CHAPTER 16

HYDROCARBONS

After completing this lesson, you will be able to:

- Classify hydrocarbons as aliphatic and aromatic
- Describe nomenclature of alkanes and cycloalkanes
- Describe the mechanism of free radical substitution in alkanes exemplified methane and ethane
- Describe the structure and reactivity of alkenes as exemplified by ethane
- Describe what is meant by the term delocalized electrons in the context of the benzene ring
- Describe addition reactions of benzene and methyl benzene
- Describe acidity of alkynes

QI. Define and explain different types of Hydrocarbons.

Answer

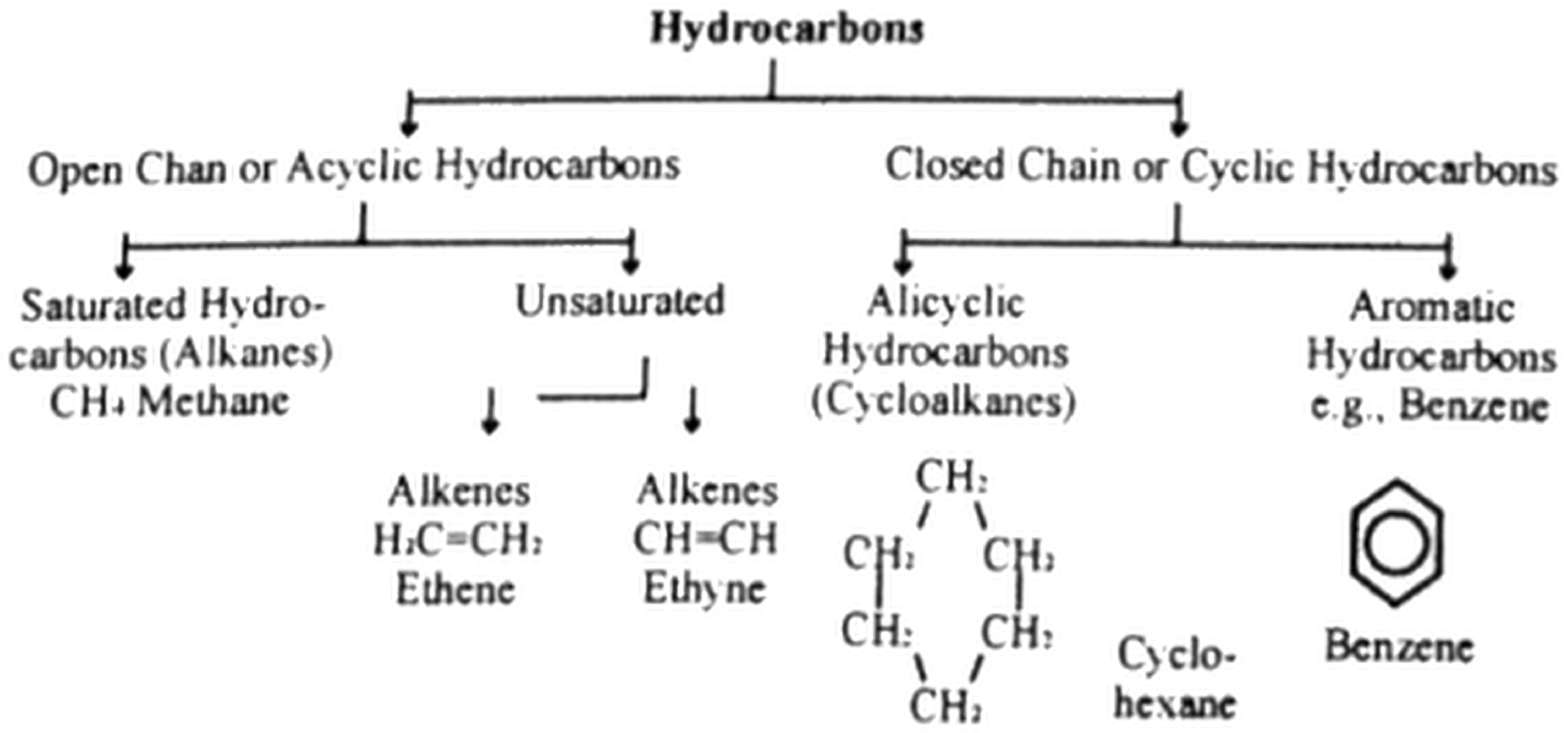
Definition

"Organic compounds which contain carbon and hydrogen only' are called hydrocarbons. "

The ability of carbon atoms to attach with each other to form a chain or ring is called Catenation.

Types of Hydrocarbons

Hydrocarbons have been divided into various classes on the basis of their structure as shown below:



Open Chain Hydrocarbons

The hydrocarbons in which carbon atoms attached with each other to form open are chains are called open chain hydrocarbons.

Types:

1) Saturated Hydrocarbons (Alkanes or Paraffins)

2) Unsaturated hydrocarbons (Alkenes or Olefins) and (Alkynes or Acetylenes)

Explanation And examples

Saturated	Unsaturated
These are the hydrocarbons in which carbon atoms are attached with each other through single bonds. Each carbon atom is Sp^3 hybridized. For example. Alkanes, $CH_3—CH_2—CH_2–CH_2-CH_2$ pentene (Straight Chain)	These are the hydrocarbons in which at least two carbon atoms are attached through double or triple bonds, and are sp^2 or sp hybridized. For examples and alkynes. (i) Alkene or Olefins: These the hydrocarbons in which at least two carbon atoms are which cause to from a double the carbon atoms. Alkenes may

$CH_{23} - CH - CH_2 - CH_3$ | CH_3 2- Methyl Butane (branched Chain) No further atoms or group of atoms can be attached to the carbon atoms of such hydrocarbons. This is why they are known as saturated hydrocarbons.	be straight chain or branched chain . $CH_2 = CH—CH_2 — CH_2 —CH_3$ 1 – pentene (straight chain) $CH2 = CH - CH - CH3$ | CH_3 3-MethyM-Batxe (Branched Chain) (i) Alkynes or acetylene These are the unsaturated hydrocarbons in which at least two carbon atoms are sp hybridized, which cause to form a triple bond between these carbon atoms. Alkynes may be straight chain or branched chain $CH = C — CH_2 — CH_2—CH_3$ I -pentene (Straight Chain) $CH = C - C - CH - CH_3$ | CH_3 3 – Methyl – 1 – Butyne (Branched Chain)

Closed Chain Hydrocarbons:

These are the hydrocarbons in which carbon atoms attach with each other to form rings.

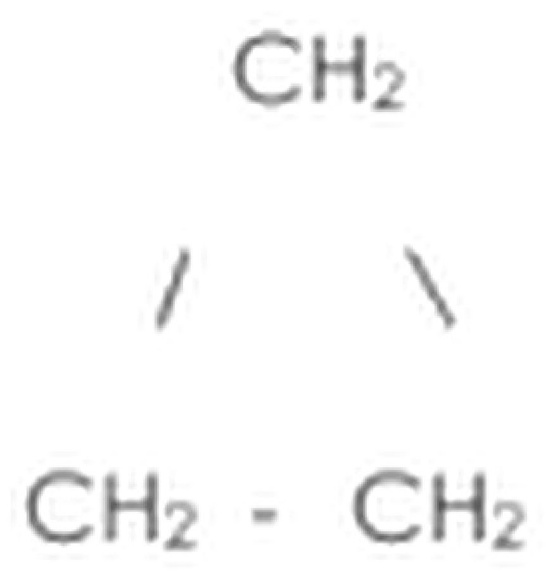
Types:

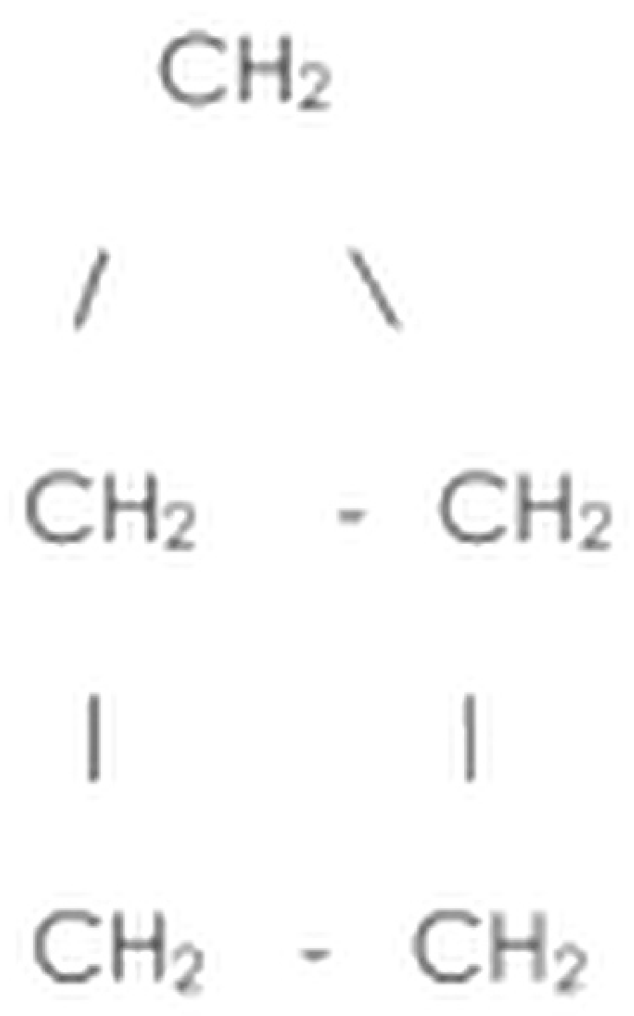
These hydrocarbons are of two types.

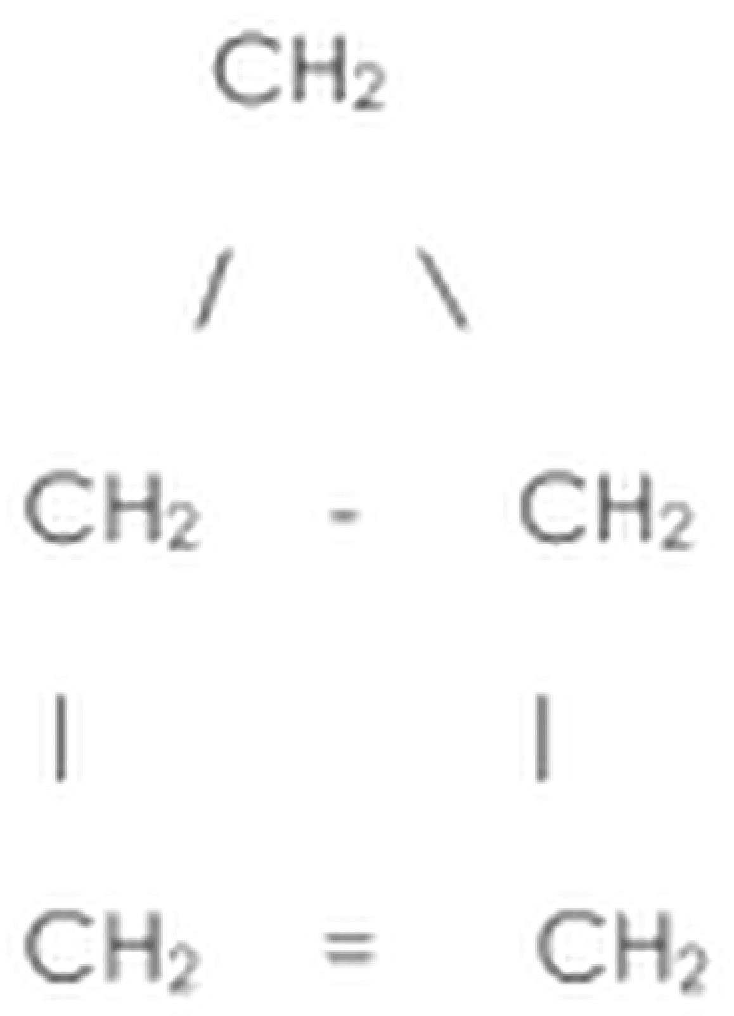
I) Alicyclic Hydrocarbons. **2)** Aromatic Hydrocarbons.

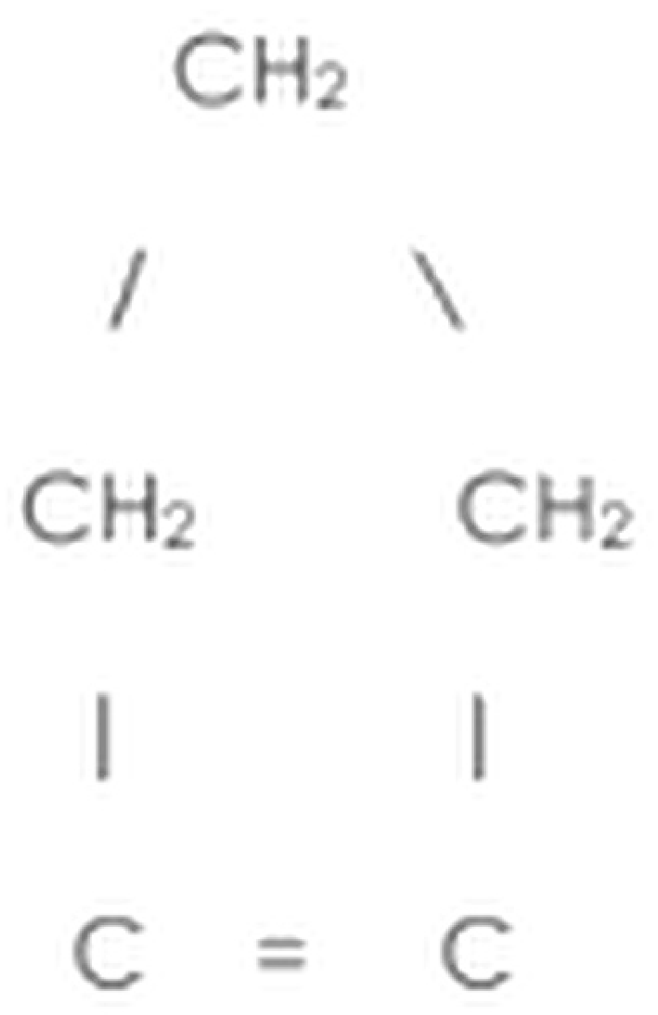
1) Alicyclic Hydrocarbons:

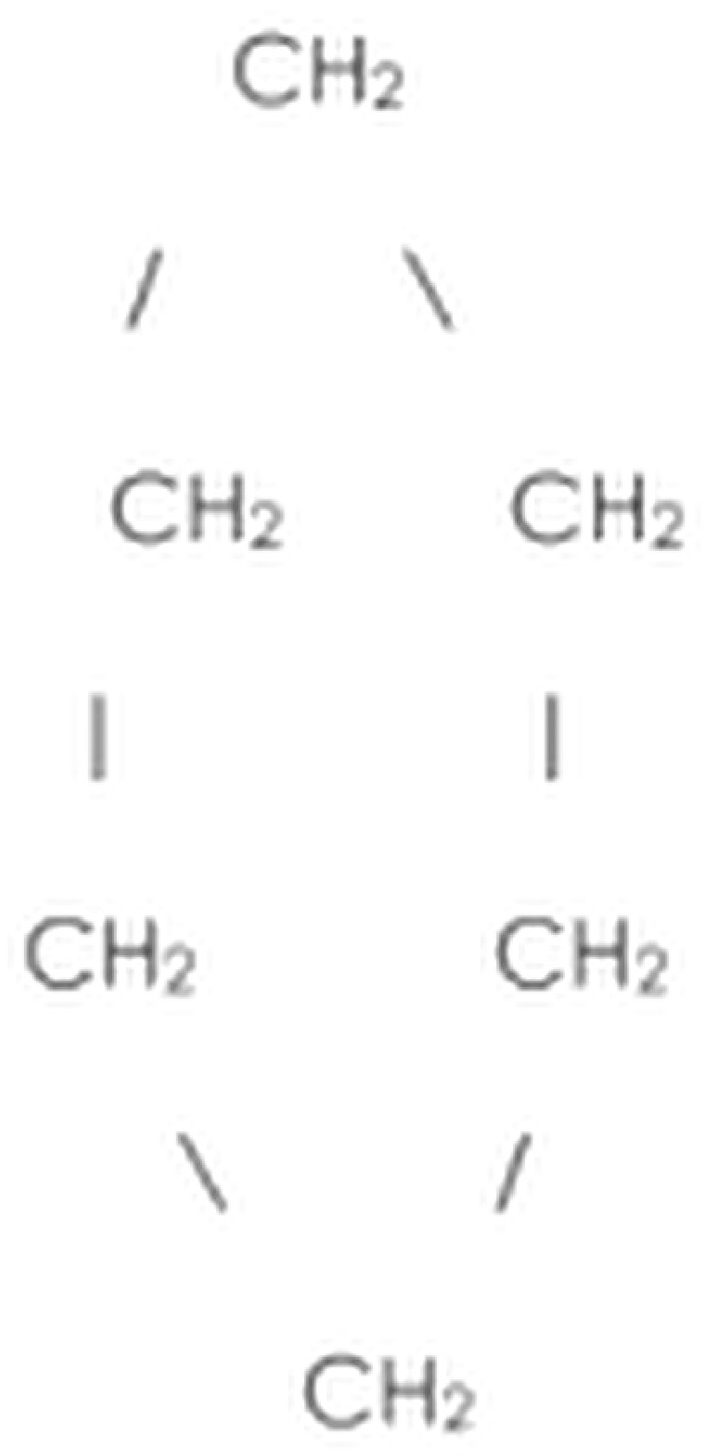
Non-benzenoid cyclic hydrocarbons are alicyclic hydrocarbons.


Cyclopropane


cyclopentane


cyclopentane


Cyclopentane


cyclohexane

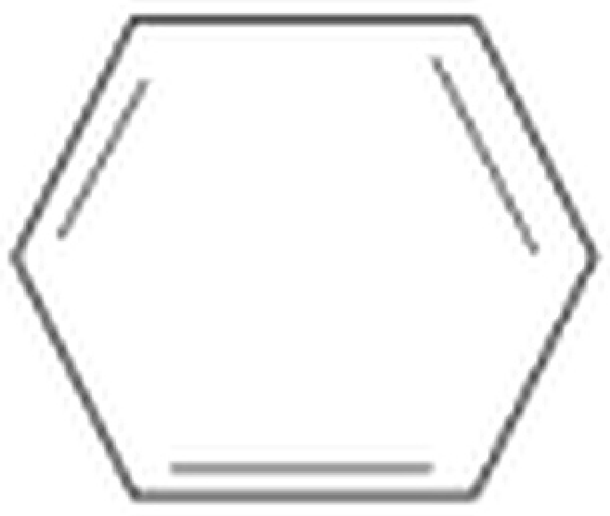
Alicyclic hydrocarbons possess two hydrogen atoms less than their corresponding open chain hydrocarbons.

2) Aromatic Hydrocarbons:

Benzenoid cyclic hydrocarbons are known as aromatic hydrocarbons. In these compounds all the carbon atoms present in the ring are sp2hybridized. Benzene, which is the simplest aromatic hydrocarbon, has a regular hexagonal structure with alternate single or double bonds between carbon atoms.

```
      H
      |
      C
     // \
H – C     C – H
    |     | |
H – C      C – H
     \\    /
       C
       |
       H
```

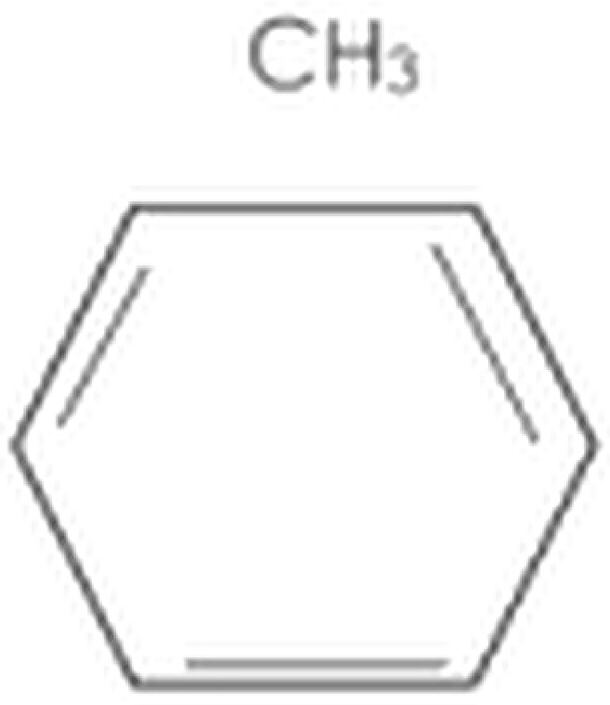
or



benzene

```
     CH3
      |
      C
     // \
H – C     C – H
    |     | |
H – C      C – H
     \\    /
       C
```

or



toluene

```
              |
              H


          H      H
          |      |
          C      C
         // \  /  \\
     H – C    C    C - H
         |    | |          |
     H – C    C     C - H
         \\   / \   //
           C      C
           |      |
           H      H
```

or

Napthalene

Alkanes and Cycloalkanes

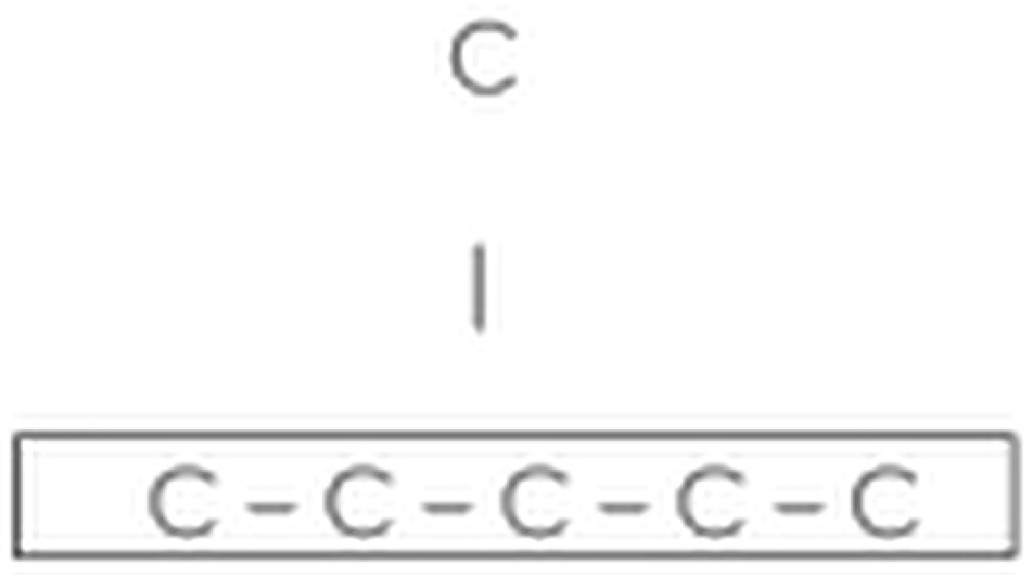
Alkanes

Simplest organic molecules with only C and H atoms. Commercially important as fuels and oils.

Nomenclature:

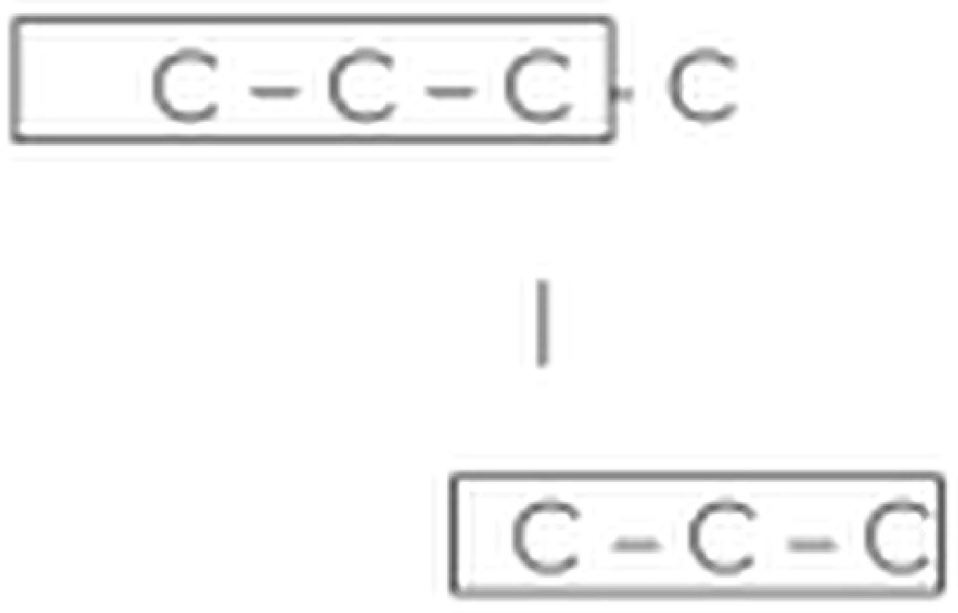
The I.U.P.A.C rules of naming alkanes are as:

I) Locate the largest continuous chain of carbon atoms independent of direction of the chain. It is called main chain, stem, principal chain or parent chain.



Longest Chain

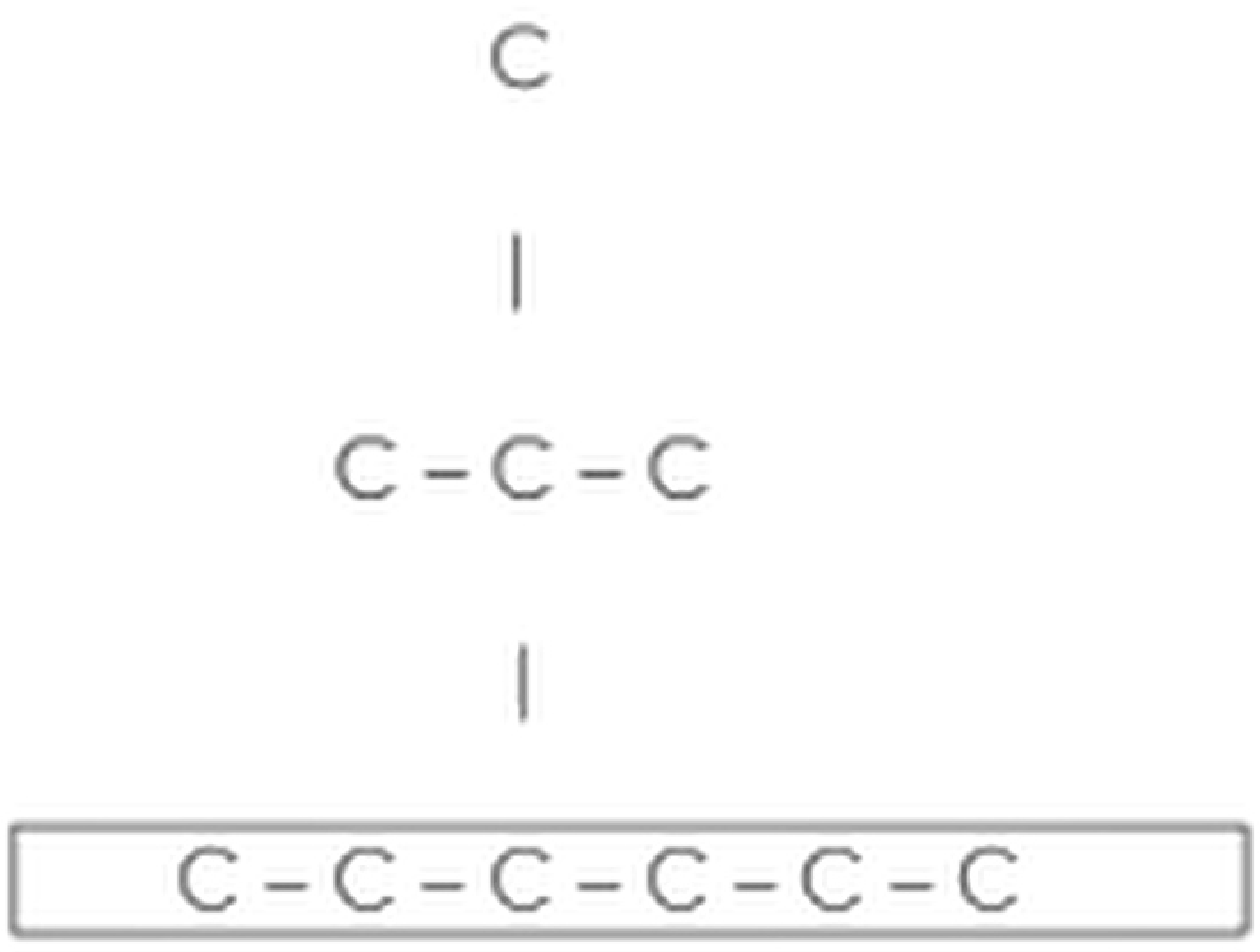
(Horizontal)



Longest Chain

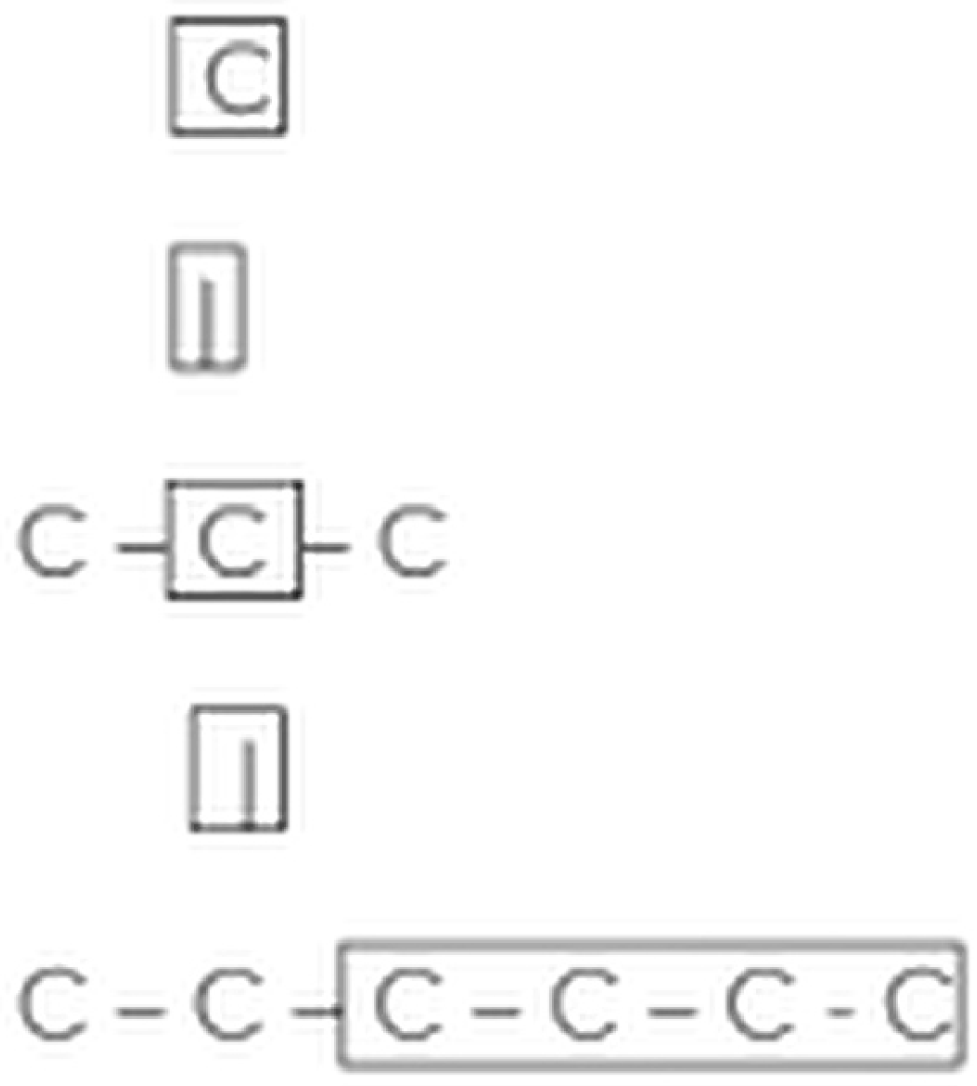
(Zig - Zag)

If there are two or more chains of equal lengths, the chain with larger number of branches is selected as main chain.



One branch

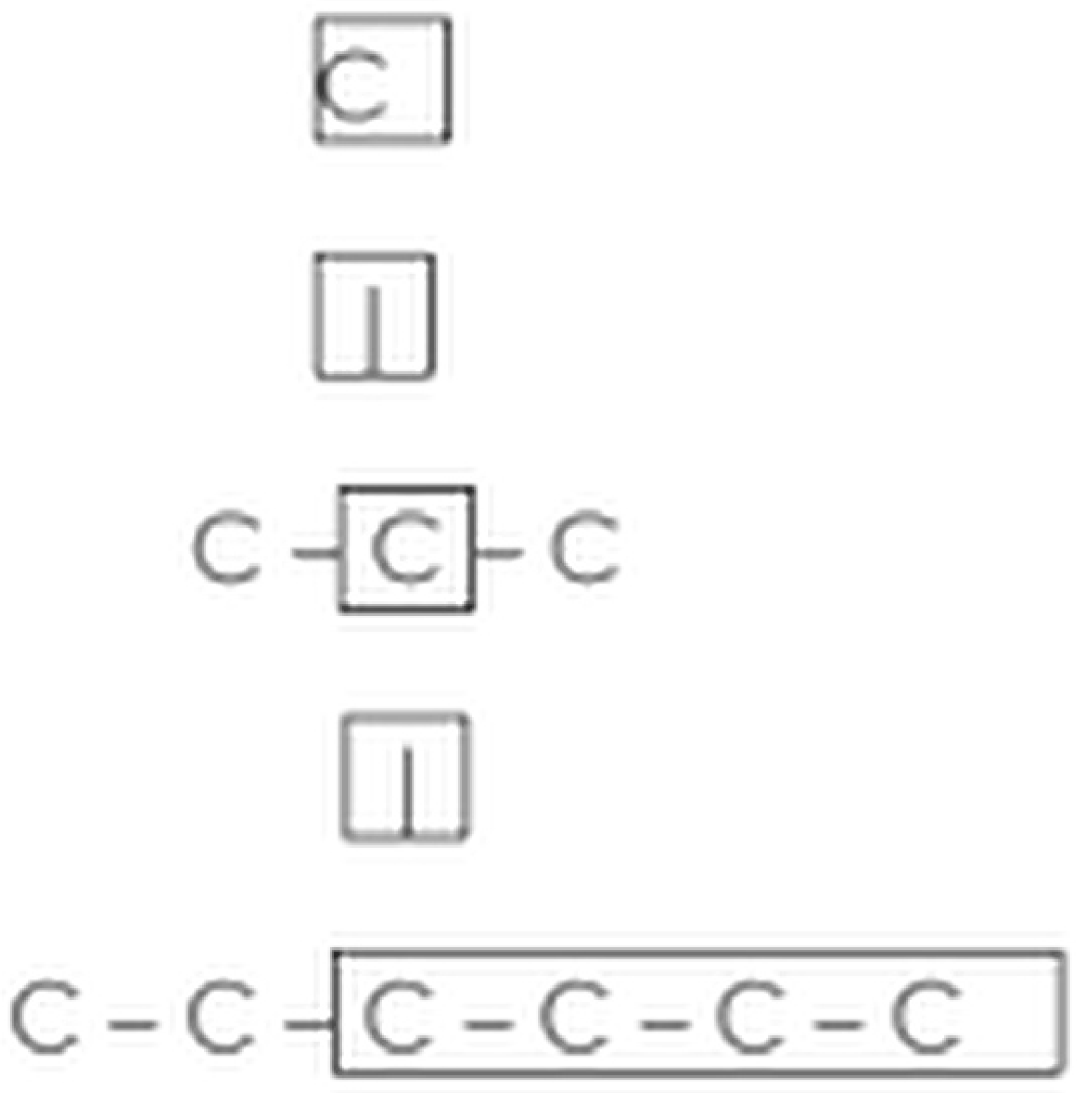
(Not main Chain)

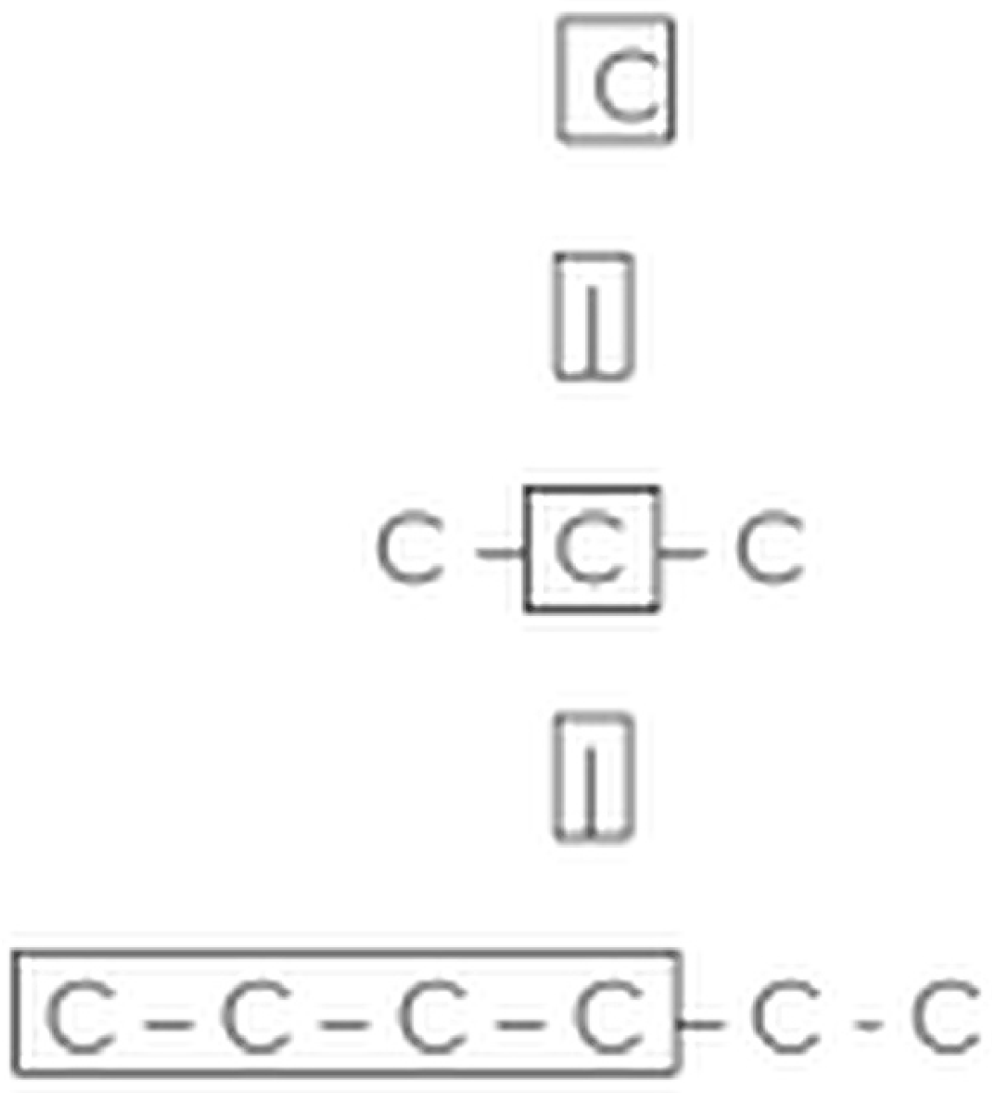


Three branches

(main chain)

2) Number the main chain starting from the end nearest to the substituent.





(Incorrect) (Correct)

3) When two identical substituents are present at equal distance from either end, number the chain starting with end which gives their minimum sum.

$C-\overset{\overset{C}{|}}{C}-C-\overset{\overset{C}{|}}{C}-\overset{\overset{C}{|}}{C}-C$

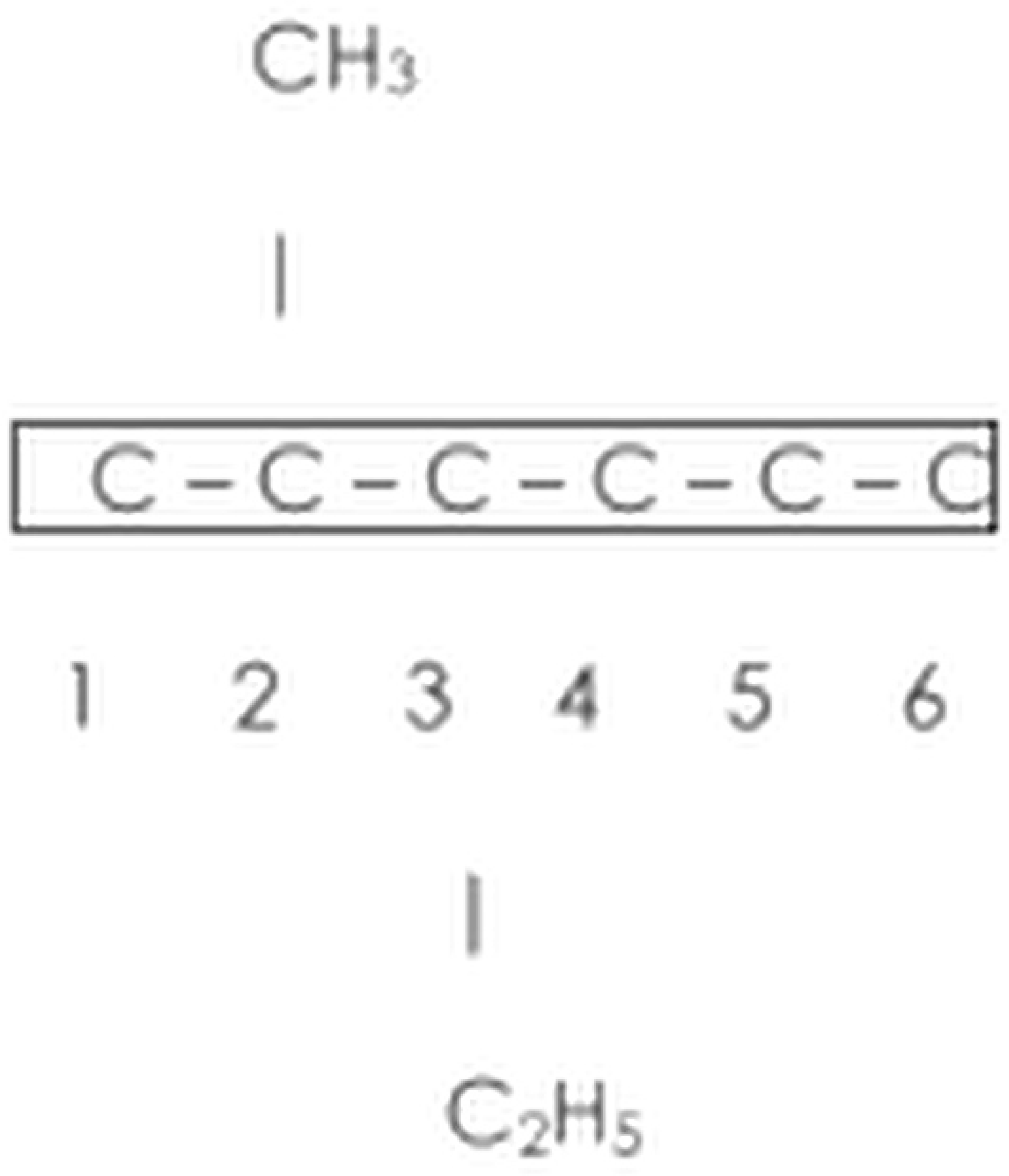
1 2 3 4 5 6

6 5 4 3 2 1 ← (Correct)

Since the sum of number 2 + 3 + 5 = 10, is less than 2 + 4 + 5 = 11, the correct numbering starts from the right.

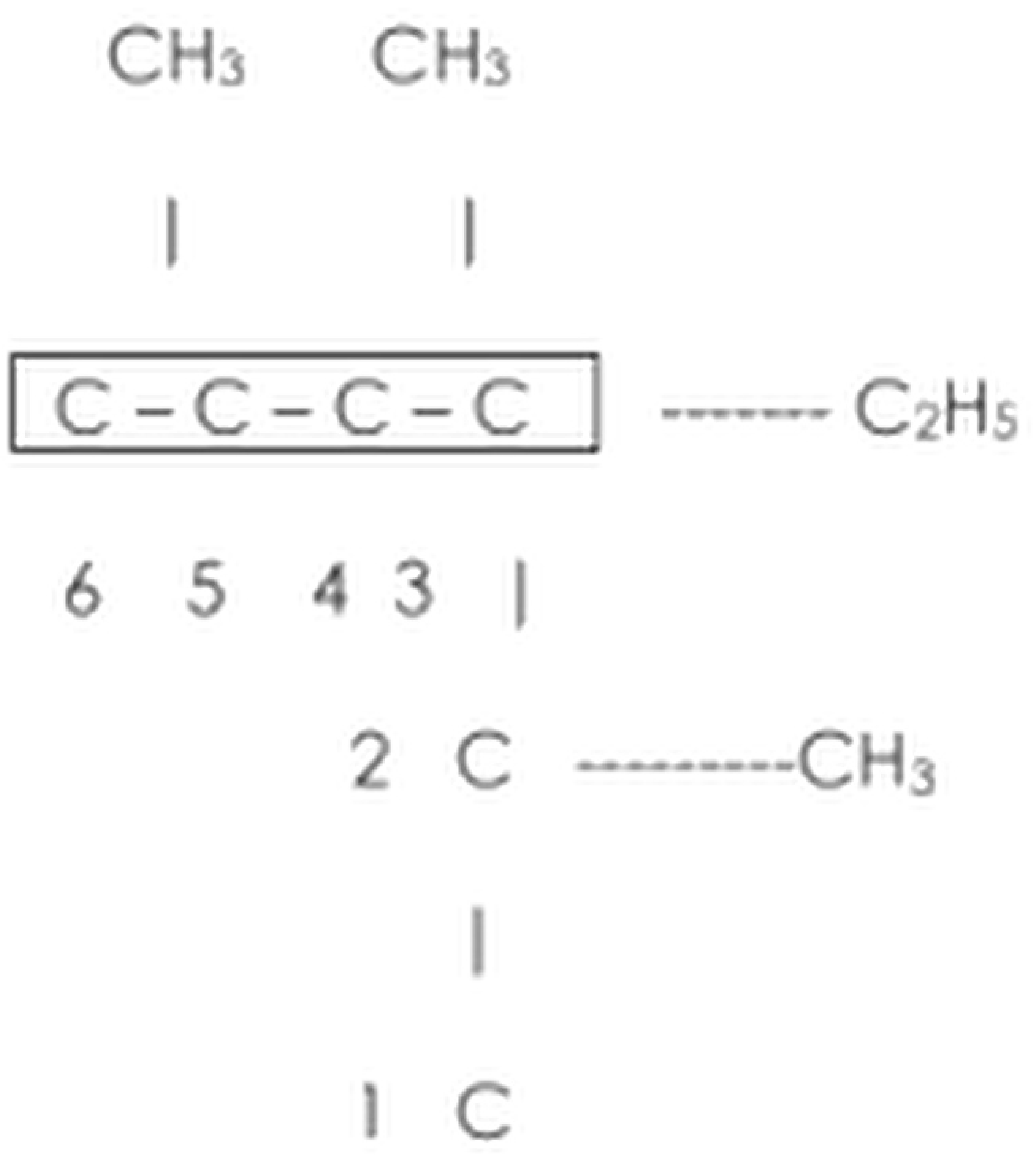
5) The position of substituent is indicated by the number of c-atom to which it is attached. The number is prefixed to the name of group separated by hyphen.

6) Names of alkyl groups are written before the name of parent hydrocarbon in alphabetical order or in order of increasing size, separated by hyphen.



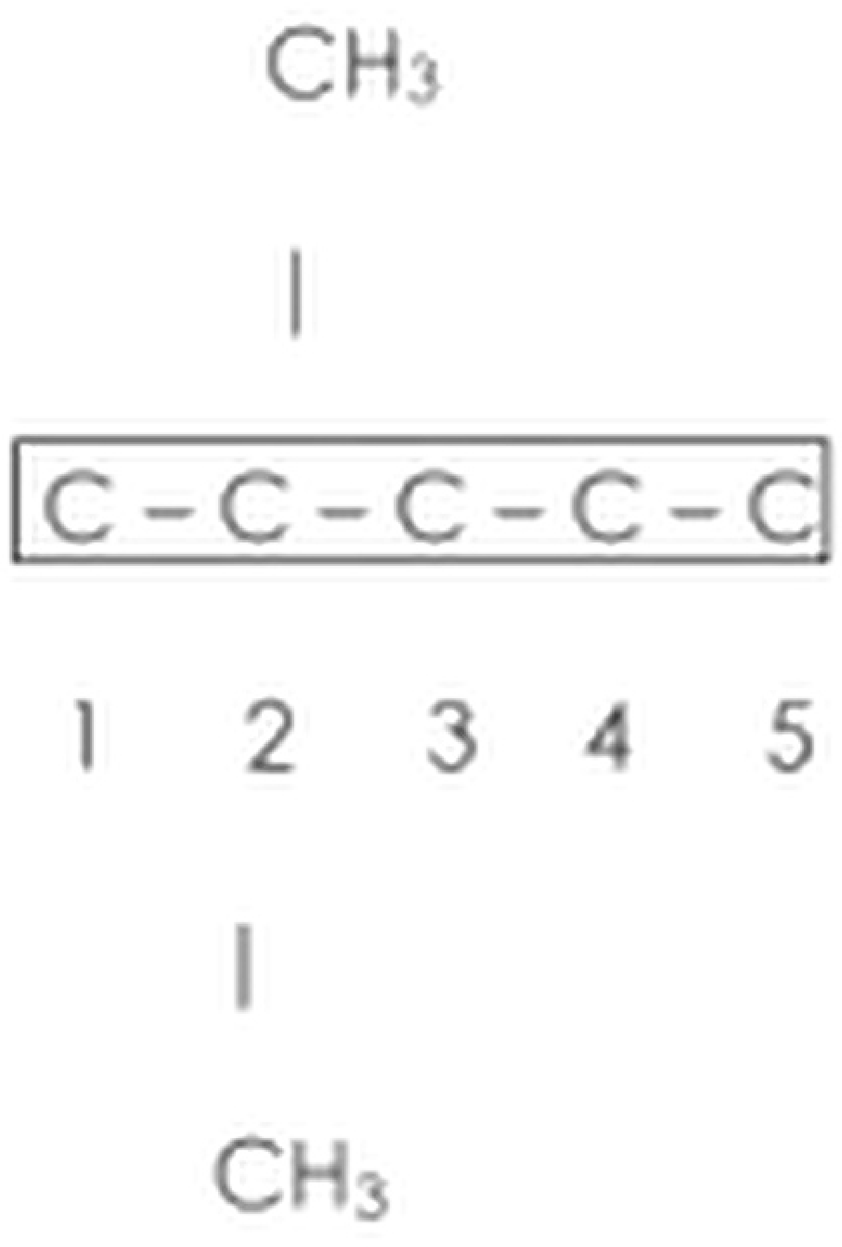
$C-\overset{\overset{CH_3}{|}}{C}-\underset{\underset{C_2H_5}{|}}{C}-C-C-C$

7) When two or more like groups are present, their numbers are indicated by prefixes di, tri-,tetra-, etc. Their numbers are grouped together and are separated by commas.



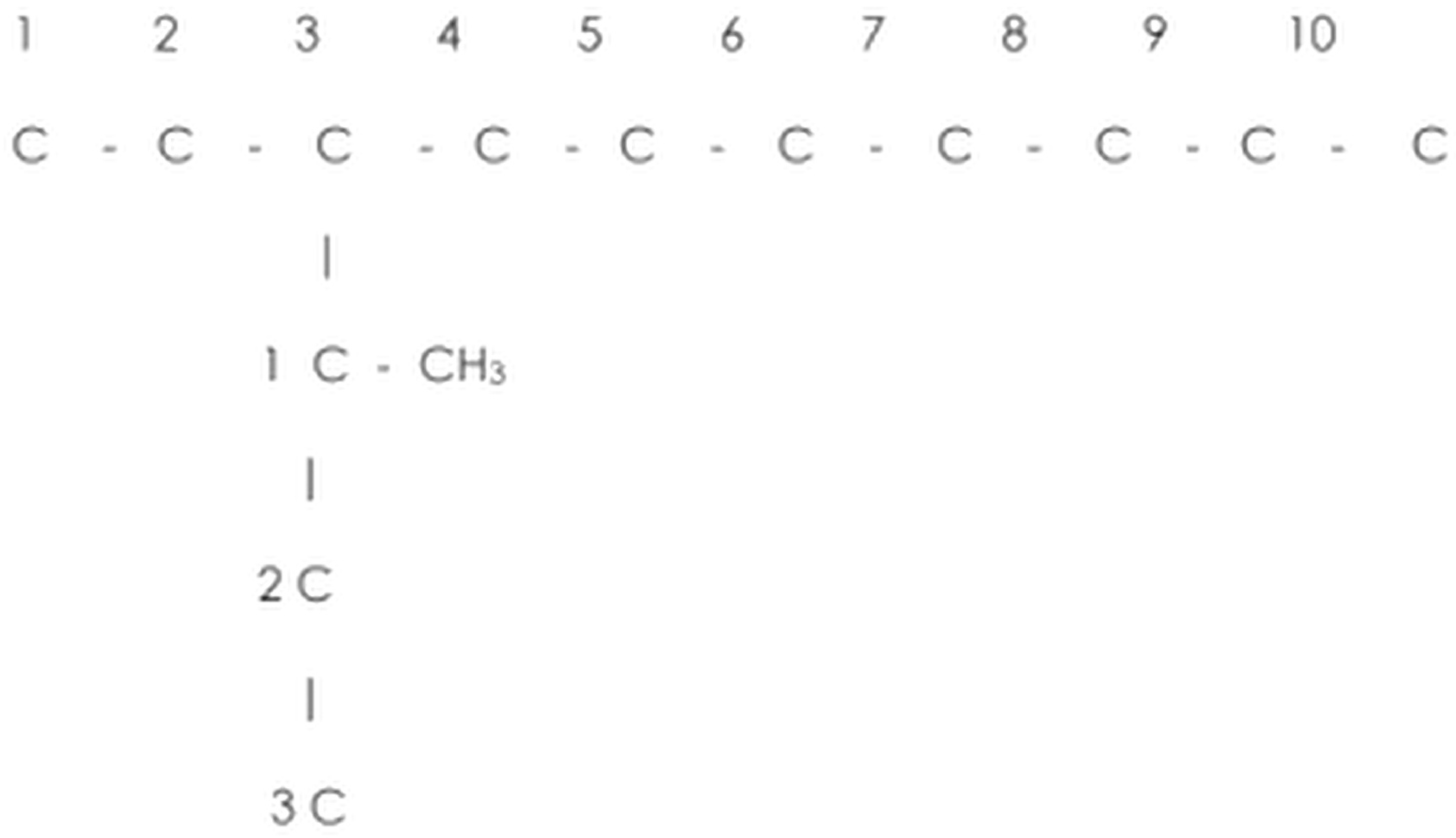
$$\begin{array}{l} \quad CH_3 \quad\; CH_3 \\ \quad | \qquad\quad | \\ \boxed{C-C-C-C} \text{ ------- } C_2H_5 \\ 6 \;\; 5 \;\; 4 \; 3 \;\; | \\ \qquad\quad 2 \;\; C \text{ ---------} CH_3 \\ \qquad\qquad\;\; | \\ \qquad\quad 1 \;\; C \end{array}$$

8) If two identical groups appear at the same c-atom, the number is separated twice, separated by commas.



$$\begin{array}{l} \qquad CH_3 \\ \qquad | \\ \boxed{C-C-C-C-C} \\ 1 \;\; 2 \;\; 3 \;\; 4 \;\; 5 \\ \quad\; | \\ \quad CH_3 \end{array}$$

9) The longest chain of the substituent is numbered starting with the attached directly to the main chain. Parentheses are used to separate the numbering of the substituent and the main chain.



