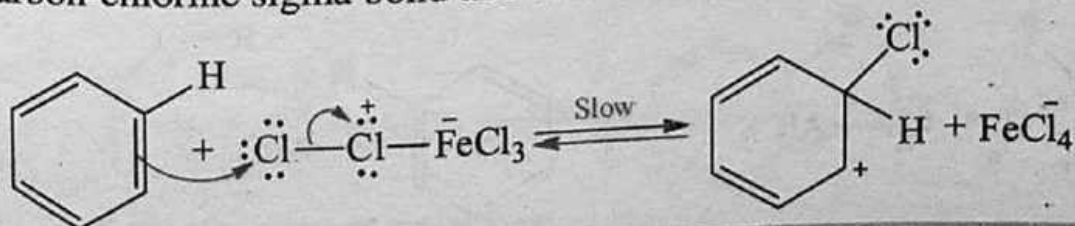
Mechanism

Step 1: Chlorine reacts with FeCl_3 to produce a Lewis acid-base complex (electrophile).

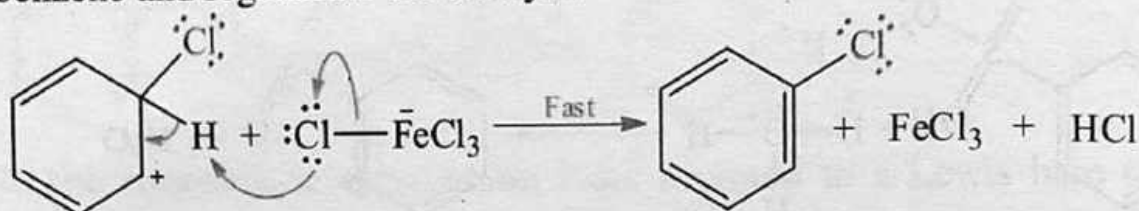


The complex has weak and polar chlorine-chlorine bond and acts as a source of chloronium ion (Cl^+).

Step 2: The benzene ring donates an electron pair to the terminal chlorine, forming a new carbon-chlorine sigma bond and forms an arenium ion along with a base (FeCl_4^-).



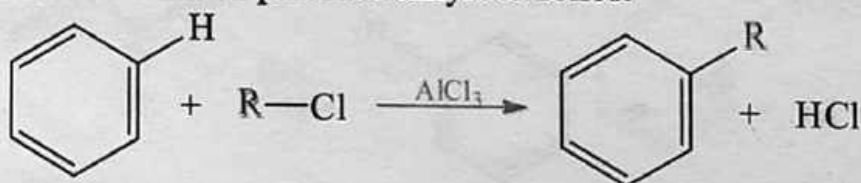
Step 3: A base (FeCl_4^-) removes the proton from the arenium ion to form chlorobenzene and regenerate the catalyst.



16.8.5.2.5 Friedel-Crafts Alkylation

Charles Friedel, a French chemist, and James Crafts, an American chemist, discovered new methods for the preparation of alkylbenzenes and acylbenzenes in 1877. Because of this, these reactions are known as Friedel-Crafts alkylation and acylation reactions. We are going to study the Friedel-Crafts alkylation here and Friedel-Crafts acylation in the next section (16.8.5.2.6).

The replacement of hydrogen of benzene by an alkyl group ($-\text{R}$) is called alkylation. Benzene reacts with alkyl halide in the presence of Lewis acids such as aluminium chloride to produce alkylbenzenes.

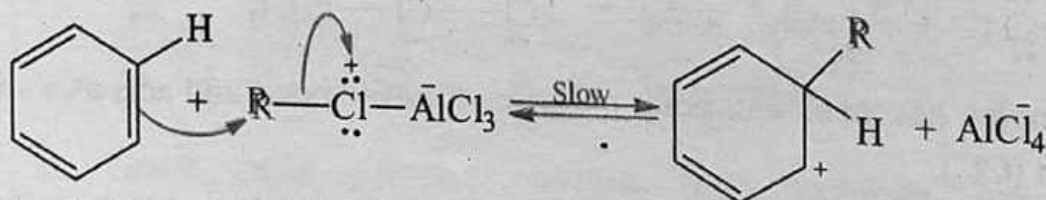


Mechanism

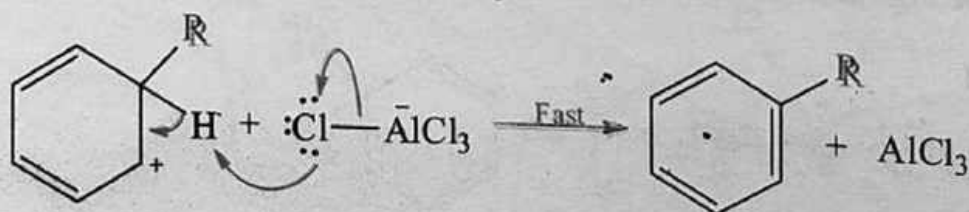
Step 1: Lewis acid (AlCl_3) reacts with alkyl chloride to produce a Lewis acid-base complex that serves as a source of an electrophile.



