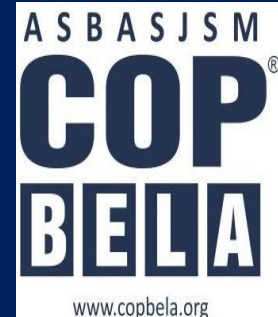




**Amar Shaheed Baba Ajit Singh Jujhar Singh Memorial**  
**COLLEGE OF PHARMACY**  
**(An Autonomous College)**  
**BELA (Ropar) Punjab**



Name of Unit	Alkanes, Alkenes and Conjugated Dienes
Subject /Course	Pharmaceutical Organic Chemistry-I
Subject/Course ID	BP202T
Class: B.Pharm.Semester	II
Course coordinator	Ms. Sukhwinder Kaur, Ms. Mandeep Kaur
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**Learning Outcome of Module 02**

LO	Learning Outcome	Course Outcome Code
LO1	To gain the knowledge of Alkanes, aAlkenes, Conjugated dienes, Its classification and Nomenclature.	BP 202.1
LO2	To understand various method of preparation of alkanes,alkenes and Conjugated dienes.	BP 202.4
LO3	To gain the knowledge about hybridization	BP202.5
LO4	To understand physical and Chemical properties of Alkanes, alkenes and Conjugated dienes.	BP 202.1

**Content Table**

<b>Topic</b>
<ul style="list-style-type: none"><li>• Introduction of Alkanes, Alkenes and Conjugated dienes.</li><li>• Classification of Alkanes, Alkenes and Conjugated dienes &amp; Nomenclature</li><li>• Hybridization of Alkanes, Alkenes and Conjugated dienes.</li><li>• Method of Preparation of Alkanes, Alkenes and Conjugated dienes.</li><li>• Properties of Alkanes, Alkenes and Conjugated dienes.</li></ul>

## INTRODUCTION OF ALKANES

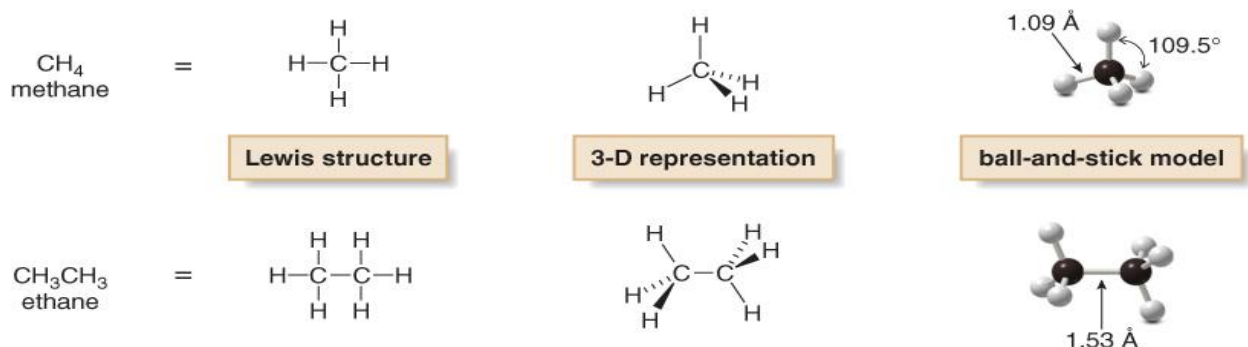
Alkanes are the simplest organic compounds made of carbon and hydrogen only. Alkanes are aliphatic hydrocarbons having **C—C and C—H  $\sigma$  bonds**. They can be categorized as acyclic or cyclic.

**Acyclic alkanes** have the molecular formula  $C_nH_{2n+2}$  (where  $n$  = an integer) and contain only linear and branched chains of carbon atoms. They are also called **saturated hydrocarbons** because they have the maximum number of hydrogen atoms per carbon.

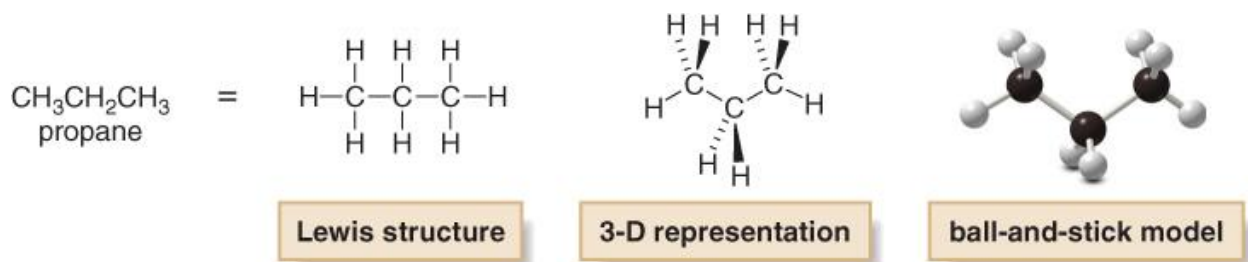
**Cycloalkanes** contain carbons joined in one or more rings. Because their general formula is  $C_nH_{2n}$ , they have two fewer H atoms than an acyclic alkane with the same number of carbons.

### Acyclic alkanes having One to Five C Atoms

- All C atoms in an alkane are surrounded by four groups, making them  $sp^3$  hybridized and tetrahedral, and all bond angles are  $109.5^\circ$ .
- The 3-D representations and ball-and-stick models for these alkanes indicate the tetrahedral geometry around each C atom.



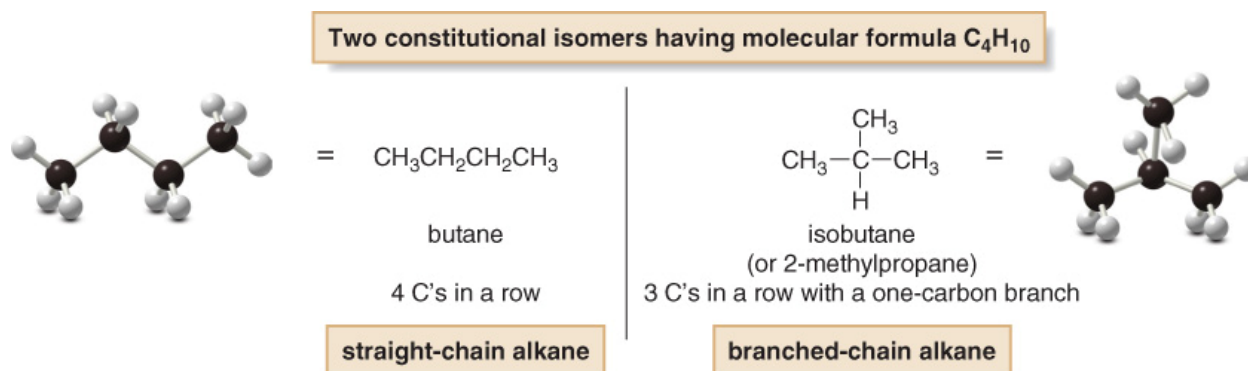
- The three-carbon alkane called propane, has a molecular formula  $C_3H_8$ . Note in the 3-D drawing that each C atom has two bonds in the plane (solid lines), one bond in front (on a wedge) and one bond behind the plane (on a dashed line).



- Additionally, in propane and higher molecular weight alkanes, the carbon skeleton can be drawn in a variety of ways and still represent the same molecule. For example, the three carbons of propane can be drawn in a horizontal row or with a bend. These representations are equivalent.
- In a Lewis structure, the bends in a carbon chain don't matter.

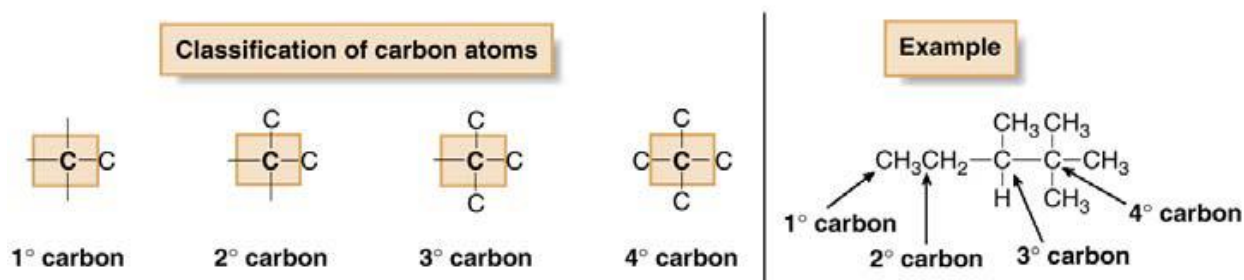


- There are two different ways to arrange four carbons, giving two compounds with molecular formula  $\text{C}_4\text{H}_{10}$ , named butane and isobutane.
- Butane and isobutane are **isomers**—two different compounds with the same molecular formula. Specifically, they are constitutional or structural isomers.
- **Constitutional isomers** differ in the way the atoms are connected to each other.



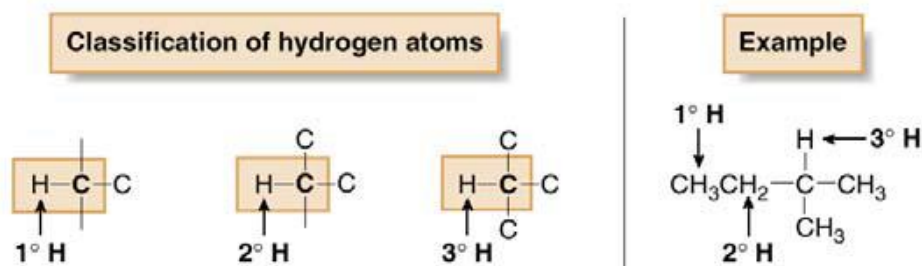
- Carbon atoms in alkanes and other organic compounds are classified by the number of other carbons directly bonded to them.

- A *primary carbon* ( $1^\circ$  carbon) is bonded to *one* other C atom.
- A *secondary carbon* ( $2^\circ$  carbon) is bonded to *two* other C atoms.
- A *tertiary carbon* ( $3^\circ$  carbon) is bonded to *three* other C atoms.
- A *quaternary carbon* ( $4^\circ$  carbon) is bonded to *four* other C atoms.



- Hydrogen atoms are classified as primary ( $1^\circ$ ), secondary ( $2^\circ$ ), or tertiary ( $3^\circ$ ) depending on the type of carbon atom to which they are bonded.

- A *primary hydrogen* ( $1^\circ$  H) is on a C bonded to one other C atom.
- A *secondary hydrogen* ( $2^\circ$  H) is on a C bonded to two other C atoms.
- A *tertiary hydrogen* ( $3^\circ$  H) is on a C bonded to three other C atoms.



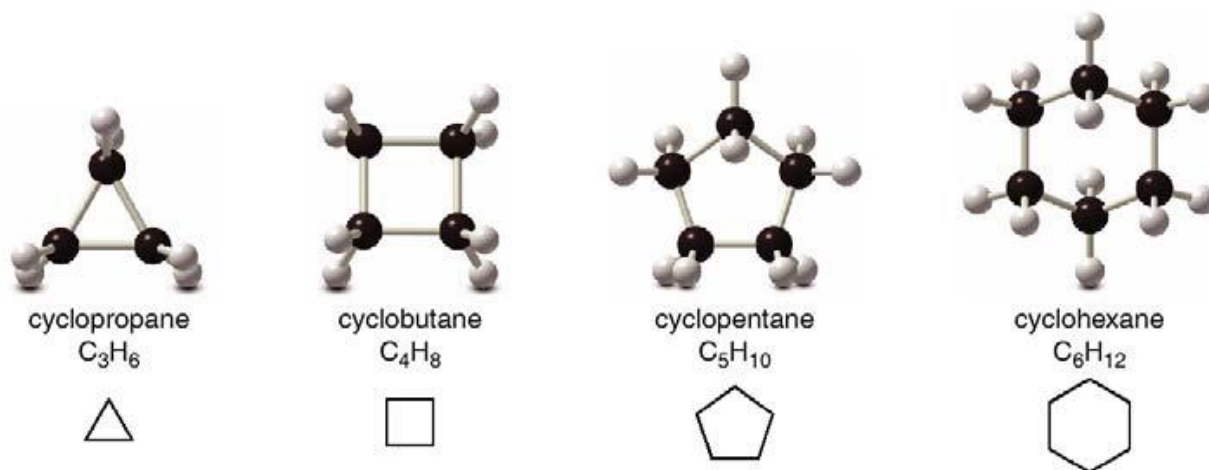
- The maximum number of possible constitutional isomers increases dramatically as the number of carbon atoms in the alkane increases. For example, there are 75 possible isomers for an alkane having 10 carbon atoms, but 366,319 possible isomers for one having 20 carbons.