5-(1 – Methyl Propyle) – Decane

The structural formula and names for the simple alkanes are shown in the following table.

Number of C atoms	Formula	Line Drawing	Alkane Name
1	CH_4	N/A	methane
2	C_2H_6		Ethane
3	C_3H_8 or $CH_3(CH_2)_2CH_3$		Propane
4	C_4H_{10} or $CH_3(CH_2)_3CH_3$		Butane
5	C_5H_{12} or $CH_3(CH_2)_4CH_3$		Pentane
6	C_6H_{14} or		Hexane

	$CH_3(CH_2)_4CH_3$		
7	C_7H_{16} or $CH_3(CH_2)_5CH_3$		Heptane
8	C_8H_{18} or $CH_3(CH_2)_6CH_3$		Octane
9	C_9H_{20} or $CH_3(CH_2)_7CH_3$		Nonane

Q2. Give physical properties of alkanes.

Answer

a) Methane to Butane is colorless, odorless gases while pentane to heptadecane (C5 to Cl 7) is colorless, odorless liquids. The higher members from C18 onwards are waxy solids, which are also colorless and odorless.

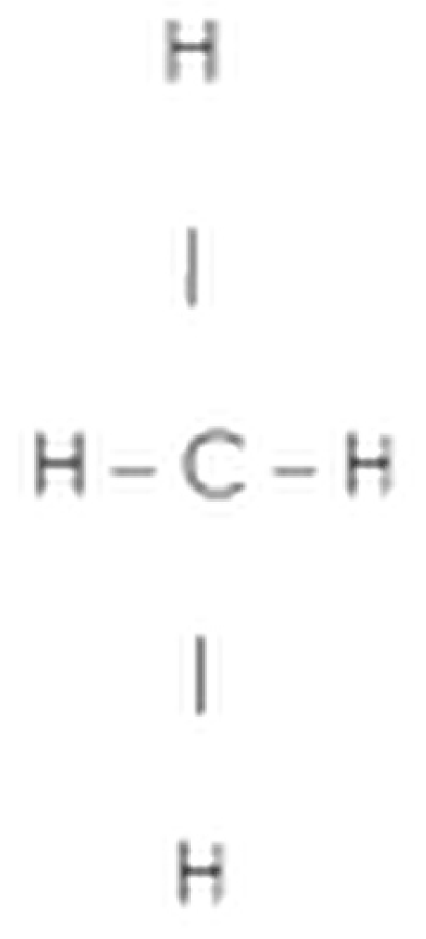
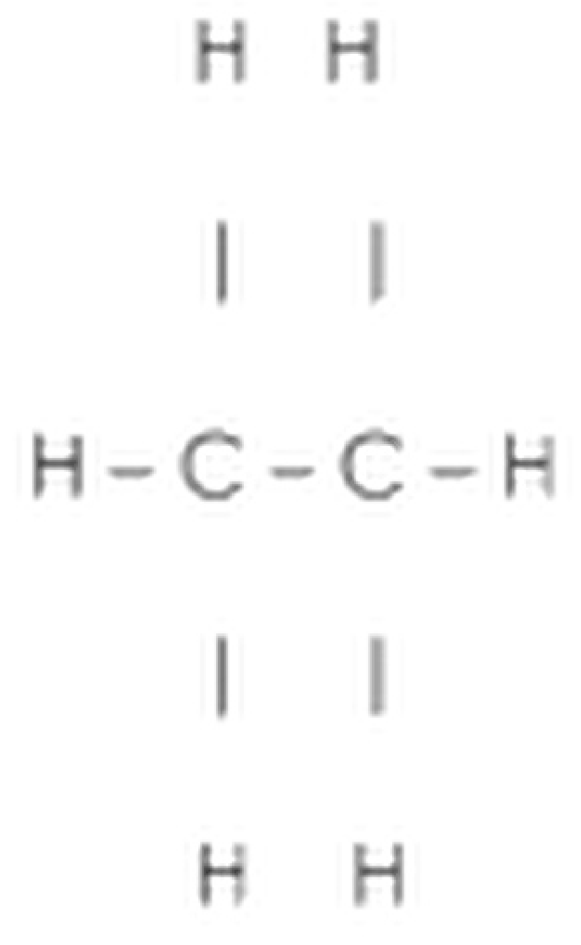
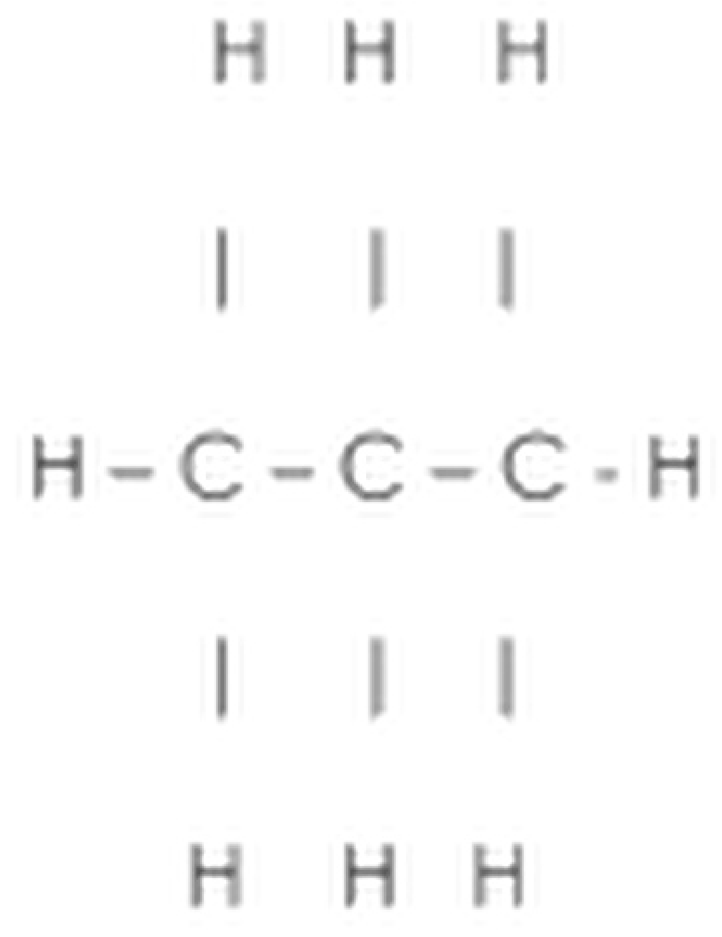
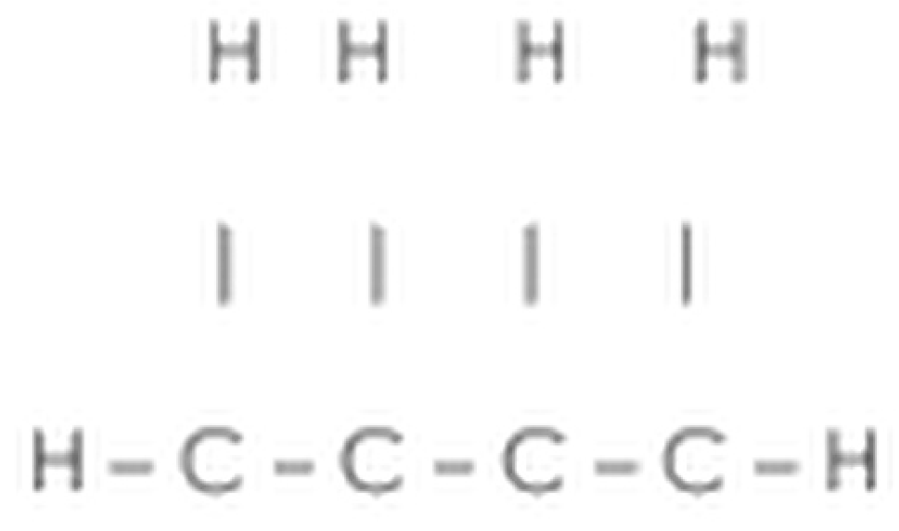
b) Alkanes are non-polar or very weakly polar and are insoluble in polar solvents like water, but soluble in non-polar solvents like benzene, ether, carbon tetra chloride, etc.

c) Their boiling points, melting points, density etc increase with the increase in number of carbon atoms, whereas solubility decreases with the increase in mass. The boiling points increases by 20 to 30^{0}C for addition of each CH2 group to the molecule. However, the boiling points of alkanes, having branched chain structures are lower than

their isomeric normal chain alkanes, e.g. n-butane has a higher boiling point 550C) then iso-butane -102^{0}C).

Structure

Alkanes are the simplest organic compounds, comprised of only sp^3 hybridized C and H atoms connected by s bonds. They have a generic formula of CnH2n+2 (a relationship that also defines the maximum number of hydrogen atoms that can be present for a given number of C atoms). Structures of the simple CI to C4 alkanes are shown below in a variety of representations. As the number of C atoms increases then other isomeric structures are possible

Methane CH_4 (b.pt. = 160^{0}C)	 $\begin{array}{c} H \\ \vert \\ H - C - H \\ \vert \\ H \end{array}$
Ethane C_2H_6 (b.pt. = 89^{0}C)	 $\begin{array}{cccc} & H & H & \\ & \vert & \vert & \\ H - & C - & C & - H \\ & \vert & \vert & \\ & H & H & \end{array}$
Propane C_3H_8 (b.pt. = 42^{0}C)	 $\begin{array}{ccccc} & H & H & H & \\ & \vert & \vert & \vert & \\ H - & C - & C - & C & - H \\ & \vert & \vert & \vert & \\ & H & H & H & \end{array}$
Butane C_4H_{10} (b.pt. =	 $\begin{array}{cccccc} & H & H & H & H & \\ & \vert & \vert & \vert & \vert & \\ H - & C - & C - & C - & C & - H \end{array}$

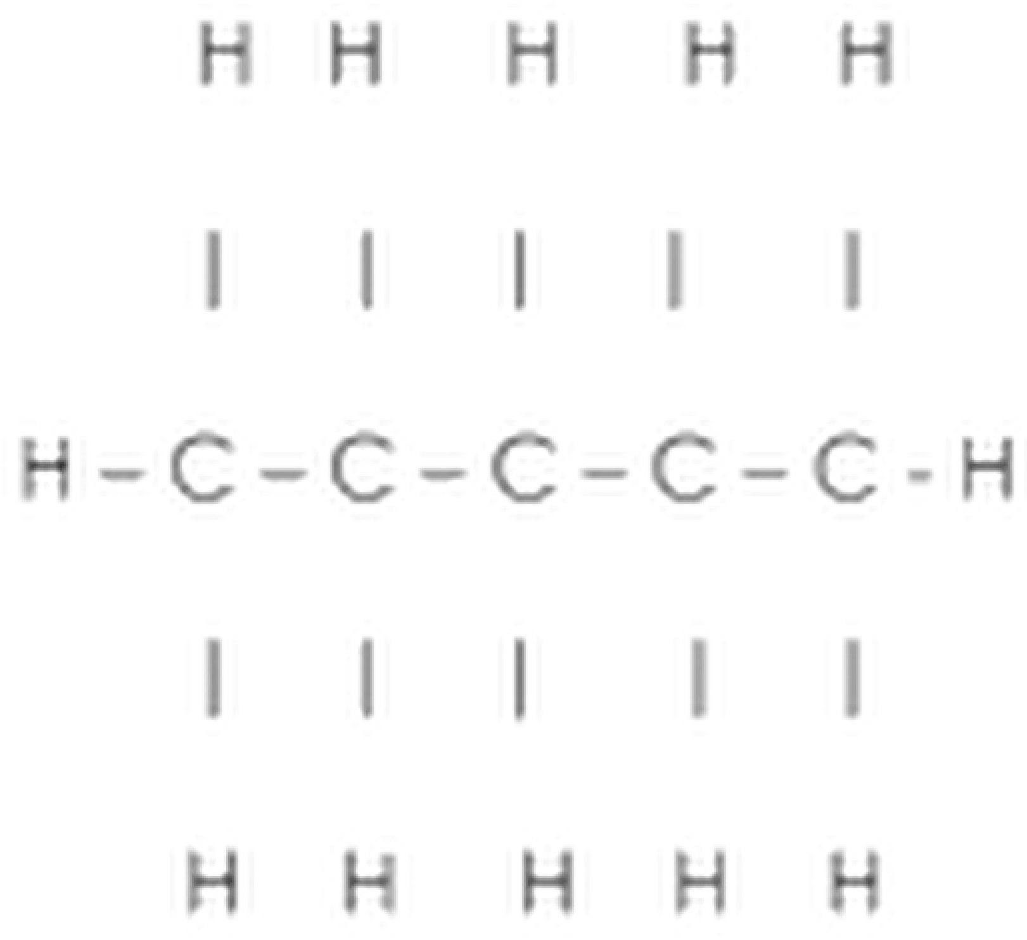
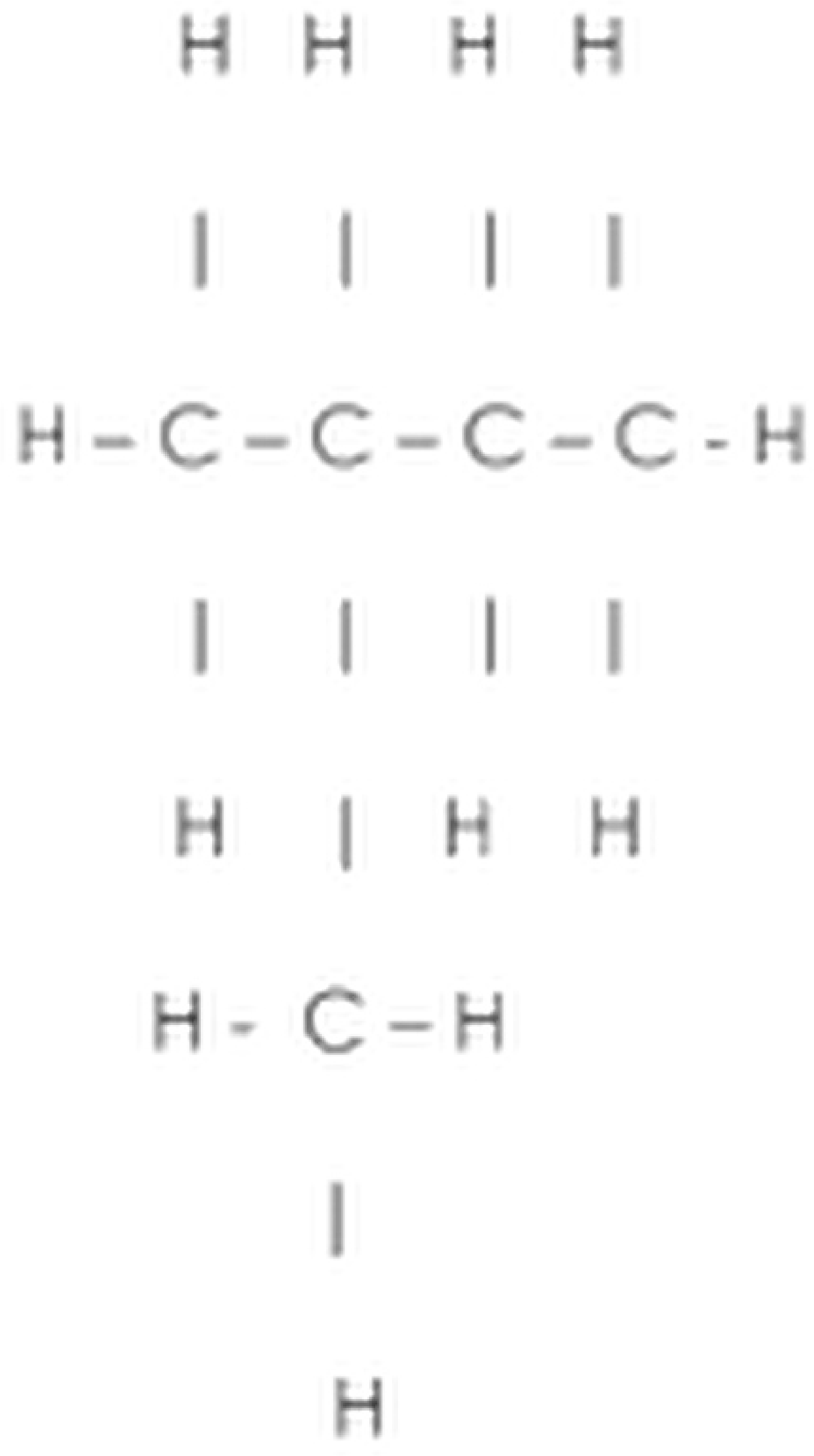
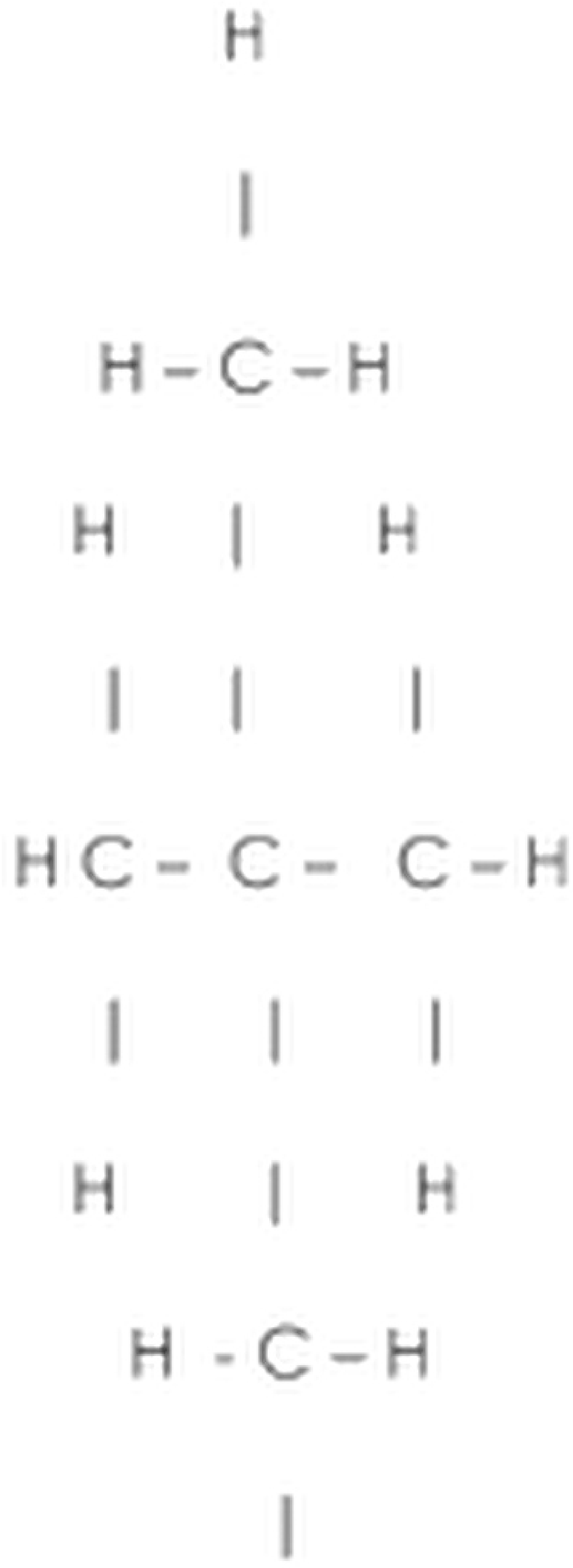
0.4^{0}C)	| | | | H H H H

Isomeric Alkanes:

The molecular formula for the CI to C3 alkanes lead to single, unique structures. However, for C4H10, there are two possible constitutional isomers. It is important to be able to recognize isomers because there can have different chemical, physical properties and biological properties. The constitutional isomers of C4Hi0 are shown below along with some properties:

n- butane	H H H H | | | | H – C – C – C – C – H | | | | H H H H	m.pt. = -139^{0}C b.pt. = -0.4^{0}C DH_f = -125.6 KJ/mol = (-30.0 Kcal/mol) DH_c = -2877 KJ/mol (-687 kcal/mol)
isobutane	H H H | | | H – C – C – C - H | | | H | H H - C – H | H	m.pt. = -161^{0}C b.pt. = -10.2^{0}C DH_f = -135.6 KJ/mol = (-32.4 Kcal/mol) DH_c = -2868 KJ/mol (-685 kcal/mol)

C_5H_{12} has three possible constitutional isomers:

n- pentane	 $\begin{array}{ccccccc} & H & H & H & H & H & \\ & \vert & \vert & \vert & \vert & \vert & \\ H- & C- & C- & C- & C- & C & -H \\ & \vert & \vert & \vert & \vert & \vert & \\ & H & H & H & H & H & \end{array}$	b.pt. = $36.1^{0}C$ DH_f = -147 KJ/mol = (-35.1 Kcal/mol) DH_c = -3509 KJ/mol (-839 kcal/mol)
Isopentane	 $\begin{array}{cccccc} & H & H & H & H & \\ & \vert & \vert & \vert & \vert & \\ H- & C- & C- & C- & C & -H \\ & \vert & \vert & \vert & \vert & \\ & H & \vert & H & H & \\ & H- & C & -H & & \\ & & \vert & & & \\ & & H & & & \end{array}$	b.pt. = $30^{0}C$ DH_f = -154.1 KJ/mol = (-36.8 Kcal/mol) DH_c = -3502 KJ/mol (-837 kcal/mol)
neopentane	 $\begin{array}{ccccc} & & H & & \\ & & \vert & & \\ & H- & C & -H & \\ & H & \vert & H & \\ & \vert & \vert & \vert & \\ H & C- & C- & C & -H \\ & \vert & \vert & \vert & \\ & H & \vert & H & \\ & H- & C & -H & \\ & & \vert & & \end{array}$	b.pt. = $9.5^{0}C$ DH_f = -168.0 KJ/mol = (-40.1 Kcal/mol) DH_c = -3493 KJ/mol (-835 kcal/mol)

	H	

Q3. What is relative stability and reactivity?

Answer

Branched alkanes are more stable than linear alkanes, e.g. 2-methylpropane is more stable than n-butane.

Reactivity

The Alkanes or Paraffins are inert towards acids, alkalis, oxidizing and reducing agents under normal conditions.

Explanation:

The unreactivity of Alkanes can be explained on the basis of inerü1ess of a ô bond and non-polar C-H/C-C bonds.

i) Inertness of ð bond

In a ô bond the electrons are very tightly held between the nuclei. A lot of energy is required to break it. Moreover, the electrons present in a ô bond can neither attack on any electrophile nor a nucleophile can attack on them. Hence Alkanes less reactive. .

ii) Non-polar Bonds:

The electro negativity of carbon (2.5) and hydrogen (2. I) do not differ appreciably and the bonding electrons between C-H and C-C are equally shared making them almost non0polar. In view of this, the ionic reagents such as acids, alkalis, oxidizing agents, etc find no reaction in the alkane molecules to which they could be attached. However, under suitable condition, Alkanes give two types of reactions.

i) Thermal and Catalytic Reactions

ii) Substituted Reactions.

These reactions take place at high temperature or on absorption of light energy through the formation of highly reactive free radicals.

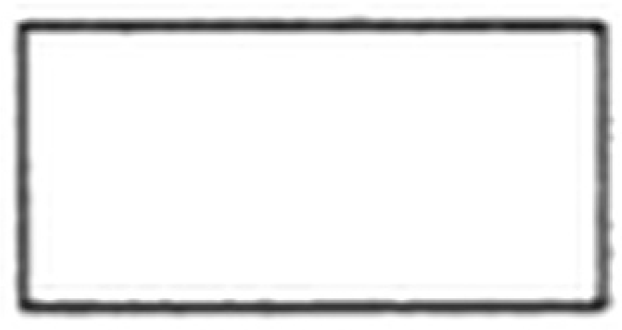
iii) Cycloalkanes

Another type of molecule containing only sp^3 hybridized C and H atoms connected by s bonds is possible with a ring of 3 or more C atoms. These are the cycloalkanes which are fairly common in the world of organic chemistry, both man-made and natural.

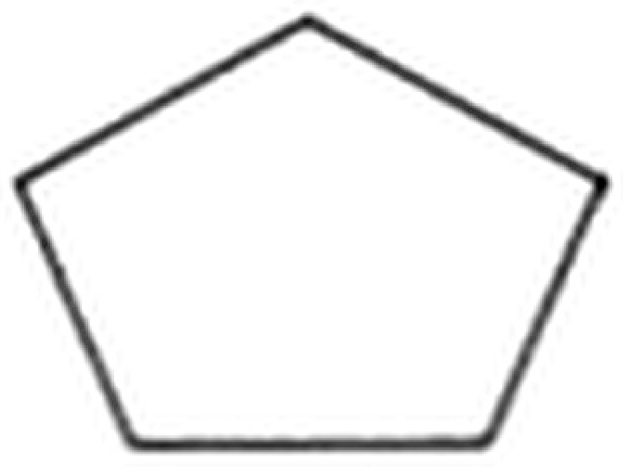
1) Nomenclature:

According to IUPAC system, cyclo alkanes with one ring are named by prefixing cyclo to the name of the corresponding alkane having the same number of carbon atoms as the ring, e.g.,

Cyclo
Propane



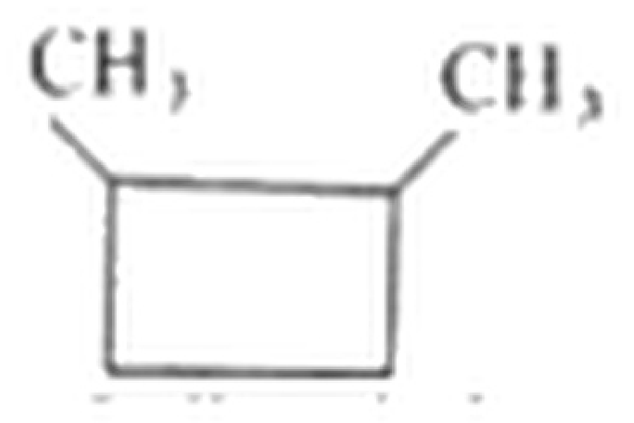
Cyclo
Butane



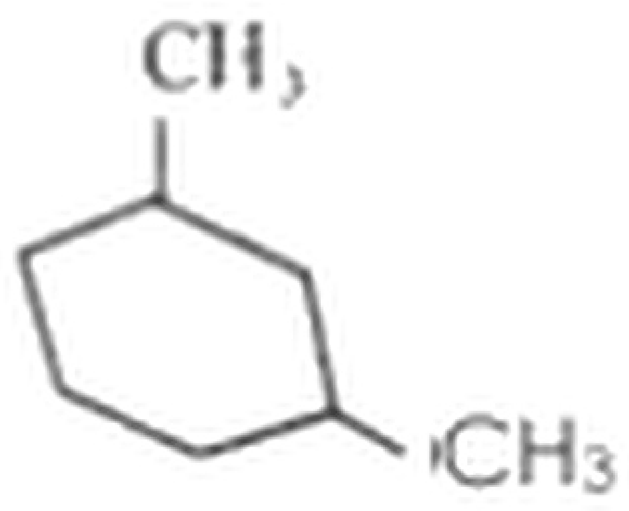
Cyclo
pentane

The substituents are numbered in such a way that the sum of numbers is kept minimum, e.g.,

Methyl
Cyclo propane



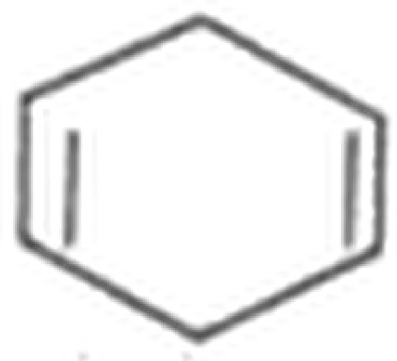
1.2 – dimethyl
cyclo butane
(not 1.4 – dimethyl....)



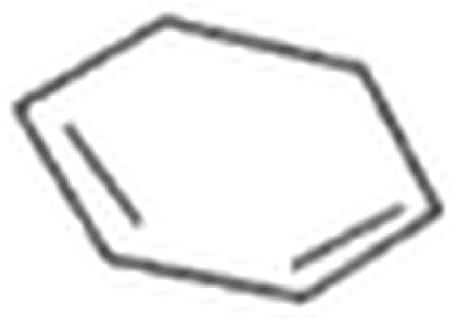
1,3 – dimethyl cyclo
hexane
(Not 1,5 – dimethyl ......)

If the alicyclic hydrocarbon is unsaturated, the rules applied to alkenes (for double bond) or alkynes (for triple bond) are used, e.g.

Cyclo penience



Cyclo hexane -1, 4 – diene



1,3 – Cyclo hexadine

Multiple bonds are given the lowest possible number.

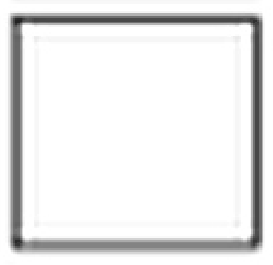
2) Physical Properties:

Like alkanes, the low polarity of all the bonds in cycloalkanes means that the only intermolecular forces between molecules of cycloalkanes are the very weak induced dipole - induced dipole forces, also known as Landon forces which are easily overcome. As a result, compared to other functional groups, but like alkanes, cycloalkanes tend to have low melting and boiling points.

3) Structure:

They have a generic formula of C_nH_{2n}. (note: there 2 less H atoms compared to the analogous alkane).

The C3 to C6 cycloalkanes are shown below in a variety of representations.

Cyclopropane C_3H_6	
Cyclobutane C_4H_8	
Cyclopentane C_5H_{10}	

Cyclohexane C_6H_{12}	

4) **Reactivity:**

Very similar reactivity to the closely related alkanes which have the same types of bonds.

Since C and H atoms have very similar electronegativities, both the C-H and C-C bonds are non-polar.

As a result, cycloalkanes, like alkanes, are not a very reactive functional group.

Q4. Give mechanism of free radical reactions.

Answer

Interesting Information:

When reaction mechanisms are being described, a 'curly arrow' is sometimes used to show the movement of a pair of electrons. The beginning of the arrow shows where the electron pair starts from and the arrow head shows where the pair ends up. Figure 16.1 shows an example.

$$\mathrm{Br^{-}}\quad {}^{+}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{H} \longrightarrow \mathrm{Br}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{H}$$

Figure 16.1

The arrows a pair of electrons moving from the Br-ion to the region between the bromine and the carbon, were it forms a covalent bond between the atoms. The same reaction is shown again below, with all the bonding electrons indicated.

Figure 16.2

A half-arrow is used to show the movement of a single electron in reactions involving free radicals. The beginning of the arrow shows where the single electron starts from and the half-arrow head shows where it ends up. For example, the reaction

$$H \quad Cl-Cl \longrightarrow H-Cl \quad Cl^{\bullet}$$

Would be shown as

This is shown again below, with all the bonding electrons indicated.

Figure 16.3 summarizes the way curly arrows and half-arrows are used.

Curly arrows show the movement of an electron pair

Electron

Pair starts ….. finished here

Here……

Curly half arrows show the movement of a single.

Unpaired electron

Electron

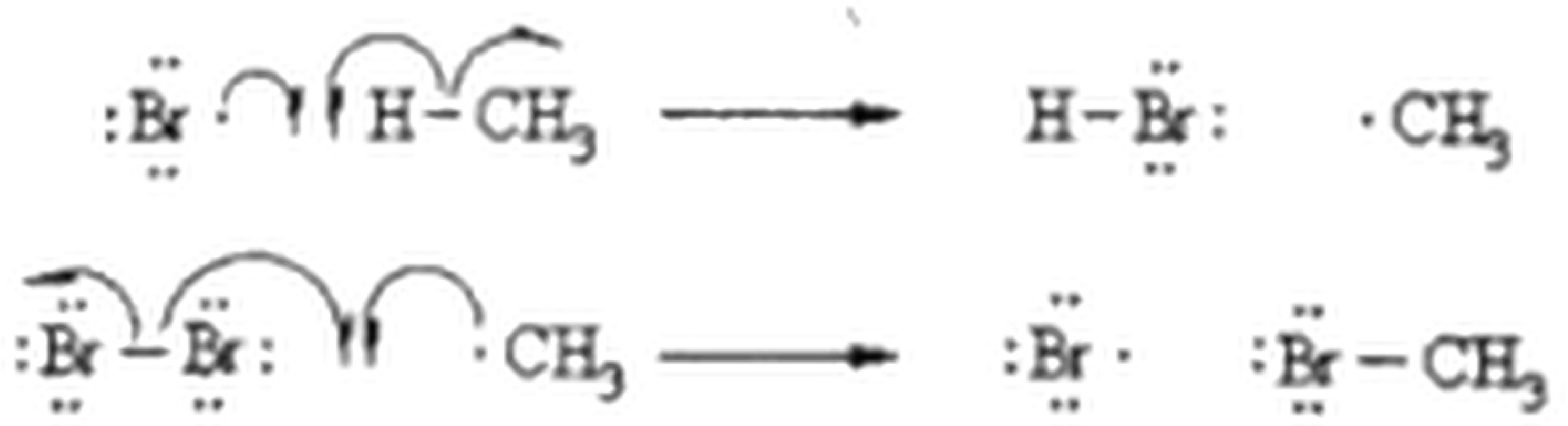
Pair starts ….. finished here

The mechanism for the bromination of methane is shown below, but the mechanism for chlorination or higher alkanes is the same. Note that it contains three distinct types of steps, depending on the net change in the number of radicals that are present.

RADICAL CHAIN MECHANISM FOR REACTION OF METHANE WITH Br_2

Step 1 (Initiation)

Heat or uv light cause the weak halogen bond to undergo homolytic cleavage to generate two bromine radicals and starting the chain process.



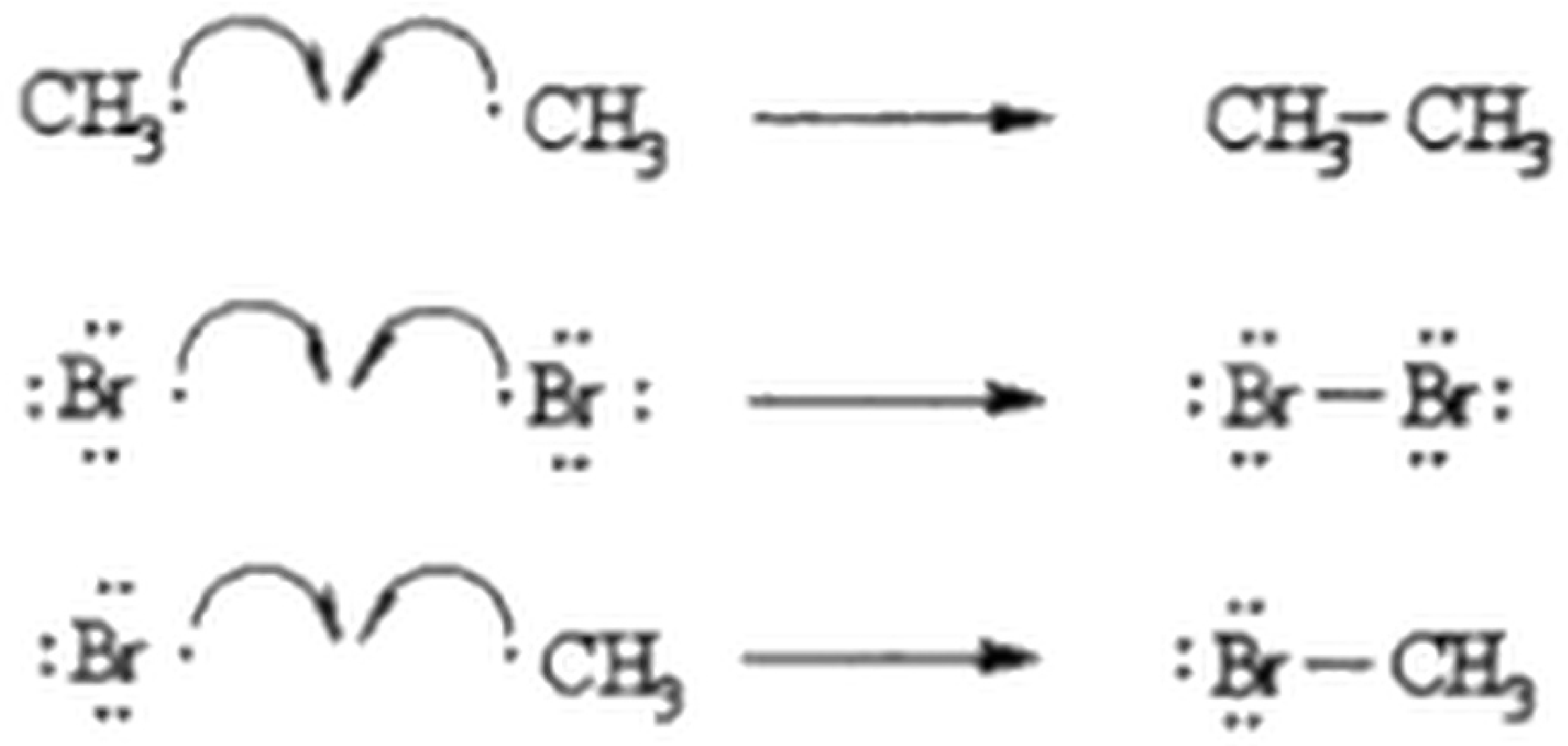
Step 2 (Propagation)

(a) A bromine radical abstracts a hydrogen to form HBr and a methyl radical, then

(b) The methyl radical abstracts a bromine atom from another molecule of Br2 to form the methyl bromine product and another bromine radical, which can

Step 3 (Termination)

Various reactions between the possible pairs of radicals allow for the formation of ethane, Br_2 or the product, methyl bromide. These reactions remove radicals and do not perpetuate the cycle



Q5. Give oxidation and reduction reactions of organic compounds.

Answer

Oxidation, [O], and reduction, [R], are opposites and both must occur simultaneously, hence redox reactions.

Organic chemists will normally describe a reaction as cither oxidation or reduction depending on the fate of the major organic component.

Oxidation

- more C-O bonds (or other atoms more electronegative than C)
- less C-H bonds
- loss of electrons
- increased oxidation state, e.g. +1 to +3 (see below)

Reduction

more C-H bonds

less C-O bonds (or other atoms more electronegative than C)

gain of electrons decreased oxidation state, e.g. +1 to -l (see below)

Alkene

Nomenclature:

IUPAC system for naming Alkenes are as:

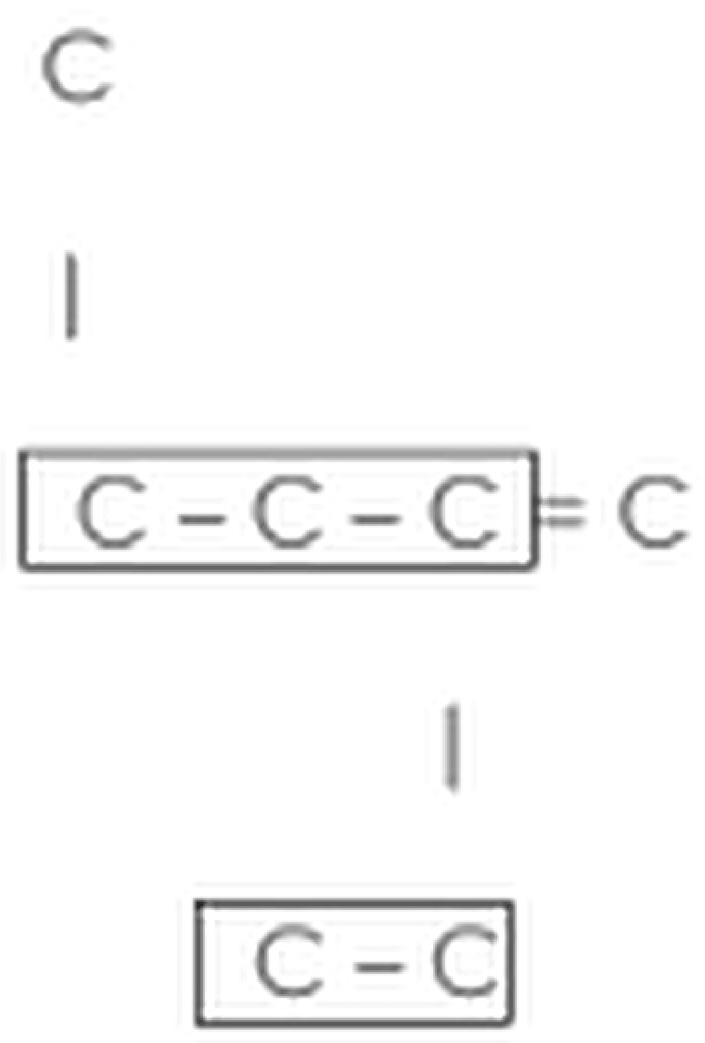
I) The longest continuous chain containing double bond is selected as parent chain.

$$\begin{array}{l} \quad C \\ \quad | \\ \boxed{C-C-C=C} \\ \qquad\quad | \\ \qquad\quad C-C \end{array}$$

The parent chain

Containing double

Bond (correct)



$$\begin{array}{l} \quad C \\ \quad | \\ \boxed{C-C-C}=C \\ \qquad\qquad\quad | \\ \qquad\quad \boxed{C-C} \end{array}$$

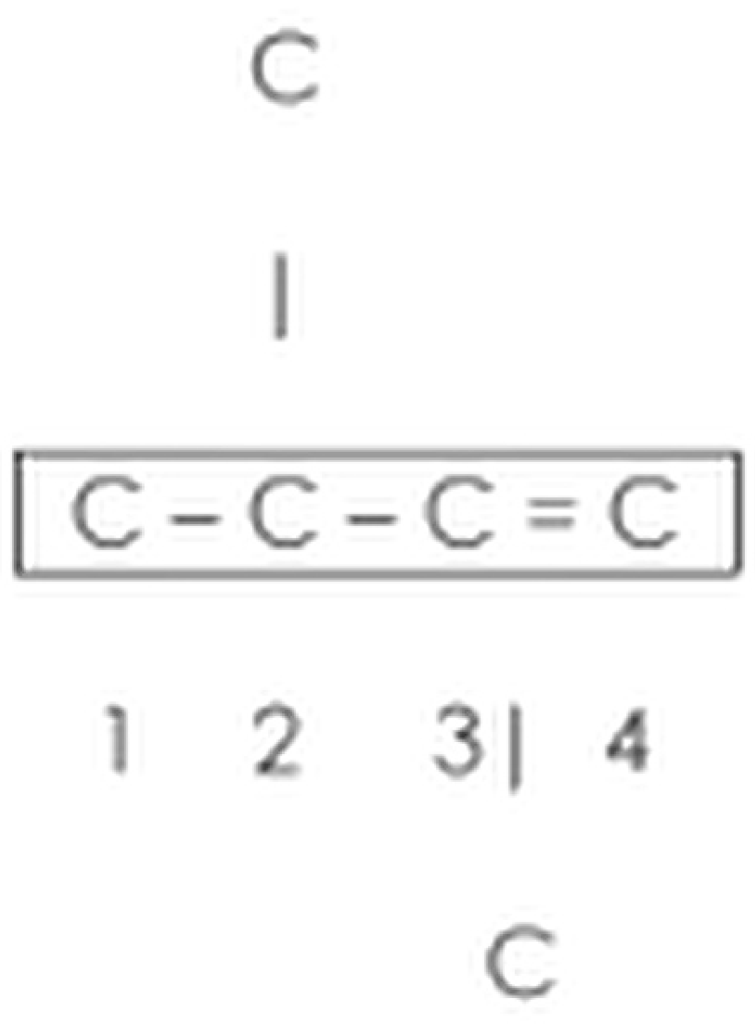
Longest chain with

no double bond

(incorrect)

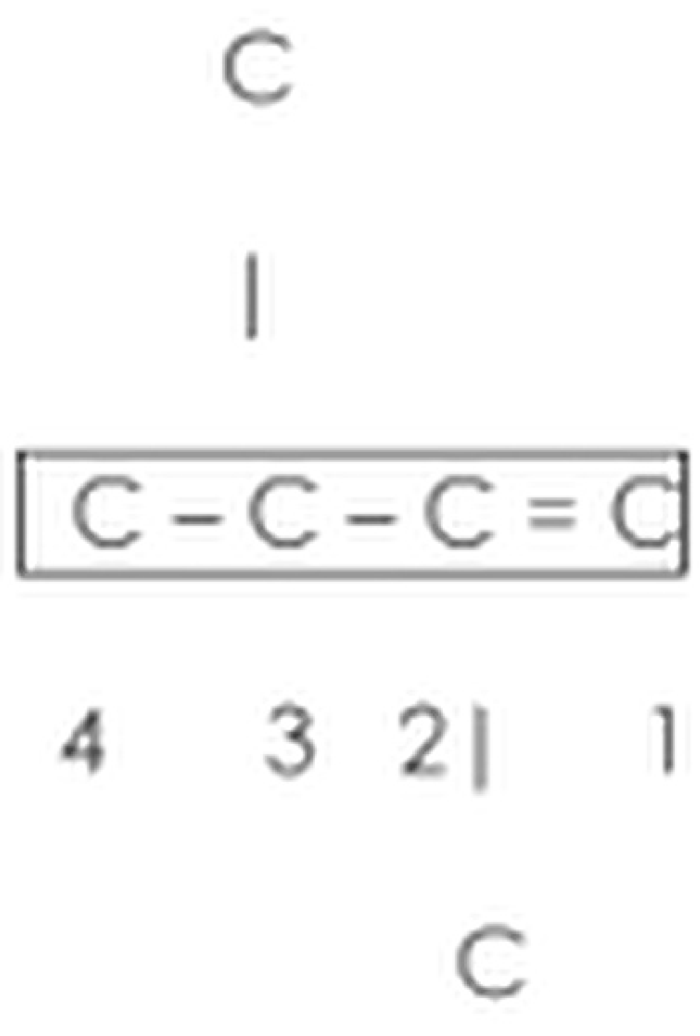
2) The ending 'ane' is replaced by 'ene'.

3) The chain is numbered in such a manner as to give minimum number to the doubly bonded C-atoms.



$$\begin{array}{l} \quad C \\ \quad | \\ \boxed{C-C-C=C} \\ 1\quad 2\quad 3|\;\; 4 \\ \qquad\quad\;\; C \end{array}$$

(incorrect)

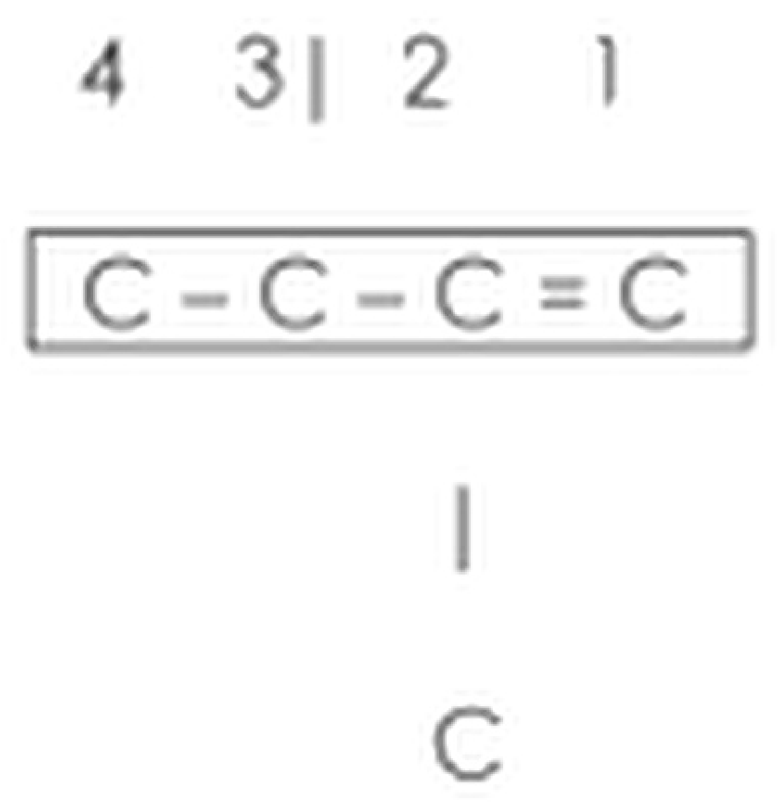


$$\begin{array}{l} \quad C \\ \quad | \\ \boxed{C-C-C=C} \\ 4\quad 3\quad 2|\;\; 1 \\ \qquad\quad\;\; C \end{array}$$

(correct)

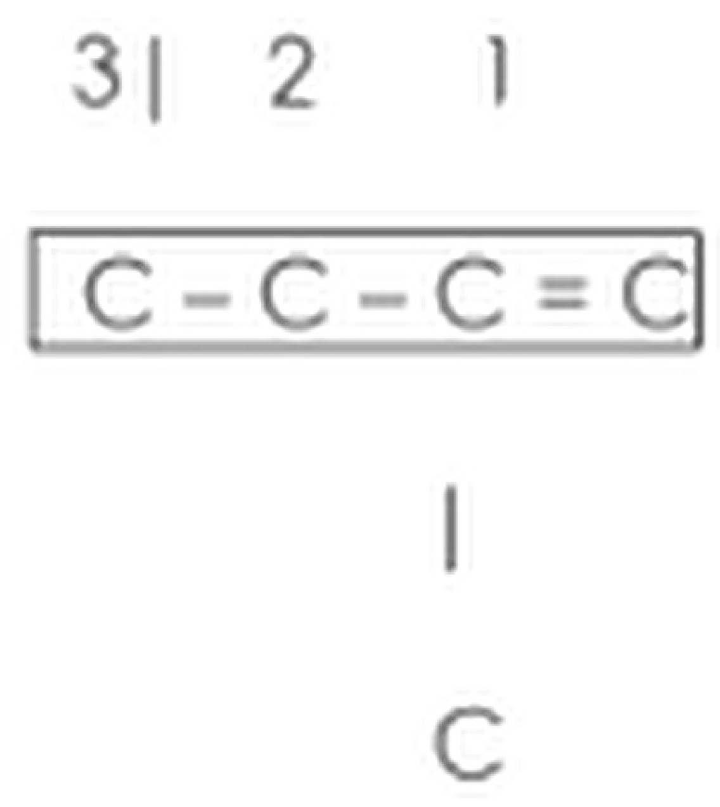
4) The position of double bond is indicated by the lower number of C-atom.

C C



$$\begin{array}{l}4\ \ 3|\ 2\ \ 1\\ \boxed{C-C-C=C}\\ \qquad\ \ |\\ \qquad\ \ C\end{array}$$

2 – ene (incorrect)



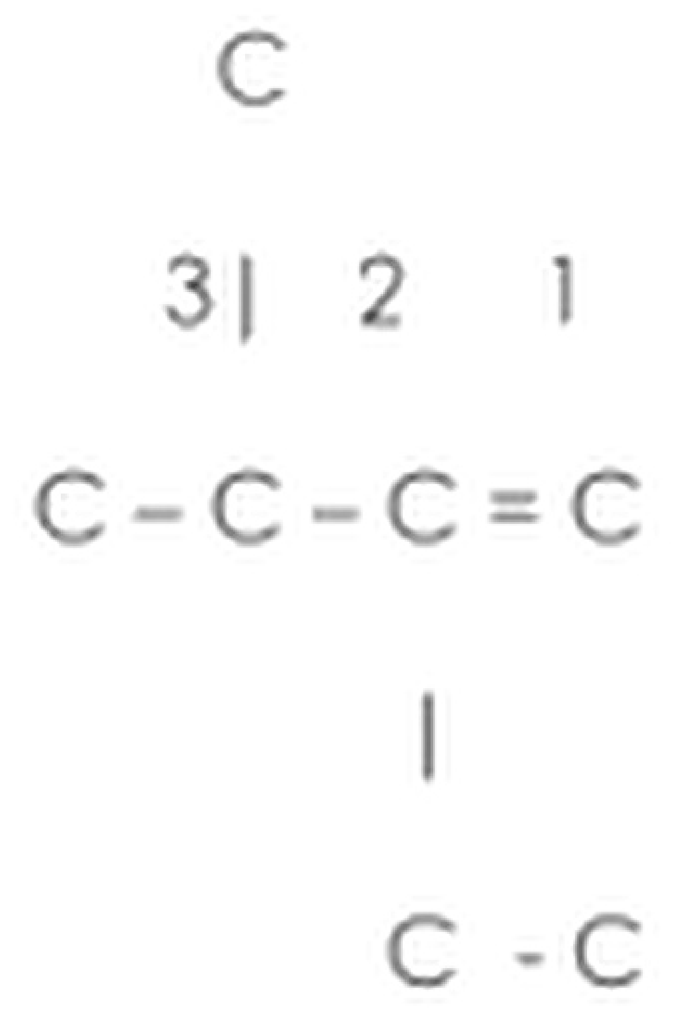
$$\begin{array}{l}4\ \ 3|\ 2\ \ 1\\ \boxed{C-C-C=C}\\ \qquad\ \ |\\ \qquad\ \ C\end{array}$$

1 – ene (correct)

5) The lower number of C-atom is placed before the name of parent alkene.

6) The presence of more than double bond is indicated by the suffix -diene for two double bonds, for three double bonds and so on.

7) Alkyl Coups are indicated by the methods mentioned in alkane.



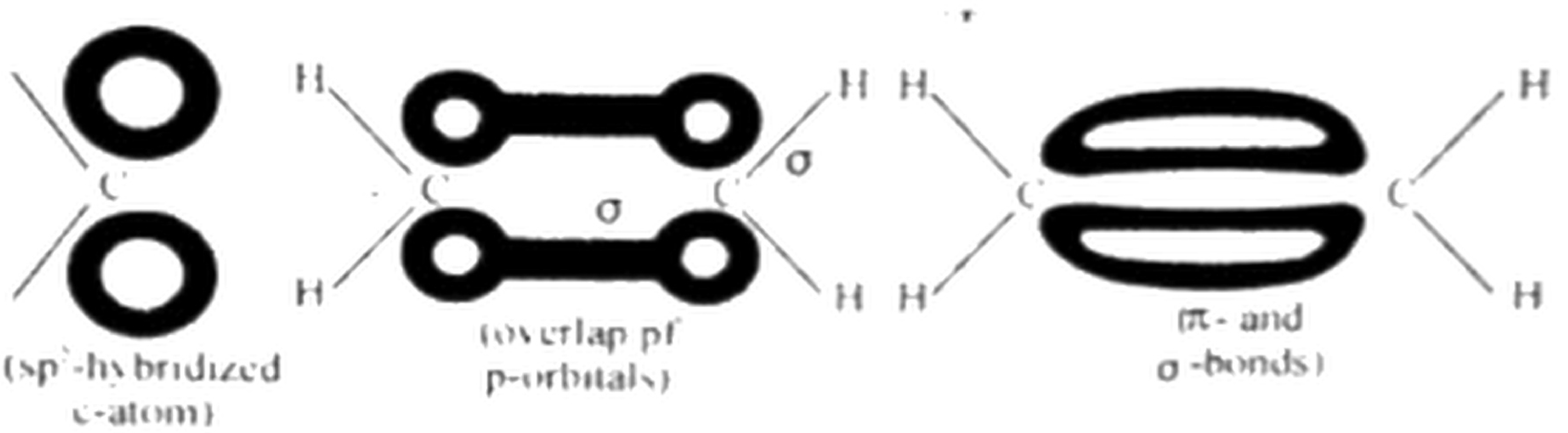
$$\begin{array}{l}\quad C\\ \quad 3|\ \ 2\ \ 1\\ C-C-C=C\\ \qquad\ \ |\\ \qquad\ \ C-C\end{array}$$

2 – ethyl – 3 – methyl – 1 - butene

Q6. Give Structure of alkanes.