Step 2: The benzene ring donates an electron pair to the alkyl group, forming the arenium ion and a base (AlCl_4^-).

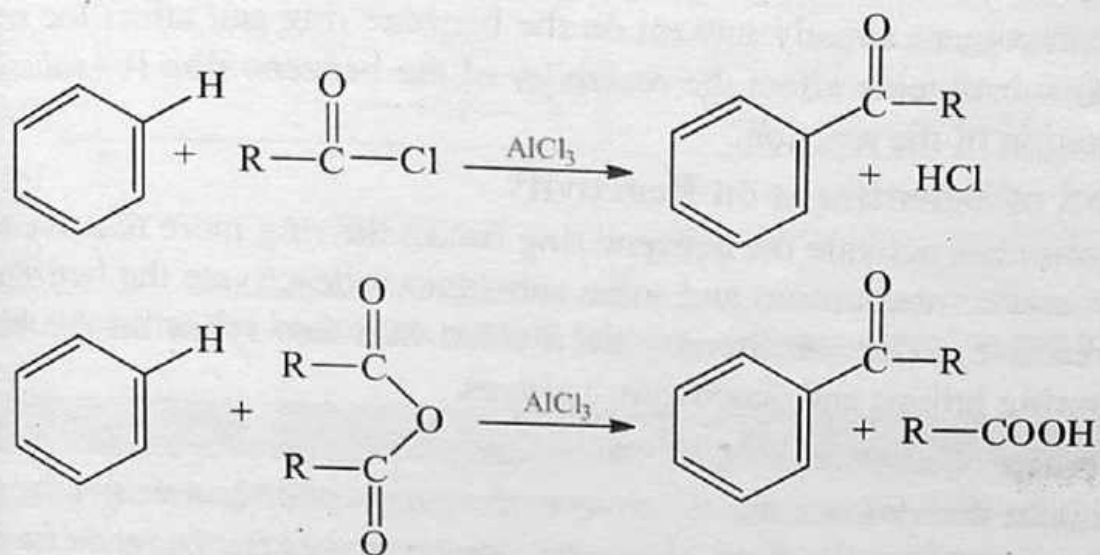


Step 3: A base (AlCl_4^-) removes the proton from the arenium ion to form alkylbenzene and regenerate the catalyst.



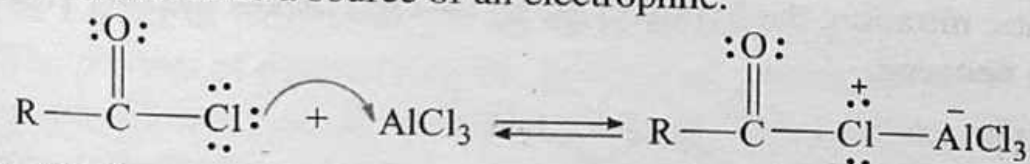
16.8.5.2.6 Friedel-Crafts Acylation

The replacement of hydrogen of benzene by an acyl group ($-\text{COR}$) is called acylation. Benzene reacts with acyl halides (also called acid halides) or acid anhydride in the presence of Lewis acids to produce acylbenzene.

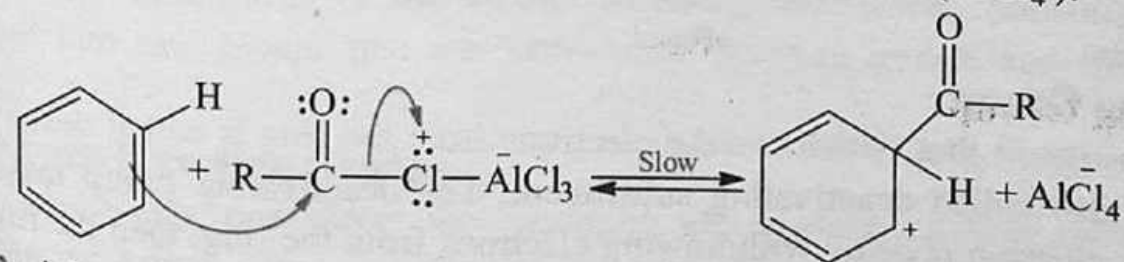


Mechanism

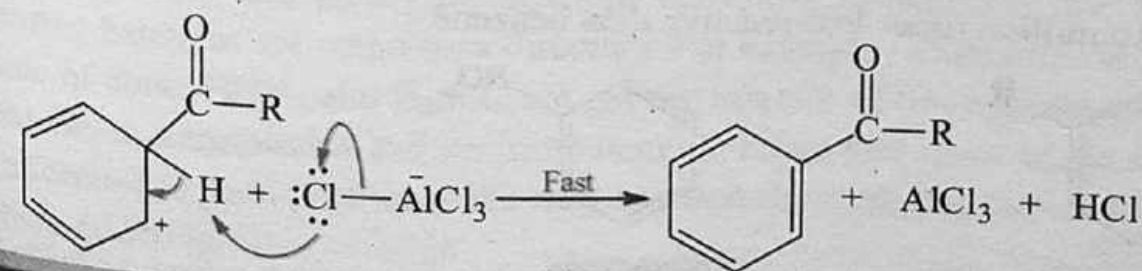
Step 1: Lewis acid (AlCl_3) reacts with acyl chloride to produce a Lewis acid-base complex that serves as a source of an electrophile.