- The suffix “ane” identifies a molecule as an alkane.
- By increasing the number of carbons in an alkane by a  $\text{CH}_2$  group, one obtains a “homologous series” of alkanes, as shown in Table
- The  $\text{CH}_2$  group is called “methylene.”

Number of C atoms	Molecular formula	Name ( <i>n</i> -alkane)	Number of constitutional isomers
1	$\text{CH}_4$	methane	—
2	$\text{C}_2\text{H}_6$	ethane	—
3	$\text{C}_3\text{H}_8$	propane	—
4	$\text{C}_4\text{H}_{10}$	butane	2
5	$\text{C}_5\text{H}_{12}$	pentane	3
6	$\text{C}_6\text{H}_{14}$	hexane	5
7	$\text{C}_7\text{H}_{16}$	heptane	9
8	$\text{C}_8\text{H}_{18}$	octane	18
9	$\text{C}_9\text{H}_{20}$	nonane	35
10	$\text{C}_{10}\text{H}_{22}$	decane	75
20	$\text{C}_{20}\text{H}_{42}$	eicosane	366,319

## Cycloalkanes

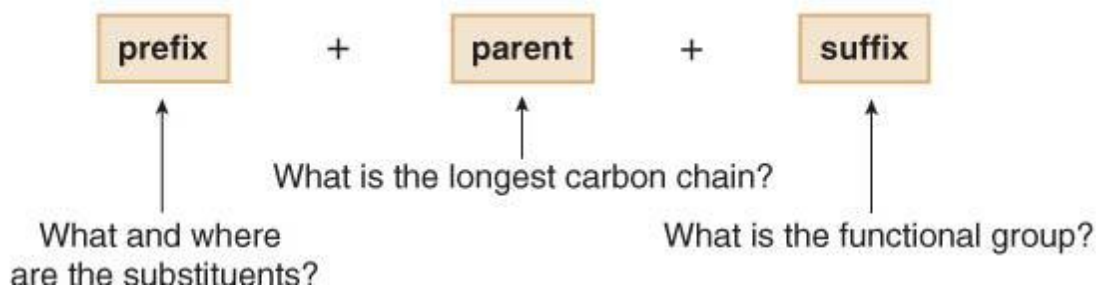
Cycloalkanes have molecular formula  $\text{C}_n\text{H}_{2n}$  and contain carbon atoms arranged in a ring. Simple cycloalkanes are named by adding the prefix *cyclo-* to the name of the acyclic alkane having the same number of carbons.



## NAMING ALKANES

The name of every organic molecule has 3 parts:

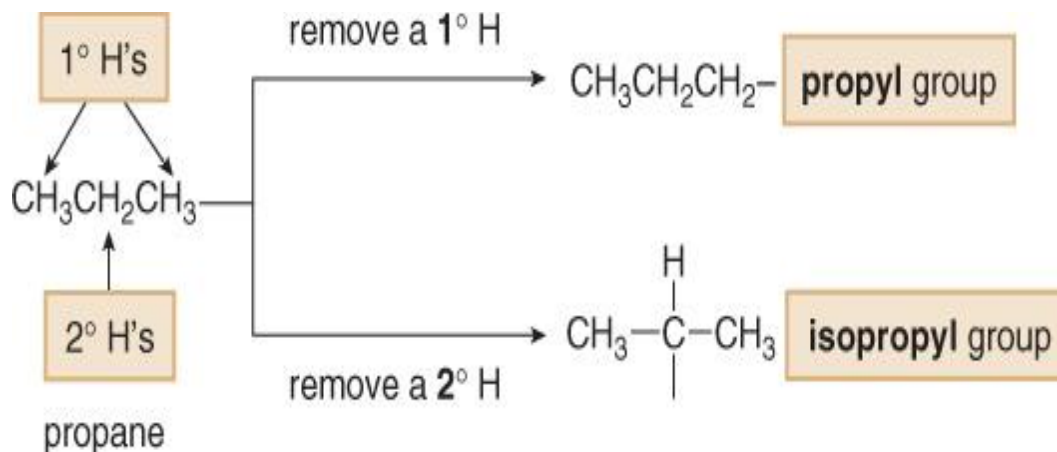
1. The parent name indicates the number of carbons in the longest continuous chain.
2. The suffix indicates what functional group is present.
3. The prefix tells us the identity, location, and number of substituents attached to the carbon chain.



### 1. Naming Substituents

- Carbon substituents bonded to a long carbon chain are called alkyl groups.
- An alkyl group is formed by removing one H atom from an alkane.
- To name an alkyl group, change the *-ane* ending of the parent alkane to *-yl*. Thus, methane ( $\text{CH}_4$ ) becomes methyl ( $\text{CH}_3-$ ) and ethane ( $\text{CH}_3\text{CH}_3$ ) becomes ethyl ( $\text{CH}_3\text{CH}_2-$ ).

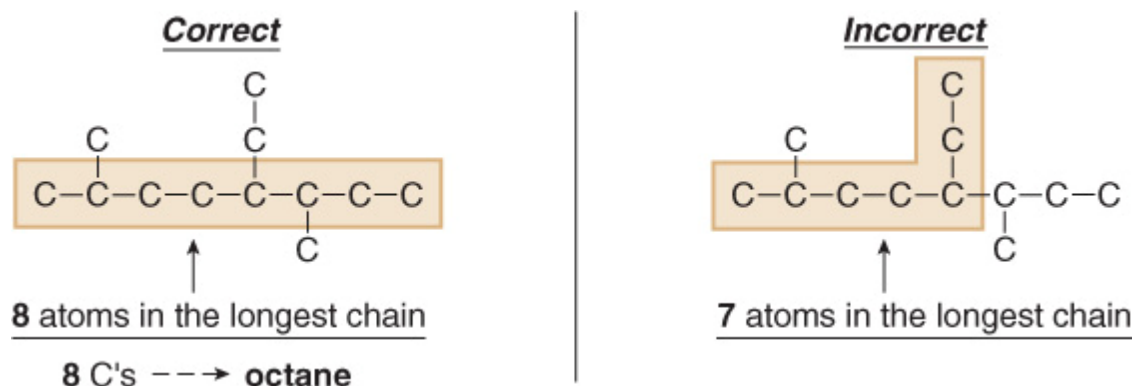
Naming three- or four-carbon alkyl groups is more complicated because the parent hydrocarbons have more than one type of hydrogen atom. For example, propane has both  $1^\circ$  and  $2^\circ$  H atoms, and removal of each of these H atoms forms a different alkyl group with a different name, propyl or isopropyl.



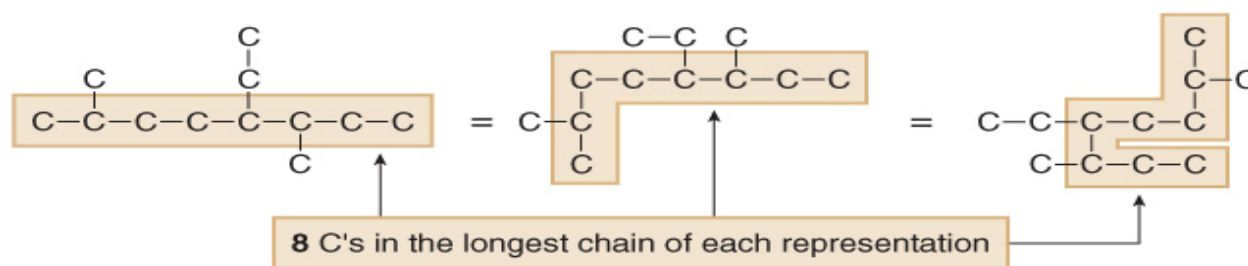


## NAMING AN ACYCLIC ALKANE

1. Find the parent carbon chain and add the suffix.



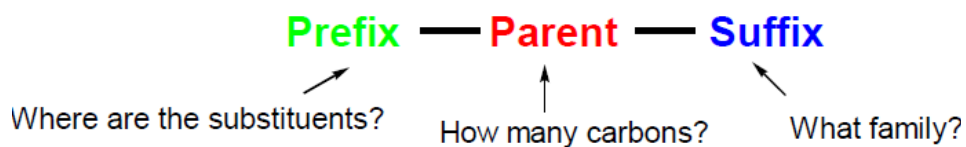
Note that it does not matter if the chain is straight or it bends.



## ORGANIC COMPOUNDS: ALKANES AND CYCLOALKANES

IUPAC: International Union of Pure and Applied Chemistry

### Naming Alkanes



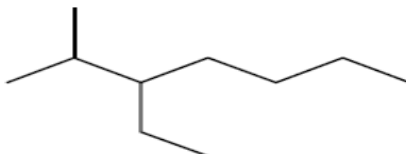
### Step 1. Find the parent hydrocarbon.

a) the longest continuous chain of carbon atoms



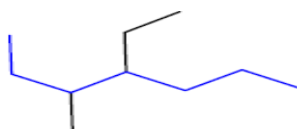


**b) if two different chains of equal length are present ; choose the one with the larger number of branch points**



**Step 2. Number the atoms in the main chain.**

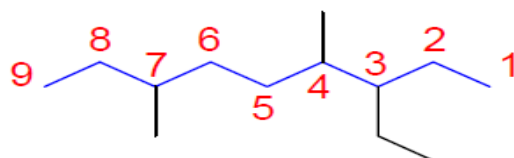
**a) beginning at the end nearer the first branch point**



heptane

**Step 3. Identify and number the substituents.**

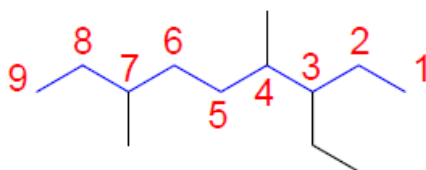
**a) assign a number to each substituent according to its point of attachment to the main chain**



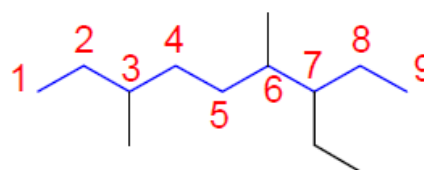
3-ethyl  
4-methyl  
7-methyl

a nonane

**b) if there is branching an equal distance away from both ends; begin the end nearer the second branch point**

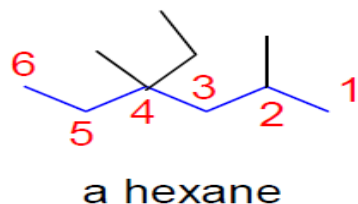


3,4,7



3,6,7

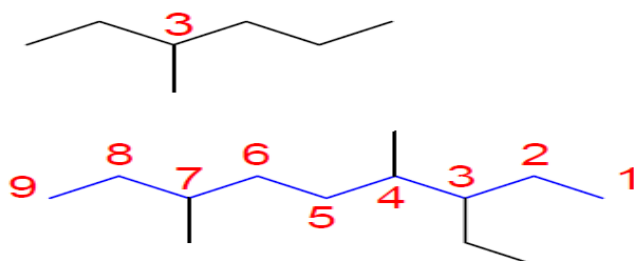
b) If there are **two substituents** on the same carbon, give them both the same number.