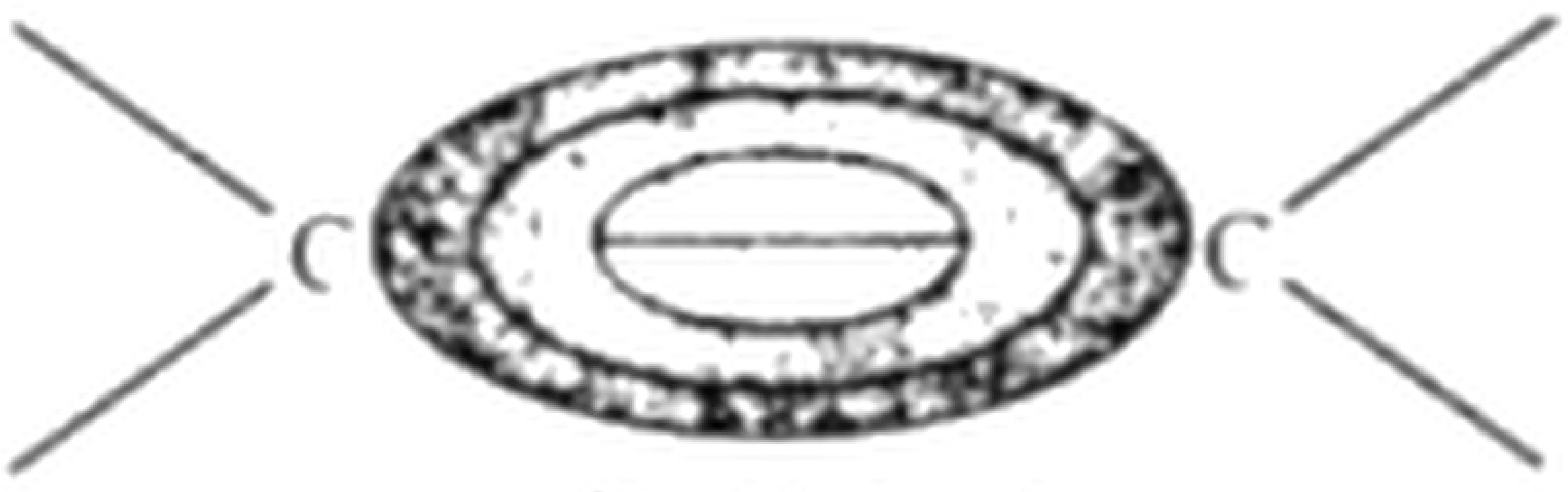
Answer

The carbon atoms linked through π-bon d are sp2 hybridized. Therefore, each atom carries three sp2-hybrids and one p-orbital. The p-orbital overlap to form x-bond and hybrid orbitals form a-bonds due to linear overlap.



The carbon-carbon distance in ethane is shorter (I .34A) than the C-C bond distance of ethane (I .54A). It is due to increased electron density between carbon atoms.


Single bond


Double bond

Carbon atoms are coplanar, and the rotation of one e-atom with respect to other is restricted which results in c is-trans isomerism in alkene.

Q7. Give preparation of alkenes.

1) Dehydration of Alcohols

Removal of water molecule is called dehydration.

Example

When vapors of alcohol are passed over heated alumina, dehydration takes place with the formation of alkene.

$$R - CH_2 - CH_2 \xrightarrow{Al_2O_3} R - CH = CH_2 + H_2O$$

| 340 – 450°C

OH

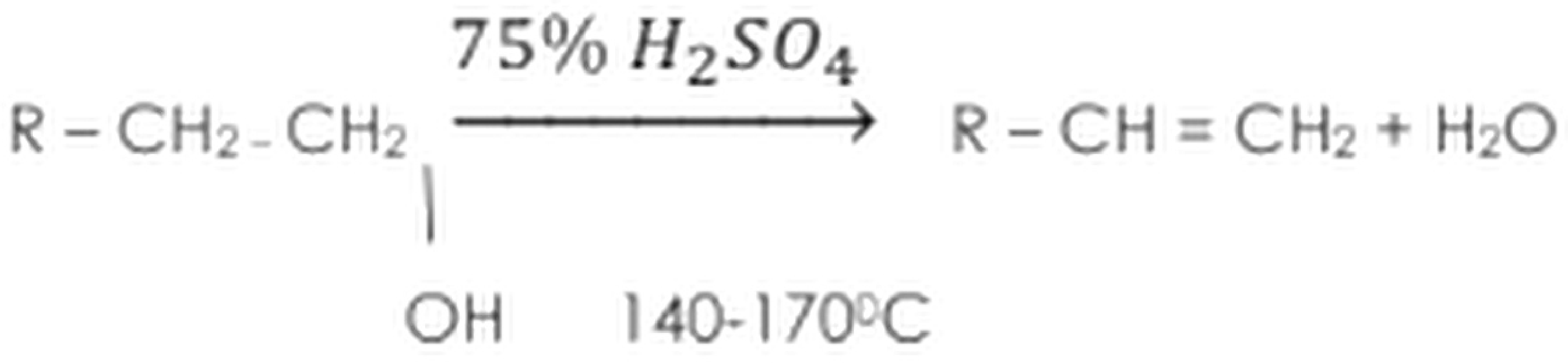
Alcohol Alkene

P_4O_{10}, H_2SO_4, H_3PO_4 are also used for dehydration. The ease of dehydration of various alcohols is in the order.

Ter.alcohol > sec.alcohol > pri.alcohol

Example:

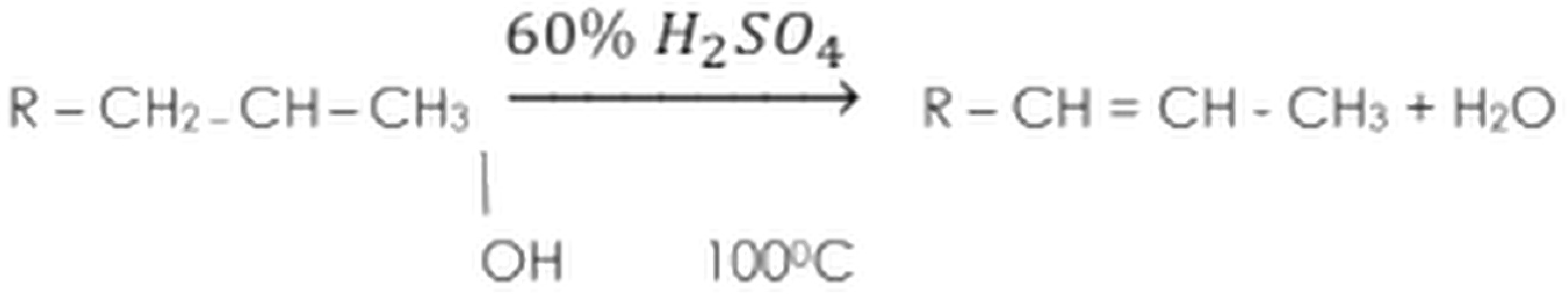
(i) Primary Alcohol:



$$R-CH_2-\underset{\underset{OH}{|}}{CH_2} \xrightarrow[140\text{-}170^{0}C]{75\%\ H_2SO_4} R-CH=CH_2+H_2O$$

Primary Alcohol

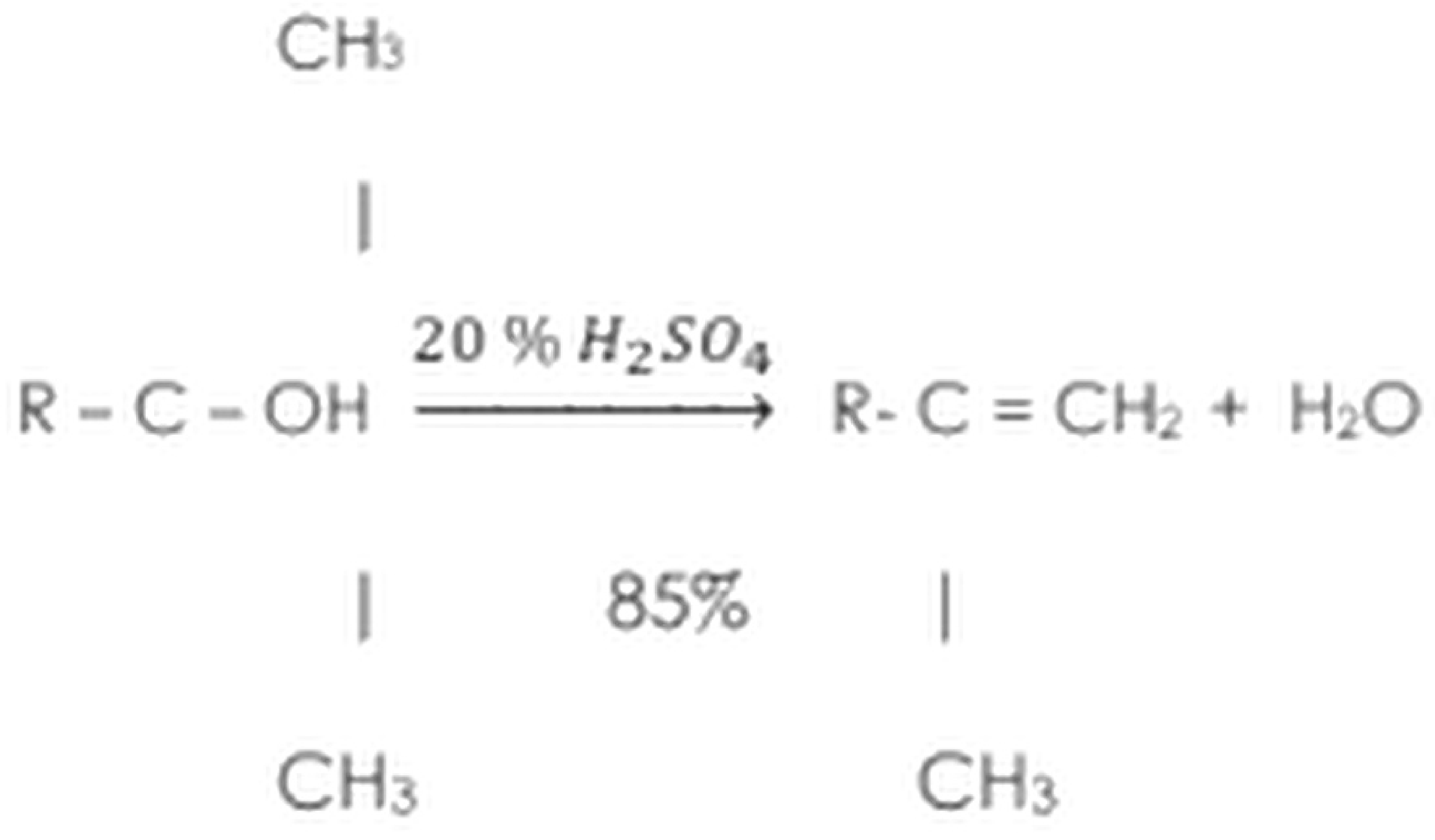
(ii) Secondary Alcohol:



$$R-CH_2-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow[100^{0}C]{60\%\ H_2SO_4} R-CH=CH-CH_3+H_2O$$

Secondary Alcohol

(iii)



$$R - \overset{CH_3}{\underset{CH_3}{C}} - OH \xrightarrow[85\%]{20\ \%\ H_2SO_4} R- \underset{CH_3}{C} = CH_2 + H_2O$$

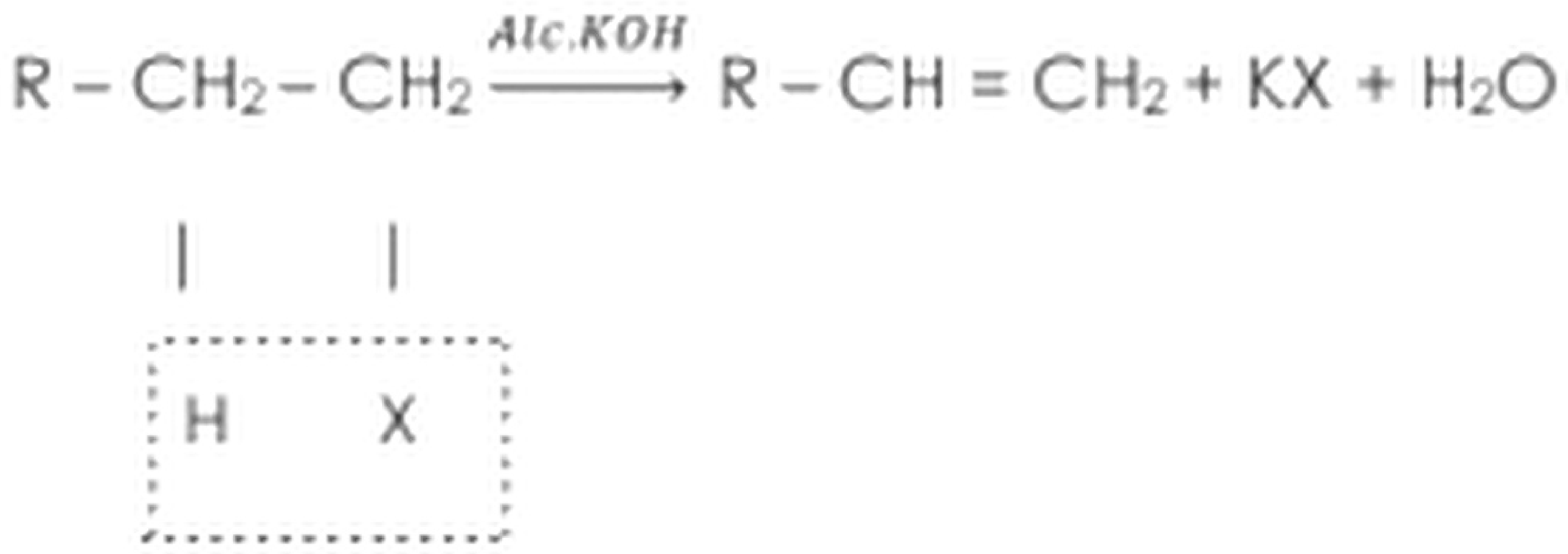
Tertiary Alcohol

2) Dehydrohalogenation of Alkyl Halides

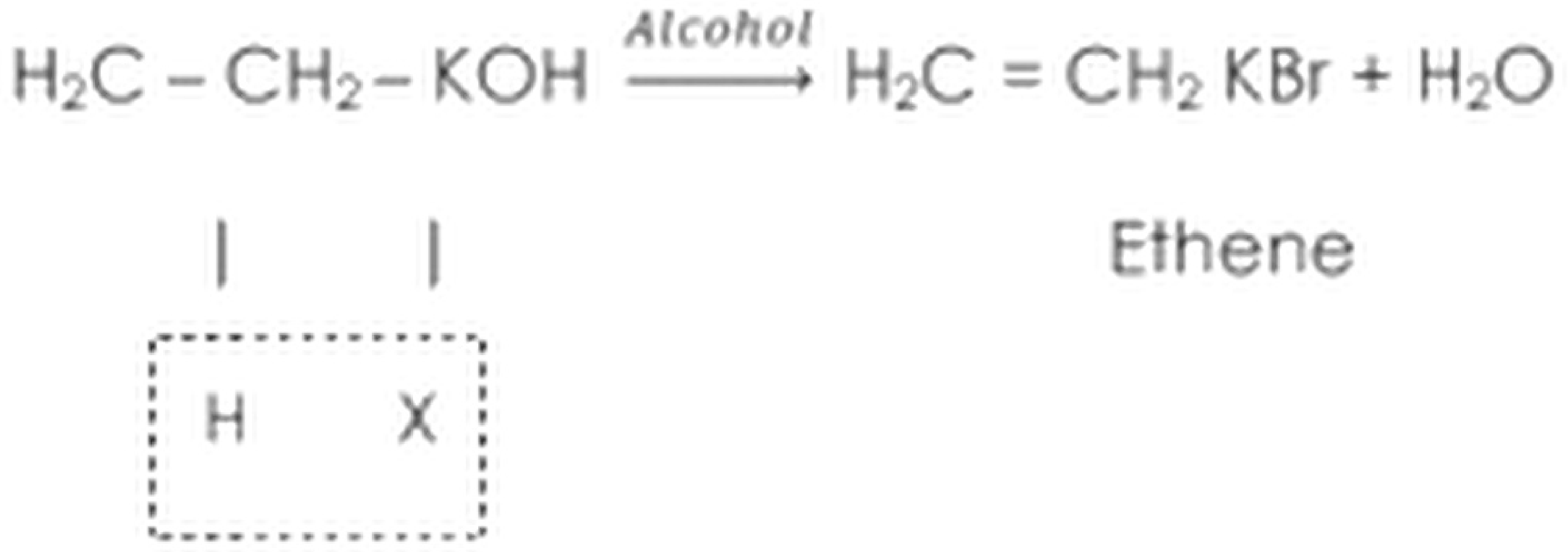
Removal of hydrogen halide (HX) from alky halides is called Dehydrohalogenation"

Example

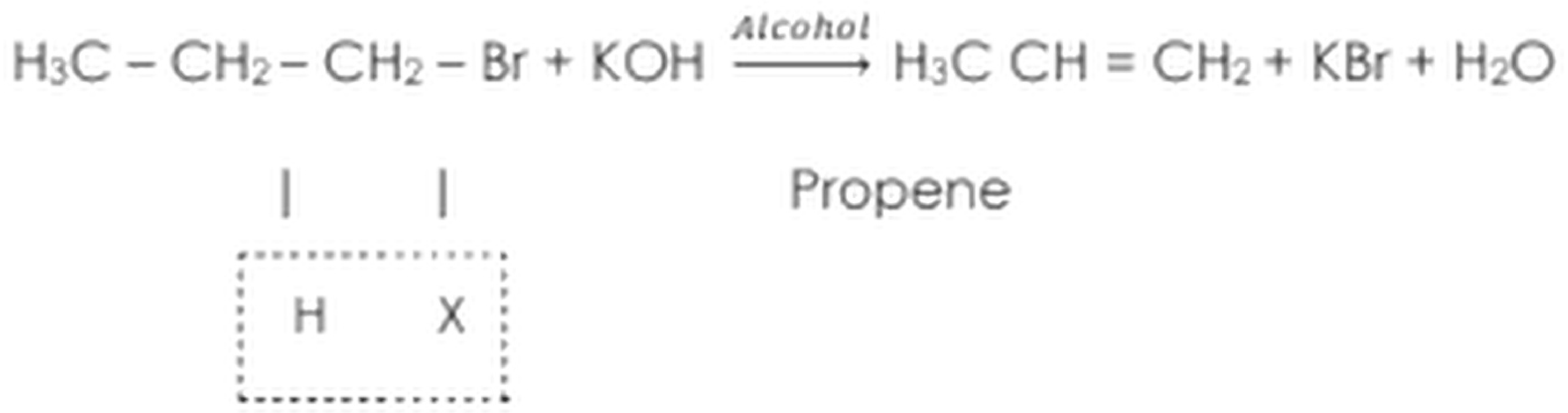
Alkyl halides on heating with alcoholic potassium hydroxide undergo Dehydrohalogenation to form alkenes.



$$R - \underset{H}{CH_2} - \underset{X}{CH_2} \xrightarrow{Alc.KOH} R - CH = CH_2 + KX + H_2O$$



$$\underset{H}{H_2C} - \underset{X}{CH_2} - KOH \xrightarrow{Alcohol} \underset{\text{Ethene}}{H_2C = CH_2}\ KBr + H_2O$$



$$H_3C-CH_2-CH_2-Br + KOH \xrightarrow{Alcohol} H_3C\ CH = CH_2 + KBr + H_2O$$

Propene

Q8. Give diffractions of alkanes.

Answer

1) Hydrogenation

A process in which a molecule of hydrogen is added to an akene is in the presence of a catalyst and at moderate pressure (I-5atm) to give a saturated compound is known as catalytic hydrogenation.

Explanation

It is a highly exothermic process and 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 about 120kJmole-I for each double bond present in a molecule. The catalysts employed are Pt, Pd and Raney Nickel.

Raney Nickel

It is prepared by treating a Ni — Al alloy with caustic soda.

$$Ni - Al + NaOH + H_2O \longrightarrow Ni + NaAlO_2 + 3/2\ H_2$$

$$H_3C - CH - CH = CH_2 + H_2 \xrightarrow{Ni} H_3C - CH - CH_2 - CH_3$$

3- Methyl – 1 – butane iso Pentane

Benzene Cyclohexane

Catalytic hydrogenation of alkenes is used in the laboratory as well as in industry. In industry, it is used for the manufacture of vegetable ghee from vegetable oils. In the laboratory, it is used as a synthetic as well as an analytical tool.

2) Hydrohalogenation

Alkenes react with aqueous solution of halogen acid to form alkyl halides.

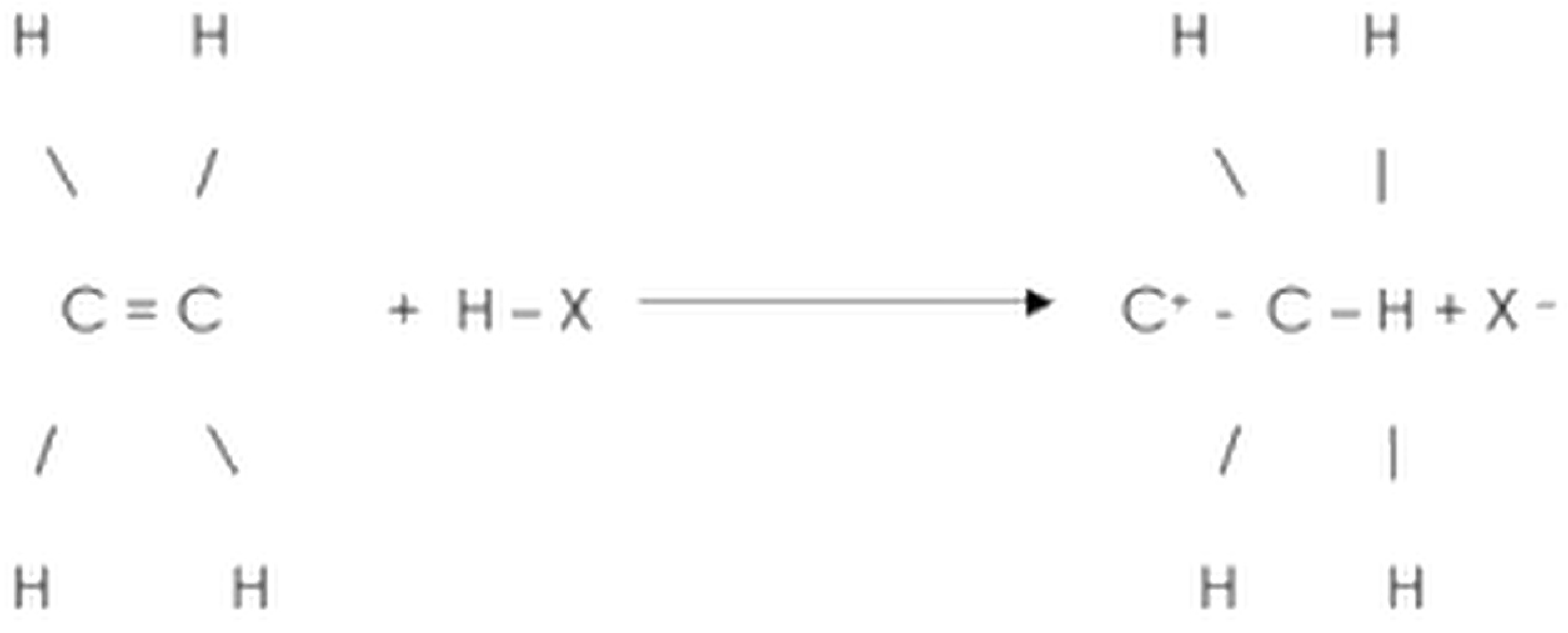
$$R - CH = CH_2 + HX \longrightarrow \underset{\displaystyle X}{\underset{|}{RCH}} - CH_3$$

$$H_2C = CH_2 + HCl \longrightarrow H_3C - \underset{\displaystyle Cl}{\underset{|}{CH_2}}$$

The order of reactivity of halogen acids is HI>HBr>HCl

Mechanism of Reaction:

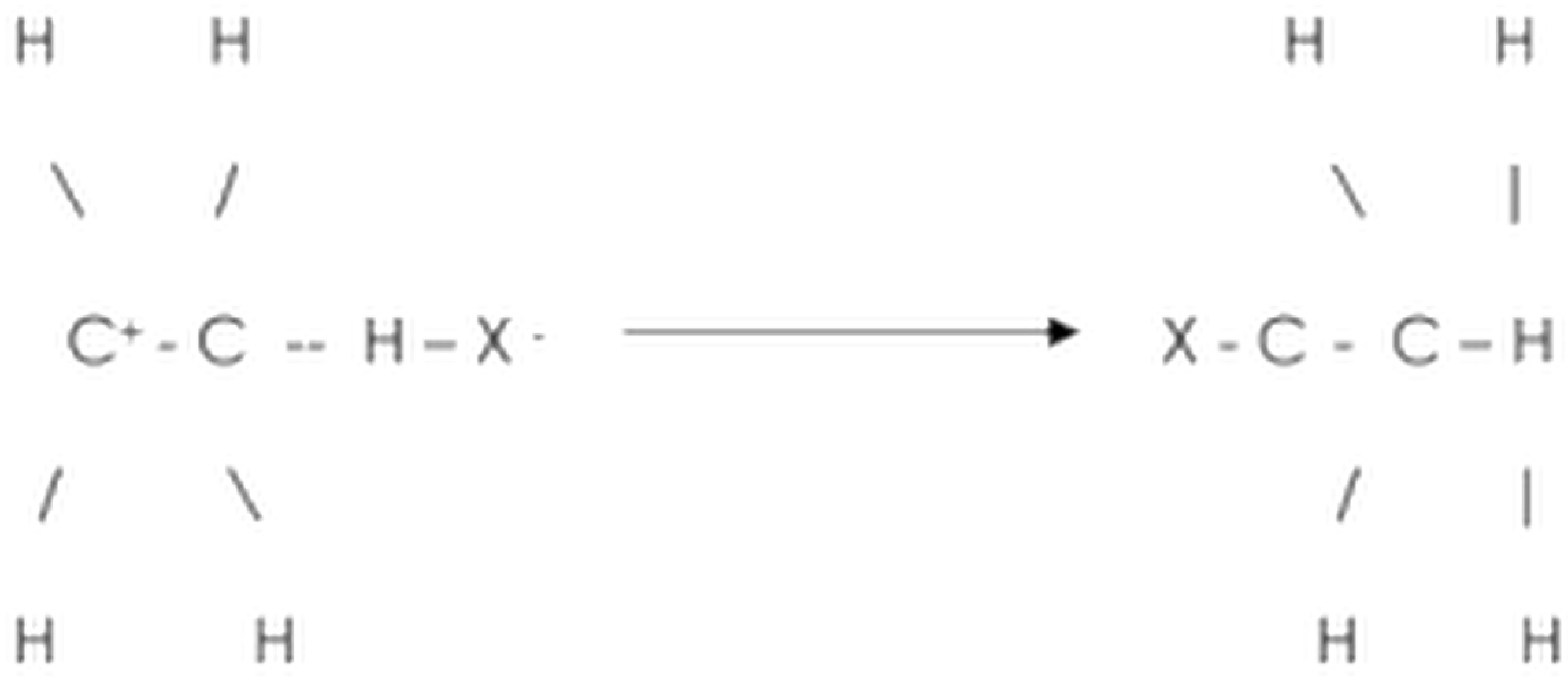
The addition of a hydrogen halide to an alkene takes place in two steps. Alkene accepts the proton of hydrogen halide to form a carbocation.



$$\begin{array}{c} H \quad\quad H \\ \backslash \quad\quad / \\ C = C \\ / \quad\quad \backslash \\ H \quad\quad H \end{array} \quad + \; H - X \longrightarrow \begin{array}{c} H \quad\quad H \\ \backslash \quad\quad | \\ C^{+} - C - H \\ / \quad\quad | \\ H \quad\quad H \end{array} + X^{-}$$

(Carbocation)

The carbocation then reacts with the halide ion.

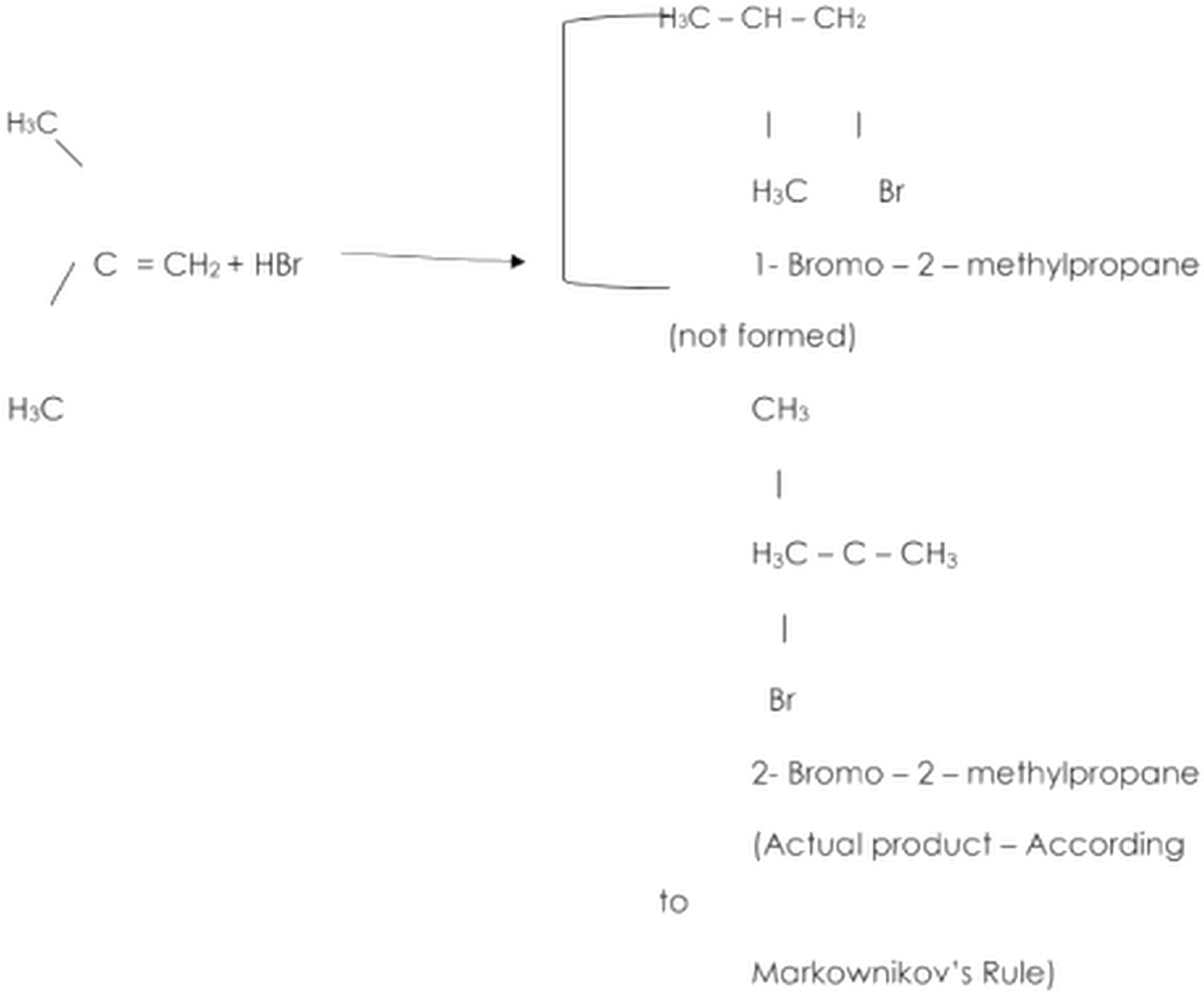


$$\begin{array}{c} H \quad\quad H \\ \backslash \quad\quad / \\ C^{+} - C \;\text{--}\; H - X^{-} \\ / \quad\quad \backslash \\ H \quad\quad H \end{array} \longrightarrow \begin{array}{c} H \quad\quad H \\ \backslash \quad\quad | \\ X - C - C - H \\ / \quad\quad | \\ H \quad\quad H \end{array}$$

Markownikov's Rule:

The addition of hydrogen halide over an unsymmetrical alkene is according to Markownikov's Rule. Which states that; in the addition of an unsymmetrical reagent to an unsymmetrical alkene, the negative part of the adding reagent goes to that carbon, consisting the double bond, which has least number of hydrogen atoms.

Example



$$\begin{matrix} H_3C \\ \quad C=CH_2+HBr \\ H_3C \end{matrix} \longrightarrow \left[\begin{matrix} \underset{H_3C}{\underset{|}{H_3C-CH}}-\underset{Br}{\underset{|}{CH_2}} \\ \\ H_3C-\overset{CH_3}{\overset{|}{\underset{Br}{\underset{|}{C}}}}-CH_3 \end{matrix} \right.$$

1- Bromo – 2 – methylpropane

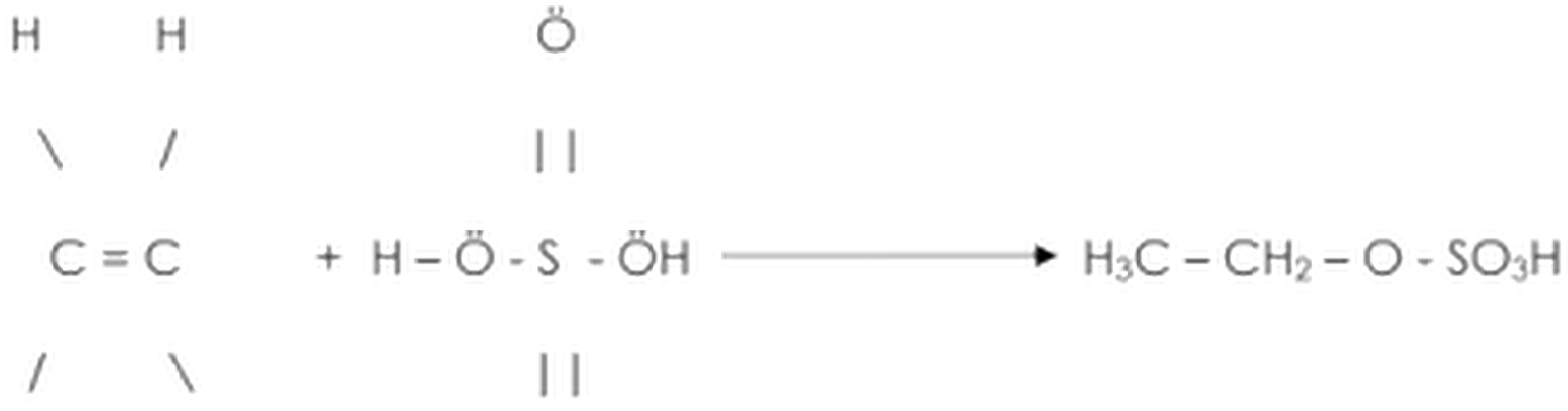
(not formed)

2- Bromo – 2 – methylpropane

(Actual product – According to Markownikov's Rule)

3) Hydration

Addition of water is called hydration. Some reactive alkenes react with water in the presence of suitable substances as acid etc. to form alcohol. It is possible as alkenes are soluble cold concentrated sulfuric acid. They react by addition to form alkyl hydrogen sulphate.



$$\begin{matrix} H & & H \\ & C=C & \\ / & & \backslash \end{matrix} + H-\ddot{O}-\overset{\ddot{O}}{\overset{||}{\underset{||}{S}}}-\ddot{O}H \longrightarrow H_3C-CH_2-O-SO_3H$$

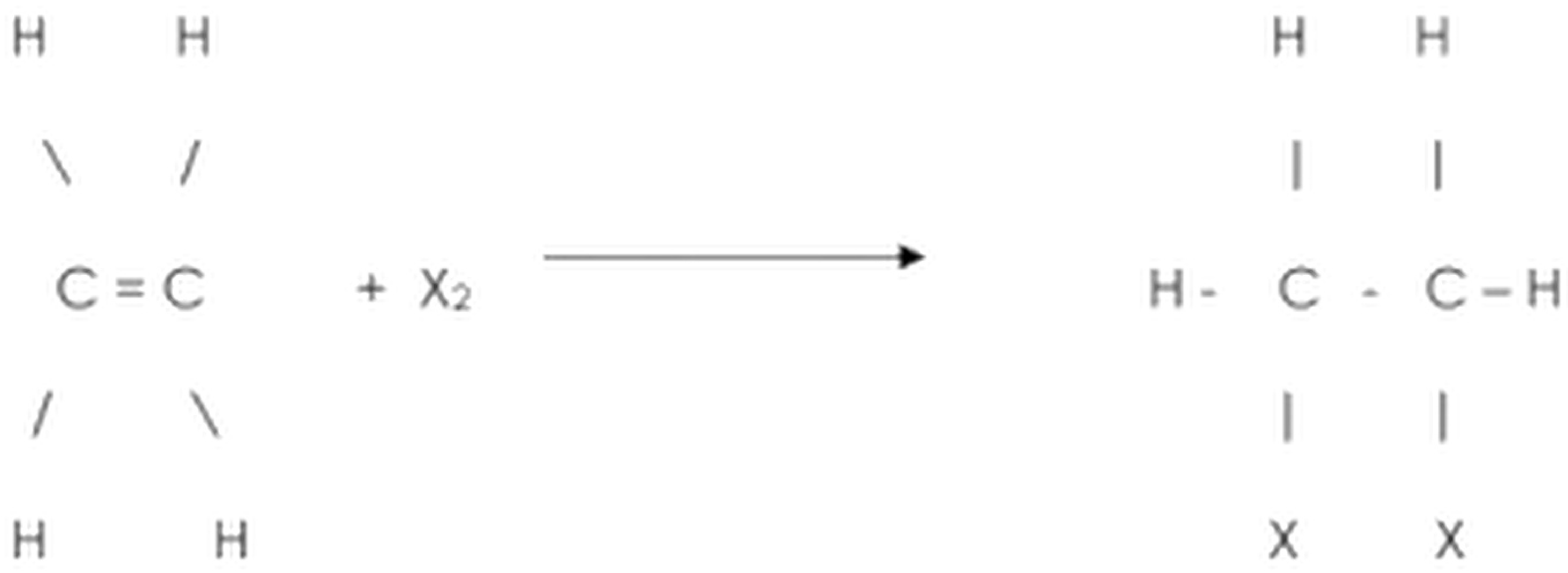
H H Ö

These alkyl hydrogen sulphates on boiling with water decompose to give corresponding alcohols.

$$H_2C - CH_2 - O - SO_3H + H_2O \xrightarrow{100^\circ C} H_3C - CH_2 - OH - H_2SO_4$$

4) Halogenation

The alkenes react with halogen in an inert solvent like carbon tetrachloride at room temperature to give vicinaldihalides or 1,2 dihalogenated products.

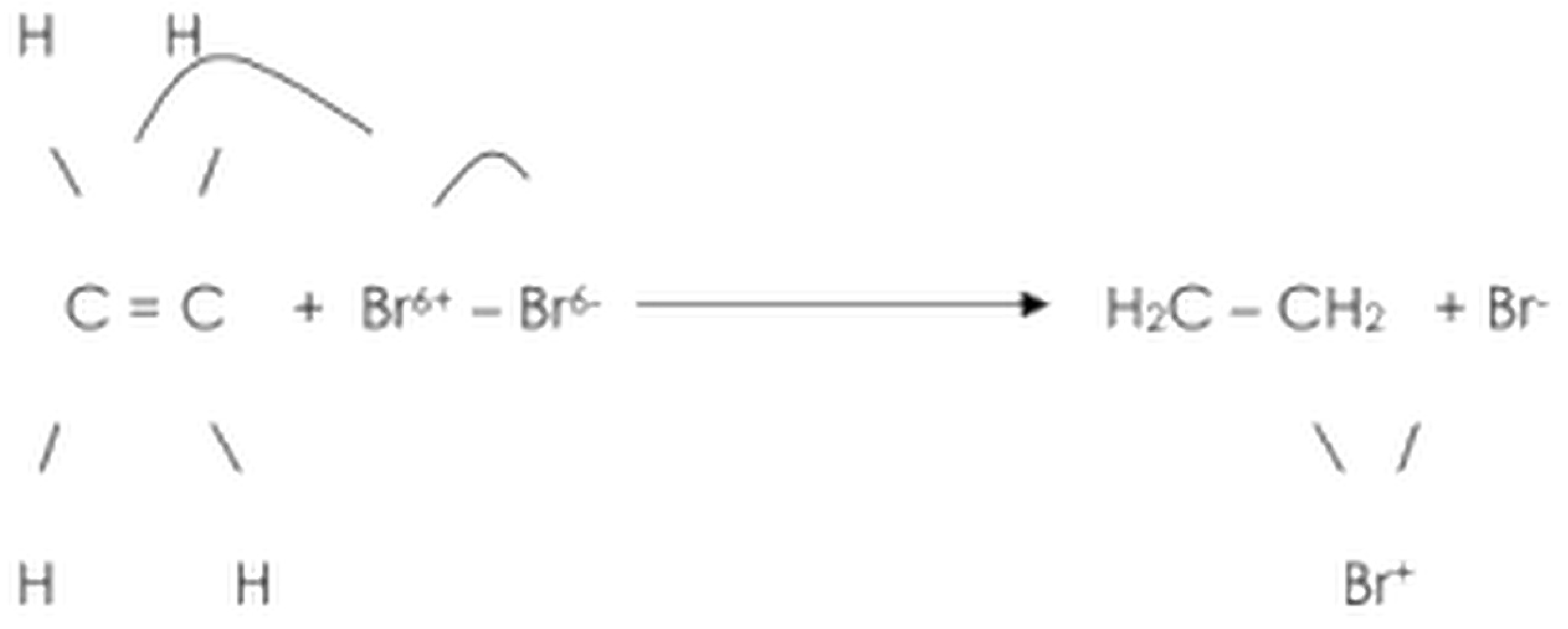


(Vicinal dihalide)

Br_2 and Cl_2 are effective electrophilic reagents. Fluorine is too reactive to control the reaction. Iodine does not react.

Mechanism

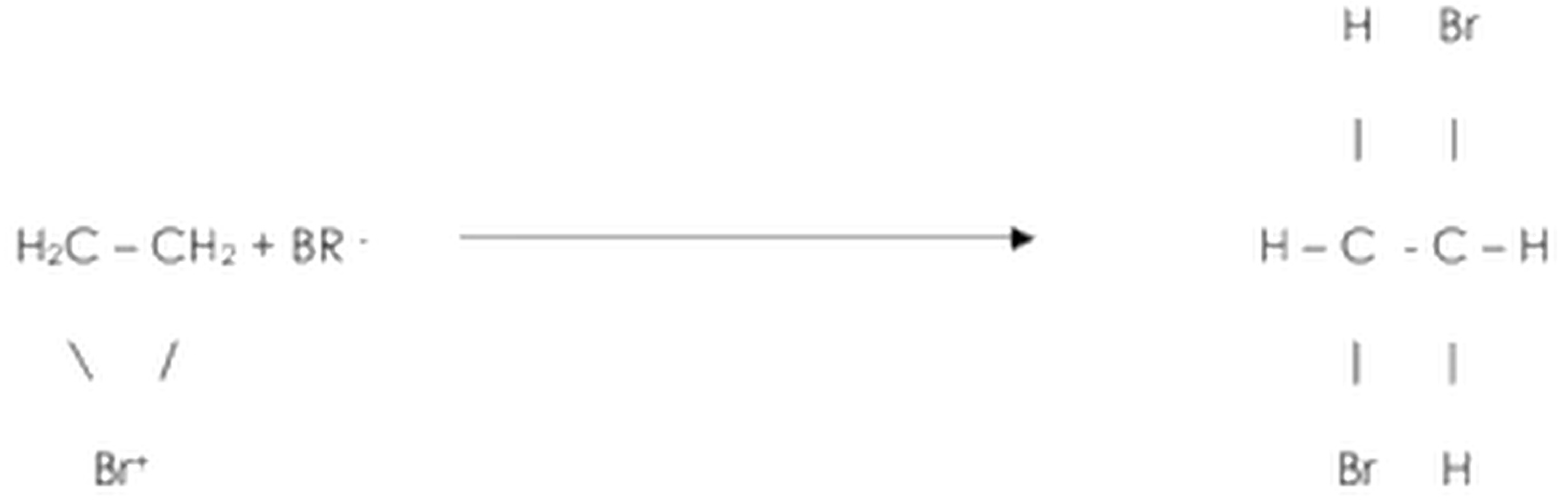
a) A bromine molecule becomes polarized as it approaches the alkene. This polarized bromine molecule transfers a positive bromine atom to the alkene resulting in the formation of a bromonium ion.



$$\mathrm{H_2C{=}CH_2} + Br^{\delta+}-Br^{\delta-} \longrightarrow \underset{\diagdown\ \diagup \atop Br^+}{H_2C-CH_2} + Br^-$$

Bromonium ion

b) The nucleophilic bromide ion then attacks on the carbon of the bromonium ions to form Vic. Dibromide and the color of bromine is discharged.



$$\underset{\diagdown\ \diagup \atop Br^+}{H_2C-CH_2} + BR^- \longrightarrow H-\underset{Br}{\overset{H}{C}}-\underset{H}{\overset{Br}{C}}-H$$

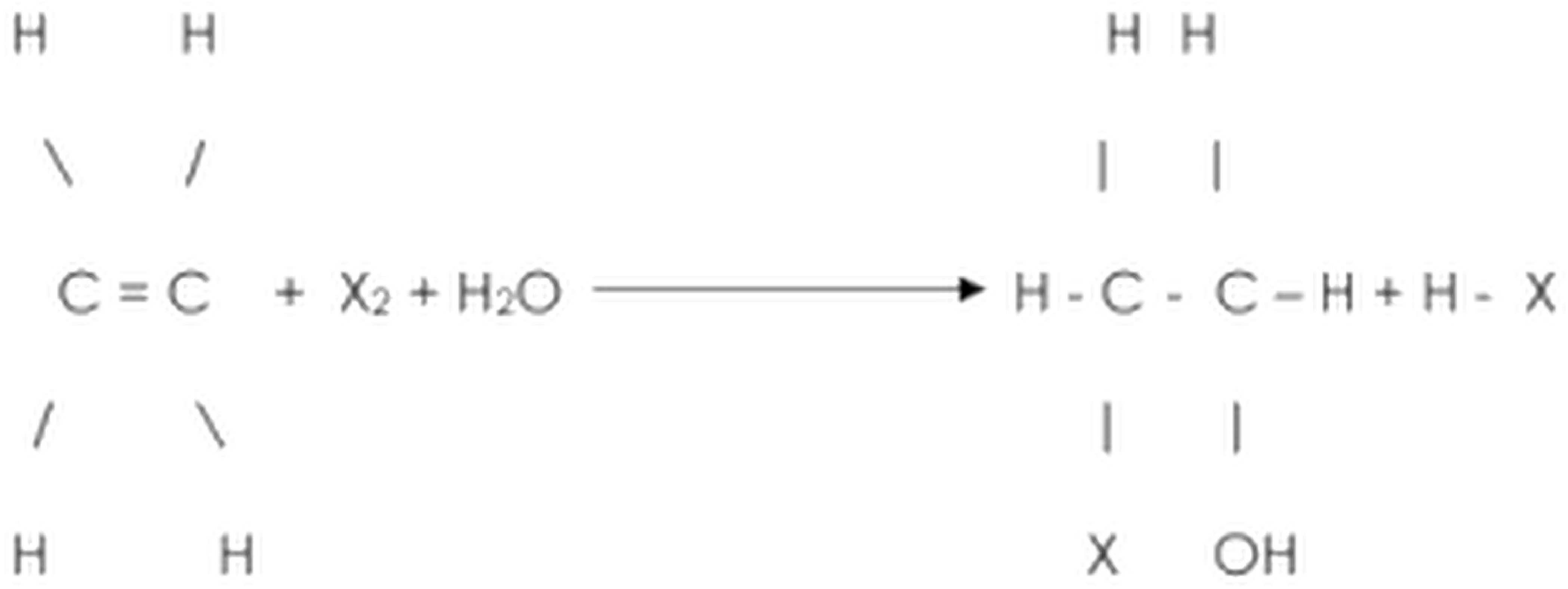
Bromonium ion 1,2 - Dibromethane

This test is applied for the detection of double bond in a molecule.

5) Halohydration

Addition of hypohalous acid (HOX) is called halohydration.

Alkenes react with hypohalous acid to give Halohydrin: In this reaction, molecules of the solvent become reactants too.

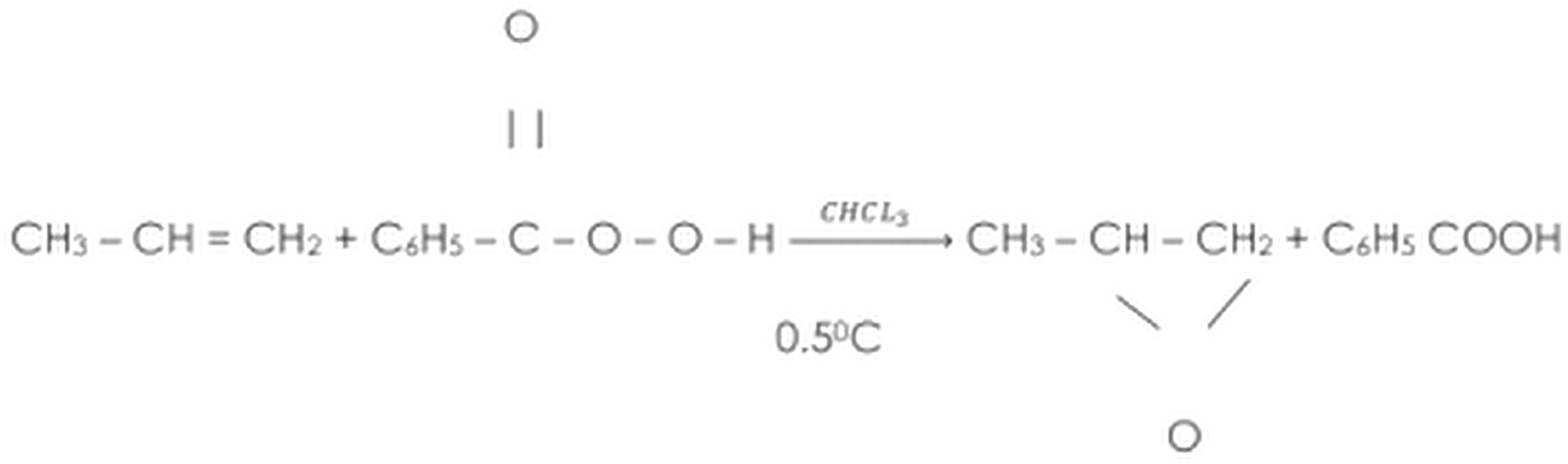


$$\overset{H}{\underset{H}{C}}=\overset{H}{\underset{H}{C}} + X_2 + H_2O \longrightarrow H-\underset{X}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-H + H-X$$

X_2 = Cl_2 or Br_2 (Halohydrin)

6) Epoxidation

It is the formation of epoxides. Peracids such as per oxyacetic acid or peroxy benzoic acid react with alkenes to form epoxides.

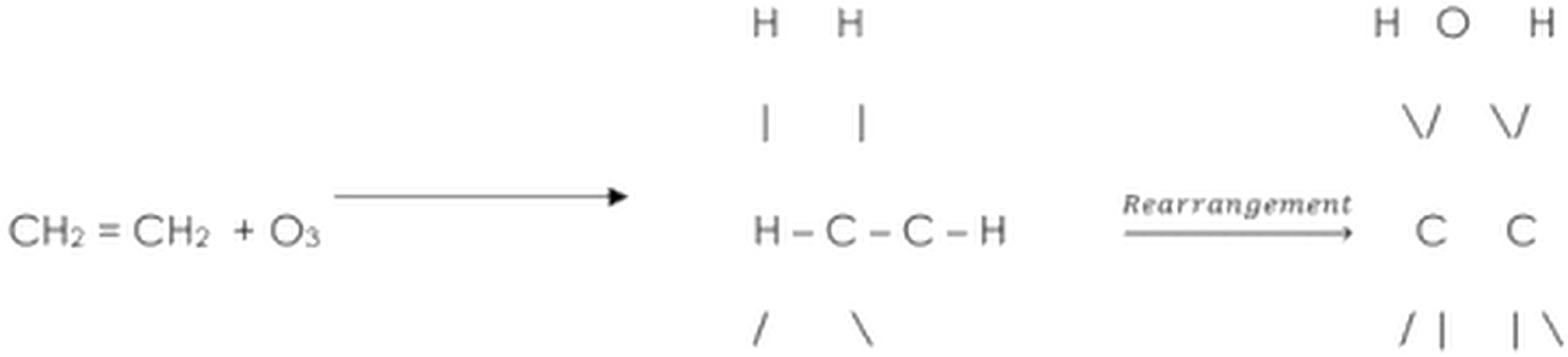


$$CH_3-CH=CH_2 + C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-H \xrightarrow[0.5^0C]{CHCL_3} CH_3-\underbrace{CH-CH_2}_{O} + C_6H_5COOH$$

(Epoxy propane) Benzoic Acid

7) Ozonolysis

Ozone (O_3) reacts vigorously with alkenes to fom unstable molozonide. It rearranges spontaneously to form an ozonide.



$$CH_2=CH_2 + O_3 \longrightarrow H-\overset{H}{C}-\overset{H}{C}-H \xrightarrow{Rearrangement} C \quad C$$

Molozonide (unstable) Ozonide

Reduction Ozonide:

Ozonides are unstable compounds and are reduced directly on treatment with zinc and H20. The reduction produces carbonyl compounds (aldehydes or ketones).

$$C \quad C + 2H_2O \longrightarrow 2H-C=O + 2H_2O_2$$

Formaldehyde

$$H_2O_2 + Zn \longrightarrow ZnO + H_2O$$

Ozonolysis is used to locate the position of double bond in an alkene. The C-atom of double bond is changed to group.

8) Polymerization

Polymerization is a process in which a small organic molecules which are called monomers combine together to form larger molecules. The substances so produced are called polymers.

Ethene polymerizes to polythene at 400 ^{0}C at a pressure of 100 atm.

400_0C

$nCH_2 = CH_2 \rightarrow \_(\_CH_2\_CH_2\_)\ n\_$

Pressure = 100 atm Polythene

Traces of O_2(0.1%) (Polyethylene)

A good quality polythene is obtained when ethane is. polymerized in the presence of aluminium triethyl $Al(C_2H_5)$ and titanium tetrachloride ($TiCl_4$).