Step 2: The benzene ring donates an electron pair to the carbon of carbonyl group of Lewis acid-base complex, forming the arenium ion and a base (AlCl_4^-).



Step 3: A base (FeCl_4^-) removes the proton from the arenium ion to form acylbenzene and regenerate the catalyst.



16.8.5.2.7 Substituent Effects on Benzene Ring

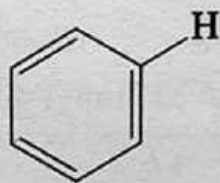
Only one product can be produced when an electrophilic substitution takes place on benzene. It is because all the available sites of benzene ring are equivalent. But what would happen if we were to carry out a reaction on a benzene ring that already has a substituent? A substituent already present on the benzene ring can affect the reaction in two ways: (a) substituents affect the reactivity of the benzene ring (b) substituents affect the orientation of the reaction.

A) The Effect of Substituent on Reactivity

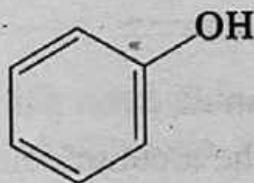
Some substituents activate the benzene ring (make the ring more reactive toward electrophilic aromatic substitution) and some substituents deactivate the benzene ring (make it less reactive). The substituents are divided into two types on the basis of reactivity: activating groups and deactivating groups.

Activating Group

A substituent that donates the electrons to the ring is called an activating group. It is also called activating substituent. Activating group makes the benzene ring more electron rich by donating electrons to the ring, then the ring will be more reactive towards electrophilic aromatic substitution and the reaction will occur faster. For example, in aromatic nitration, the hydroxyl group (—OH) makes the ring 1000 times more reactive than benzene.



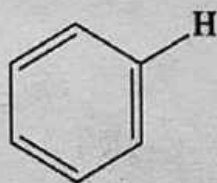
Benzene



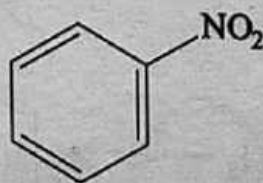
Phenol

Deactivating Group

A substituent that withdraws the electrons from the ring is called a deactivating group. It is also called deactivating substituent. The deactivating group makes the benzene ring electron poor by withdrawing electrons from the ring, then the ring will be less reactive towards electrophilic aromatic substitution and the reaction will occur slower. For example, in aromatic nitration, the nitro group (—NO_2) makes the ring more than 10 million times less reactive than benzene.



Benzene



Nitrobenzene

Table 16.8: Activating and Deactivating Groups

Activating Groups			Deactivating Groups		
Strong	Moderate	Weak	Strong	Moderate	Weak
$\text{—}\ddot{\text{O}}\text{—}$	$\text{—}\ddot{\text{N}}\text{COR}$	—R	—NO_2	—COCl	—X
$\text{—}\ddot{\text{N}}\text{R}_2$	$\text{—}\ddot{\text{O}}\text{COR}$	$\text{—C}_6\text{H}_5$	$\text{—}\overset{+}{\text{N}}\text{R}_3$	—COOH	
$\text{—}\ddot{\text{N}}\text{H}_2$		—CH=CR_2	$\text{—SO}_3\text{H}$	—COOR	
$\text{—}\ddot{\text{O}}\text{H}$			—CN	—COR	
$\text{—}\ddot{\text{O}}\text{R}$			—CF_3	—CHO	

Notices that the hydrogen atom is taken as a standard and is regarded as having no effect.

Keep in Mind

Activating groups are alkyl groups, phenyl groups or they have an atom esp. N or O atom with a lone pair of electrons attached directly to the benzene ring.

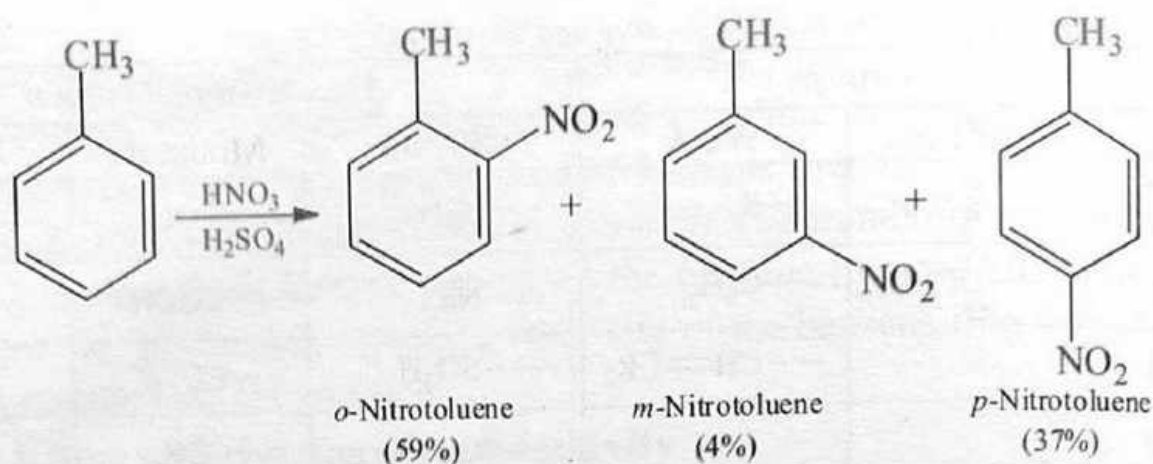
Deactivating groups are either halogens or they have an atom with full or partial positive charge attached to the benzene ring.