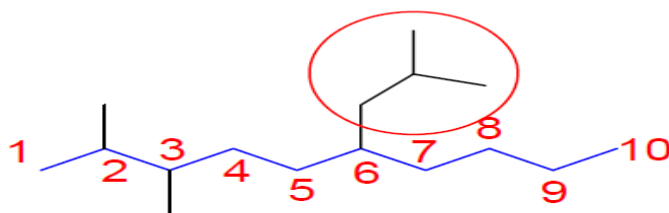
2-methyl  
4-methyl  
4-ethyl

**Step 4. Write the name as a single word.**

- use **hyphens** to separate the different prefixes
- use **comma** to separate numbers
- cite in **alphabetical order**
- more than one identical substituents; **di-, tri-, tetra-...**  
(Don't use these prefixes for alphabetizing purposes)

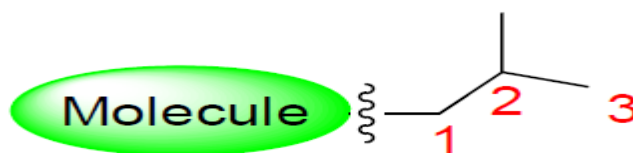


**Step 5. Name a complex substituent just as though it were itself a compound.**

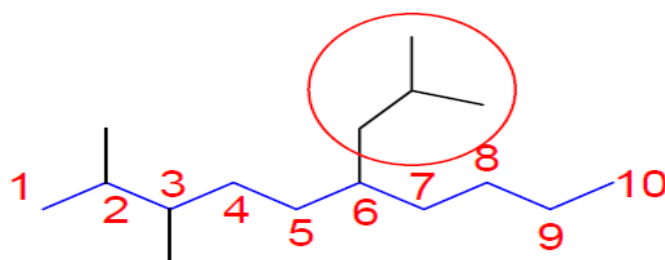


2,3,6-trisubstituted decane

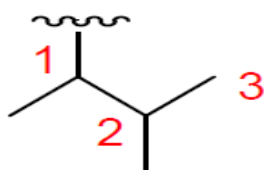
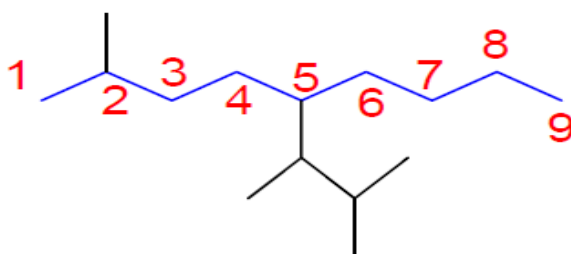
- begin numbering at the point of attachment



The substituent is alphabetized according to the first letter of its complete name (including any numerical prefix) and is set off in parentheses.



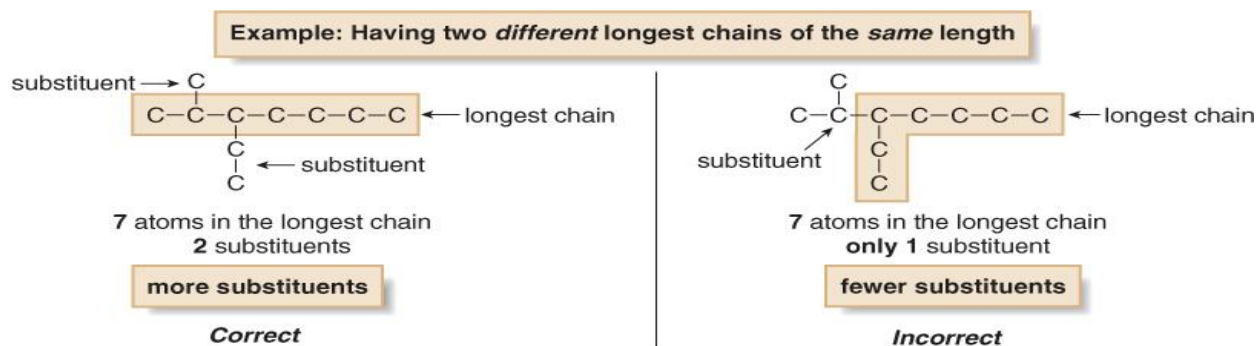
- alphabetizing the substituent: the **first letter of the complete name** (including any numerical prefix of the complex substituent)



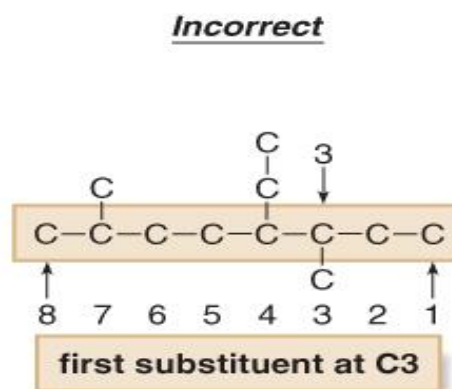
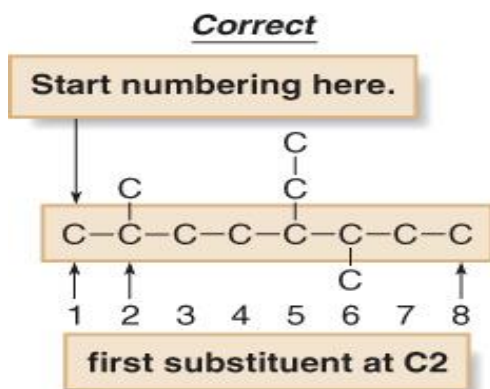
5-(1,2-dimethylpropyl)

2-methyl

Also note that if there are two chains of equal length, pick the chain with more substituents. In the following example, two different chains in the same alkane have seven C atoms. We circle the longest continuous chain as shown in the diagram on the left, since this results in the greater number of substituents.



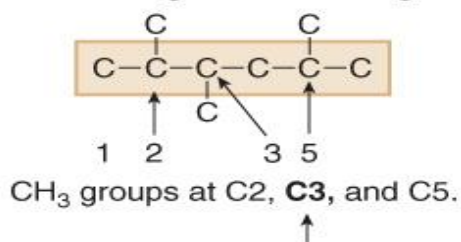
2. Number the atoms in the carbon chain to give the first substituent the lowest number.



If the first substituent is the same distance from both ends, number the chain to give the second substituent the lower number.

**Example: Giving a lower number to the *second* substituent**

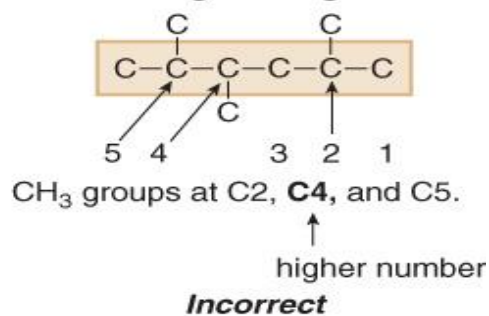
Numbering from *left* to right



The second substituent has a lower number.

**Correct**

Numbering from *right* to left

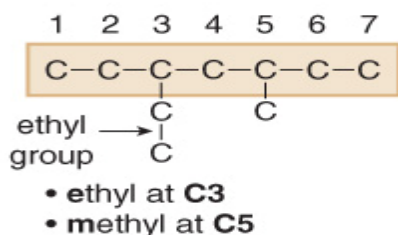


**Incorrect**

When numbering a carbon chain results in the same numbers from either end of the chain, assign the lower number alphabetically to the first substituent.

**Example: Two *different* groups *equidistant* from the ends**

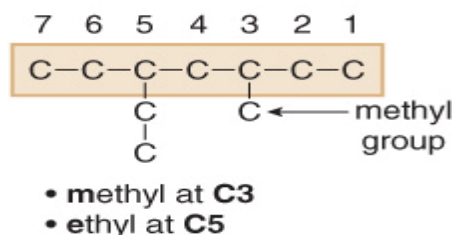
Numbering from *left* to right



Earlier letter → lower number

**Correct**

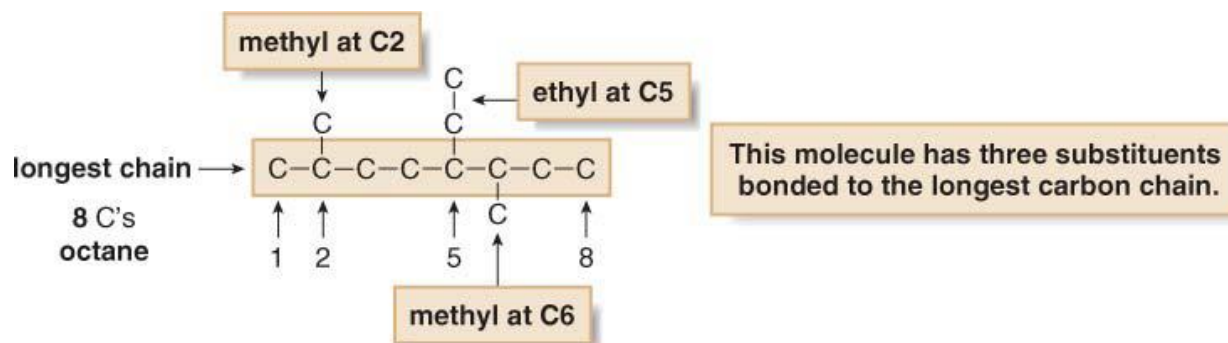
Numbering from *right* to left



**Incorrect**

3. Name and number the substituents.

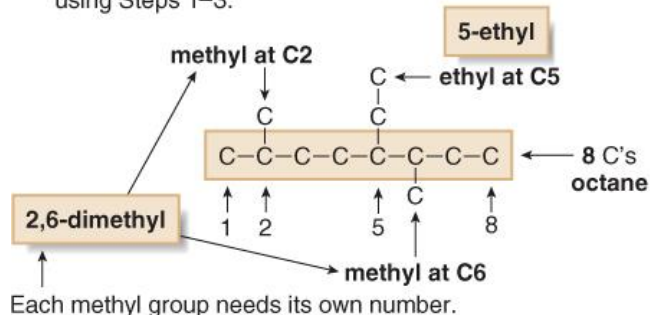
- Name the substituents as alkyl groups.
- Every carbon belongs to either the longest chain or a substituent, not both.
- Each substituent needs its own number.
- If two or more identical substituents are bonded to the longest chain, use prefixes to indicate how many: di- for two groups, tri- for three groups, tetra- for four groups, and so forth.



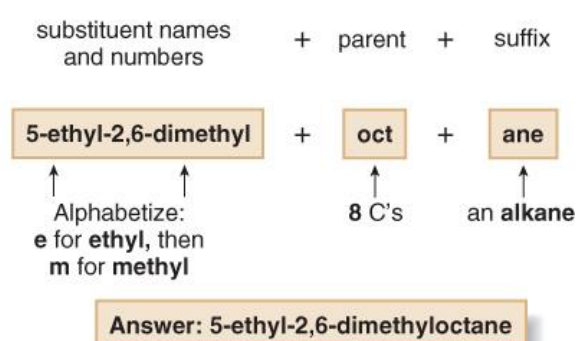
4. Combine substituent names and numbers + parent and suffix.

- Precede the name of the parent by the names of the substituents.
- Alphabetize the names of the substituents, ignoring all prefixes except iso, as in isopropyl and isobutyl.
- Precede the name of each substituent by the number that indicates its location.
- Separate numbers by commas and separate numbers from letters by hyphens. The name of an alkane is a single word, with no spaces after hyphens and commas.

[1] Identify all the pieces of a compound, using Steps 1–3.

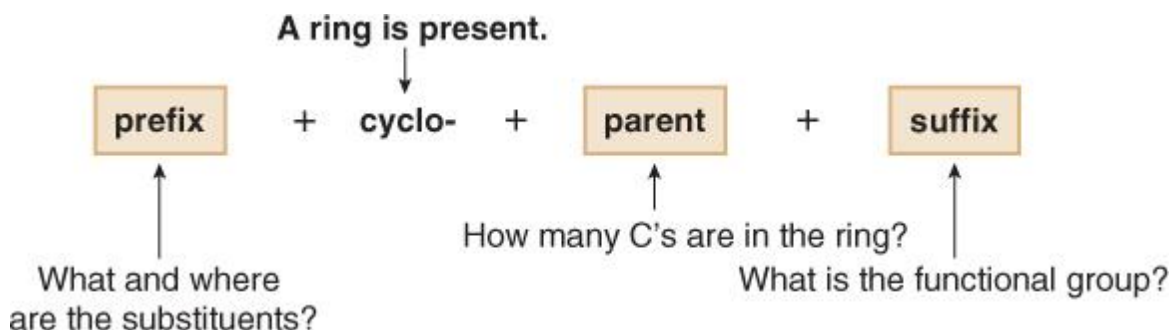


[2] Then, put the pieces of the name together.

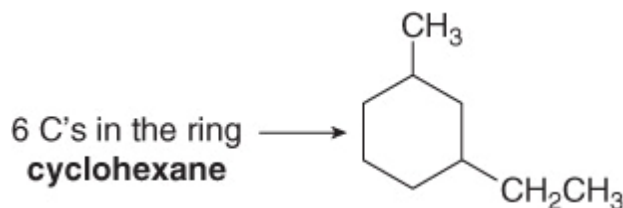


## NAMING CYCLOALKANES

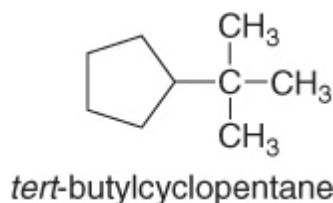
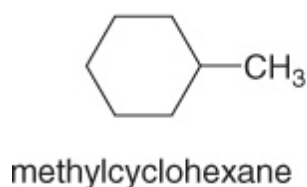
Cycloalkanes are named by using similar rules, but the prefix *cyclo* immediately precedes the name of the parent.



