Unit

1

Alkanes, Alkenes and Alkynes

(By : Dr. B. C. Dixit &
Dr. H. R. Maradiya)

1.1 Introduction :

In the early stages of the development of chemistry it was believed that substance derived from living matters can not be synthesized in laboratories. This view was called the *vital force theory*. This view was discarded after the first organic compound, urea, was synthesized in the laboratory by German Scientist Wohler.

In 1828 he prepared urea (NH_2CONH_2) in laboratory by heating potassium cyanate (KCNO) and ammonium chloride (NH_4Cl).

$$KCNO + NH_4Cl \xrightarrow{\text{Heat}} NH_4CNO + KCl$$

$$NH_4CNO \xrightarrow{\text{Heat}} \underset{\text{Urea}}{NH_2CONH_2}$$

1.2 Organic Chemistry :

The word "organic" was introduced by Berzelius in 1780 to introduce chemicals which were obtained from living sources.

Organic chemistry has long been regarded as a separate and unique branch of chemistry, organic chemistry is the body of knowledge which is concerned with the physical and chemical properties of the broad group of carbon compounds containing hydrogen and one or more additional elements like oxygen, nitrogen, sulphur etc. However, compounds of carbon containing only carbon and oxygen like CO, CO_2, CO_3^{-2} are not studied under organic chemistry. Similarly, compounds containing carbon and nitrogen are not considered to be organic compounds.

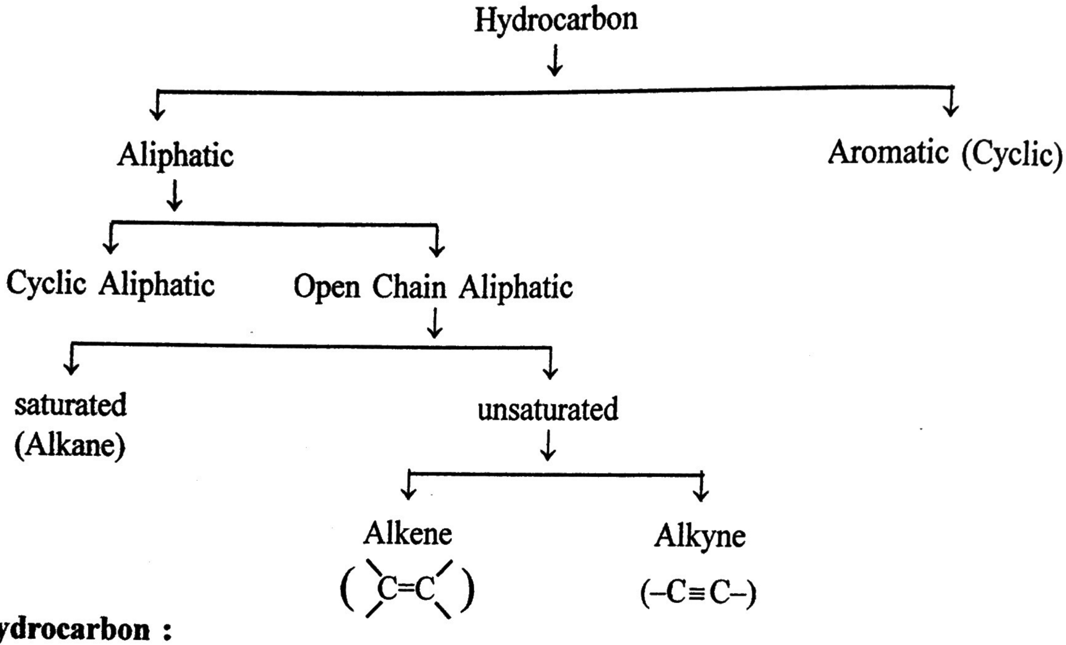
To understand organic chemistry, knowledge of valency of atoms is essential.

Valency of different atoms :

Atom	Valency
H	1
O	2
N	3
C	4
S	2, 4 or 6

Carbon atom has an unique property by the virtue of which it forms regular covalent bonds with other carbon atoms. This property of carbon atom is known as **catenation.** Due to tetravalency. It is able to form stable C–C bond and multiple bonds like C=C, C≡C, C=S, C≡N etc.

- **Classification of hydrocarbon :**



Hydrocarbon :

The compounds that contain only carbon and hydrogen atoms are known as hydrocarbons. e.g. Methane (CH_4), Ethane (C_2H_6) etc.

Saturated hydrocarbon :

A hydrocarbon in which the four valencies of each carbon atom are satisfied by single covalent bonds is called a saturated hydrocarbon. e.g. methane, ethane, propane etc.

Unsaturated hydrocarbon :

It is a compound in which, carbon atom is bonded to another carbon atom by a double bond OR triple bond are called unsaturated hydrocarbon. e.g. Ethylene, propylene etc.

Alkanes : Alkanes or paraffins are hydrocarbons in which carbon atoms form single bonds with one another. Their general formula is C_nH_{2n+2} where 'n' is the number of carbon atoms. e.g. Methane, Ethane etc.

Alkenes : The acyclic unsaturated hydrocarbons which contain carbon - carbon double bonds are called alkenes. These are also called olefins (olefiant = oil forming). They have the general formula C_nH_{2n}, each having two less hydrogen atoms than the corresponding alkane, C_nH_{2n+2}. e.g. Ethene, Propene etc.

Alkynes : The acyclic unsaturated hydrocarbons which contain carbon - carbon triple bonds are called alkynes. They have the general formula C_nH_{2n-2}. e.g. Ethyne.

Alkyl groups :

The group having general formula C_nH_{2n+1} is known as alkyl group. One hydrogen remove from alkane give corresponding alkyl group and is named simply by dropping '–ane' from the name of corresponding alkane and replacing it by '–yl'. The general formula of alkyl group is C_nH_{2n+1} e.g. $-CH_3$, C_2H_5 etc.

Cycloalkane :

Saturated hydrocarbon in which the carbon atoms are arranged to form a closed ring is called cycloalkane. e.g. cyclohexane. They are alkanes that contain a ring of three or more carbons having general formula C_nH_{2n}.

The general formula of alkane is : C_nH_{2n+2} e.g Methane, ethane etc.
The general formula of alkene is : C_nH_{2n} e.g. Ethylene, Propylene etc.
The general formula of alkyne is : C_nH_{2n-2} e.g. Acetylene (Ethyne).
The general formula of cycloalkane is : C_nH_{2n} e.g. Cyclopropane, Cyclohexane.

1.3 Alkyl groups :

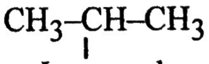
Names are given to certain groups that constantly appear as structural units of organic molecules. For example chloromethane, CH_3Cl, is known as methyl chloride. The CH_3 group is called methyl wherever it appears, CH_3Br being methyl bromide; CH_3I, methyl iodide; and CH_3OH, methyl alcohol. In an analogous way, the C_2H_5 group is ethyl; C_3H_7, propyl, C_4H_9, butyl and so on.

These groups are named simply by dropping –ane from the name of the corresponding alkane and replacing it by –yl. They are known collectively as alkyl groups. The general formula for an alkyl groups is C_nH_{2n+1}, since it contains one less hydrogen than the parent alkane C_nH_{2n+2}. e.g. $-CH_3$, $-CH_2CH_3$ etc.

Among the alkyl groups the property of isomerism is observed. There is only one methyl chloride or ethylchloride, and correspondingly only one methyl group or ethyl group. However, there are **two propyl groups**, as shown below. Both these groups contains the propane chain.

$CH_3-CH_2-CH_2^-$

n–Propyl



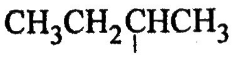
$CH_3-\underset{|}{C}H-CH_3$

Isopropyl

Similarly there are **FOUR butyl groups**, two derived from the straight chain n-butane and two desired from the branched chain isobutane. These are given the designations n - (normal), sec - (secondary), and tert - (tertiary), as shown below. Again the difference between isobutyl and tert-butyl lies in the point of attachment of the alkyl groups to the rest of the molecule.

$CH_3CH_2CH_2CH_2-$

n-Butyl group

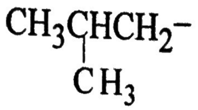


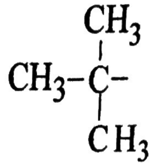
$CH_3CH_2\underset{|}{C}HCH_3$

or

$CH_3\underset{|}{C}HCH_2CH_3$

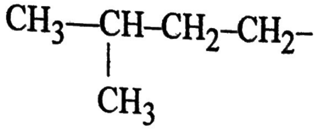
Sec.-butyl group


$CH_3\underset{\underset{CH_3}{|}}{C}HCH_2-$

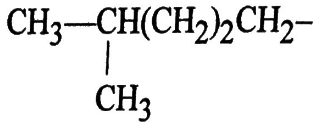

$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-$

Isobutyl group tert-butyl group

Pentane has **FIVE** pentyl groups.


$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-$

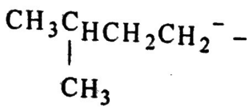
Isopentyl group

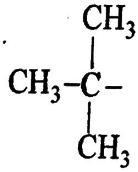

$CH_3-\underset{\underset{CH_3}{|}}{CH}(CH_2)_2CH_2-$

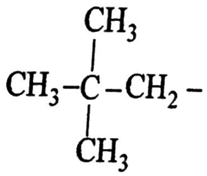
Isohexyl group

$CH_3CH_2CH_2CH_2CH_2^-$, $CH_3\underset{|}{CH}CH_2CH_2CH_3$ or $CH_3CH_2CH_2\underset{|}{CH}CH_3$

n-pentyl sec-pentyl


$CH_3\underset{\underset{CH_3}{|}}{C}HCH_2CH_2^- -$


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


$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-$

Isopentyl t-pentyl Neopentyl

If the branching occurs at any other position, or if the point of attachment is at any other position, this name does not apply (n– and iso–).