B) The Effect of Substituents on Orientation

The process of determining the position of second incoming substituent on the monosubstituted benzene is called orientation. The position of second incoming substituent (electrophile) depends upon the nature of first substituent already present on the benzene ring. Because the first substituent activates or deactivates the benzene ring and provides a site for the second incoming substituent. Substituents can be classified into two groups that are: ortho-para directing groups and meta directing groups.

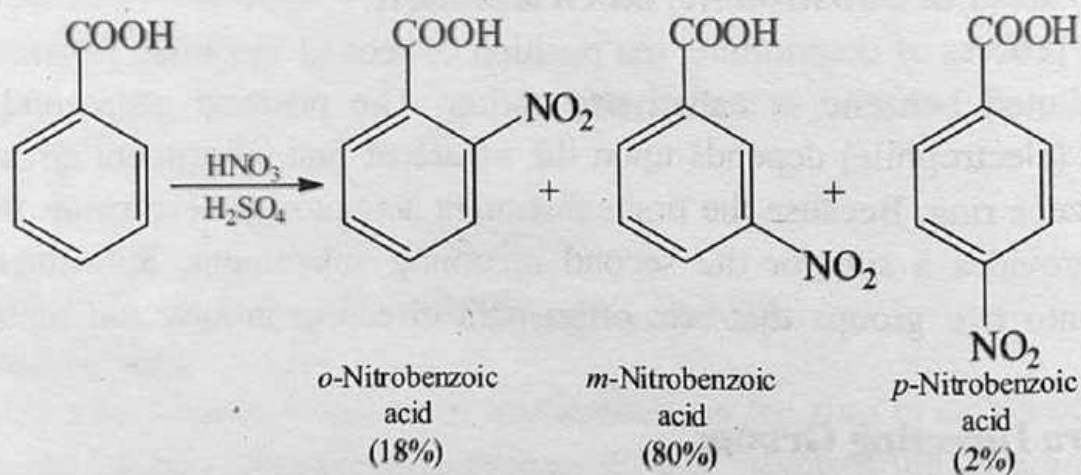
Ortho-para Directing Groups

Substituents that direct the incoming electrophile towards ortho and para positions are called ortho-para directing groups. They are electron releasing groups and activates primarily the ortho and para positions. Hence, the attack of electrophile may occur at ortho and para positions. All activating substituents and the weakly deactivating halogens are ortho-para directors. For example, when toluene reacts with a mixture of conc. HNO_3 and H_2SO_4 , we get the mixture of three products that are o-nitrotoluene, m-nitrotoluene and p-nitrotoluene. We find that most of the substitution occur at ortho and para positions. We may say that the methyl group of toluene is an ortho-para directing.



Meta Directing Groups

Substituents that direct the incoming electrophile towards meta positions are called meta directing groups. They are electron withdrawing groups and deactivate primarily the ortho and para positions. Hence, the attack of electrophile may occur at metapositions. All moderately and strongly deactivating substituents are metadirectors. For example, when benzoic acid reacts with a mixture of conc. HNO_3 and H_2SO_4 at 100°C , we get the mixture of about 80% of the *m*-nitrobenzoic acid, 18% *o*-nitrobenzoic acid and 2% *p*-nitrobenzoic acid. We find that most of the substitution occurs at meta positions. We may say that the carboxyl group of benzoic acid is metadirecting.



Keep in Mind

Monosubstituted benzenes that give mainly ortho and para products usually react faster than benzene. Monosubstituted benzenes that give mainly meta product always react more slowly than benzene.