Interesting Information

Examples of natural and synthetic polymers

	Polymer	Monomer	where you find it
Natural	protein	ammo acids	wool, silk, etc.
	starch	glucose	potato, wheat, etc
	cellulose	glucose	paper, wood, dietary fibre
	DNA	nucleotides	chromosomes, genes
Synthetic	poly (ethane)	ethane	bags, washing-up bowls, etc.
	poly (chloroethene) (PVC)	chloroethene	fabric coatings, electrical
	poly (phenylethene)	phenylethene	Insulation
	(polystyrene)		toys, expanded polystyrene
	Polyster	ehthane-l.2- diol and benzene- 1,2dicarboxylic acid	skirts, shirts, trousers

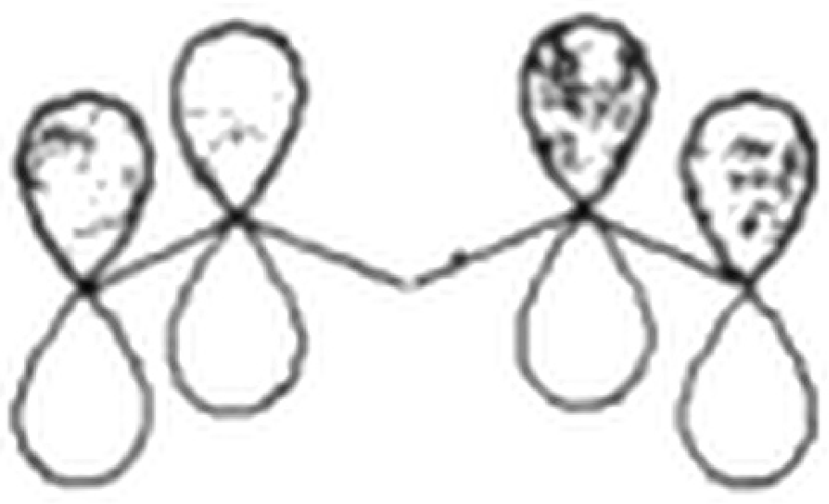
Q9. What is conjugation?

Answer

The word "conjugation" is derived from a Latin word that means "to link together". In organic chemistry, it is used to describe the situation that occurs when p systems are "linked together".

- An "isolated' p system exists only between a single pair of adjacent atoms (e.g. C=C)
- An "extended' p system exists over a longer series of atoms (e.g. C=C-C=C or C=CC=O etc..
- An extended p system results in an extension of the chemical reactivity.
- The fundamental requirement for the existence of a conjugated system is revealed if one considers the orbital involved in the bonding within the system.
- A conjugated system requires that there is a continuous array of "p" orbitals that can align to produce a bonding overlap along the whole system.
- If a position in the chain does not provide a "p" orbital or if geometry prevents the correct alignment, then the conjugation is broken at that point.
- You can investigate these differences by studying the following examples, pay particular attention to the "p" orbitals:

System	P System	type
Ethane		isolated

Propane		isolated
1,2 – propadiene (allene)		cumulated
1,3 - butadiene		conjugated
1,3 - pentadiene		conjugated
1, 4 - pentadiene		isolated
1,3 – cyclopentadiene		conjugated
1,3 – cyclohexadiene		Conjugated

1,4 – cyclohexadiene		Isolated
Benzene		Conjugated

The result of conjugation is that there are extra p bonding interactions between the adjacent p systems that results in an overall stabilization of the system.

Q10. What is isomerism? Explain with examples.

Answer

Compounds that have the same molecular formula but different chemical structures are called isomers and the phenomenon is called isomerism

Since isomers have the same molecular formula, the difference in their properties must be due to different modes of combination or arrangement of atoms within the molecule. There are two main types of isomerism:

(I) Structural Isomerism **(2)** Stereoisomerism

Structure Isomerism: When the isomerism is due to difference in the arrangement of atoms within the molecule, without any reference to space, the phenomenon is called Structural Isomerism. In other words, isomers are compounds that have the same molecular formula but different structural formulas. Structural isomerism is of five types:

i) Chain isomerism

ii) Position isomerism

iii) Functional isomerism

iv) Metamerism

v) Tautomerism

Stereoisomerism: When isomerism is caused by the different arrangements of atoms or groups in space, the phenomenon is called Stereoisomerism. The stereoisomers have the same structural formulas but differ in arrangement of atoms in space. In other words, stereoisomer is exhibited by such compounds which have the same structural formula but differ in configuration, (The term configuration refers to the three-dimensional arrangement of atoms that characterizes a particular compound). Stereoisomer is of two types:

(a) Geometrical or Cis-Trans Isomerism **(b)** Optical Isomerism

1) Chiral Center:

First, we will discuss plane of symmetry which help us to understand this topic.

Plane of Symmetry

A plane which divides an object into two symmetrical halves, is said to be plane of symmetry. For example, a person or a hat has a plane of symmetry (Fig. a person's hand or gloves lack plane of symmetry.

An object lacking a plane of symmetry is called dissymmetric or Chiral (pronounced as Ki-ral). A symmetric object is referred to as Achiral.

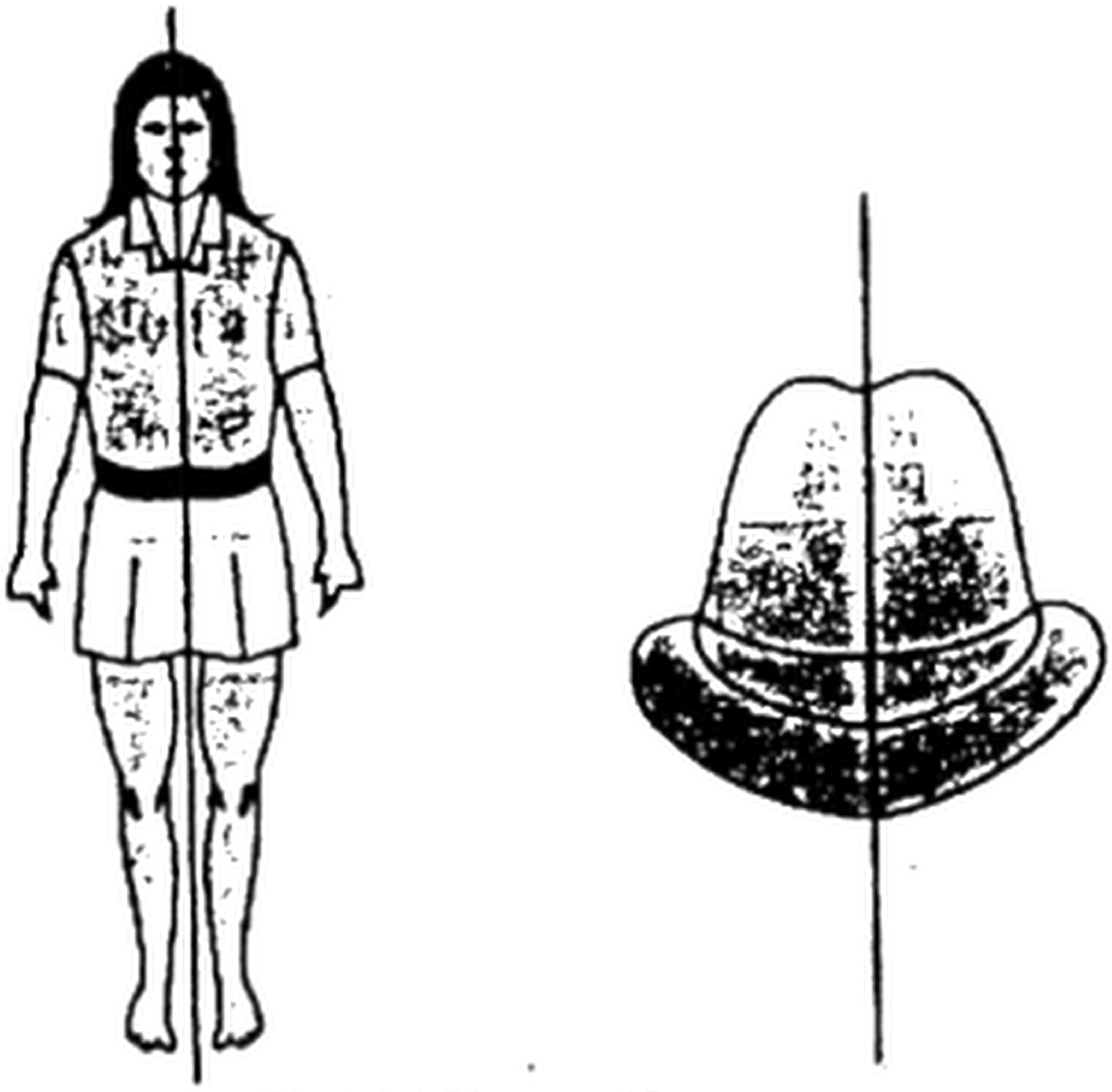


Fig.16.4 Planes of Symmetry

A dissymmetric object cannot be superimposed on its mirror image. A left hand for example does not possess a plane of symmetry, and its mirror image is not another left hand but a right hand (Fig.). The two are not identical because they cannot be superimposed. If we were to lay one hand on top- of the other, the fingers and the thumb would clash.

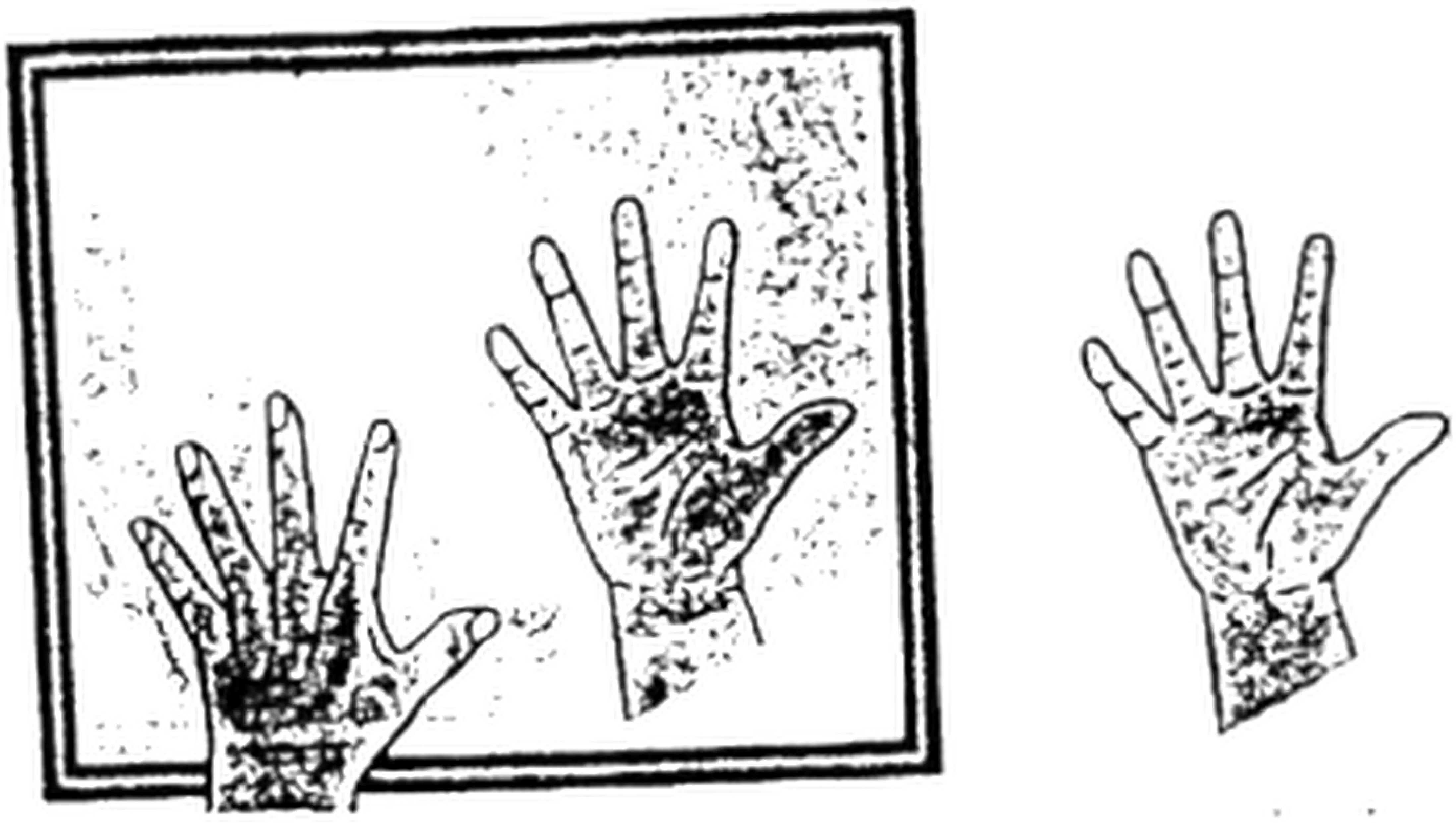


Fig. 16.5 The mirror image relationship of the left hands, notice that right hand is the mirror image of the left hand.

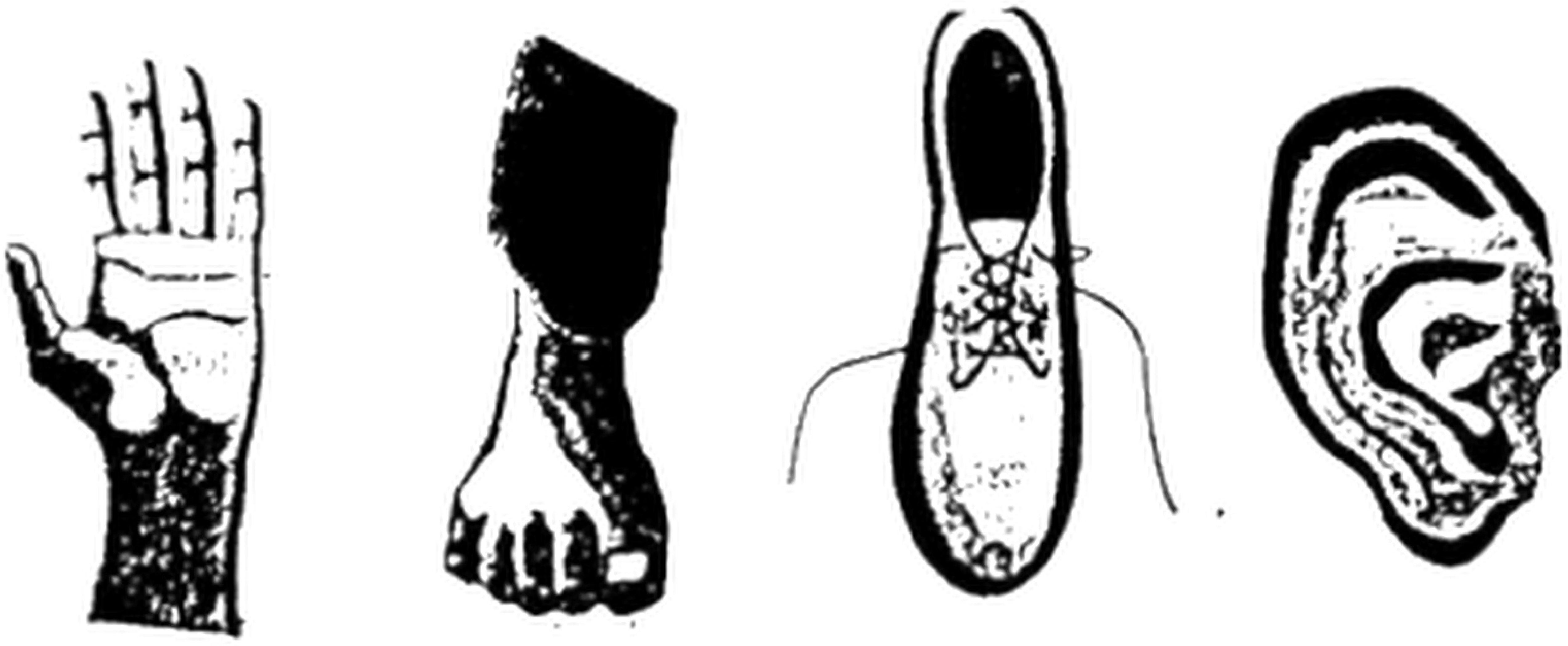


Fig 16.6 Chiral objects

Achiral molecule has at least one asymmetric center and does not have a plane of symmetry.

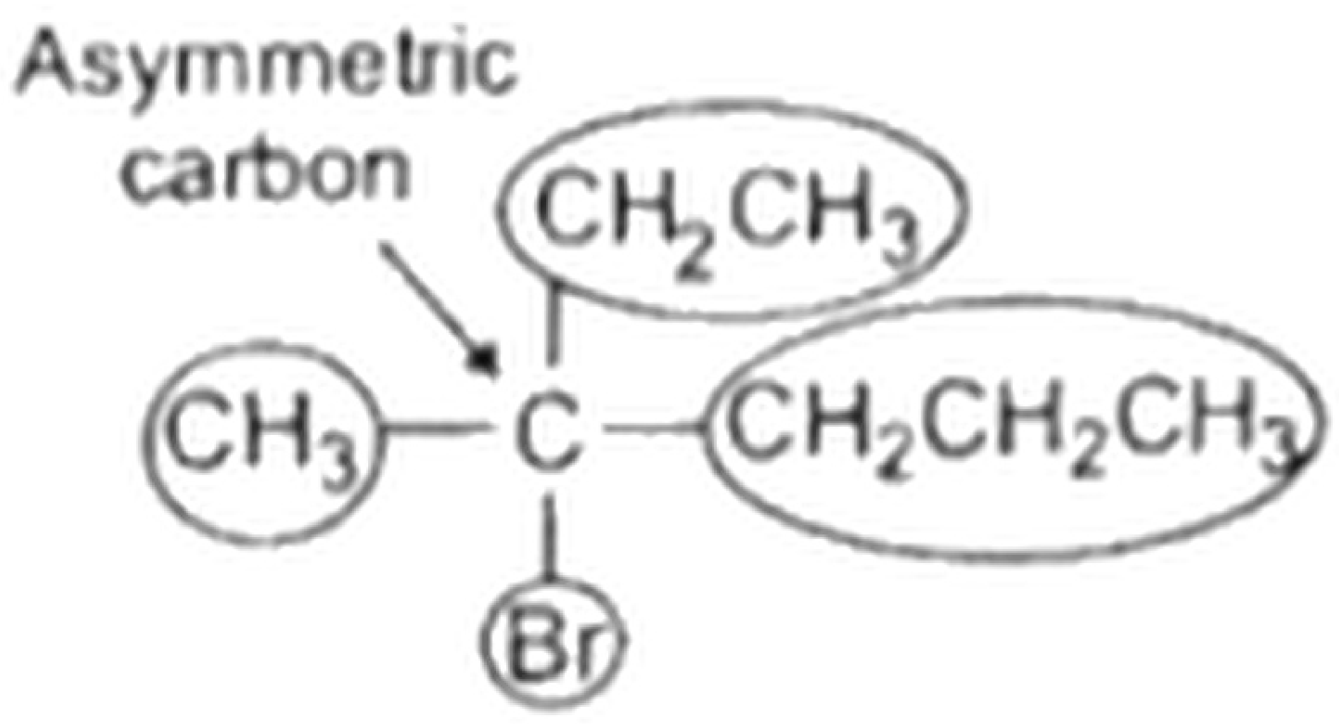
Fig 16.7 Achiral objects

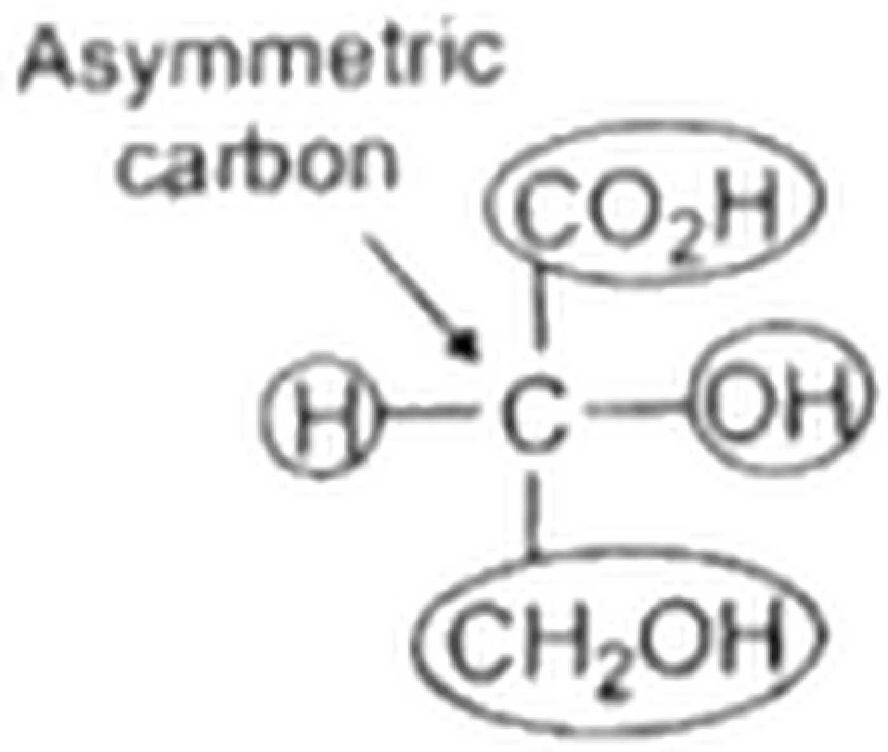
An achiral molecule has a plane of symmetry

2) **Carbon-Based Chiral Centers:**

A carbon atom which is bonded to four different groups is called an Asymmetric Carbon Atom.

Examples are:





The term asymmetric carbon atom is rather misleading. It only means that a carbon atom is bonded to four different groups and that a molecule of this type lacks plane of symmetry. Such a molecule is called asymmetric (Latin a = without), that is, without symmetry. Presently the term Dissymmetric or Chiral Molecules is often for asymmetric molecules.

3) **Optical Activity:**

Light from ordinary electric lamp is composed of waves vibrating in many & different planes. When it is passed through Nicol prism (made of calcite, CaC03) or Polaroid lens, light is found to vibrate in only one plane, and is said to be plane-polarized or simply polarized. The diagrams illustrate the vibrations of ordinary and polarized light from a beam propagated perpendicularly to the plane or paper. Solutions of some organic compounds have the ability to rotate the plane of polarized light. These compounds are said to be Optically Active. This property of a compound is called Optical Activity.

Optical activity in a compound is detected and measured by means of a Polarimeter. When a solution of a known concentration of an optically active material is placed in the polarimeter, the beam of polarized light is rotated through a certain number of degrees, either to the right (clockwise) or to the left (antic-clockwise). The compound which rotates the plane of polarized light to the right (clockwise) is said to be Dextrorotatory. It is indi9cated by the sign (+). The compound which rotates the plane of polarized light to the left (anticlockwise) is said to Levorotatory. It is indicated by the sign G). The magnitude of rotation in degrees is referred to as observed rotation, alpha, Fig shows the part of polarimeter.

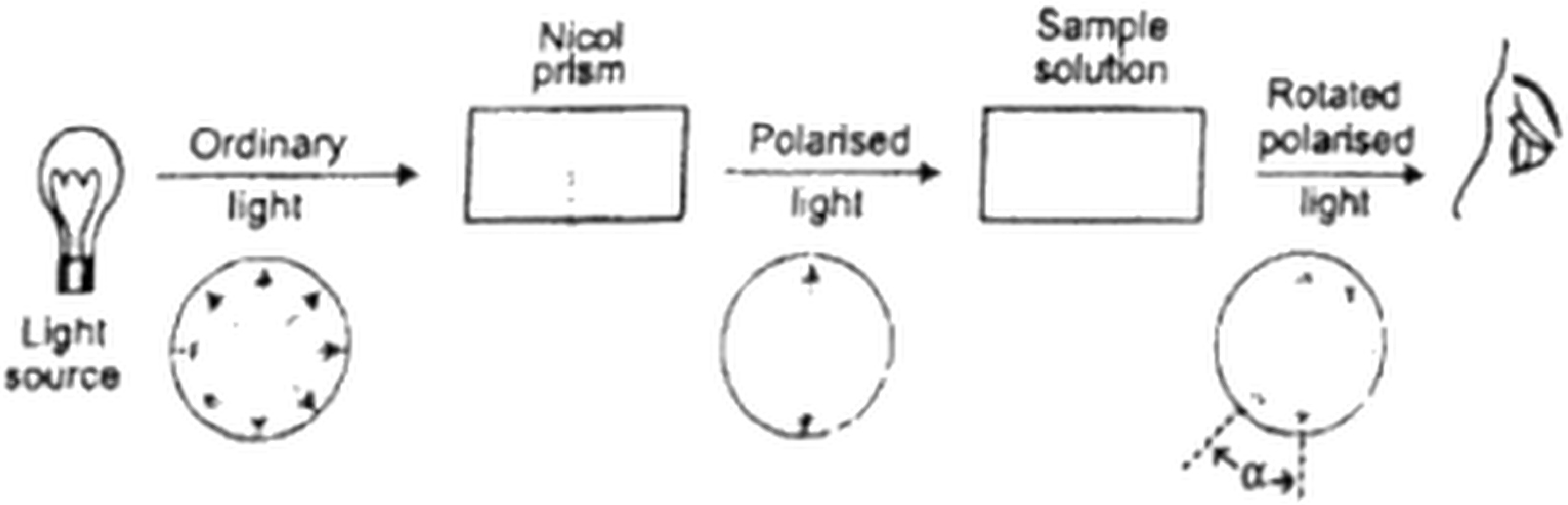


Fig.16.8 A simple polarimeter in operation

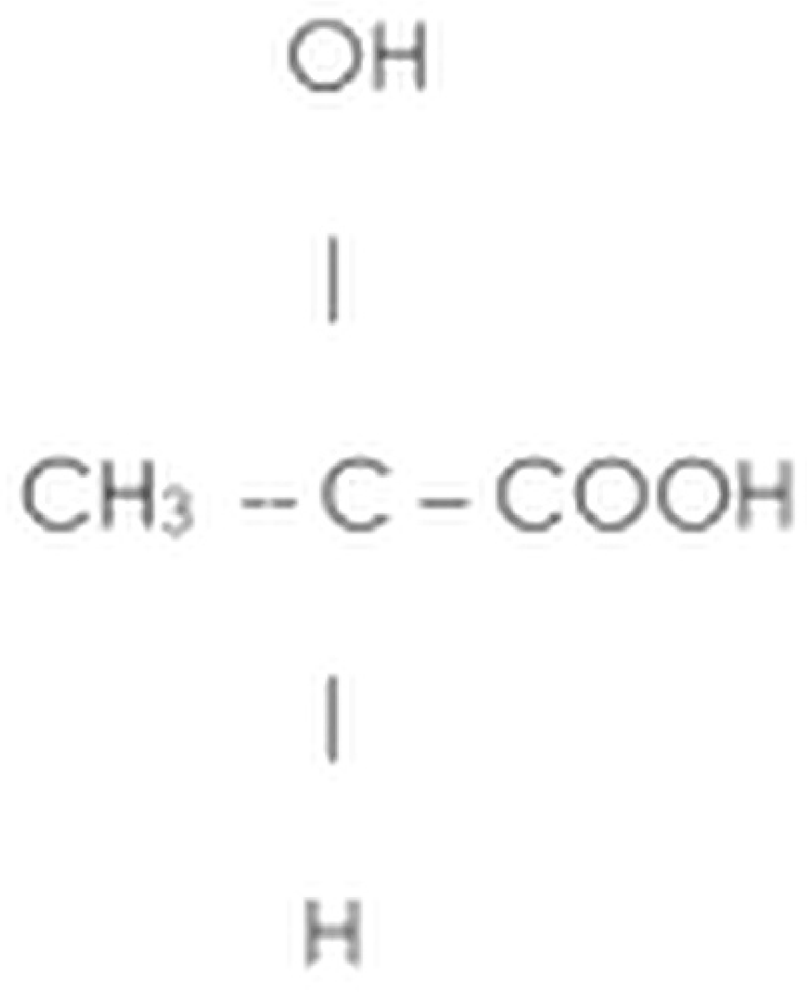
4) Optical Isomerism

An optically active compound can exist in two isomeric forms which rotate the plane polarized light in opposite directions. These are called Optical Isomers and the phenomenon is known as Optical Isomerism.

The isomer which rotates the plane of polarized light to the right (clockwise direction) is known as Dextrorotatory Isomer or (+) isomer. The isomer which rotates the plane of polarized light to the left (anticlockwise direction) is known as the Laevorotatory Isomer or (-) isomer.

Optical Isomerism of Lactic Acid

Lactic acid (2-Hydroxypropaoic acid) is an example of a compound which shows optical isomerism. It contains one asymmetric carbon atom.



$$CH_3 - \overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}} - COOH$$

Lactic Acid. The Asymmetric carbon is shown by an asterisk.

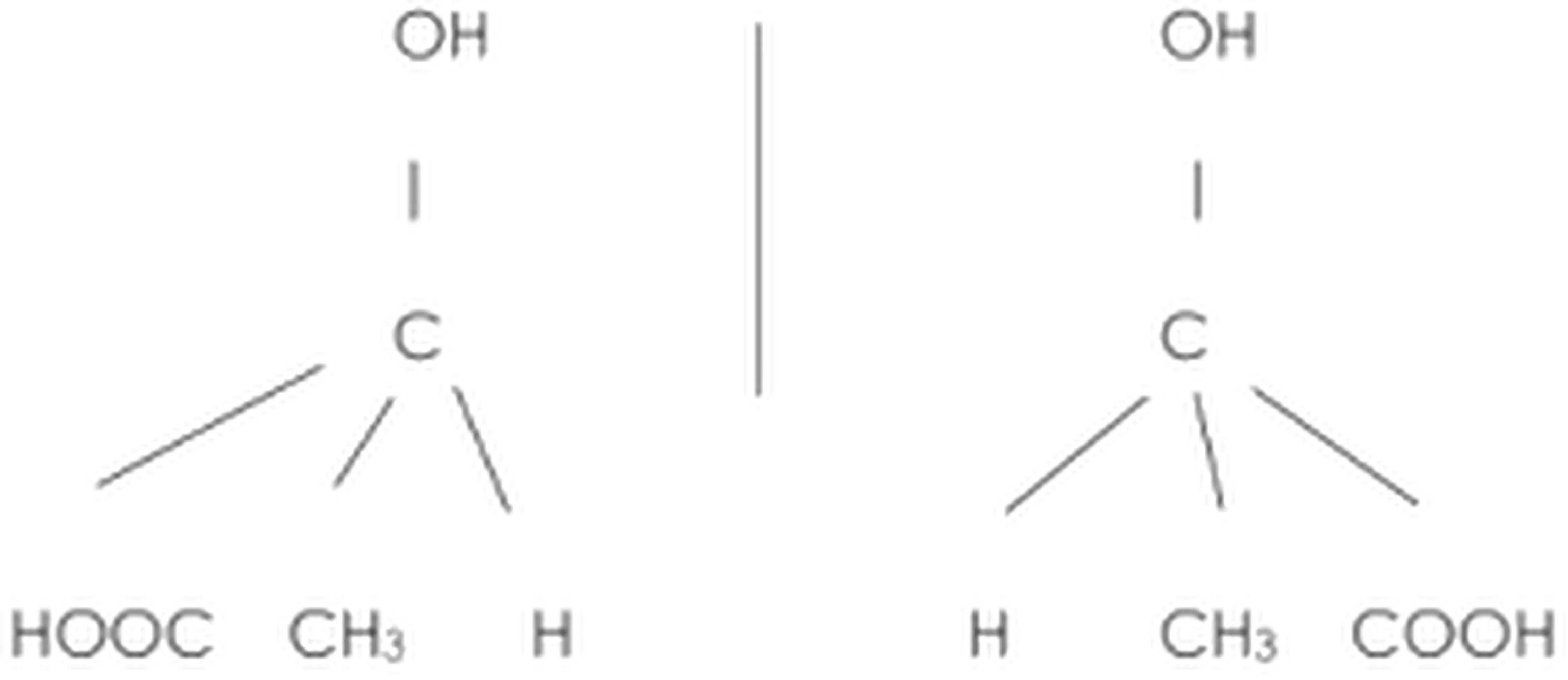
Two three dimensional structures are possible for Lactic acid

These structures are not identical because they cannot be superimposed on each other. On the mirror image of the other, such non-superimposable mirror image forms are optical isomers and called enantiomers. Thus, three forms of lactic acid are known. Two are optically active and this is optically inactive.

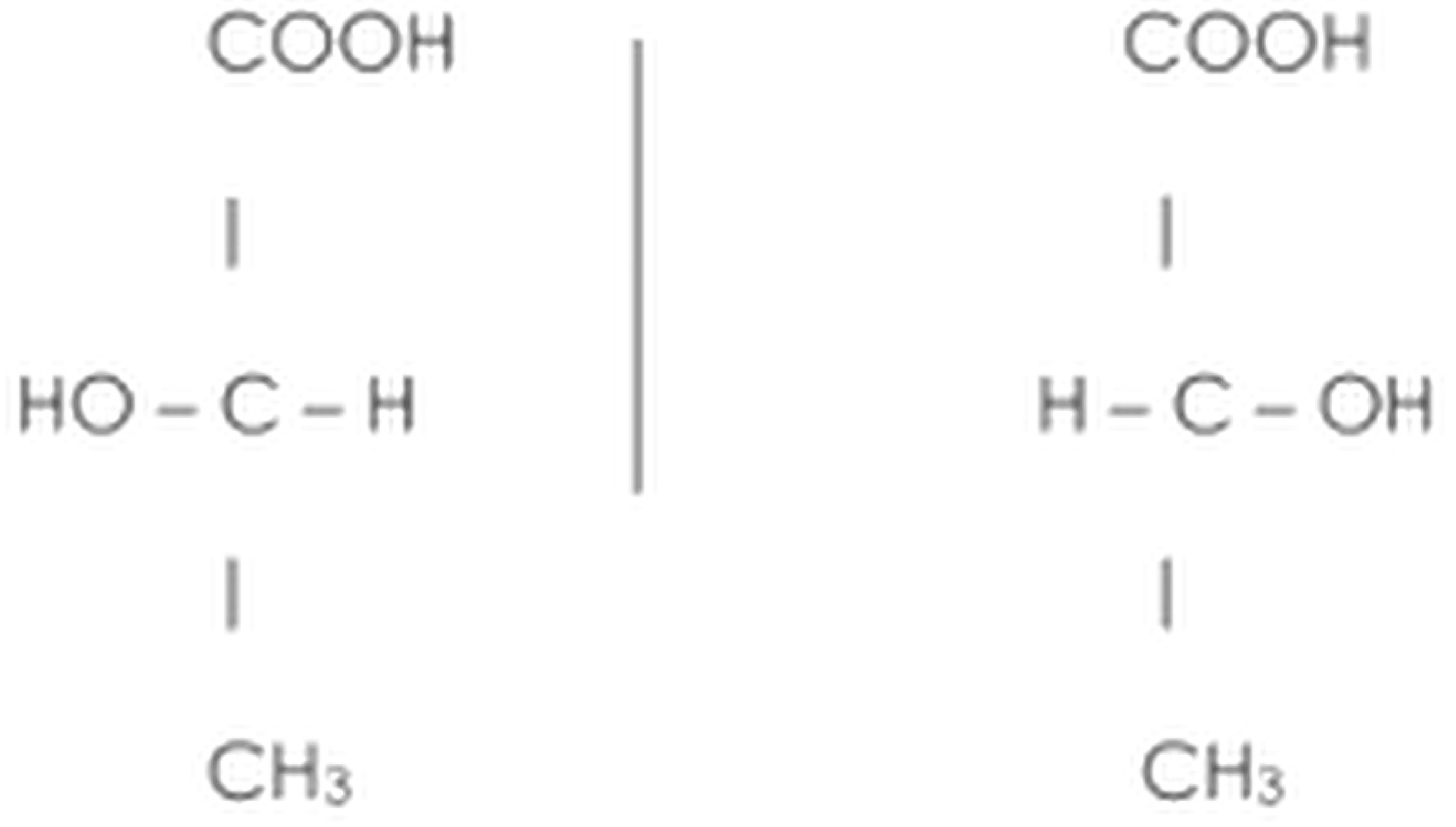
(+) Lactic Acid: it rotates the plane of polarized light to the right (clockwise direction) is called dextrorotatory.

(-) Lactic Acid: it rotates the plane of polarized light to the left (anticlockwise direction) is called laevorotatory. (-) Lactic acid is the mirror image of (+) lactic acid and vice versa.

(±) Lactic Acid: it does not rotate the plane of polarized light. That is, it is optically inactive. It is an equimolar mixture of (+) and (-) forms (racemic mixture).



Mirror



$$\begin{array}{c} COOH \\ | \\ HO-C-H \\ | \\ CH_3 \end{array} \quad \Bigg| \quad \begin{array}{c} COOH \\ | \\ H-C-OH \\ | \\ CH_3 \end{array}$$

Equimoler mixture of
(+) and (-) forms
(racemeric mixture)

(+) Acid	(-) Acid	(+) Acid
Mp = 26⁰C	mp = 26⁰C	mp = 18⁰C

Optically Active

Optically inactive

Optical Isomerism of Tartaric Acid

Tartaric acid (2,3-Dihydroxybutuiedioic acid) contains two asymmetric carbon atoms.

OH

|

H – C – COOH Tartaric acid. The two asymmetric

| carbons are shown by asterisks.

H – C – COOH

|

OH

Four forms of Eid are known. Two of them are optically active and two are optically inactive. The optically active forms related to as an object to its mirror image. That is, they are enantiomers.

Mirror

COOH | COOH COOH

| | |

H – C – COOH | HO – C – H H – C – OH Equimolar mixture of

| | | | (+) and (-)

forms | H – C – COOH H – C – OH H – C –

OH (Racemic Mixure)

| | |

COOH COOH COOH

(+) Acid (-)Acid mono acid (+) Acid

Mp = 170 C mp = 170 C mp = 143 C mp = 206 C

(+)Tanar'c Add; it rotates the plane of polarized light to the left (anticlockwise direction is called laevorotaory. (-) Lactic acid is mirror of (+) Lactic acid and vice versa.

(-) Tartaric Acid: it rotates the plane of polarized light to the right (clockwise direction) is called dextrorotatory.

(±) Tartaric Acid: it does not rotate the plane of polarized light. That is, it is optically inactive. It is an equimolar mixture of (+) and (-) forms (racemic mixture).

Q11. What is stereoisomerism (Geometric isomerism)?

Answer

Its definition has been given in the start of this topic i.e. 16.6.0. it is of two types:

I) Optical isomerism (already discussed in sections 16.6.3 and 16.6.4)

2) Geometric or Cis-trans Isomerism

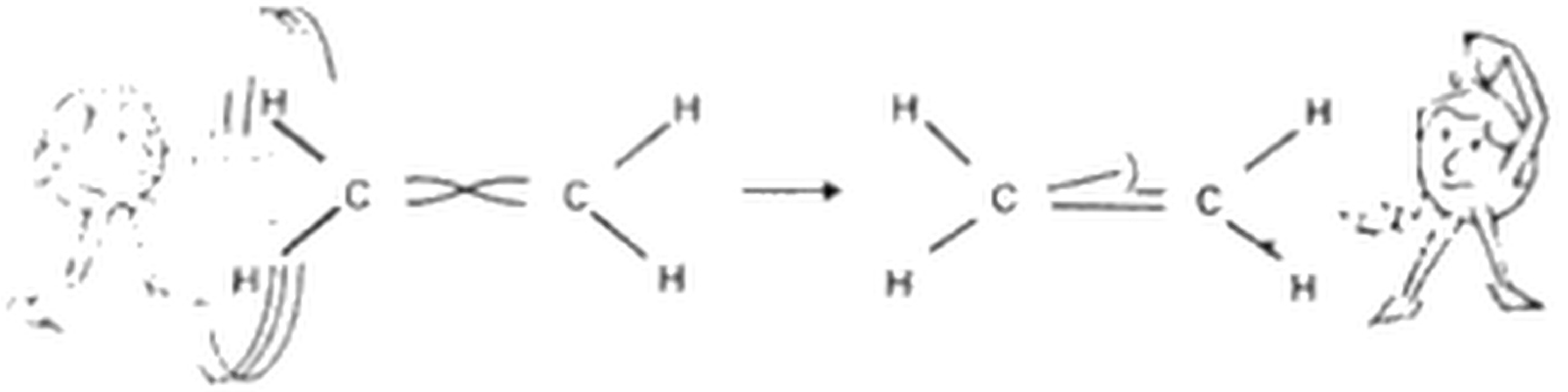
Its explanation is given below

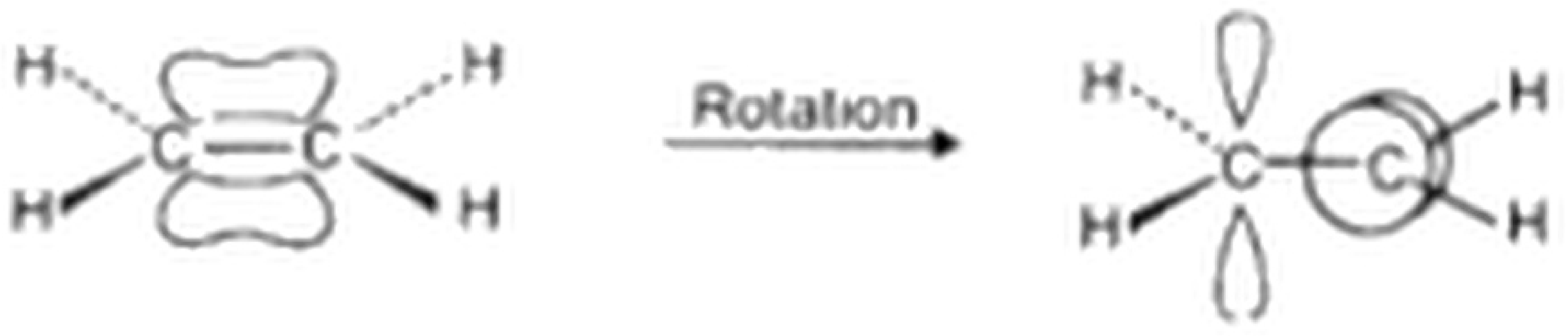
Geometrical Isomerism

Geometrical isomerism (also called cis-trans isomerism) results from a restriction in rotation about double bonds, or about single bonds in cyclic compounds.

i) Geometrical Isomerism in Alkenes

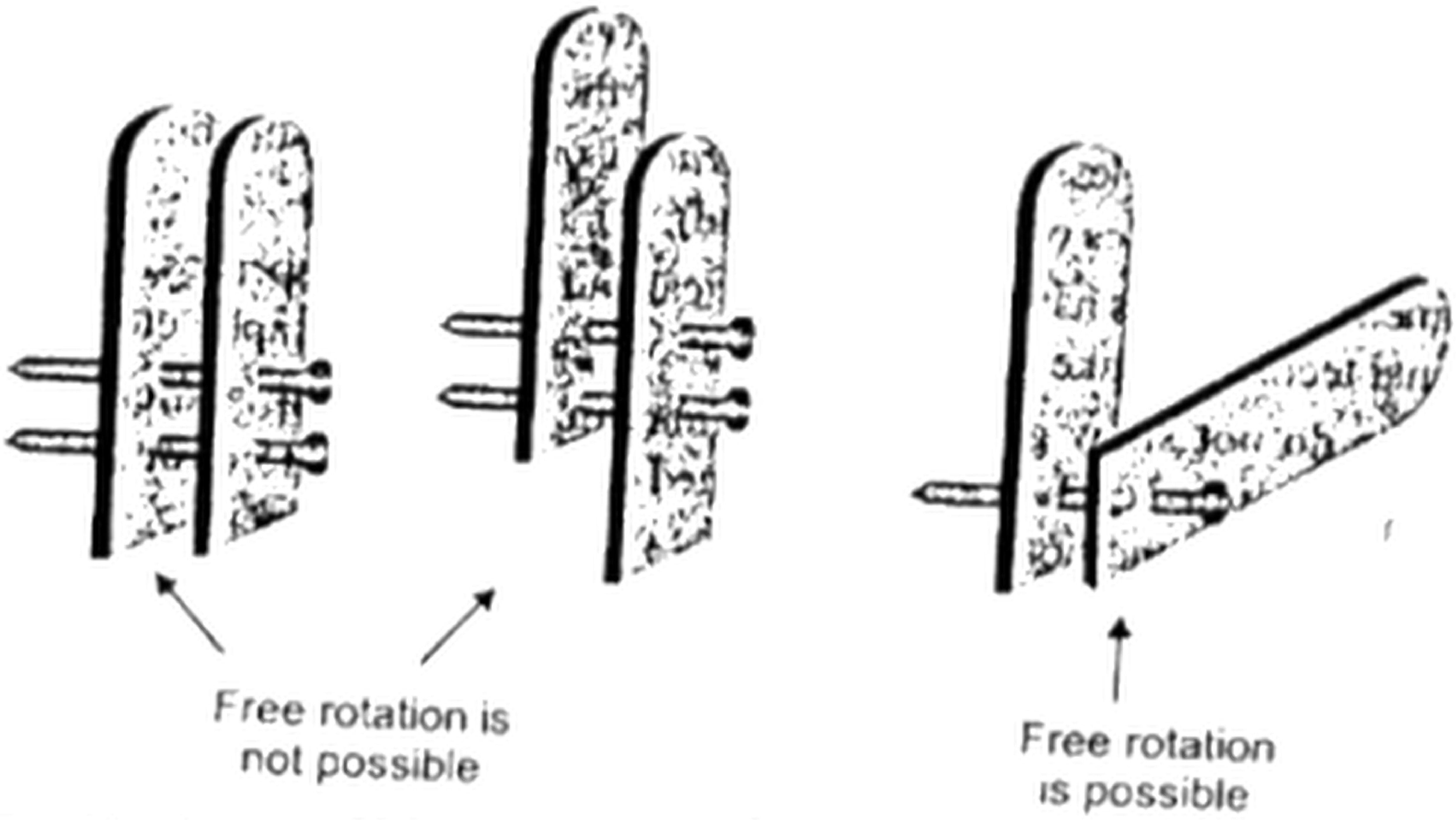
The carbon atoms of the carbon-carbon double bond are sp^2 hybridized. The carbon-carbon double bond consists of a sigma bond and a pi bond. The sigma bond is formed by the overlap of sp^2 hybrid orbitals, the pi bond is formed by the overlap of p orbitals. The presence of the pi bond locks eh molecule in one position. The two carbon atoms of the C=C bond and the four atoms that are attached to them lie in one plane and their position in space are fixed. Rotation around the C=C bond is the possible because rotation would break the pi bond.



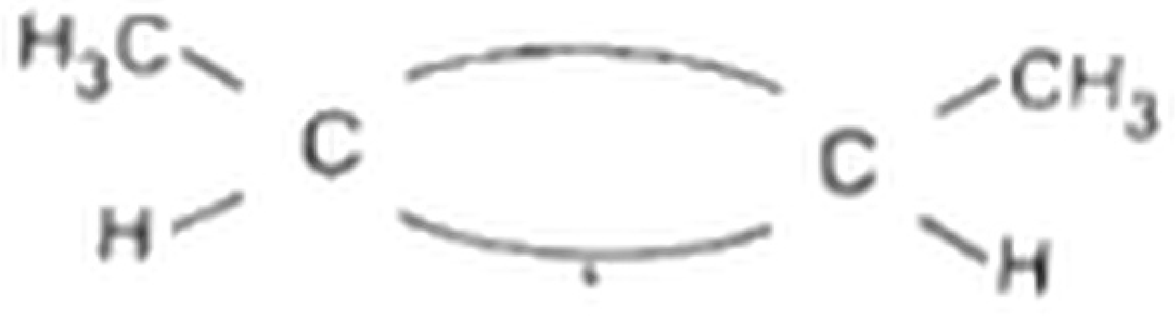


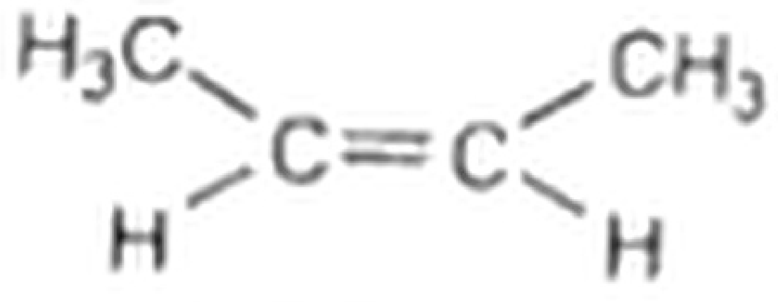
Rotation about pi bond is not possible because it would break the pi bond

This restriction of rotation about the carbon-carbon double bond is responsible for the geometrical isomerism in alkenes. A popular analogy for this situation is based upon two bonds and two nails. Driving one nail through two boards will not prevent free rotation of the two bonds. But once a second nail used, the boards cannot be freely rotated.



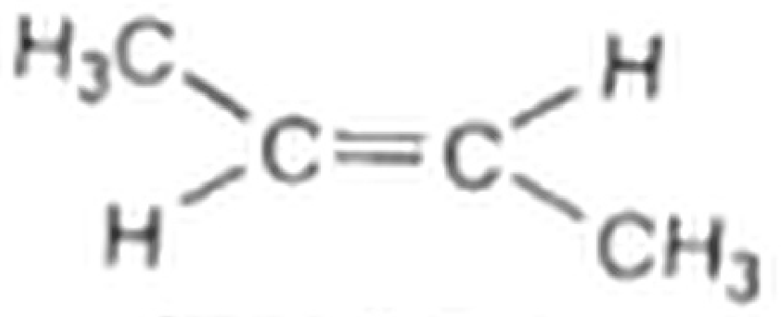
Consider the case of 2-butene. It exists in two special arrangements:





cis-2-Butene
(bp 4°C)

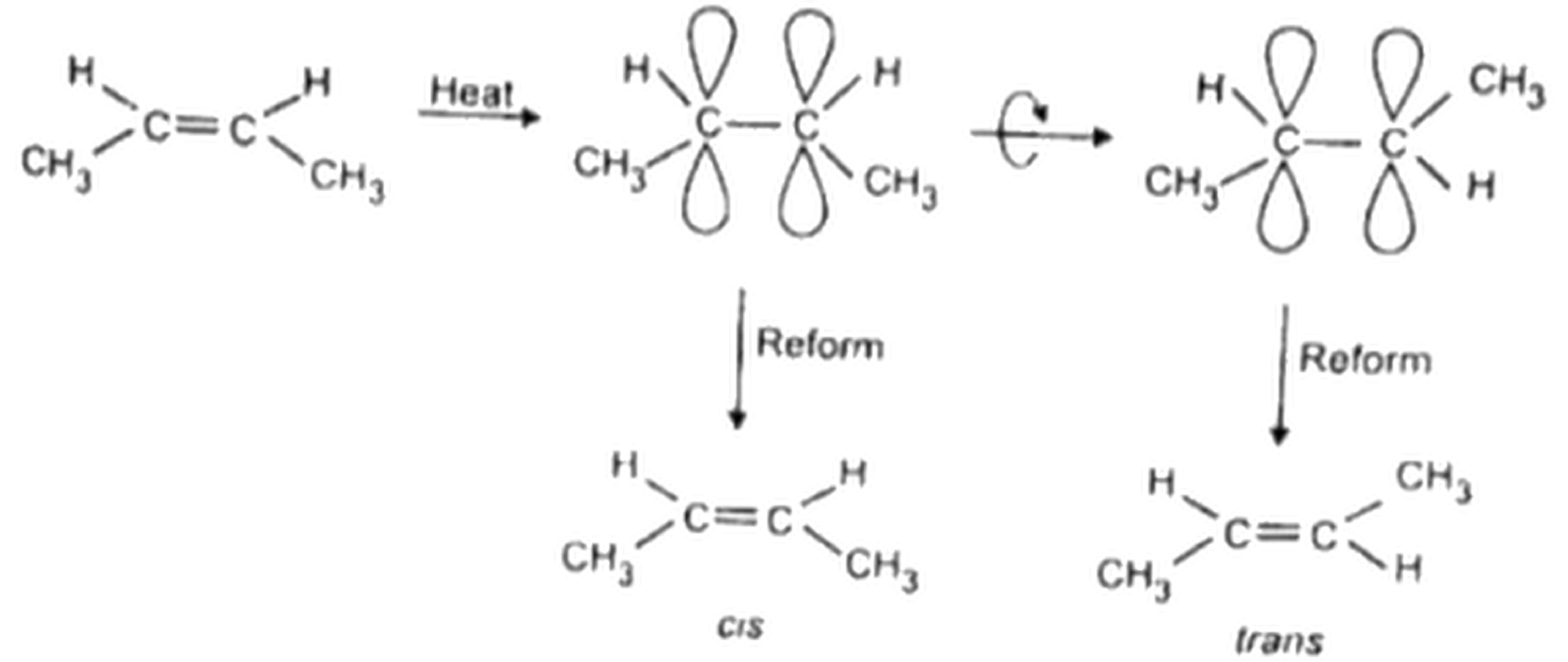
and



trans-2-Butene
(bp 1°C)

These two compounds are referred to as geometrical isomers and are distinguished from each other by the terms cis and trans. The cis isomer is one in which two similar groups are on the same side of the double bond. The trans isomer is that in which two similar groups are on the opposite sides of double bond. Consequently, this type of isomerism is often called cis-trans isomers. Geometrical isomers are stereoisomer, because they have the same structural formula but different special arrangement of atoms.

The conversion of cis-isomer into trans-isomer or vice versa is possible only if either isomer is heated to a high temperature or absorbs light. The heat supplies the energy (about 62 Kcal/mole) to break the pi bond so that rotation about sigma bond becomes possible. Upon cooling, the reformation of the pi bond can take place in two way giving mixture of tarns-2-butene plus cis-2-butene.



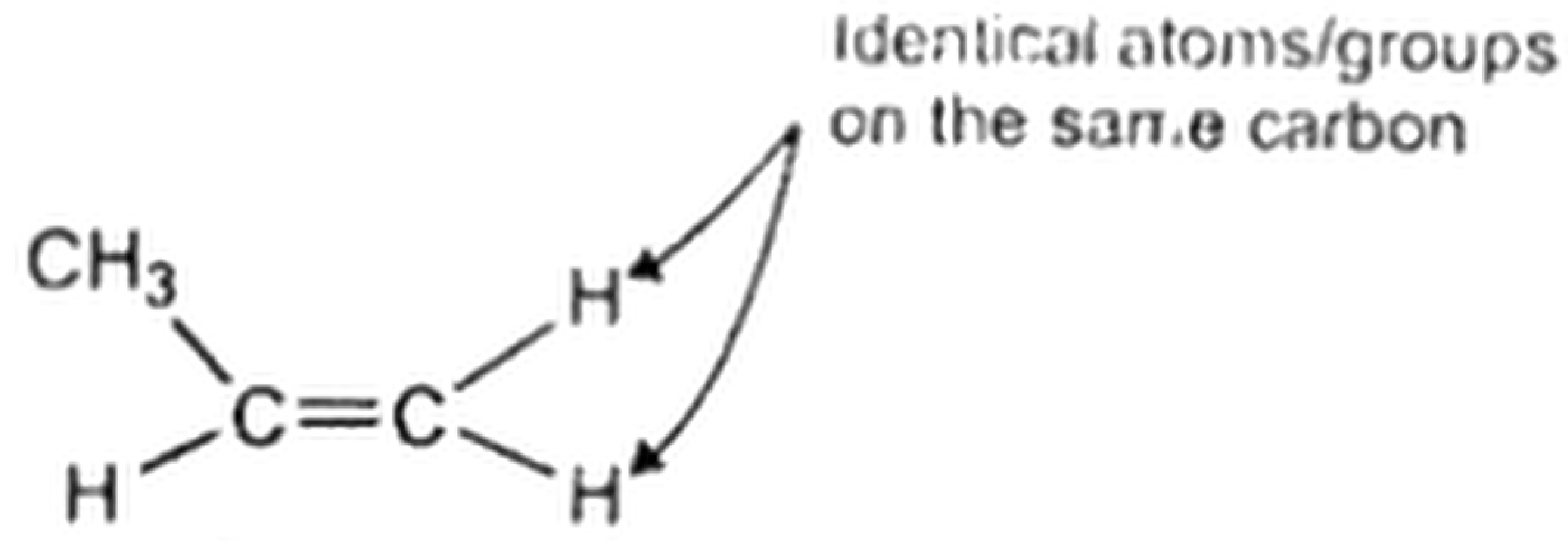
The trans isomers are more stable than the corresponding cis isomers. This is because, in cis isomer, the bulky groups are on the same side of the double bond. The stearic repulsion of groups makes the cis isomers less stable than the isomer in which the bulky groups are far (they are on the opposite sides of the double bond).