- Find the parent cycloalkane.

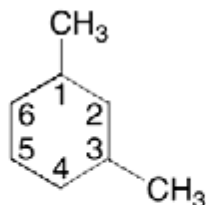


- Name and number the substituents. No number is needed to indicate the location of a single substituent.



For rings with more than one substituent, begin numbering at one substituent and proceed around the ring to give the second substituent the lowest number.

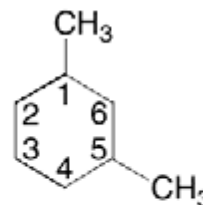
**numbering clockwise**



CH<sub>3</sub> groups at C1 and C3  
The 2<sup>nd</sup> substituent has a lower number.

**Correct: 1,3-dimethylcyclohexane**

**numbering counterclockwise**



CH<sub>3</sub> groups at C1 and C5

**Incorrect: 1,5-dimethylcyclohexane**

With two different substituents, number the ring to assign the lower number to the substituents alphabetically.

**Begin numbering at the ethyl group.**



earlier letter → lower number

**Correct: 1-ethyl-3-methylcyclohexane**

**Begin numbering at the methyl group.**



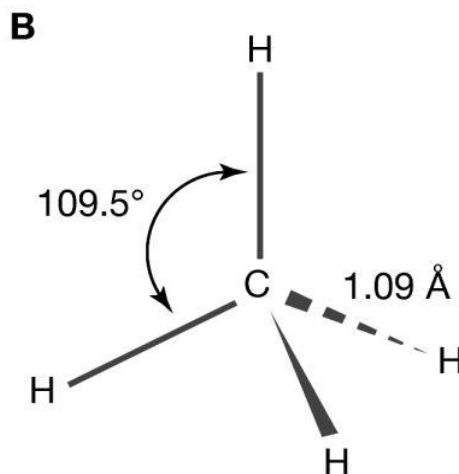
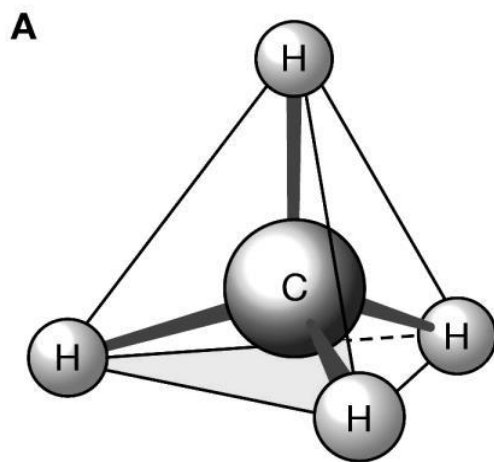
**Incorrect: 3-ethyl-1-methylcyclohexane**

## SP<sup>3</sup> HYBRIDIZATION

The process of formation of 4 equivalent orbitals from hybridization or mixing up of one S and three P orbitals is known as sp<sup>3</sup> hybridization. sp<sup>3</sup> hybrid orbitals and properties of sigma bonds.

### Characteristics:

- sp<sup>3</sup> has 25% s and 75% p character.
- The 4 sp<sup>3</sup> hybrids point towards the corners of a tetrahedron at 109.5° to each other.
- Each sp<sup>3</sup> hybrid is involved in a σ bond.

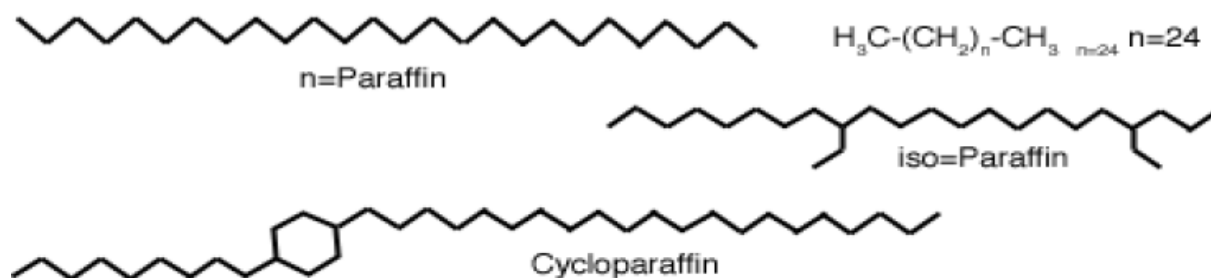


*Methane*



## PARAFFIN

- Paraffin's, more commonly referred to as alkanes, are the chemical family of saturated hydrocarbons.
- The general formula is  $C_nH_{2n+2}$ , C being a carbon atom, H a hydrogen atom, and „n“ an integer.
- The paraffin's are major constituents of natural gas and petroleum.
- Paraffin's containing fewer than 5 carbon atoms per molecule are usually gaseous at room temperature, those having 5 to 15 carbon atoms are usually liquids, and the straight-chain paraffins having more than 15 carbon atoms per molecule are solids.
- Branched-chain paraffin's have a much higher octane number rating than straight-chain paraffin's and, therefore, are the more desirable constituents of gasoline.
- The hydrocarbons are immiscible with water. All paraffin's are colourless.
- Paraffin is a strong-smelling liquid which is used as a fuel in heaters, lamps, and engines.



## Paraffin wax

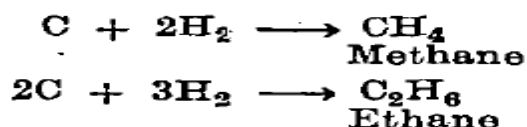
- It is also known as American English paraffin, is a white wax obtained from petrol or coal. It is used to make candles and in beauty treatments.
- The term "wax" simply refers to saturated hydrocarbons that contain more than 16 carbon atoms in the paraffin series ( $C_{16}-C_{40}$ ) and are in solid state at room temperature. Chemically, natural waxes are defined as long chain esters, monohydric (one hydroxyl group), or alcohols with long chain fatty acids. The majority of the waxes present in crude oil are considered synthetic paraffin waxes with non-oxidized saturated alkanes.

## Uses of Paraffin

1. Medicinal liquid paraffin, also known as *paraffinum liquidum*, is a very highly refined mineral oil used in cosmetics and for medical purposes.
2. Liquid paraffin has many uses in the medical field. Because liquid paraffin passes through the body's intestinal tract without being absorbed, it can be used as a laxative to limit the amount of water removed from the stool and ease constipation.
3. Liquid paraffin is considered to have a limited usefulness as an occasional laxative.
4. Liquid paraffin will reveal that this common personal care ingredient is used in many skin products, including creams, lotions, lip balm, soap, and even eczema ointments.
5. In burns treatment that involved covering the affected area with a combination of waxes and oils including paraffin wax; this petroleum-derived substance created a barrier for the skin to heal and was seen as a very effective treatment.
6. Paraffin wax were developed, the most popular of which was giving hot wax baths to patients suffering from a variety of ailments, in particular rheumatism and joint pain. The wax would be used to soften the skin and the intense heat would soothe the muscles and ready them for massage treatment.
7. White soft paraffin with liquid paraffin is used as a barrier cream by providing a layer of oil on the surface of the skin to prevent water evaporating from the skin surface. It is an emollient, sometimes known as skin lubricant. It is used to soothe, smooth and hydrate the skin.

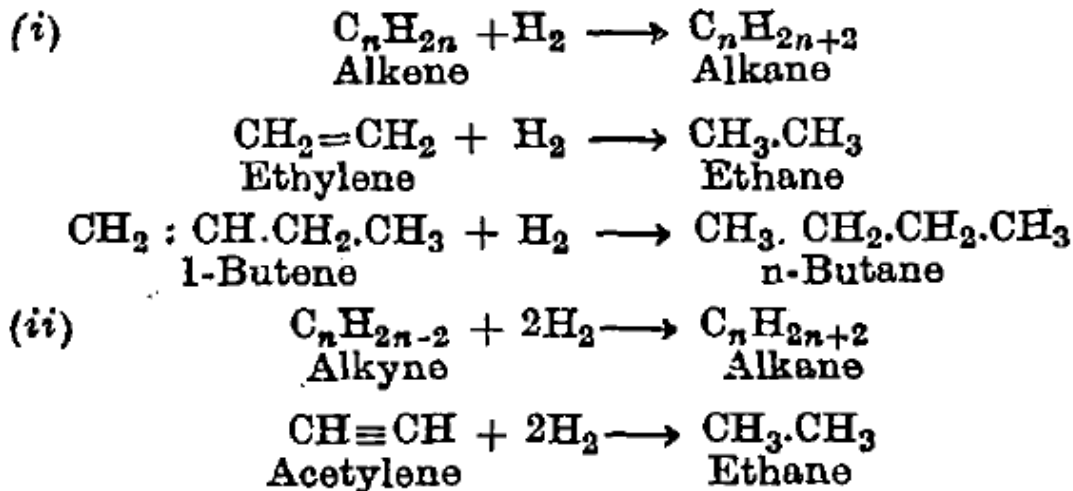
## METHOD OF PREPARATION

**(1) Direct synthesis from elements.** The lower hydrocarbons, methane and ethane are formed by passing the electric arc between carbon electrodes in an atmosphere of hydrogen. At the temperature of the arc (1200°) carbon and hydrogen combine together to form alkanes.



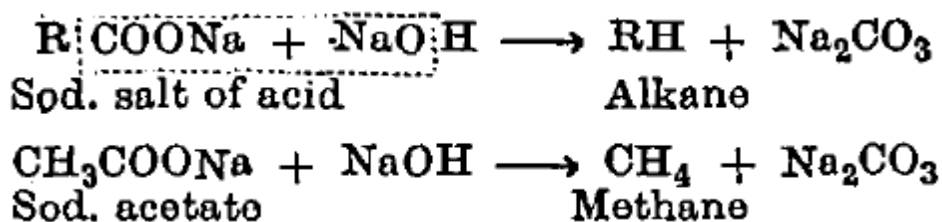
**(2) Hydrogenation of unsaturated hydrocarbons.** Alkanes are formed by passing a mixture of an unsaturated hydrocarbon and hydrogen over finely divided nickel (or platinum) at 250° to 300°C.

(Also known as Sabatier and Senderens Reaction).

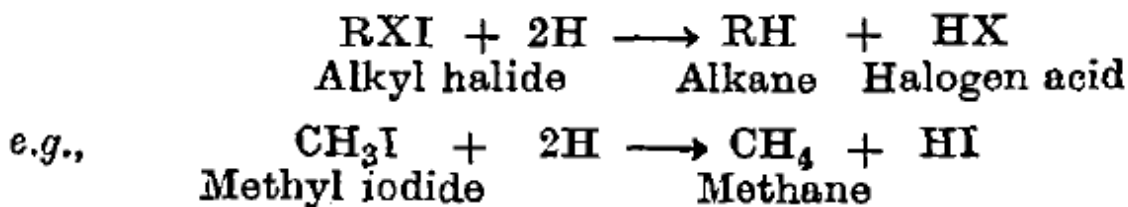


Since unsaturated hydrocarbons are obtained in large quantities by the cracking of petroleum, this method is now used for the technical preparation of alkanes.

**(3) Decarboxylation of a fatty acid.** When the sodium salt of a fatty acid  $\text{R}\cdot\text{COONa}$ , is heated with soda lime ( $\text{NaOH}+\text{CaO}$ ), a molecule of carbon dioxide is split off as carbonate and an alkane obtained.



**(4) Reduction of alkyl halides.** When reduced with nascent hydrogen, alkyl halides are converted to the corresponding alkanes.

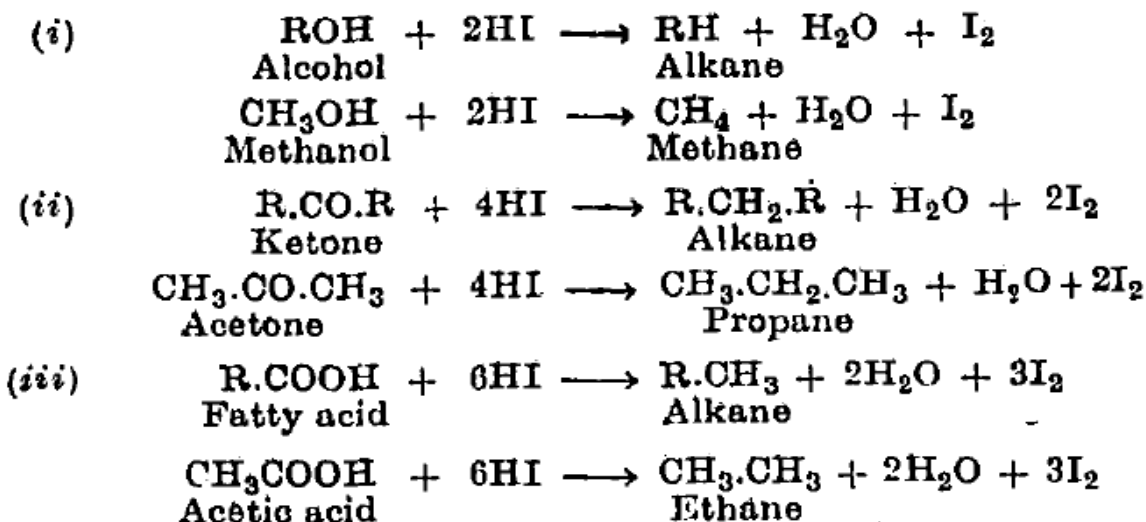


The common reducing agents employed for the purpose are zinc and hydrochloric acid; hot hydrogen iodide; and zinc.copper couple and alcohol.