16.8.5.2.8 Formation of Polysubstituted Benzenes

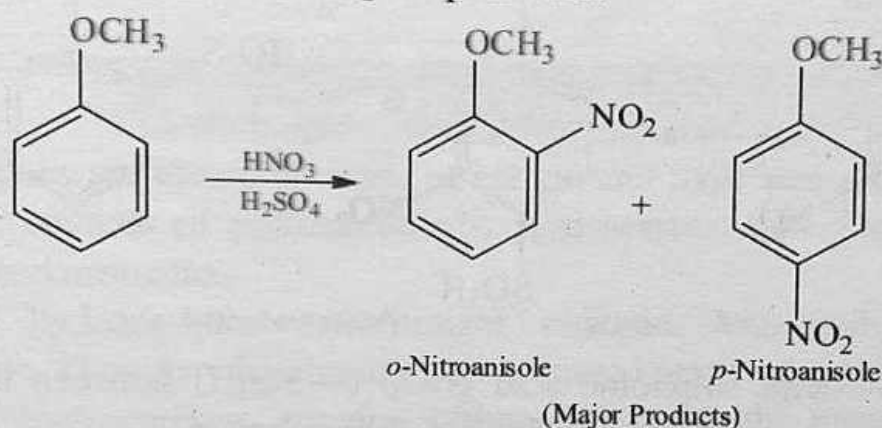
The substitution pattern of electrophilic substitution reactions can be controlled by the substituent group already present on the benzene ring other than hydrogen. The activating group such as methyl, hydroxyl, and methoxy on a benzene ring directs the

electrophile to ortho and para positions of the ring whereas the deactivating groups such as nitro, carboxyl and aldehyde except halogens directs the electrophile to meta positions. If there is competition between ortho-para and meta directing groups, ortho-para directing groups predominate.

Formation of Disubstituted Benzenes

The position of the second substituent depends upon the nature of the first substituents already bonded to the ring.

Consider the example of nitration of anisole. The methoxy group of phenol is electron releasing group and is ortho-para director. It sends the second substituent (electrophile) mostly to the ortho and para positions.

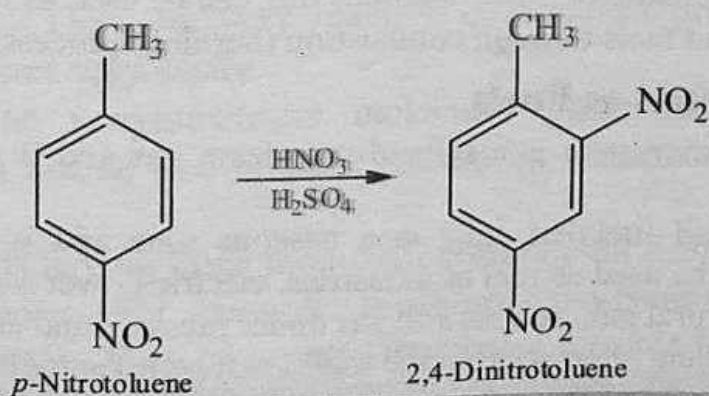


The ortho and para products can be separated by several methods because they have different physical properties.

Formation of Trisubstituted Benzenes

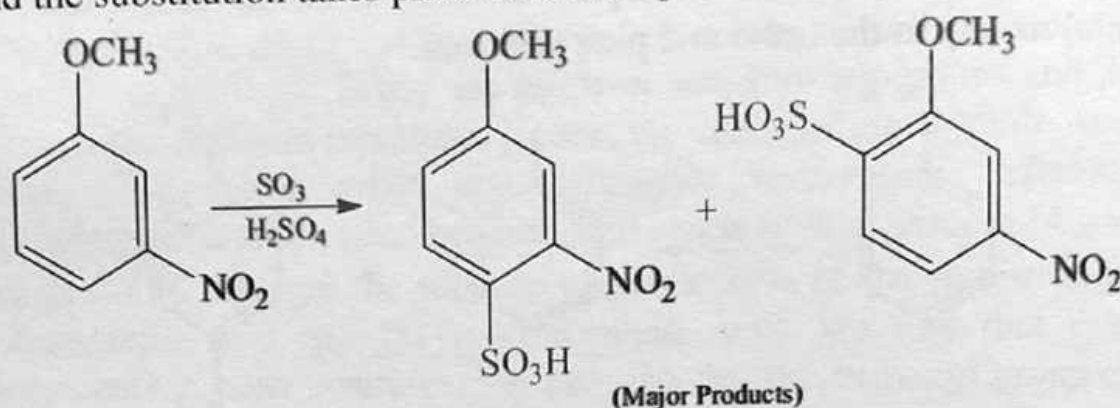
The position of third substituent depends upon the nature of both the substituents that are already bonded to the benzene ring.

Example 1: If the two substituents direct the new substituent to same positions, then neither group will dominate. Consider the example of nitration of *p*-nitrotoluene. It has two substituents: the methyl group and nitro group. The methyl group in *p*-nitrotoluene is ortho-para director and the nitro group is meta director.



In this example, the methyl group directs the incoming substituent to the ortho positions only because the para position is already blocked and the nitro group directs the incoming substituent to the meta position to the nitro group. In this example, both the methyl group and nitro group direct the incoming substituent to the same positions. Since the two positions are identical and only one product is formed.

Example 2: If the two substituents direct the new substituent to different positions, the more powerful group predominates. Consider the example of m-nitroanisole. The methoxy group in m-nitroanisole is a stronger activating group as compared to nitro group, and the substitution takes place ortho and para to the methoxy group.



The isomer with sulphonic acid group ($-\text{SO}_3\text{H}$) between the $-\text{OCH}_3$ and $-\text{NO}_2$ is a very minor product because of steric hindrance.