The geometrical isomers have different physical and chemical properties. They can be separated by conventional isomers have different physical techniques like fractional distillation, gas chromatography etc.

All alkenes do not show geometrical isomerism. Geometrical isomerism is possible only when each double bonded carbon atoms is attached to two different atoms or groups. The following examples illustrate this condition for the existence of geometrical isomers.

Example 1. Consider the case of Propene

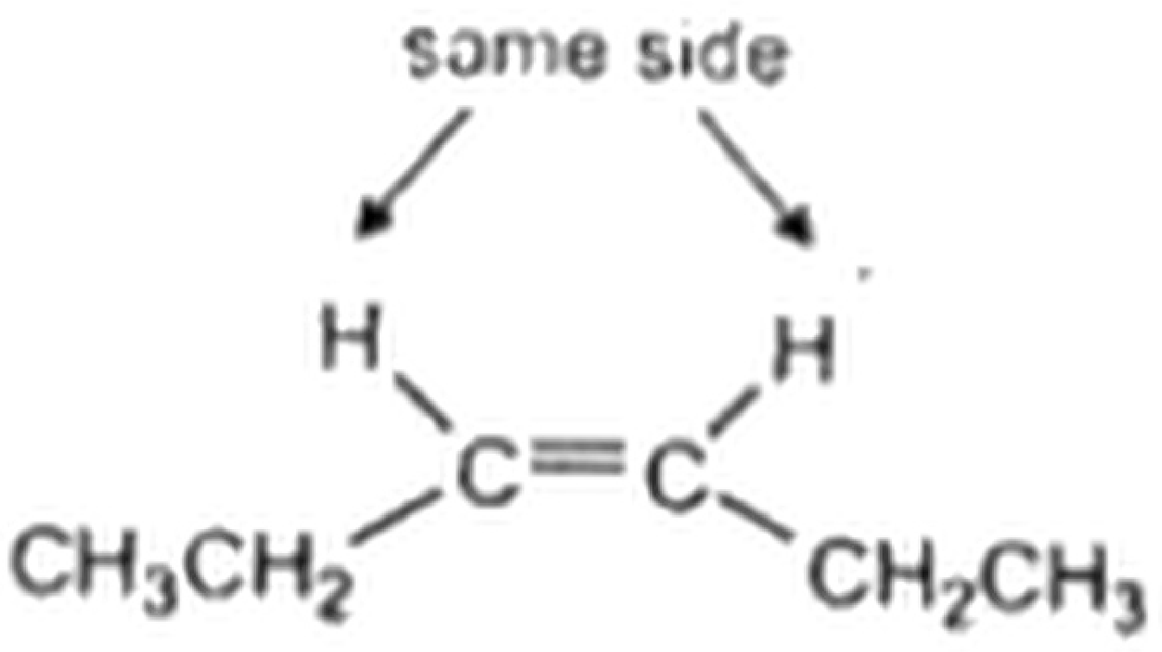
No geometrical isomers are possible for propene ($CH_3CH=_{CH2}$). This is because one of double bonded carbons has two identical groups (H atoms) attached to it.



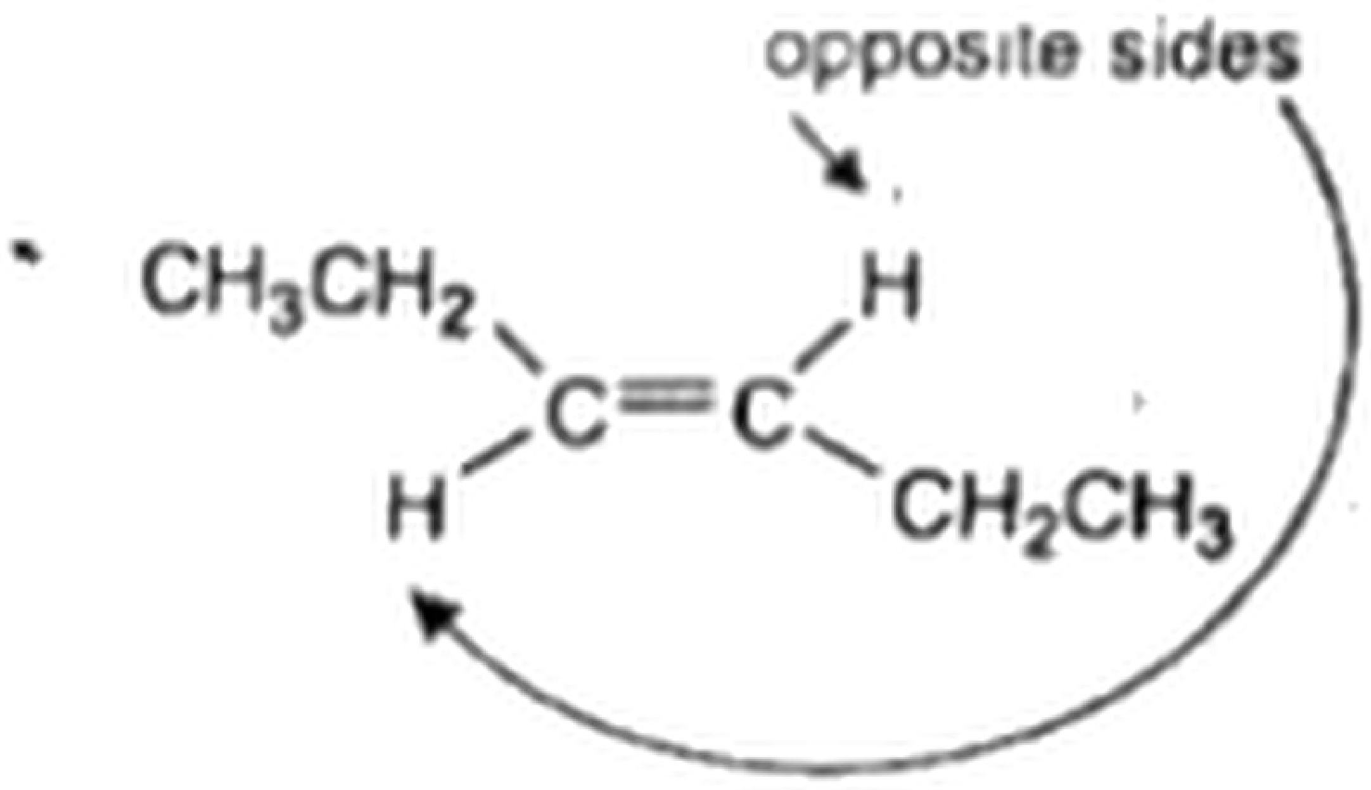
Propene

Example 2. Consider the case of 3-Hexene

Geometrical isomers are possible or 3-hexene ($CH_3CH_2CH=CHCHCH$). This is because each double bonded carbon atom is attached to two different YOUPS (CHCH and H). the cis and trans isomers of 3-hexene shown below:



cis-3-Hexene



trans-3-Hexene

Example 3. Consider the case of Butenedioic acid.

Geometrical isomers are possible for butenedioic acid (HOOC-CH=CH-COOH). This because each double bonded carbon atoms ahs two different groups attached to it (H and COOH).

H COOH

\ /

C

| |

C

H COOH

\ /

C

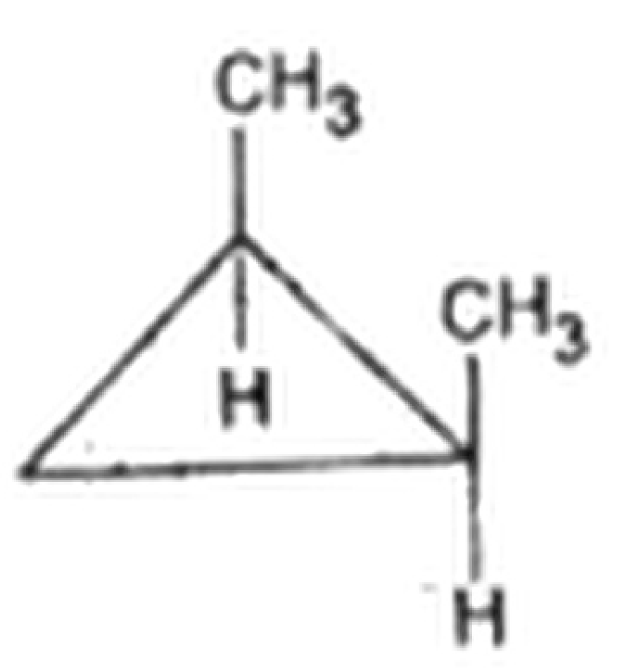
| |

C

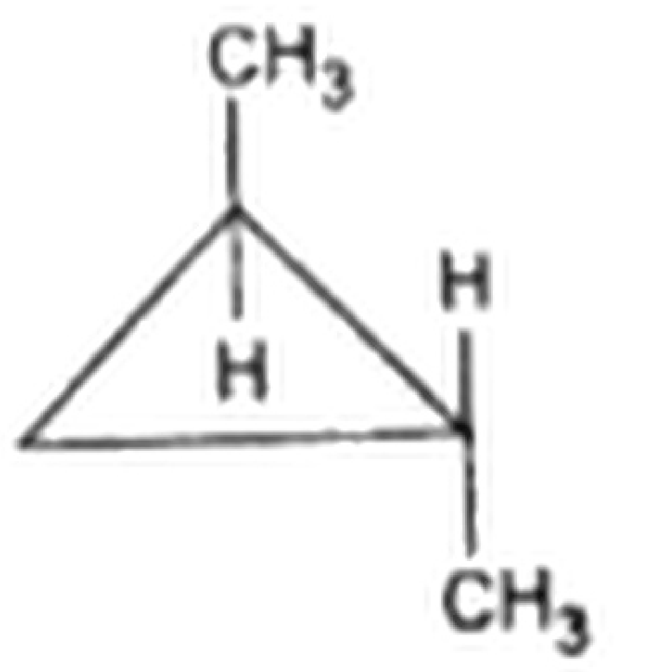
/ \	/ \
HOOC H	H COOH
Trans- Butenedioic acid	cis- Butenedioic Acid
(fumaric acid)	(Maleic Acid)
mp 130^{0}C	mp 288^{0}C

2) Geometrical Isomerism in Cyclic Compounds

Geometrical isomerism is also possible in cyclic compounds. There can be no rotation about carbon-carbon single bonds forming a ring because rotation would break the bonds and break ring. For example, 1,2-dimethylcyclopropane exists in two isomeric forms.

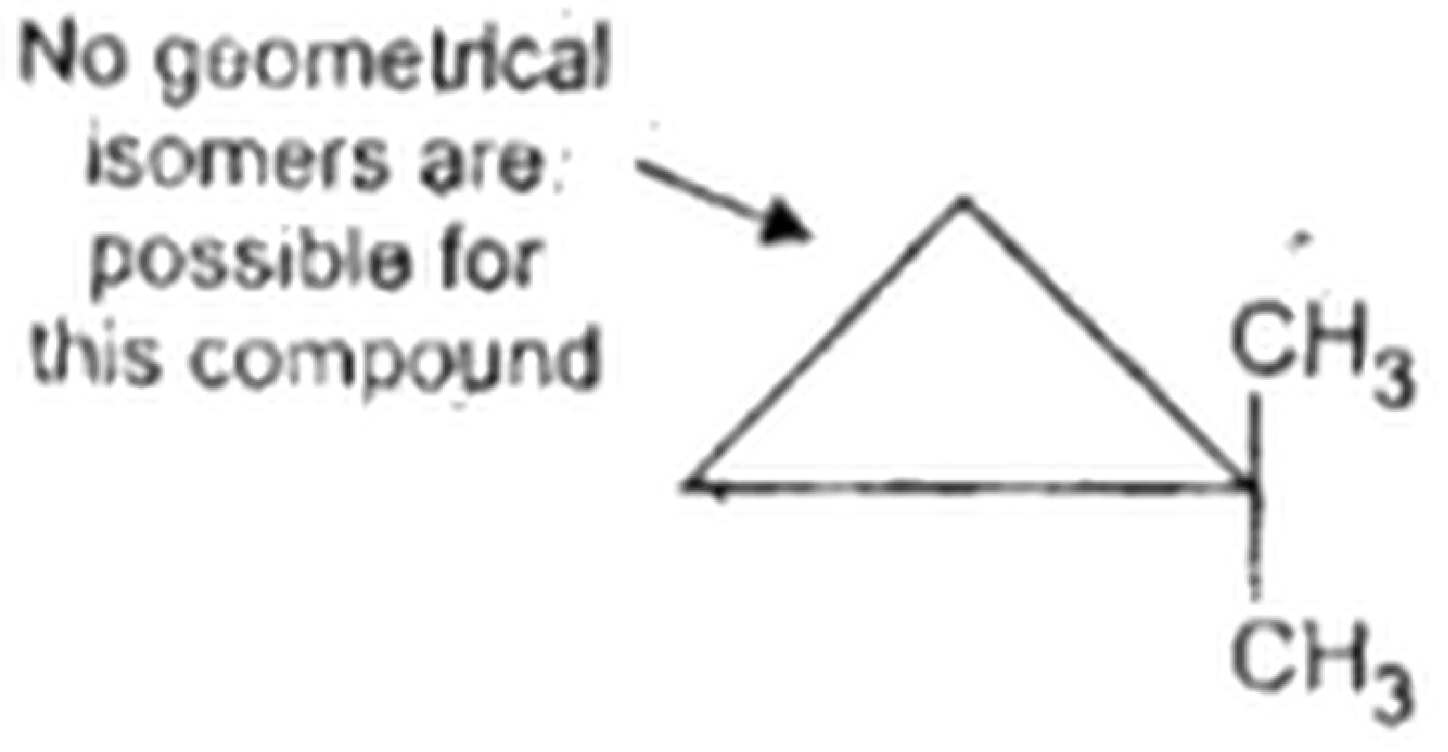


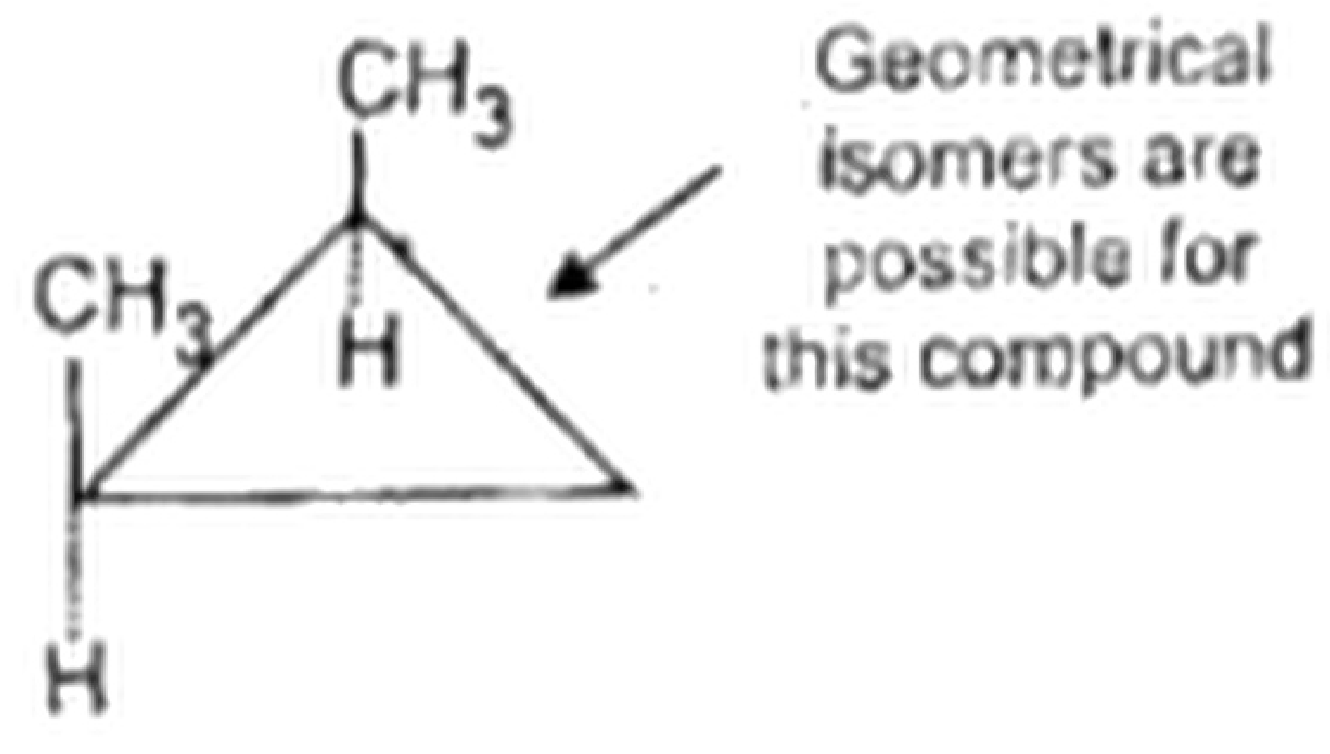
cis



trans

In cis-l ,2-dimethylcyclopropane the two methyl groups are on the same side of ring. In 1,2-dimethylcyclopropane, they are on sides. A requirement for geometrical isomerism in cyclic compounds is that there must be at lean two other groups beside hydrogen on the ring and these must be on different ring carbon atoms. Fr example, no geometrical isomers possible for 1,1-dimethylcyclopropane.





Q12. Define and explain structural isomerism.

Answer

In structural isomerism the isomers have the same molecular formula but differ in structural formula, that is, in the order in which the different atoms are linked in the molecule. Structural isomerism if of five types:

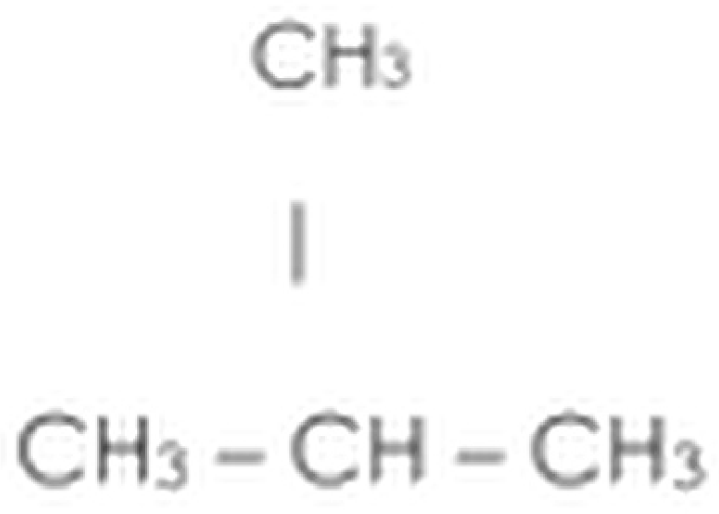
1) Chain Isomerism

Chain isomers have the same molecular formula but differ in order in which the carbon atoms are bonded to each other.

Example 1. n-Butane and Isobutane

$CH_3 - CH_2 - CH - CH_3$

n-Butane



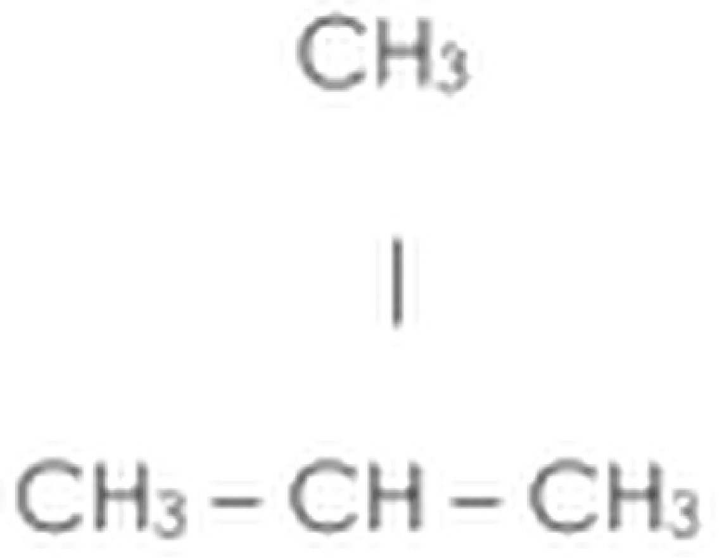
$$\begin{array}{c} CH_3 \\ | \\ CH_3 - CH - CH_3 \end{array}$$

Isobutane

Example 2. 2-Methylbutane and 2,2-Dimethylpropane

$CH_3 - CH_2 - CH - CH_3$

2 – Methylbutane



$$\begin{array}{c} CH_3 \\ | \\ CH_3 - CH - CH_3 \end{array}$$

Isobutane

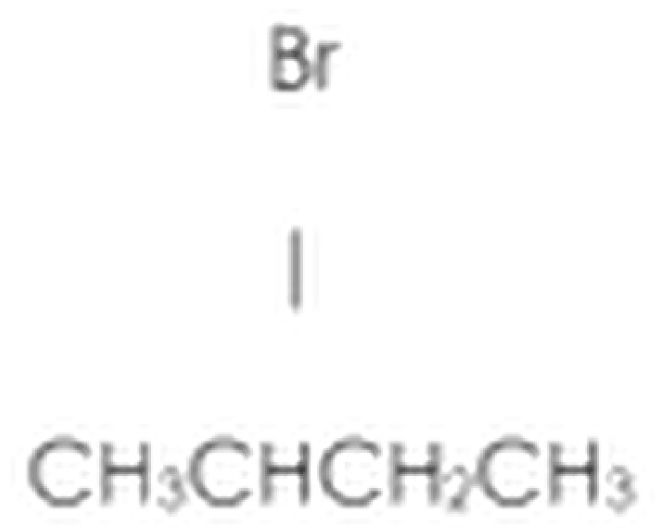
2) Position Isomerism

Position isomers have the same molecular formula but different in the position of a functional group on the carbon chain.

Example 1. I-Bromobutane and 2-Bromobutane

$CH_3CH_2CH_2CH_2Br$

1-Bromobutane


$$\begin{array}{c} Br \\ | \\ CH_3CHCH_2CH_3 \end{array}$$

2-Bromobutane

Example 2. n-Propyl alcohol and Isopropyl alcohol

$CH_3 - CH_2 - CH_2OH$

n-Propyl alcohol


$$\begin{array}{c} OH \\ | \end{array}$$

Isopropyl alcohol

Example 3. I-Butene and 2-Butene

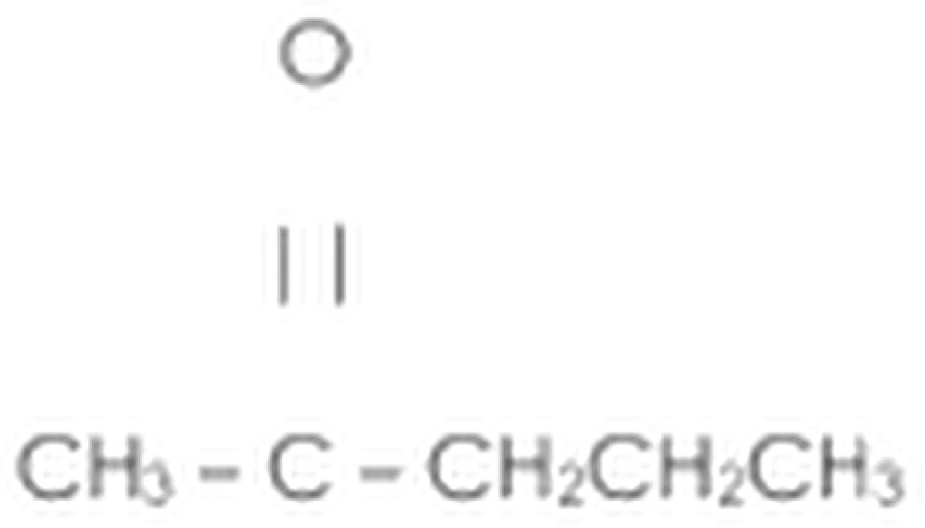
$CH_3CH_2CH{=}CH_2$

I-Butene

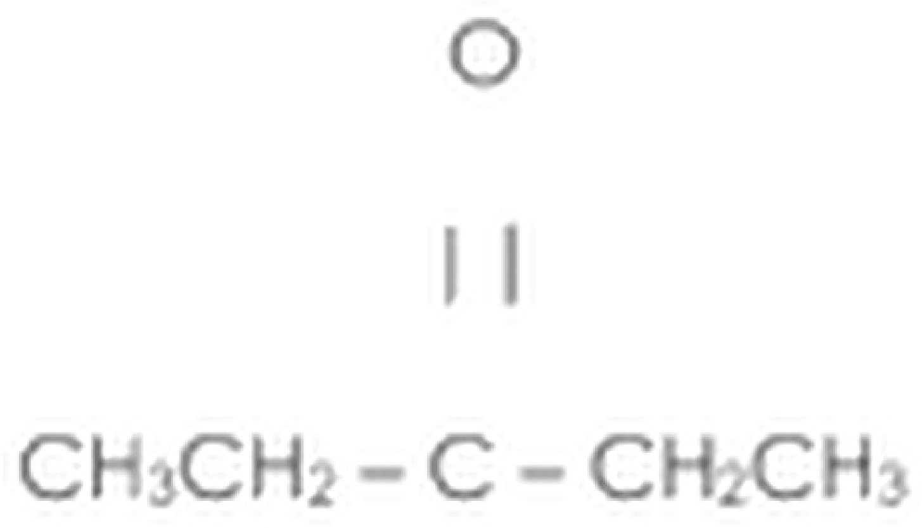
$CH_3CH = CHCH_3$

2-Butene

Example 4. 2-Pentanone and 3-Pentanone


$$\begin{array}{c} O \\ || \\ CH_3 - C - CH_2CH_2CH_3 \end{array}$$

2- Pentanone


$$\begin{array}{c} O \\ || \\ CH_3CH_2 - C - CH_2CH_3 \end{array}$$

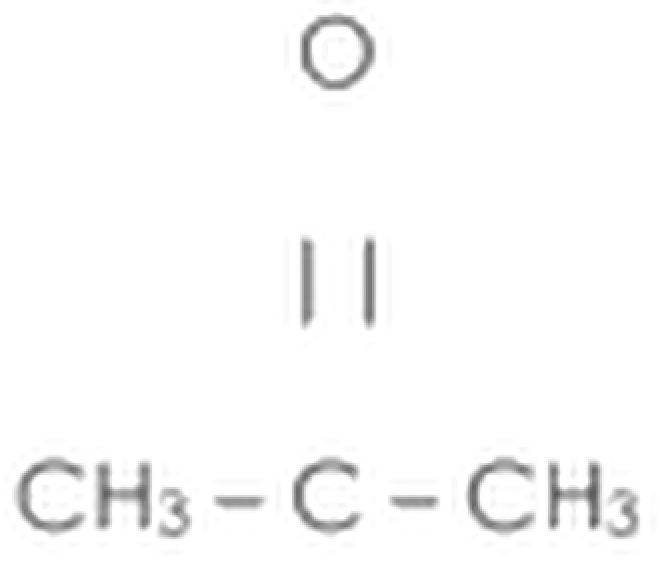
3_Pentanone

$CH_3 - CH - CH_3$

3) Functional Isomerism

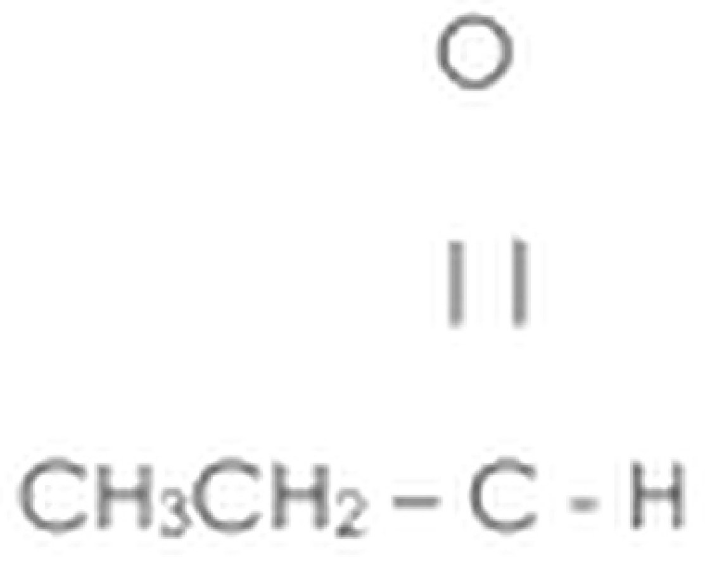
Functional isomers have the same molecular formula but different functional groups.

Example 1. Acetone and Propionaldehyde



$CH_3-\overset{\overset{O}{||}}{C}-CH_3$

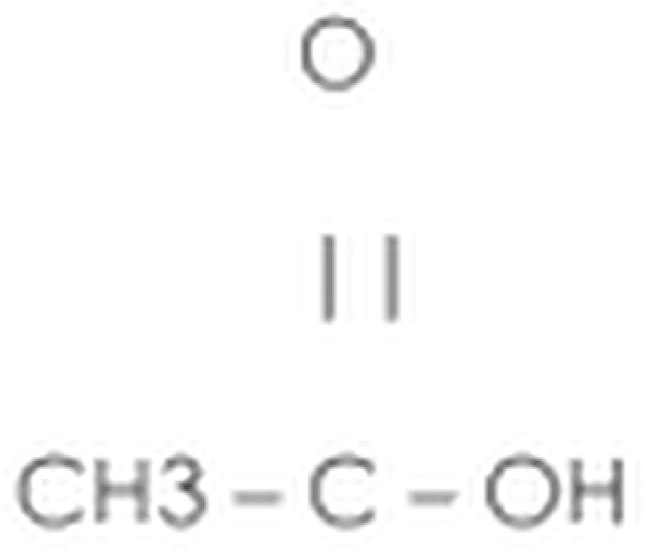
Acetone



$CH_3CH_2-\overset{\overset{O}{||}}{C}-H$

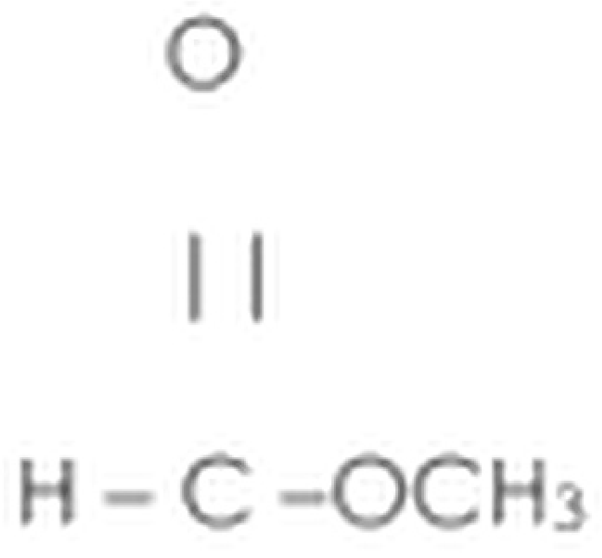
Propionaldehyde

Example 2: Acetic acid and Methyl formate



$CH3-\overset{\overset{O}{||}}{C}-OH$

Acetic acid



$H-\overset{\overset{O}{||}}{C}-OCH_3$

Methyl formate

4) **Metamerism**

This type of isomerism is due to the unequal distribution of carbon atoms on either side of the functional group. Members belong to the same homologous series.

Example 1. Diethyl ether and Methyl propyl ether

$CH_3CH_2 - O — CH_2CH_3$

Diethyl ether

$CH3 – O – CH_2CH_2CH_3$

Methyl propyl ether

Example 2. Diethylamine and Methylpropylamine

$CH_3CH_2 – O – CH_2CH_3$

Diethylamine

$CH_3CH_2CH_2 – NH – CH_3$

Methylpropylamine

5) **Tautomerism**

A type of isomerism in which a compound exists simultaneously in two forms in equilibrium with one another e.g. H-C= H-N=C. it involves the shifting of position of hydrogen atom. This type of hydrogen atom is known as "mobile" hydrogen.

$$\mathrm{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CO_2C_2H_5 \longleftrightarrow CH_3-\overset{\overset{\displaystyle OH}{|}}{C}=H-CO_2C_2H_5}$$

Keto-Form Enol-Form

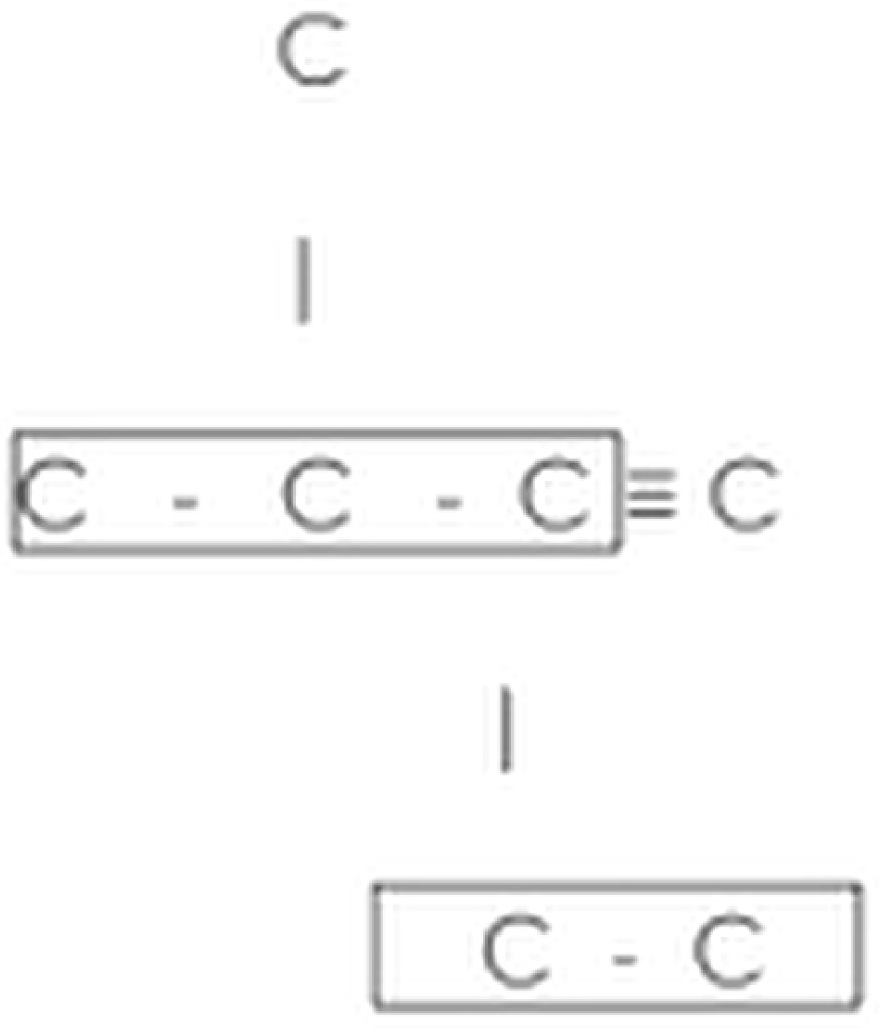
Alkynes

Nomenclature:

IUPAC System:

I) The parent hydrocarbon is the continuous chain containing triple bond.

2) The ending 'ane' of the alkane is charged by _yne.



$$\boxed{C-\overset{\overset{\displaystyle C}{|}}{C}-\underset{\underset{\displaystyle \boxed{C-C}}{|}}{C}}\equiv C$$

(longest chain without

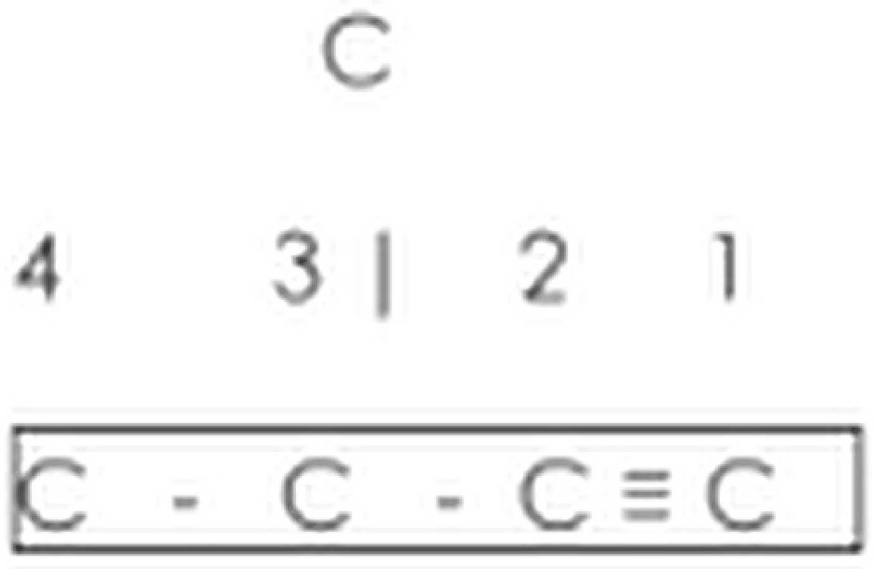
Triple bond- Not main chain)

$$\boxed{C-\overset{\overset{\displaystyle C}{|}}{C}-\underset{\underset{\displaystyle C-C}{|}}{C}\equiv C}$$

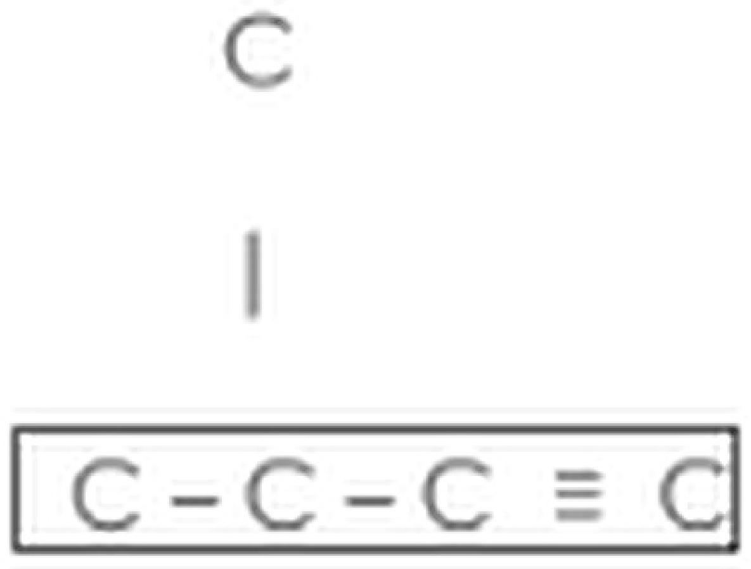
(chain with triple bond-

main chain)

3) The main chain is numbered starting from the terminal carbon nearer to the triple bond.



$$\boxed{\overset{4}{C}-\overset{\overset{\displaystyle C}{|}}{\overset{3}{C}}-\overset{2}{C}\equiv\overset{1}{C}}$$



$$\boxed{C-\overset{\overset{\displaystyle C}{|}}{C}-C\equiv C}$$

|

C - C

(correct)

1 2 3| 4

C – C

(incorrect)

4) Triple bond is given the number of the lower carbon atom attached to triple bond separated by hyphen.

5) If two or more triple bonds are there in the molecule, use the prefixes di-, tri-, etc.

6) Alkyl groups are indicated by the methods described while naming alkanes.

Naming of Molecules Containing Both the Double and Triple Bonds:

1) The suffix 'ene' is used to denote the presence of Double bond the suffix —yne to denote the presence of triple bond.

2) The suffix —'ene' always precedes —'yne' in the name of compound, even when the double bond is assigned the large number.

3) The position number for the double bond is placed before the name of parent hydrocarbon.

4) The position number of triple bond is placed between —'ene' and —'yne'.

5) If same number would result from each terminal, the double bond is given the lower possible number. e.g,

$$\overset{1}{CH_2} = \overset{2}{CH} - \overset{3}{CH_2} - \overset{4}{C} \equiv \overset{5}{CH}$$

1 – Pentene – 4 - yne

Activity

Give the IUPAC name of the following:

a) $CH_3CH_2\,C \equiv CH$
b) $CH \equiv C - C \equiv CH$
c) $CH_2 = CH = C \equiv C$
d) $CH \equiv - C \equiv - CH \equiv C = CH - CH_3$
e) $CH_3 - CH_2 - C \equiv C - CH_2 - CH_3$

Relative Stability

Alkynes are more stable as compared to alkenes due to the presence of extra pi-bond. That is why alkynes are less reactive than alkene. This can be supported if we compare thermodynamic data of alkynes and alkenes, i.e.

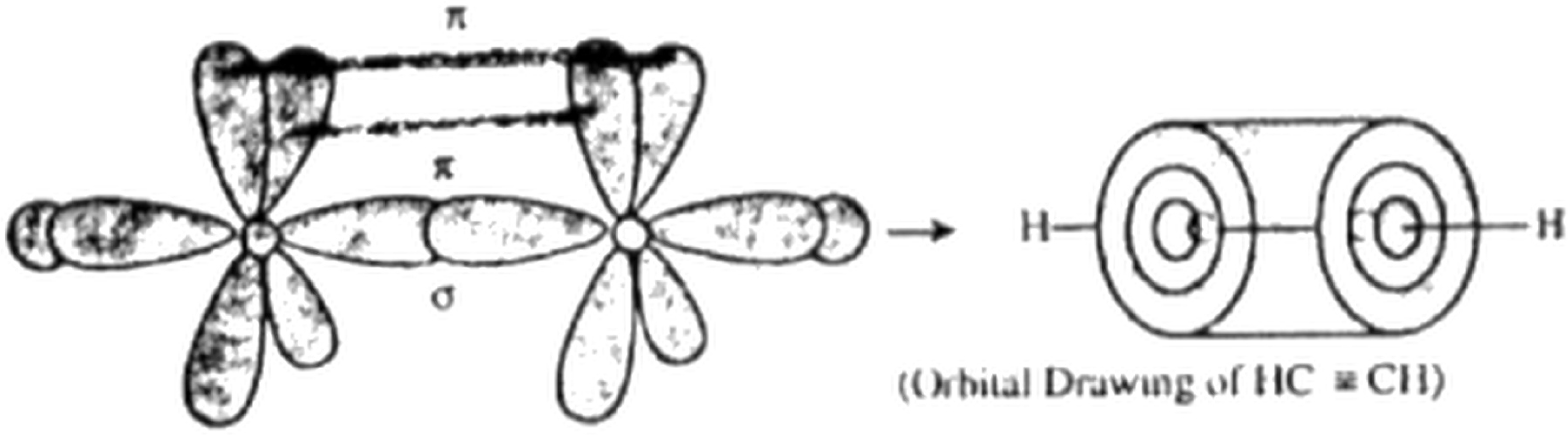
OH of I-Hexyne = 290 kj/mol while

OH of IHexene = 126 kj/mol.

Q13. Give structure of alkynes.

Answer

The two carbons of acetylene (alkyne) are sp-hybridized. They are linked by a sigma bond due to sp-sp orbitals overlap. The unhybridized two p-orbitals on one carbon overlap with two p-orbitals on other carbon to form two pi-bonds. The cloud pf pi- electrons is present cylindrically about the carbon-carbon sigma-bond.



(Orbital Drawing of HC ≡ CH)

Rotation about carbon-carbon sigma bond does not cause any change in energy and electron density. It is a linear molecule, and hence geometrical isomer is not observed in it.

Physical Properties Alkynes.

In general, alkynes are non-polar and are insoluble in water but soluble in non-polar organic solvents.

Q14. Preparation of Alkynes by Elimination Reactions.

Answer

Alkynes can be prepared by the following methods:

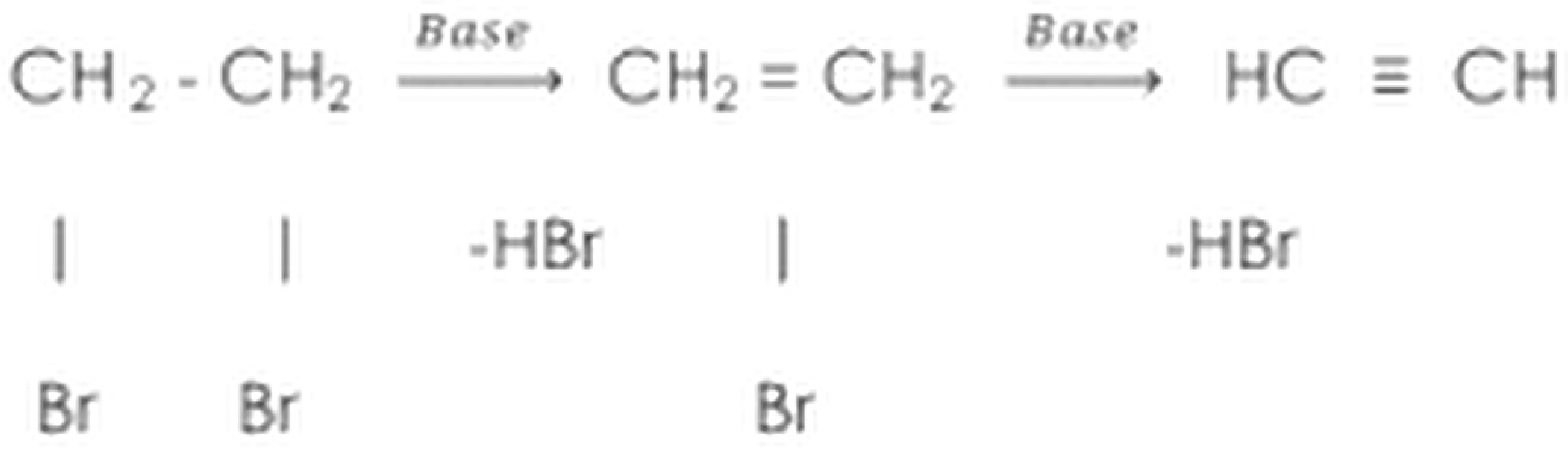
i) Elimination reaction **(ii)** Alkylation of sodium acetylide.

But we discuss here only elimination reactions

i) Elimination of Hydrogen Halide:

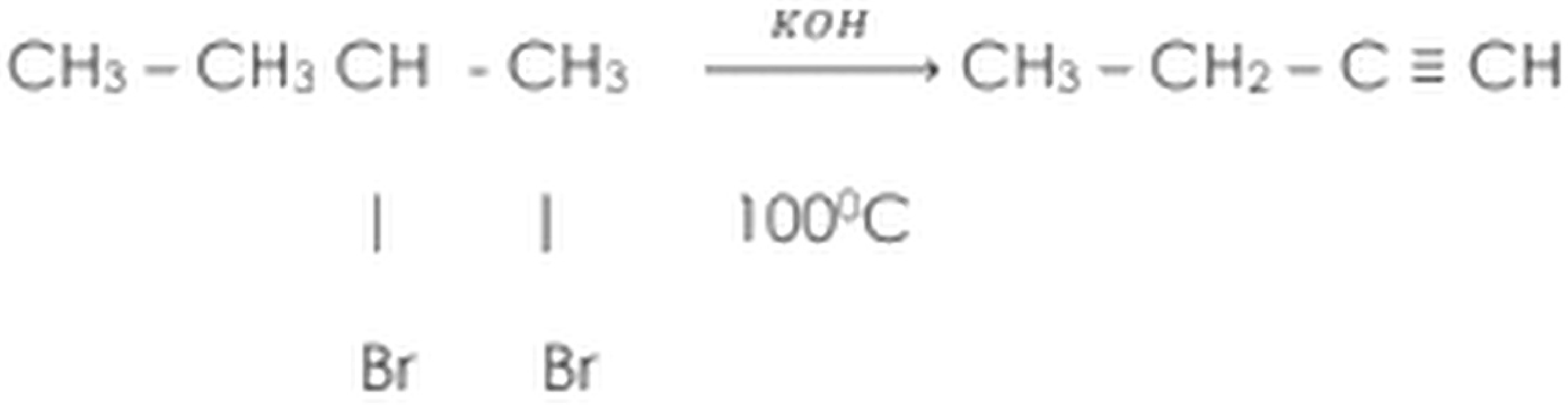
Alkynes can be prepared by dehydrohalogenation of vicinal and germinal dihalides in the presence of some alkaline reagents.

a) A vicinal dihalide contains two halogen atoms on adjacent carbon atoms.



$$\underset{Br}{\underset{|}{CH_2}} - \underset{Br}{\underset{|}{CH_2}} \xrightarrow[-HBr]{Base} CH_2 = \underset{Br}{\underset{|}{CH_2}} \xrightarrow[-HBr]{Base} HC \equiv CH$$

Higher alkynes arc also formed in the presence of alcoholic KOH, e.g.,



$$CH_3 - CH_3\ \underset{Br}{\underset{|}{CH}} - \underset{Br}{\underset{|}{CH_3}} \xrightarrow[100^0C]{KOH} CH_3 - CH_2 - C \equiv CH$$

1- butyne

In the presence of strong base such as KOH and at high temperature bond at terminal c-atom migrates to give more disubstituted alkyne.

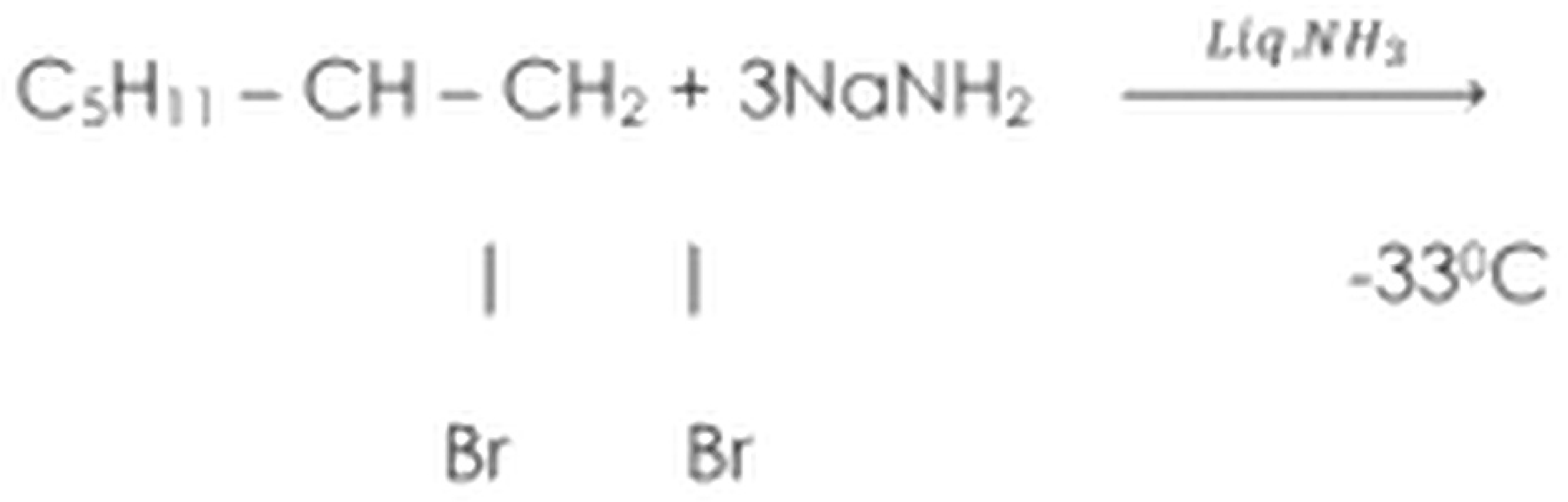
$$CH_3 - CH_3 - C \equiv CH \xrightarrow{\Delta} CH_3 - C \equiv C - CH_3$$

1- butyne 2 butyne

Therefore, alcoholic KOH is useful when rearrangement is not possible,

$$C_6H_5-\underset{Br}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH}}-C_6H_5 \xrightarrow[\text{Alc. }100-200^0C]{KOH} C_6H_5-C\equiv C-C_6H_5$$

I -alkynes can be prepared from vic-dihalides with sodium amide in liquid ammonia

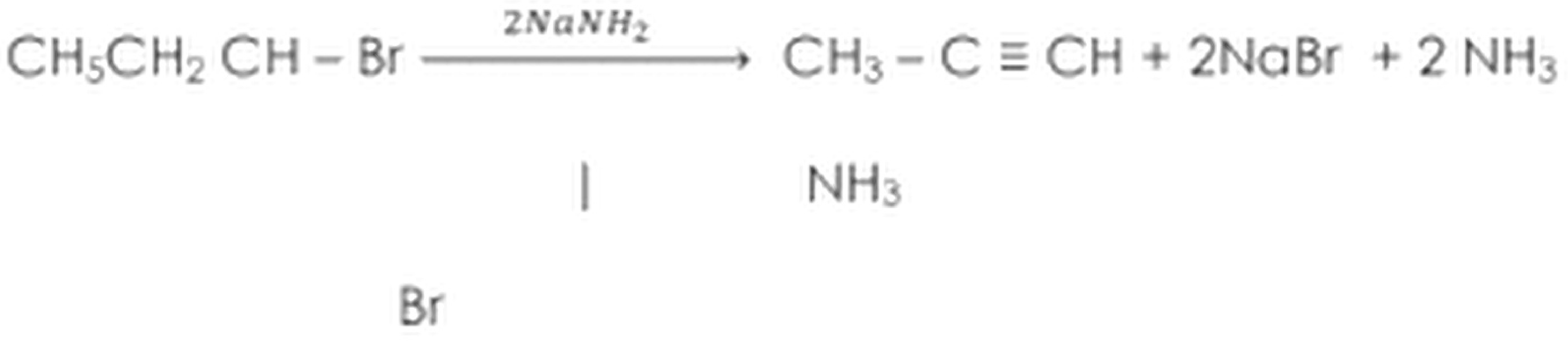


$$C_5H_{11}-\underset{Br}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH_2}}+3NaNH_2 \xrightarrow[-33^0C]{Liq.NH_3}$$

$$C_5H_{11}\,C\equiv CNa \xrightarrow{H_2O} C_6H_5C\equiv CH$$

a) Germinal Dihalide:

A dihalide containing two halogen atoms linked with the same carbon atom) on treatment with strong base gives alkyne, e.g.,



$$CH_5CH_2\,\underset{Br}{\underset{|}{CH}}-Br \xrightarrow[NH_3]{2NaNH_2} CH_3-C\equiv CH+2NaBr+2\,NH_3$$

Acetylene (alkyne) is an unsaturated hydrocarbon and shows addition reactions. It also undergoes substitute reactions due to easy cleavage of C-H bond. The pi-electrons Ee present cylindrically symmetrical about carbon-carbon sigma bond and the removal of terminal hydrogen is possible without disturbing carbon —

carbon boding. Therefore electrophile substitute reactions are possible in acetyl and I -alkynes.

Q15. What is meant by acidity of terminal alkynes?