This method for the preparation of alkanes is used when pure hydrocarbons are needed.

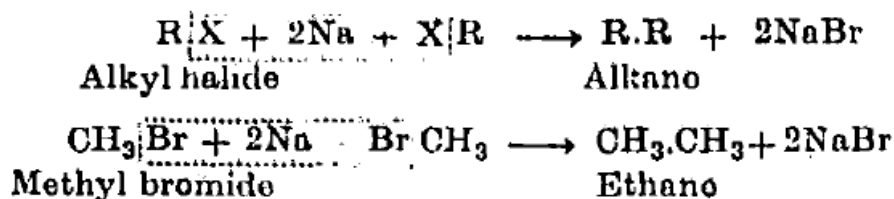
**(5) Reduction of alcohols, ketones and fatty acids.**

Alcohols, ketones and fatty acids when reduced with hot hydriodic acid and red phosphorus form alkanes.

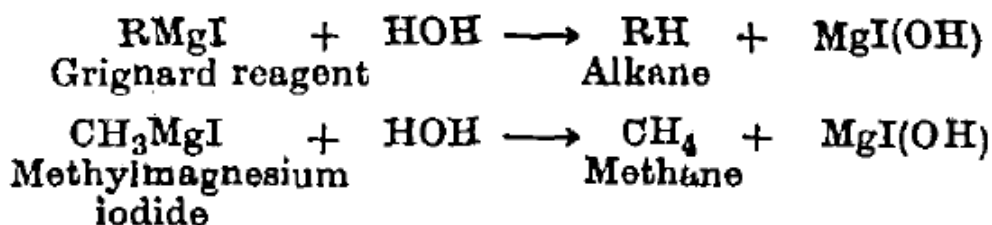


This method is particularly important for the preparation of higher alkanes from fatty acids which are easily obtained by the hydrolysis of fats.

**(6) Action of sodium on alkyl halides (Wurtz Reaction).** Higher alkanes are produced by heating an alkyl halide with sodium metal in dry ether solution. Two molecules of the alkyl halide react with two atoms of sodium to give alkane with double the number of carbon atoms present in the former.

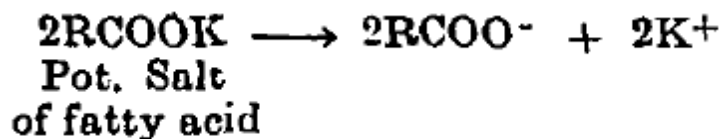


**(7) From Grignard Reagents.** Alkylmagnesium halides (Grignard reagents) when decomposed with water yield pure alkanes.



## (8) Electrolysis of salts of fatty acids (*Kolbe's Method*).

When concentrated solution of sodium or potassium salt of a fatty acid is electrolysed, a higher alkane is obtained.



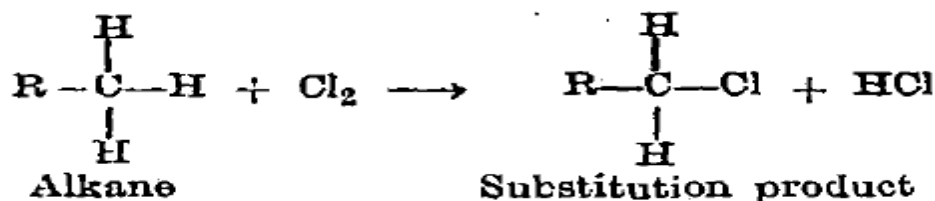
## PHYSICAL CHARACTERISTICS

- (1) The first four hydrocarbons methane, ethane, propane and butane are colourless, Odourless gases. The next eleven members (C<sub>5</sub>H<sub>12</sub> to C<sub>15</sub>H<sub>32</sub>) are colourless liquids having "benzine" odour. The higher alkanes are solids with no colour or odour.
- (2) Alkanes are the most volatile organic compounds, their boiling points being the lowest when compared with those of any of their derivatives.
- (3) The liquid alkanes are lighter than water.
- (4) They are almost insoluble in water but dissolve freely in organic solvents like ether acetone, and carbon tetrachloride.
- (5) Their boiling points and specific gravities increase with rise of molecular weight. Among the lower members, a difference of CH<sub>2</sub> corresponds to an increase of about 30° in the boiling point.

## CHEMICAL REACTIONS

(i) **STABILITY.** They are characterised by their stability to most chemical reagents. The four valencies of the carbon atoms being fully satisfied, there is no scope for further addition of hydrogen, halogens etc. Moreover a carbon-to-carbon linkage is unusually *strong* and cannot be ruptured by even such reagents as potassium permanganate, chromic acid etc.

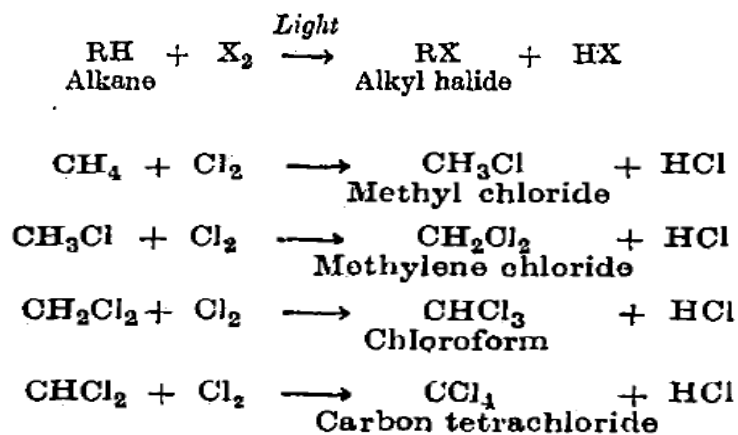
(ii) **SUBSTITUTION REACTIONS.** The linkage between carbon and hydrogen is comparatively weak so that the hydrogen atoms can be replaced by other atoms or groups giving substitution products.



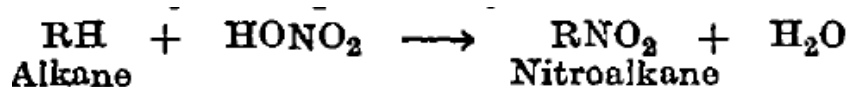
**(iii) OXIDATION REACTIONS.** When burnt in air or oxygen, the alkanes are decomposed to form carbon dioxide and water. On slow combustion the products are found to contain aldehydes and fatty acids.

The general reactions of alkanes are described below:

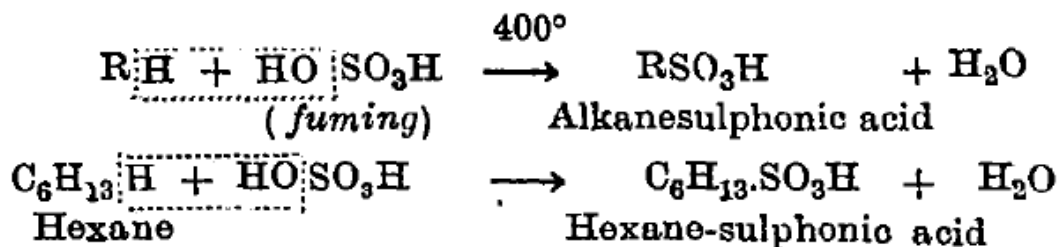
**(1) Halogenation.** Chlorine and bromine can substitute the hydrogen atoms of alkanes with considerable ease, chlorine being more reactive than bromine. Thus by the action of chlorine at ordinary temperature in diffused daylight all the four hydrogen atoms of methane can be successively replaced by chlorine atoms.



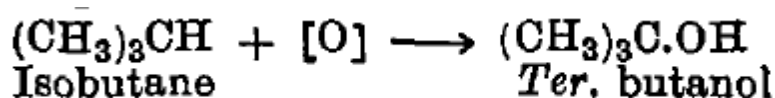
**(2) Nitration.** Nitric acid has no action on lower alkanes but by its long, continued action on higher hydrocarbons one of their hydrogen atoms may be replaced by a nitro-group, NO<sub>2</sub> (Nitration).



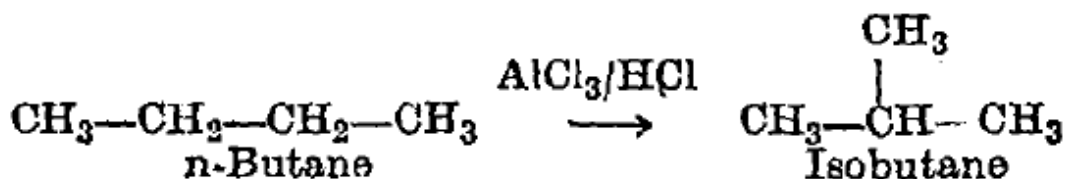
**(3) Sulphonation.** Alkanes react with fuming sulphuric acid at elevated temperatures to produce alkane sulphonic acids.



**(4) Oxidation:** Normal alkanes are not oxidised by potassium permanganate but the latter oxidises a tertiary hydrogen atom to a hydroxy group. Thus isobutane is oxidised to tertiary butanol.

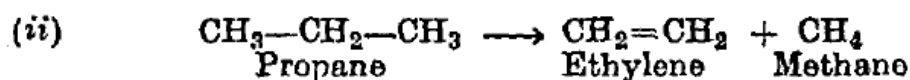
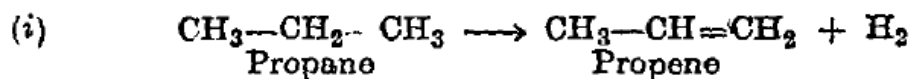


**(5) Isomerisation.** n-Alkanes in the presence of aluminium chloride and hydrogen chloride or of aluminium bromide and hydrogen bromide are converted to their branched-chain isomers.

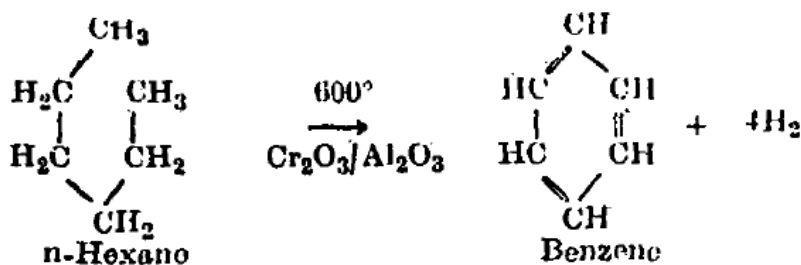


**(6) Pyrolysis.** By the term pyrolysis (Gr., pyr = fire ; lysis = loosing) is meant the conversion of an organic substance to one or more new substances by the action of heat alone. When the vapours of a higher alkane are heated at elevated temperature (500° or more) in the absence of oxygen, chemical decomposition occurs in two ways:

- By fission of C-H linkages to form an unsaturated hydrocarbon and hydrogen gas ; and
- By fission of C-C linkages to give simpler hydrocarbons - one alkane and one alkene.



**(i) Aromatisation.** The alkanes containing six or more carbon atoms are converted into aromatic hydrocarbons at high temperature in the presence of catalyst. Thus, n-hexane and n-heptane when passed over chromium trioxide supported on aluminium trioxide at 600°, yield benzene and Toluene.