Society, Technology and Science

Importance of Various Hydrocarbons as Fuels for the Future Energy Needs

Fuels are naturally occurring combustible substances that act as a source of heat energy or raw materials for the chemical industry. Hydrocarbons (compounds of hydrogen and carbon) are mainly used as fuels. Fuels include from methane to higher hydrocarbons containing seventeen carbon atoms. Some of the important hydrocarbons that are used as fuels are LPG, natural gas, gasoline, kerosene oil, and diesel. The higher hydrocarbons having more than seventeen carbon atoms are present in heavy oil fractions. They can be cracked to get gasoline and other hydrocarbons that can be used as fuel in various sectors. Energy is obtained from fuels through combustion (burning) process.

Uses of Hydrocarbons as Fuels

LPG (liquefied petroleum gas) is a refined petroleum gas and is used as camping and domestic fuel.

Natural Gas is a fossil fuel that exist in a gaseous state and is composed mainly of methane (CH_4). It can be used as fuel in industries, electric power stations and homes.

CNG (compressed natural gas) is a natural gas under pressure and can be used as cheaper, greener and more efficient alternative to the traditional petrol and diesel fuels for vehicles.

Gasoline is used as a fuel for cars, motorbikes, trucks, boats and other transport vehicles.

Kerosene oil is widely used to power jet engines of aeroplanes and some rocket engines. It is used to fuel lamps and lanterns because it has low explosion hazard and burns relatively cleanly. It is also used in stoves for cooking.

Diesel is used as a fuel for trucks, buses, tractors, tanks and central heating systems. It is also used in diesel engine generators to generate electricity.

Coal is not hydrocarbon. It is made up almost entirely of carbon. It is mainly used in power generation. It is also used as household fuel for cooking and heating.

Fuel oil is derived from crude petroleum either as a distillate or a residue at the oil refinery and is the most widely used liquid fuel for power generation and ships. Fuel oil has more than sixteen carbon atoms.

Paraffin wax is an alkane with approximately 25 carbon atoms, and is used as fuel for candles.

Summary of Facts and Concepts

- Hydrocarbons are the compounds of carbon and hydrogen atoms only. They are the major sources of petrochemicals. Hydrocarbons are broadly classified as aliphatic and aromatic.
- Aliphatic hydrocarbons are straight chained, branched or non-aromatic compounds. They may be classified as saturated or unsaturated.
- Saturated hydrocarbons contain carbon-carbon single bonds. They are also known as alkanes or paraffins. They have no functional groups. They have general formula C_nH_{2n+2} .
- Alkanes react with halogens by free radical mechanism to produce alkyl halides. The mechanism occurs in three steps: (i) initiation (ii) propagation and (iii) termination.
- Complete oxidation of alkanes give carbon dioxide, water vapours and energy.
- Unsaturated hydrocarbons contain one or more carbon-carbon multiple bonds. They are further divided into alkenes and alkynes.
- Alkenes are unsaturated hydrocarbons, which contain one or more carbon-carbon double bonds. They are also known as olefins. They have general formula C_nH_{2n} . They are very reactive compounds and undergo electrophilic addition reactions very easily.
- Addition of an unsymmetrical molecule (polar reagent) such as HX to unsymmetrical alkene like propene, occurs in accordance with Markovnikov's rule.
- The compounds having same molecular formula but different structural formulas are called isomers. For example, n-pentane, iso-pentane and neo-pentane are isomers of pentane. They have same molecular formula but different structures.

- Alkynes are unsaturated hydrocarbons, which contain one or more carbon-carbon triple bonds. They have general formula C_nH_{2n-2} . They are produced during cracking of petroleum.
- Alkynes undergo addition reactions like alkenes but alkynes add two molecules of reagent instead of one. They occur in two steps.
- Terminal alkynes contain weakly acidic hydrogen, hence the hydrogen atoms of alkynes can be replaced readily by metals such as Na, Ag, or Cu to form ionic compounds.
- Hydrocarbons which have at least one benzene ring in their structures are called aromatic hydrocarbons. The term "aromatic" is derived from the Greek word "aroma" meaning fragrant.
- The molecule of benzene consists of a ring of six carbon atoms with one hydrogen atom bonded to each carbon. Benzene was discovered by Michael Faraday in 1825.
- Resonance is the process in which two or more structures are written for a compound which differ only in the arrangement of electrons. The resonance is represented by placing a double headed arrow ($\longleftrightarrow$) between resonance structures.
- The difference between the energy of the actual molecule (a resonance hybrid) and the most stable resonance structure is called resonance energy. The resonance energy of benzene is 152 kJ/mol. The process of resonance makes benzene more stable than the other unsaturated hydrocarbons.
- Benzene is less reactive than alkenes and alkynes towards electrophilic addition reactions. The most common reactions of benzene are electrophilic substitution reactions.
- Some substituents activate the benzene ring while some others deactivate the benzene ring. On the basis of reactivity, the substituents are divided into two types: activating groups and deactivating groups.