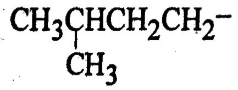
1.4 Common names of alkanes :

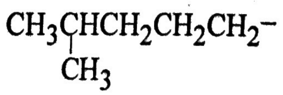
The prefix *n*–, iso– and neo– are used to differentiate the various butanes and pentanes. However, the prefix *n*– can be used for any alkane, in which all carbon atoms form a single continuous chain without branching and its point of attachement is the very end carbon of the molecule.

$CH_3CH_2CH_2CH_2CH_2-$ $CH_3(CH_2)_4CH_2-$

n–Pentyl n–Hexyl

The prefix iso- is used to designate an alkyl group (of six carbons of fewer) that has a single on carbon branch on the next to last carbon of a chain and has the point of attachment at the opposite end of the chain e.g.


$CH_3\underset{\underset{CH_3}{|}}{C}HCH_2CH_2-$

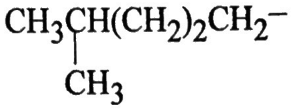

$CH_3\underset{\underset{CH_3}{|}}{C}HCH_2CH_2CH_2-$

Isopenctyl group Isohexyl group

An isoalkane is compound of six carbon or fewer in which all carbon except one form a continuous chain and that one is attached to the next to end carbon.

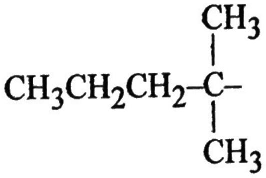
$CH_3CH_2CH_2CH_2CH_2CH_2-$

n–hexyl group



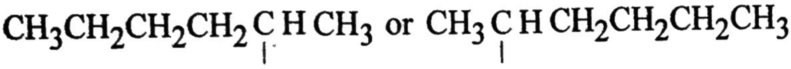
$CH_3\underset{CH_3}{\underset{|}{C}}H(CH_2)_2CH_2-$

isohexyl group



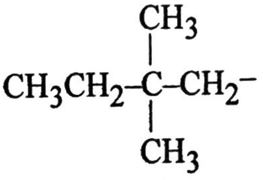
$CH_3CH_2CH_2-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-$

t–hexyl group



$CH_3CH_2CH_2CH_2\underset{|}{C}HCH_3$ or $CH_3\underset{|}{C}HCH_2CH_2CH_2CH_3$

Sec. hexyl group



$CH_3CH_2-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2-$

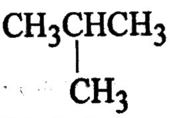
neohexyl group

1.5 IUPAC names of alkanes :

For naming of any higher alkanes, IUPAC (International Union of Pure and Applied Chemistry) system follow the same pattern for all families of organic compounds.

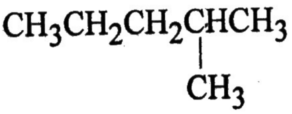
The rules of the IUPAC system are :

1. Select the longest continuous chain of parent structure and then consider the compound to have derived from this structure by the replacement of hydrogen of various alkyl groups. Isobutane (I) can be consider to arise from propane by the replacement of a hydrogen atom by methyl group and thus may be named methyl propane, 2–methyl pentane (II) and 3–methyl pentane (III) can arise from n–pentane by the replacement of hydrogen atom by methyl group.



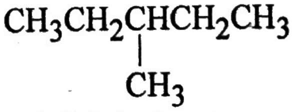
$CH_3\underset{CH_3}{\underset{|}{C}}HCH_3$

2–Methylpropane
(Isobutane)
I



$CH_3CH_2CH_2\underset{CH_3}{\underset{|}{C}}HCH_3$

2–Methylpentane
(Isohexane)
II



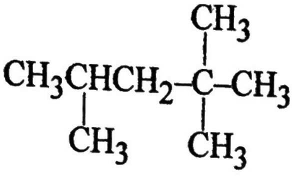
$CH_3CH_2\underset{CH_3}{\underset{|}{C}}HCH_2CH_3$

3–Methylpentane

III

2. Identify the group attached to parent chain.
3. Arrange the name of groups attached alphabetically.
4. Numbering of the carbon chain is given in such a way so that the substituted carbon should gets the **lowest possible** number. Numbering of the parent carbon chain, start either from Left Hand Side or Right Hand Side at whichever end results in the use of the lowest numbers; thus II is called 2–methyl pentane rather than 4–methyl pentane.

5. If the same alkyl group present as a side chain; indicated by the prefix di, tri, tetra etc. and the position of each group is indicate by various number as in 2,2,4–trimethyl pentane (IV).

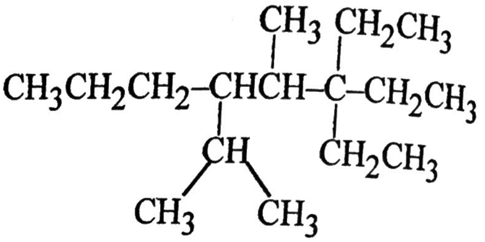


$$CH_3\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3$$

(Isooctane)

IUPAC : 2,2,4–trimethylpentane

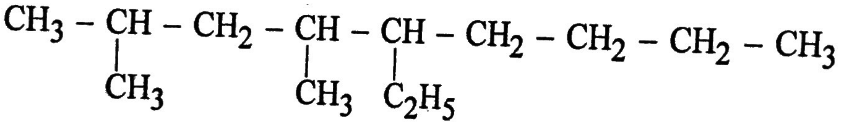
IV



3,3–diethyl–5–isopropyl–4–methyloctane.

V

6. If their are several different alkyl groups attached to the parent chain name them in alphabetical order as in 3,3–diethyl–5–isopropyl–4–methyl octane (V) (Note : iso propyl comes before methyl, would come after ethyl or diethyl). Let us now practice the application of the rules of momenclature of alkanes. We select the following example :



$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}-\underset{\underset{\displaystyle C_2H_5}{|}}{CH}-CH_2-CH_2-CH_2-CH_3$$

→ Longest continuous chain of carbon atom contains nine carbon atom. So parent alkane is nonane.

→ In order that locants of the two methyl group and one ethyl groups attached to the parent are the smallest, number of carbon atoms of parent chain is done from the left hand side : in doing so locants of two methyl groups and the ethyl groups are 2, 4 and 5 respectively. The numbering from the right hand side is not permitted as the locants of the said groups will than be 6, 8 and 5 respectively. These are not the lowest possible numbers. Hence numbering from right hand side is not permitted.

→ Thus, the name of alkane is 5–Ethyl–2,4–dimethylnonane, and can not be named as : 2,4–Dimethyl–5–ethyl nonane.

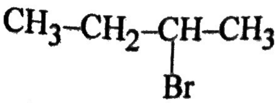
The alkyl halides are named as haloalkanes; that is halogen is simply treated as a side chain. We first name the alkane as parent name and then add fluoro, chloro, bromo or iodo, together with any needed numbers as a prefixes.

CH_3CH_2Cl

1–Chloroethane

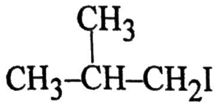
$CH_3CH_2CH_2Br$

1–Bromopropane



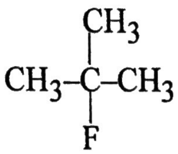
$$CH_3-CH_2-\underset{\underset{\displaystyle Br}{|}}{CH}-CH_3$$

2–Bromobutane



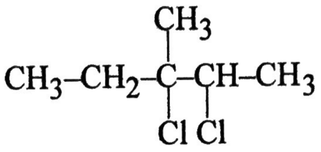
$$CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}}}H-CH_2I$$

1–Iodo–2–methyl propane



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

2–Fluoro–2–methyl propane

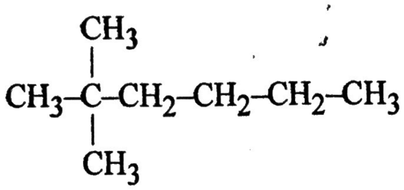


$$CH_3-CH_2-\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{Cl}{|}}{C}H-CH_3$$

2,3–Dichloro–3–methyl pentane

Q. 1 The following names are objectionable write corret name and their structure.

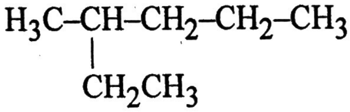
(1) 1,1,1–Trimethylpentane



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_2-CH_2-CH_3$$

2,2–Dimethylhexane

(2) 2–Ethylpentane



$$H_3C-\underset{\underset{CH_2CH_3}{|}}{CH}-CH_2-CH_2-CH_3$$

3–Methylhexane

(3) 3–Pentene

$H_3C-CH_2-HC=CH-CH_3$

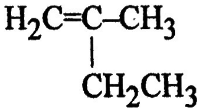
2–Pentene

(4) 6–Octene

$CH_3HC=CHCHCH_2CH_2CH_2CH_3$

2–Octene

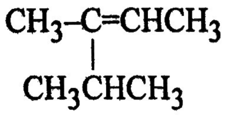
(5) 2–Ethyl–1–propene



$$H_2C=\underset{\underset{CH_2CH_3}{|}}{C}-CH_3$$

2–Methyl–1–butene

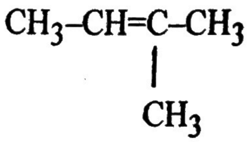
(6) 2–Isopropyl–2–butene



$$CH_3-\underset{\underset{CH_3CHCH_3}{|}}{C}=CHCH_3$$

3,4–Dimethyl–2–pentene

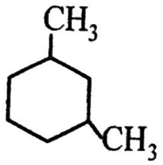
(7) 3–methyl–2–butene :



$$CH_3-CH=\underset{\substack{|\\ CH_3}}{C}-CH_3$$

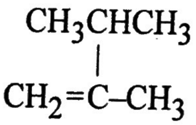
2–methyl–2–butene

(8) 1,5–dimethylcyclohexane.



1,3–dimethylcyclohexane.