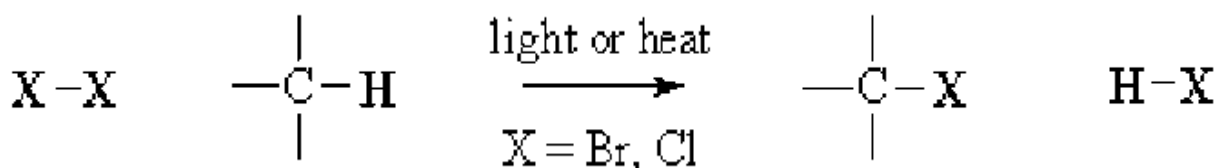




## HALOGENATION OF ALKANES (FREE RADICAL SUBSTITUTION REACTION)

The reaction of a halogen with an alkane in the presence of ultraviolet (UV) light or heat leads to the formation of a haloalkane (alkyl halide). An example is the chlorination of methane. It is also known as Radical Halogenation of Alkanes. Reaction type is Free Radical Substitution Reaction.

- When treated with Br<sub>2</sub> or Cl<sub>2</sub>, radical substitution of R-H generates the alkyl halide and HX.
- Alkane R-H relative reactivity order: tertiary > secondary > primary > methyl.
- Halogen reactivity F<sub>2</sub> > Cl<sub>2</sub> > Br<sub>2</sub> > I<sub>2</sub>.
- Only chlorination and bromination are useful in the laboratory.
- Bromination is selective for the R-H that gives the most stable radical. Chlorination is less selective.



- Mechanism Of Halogenation	Radical chain mechanism for reaction of methane with Cl <sub>2</sub>
<p><b>Initiation Step</b></p> $\text{X}_2 \xrightarrow{\text{uv}} \text{X}^\bullet + \text{X}^\bullet$ <p><b>Propagation Steps</b></p> $\text{RH} + \text{X}^\bullet \longrightarrow \text{R}^\bullet + \text{HX}$ $\text{R}^\bullet + \text{X}_2 \longrightarrow \text{RX} + \text{X}^\bullet$ <p><b>Termination Steps</b></p> $\text{X}^\bullet + \text{X}^\bullet \longrightarrow \text{X}_2$ $\text{X}^\bullet + \text{R}^\bullet \longrightarrow \text{RX}$ $\text{R}^\bullet + \text{R}^\bullet \longrightarrow \text{R-R}$	<ul style="list-style-type: none"> <li>• <b>Chain - initiating steps:</b> steps in which the chain reaction starts</li> <math display="block">\text{Cl}-\text{Cl} \xrightarrow{\text{energy}} 2 \text{Cl}^\bullet</math> <li>• <b>Chain propagating steps:</b> steps which keep to the reaction going</li> <math display="block">\text{Cl}^\bullet + \text{CH}_4 \longrightarrow \text{CH}_3^\bullet + \text{HCl}</math> <math display="block">\text{CH}_3^\bullet + \text{Cl}_2 \longrightarrow \text{CH}_3\text{Cl} + \text{Cl}^\bullet</math> <li>• <b>Chain - terminating:</b> steps which might occur which causes the chain reaction to stop</li> <math display="block">\text{Cl}^\bullet + \text{Cl}^\bullet \longrightarrow \text{Cl}_2</math> <math display="block">\text{CH}_3^\bullet + \text{CH}_3^\bullet \longrightarrow \text{C}_2\text{H}_6</math> <math display="block">\text{CH}_3^\bullet + \text{Cl}^\bullet \longrightarrow \text{CH}_3\text{Cl}</math> </ul>

## ALKENES

Alkenes are unsaturated aliphatic hydrocarbons having two hydrogen atoms less than alkanes and there is presence of double bond in their molecules. The general formula of alkene is  $C_nH_{2n}$ . Where  $n = 2, 3, 4, \dots$  etc. Alkenes are also known as olefins. Unsaturated hydrocarbons having two or three double bonds are called as alkadienes and alkatrienes. Unsaturated hydrocarbons having several double bonds are known as polyenes

### NOMENCALTURE OF ALKENES

Alkenes are named by their common name and IUPAC names

1. **Common System** – The common name is obtained by replacing the suffix -ane from the name of corresponding alkane by -ylene i.e. **Alkane-ane + ylene = Alkylene**.  
E.g Ethylene, propylene, Butylene.
2. **IUPAC System**- The name is derived by replacing the suffix -ane of the corresponding alkane by -ene i.e. **Alkane-ane+ene = Alkene**.

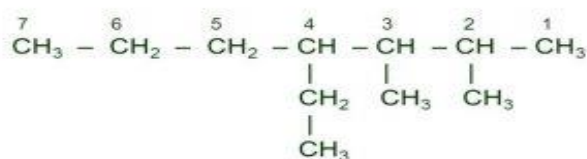
### RULES FOR NAMING ALKENES ACCORDING TO IUPAC SYSTEM

**RULE1:** The longest carbon chain containing the double bond is chosen as the parent alkene

**RULE2:** Position of the double bond and substituent are indicated by Arabic numerals 1,2,3,... etc and numbering is done from the side which give lowest number to the double bond. Also the carbon chain is number to the double bond. Also the carbon chain is numbered in such a way that the substituent if present gets the lower number.

**RULE3:** Name of the substituent on carbon chain is prefixed, preceded by its position, to the name of parent alkene.

**RULE4:** If the substituent is repeated two, three or four times the prefix di, tri, tetra is used.

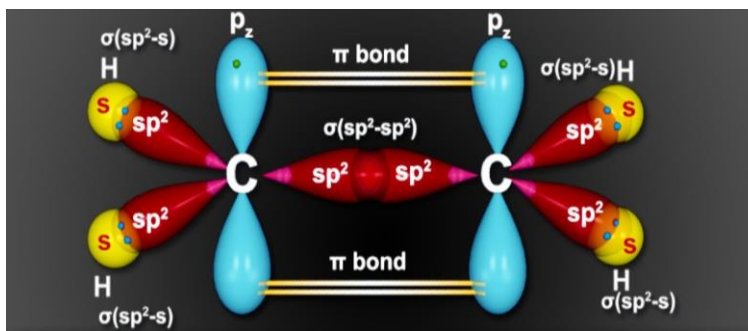


4-ethyl-2,3-dimethylheptane

Formula	Structure	Common Name	IUPAC Name
$C_2H_4$	$H_2C=CH_2$	Ethylene	Ethene
$C_3H_6$	$H_3C-CH=CH_2$	Propylene	Propene
$C_4H_8$	$H_3C-CH_2-CH=CH_2$	Butylene	1-Butene

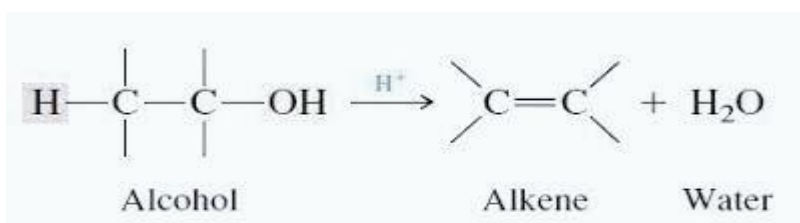
### HYBRIDIZATION IN ALKENES- $SP^2$ HYBRIDIZATION

In ethylene the carbon atoms are  $Sp^2$  hybridized, they are attached to each other by a sigma and a pi bond. The sigma bond results from overlap of one  $sp^2$  hybrid orbital from one with  $sp^2$  hybrid orbital of another carbon. The pi bond is formed from the overlapping of unhybridized orbitals. The remaining  $sp^2$  orbital form sigma bond with hydrogen atoms.

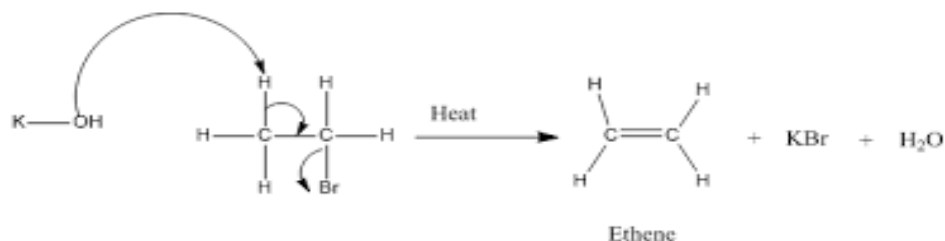


### METHOD OF PREPARATION OF ALKENES

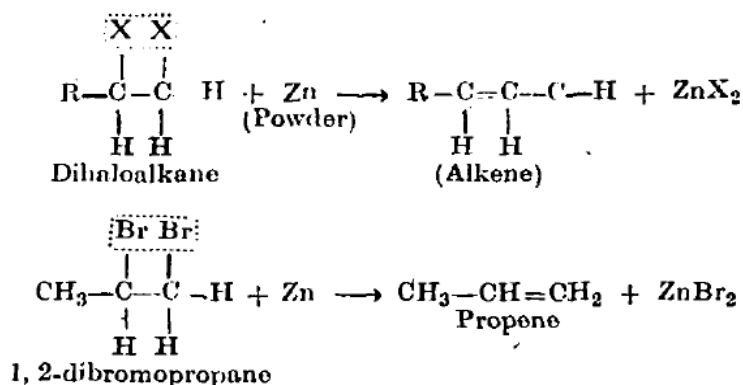
- 1. DEHYDRATION OF ALCOHOLS-** The dehydration reaction of alcohols to generate alkene proceeds by heating the alcohols in the presence of a strong acid, such as sulfuric or phosphoric acid, at high temperatures.



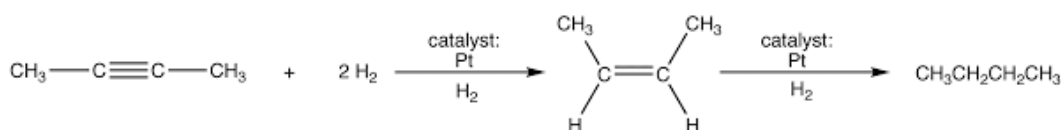
- 2. DEHYDROHALOGENATION OF ALKYL HALIDE-** When an alkyl halide is heated with concentrated solution of KOH, a molecule of hydrogen halide eliminated and an alkene forms. This reaction is called dehydrohalogenation.



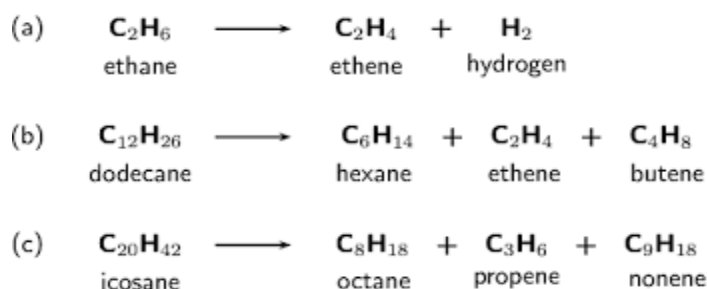
- 3. BY DEHALOGENATION OF DIHALOALKANES WITH ZINC-** When dihalogen derivatives of alkenes having the two halogen atoms on adjacent carbons are heated with an active metal like zinc the latter removes the halogen atoms to form alkenes.



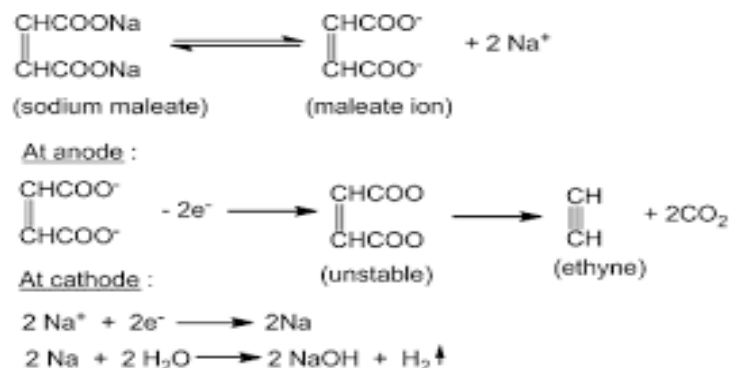
- 4. BY PARTIAL HYDROGENATION OF ALKYNES-** The alkyne mixed with hydrogen gas is passed over finely divided platinum or palladium, or heated nickel, when it adds only two H atoms to give alkene.



- 5. BY CRACKING.** The higher alkanes when heated to a high temperature decompose to give a lower alkene along with alkane.



**6. BY ELECTROLYSIS OF SALTS OF DICARBOXYLIC ACIDS.** Alkenes are formed by the electrolysis of aqueous solutions of potassium salts of dibasic acids of the succinic acid series.



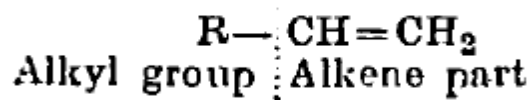
**PHYSICAL PROPERTIES-** In general, alkenes resemble alkanes in their physical properties.