Multiple Choice Questions

- Q. Select one answer from the given choices for each question:
- The compounds of carbon and hydrogen in which all the four valencies of carbon are fully satisfied are termed as:

(a) Alkanes	(b) Alkenes
(c) Alkynes	(d) Alkanols
 - Acetylene is the example of:

(a) Alkane	(b) Alkene
(c) Alkyne	(d) Enyne

iii) The addition of unsymmetrical reagent to an unsymmetrical alkene follows the rule:

- (a) Pauli's exclusion principle (b) Hund's rule
- (c) Aufbau principle (d) Markownikov's rule

iv) The geometry of alkanes is:

- (a) Linear (b) Triangular
- (c) Tetrahedral (d) Octahedral

v) Alkanes are colourless and odourless liquids when they have:

- (a) Less than five carbons (b) Five to seventeen carbons
- (c) One to seventeen carbons (d) More than seventeen carbons

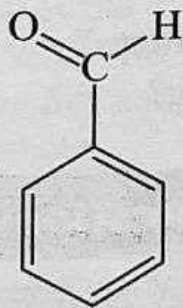
vi) The isomers of a compound have same:

- (a) Physical properties (b) Chemical properties
- (c) Structural formulas (d) Molecular masses

vii) Which type of substitution reaction occurs in benzene easily?

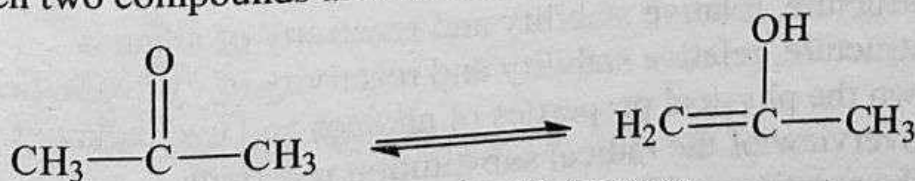
- (a) Electrophilic substitution reaction
- (b) Nucleophilic substitution reaction
- (c) Both occurs simultaneously
- (d) None of the reaction takes place

viii) The substituent ($-\text{CHO}$) as shown attach to benzene ring is said to be:



- (a) Activator to the ring
- (b) Deactivator to the ring
- (c) It does nothing to the ring
- (d) It is just a functional group

ix) The given two compounds are of each other



- (a) Skeletal isomers (b) Metameres

- (c) Tautomers (d) Positional isomers
- x) Two optical isomers such as (+) lactic acid and (–) lactic acid, have:
- (a) Same physical and chemical properties
 - (b) Same physical but different chemical properties
 - (c) Different physical but same chemical properties
 - (d) Same behavior towards plane of polarized light

Short Answer Questions

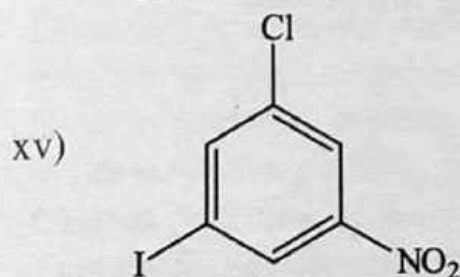
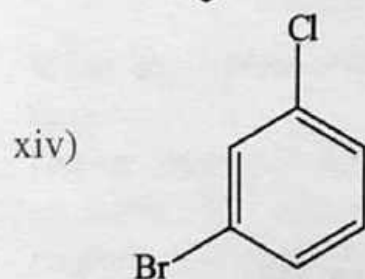
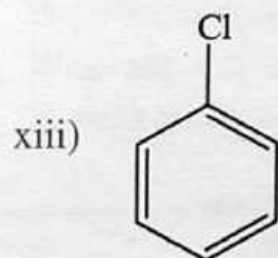
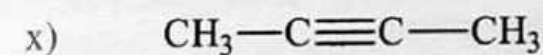
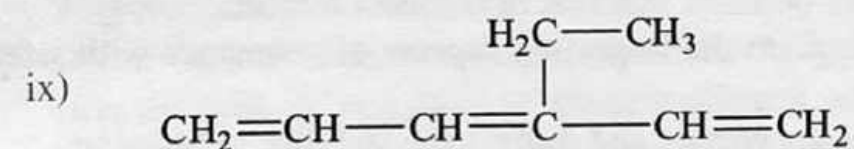
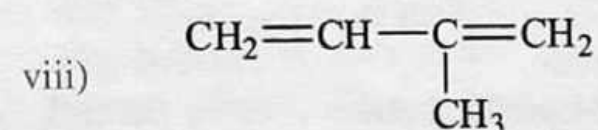
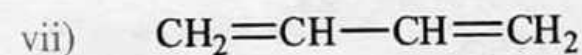
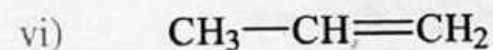
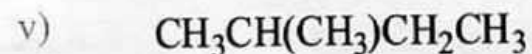
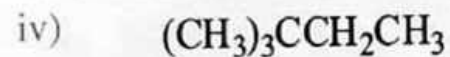
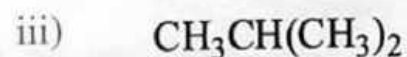
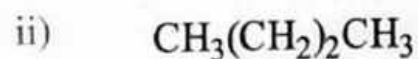
- Q.1. Why alkanes are less reactive than alkenes?
- Q.2. Why alkenes are more reactive than alkynes?
- Q.3. Why benzene is less reactive than alkenes?
- Q.4. Explain why cis-alkenes are generally less stable than their trans-isomers
- Q.5. Why a substituent directs an incoming electrophile to a particular position?
- Q.6. Define radical, homolytic fission and heterolytic fission.
- Q.7. Give the order of reactivity of alkanes, alkenes, alkynes and benzene.
- Q.8. Why alkynes are acidic in nature?
- Q.9. What is electrophilic substitution of benzene?
- Q.10. Why benzene does undergo electrophilic substitution reaction?
- Q.11. Why benzene does not undergo electrophilic addition?
- Q.12. Why benzene acts as a nucleophile?
- Q.13. What are activating and deactivating groups?
- Q.14. Is nitro group activating or deactivating?