Answer

$$R - C \equiv C - H \xrightarrow{B} R - C \equiv C{:}\ B - H$$

$$R - C \equiv C - H \xrightarrow{B} R - C \equiv C{:} \quad B - H$$

In ethyne and other terminal alkynes like propyne, the hydrogen atom is bonded to the carbon atoms with sp-s overlap. An sp hybrid orbital has 50% S-character in it and renders the carbon atoms more electronegative. As a result, the sp hybridized carbon atom of a terminal alkyne pulls the electrons more strongly making the attached hydrogen atom slightly acidic.

$$H - C \equiv C^{\delta-} - H^{\delta+}$$

This $H^{\delta+}$ can be substituted with metal. Thus substitution reaction occurs due to $H^{\delta+}$:

Examples:

i) When I-alkyne or ethyne is treated with sodamide in liquid ammonia or passed over molten sodium, alkynides or acetylides are obtained.

$$R - C \equiv CH + 2NaNH_2 \xrightarrow{Liq. NH_3} R - C \equiv C^- Na^+ + NH_3$$

$$HC \equiv CH + 2Na \longrightarrow Na^+ C^- \equiv C^- Na^+ + H_2$$

Sodium Acetylide

Sodium acetylide is a very valuable reagent for chemical synthesis and is essentially ionic in nature.

(ii) Acetylides of copper and silver are obtained by passing acetylene in the ammoniacal solution of cuprous chloride and silver nitrate respectively.

$$HC \equiv CH + Cu_2Cl_2 \rightarrow CuC \equiv CCu + 2NH_4Cl + 2H_2O$$

Dicopper acetylide or copper

Ehtynide (Reddish brown)

(iii)

$$HC \equiv CH + 2AgNO_3 + 2NH_4OH \rightarrow AgC \equiv Cag + 2\ NH_4NO_3 + 2H_2O$$

Disilver acetylide or silver

Ethynide. (white ppt)

Silver and copper acetylides react with acids to regnerate alkynes.

$$AgC \equiv Cag + \text{dil. } H_2SO_4 \longrightarrow HC \equiv CH + Ag_2SO_4$$

$$AgC \equiv Cag + \text{dil. } HNO_3 \longrightarrow HC \equiv CH + 2\ AgNO_3$$

These alkynides are used for the preparation, purification separation, and identification of alkynes.

Q16. Give addition reactions of alkynes.

Answer

I) Alkynes undergo addition reactions in an analogous fashion to those of alkenes.

2) The high electron density of the p bonds makes them nucleophilic.

3) Two factors influence the relative reactivity of alkynes compared to alkenes:

4) increased nucleophilicity of the starting p system, and

5) stability of any intermediates (for example carbocations)

1) Hydrogenation

Alkynes react with hydrogen gas in the presence of suitable catalysts like finely divided Ni, Pt or Pd. In the first step alkenes are formed which them take up another molecule of hydrogen to form an alkaline.

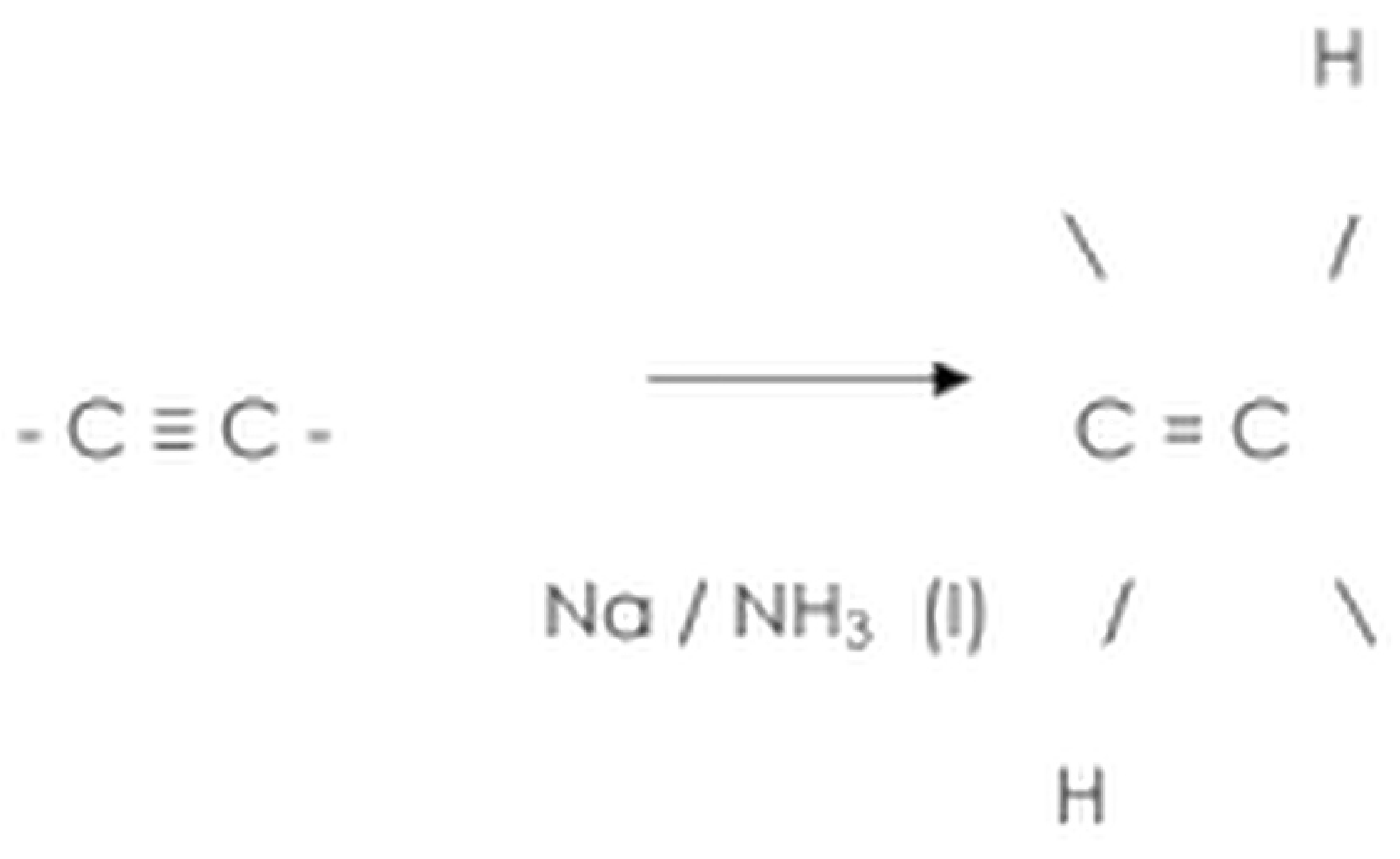
$$HC \equiv CH + H_2 \xrightarrow[\text{Heat}]{Ni} H_2C = CH_2$$

Ethyne

$$CH_2 = CH_2 + H_2 \xrightarrow[\text{Heat}]{Ni} H_3C = CH_3$$

Ethyne

2) Dissolving Metal Reduction:



$$- C \equiv C - \xrightarrow[\text{Na / NH}_3\ (l)]{} C = C$$

Reaction Type: Addition

Elaboration

- Alkynes can be reduced to trans-alkenes using Na in NH3 (liq.)
- This reaction is stereospecific giving only the trans-alkene via an anti-addition.
- Note that the stereochemistry of this reaction complements that of catalytic hydrogenation (syn)

- The reaction proceeds via single electron transfer from the Na with H coming from the NH3
- These reaction conditions do not reduce alkenes, hence the product is the alkene.

3) Hydrohalogenation

Alkynes react with hydrogen chloride and hydrogen bromide to form dihaloalkenes. The reaction occurs in accordance with Markownikov's rule.

$$HC \equiv CH + H - Br \longrightarrow H_2C = \underset{\underset{Br}{|}}{CH}$$

Ethyne

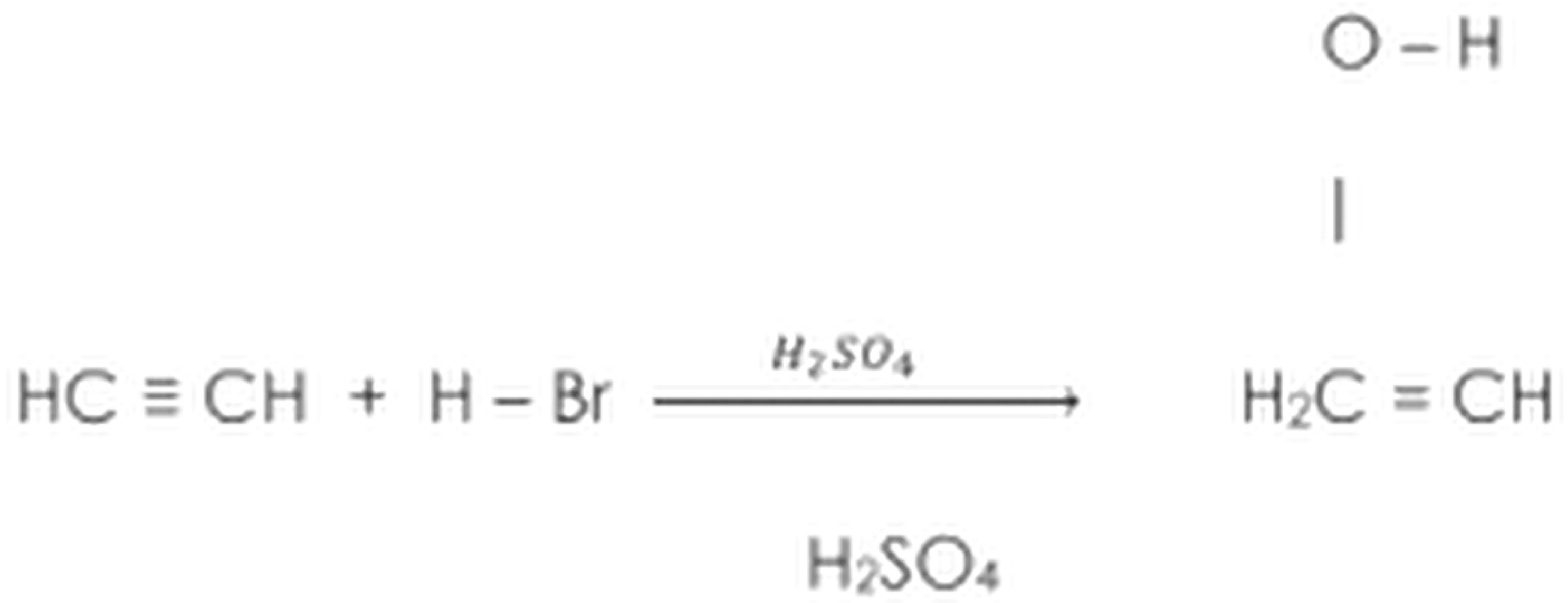
Vinyl bromide

$$HC \equiv \underset{\underset{Br}{|}}{CH} + H - Br \xrightarrow[\text{Additon}]{Markownikov's} H_3C - CH\genfrac{}{}{0pt}{}{/\,Br}{\backslash\,Br}$$

1,1 - Dibromoethanac

4) Hydration

Water adds to acetylene in the presence of mercuric sulphate dissolved in sulphuric acid at 75^{0}C.



$$HC\equiv CH\ +\ H-Br \xrightarrow[H_2SO_4]{H_2SO_4} \overset{\overset{O-H}{|}}{H_2C}=CH$$

vinyl alcohol

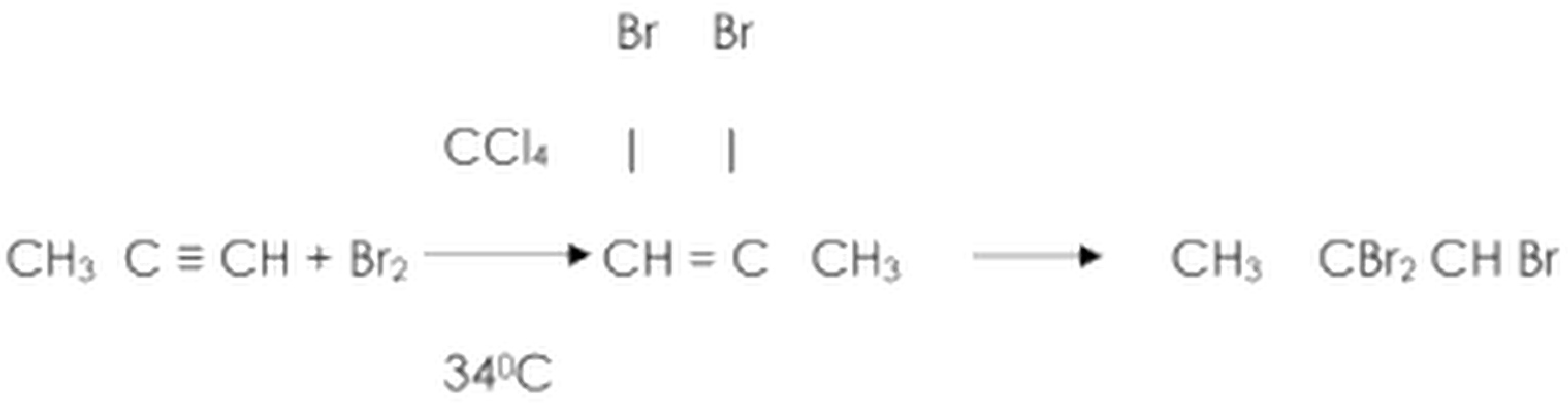
Rearrangement of Alcohol:

Vinyl alcohol is an unstable. It has hydroxyl group attached to a doubly bonded carbon atom and isomerizes to acetaldehyde.

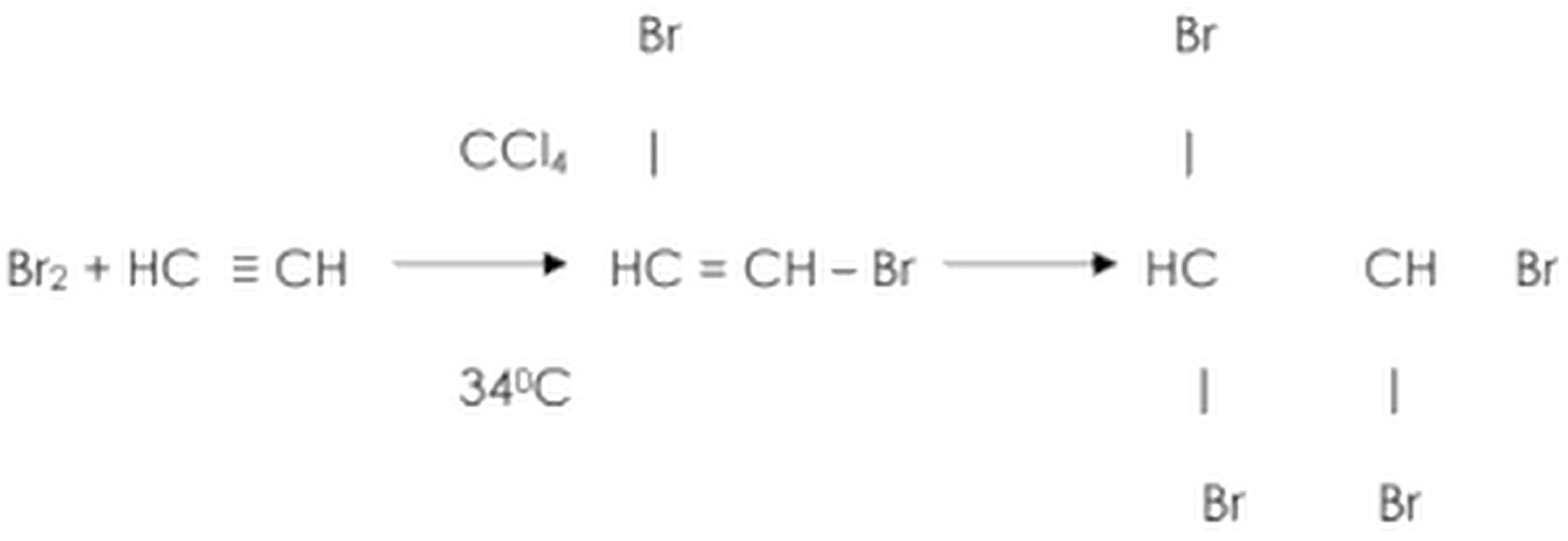
This reaction is industrially important because aldehydes can be by this method.

5) Bromination

Chlorine and bromine to the acetylenic triple in the presence of lewis acid as catalyst



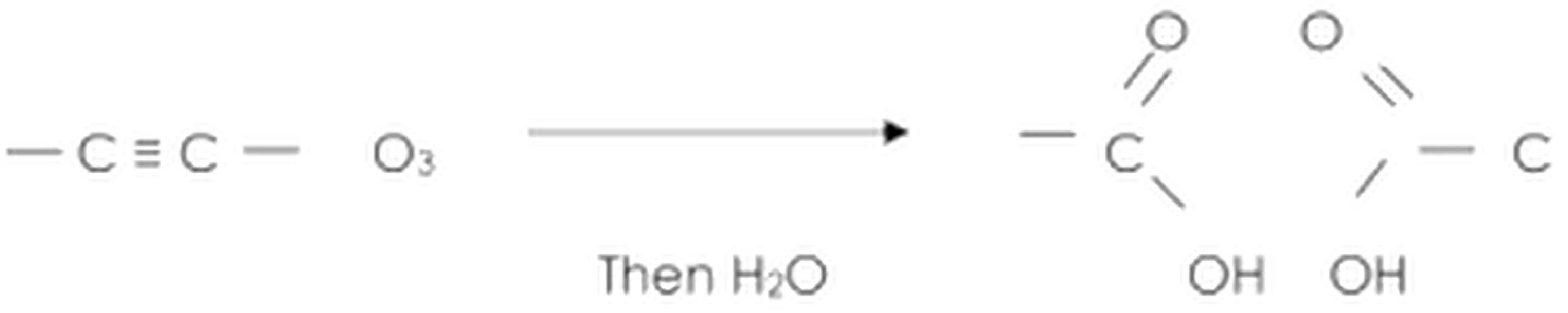
$$CH_3\ \ C\equiv CH + Br_2 \xrightarrow[34^0C]{CCl_4} \overset{\overset{Br}{|}}{CH}=\overset{\overset{Br}{|}}{C}\ \ CH_3 \longrightarrow CH_3\ \ CBr_2\ CH\ Br$$



$$Br_2 + HC\ \equiv CH \xrightarrow[34^0C]{CCl_4} \overset{\overset{Br}{|}}{HC}=CH-Br \longrightarrow \underset{\underset{Br}{|}}{\overset{\overset{Br}{|}}{HC}}\qquad \underset{\underset{Br}{|}}{CH}\quad Br$$

The Halogenation may be stopped at the dihaloalkene stage because the double bond of dihaloalkene is less nucleophilic than even triple bond itself.

6) Ozonolysis



When ozone reacts with alkyne followed by aqueous work up we get 2XC02H.

Benzene and Substituted Benzenes

Discovered by	=	Michael Faraday
Isolated by	=	Hoffmann
Molecular formula	=	C_6H_6
Molecular weight	=	(i)Resonance
		(ii) Electrophilic substitution reaction

Michael Faraday discovered benzene in 1825, during the destructive distillation of vegetable oil. Hoffmann isolated it form coal tar.

As a functional group, benzene and substituted benzenes are called arenes.

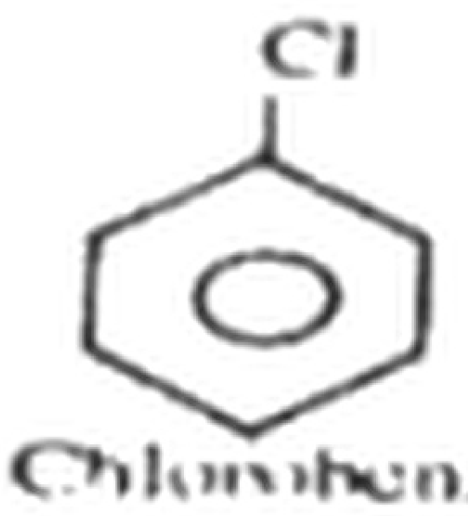
Nomenclature

Mono Substituted Benzenes:

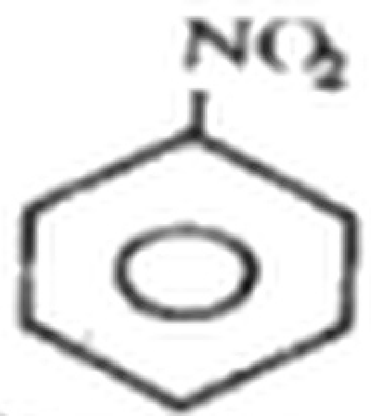
a) Common system naming:

The following procedures are adopted for naming mono substituted benzenes:

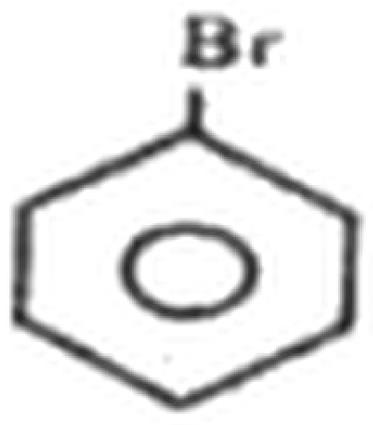
(I) Parent name is benzene and the substituent is indicated by a prefix, e.g,.



Chlorobenzene



Nitrobenzene



Bromobenzene

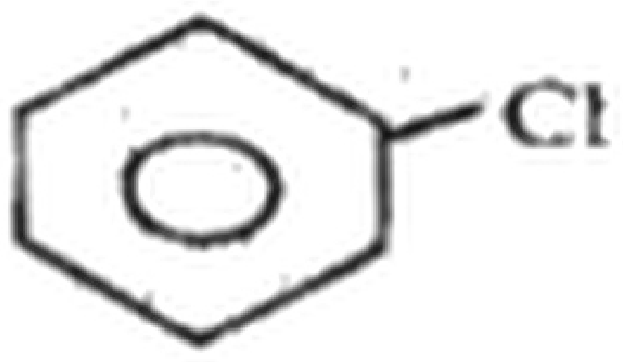
2) The substituent and the benzene ring taken together may from s new parent name. The largest parent name is preferred e.g., C6HsCH3 may be named as:

i. Methyl benzene

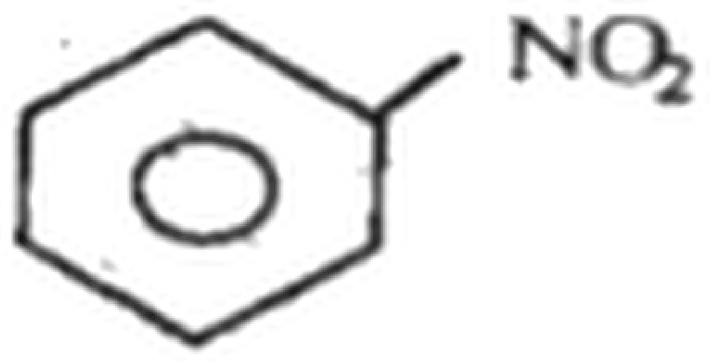
ii. Phenyl methane. According to 'The largest rule" methyl benzene is preferred.

IUPAC System of Naming:

Mono substituted derivatives of benzene are named by prefixing the name of substituted to the word 'benzene'. e.g.

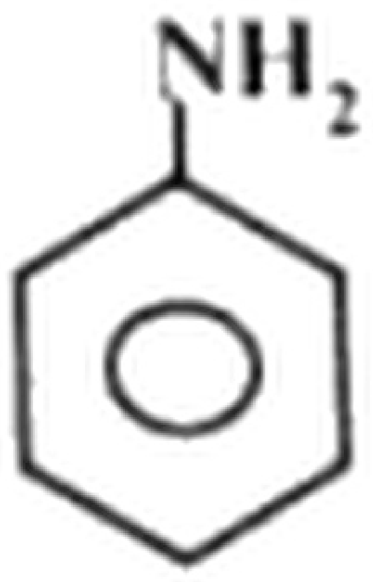
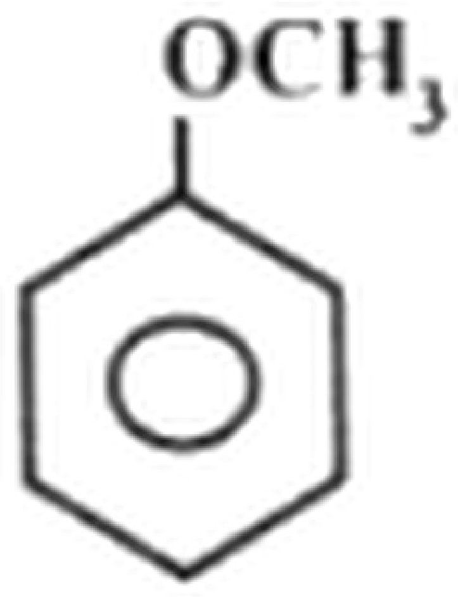
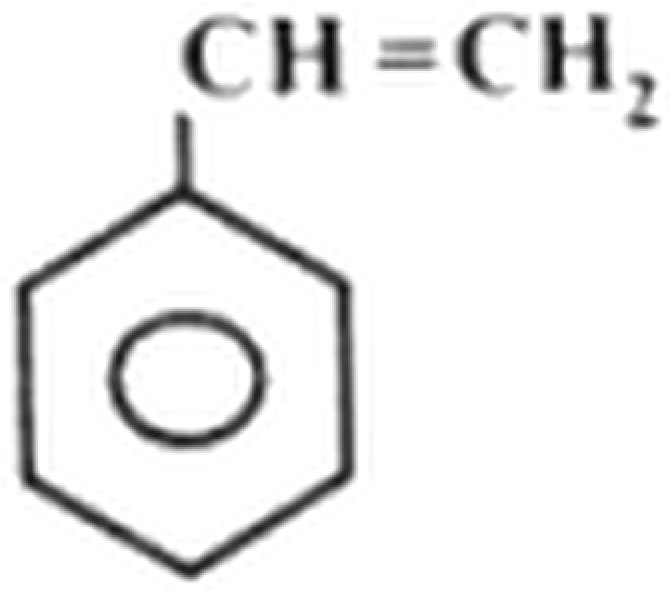


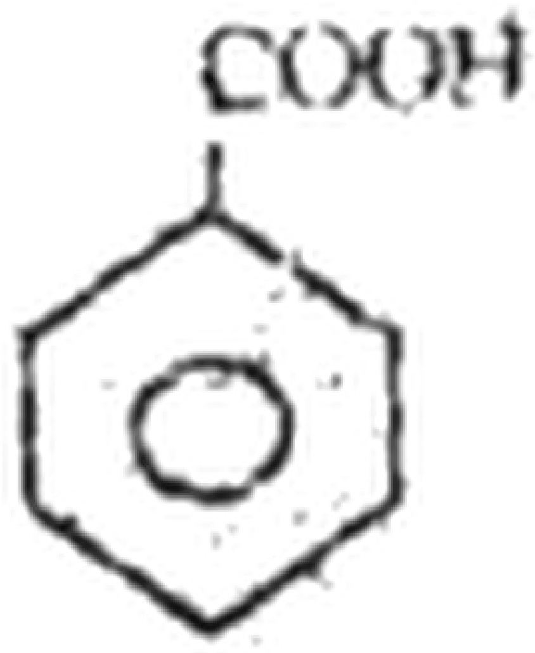
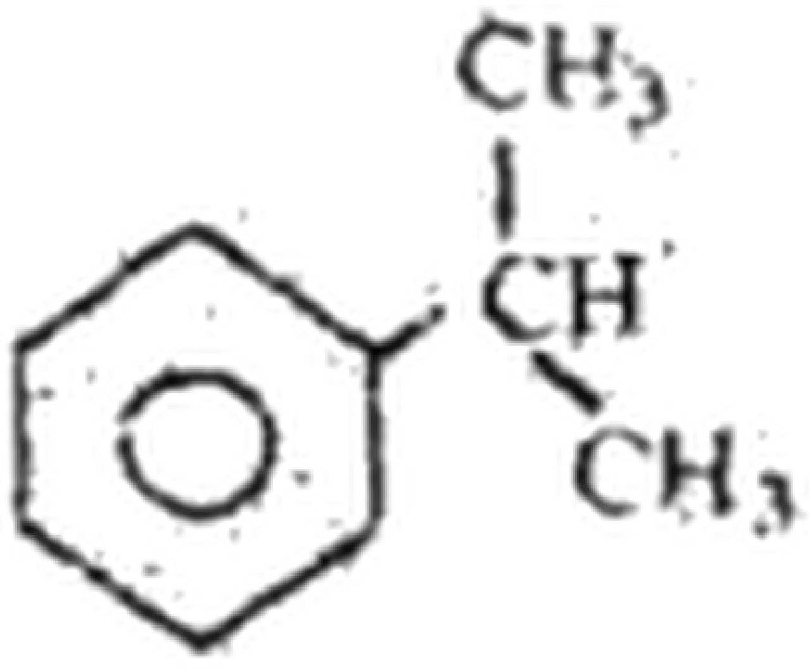
Chlorobenzene



Nitrobenzene

Many aromatic compounds have been known by their common or trivial names which are still in use. IUPAC system retains these names: A few are given below:

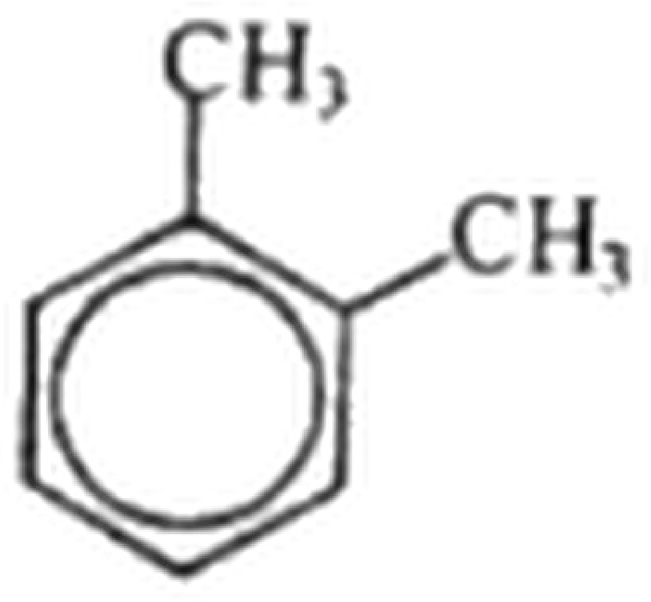
Structure	Names	Structure	Names
	Toluene		Phenol
	Aniline		Anisole
	Sturene		Nitrobenzene

	Benzoic acid		Cumene
	Bromobenzene		

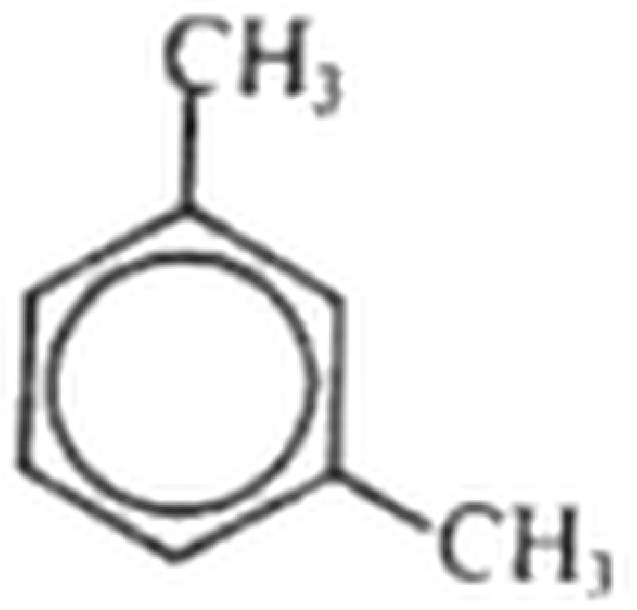
Q17. What is distributed benzene?

Answer

I) When there are two substituents on benzene ring their relative positions are indicated by prefixes ortho (o), Meta (m) and Para (p) in common system of naming and by numerals while naming according to IUPAC system, e.g.,



o-Dimethylbenzene

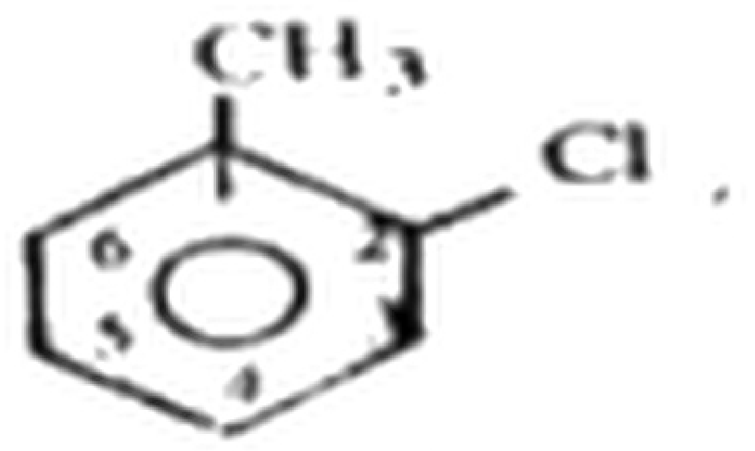


m-Dimethylbenzene

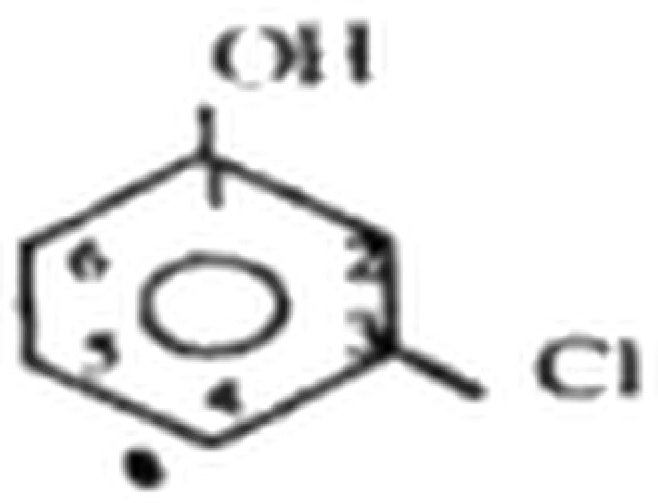
p-Dimethylbenzene

2) If the substituents are different and one of them is an alkyl group the numbering is started from the ring carbon which is linked to the alkyl group and the second substituent gets the lowest possible number.

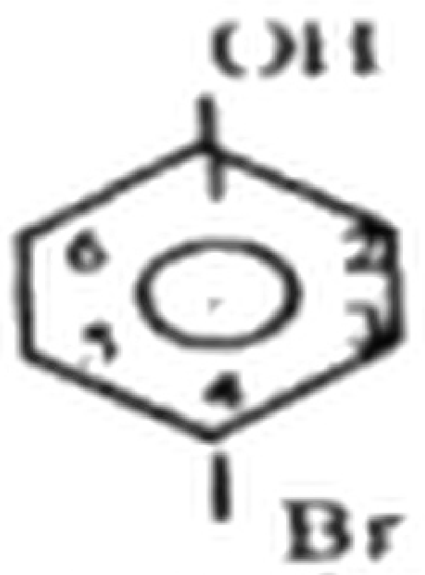
3) When a common name is used, the substituent which is responsible for name, e.g., CH3 in toluene, and —OH in phenol, is considered to be on carbon -I, i.e., numbering is started from the carbon of ring bearing that group such a distributed compound is named as derivative of that parent, e.g,.



o -chlorotoulene
2 - chlorotoulene
(IUPAC)

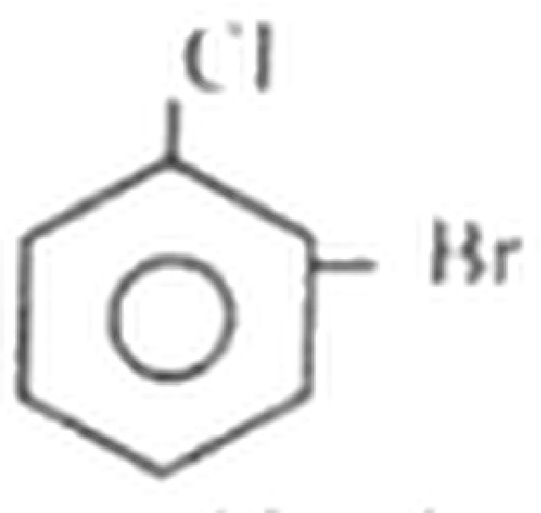


m - chlorophenol
3 - chlorophenol
(IUPAC)

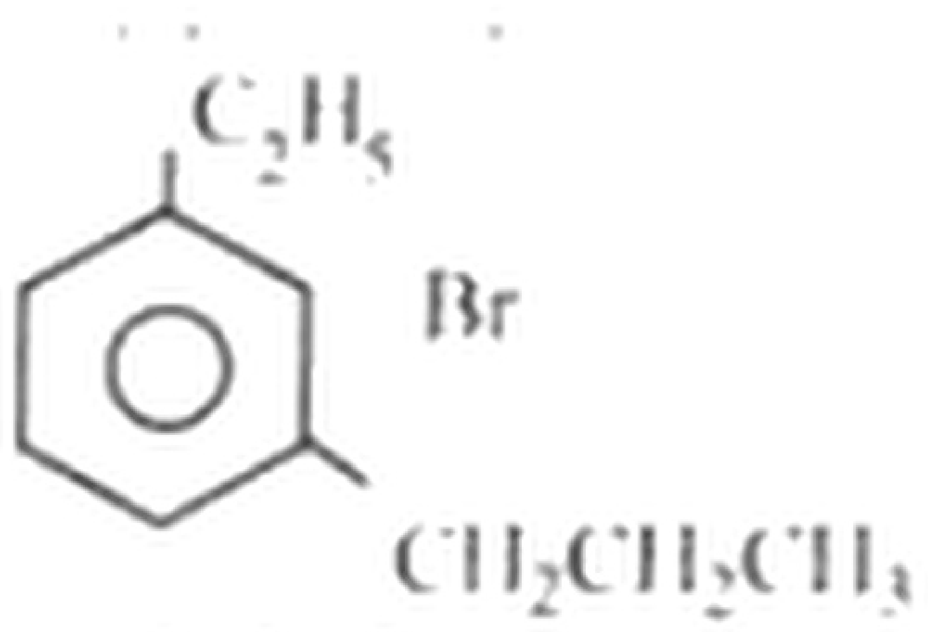


p - bromonitrobenzene
4 - bromonitrobenzene
(IUPAC)

4) When two substituents are different, they are usually put in alphabetical order, e.g.

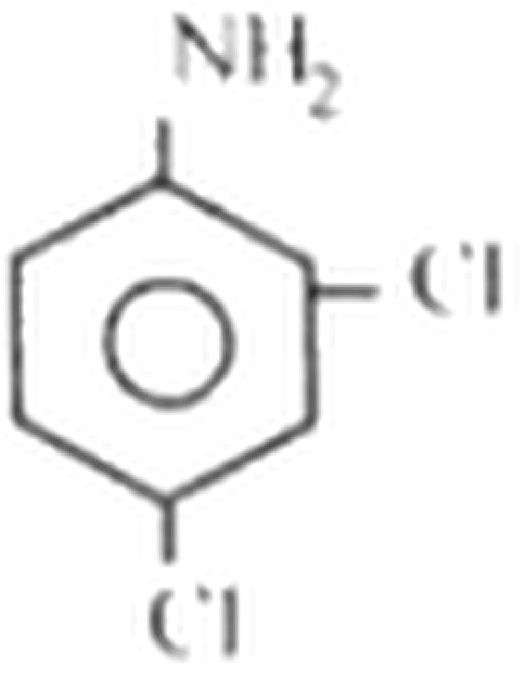


o - bromochlorobenzene
1 - bromochlorobenzene
(IUPAC)

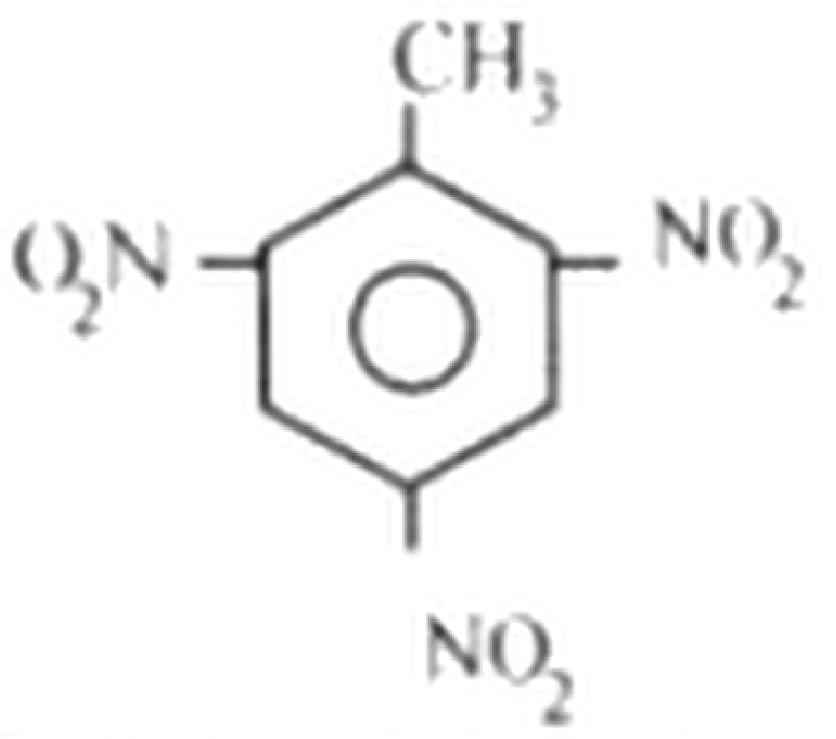


1 - ethyl - 3 - propyl
benzene (IUPAC)

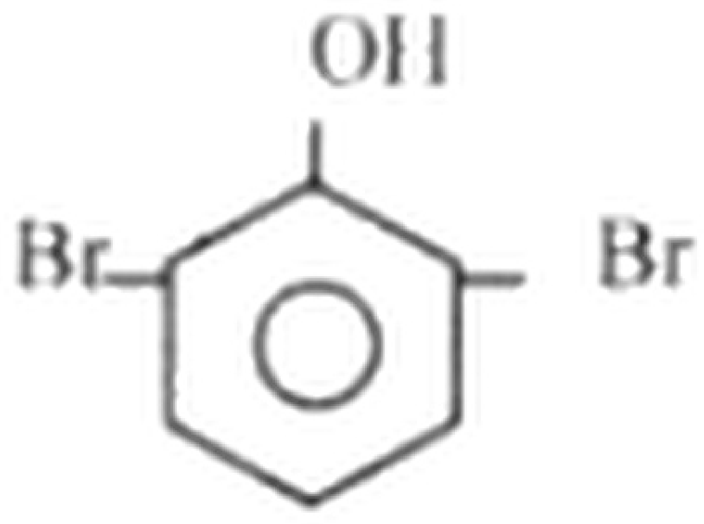
5) Poly substituted benzenes are named by numbering the substituent to ring so as to give the substituents lowest possible numbers. The last-named substituent is assumed to be at position number I. This number is not indicated in the name.



2.4 - dichloro aniline

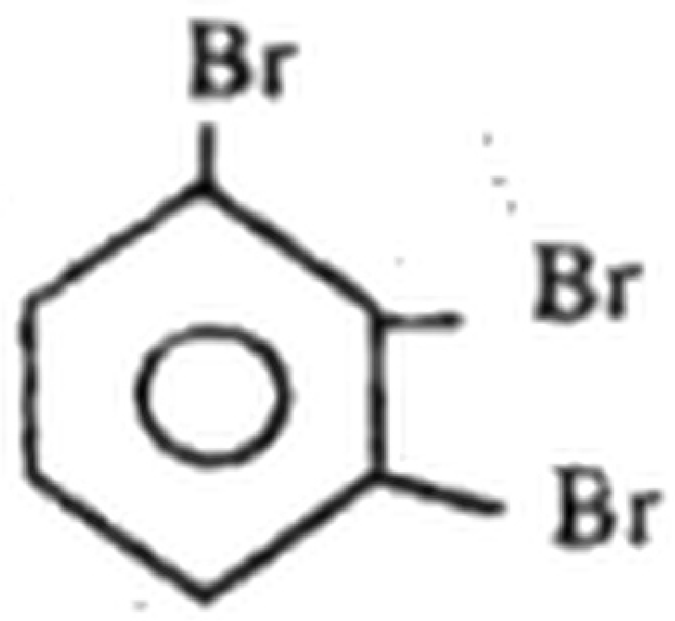


2, 4, 6 - trinitrotoluene
(TNT)

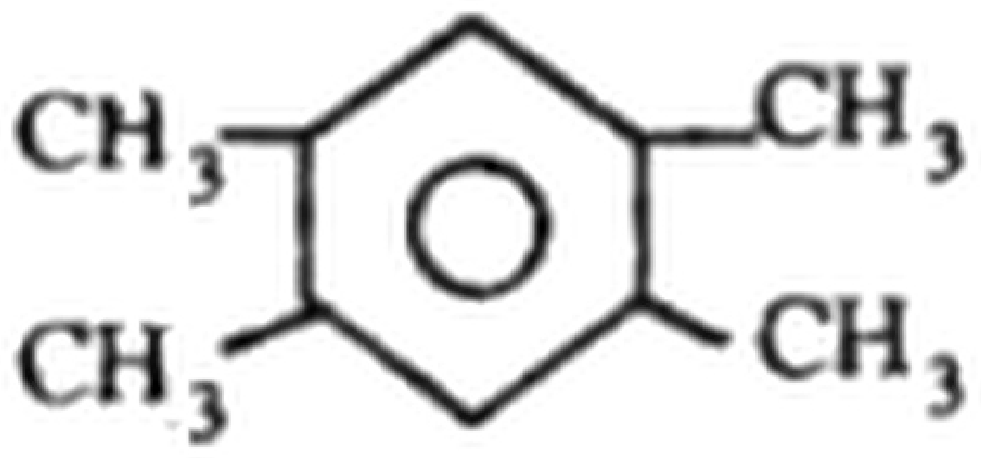


2, 6 - dibromophenol

6) If the substituents are all alike their positions are indicated by numbering the substituents in a manner so as to give the lowest number to the substituents.

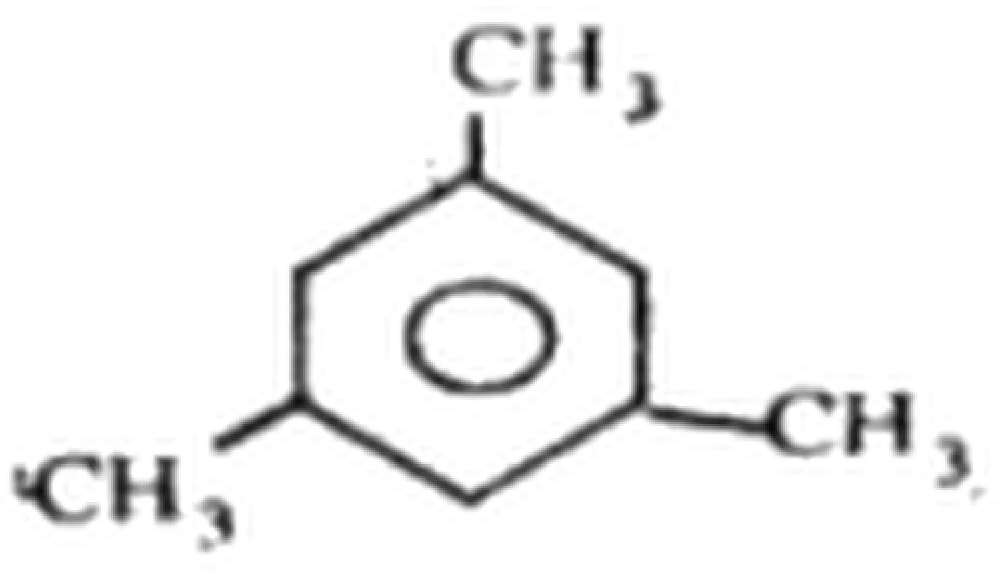


1, 2, 3 - tribromobenzene

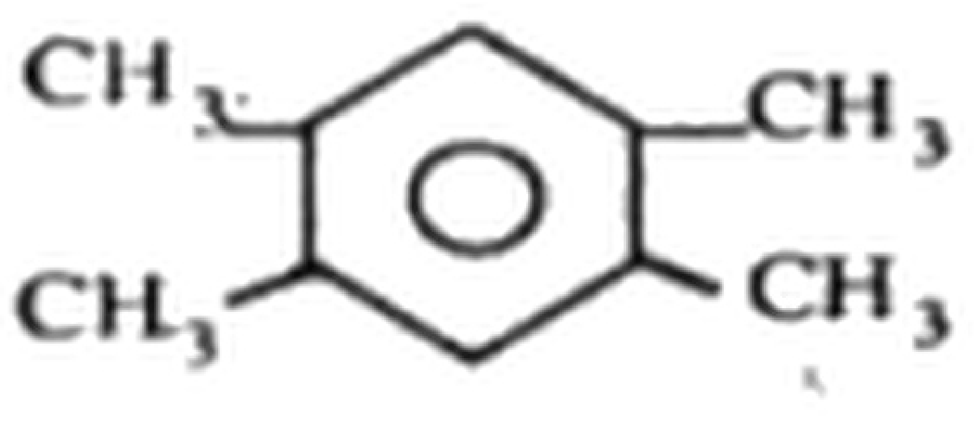


1, 2, 4, 5 - tetramethylbenzene

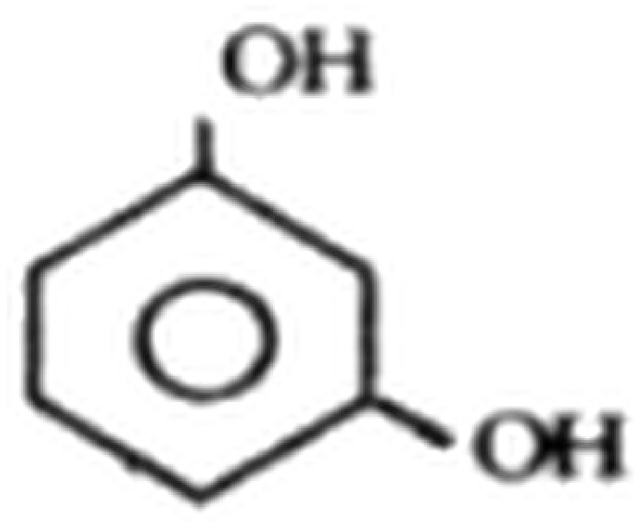
7) Some poly substituted are still known by their common name.



mesitylene



durene

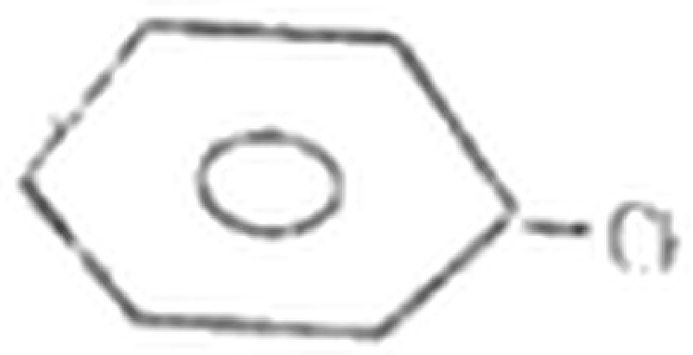


Resorcinol

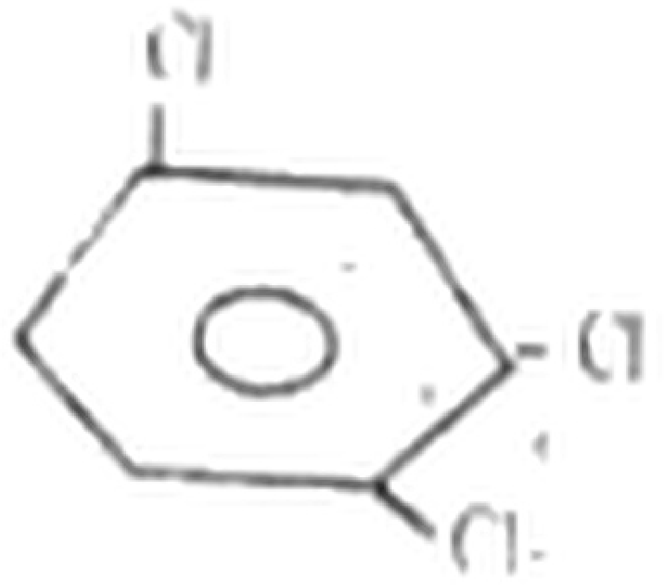
Activity:

1- Give the suitable name to each of following:

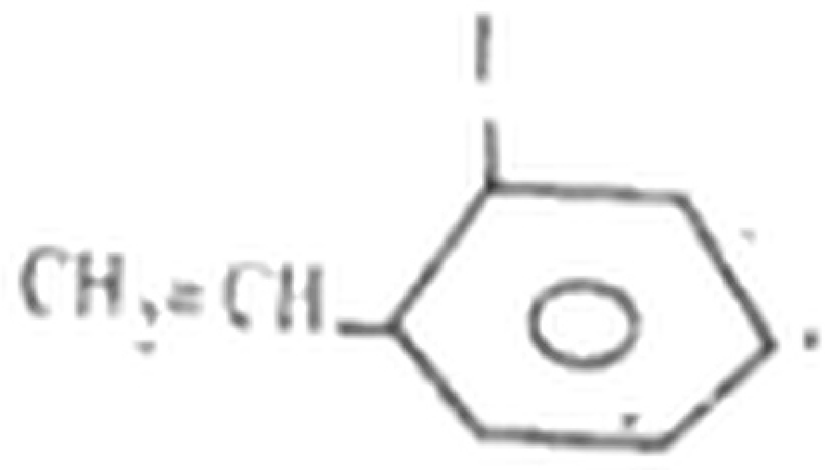
(a)



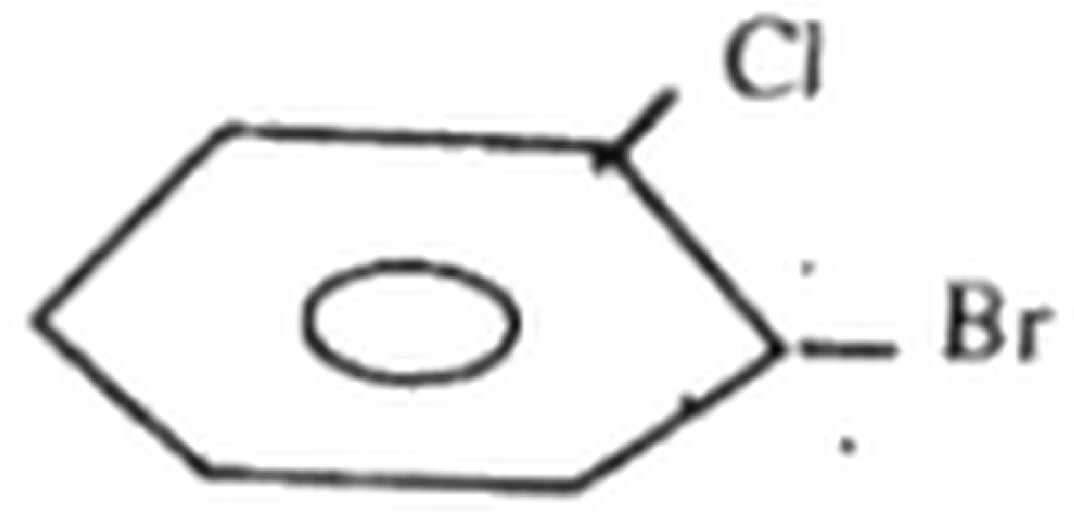
(b)



(c)

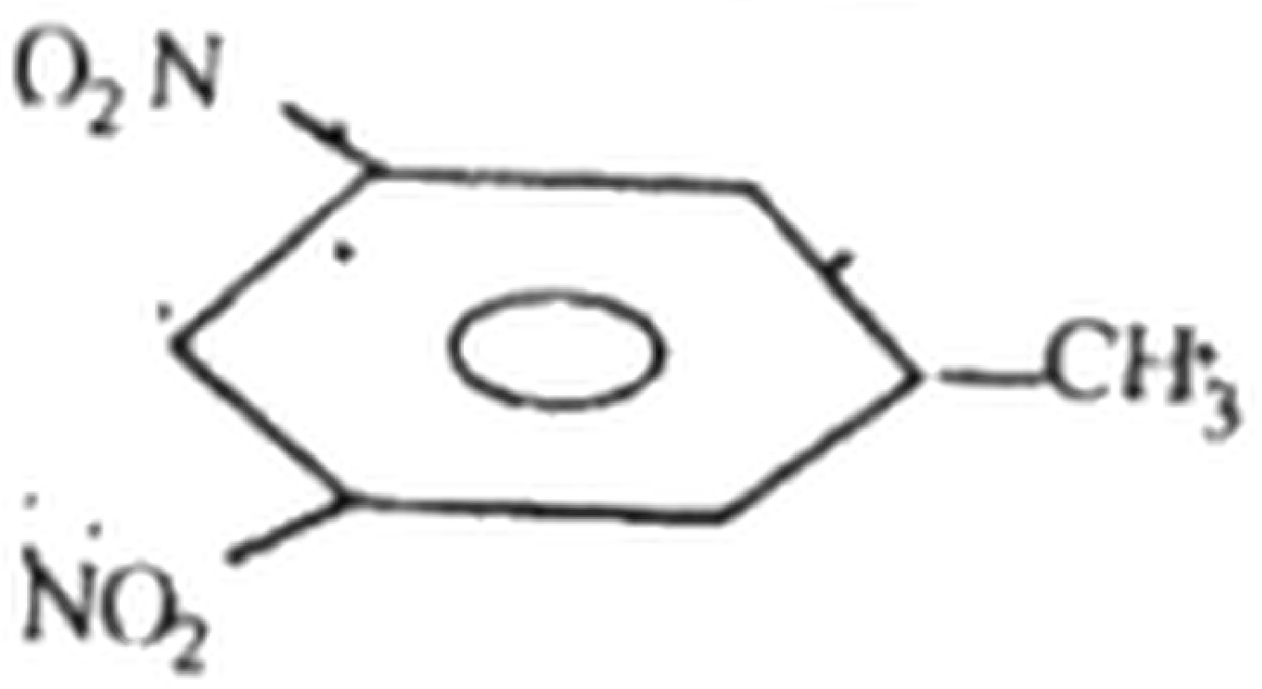


(d)



(e)

(f)

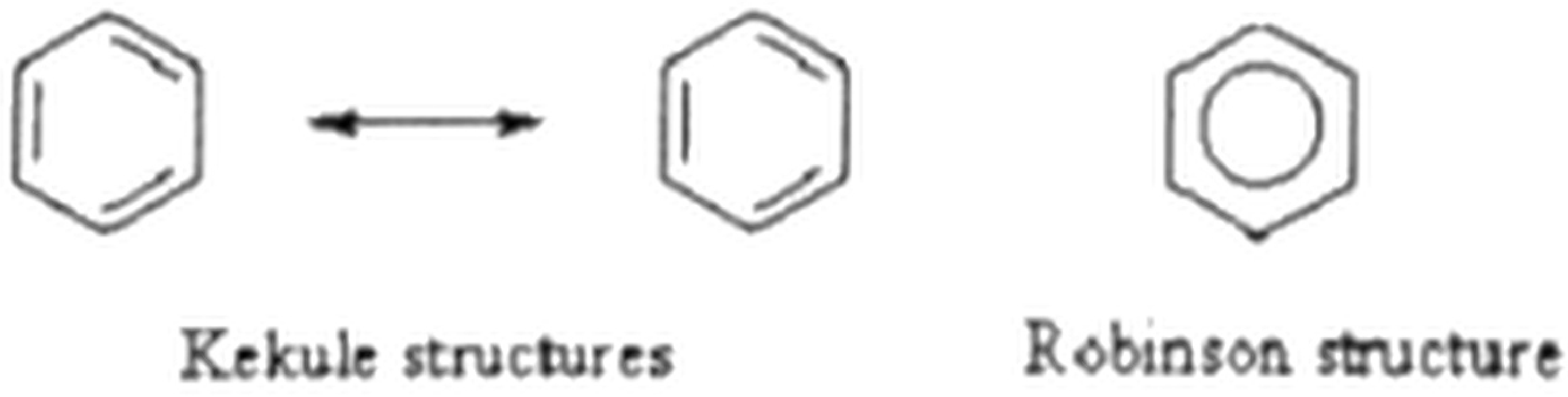


(g)

Physical Properties

In the absence of polar substituents, arenes are typical of hydrocarbons: low melting and boiling points, low solubility in polar solvents.