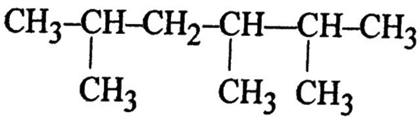
(9) 2–isopropyl–1–propene



$$CH_2=\overset{\substack{CH_3CHCH_3\\ |}}{C}-CH_3$$

2,3-dimethyl-1-butene

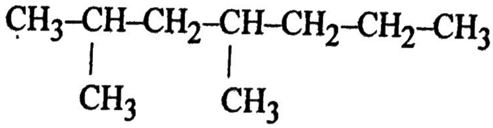
(10) 2,4,5–trimethylhexane



$$CH_3-\underset{\substack{|\\ CH_3}}{CH}-CH_2-\underset{\substack{|\\ CH_3}}{CH}-\underset{\substack{|\\ CH_3}}{CH}-CH_3$$

2,3,5–trimethylhexane

(11) 1,1,3–trimethylhexane.



$$CH_3-\underset{\substack{|\\ CH_3}}{CH}-CH_2-\underset{\substack{|\\ CH_3}}{CH}-CH_2-CH_2-CH_3$$

2,4–dimethylheptane.

(12) 3–butene

$CH_3-CH_2-CH=CH_2$

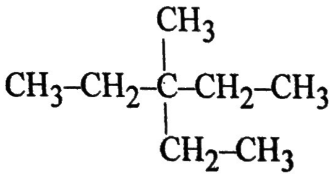
1–butene

(13) 1–methyl–1–heptene

$CH_3-CH=CH-CH_2-CH_2-CH_2-CH_2-CH_3$

2–Octene (Not 6-Octene)

(14) 2,2–diethylbutane



$$CH_3{-}CH_2{-}\underset{\displaystyle CH_2{-}CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}{-}CH_2{-}CH_3$$

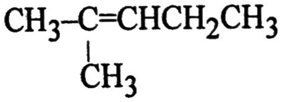
3–ethyl–3–methylpentane

(15) 1–ethylpentane

$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3$

Heptane

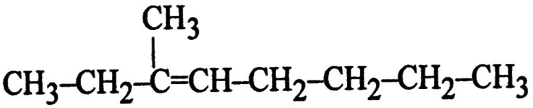
(16) 1,1-dimethyl-1-butene



$$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CHCH_2CH_3$$

2-methyl-2-pentene

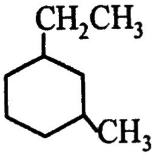
(17) 2–ethyl–2–heptene



$$CH_3{-}CH_2{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH{-}CH_2{-}CH_2{-}CH_2{-}CH_3$$

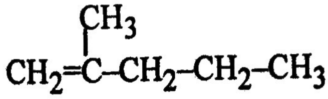
3–methyl–3-octene

(18) 1–ethyl–5–methylcyclohexane



1–ethyl–3–methylcyclohexane.

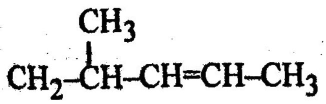
(19) 2–n-propyl–1–propene.



$$CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH_2{-}CH_2{-}CH_3$$

2–methyl–1–pentene

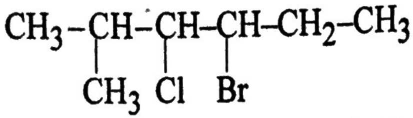
(20) 1,1–dimethyl–2–butene



$$CH_2{-}\overset{\displaystyle CH_3}{\overset{|}{CH}}{-}CH{=}CH{-}CH_3$$

4–methyl–2–pentene.

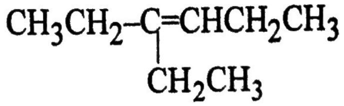
(21) 2–methyl–3–chloro–4–bromohexane.



$$CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH}}-CH_2-CH_3$$

4–bromo–3–chloro–2–methylhexane

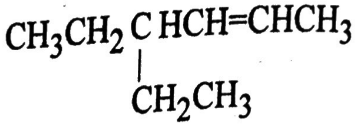
(22) 1,1-diethyl-1-butene



$$CH_3CH_2-\underset{CH_2CH_3}{\underset{|}{C}}=CHCH_2CH_3$$

3-ethyl-3-hexene

(23) 1,1-diethyl-2-butene



$$CH_3CH_2\underset{CH_2CH_3}{\underset{|}{C}}HCH=CHCH_3$$

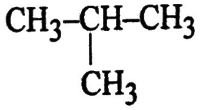
4-ethyl-2-hexene

Q. 2 Give all possible isomers of the following aliphatic compound and give their correct structures and IUPAC as well as common name.

(a) C_4H_{10} :

$CH_3-CH_2-CH_2-CH_3$

n–Butane



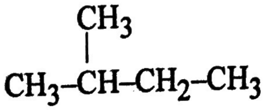
$$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_3$$

Isobutane [2–methylpropane]

(b) C_5H_{12} :

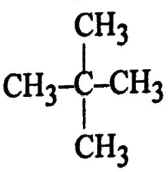
$CH_3-CH_2-CH_2-CH_2-CH_3$

n–pentane



$$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_3$$

Isopentane [2–methylbutane]



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

Neopentane [2,2–dimethylpropane]

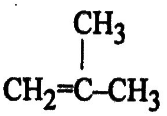
(c) C_4H_8 :

$CH_2=CH-CH_2-CH_3$

1–Butene

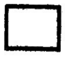
$CH_3-CH=CH-CH_3$

2–Butene



$$CH_2=\overset{CH_3}{\overset{|}{C}}-CH_3$$

Isobutene or Isobutylene [2–methyl–1–propene]



Cyclobutane

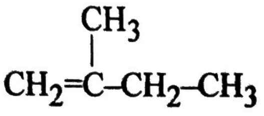
(d) C_5H_{10}

$CH_2{=}CH{-}CH_2{-}CH_2CH_3$

1–pentene

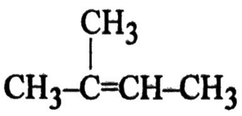
$CH_3{-}CH{=}CH{-}CH_2{-}CH_3$

2–petene



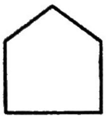
$CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}CH_2{-}CH_3$

2–methyl–1–butene

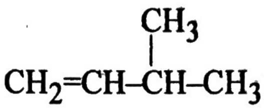


$CH_3{-}\overset{\overset{CH_3}{|}}{C}{=}CH{-}CH_3$

2-methyl-2-butene



Cyclopentane

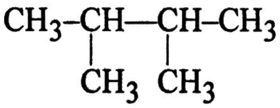


$CH_2{=}CH{-}\overset{\overset{CH_3}{|}}{CH}{-}CH_3$

3–methyl–1–butene

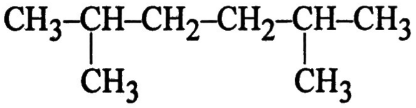
Q. 3 Give the structured formula of following compounds :

(a) 2,3–dimethylbutane



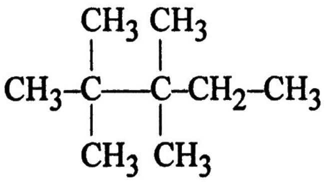
$CH_3{-}\underset{\underset{CH_3}{|}}{CH}{-}\underset{\underset{CH_3}{|}}{CH}{-}CH_3$

(b) 2,5–dimethylhexane



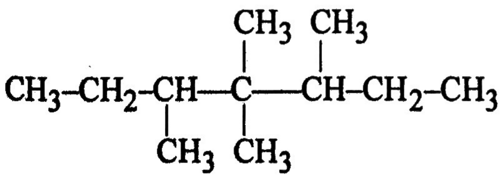
$CH_3{-}\underset{\underset{CH_3}{|}}{CH}{-}CH_2{-}CH_2{-}\underset{\underset{CH_3}{|}}{CH}{-}CH_3$

(c) 2,2,3,3–tetramethylpentane.



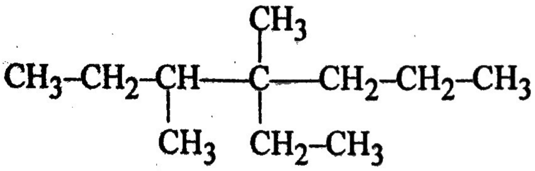
$CH_3{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_2{-}CH_3$

(d) 3,4,4,5–tetramethylheptane



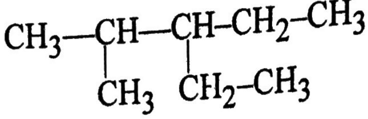
$CH_3{-}CH_2{-}\underset{\underset{CH_3}{|}}{CH}{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}\overset{\overset{CH_3}{|}}{CH}{-}CH_2{-}CH_3$

(e) 4–ethyl–3,4–dimethylheptane.



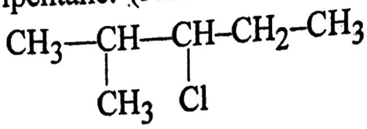
$CH_3{-}CH_2{-}\underset{\underset{CH_3}{|}}{CH}{-}\underset{\underset{CH_2-CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_2{-}CH_2{-}CH_3$

(f) 3–ethyl–2-methylpentane. (3-isopropylpentane)



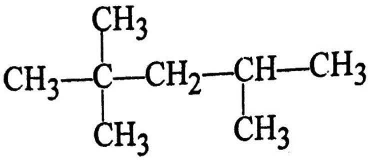
$CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{CH_2-CH_3}{\underset{|}{CH}}-CH_2-CH_3$

(g) 3–chloro–2–methylpentane. (Not 3-chloro-4-Methylpentane)



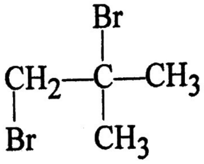
$CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH}}-CH_2-CH_3$

(h) 2,2,4–trimethylpentane. (Isooctane)



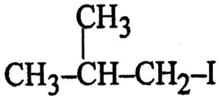
$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_3$

(i) 1,2–dibromo–2–methylpropane.