Long Answer Questions

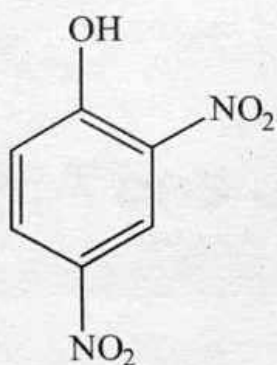
- Q.1. What are hydrocarbons? How are they classified? Give an example of each type.
- Q.2. Define nomenclature. Give historical background of common and IUPAC systems.
- Q.3. Explain nomenclature of straight chain and branched chain alkanes
- Q.4. Describe the nomenclature of cycloalkanes.
- Q.5. Explain structure, relative stability and reactivity of alkanes.
- Q.6. Explain structure, relative stability and reactivity of cycloalkanes.
- Q.7. Write down the physical properties of alkanes and cycloalkanes.
- Q.8. Give an overview of the radical substitution reactions.
- Q.9. Explain the reaction mechanism of free radical.

- Q.10. Describe the oxidation of organic compounds.
- Q.11. What are alkenes? Explain the nomenclature of alkenes.
- Q.12. Describe the relative stability, structure and reactivity of alkenes.
- Q.13. Write down the methods for the preparation of alkenes in detail.
- Q.14. What are the physical and chemical properties of alkenes? Explain.
- Q.15. Describe the concept of conjugation in alkenes. Your focus should be on dienes.
- Q.16. What is isomerism? Explain different types of isomerism.
- Q.17. What are alkynes? Explain the nomenclature of alkynes.
- Q.18. Explain relative stability, structure and reactivity of alkynes.
- Q.19. Give the general methods for the preparation of alkynes.
- Q.20. Write down the physical properties of alkynes.
- Q.21. What do you know about addition reactions of alkyne? Explain.
- Q.22. Define benzene and give its classification.
- Q.23. Explain the nomenclature of aromatic hydrocarbons.
- Q.24. Explain the structure of benzene in terms of molecular orbital theory.
- Q.25. What is resonance? Explain the important aspects of resonance with reference to benzene.
- Q.26. Define the term resonance energy and discuss the stability of benzene.
- Q.27. Draw the structures for the following hydrocarbons:
- 2-Methylhexane
 - 3-Methylheptane
 - 4-Ethyl-3-methylheptane
 - 2,2,4-trimethylhexane
 - 4-Ethyl-2-methylhexane
 - 3-Ethyl-3-methylhexane
 - 2,3-dimethylbutane
 - 2,3,4-trimethylpentane
 - 3-ethyl-2,2-dimethylpentane
 - 5-ethyl-2,6-dimethyloctane
 - Methylcyclopentane
 - Ethylcyclohexane
 - 1-ethyl-2-methylcyclopentane
 - 1,1,2-trimethylcyclopentane
- Q.28. Write the structural formulas of the following compounds:
- 3-hexene
 - 2,3-heptadiene
 - Hepta-2,4-diene
 - 1,3-dimethylcyclohexane
 - TNT
 - Picric acid

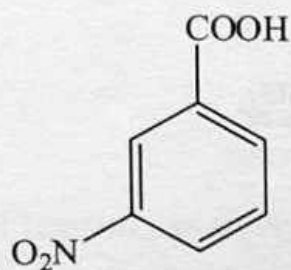
2.29. Give the IUPAC names of the following compounds:



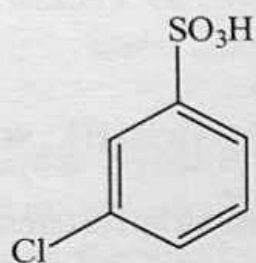
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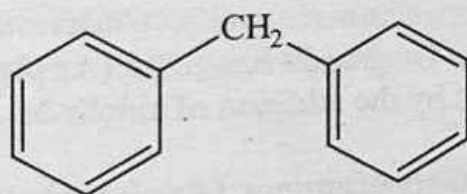
xvii)



xviii)



xix)



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