1. The first three alkenes - ethene, propene, and butenes are gases at ordinary temperature; the next fourteen members are liquids and the hydrocarbons with more than 18 carbon atoms in the molecule are solids. They are all colourless and odourless except ethene which has a rather pleasant odor.
2. They are little less volatile than the corresponding alkanes. Their boiling and melting points are slightly higher than those of alkane containing the same number of carbon atoms.
3. They are only slightly soluble in water but dissolve freely in organic solvents.
4. The lower alkenes are powerful general anaesthetics.
5. Their boiling points, melting points, and specific gravities, in general, rise with increase of molecular weight in the homologous series.

## CHEMICAL CHARACTERISTICS

The molecule of an alkene (other than ethylene) consists of two parts:

- (a) an alkyl group, R ; and
- (b) the alkene part or group containing the doubly bonded carbon atoms.

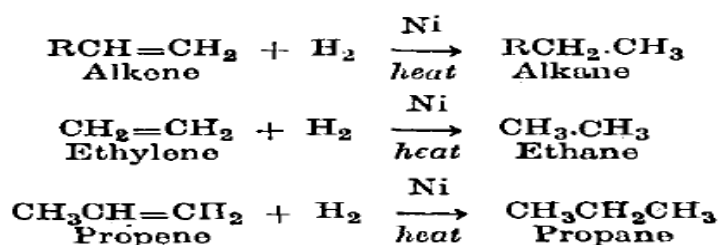


In general, alkenes give the following types of reactions.

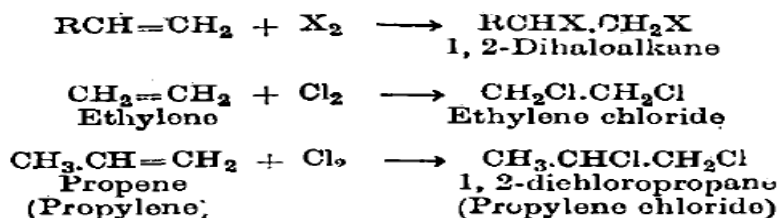
- 1. ADDITION REACTIONS.** In these reactions, the reagent adds along the double bond which is then converted to a single bond.
- 2. OXIDATION REACTIONS.** The double bond being a weak spot in the molecule is readily attacked by strong oxidising agents. The molecule of an alkene is, therefore, oxidised at this point, giving two simple oxidation products which may be aldehydes ketones or fatty acids.
- 3. SUBSTITUTION REACTIONS.** The alkyl group is capable of undergoing substitution reactions and one or more hydrogen atoms in it may be replaced by monovalent atoms or groups. For example. it can be chlorinated easily. The alkene part of the molecule does not give substitution reactions.
- 4. POLYMERISATION.** The valency bonds constituting the double bond are not in a stable condition. They become all the more labile at high temperature. Thus many molecules of an alkene may join together to form compound of higher molecular weights.

The general reactions of alkenes are given below.

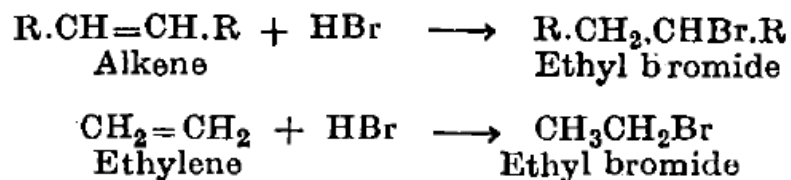
- 1. Addition of Hydrogen.** When the vapours of an alkene mixed with hydrogen are passed over finely divided nickel at high temperature, it adds a molecule of hydrogen at the double bond giving alkane.



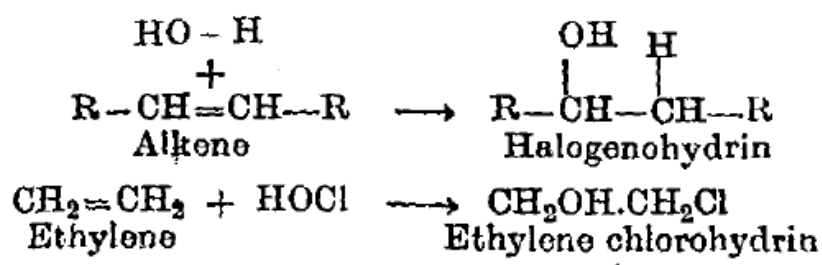
- 2. Addition of Halogens.** Alkenes react readily with halogens by addition, forming dihalogen derivatives.



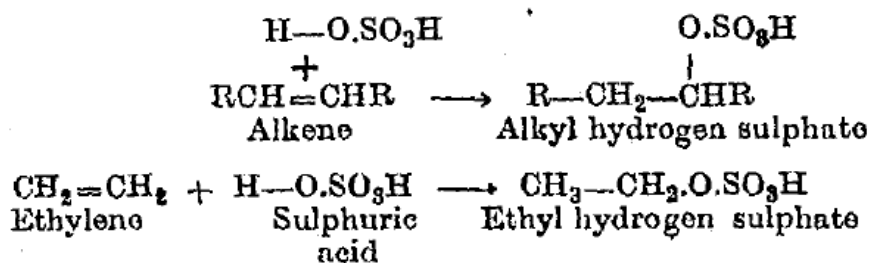
**3. Addition of Halogen acids.** Addition of halogen acids to alkenes gives alkyl halides.



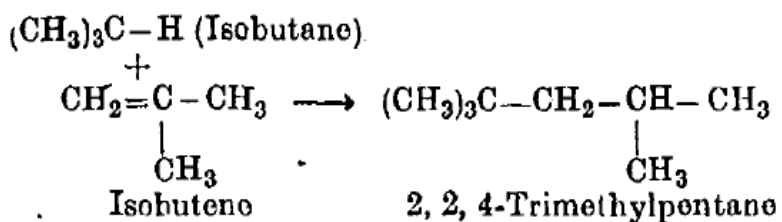
**4. Addition of Hypohalous acids.** Hypochlorous acid, and to a less extent hypobromous acid, reacts with alkenes to form halogenohydrins.



**5. Addition of Sulphuric Acid.** Alkenes react with concentrated sulphuric acid to form alkyl hydrogen sulphates.

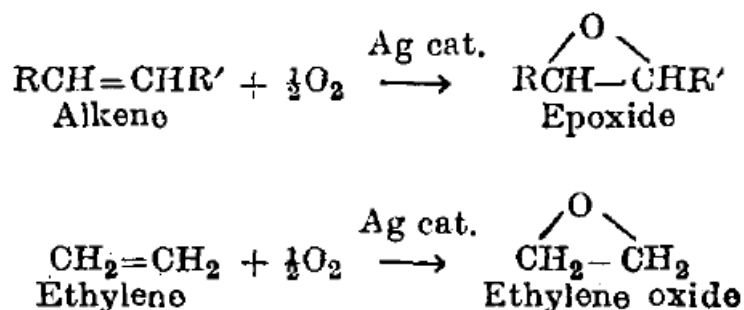


**6. Alkylation.** The addition of alkanes to alkenes is carried in the presence of an acid catalyst (HF, AlCl<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> etc.)

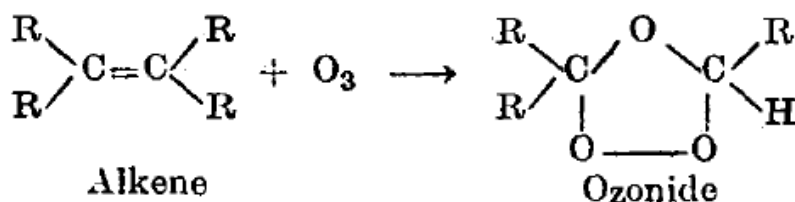




- 7. Addition of Oxygen.** Lower alkenes react with oxygen by addition in the presence of If special catalyst to form **epoxides**.

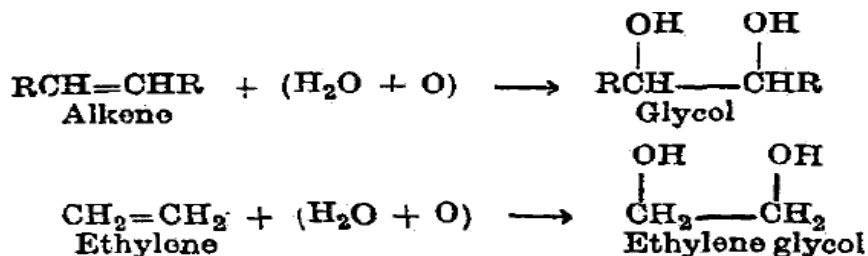


- 8. Addition of Ozone.** When ozone is passed through an alkene dissolved in an inert solvent, it adds across the double bond to form an **Ozonide**.

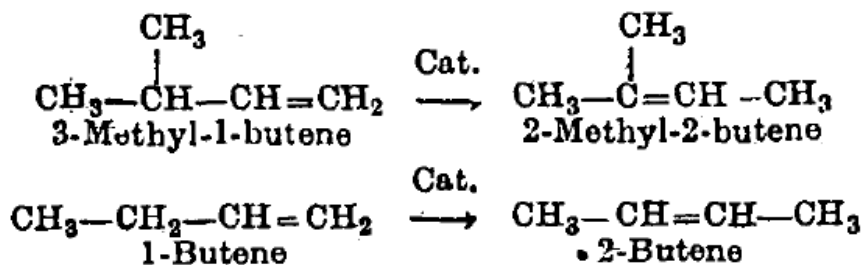


- 9. Oxidation Reactions.** Alkenes are more readily oxidised than the alkanes, the site of attack being the. double bond. The nature of the oxidation products obtained in a particular case depends upon the strength of the oxidising agent employed.

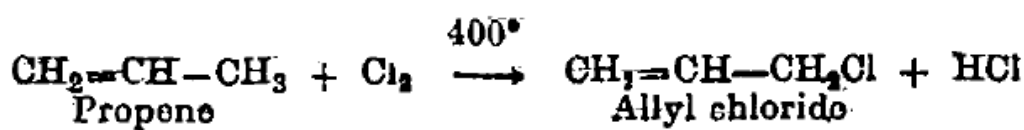
- A) WITH MILD OXIDISING AGENT.** When treated with 1 percent potassium permanganate solution, an alkene adds two (OH) groups at the double bond and thus forms a glycol.



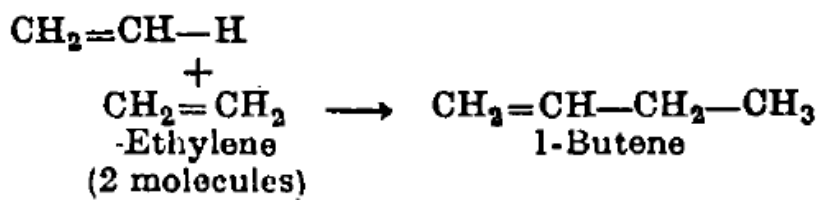
**Isomerisation**-The alkenes on heating or in the presence of a catalyst, undergo isomerisation when the double bond shifts to a carbon atom with greater, branching or one centrally located in the molecule.



**Substitution Reactions** - When alkenes are chlorinated at high temperature, it results in a product formed by substitution in the alkyl group.

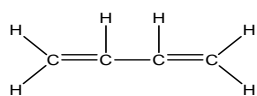


**Polymerisation**- At high temperature and in the presence of acid catalyst alkene molecules add to one another to form polymers.

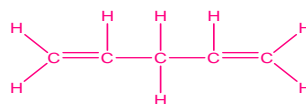


### CONJUGATED DIENES

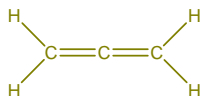
- + Alkenes containing 2 Carbon double bonds (C=C) are called dienes or alkadienes.
- + If the double bonds are separated by one single bond, the diene is called as Conjugated dienes.
- + If the double bond is separated by more than one double bond, the diene is called as Non-Conjugated diene or Isolated diene.
- + If the double bond is adjacent to each other, the diene is called as Cumulative diene.



Conjugated Diene

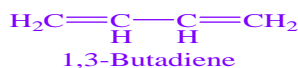


Non-Conjugated diene

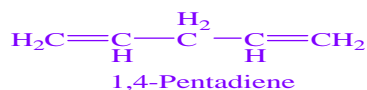


Cumulative Diene

- Dienes are named by the IUPAC system in the same way as alkenes except that ending **adiene** is used.
- The positions of the double bond are numbered to give the first carbon of each double bond a minimum number.