Structure (Molecular Orbital Aspects)



All 12 atoms in benzene, C6H6, lie in the same plane.

Benzene has a planar, cyclic, conjugated structure.

If one draws benzene as alternating C=C and C-C then the two different Kekule structures are obtained.

These are two equally valid resonance contributors.

Alternatively, these two forms can be combined in the resonance hybrid and the conjugated system represented by a circle as in the Robinson structure.

Note that all of the CC bonds are 1.4 Å (between typical C=C and C-C distances).

Which representation is best?

In benzene all the CC bonds are known to be of equal length (above) so there are no C=C and C.C. This is best represented by the resonance hybrid in the Robinson form.

However, since the key to organic chemistry is being able to understand mechanisms and drawing curved arrows to account for the positions of the electrons, the Kekule structures give a more precise description of the electron positions that can avoid confusion. Therefore, it is n good idea to use a Kekule representation.

Q18.Write down molecular orbital structure of Benzene (Modern structures of Benzene).

Answer

Kekule's structure failed to explain as to why

I) Benzene is less reactive

2) It shows dual character, i.e., it shows addition as well as substitute reaction.

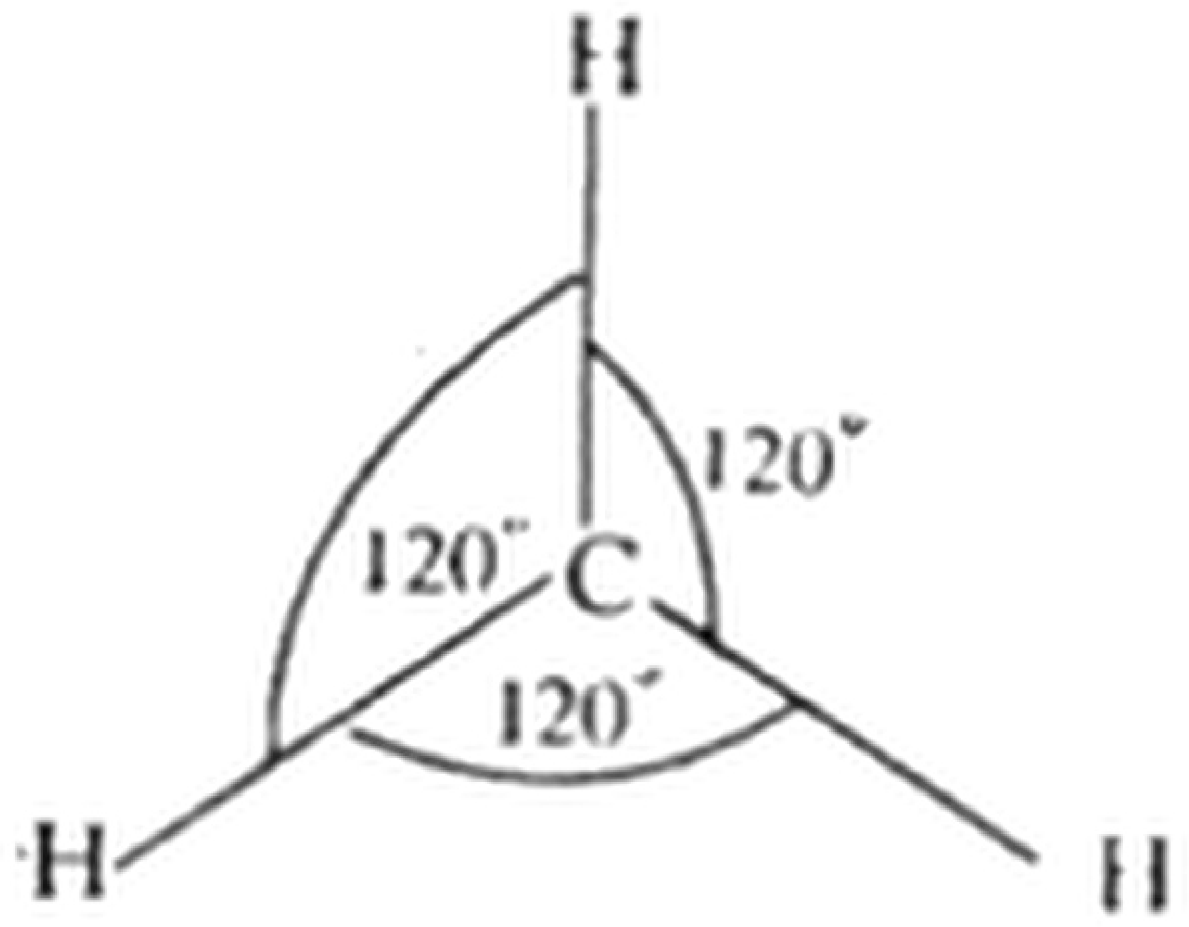
3) It has less heat of formation, and

4) It has equal C-C bonds.

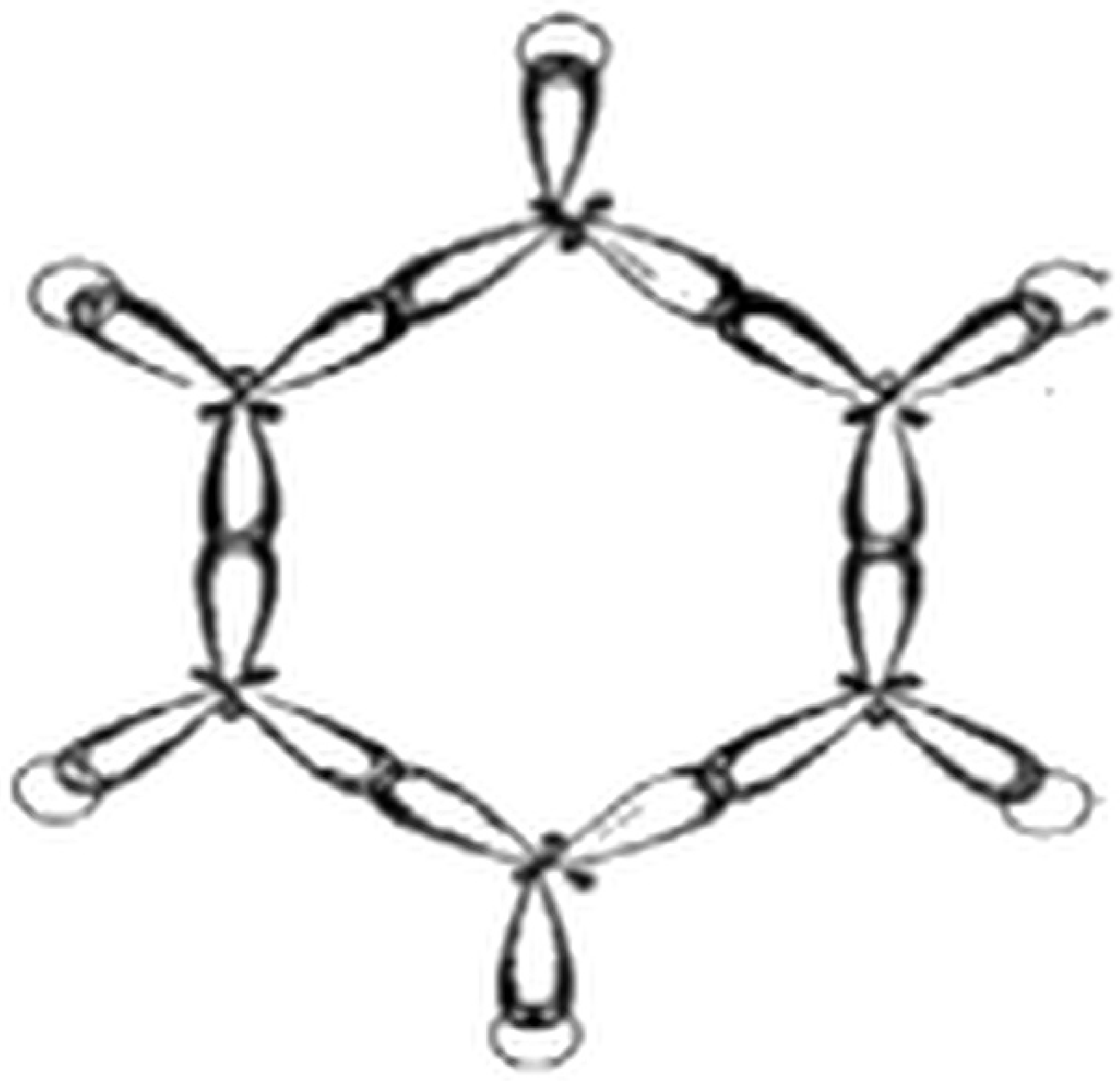
Spectroscopic studies and X-rays analysis have shown that benzene is a regular, flat planar hexagon. All six hydrogen atoms are co-planar with six carbon atoms. The bond angles are:

1) C-C-C=120, and (ii) C-C-H=120

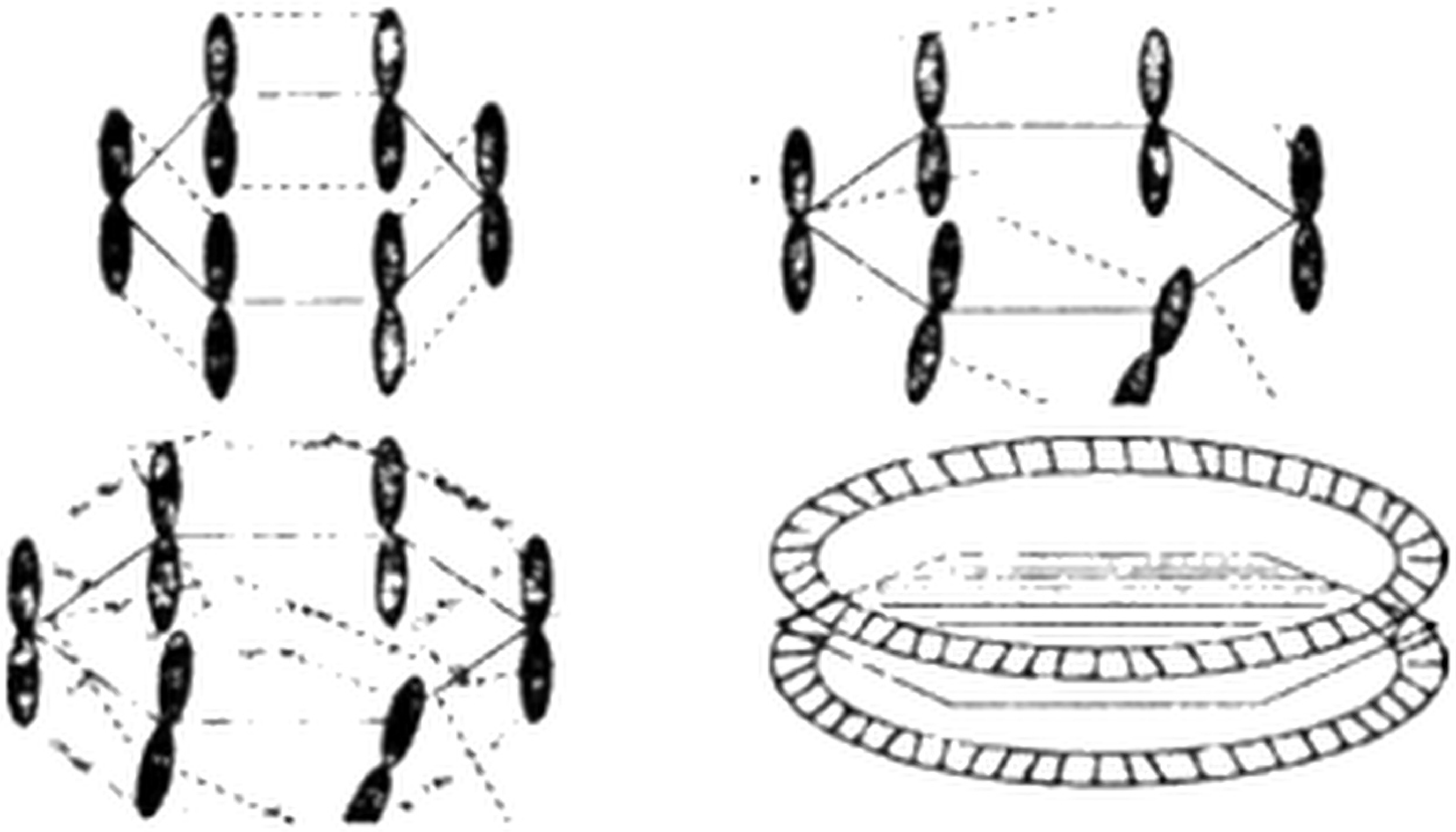
Thus, each C-atom is in a state of sp^2-hybridization because each C-atom is attached to three atoms.



Combination of such six structures and overlap of six hydrogen atoms (Isl) produces the following sigma frame work of benzene.



Six atomic p-orbitals one on each c-atom, are present perpendicular to this sigma bonding. Each p-orbital is in a position to overlap in parallel manners with neighboring p-orbitals to give a continuous sheath of negative charges as:



It results in extensive delocalized pi-bonding which spreads oval all the carbon nuclei of benzene. Delocalization of p-orbitals over the entire ring produces sand which like structure of benzene and decreases the energy of molecule. Consequently, the molecule becomes more stable and less reactive.

According to this molecular orbital picture each carbon-carbon bond in benzene consists of one full sigma-bond and half a pi-bond. Because of this reason, the carbon-carbon bond length is equal and benzene shows substitution as well as addition reactions.

MODERN REPRESENTATION OF BENZENE

With the help of molecular orbital behaviour we conclude that benzene has A regular hexagonal structure with an inscribed circle. A hexagon with alternate double and single bonds.

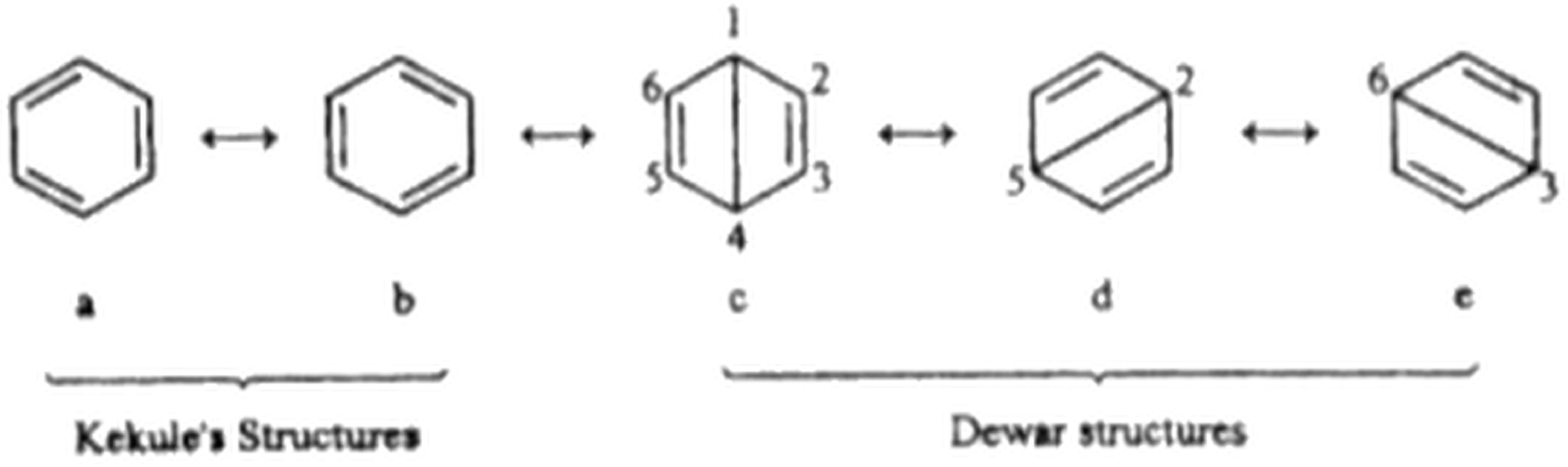
16.8.4. Resonance, Resonance Energy and Stabilization

I) Resonance:

"The possibility of different pairing schemes of valence electrons of atom is called resonance" and the different structures thus arranged are called "Resonance Structures".

Explanation:

The resonance is represented by a double-headed arrow e.g. the following different pairing schemes of the fourth valence (the p-electrons) of carbon atoms are possible in benzene. This gives the following resonating structures of benzene:



(a), (b) were proposed by Kekule and c, d, e were proposed by Dewar. The stability of a molecule increases with increase in the number of its resonance structures. Thus molecule of benzene is chemically quite stable.

In fact the structure of benzene is a resonance hybrid of all five structures, (a), (b), (c), (d), and (e) in which the Kekule's structure (a) and (b) have the larger contribution and Dewar's structures contribute a little. Therefore, benzene molecule can be represented by either of the two Kekule's structure.

The three alternate single and double bonds in the above structure are called conjugate bonds of resonating bonds.

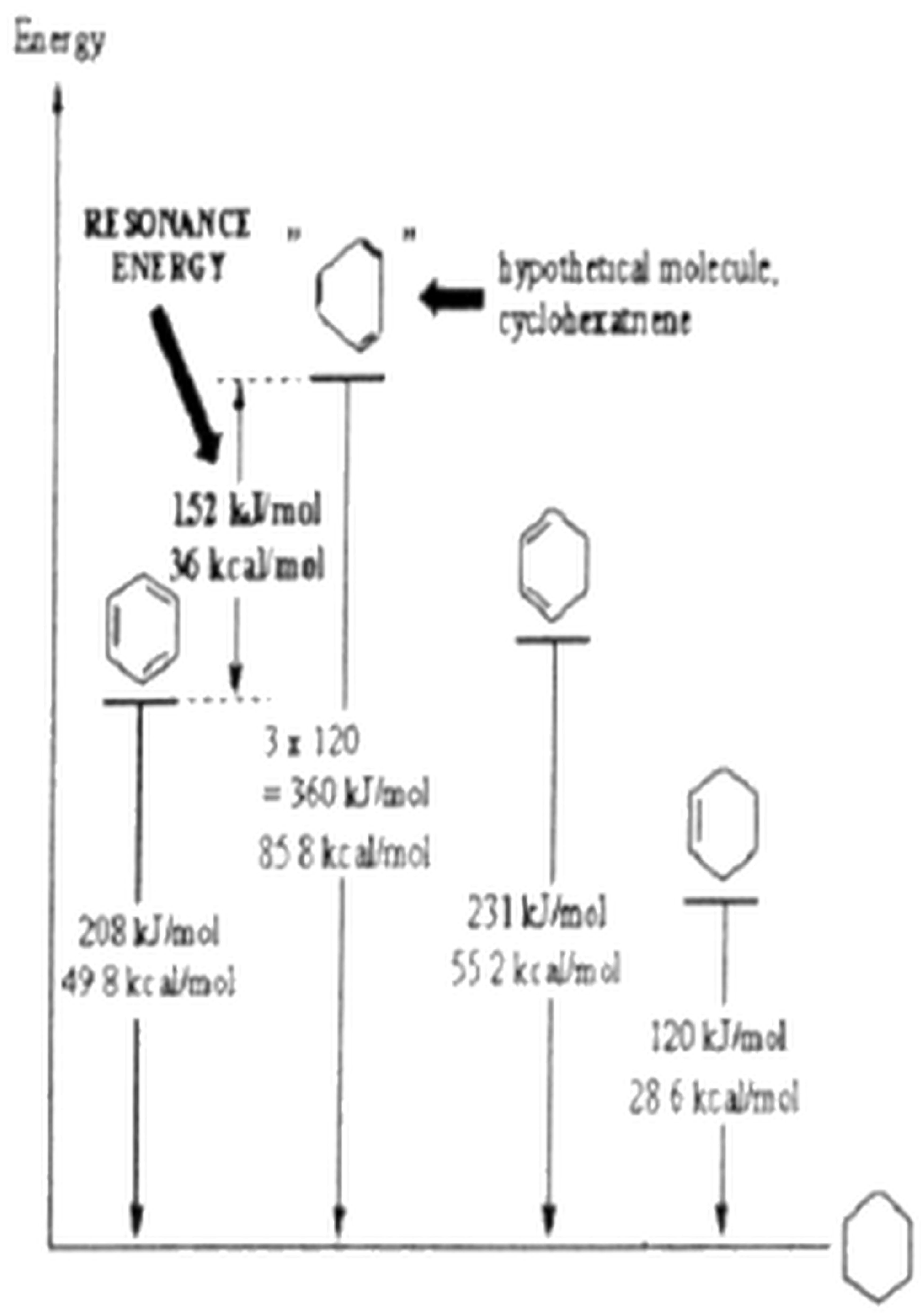
Since the structure of benzene is a resonance hybrid, therefore all the C-C bond lengths are equal but different from those in alkanes, alkenes and alkynes. It is intermediate between those in alkanes and alkenes. The resonating single and double bonds in benzene can better be represented as follows.

Benzene

Q19.What is resonance energy? Explain with Benzene.

Answer

The resonance energy of a compound is a measure of the extra stability of the conjugated system compared to the corresponding number of isolated double bonds. This can be calculated from experimental measurements.



The diagram shows the experimental heats of hydrogenation, AHh, for three molecules, benzene, 1,3cyclohexadiene and cyclohexene. These are related in that under appropriate conditions they can all be reduced to the same product, cyclohexane.

The AHh for "cyclohexaftne", a hypothetical molecule in which the double bonds are assumed to be isolated from each other, is calculated to be 3 times the value for cyclohexene. This value reflects the energy we could expect to be released from 3 isolated C=C.

By comparing this value with the experimental value for benzene, we can conclude that benzene is 152 kJ or 36 kcal / mol more stable than the hypothetical system. This is the resonance energy for benzene.

Reactivity and Reactions

The image shows the electrostatic potential for benzene.

The more red an area is, the higher the electron density and the more blue an area is, the lower the electron density. Note the nucleophilic character of the aromatic p system.

The reactivity issues can be separated into two types of reactions: reactions of electrophiles directly on the aromatic ring, and reactions of the substituents (since the neighboring aromatic group influences its reactivity).

For reactions directly on the aromatic ring:

The cyclic array of p-bonds is a region of high electron density so arenes are typically nucleophiles (like alkenes and alkynes).

Unlike alkenes and alkynes (which undergo addition reactions), arenes typically undergo substitution reactions in which a group (usually -H) is replaced and the aromatic system is retained.

The stability of the aromatic system favors substitution over addition which would destroy the aromatic system.

ADDITION REACTIONS of Benzene

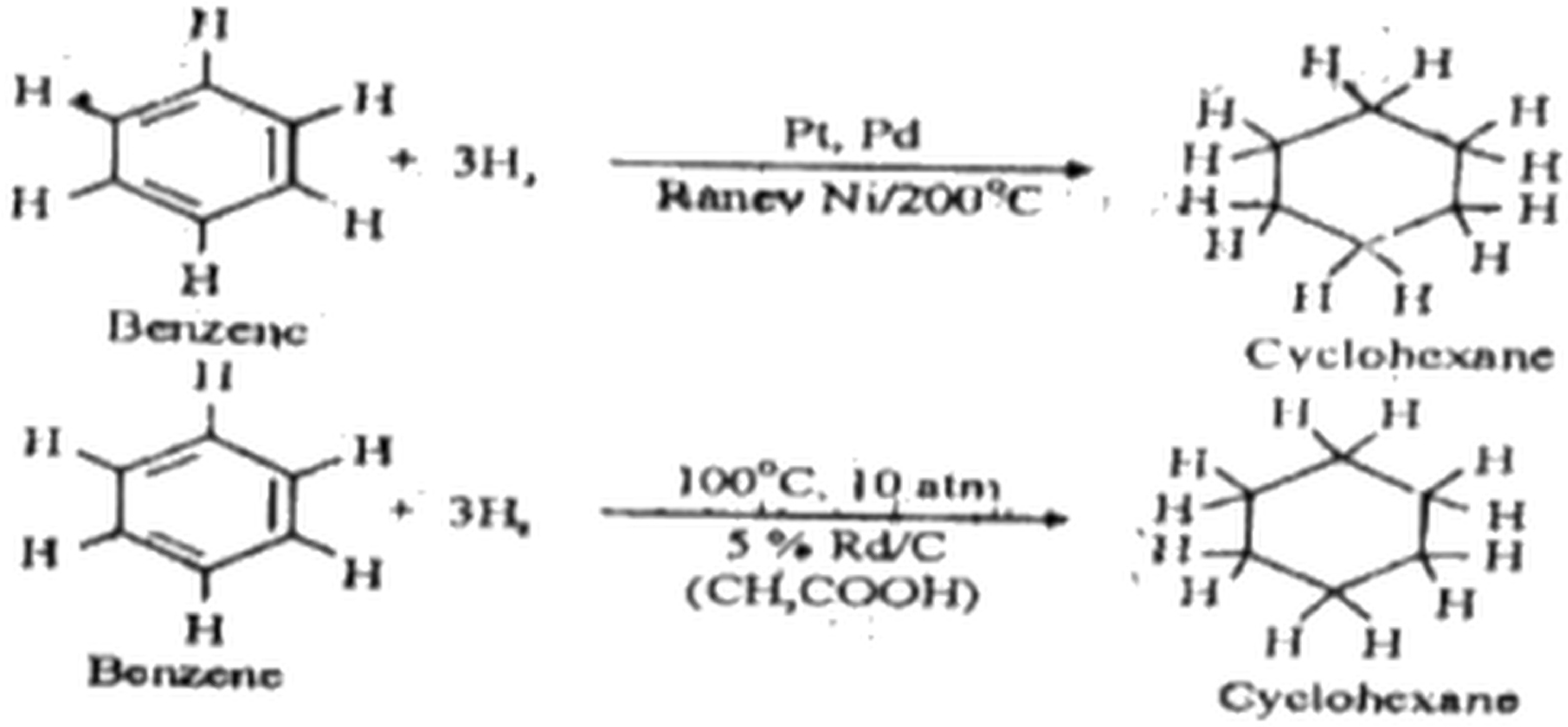
Benzene is highly unsaturated compound. It has three double bonds in it. But it does not undergo addition reaction happily. The reason is that it shows resonance. The delocalization of six pi-electrons makes it extra stable.

So, for addition reaction benzene requires more vigorous condition than that of alkenes and alkynes.

1) Catalytic Hydrogenation

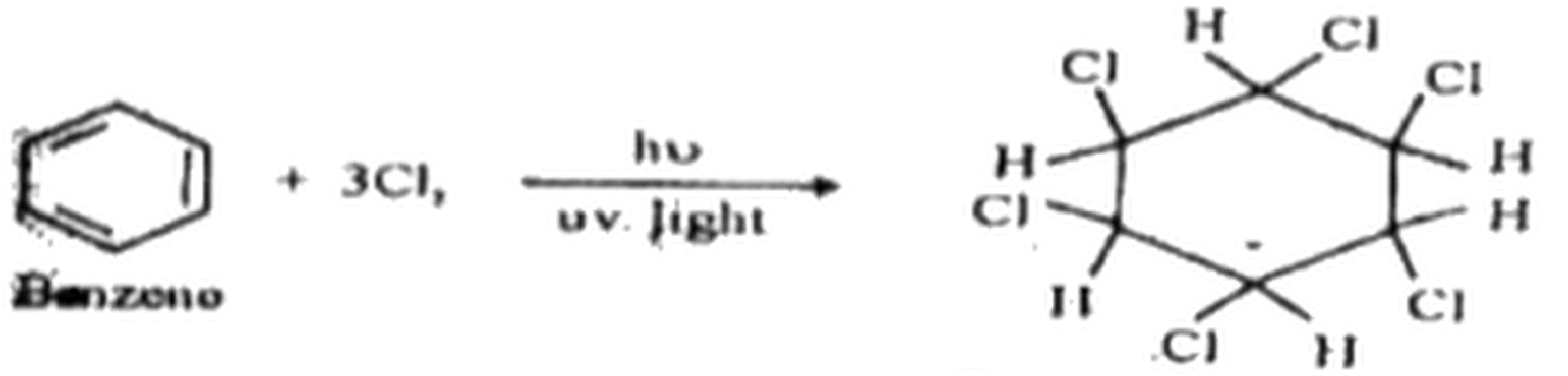
Benzene can be hydrogenated in the presence of a catalyst as Pt, Pd, or Raney Ni only at higher temperature and pressures.

If we use the metals like Ru, Rh, supported at carbon then hydrogenation becomes easier

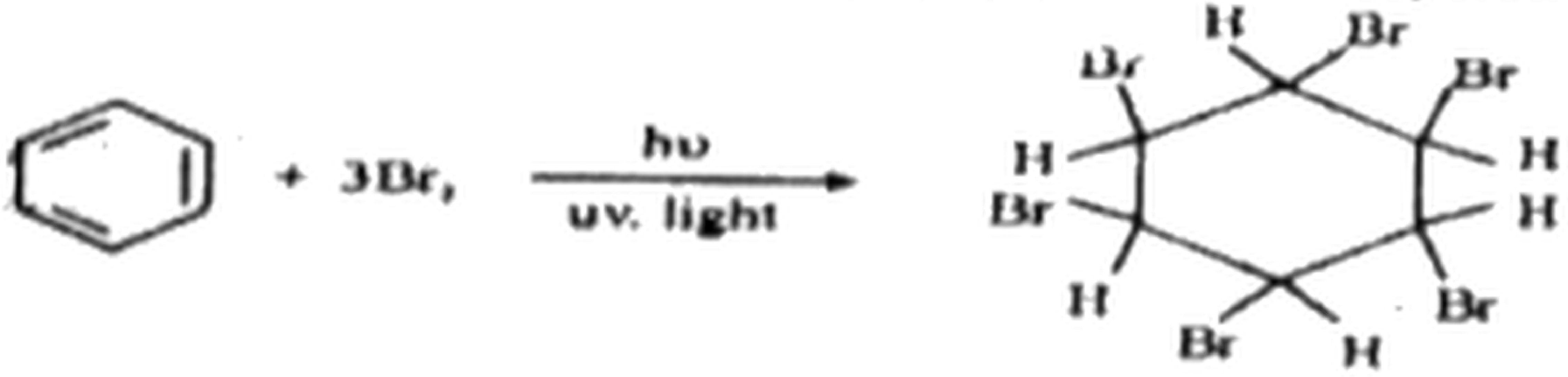


2) Addition of Halogens

Benzene can add three molecules of chlorine or bromine under the influence of light. The benzene ring becomes saturated, and we get benzene hexachloride and benzene hexabromide. This reaction shows that benzene has three double bonds in the ring.



Benzene hexachloride
1, 2, 3, 4, 5, 6-hexachlorocyclohexane



Benzene hexabromide
1, 2, 3, 4, 5, 6-hexabromocyclohexane

Reaction of Fa and I_2:

The reaction of F_2 with benzene is very vigorous, while with I_2 it is very slow.

Conclusion:

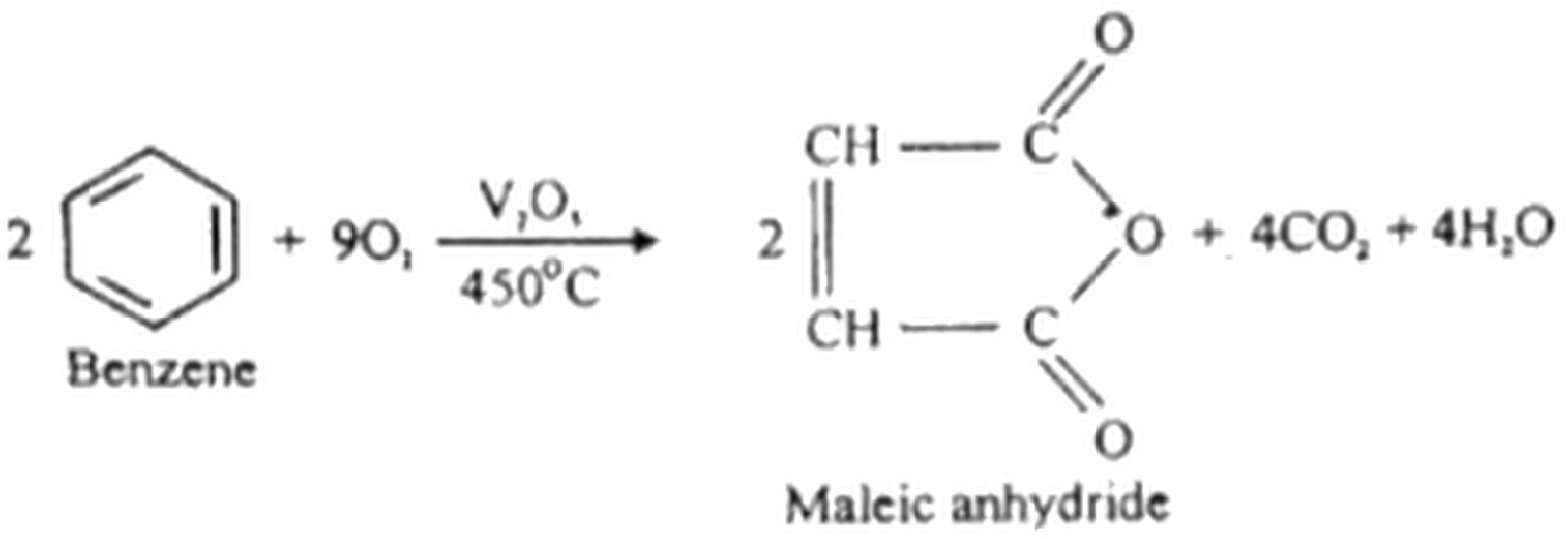
The addition reaction of hydrogen and chlorine show that benzene is unsaturated hydrocarbon and has three double bonds in it.

3) Oxidation Reactions

Benzene is stable towards general oxidizing agents. However, it can be oxidized under certain conditions:

i) Catalytic Oxidation

When benzene is oxidized with air in the presence of V20s at 450^0C, then we get maleic anhydride



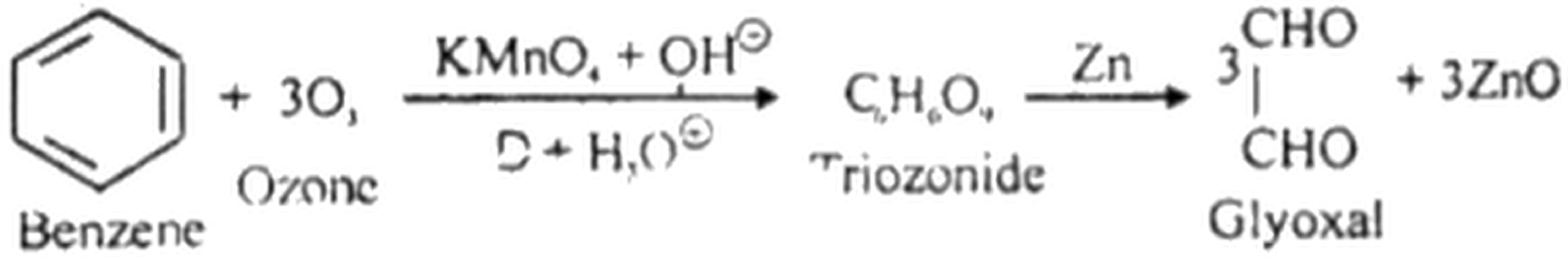
This is commercial method for the preparation of maleic anhydride. Benzene is not oxidized by $KMnO_4$ or $K_2Cr_2O_7$.

ii) Combustion:

When benzene is burnt in the presence of air or oxygen, C02 and H20 are produced, just like other aliphatic hydrocarbons

iii) Ozonolysis:

Benzene reacts with ozone and gives glyoxal. First of all triozonide is produced as an intermediate



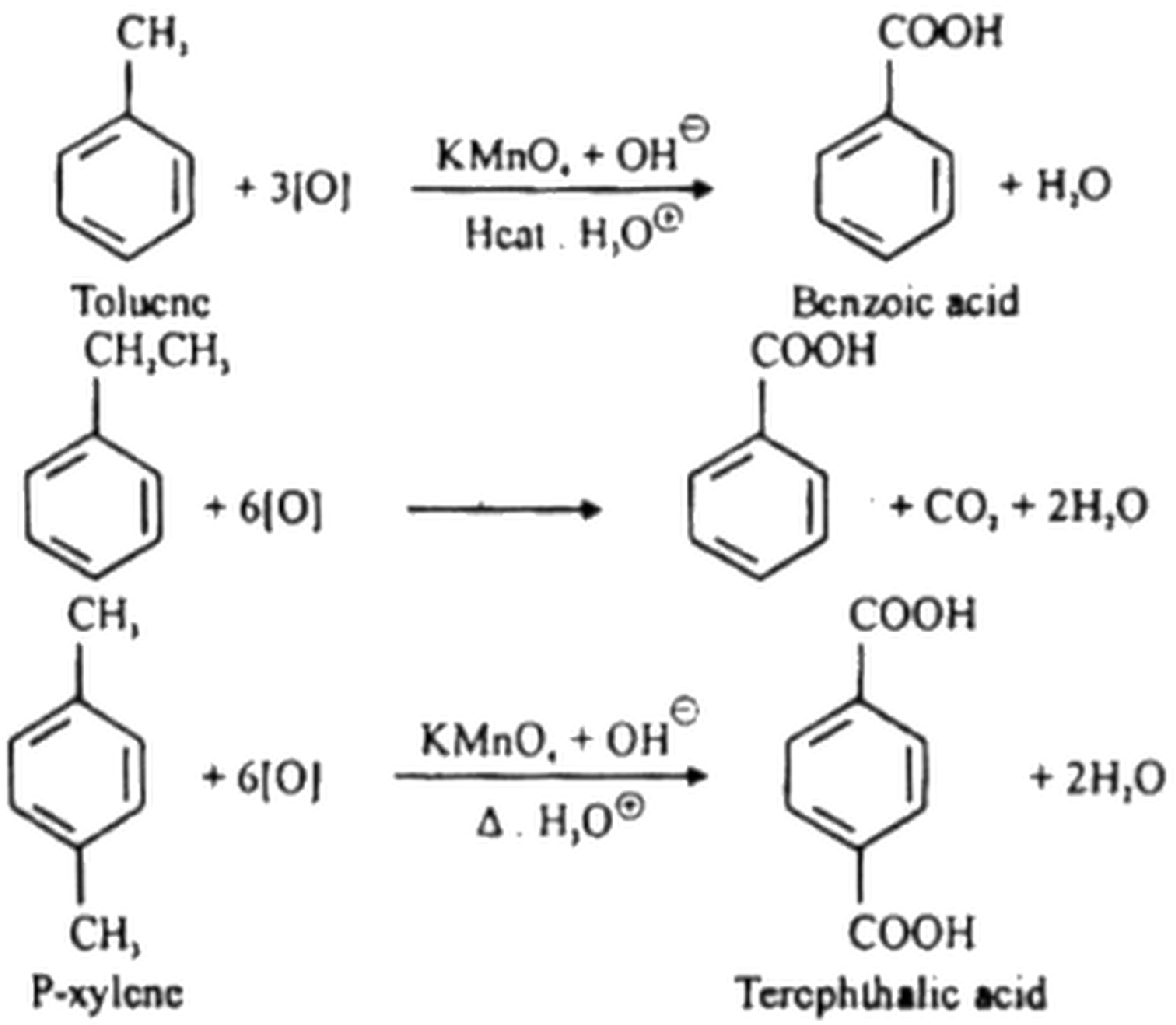
iv) Oxidation of side chain:

Alkyl groups present in the benzene ring are oxidized into carboxylic groups. The oxidizing agents are:

1) $KMnO_4 + H_2SO_4$

2) $K_2Cr_2O_7 + H_2SO_4$

3) Dil. HNO_3



Conclusion:

When both methyl groups are oxidized and benzene ring remains unaffected, then it means that benzene ring is stable towards oxidizing agents.

Q20. Give electrophilic aromatic substitution reactions of benzene.

Answer

General Introduction

The pi-electrons of benzene are highly stabilized due to resonance. They are not readily available for the electrophilic attack like the electros of alkenes. They do not assist in the attack of weak electrophiles. Hence more powerful electrophiles are required for a successful attack to penetrate and break the continuous sheath of electron cloud in benzene.

Explanation and Example:

Substitution of halogen in benzene requires iron or corresponding ferric halide as catalyst. It reacts with halogen molecule to produce a powerful electrophile:

1) **Formation of a strong electrophile (X+)**

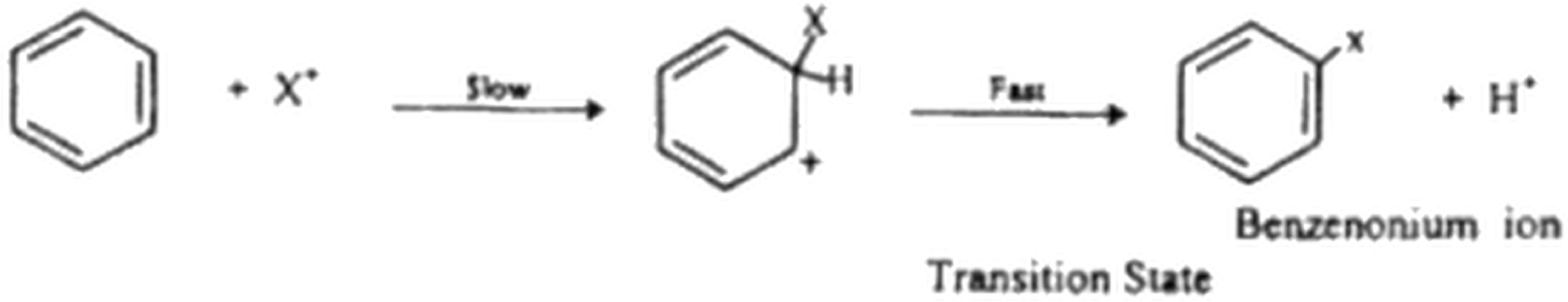
$$2Fe + 3X_2 \rightarrow 2FeX_3$$

$$FeX_3 + X_2 \rightarrow Fex^{-}_4 + X^{+}$$

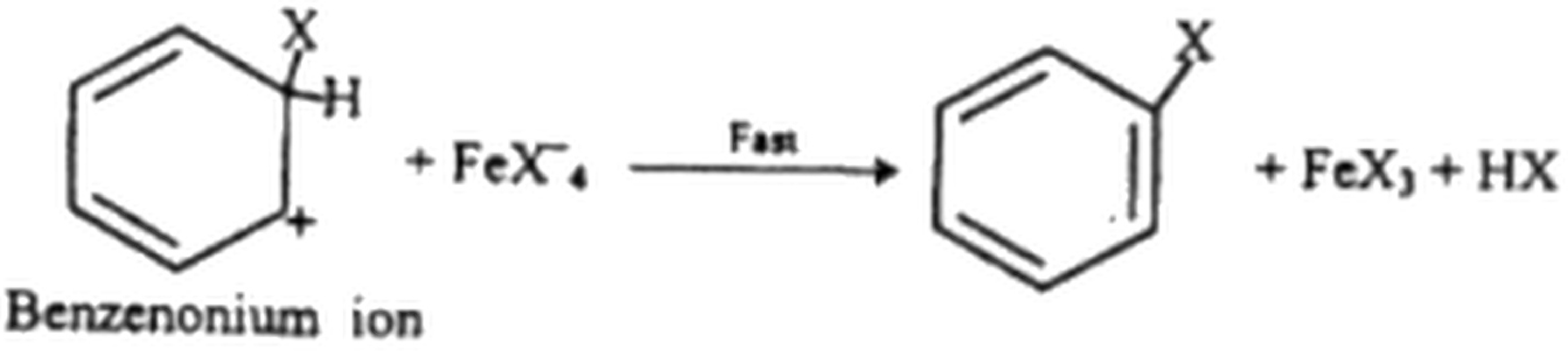
Tetra haloferrate ion (III) Halogenoium ion

2) **Attack of electrophile at pi-bond:**

The halogenation ion thus produced attacks as a powerful electrophile on the electrons of benzene ring.

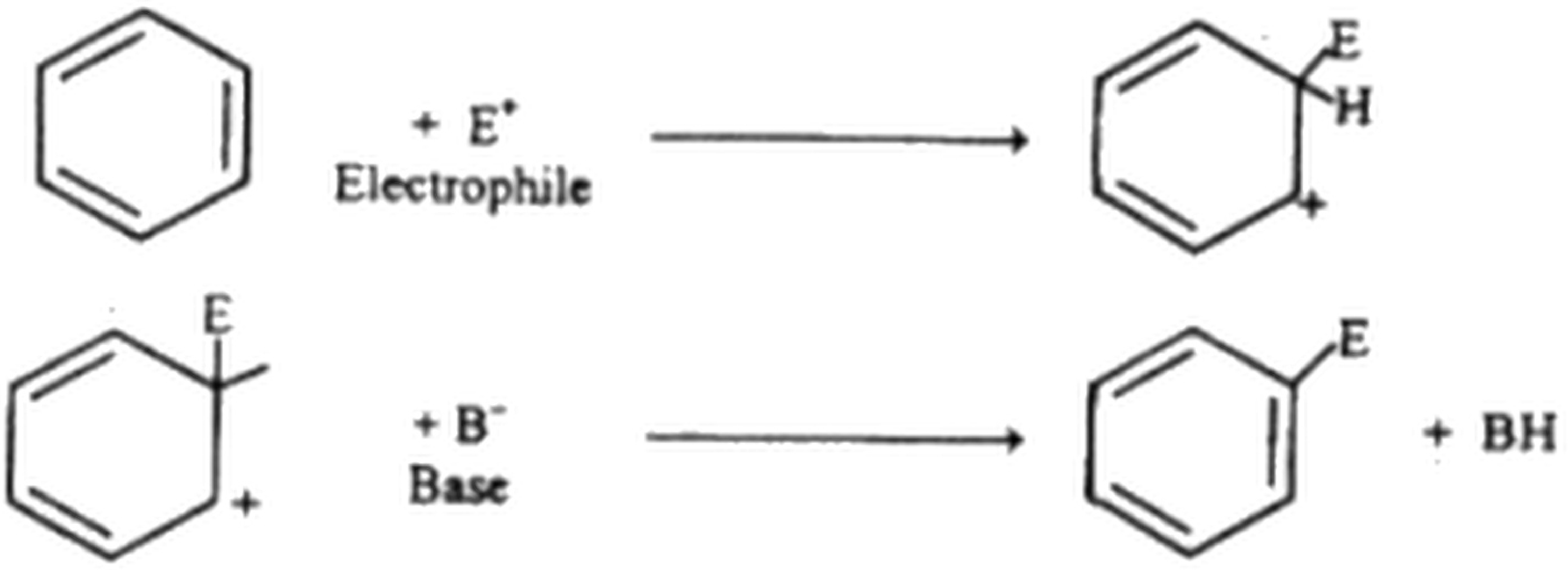


It had benzene unstable. The stability is retained by. the removal of H-atom to give substitution product.

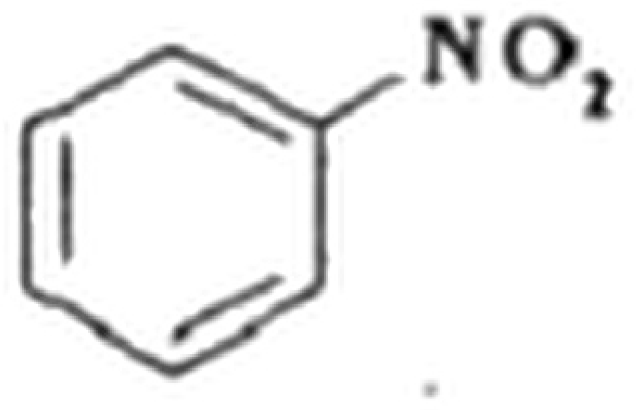
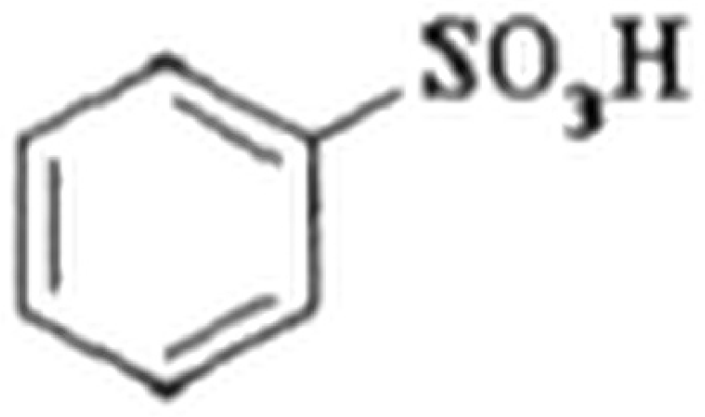
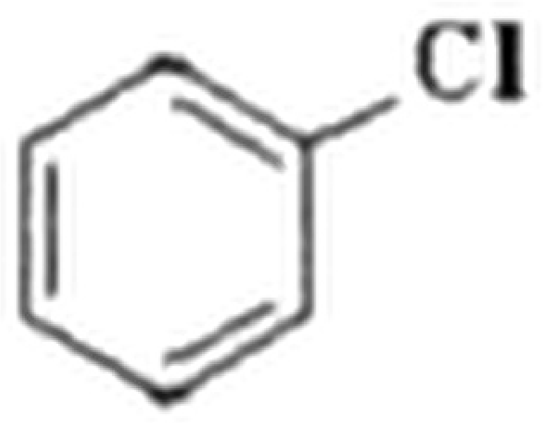
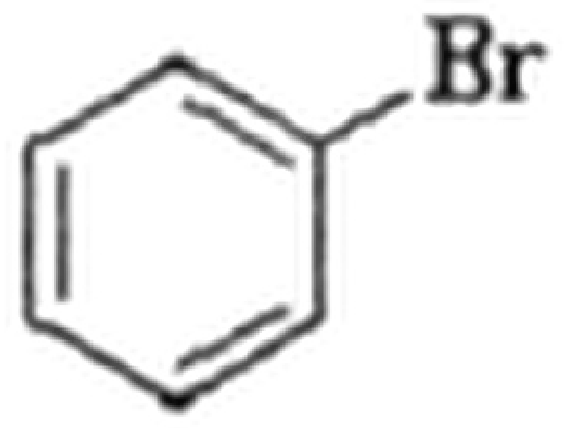


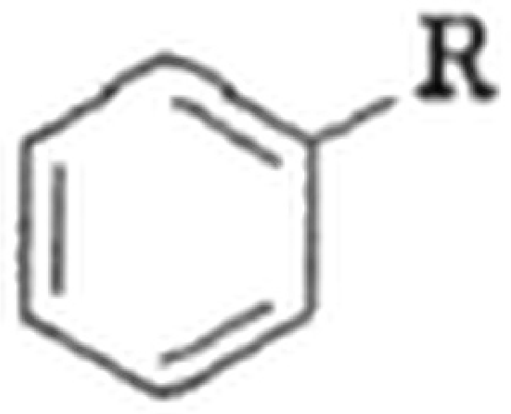
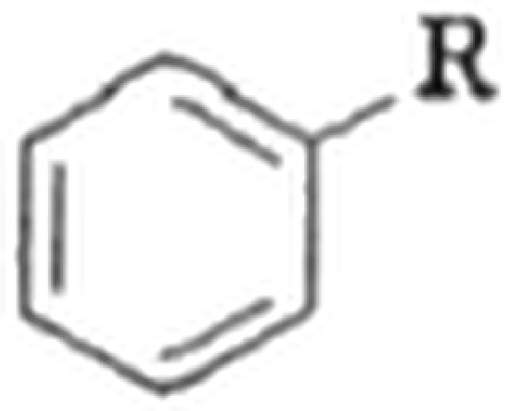
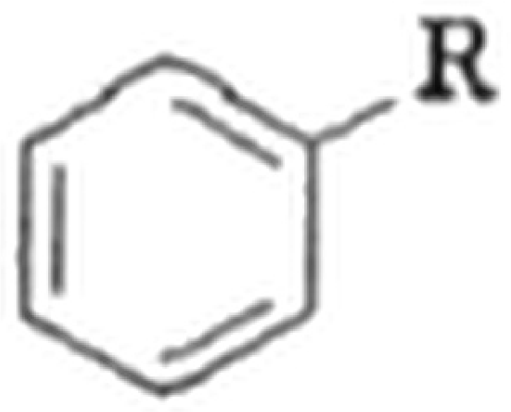
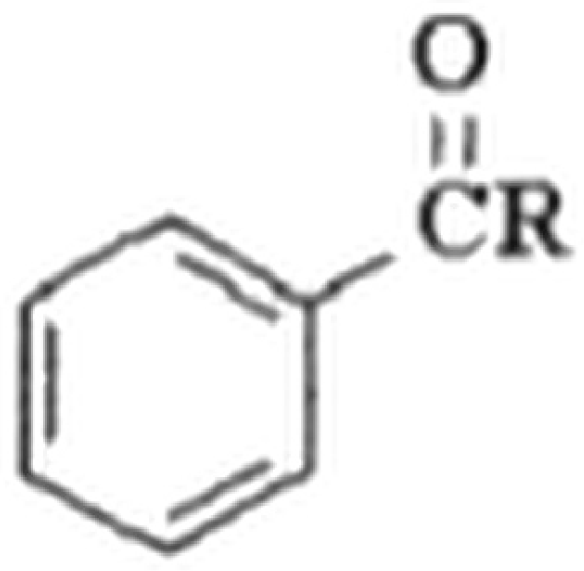
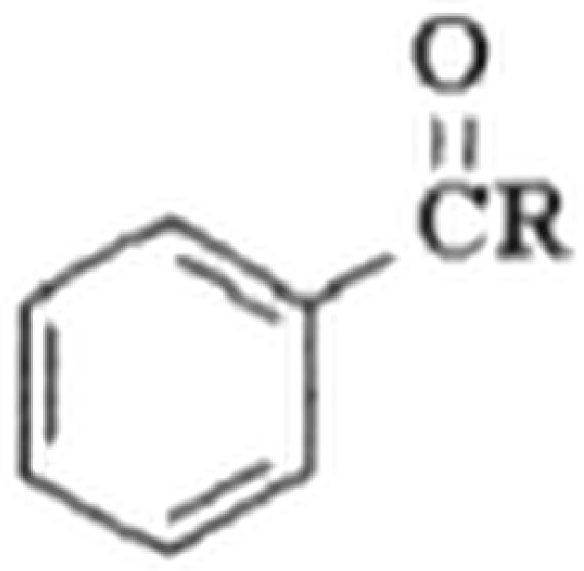
General Pattern of Substitution

The general pattern of the chemical reactivity of benzene towards electrophiles can be shown as follows.