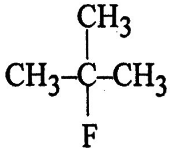
$\underset{Br}{\underset{|}{CH_2}}-\overset{Br}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3$

(j) 1–iodo–2–methylpropane.



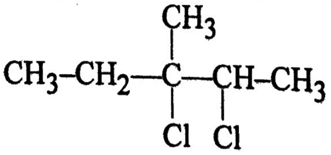
$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-I$

(k) 2–Fluoro–2–methylpropane.



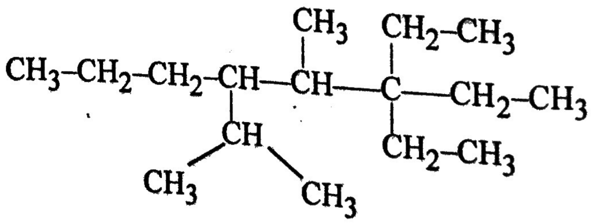
$CH_3-\overset{CH_3}{\overset{|}{\underset{F}{\underset{|}{C}}}}-CH_3$

(l) 2,3–dichloro–3–methylpentane. (Not 3,4-dichloro-3-Methylpentane)



$CH_3-CH_2-\overset{CH_3}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}-\underset{Cl}{\underset{|}{CH}}-CH_3$

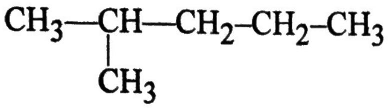
(m) 3,3–diethyl–5–isopropyl–4–methyloctane.



Q. 4 Draw the correct structural formula and give their IUPAC names of the following.

(a) $(CH_3)_2\ CH\ CH_2\ CH_2\ CH_3$

Ans.

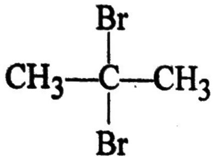


$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2-CH_2-CH_3$$

2-Methylpentane

(b) $CH_3CBr_2CH_3$

Ans.

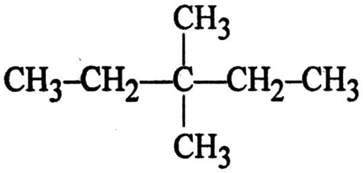


$$CH_3-\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}-CH_3$$

2,2-dibromopropane

(c) $CH_3CH_2C(CH_3)_2CH_2CH_3$

Ans.

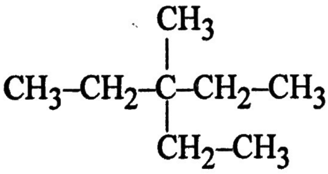


$$CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2-CH_3$$

3,3–dimethylpentane.

(d) $(C_2H_5)_2\ C\ (CH_3)\ CH_2CH_3$

Ans.

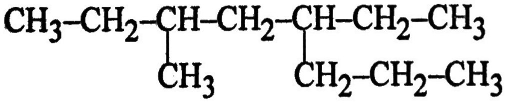


$$CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_2-CH_3}{|}}{C}}-CH_2-CH_3$$

3-ethyl-3-methylpentane

(e) $CH_3CH_2CH(CH_3)\ CH_2CH\ (n-C_3H_7)\ CH_2CH_3$

Ans.

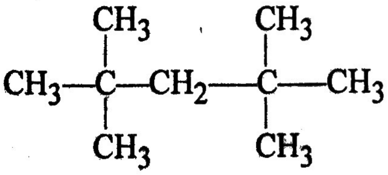


$$CH_3-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2-\underset{\underset{\displaystyle CH_2-CH_2-CH_3}{|}}{CH}-CH_2-CH_3$$

3-ethyl-5-methyloctane

(f) $(CH_3)_3C\ CH_2C(CH_3)_3$

Ans.

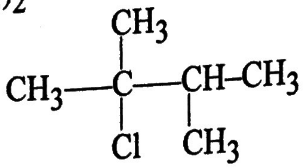


$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3$$

2,2,4,4-tetramethylpentane

(g) $(CH_3)_2ClCH(CH_3)_2$

Ans.

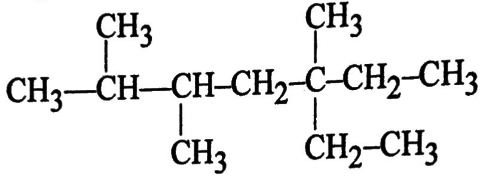


$$CH_3-\overset{CH_3}{\underset{Cl}{C}}-\underset{CH_3}{CH}-CH_3$$

2-chloro-2,3-dimethylbutane.

(h) $(CH_3)_2\ CH\ CH\ (CH_3)\ CH_2\ C\ (C_2H_5)_2\ CH_3$

Ans.

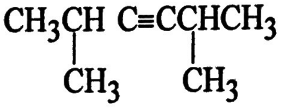


$$CH_3-\overset{CH_3}{CH}-\underset{CH_3}{CH}-CH_2-\overset{CH_3}{\underset{CH_2-CH_3}{C}}-CH_2-CH_3$$

5-ethyl-2,3,5-trimethylheptane.

(i) $(CH_3)_2CHC{\equiv}CCH(CH_3)_2$

Ans.

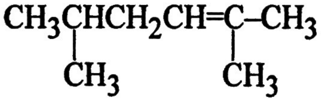


$$CH_3\underset{CH_3}{CH}\ C{\equiv}C\underset{CH_3}{C}HCH_3$$

2,5–dimethyl–3–hexyne

(j) $(CH_3)_2CHCH_2CH{=}C(CH_3)_2$

Ans.

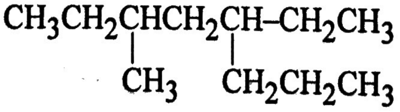


$$CH_3\underset{CH_3}{C}HCH_2CH{=}\underset{CH_3}{C}-CH_3$$

2,5–dimethyl–2–hexene

(k) $CH_3CH_2CH(CH_3)CH_2CH(n{-}C_3H_7)C_2H_5$

Ans.

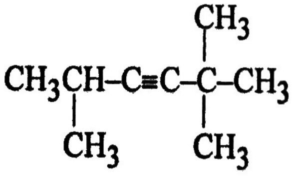


$$CH_3CH_2\underset{CH_3}{C}HCH_2\underset{CH_2CH_2CH_3}{C}H-CH_2CH_3$$

5–ethyl–3–methyloctane

(l) $(CH_3)_2CHC{\equiv}C-C(CH_3)_3$

Ans.

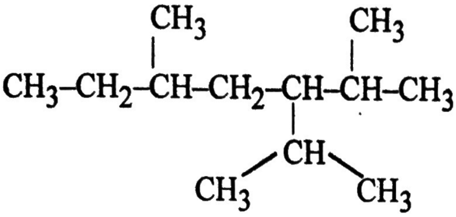


$$CH_3\underset{CH_3}{C}H-C{\equiv}C-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$

2,2,5–trimethyl–3–hexyne

(m) $CH_3\ CH_2\ CH\ (CH_3)\ CH_2\ CH\ (iso - C_3H_7)\ CH\ (CH_3)_2$

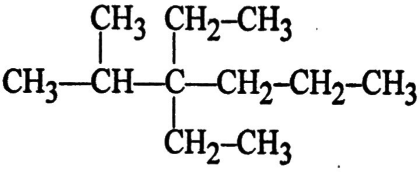
Ans.



3-Isopropyl-2,5-di-methylheptane

(n) $(CH_3)_2CHC(C_2H_5)_2\ CH_2\ CH_2\ CH_3$

Ans.

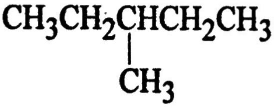


$$CH_3\!-\!\underset{}{\overset{CH_3}{\overset{|}{C}H}}\!-\!\underset{\underset{CH_2-CH_3}{|}}{\overset{\overset{CH_2-CH_3}{|}}{C}}\!-\!CH_2\!-\!CH_2\!-\!CH_3$$

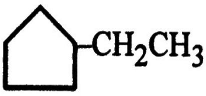
3,3-diethyl-2-methylhexane

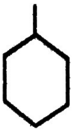
Q. 5 Some Common Structures and their names :

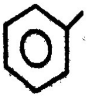
(1)  i.e. $CH_3CH_2CH_2CH_3$ → n–Butane

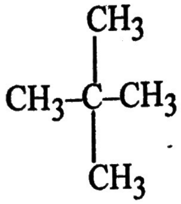
(2)  i.e.  $CH_3CH_2\underset{\underset{CH_3}{|}}{C}HCH_2CH_3$ → 3–Methylpentane

(3)  i.e. $CH_2 = CH\text{–}CH = CH_2$ → 1,3–Butadiene

(4)  i.e.  → Ethyl cyclopentane

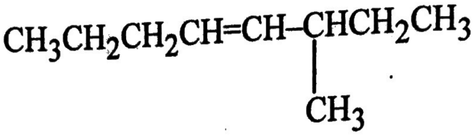
(5)  → methyl cyclohexane

(6)  or  → Toluene

(7)  or  i.e. 

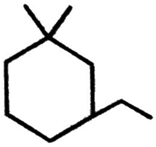
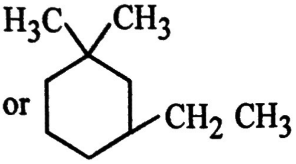
$$\begin{array}{c} CH_3 \\ | \\ CH_3-C-CH_3 \\ | \\ CH_3 \end{array}$$

→ Neopentane (2,2-dimethylpropane)

(8)  i.e. 