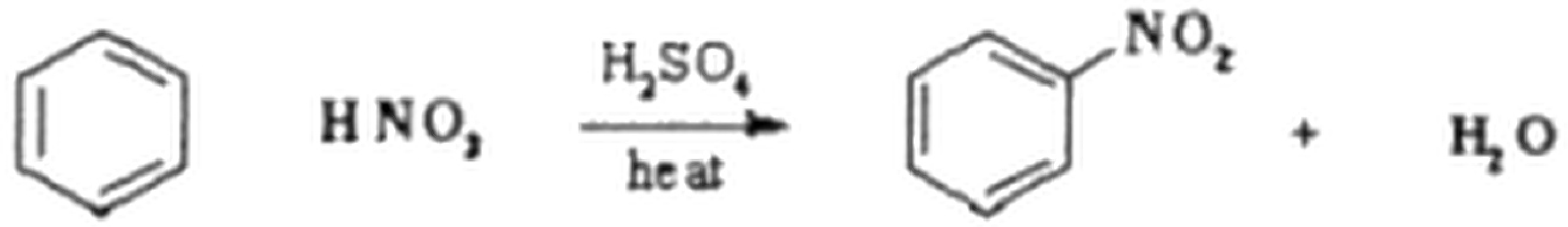


Substitution is preferred over addition in order to preserve the stable aromatic character

Reaction	Reagents	Electrophile	Product	Comments
Nitration	HNO_3 / H_2SO_4	NO_2^+		E+ formed by loss of water from nitric acid
Sulfonation	H_2SO_4 or SO_3 / H_2SO_4	SO_3		Reversible
Halogenation	Cl_2 / Fe or $FeCl_3$	Cl^+		E+ formed by Lewis acid removing Cl
	Br2 / Fe or $FeBr_3$	Br^+		E+ formed by Lewis acid removing Br

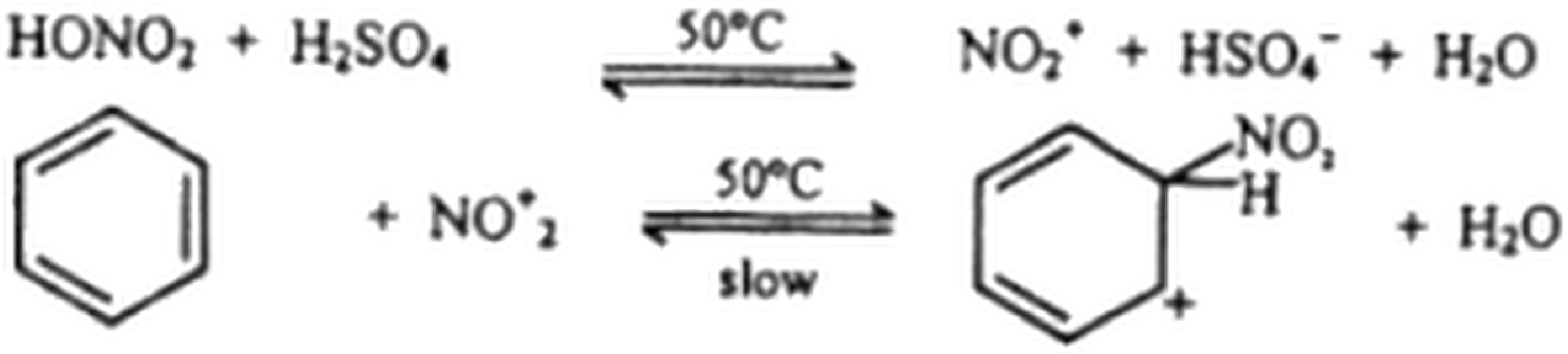
Alkylation	$R - Cl$ / $AlCl_3$	R^+		E+ formed by Lewis acid removing Cl
	$R\text{-}OH$ / H^+	R^+		E+ formed by protonation of alkene
	$C = C$ / H^+	R^+		E+ formed by Lewis acid removing Cl
Acylation	ROOCl / $AlCl_3$	RCO^+		E+ formed by Lewis acid removing Cl
	RCO_2COR / $AlCl_3$	RCO^+		E+ formed by Lewis acid removing RCO_2

Nitration



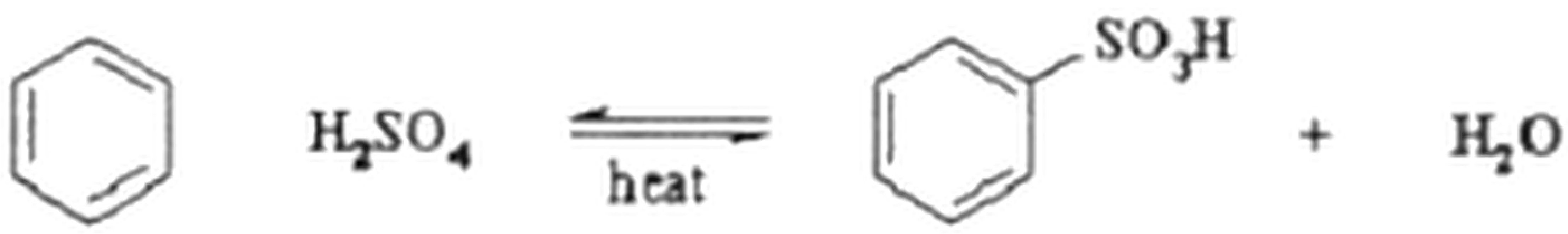
Mechanism

Sulphuric acid reacts with nitric acid to generate nitronium ion.

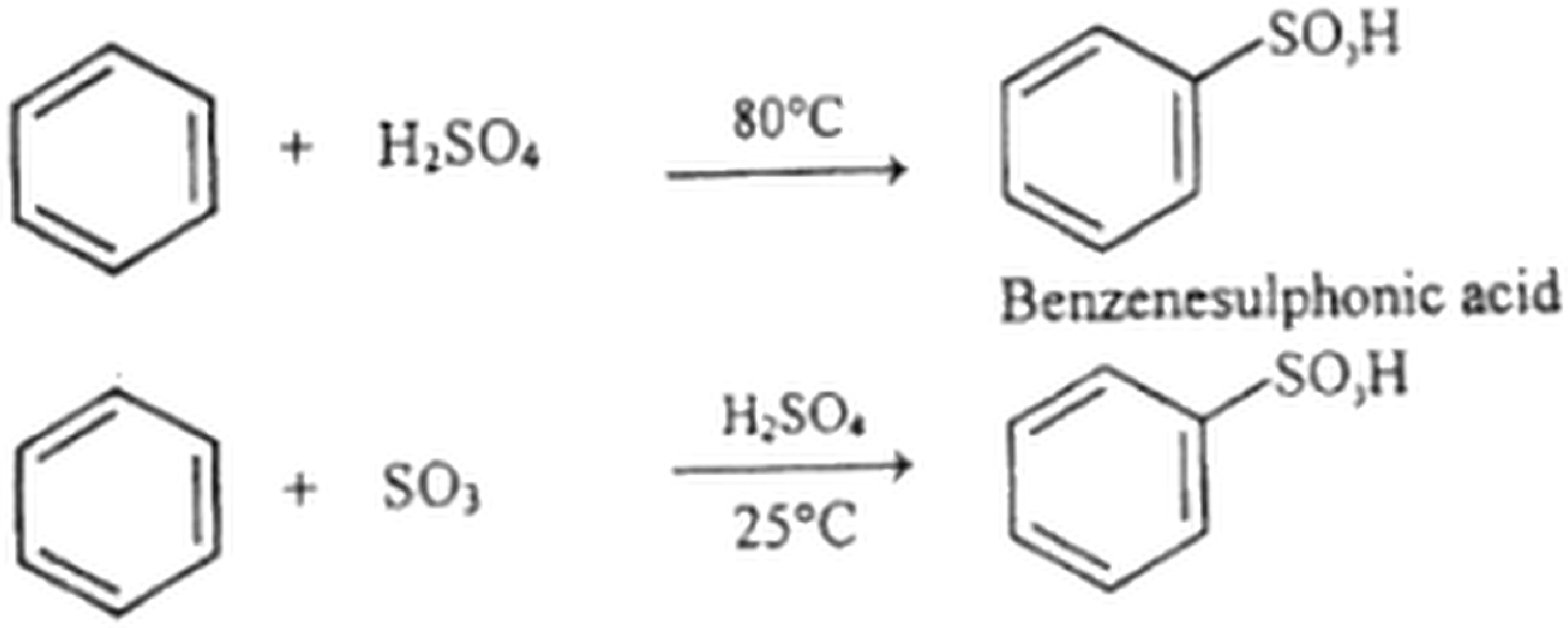


Nitrobenzene

3) Sulfonation



The introduction of sulphonic acid group in benzene rig is called Sulphonation. When benzene is heated with fuming H_2SO_4 or concentrated H_2SO_4 it yields benzene sulphonic acid. Fuming H_2SO_4 has free sulphur trioxide which is electron deficient (electrophile) and causes substitution.

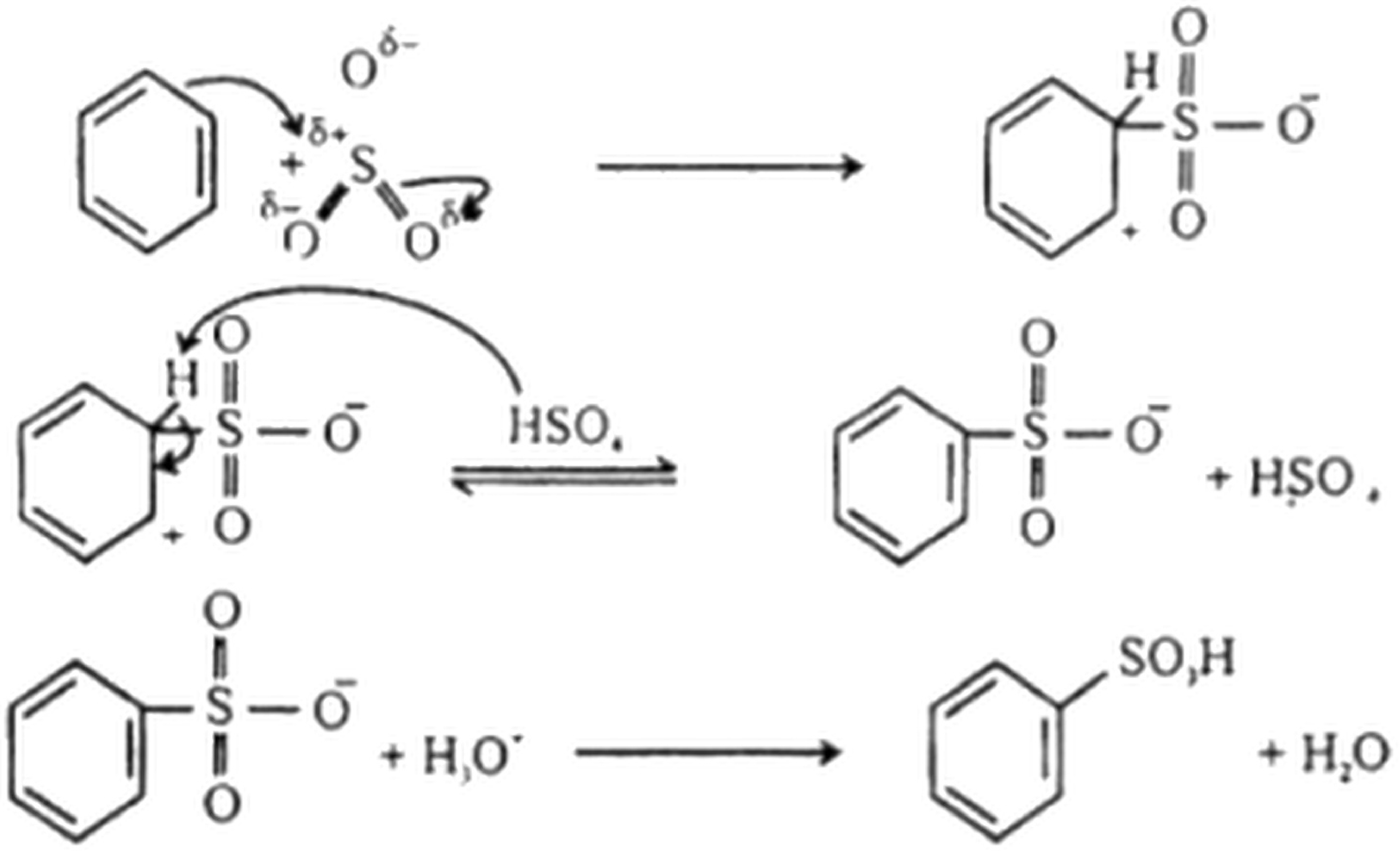


Benzenesulphonic acid

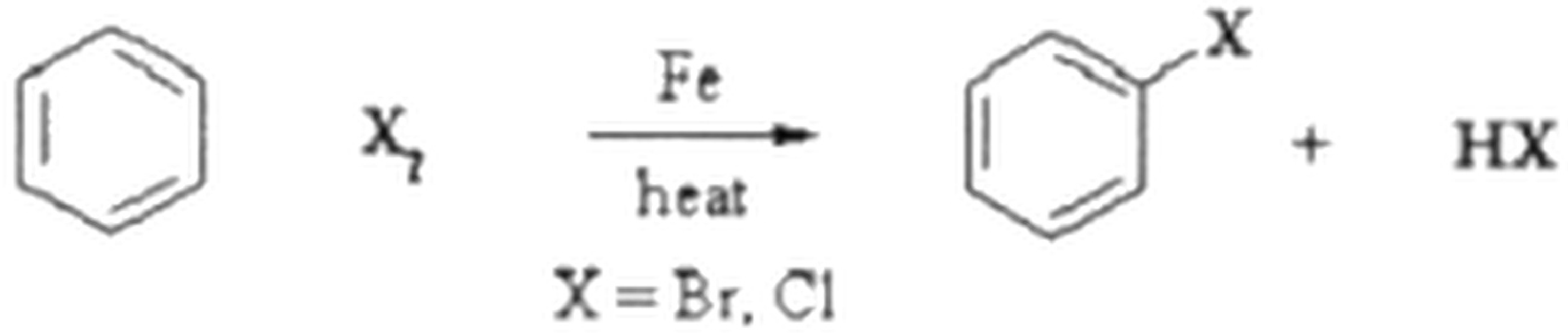
Mechanism:

When sulphuric acid alone is used, the actual electrophile in this reaction is S03

$$H_2SO_4 + H_2SO_4 \rightleftharpoons H_3O^+ + SO_3 + HSO_4^-$$



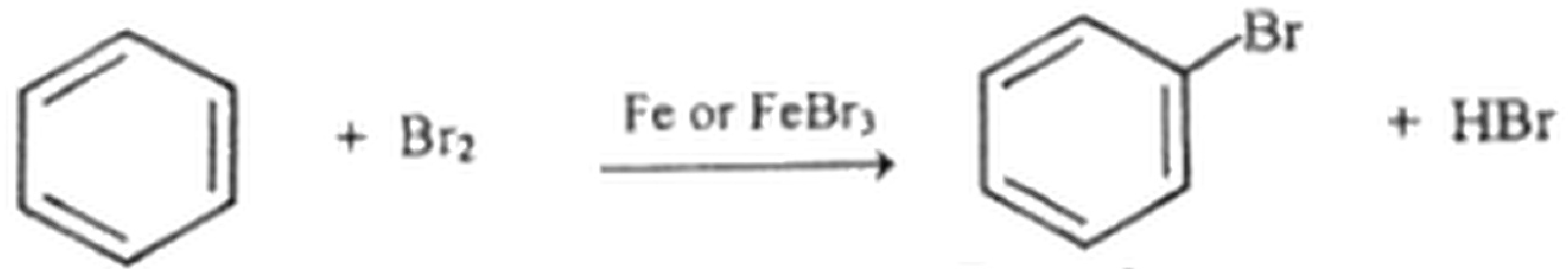
4) Halogenation



The introduction of halogen in benzene ring is called halogenation.

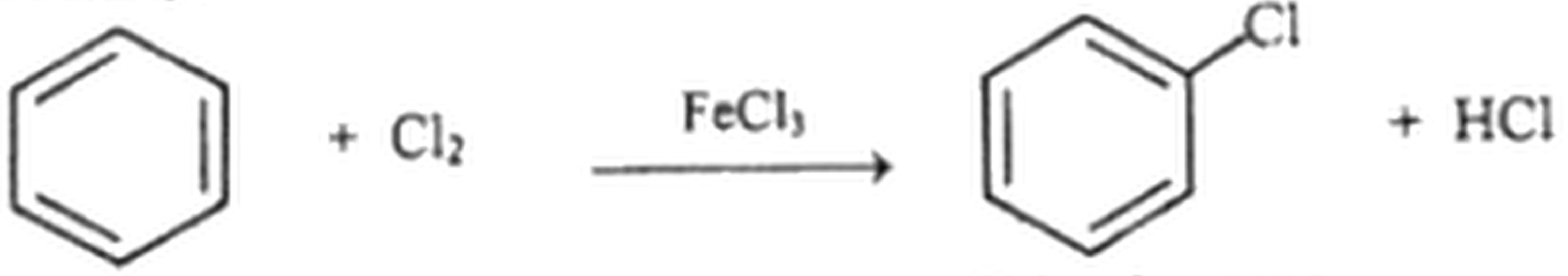
Explanation and Example:

Halogenation of benzene occurs with halogens (X) in the presence of a catalyst FeX3 or Fe. Chloroformation and bromination are normal reaction but fluorination is too vigorous to control. Iodination gives poor yield.



Bromobenzene

Similarly,



Chlorobenzene

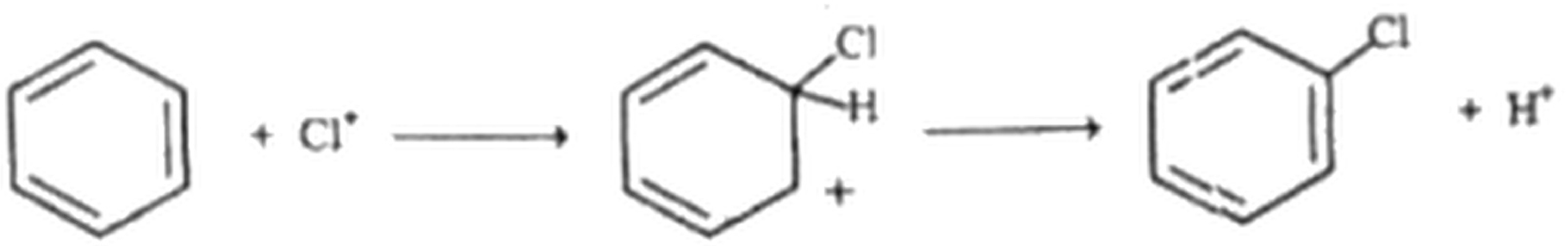
Mechanism:

The actual halogenation agent is X that is formed by the following mechanism

$$X2 + FeX3 \longrightarrow X^{+} + feX^{-}_{4}$$

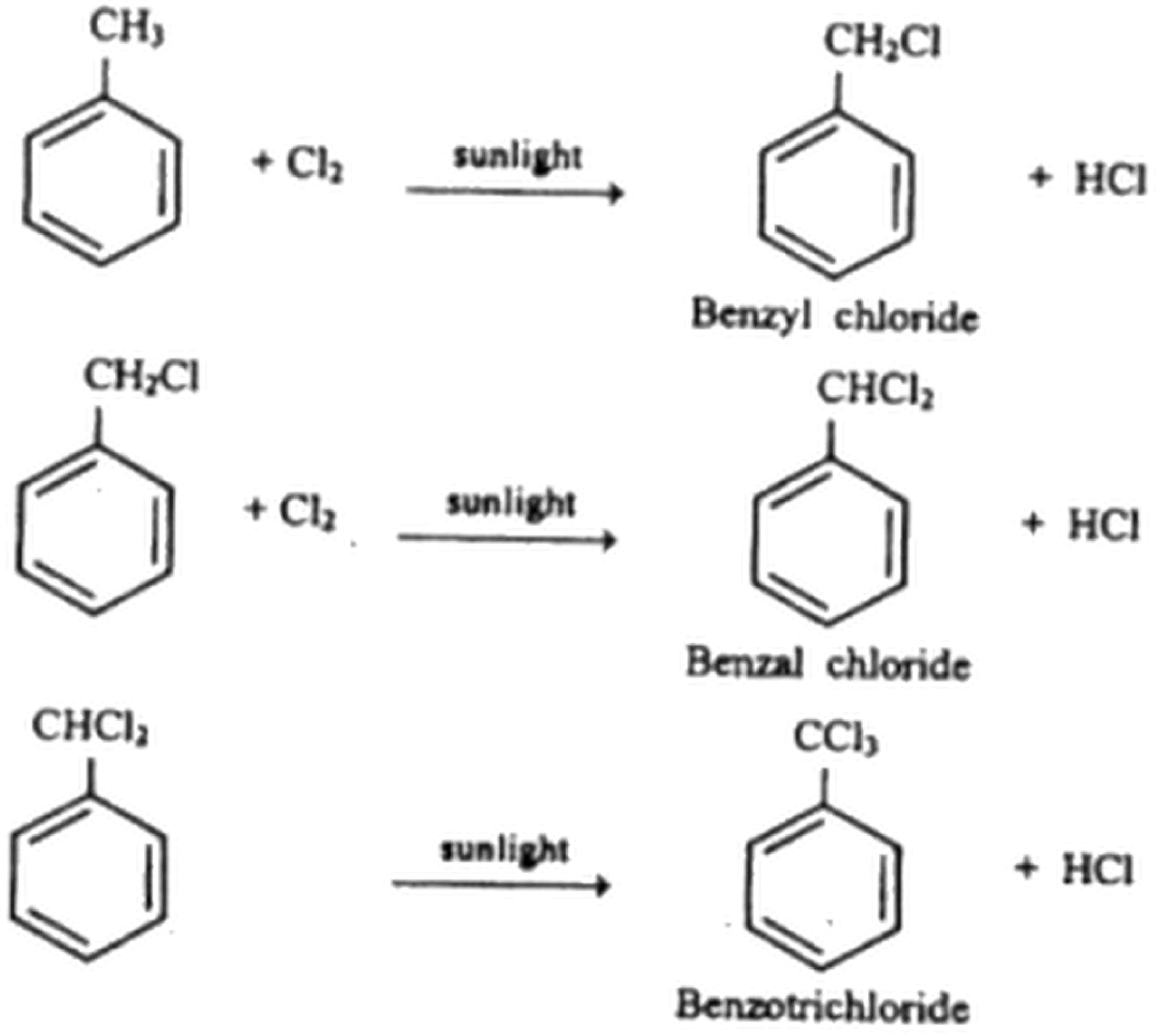
$$Cl_2 + FeCl_3 \longrightarrow Cl^{+} + FeCl^{-}_{4}$$

Cl+ being a strong electrophile is ready for successful attack on benzene.



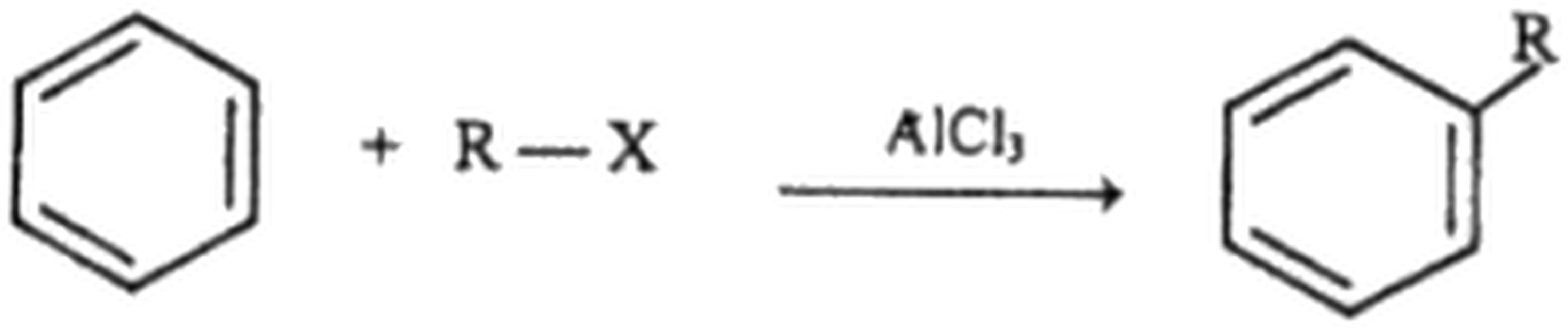
$$FeCl^{-}_{4} + H^{+} \longrightarrow HCl + FeCl_3$$,

When alkyl benzenes are treated with chlorine or bromination the presence of sunlight, only the alkyl groups are substituted.

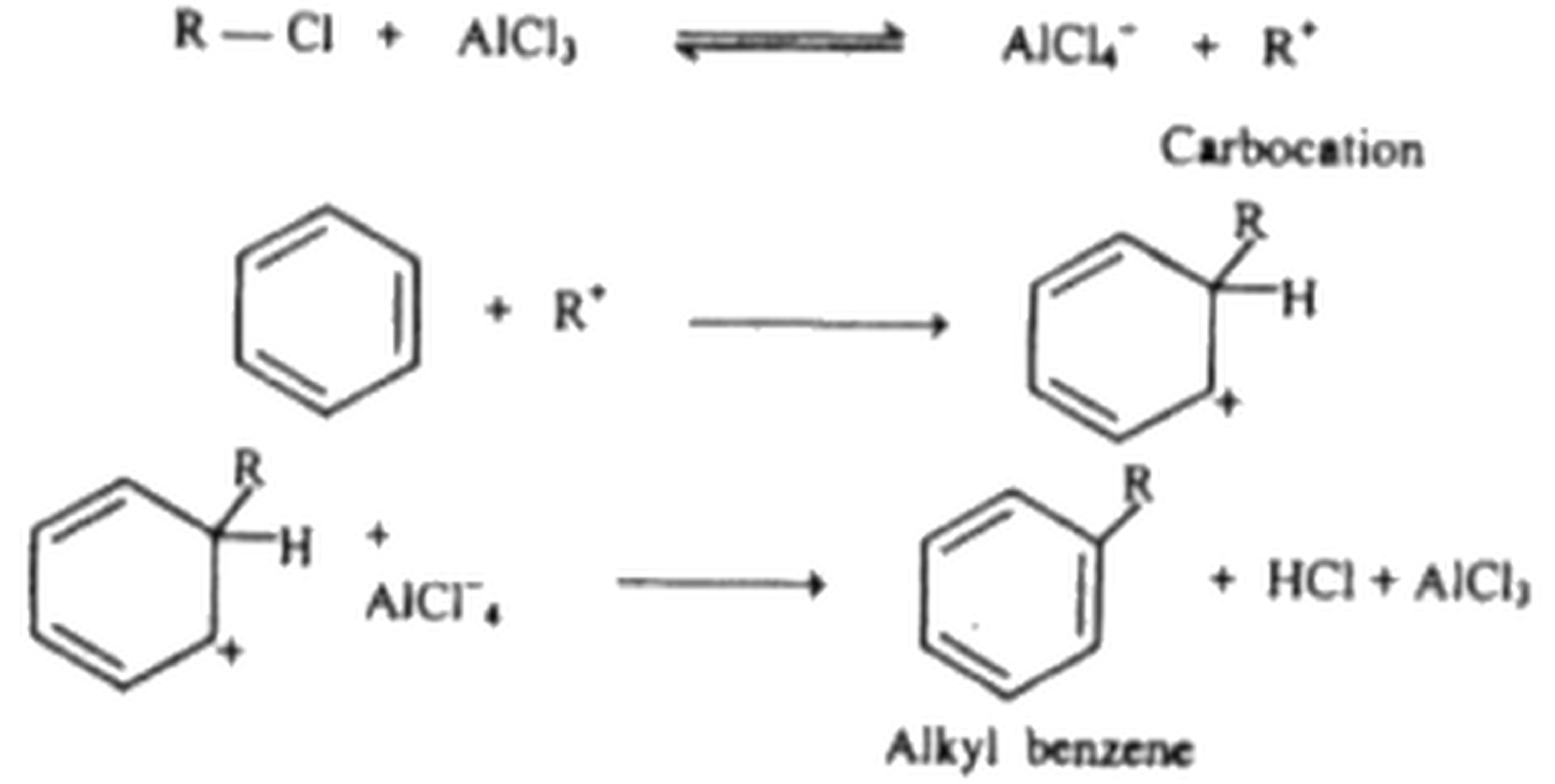


5) Friedel-Crafts Alkylation

The introduction of an alkyl group in the benzene ring in the presence of an alkyl halide and a catalyst $AlCl_3$ is called Friedel Crafts alkylation or Alkylation.



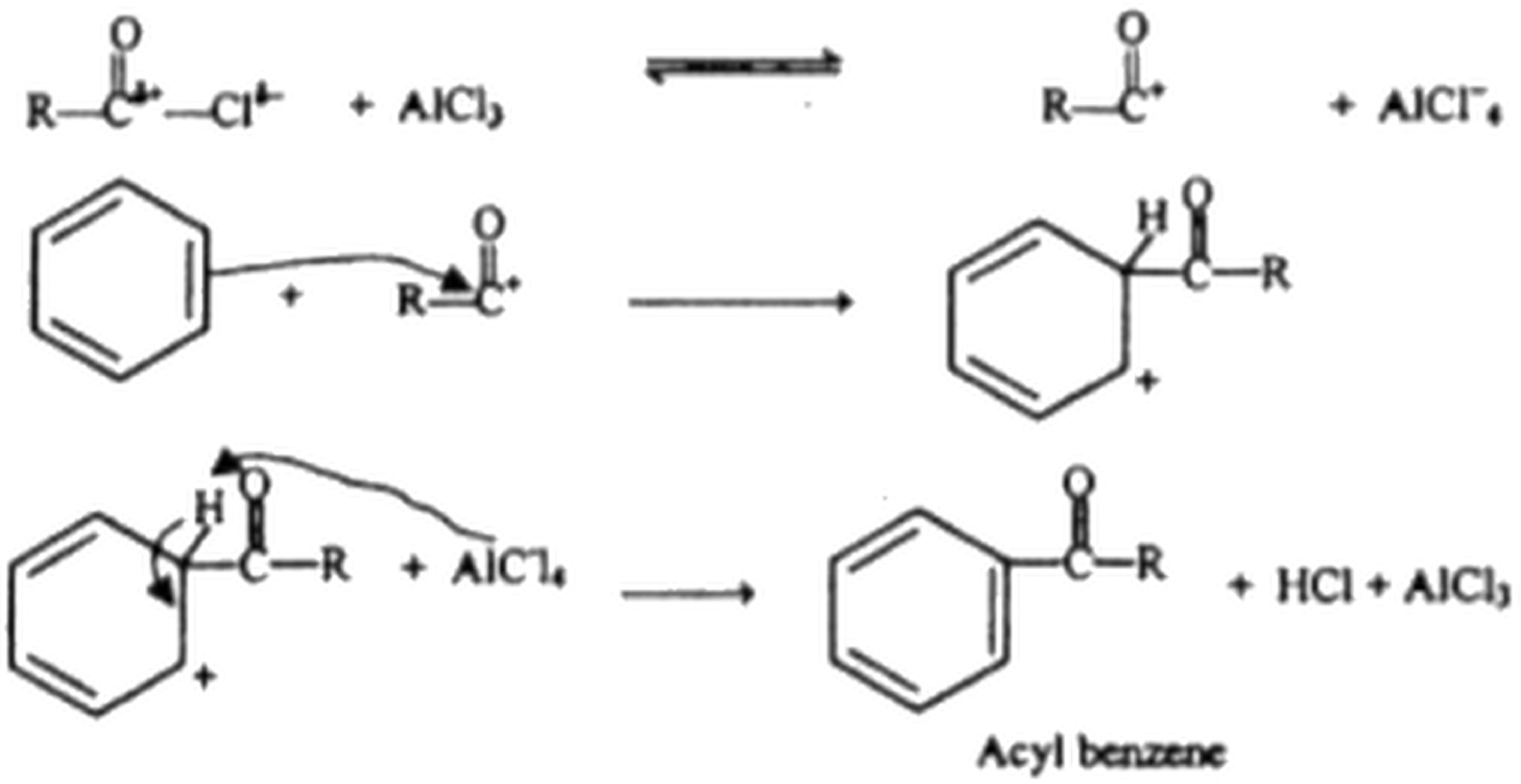
Mechanism:



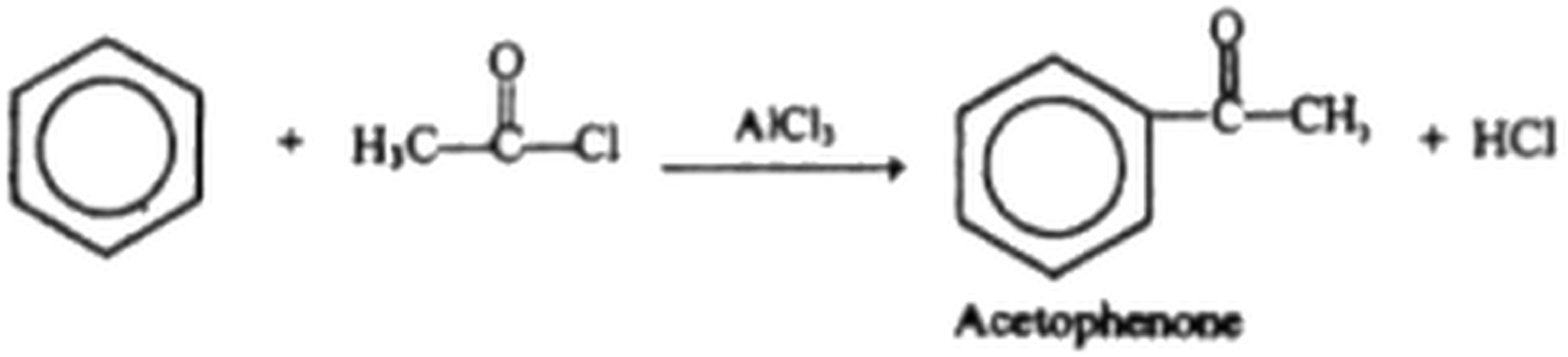
Specific Examples:

6) Friedel-Crafts Acylation

The introduction of an acyl group R-—C in the benzene ring in benzene ring in the presence of an acyl halide and a catalyst AIC13 is called Friedel Crafts Acylation or Acylation.

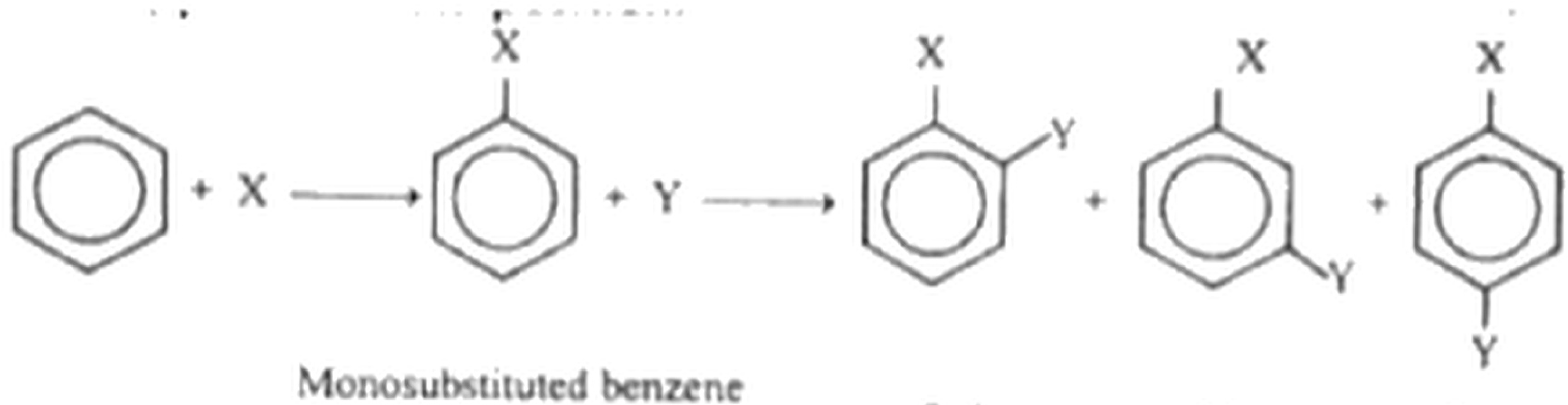


Specific Example:



7) Substituent Effects - (Table of Substituent Effects) and Making Polysubstituted Benzenes

When an electrophilic substitution reaction takes place on benzene ring, we get only one monosubstituted benzene because all the six positions in the ring are equivalent. However, the position of a second group into the ring depends on the nature of the first group. The second substituted any enter in ortho, para or meta position.

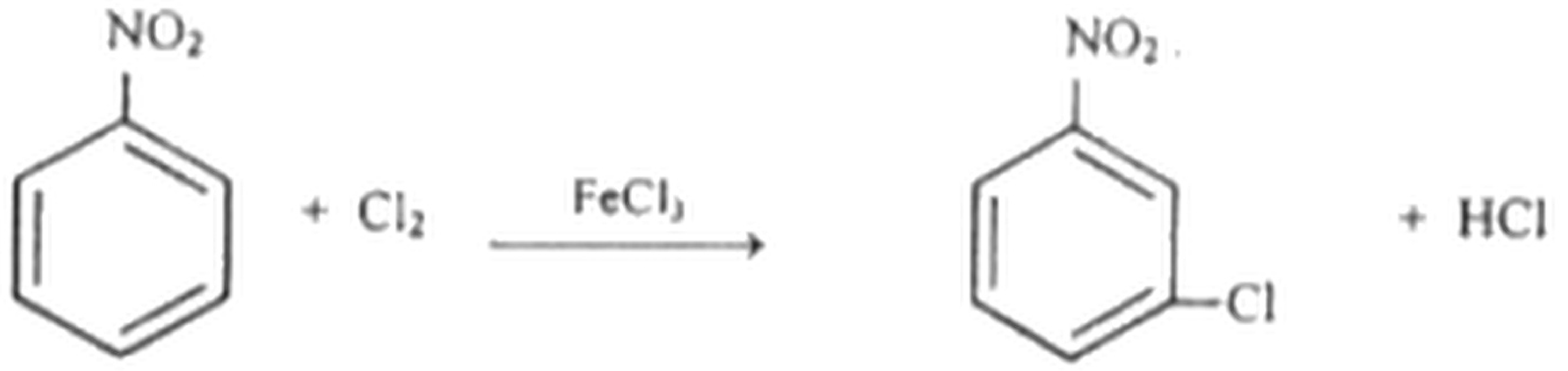


Monosubstituted benzene

Ortho Meta Para

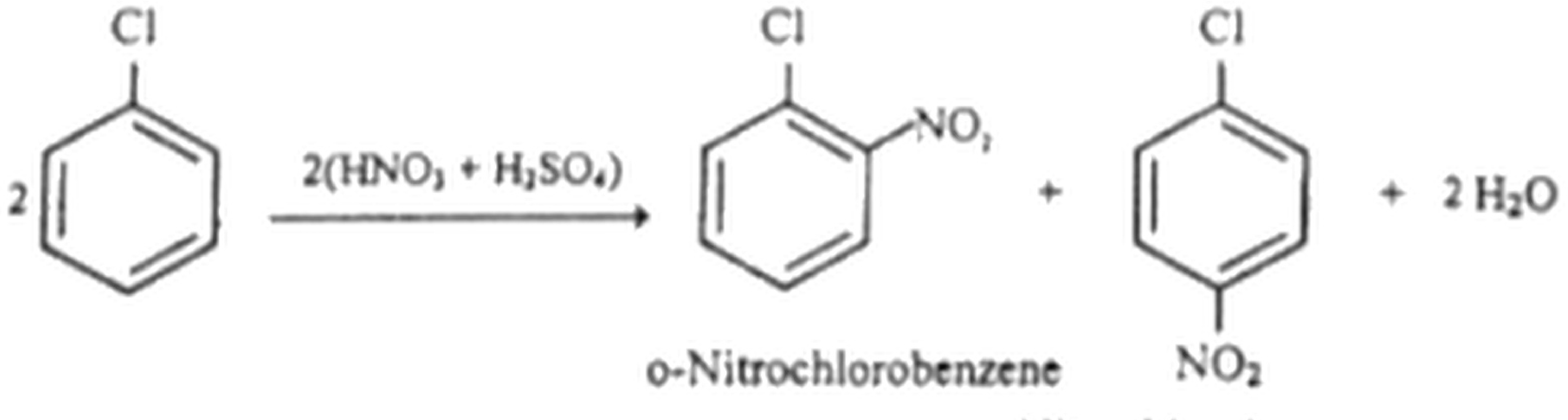
Disubstituted benzene

On chance basis 40% Ortho, 40% meta and 20% para disubstituted products are expected. However, the results do not agree with chance substitution ratio, e.g. mnitrochlorobenzene is the main product of the following halogenation reaction.



m–Nitrochlorobenzene

On the other hand, a mixture of o-nitrochloro-benzene and p-nitrochloro-benzene is obtained from the nitration of chlorobenzene.



o-Nitrochlorobenzene

p-Nitrochlorobenzene

It means that the groups already present in the benzene ring directs the second entrant and thus determines the position, which may be taken up by it. There are two types of groups:

a) Ortho- and para- directing groups

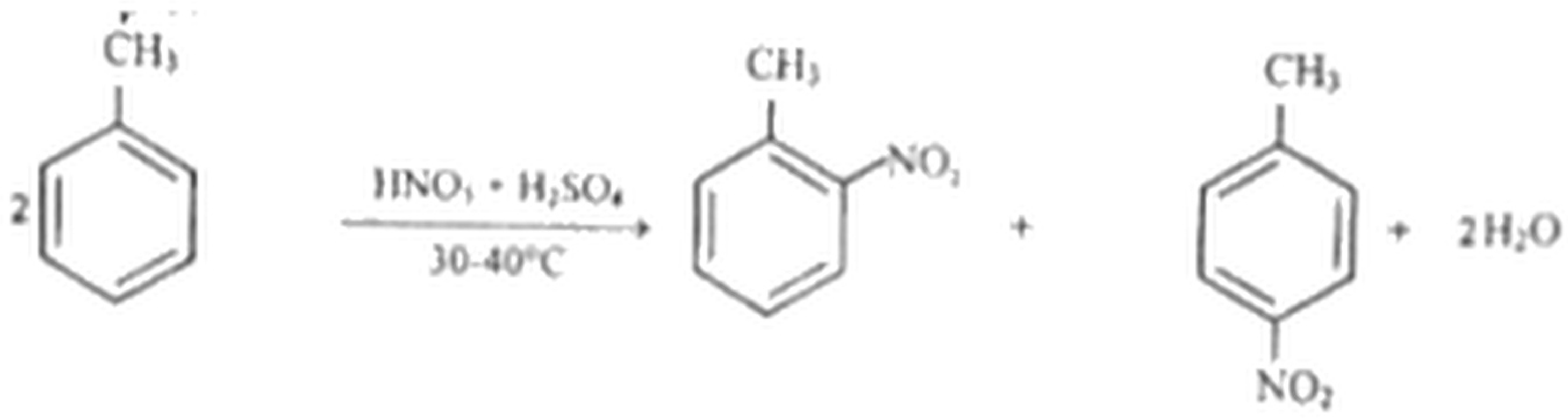
b) meta- directing groups

1) Ortho and para directing groups

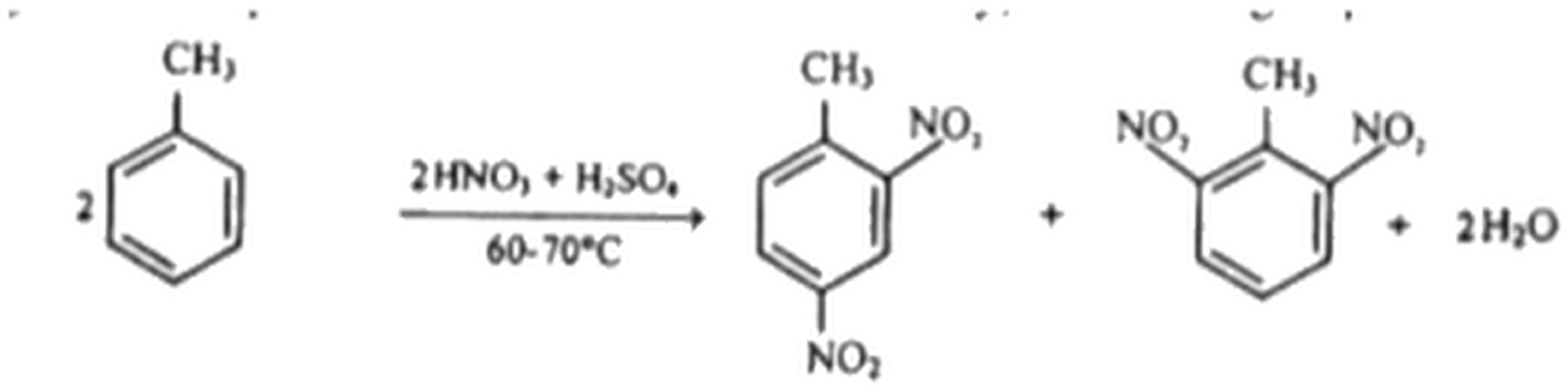
These groups release electrons towards the benzene ring, at ortho and para positions.

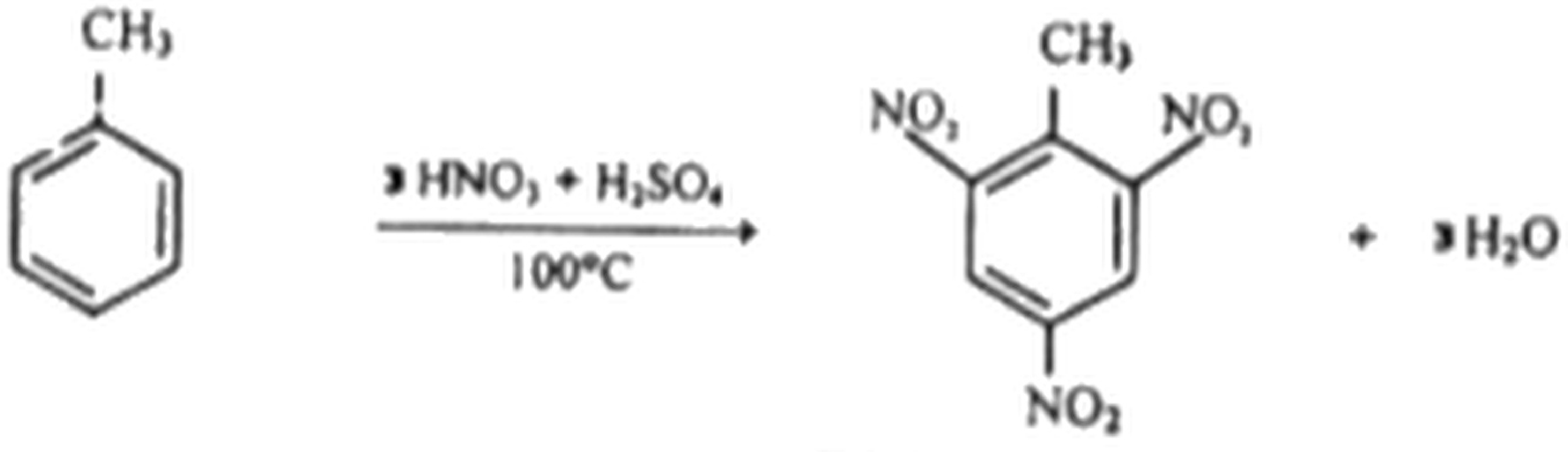
Because these positions are richer in electron for attack of an electrophile. The second group is substituted at ortho and para positions. They also enhance the reactivity of benzene ring.

Example:



The electron releasing effect of methyl groups is significant and it makes the ring a good nucleophile. Due to this increased reactivity, more nitro groups can enter the ring.





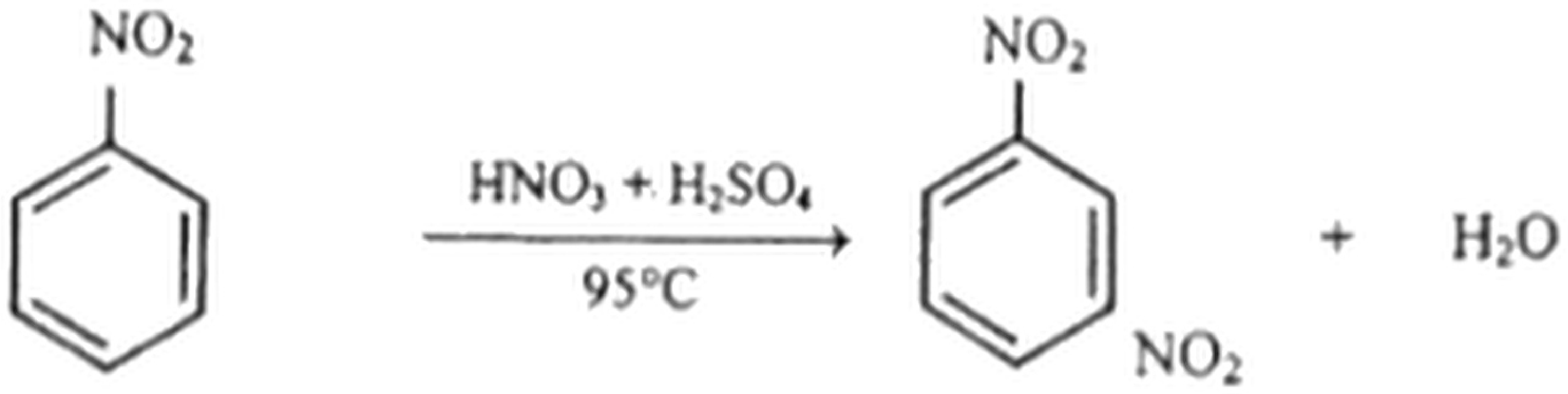
Trinitrotoluene (TNT)

Other examples of ortho and para directing groups are:

- $N(CH_3)_2$, $-HNH_2$, $-OH$, $-OCH_3$, $-Cl$, $-Br$, $-I$

2) Meta-Directing Groups

These groups withdraw the electrons of the benzene ring from ortho and para positions. Due to the electro withdrawing effect of such substituents, the of the and para position are more electrons deficient than the meta position. Thus the incoming electrophile will prefer to attack on meta position rather than ortho and para positions. These groups are called meta-directing groups. These groups decrease the chemical reactivity of benzene.



The substitution of third nitro groups is not possible because nitro group has deactivated the ring, other examples of meta directing groups are

-C ≡N, NO_2, -COOH, -CHO.

Rule:

If the electronegativity of the atom of the group attached to the benzene ring is greater than any atom of the group, the whole group will act as electron repelling, will increase the reactivity of benzene all direct the new entrant to ortho, para positions. On the other hand

If the electronegativity of such atom is less, it will be under constraint and it turn withdraw electron form the ring making it less reactive and directing the new to meta position

e.g.

(i) —NH_2 Nitrogen with greater electronegativity from hydrogen.

ii) -Cl has no other atom hence will have no danger of pulling electrons. Thus it is electron repelling and O, P directing group. Hence O, P, directing

O

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i) - N —O Nitrogen with less E.N from O. Hence meta directing.

ii) In —SO_3H E.N of oxygen is greater than that of S. hence oxygen disturbs sulphur, which in turn withdraws electrons from benzene ring hence m-directing.

Making Polysubstituted Benzenes

Since the position of electrophilic attack on a substituted benzene ring is by the substituent already present rather than the approaching electrophile, the order of events in the synthesis of polysubstituted benzenes need careful planning to ensure success.

The two factors that need to be monitored are:

I) regiochemistry

2) reactivity (for example Friedel-Crafts reactions are limited to halobenzenes and activated benzenes)

Uses of Hydrocarbons

I) Butane is used as a fuel in lighter.

2) Butane is also used in same camping stoves 3) Crude petroleum is lighter than water.

4) Coal is used for the manufacturing of synthetic petrol

5) Ethylene is the hormone that causes tomatoes and apples to ripen

6) Oxyacetylene torch is used for cutting of metals

7) Methane is used to manufacture urea fertilizer

8) Kekule was the scientist who draw the structure of benzene