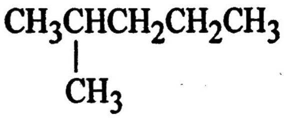
$$CH_3CH_2CH_2CH{=}CH-\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_3$$

3–methyl–4–octene

(9)  or 

1,1–dimethyl–3–ethylcyclohexane

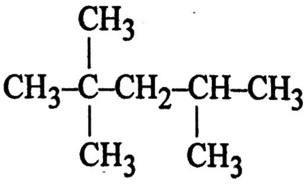
(10) Isohexane



$$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2CH_3$$

2–methylpentane

(11) Isooctane



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}H-CH_3$$

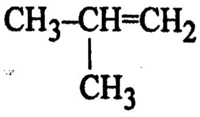
2,2,4–trimethylpentane

(12) Propylene

$CH_2{=}CHCH_3$

1–propene

(13) Isobutene [Isobutylene]



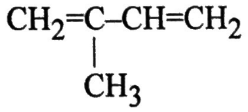
$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}H{=}CH_2$$

2–methyl–1–propene

(14) 1,3–Butadiene

$$CH_2=CH-CH=CH_2$$

(15) Isoprene



$$CH_2=\underset{CH_3}{\underset{|}{C}}-CH=CH_2$$

2–methyl–1,3–butadiene

(16) Acetylene

$$CH\equiv CH \quad \text{or} \quad HC\equiv CH$$

Ethyne

(17) Methylacetylene

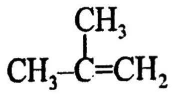
$$CH_3-C\equiv CH$$

1–propyne

1.6 Names of alkenes :

1. Select (the parent structure) the longest continuous chain that contain the carbon – carbon double bond. Depending upon the number of carbon atom; each name is derived by changing the ending–ane of the corresponding alkane name to ene.

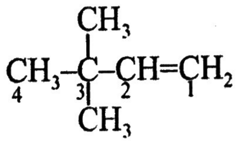
$CH_2=CH_2$	$CH_3-CH=CH_2$	$\overset{4}{CH_3}\overset{3}{CH_2}\overset{2}{CH}=\overset{1}{CH_2}$	$CH_3\ CH=CH\ CH_3$
Ethylene (Ethene)	(Propene) Propylene	1–Butene	2–Butene (cis – or trans)



$$CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2$$

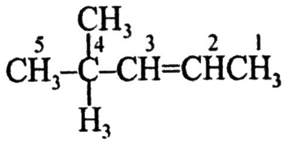
Isobutylene

(2–Methyl–1–propene)



$$\underset{4}{CH_3}-\underset{CH_3}{\overset{CH_3}{\underset{3}{C}}}-\underset{2}{CH}=\underset{1}{CH_2}$$

3,3–Dimethyl-1-butene



$$\overset{5}{CH_3}-\underset{H_3}{\overset{CH_3}{\overset{4}{C}}}-\overset{3}{CH}=\overset{2}{CH}\overset{1}{CH_3}$$

4-Methyl-2-pentene (cis – or trans)

2. Indicate the position of the double bond in the parent chain by a number. Numbering will start from the end of the chain nearest to the double bond in such a way so that first double bonded carbon get lowest number. Thus,

   $CH_2=CHCH_2CH_3$ will have correct name 1–Butene and not 3–butene.

3. Indicate by number the position of the alkyl group or other group attached to the parent chain.
4. When geometric isomer is to be specified a prefix is added : cis– or trans– or (Z)– or (E)–.

5. An alkene containing halogen is generally named as halo alkene, the unsaturated groups are given special names like vinyl $CH_2=CH-$; and allyl $CH_2=CH-CH_2-$

$CH_2=CH-Cl$

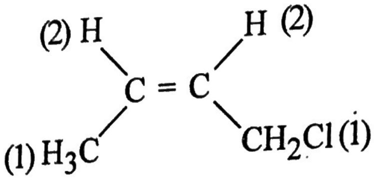
Chloro ethene

(vinyl chloride)

$\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH_2}Br$

3–bromo–1–propene

(allyl bromide)



(z)–1–chloro–2–butene

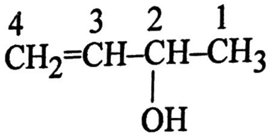
$CH_2Cl > H$

$CH_3 > H$

6. An alcohol containing double bond is named as an **alkenol** with numbers to indicated the positions of the double bond and the hydroxyl group –ol takes priority over –ene; –ol appears last in the name and, where possible is given the lower number. (Numbering start in such a way that –OH group should get Lowest number i.e. higher priority)

$\underset{1}{\overset{3}{CH_2}}=\underset{2}{\overset{2}{CH}}-\underset{3}{\overset{1}{CH_2}}OH$

(Allyl alcohol).
2–Propen–1–ol and
not 1–propen–3–ol



$\overset{4}{CH_2}=\overset{3}{CH}-\underset{OH}{\overset{2}{CH}}-\overset{1}{CH_3}$

3–buten–2–ol and not 1–buten–3–ol

Q. 6 Give the structural formula of :

(a) 3,6–dimethyl–1–octene

(b) 3–chloropropene

(c) 2,4,4–trimethyl–2–pentene

(d) trans–3,4–dimethyl–3–hexene

(e) (z)–3–chloro–4–methyl–3–hexene

(f) (E)–1–deuterio–2–chloropropene (deuterio means deuterium D)

Q. 7 Give the structure formula of :

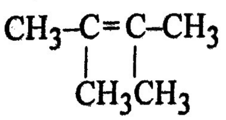
(a) 2,3-dimethyl-2-butene

(b) 3-bromo-2-methylpropene

(c) cis-2-methyl-3-heptene

(a) 2,3-dimethyl-2-butene

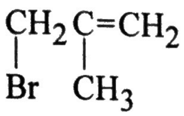
Ans. :



$CH_3-\underset{CH_3}{C}=\underset{CH_3}{C}-CH_3$

(b) 3-bromo-2-methylpropene

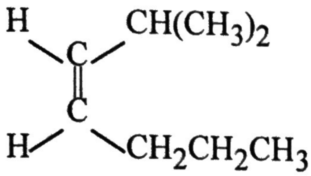
Ans. :



$\underset{Br}{CH_2}\,\underset{CH_3}{C}=CH_2$

(c) cis-2-methyl-3-heptene

Ans. :

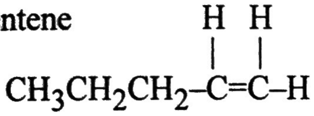


Q. 8 Give IUPAC name of :

(a) isomeric pentenes (b) isomeric chloropropenes

(a) isomeric pentenes

(1) 1-pentene

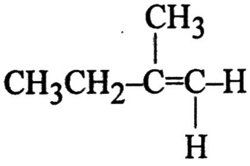


$CH_3CH_2CH_2-\overset{H}{C}=\overset{H}{C}-H$

(2) $CH_3CH_2CH=CHCH_3$

2-pentene

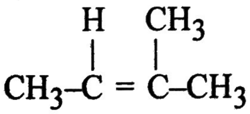
(3)



$CH_3CH_2-\overset{CH_3}{C}=\underset{H}{C}-H$

2-methyl-1-butene

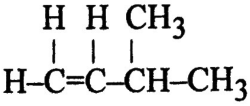
(4)



$CH_3-\overset{H}{C}=\overset{CH_3}{C}-CH_3$

2–methyl–2–butene

(5)



$H-\overset{H}{C}=\overset{H}{C}-\overset{CH_3}{CH}-CH_3$

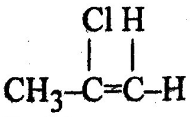
3-methyl-1-butene

(b) Isomeric chloropropenes :

(1) $CH_3CH=CHCl$

1-chloropropene

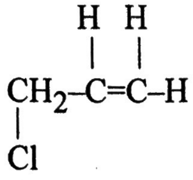
(2)



$CH_3-\overset{Cl}{C}=\overset{H}{C}-H$

2-chloropropene

(3)



$$\overset{}{\underset{\displaystyle Cl}{\underset{|}{CH_2}}}-\overset{\displaystyle H}{\overset{|}{C}}=\overset{\displaystyle H}{\overset{|}{C}}-H$$

3-chloropropene

Q. 9 Give the structural formula of :

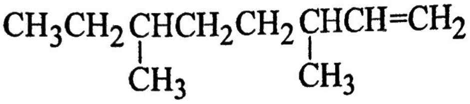
(a) 3,6-dimethyl-1-octene

(b) 3-chloropropene

(c) 2,4,4-trimethyl-2-pentene

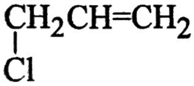
Ans. :

(a) 3,6-dimethyl-1-octene



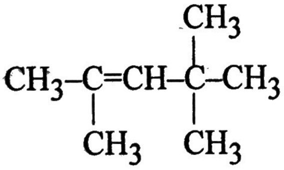
$$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{CH}}CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{CH}}CH=CH_2$$

(b) 3-chloropropene



$$\underset{\displaystyle Cl}{\underset{|}{CH_2}}CH=CH_2$$

(c) 2,4,4-trimethyl-2-pentene



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3$$

Q. 10 Draw out the structural formula and give the IUPAC name of :

(a) Isobutylene

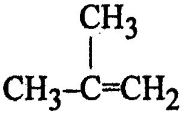
(b) $(CH_3)_3CCH=CH_2$

(c) $(CH_3CH_2)_2C=CH_2$

(d) $(CH_3)_2CHCH_2CH=C(CH_3)_2$

Ans. :

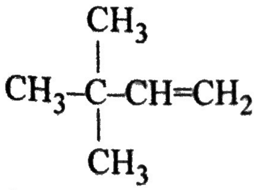
(a) Isobutylene



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH_2$$

2-methyl-1-propene

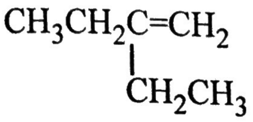
(b) $(CH_3)_3CCH=CH_2$



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH=CH_2$$

3,3-Dimethyl-1-butene

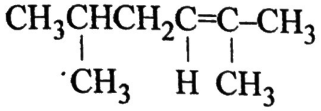
(c) $(CH_3CH_2)_2C{=}CH_2$



$CH_3CH_2C(CH_2CH_3){=}CH_2$

2-ethyl–1–butene

(d) $(CH_3)_2CHCH_2CH{=}C(CH_3)_2$



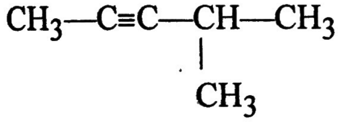
$CH_3CH(CH_3)CH_2CH{=}C(CH_3)-CH_3$

2,5-dimethyl-2-hexene

1.7 Higher alkynes : Nomenclature :

Like the alkanes and alkenes, the alkynes form a homologous series.

The alkynes are named according to two systems. In one, alkynes are considered to be derived from acetylene by replacement of one or both hydrogen atoms by alkyl groups.

$HC{\equiv}C{-}CH_3$	Methylacetylene
$H{-}C{\equiv}C{-}CH_2{-}CH_3$	Ethylacetylene (1–Butyne)
$CH_3C{\equiv}CCH_3$	Dimethylacetylene (2–Butyne)
$CH_3{-}C{\equiv}C{-}CH_3$	Dimethylacetylene (2–Butyne)
 $CH_3{-}C{\equiv}C{-}CH(CH_3){-}CH_3$	Isopropylmethylacetylene (4–Methyl–2–pentyne)

For complicate alkynes, the IUPAC rules :

(i) The parent structure is the longest continuous chain that contains the triple bond.

(ii) The position of subtituents and of the triple bond are indicated by numbers.

(iii) The triple bond is given the number of the first triply bonded carbon starting from the end of the chain nearest the triple bond.

Homologous series : It is a series of compounds in which each member of series differs from the next member by a constant amount ($-CH_2$) is called a homologous series. e.g. methane, ethane etc.

1.8 Physical properties of alkanes :

The physical properties of the alkanes follow the pattern laid down by methane and are consistent with the alkane structure. An alkane molecule have entirely covalenting. These bonds either join two atoms of the same kind and hence are non–polar, or join two atoms differ in electronegativity and hence are slightly polar. Further more, these bonds are directed in very symmetrical way, so that the slight bond polarities tend to cancel out. As a result an alkane molecule is either non–polar or very weakly polar.

Table lists certain physical constants for a number of the n–alkanes.

Table

Name	**Formula**	**M. P. °C**	**B. P. °C**	**Relative desity (at 20°C)**
Methane	CH_4	–183	–162	–
Ethane	CH_3CH_3	–172	–88.5	–
Propane	$CH_3CH_2CH_3$	–187	–42	–
n–Butane	$CH_3(CH_2)_2CH_3$	–138	0	–
n–pentane	$CH_3(CH_2)_3CH_3$	–130	36	0.626
n–Hexane	$CH_3(CH_2)_4CH_3$	–95	69	0.659
n–Heptane	$CH_3(CH_2)_5CH_3$	–90.5	98	0.684
n–Octane	$CH_3(CH_2)_6CH_3$	–57	126	0.703
n–Noname	$CH_3(CH_2)_7CH_3$	–54	151	0.718
n–Decane	$CH_3(CH_2)_8CH_3$	–30	174	0.730
Isobutane	$(CH_3)_2CHCH_3$	–159	–12	–
Isopentane	$(CH_3)_2CHCH_2CH_3$	–160	28	0.620
Neopentane	$(CH_3)_4\ C$	–17	9.5	–
Isohexane	$(CH_3)_2CH(CH_2)_2CH_3$	–154	60	0.654
3–Methylpentane	$CH_3CH_2CH(CH_3)CH_2CH_3$	–118	63	0.676
2,2–Dimethylbutane	$(CH_3)_3CCH_2CH_3$	–98	50	0.649
2,3–Dimethylbutane	$(CH_3)_2CHCH\ (CH_3)_2$	–129	58	0.668

Except for the very small alkanes the boiling point rises 20 to 30 degree for each carbon added to chain. This increment of 20–30 degree per carbon holds not only the alkanes but also for each of the homologous series that we shall study.

The first four n–alkanes are gases, but boiling point and melting point rises (increasing) as the number of carbon increasing thus the next thirteen ($C_5 - C_{17}$) are liquid and those containing 18 carbons or more are solids. **As the number of carbon atom increase in the**

n–alkane series boiling points and melting points increase. This is due to the fact that as the number of carbon atom increase, contact of surface area increase with the result that the intermolecular forces become stronger and are overcome at higher temperature. Thus n–butane, n–pentane and n–hexane have 0°, 36° and 69° boiling points respectively. In every case of alkane a branch chain isomer has lower boiling point, than straight–chain isomer and further that the more numerous the branched, the lower boiling point. Thus n–butane has boiling point of 0°C and isobutane has –12°. *n*–pentane has a boiling point of 36°, isopentane with a single branch 28° and neopentane with two branch 9.5°. This effect of branching on boiling point is observed within all families of organic compounds. **Because with increasing number of branching, the shape of the molecule tends to approach that of a sphere and due to this the contact of surface area decrease, As a result the intermolecular forces become weaker and are overcome at a lower temperature.**

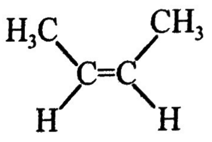
1.9 Physical property of alkenes and alkynes :

In alkenes and alkynes boiling point increases with increase in the number of carbon atoms. The lower members of each family are gases. The higher molecular weight compounds of alkenes and alkynes are waxy solids. They are insoluble in water but soluble in organic solvents. They are less dense than water. They may be polar or non-polar depending on the arrangements of atoms in the molecule.

In case of alkenes two isomers are possible :

(i) cis-isomer and (ii) trans-isomer.

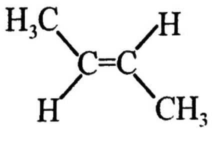
In cis-isomer, two identical groups are on the same side of double bond. in trans-isomer, the identical groups are on the opposite side of double bond. Let us consider the example of cis-2-butne and trans-2-butene.



Cis-2-butene

b.p. = + 4°C

m.p. = –139°C



Trans-2-butne

b.p. = + 1°C

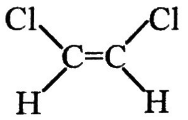
m.p. = –106°C

The difference in the m.p. and b.p. of these two isomers can be explained in terms of their **symmetry** and **polarities** respectively. In case of cis-2-butene the bond polarities of C-CH_3 bonds are not cancelled because two CH_3 groups are on same side. Thus cis-2-butene is a polar molecule. In case of trans-2-butene, the bond polarities of C–CH_3 bond C–H bonds are cancelled because two –CH_3 groups are on opposite side. Thus trans-2-butene is non-polar. **Greater** the **Polarity, higher** is the **b.p.** Thus, cis-2-butene is polar so its b.p. is higher than trans-2-butene.

It can also be seen from the structures of these two isomers that trans-2-butene is **more symmetrical** (higher symmetry) so trans-2-butene molecule can be packed very closely i.e. because of its higher symmetry, it can **fit well** into **crystalline lattice more tightly** and thus more energy is required to separated trans-isomer. Hence ~~trans~~ cis-2-butene molecule has lower symmetry so it can not fit well into crystalline lattice and thus less energy is required to separate cis-isomer. Therefore cis-2-butene has the lower m.p.

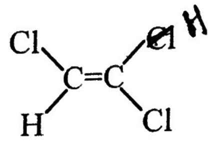
This same relationship exists for many pairs of geometric isomers. The differences in polarity and hence the differences in m.p. and b.p. are greater for alkenes that contain elements whose electro-negativities differ widely from that of carbon e.g.

(i) b.p. of cis-1,2-dichloroethene is higher than b.p. of trans-1,2-dichloroethene.
(ii) b.p. of cis-1,2-dibromoethene is higher than b.p. of trans-1,2-dibromoethane.
(iii) m.p. of trans-1,2-dichloroethene is higher than m.p. of cis-1,2-dichloroethene.



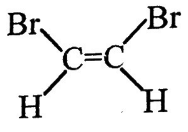
Cis

μ = 1.85 D
b.p. = 60°C
m.p. = –80°C



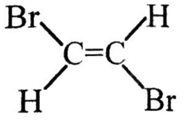
Trans

μ = 0
b.p. = 48°C
m.p. = –50°C



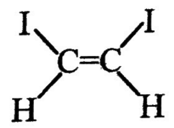
Cis

μ = 1.35 D
b.p. = 110°C
m.p. = –53°C



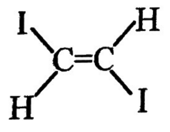
Trans

μ = 0
b.p. = 108°C
m.p. = –6°C



Cis

μ = 0.75 D
b.p. = 188°C
m.p. = –14°C



Trans

μ = 0
b.p. = 192°C
m.p. = +72°C

More symmetrical trans molecules have higher m.p. Trans molecules have less (small value) dipole moment, due to cancelled out bond polarity. Cis-molecules have lower m.p. but higher values of dipole moment due to not cancelled out bond polarity, i.e. existence of bond polarity.

1.10 Preparation of Alkane :

(1) Preparation from alkene by Hydrogenation of Alkene :

$$\rightarrow \underset{\text{Alkene}}{C_nH_{2n}} \xrightarrow{H_2/Pd \text{ or } H_2/Pt} \underset{\text{Alkane}}{C_nH_{2n+2}} \text{ (Also } H_2/Ni)$$

$$\text{eq. } \underset{\text{1–butene}}{CH_3CH_2CH=CH_2} \xrightarrow{H_2/Pd \text{ or } Pt \text{ or } H_2/Ni} \underset{\text{n–butane}}{CH_3CH_2CH_2CH_3}$$

(2) Reduction of alkyl halides :

(a) Grignard Method :

When alkyl halide react with Mg metal in presence of dry ether give corresponding Grignard reagent which upon hydrolysis give corresponding alkane e.g.

→ $$R{-}X + Mg \xrightarrow[\text{ether}]{\text{dry}} R-Mg-X \xrightarrow[H^{+}]{H_2O} \text{Alkane}$$

Alkyl halide

Grignard reagent

e.g.

$$CH_3I + Mg \xrightarrow{\text{dry ether}} CH_3Mg\,I \xrightarrow{H_2O} CH_4$$

Methyl iodide

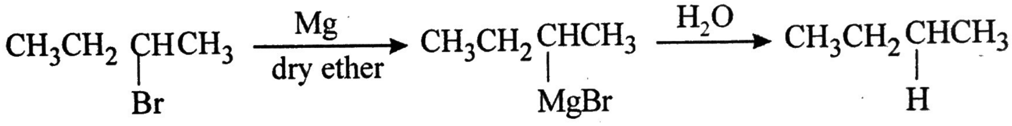
Methyl magnesium iodide

$$CH_3CH_2Br + Mg \xrightarrow{\text{dry ether}} CH_3CH_2Mg\,Br \xrightarrow{H_2O} CH_3CH_3$$

Ethyl bromide

Ethyl magnesium bromide

Ethane



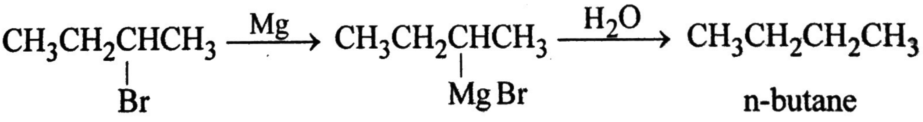
$$CH_3CH_2\underset{\underset{Br}{|}}{CH}CH_3 \xrightarrow[\text{dry ether}]{Mg} CH_3CH_2\underset{\underset{MgBr}{|}}{CH}CH_3 \xrightarrow{H_2O} CH_3CH_2\underset{\underset{H}{|}}{CH}CH_3$$

Sec. Butyl bromide

Sec. butyl magnesium bromide

n–Butane

Grignard Reagent :



$$CH_3CH_2\underset{\underset{Br}{|}}{CH}CH_3 \xrightarrow{Mg} CH_3CH_2\underset{\underset{Mg\,Br}{|}}{CH}CH_3 \xrightarrow{H_2O} CH_3CH_2CH_2CH_3$$

Sec - butyl bromide

n-butane

When a solution of an alkyl halide in dry ethyl ether, $(C_2H_5)_2O$ is allowed to stand over metallic magneisum, a vigarous reaction take place : the solution turns cloudy, begins to boil, and the magnesium metal gradually disappears. The resulting solution is known as a **Griangard reagent** (RMgX).

Grignard reagent has the **general formula** RMgX and the general name is alkylmagnesium halide. The C–Mg bond is **covalt** but highly polar and Mg–X bond is **ionic** in nature.

$$R : Mg^{\oplus} :\ddot{\underset{\cdot\cdot}{X}}:^{\ominus}$$

RMgX is called organometallic compound in which carbon bonded to a metal like Mg. The Grignard reagent RMgX is highly reactive and react with water, CO_2 and O_2. It react with water (act as storger acid) to give alkane (weaker acid).

$$\underset{\text{Stonger acid}}{RMgX + H_2O} \longrightarrow \underset{\text{Weaker acid}}{R\text{–}H} + Mg(OH)X.$$

Above reaction is simply the displacement of the we a acid R–H form from its salt by the stronger acid H_2O (HOH). Any compound containing hydrogen which attached to oxygen (H_2O), nitrogen (NH_3) is more acidic than alkane and hence can decompose the Grignard reagent e.g.

$$RMgX + NH_3 \longrightarrow R\text{–}H + Mg(NH_2)X$$

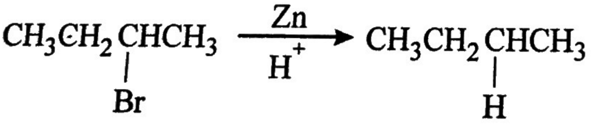
$$RMgX + R'OH \longrightarrow R\text{–}H + Mg(OR')X$$

(b) Reduction of alkyl halide by metal and acid

$$R\text{–}X + Zn + H^+ \longrightarrow \underset{\text{Alkane}}{R\text{–}H} + Zn^{+2} + X^-$$

e.g.

$$CH_3CH_2\,Br + Zn \xrightarrow{HCl} CH_3CH_3 + Zn^{2+} + Br^-$$



$$\underset{\text{Sec–butyl bromide}}{CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3} \xrightarrow[H^+]{Zn} \underset{\text{n–butane}}{CH_3CH_2\underset{\displaystyle H}{\underset{|}{C}}HCH_3}$$

Sec–butyl bromide n–butane

(3) Corey-House Reaction :

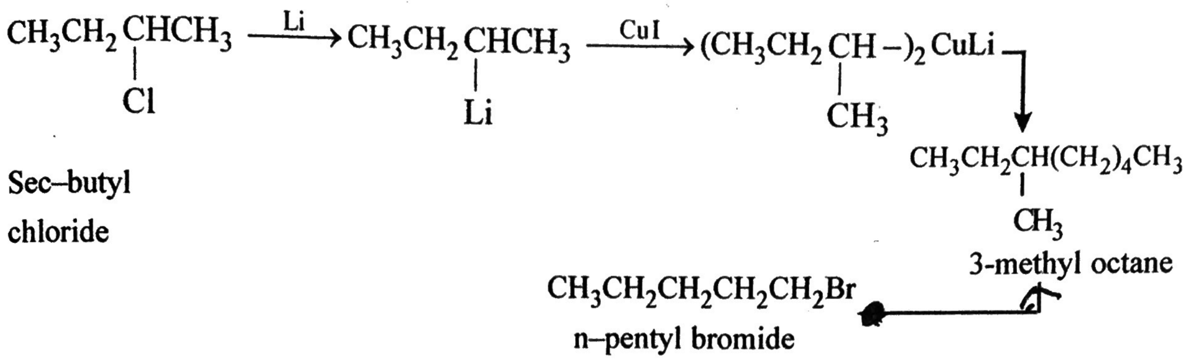
$$\underset{\text{Alkyl halide}}{R\text{–}X + Li} \longrightarrow \underset{\text{Alkyl Lithium}}{R\text{–}Li} \xrightarrow{Cu\text{–}X} \underset{\text{Lithium dialkyl Copper}}{R_2\text{-}Cu\text{-}Li} \xrightarrow[\text{must }1^\circ]{R'X} \underset{\text{Alkane}}{R\text{–}R'}$$

(R' must be n-alkylhalide)

(1) $$\underset{\text{Methyl bromide}}{CH_3Br} \xrightarrow{Li} \underset{\text{Methyl Lithium}}{CH_3Li} \xrightarrow{CuI} \underset{\text{Lithium dimethyl copper}}{(CH_3)_2\,CuLi}$$

$$\underset{\text{n–octyl iodide}}{CH_3(CH_2)_6\,CH_2I}$$

$$\rightarrow \underset{\text{n–nonane}}{CH_3(CH_2)_7CH_3}$$

(2) 

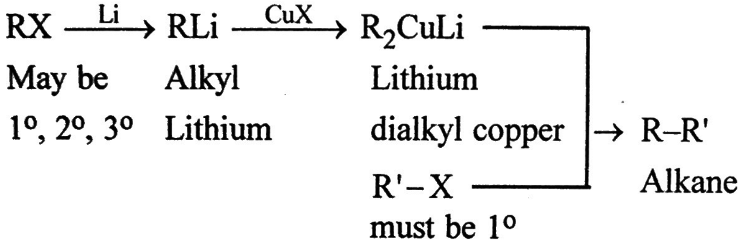
$$CH_3CH_2\underset{\displaystyle Cl}{CH}CH_3 \xrightarrow{Li} CH_3CH_2\underset{\displaystyle Li}{CH}CH_3 \xrightarrow{CuI} (CH_3CH_2\underset{\displaystyle CH_3}{CH}-)_2CuLi \xrightarrow{CH_3CH_2CH_2CH_2CH_2Br} CH_3CH_2\underset{\displaystyle CH_3}{CH}(CH_2)_4CH_3$$

Sec–butyl chloride

3-methyl octane

n–pentyl bromide

Alkyl halides react with lithium metal (Li) to give organometalic compounds which react with CuX give lithium dialkyl copper compound. This on further reaction with **1° alkyl (n-alkyl)** halides (R'X) gives alkane having longer alkyl chain. This reaction give desired (both symmetrical and unsymmetrical alkane with even or odd number of carbon atoms) alkanes by coupling of alkyl halides with organometallic compound **(Corey–House reaction).**



$$RX \xrightarrow{Li} RLi \xrightarrow{CuX} R_2CuLi \xrightarrow{R'-X} R-R'$$

RX May be 1°, 2°, 3°

RLi Alkyl Lithium

R_2CuLi Lithium dialkyl copper

R'–X must be 1°

R–R' Alkane

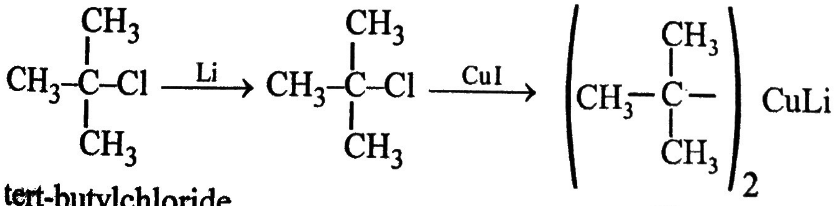
e.g.

$$CH_3CH_2Br \xrightarrow{Li} CH_3CH_2Li \xrightarrow{Cu\,I} (CH_3CH_2)_2\ CuLi$$

Ethyl bromide   Ethylithium   Lithium diethyl copper (I)

$$\underset{(I)}{(CH_3CH_2)_2\ CuLi} + \underset{\text{n–Heptyl bromide}}{CH_3(CH_2)_5CH_2Br} \longrightarrow \underset{\text{n-nonane}}{CH_3(CH_2)_7CH_3}$$

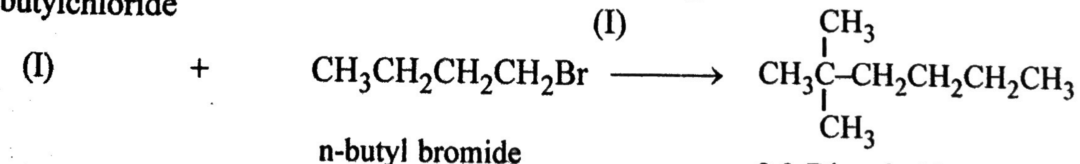
i.e. Two carbon atom (like ethylhalide) + seven carbon atoms (like n-heptylhalide → nine carbon (n-nonane)



$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-Cl \xrightarrow{Li} CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-Cl \xrightarrow{CuI} \left(CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-\right)_2 CuLi$$

tert-butylchloride

(I)



$$(I) + CH_3CH_2CH_2CH_2Br \longrightarrow CH_3\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-CH_2CH_2CH_2CH_3$$

n-butyl bromide

2,2-Dimethyl hextane

Similarly, we can synthesize 2-Methylpentane from isopropyl chloride and n-propyl halide.

→ Corey–House reaction gives **desired** alkanes by considering the reaction of alkyl halide with Lithium and copper halide (Cu–X) whereas,

→ Wurtz reaction gives **only even number** of alkanes by considering the reaction between alkyl halide and sodium metal (Na.)

(4) Wurtz Reaction :

$$\underset{\text{Alkyl halide}}{2R\text{–}X} + 2Na \longrightarrow \underset{\text{Alkane}}{R\text{–}R} + 2\,NaX$$

e.g. $2CH_3CH_2Br + 2Na \rightarrow \underset{\text{Symmetrical alkane}}{CH_3CH_2CH_2CH_3} + 2NaBr$

Two moles of alkyl halide react with two moles of sodium metal to give corresponding symmetrical alkanes. The **limitation** of this method is that only **even number** of alkanes can be prepared (symmetrical alkane).

1.11 Organometallic Compounds :

The compounds in which carbon is bonded to a metal : lithium, potassium, sodium, zinc, mercury, lead, etc. almost any metal known. Each type of organometallic compound has its own set of properties and depends on these. But any metal, it is less electronegative than carbon and carbon–metal bond is highly polar. The example of organometallic compound is Grignard reagent RMgX, R_2CuLi etc.

1.12 Classes of carbon atoms and hydrogen atoms :

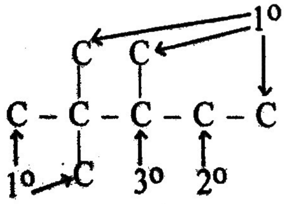
It has been found extremely useful to classify each carbon atom of an alkane with respect to the **number of other carbon atoms to which it is attached.**

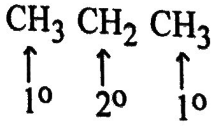
(1) A primary (1°) carbon atom is attached to only **one** other carbon atoms.

(2) A secondary (2°) carbon atom is attached to **two** other carbon atoms.

(3) A tertiary (3°) carbon atom is attached to **three** other carbon atoms.

(4) A quaternary (4°) carbon atom is attached to **four** other carbon atoms.

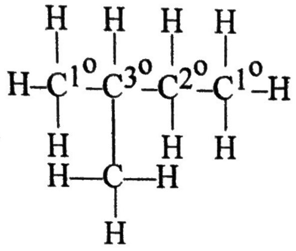


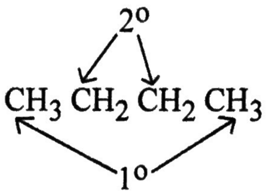


(1°, 6H) (2°, 2H)

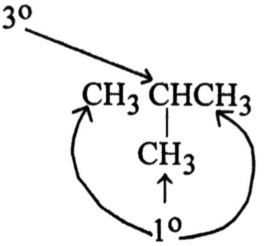
Similarly, each hydrogen atom is classified and given the same designation of primary, secondary or tertiary as the carbon atom to which it is attached.

(1°, 9H), ←
(2°, 2H),
(3°, 1H)





$CH_3CH_2CH_2CH_3$ → (1°, 6H) (2°, 4H)



$CH_3CH(CH_3)CH_3$ → (1°, 9H) (3°,1H)

Free radical : An atom or group of atoms having an odd [unpaired] electron is called free radical. e.g $Cl^\bullet$, $Br^\bullet$, $^\bullet CH_3$ etc.

Chain reaction : A reaction that involves a series of steps, each of which generates a reactive substance that brings about the next step is called chain reation. e.g. chlorination of methane.

Mechanism : Detail stepwise description of chemical reaction is known as mechanism.

1.13 Mechanism of halogenation (General mechanism) :

Halogenation of alkanes can be explained by free radical substitution mechanism. It consist of three steps.

Ist Step : Chain initiating step. Upon thermal or photo chemical decomposition homolytic cleavage take place and free radicals are generated.

$$\underset{\substack{\text{Halogen molecule} \\ (X_2 = Cl_2 \text{ or } Br_2)}}{X_2} \xrightarrow[\text{OR U.V. light}]{250^\circ - 400^\circ C} \underset{\text{(Free radical)}}{2X^\bullet} \quad \text{———— (1)}$$

It is known that halogen molecule (X_2) dissociates to two separate halogen atom ($X^\bullet$) in presence of uv–light or at high temperature. Each $X^\bullet$ radical has an unpaired electron. The energy is absorbed. So, this step is **endothermic** step.

IInd step : Chain propagating steps. Reactive particle ($X^\bullet$ free radical) is consumed and another reactive particle is generated.

$$\left.\begin{array}{ll} X^\bullet + \underset{\text{Alkane}}{R\text{–}H} \longrightarrow HX + R^\bullet & \text{———— (2)} \\ R^\bullet + X_2 \longrightarrow RX + X^\bullet & \text{———— (3)} \end{array}\right\} \text{Chain propagation}$$

Halogen radical ($X^\bullet$) formed in 1st step collides with alkane (R–H) molecule, abstract a hydrogen atom with one electron to form a molecule of hydrogen halide (HX) and alkyl radical ($R^\bullet$). The alkyl radical ($R^\bullet$) collides with X_2 molecule, abstracts a halogen atom with one electron to form a molecule of alkyl halide (RX) and halogen radical ($X^\bullet$) by this way step 2 and 3 will continue.

IIIrd Step : Chain terminating step. Reactive particles are combined (consumed) but not generated. The energy is liberated during this step, hence this step is **exothermic** step.

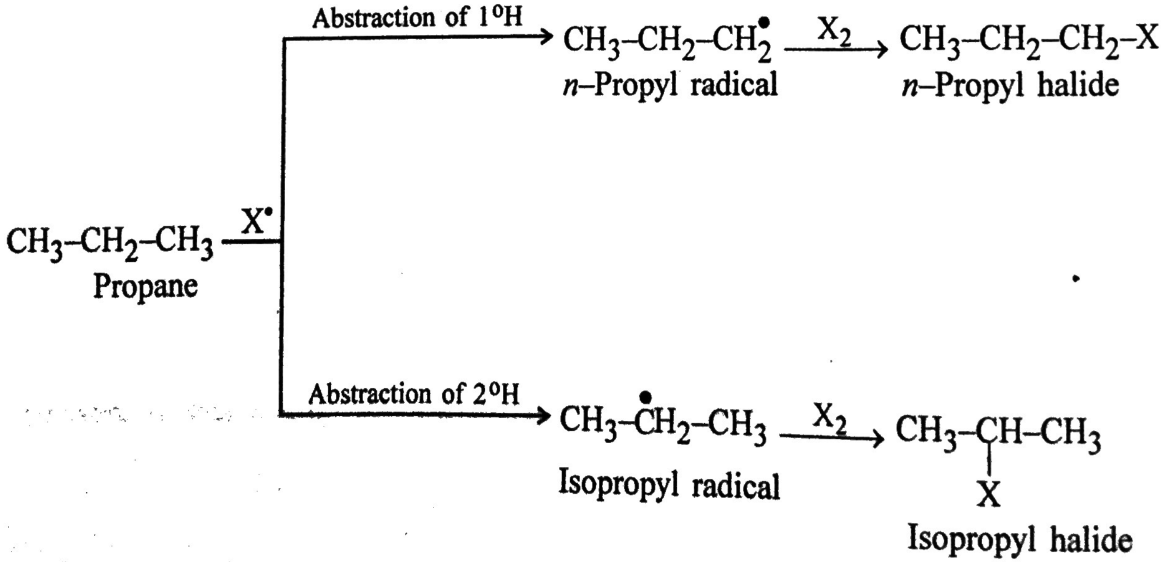
$$\left.\begin{array}{lll} X^\bullet + X^\bullet \longrightarrow X_2 & \text{\_\_\_\_\_\_\_\_} & (4) \\ R^\bullet + R^\bullet \longrightarrow R-R & \text{\_\_\_\_\_\_\_\_} & (5) \\ R^\bullet + X^\bullet \longrightarrow R-X & \text{\_\_\_\_\_\_\_\_} & (6) \end{array}\right\} \begin{array}{c}\text{Chain}\\ \text{termination}\\ \text{step}\end{array}$$

(where $R = -CH_3$, $-C_2H_5$ and X = Cl or Br)

During reaction between alkane and halogen, alkyl halide is obtained depends upon which alkyl radical is formed.

$$\underset{\text{Methane}}{CH_4 + X^\bullet} \longrightarrow \underset{\substack{\text{Methyl radical}\\ + HX}}{CH_3^\bullet} \xrightarrow{X_2} CH_3{-}X + X^\bullet$$

$$\underset{\text{Ethane}}{CH_3{-}CH_3 + X^\bullet} \longrightarrow \underset{\text{Ethyl radical}}{CH_3{-}\dot{C}H_2} \xrightarrow{X_2} CH_3{-}CH_2{-}X + X^\bullet$$



Formation of an alkyl halide is depend upon how fast the alkyl radical is formed. Formation of the alkyl radical is difficult but once formed the alkyl radical is readily converted in to the alkyl halide (see potential energy diagram).