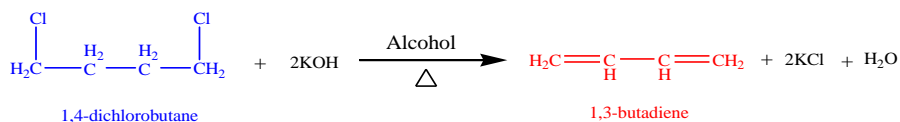
1,3-Butadiene



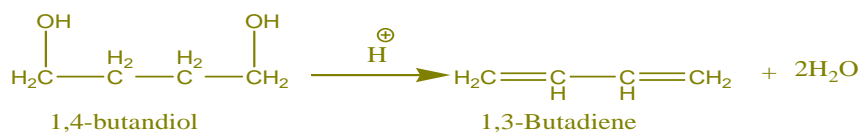
1,4-Pentadiene

## METHOD OF PREPARATION OF CONJUGATED DIENES(1,3-Butadiene)

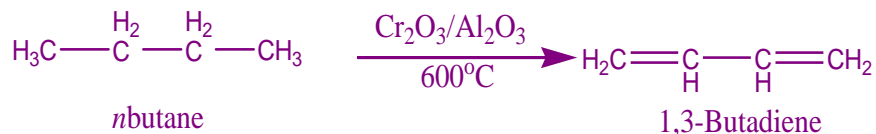
- By heating 1,4-dichlorobutane with alcoholic KOH. This is Dehydrohalogenation reaction.



- By Acid catalyzed dehydration of 1,4-butanediol



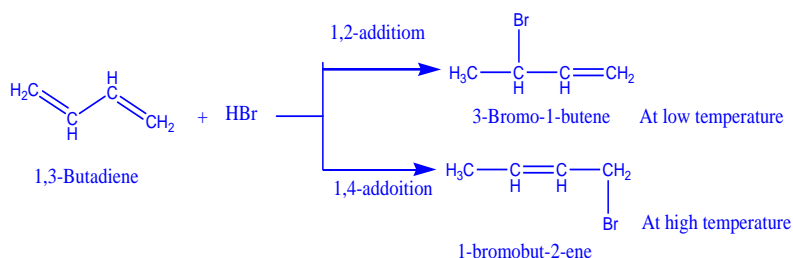
2. By catalytic dehydrogenation of *n*butane



## CHEMICAL REACTION

- Addition of Halogen acid-** 1,3-Butadiene react with HBr to yield 2 product/ compound. They are 3-bromo-1-butene and 1-Bromo-2-butene. The I<sup>st</sup> product result from 1,2-addition to one of the double bonds. The II<sup>nd</sup> product result from addition to the terminal position with the formation of new double bond between C-2 and C-3. This latter product is known as 1,4-addition.

At low temperature 1,2-addition preferred at high temperature 1,4-addition predominates.

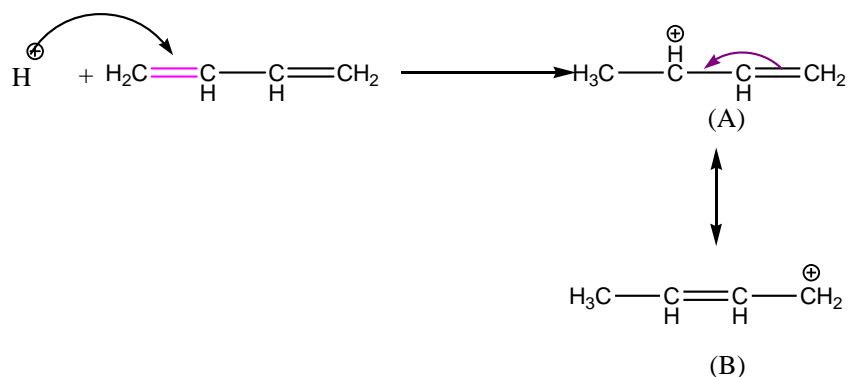


## MECHANISM

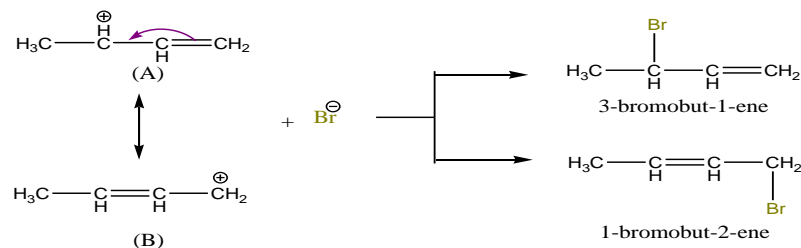
**Step-I** HBr ionizes to give proton (e<sup>-</sup>) and Br<sup>-</sup> (Nu<sup>-</sup>)



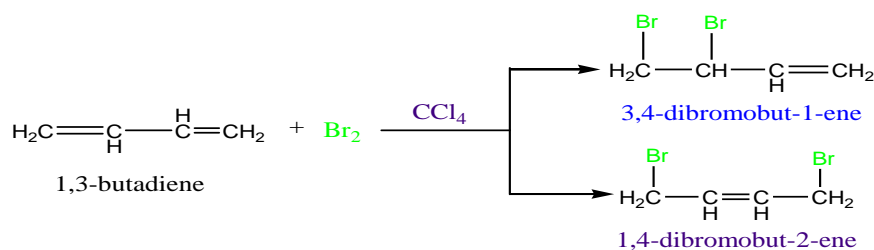
**Step-II** H<sup>+</sup> attacks double bond according to Markonikov's rule to give resonance stabalized carbonium ion.



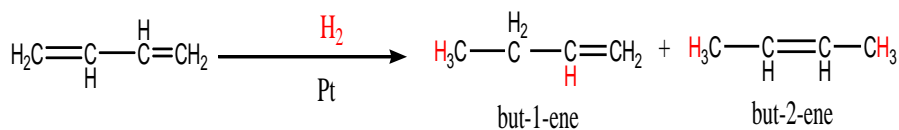
**Step-III-** Bromide ion combines with A to give 1,2-Addition product and it combines with B to give 1,4-Addition product. Thus a mixture of two compounds is obtained.



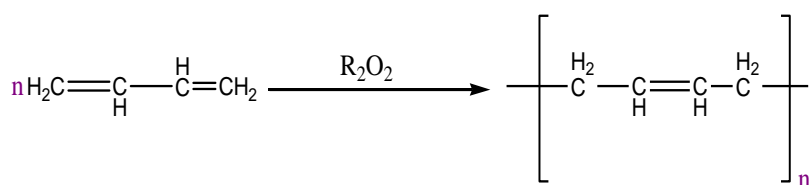
2. **Addition of Halogens-** 1,3-Butadiene react with halogen (Cl or Br) in the presence of inert solvent  $\text{CCl}_4$  to give mixture of two dibromo compounds.



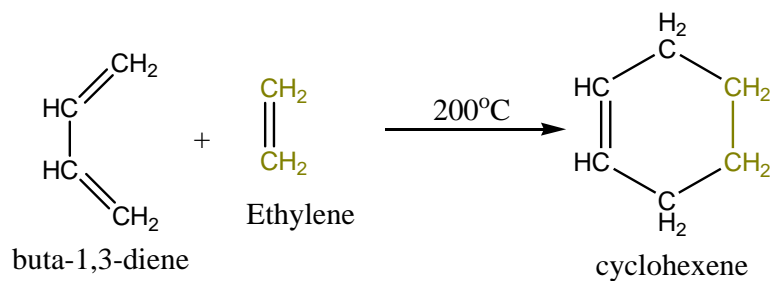
### 3. Addition of Hydrogen –



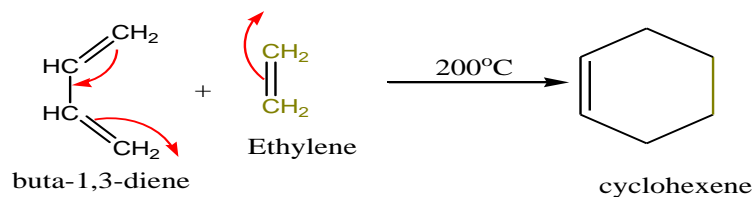
4. **Polymerization** – 1,3-Butadiene polymerizes in the presence of peroxides to give polybutadiene (Buna Rubber).



5. **Diel's Alder Reaction** – This involves the treatment of 1,3-Butadiene (or any conjugated diene) with alkene or alkyne. No catalyst is required.



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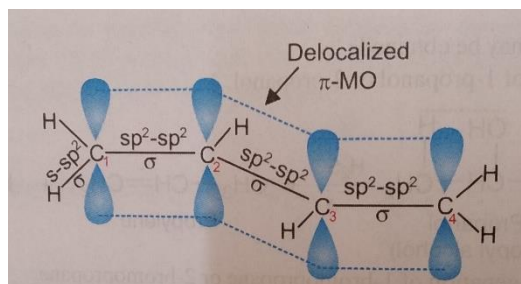


The alkene or alkyne used is **Dienophile**.

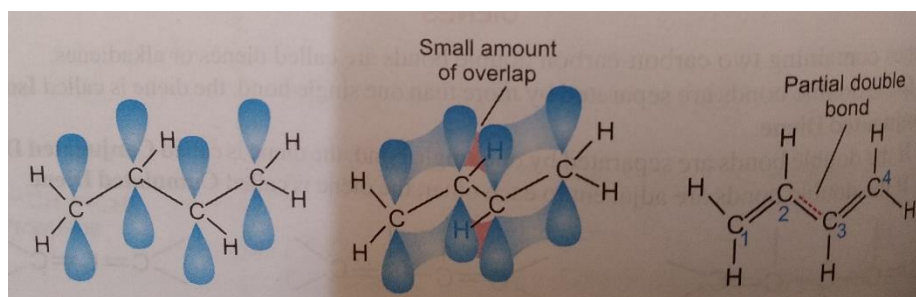
The product is called as **Diel's alder adduct**.

The net result is formation of **2 new  $\sigma$  bond** and **1 new  $\pi$  bond** at the expense of 3 original  $\pi$  bond.

## STABILITY OF CONJUGATED DIENES



All the four carbons are sp<sup>2</sup> hybridized. These sp<sup>2</sup> hybridized orbitals overlap each other and with s orbital of hydrogen atoms to form C-H and C-C  $\sigma$  bonds. Because the three bonds are formed by overlapping of sp<sup>2</sup> hybrid orbitals (Trigonal). So all the carbons and hydrogens lie in one plane each carbon contains unhybridized p orbitals.



The p orbitals of C<sub>2</sub> can overlap with p-orbitals of C<sub>1</sub> and C<sub>3</sub>. The p orbital of C<sub>3</sub> can overlap with C<sub>2</sub> and C<sub>4</sub>. So all the four p orbitals overlaps to form large  $\pi$  molecular orbitals. All pairs of  $\pi$  electrons attracted with each carbons. This overlapping spreads the charge over the large area (**Delocalization**). ***This delocalization is responsible for the stability of Conjugated dienes.***



**2 MARKS QUESTION**

- 1. Which of the following compound have planar molecules?**
  - a) **1,3-Butadiene**
  - b) Dimethyl ether
  - c) 1-Butene
  - d) Allene
- 2. Propadiene  $\text{CH}_2=\text{C}=\text{CH}_2$  is?**
  - a) A planar compound
  - b) **A cumulative diene**
  - c) An isolated diene
  - d) A conjugated diene
- 3. 1,3-butadiene has**
  - a) Only sp hybridized carbons.
  - b)  $\text{Sp}, \text{sp}^2, \text{sp}^3$  hybridized carbons.
  - c) Only  $\text{sp}^3$  hybridized carbons.
  - d) **Only  $\text{sp}^2$  hybridized carbons.**
- 4. 1,3-butadiene reacts with bromine to mainly give**
  - a) 3,4-Dibromo-1-butene
  - b) 4-Bromo-1-butene
  - c) **1,4-Dibromo-2-butene**
  - d) 1-Bromo-2-butene
- 5. Which of the following molecular formula will correspond to an alkene with double bonds?**
  - a)  **$\text{C}_4\text{H}_{10}$**
  - b)  $\text{C}_5\text{H}_{12}$
  - c)  $\text{C}_6\text{H}_{10}$
  - d)  $\text{C}_8\text{H}_{16}$
- 6. Alkadienes are classified in how many types**
  - a) **3**
  - b) 4
  - c) 6

- d) 1
7. Conjugated dienes react with which among the following to form cyclohexene?
- a) Phenol
  - b) Hexane
  - c) Tribromophenol
  - d) **Dienophile**
8. Which among the following dienes undergoes addition with the help of radical chain mechanism?
- a) Cumulative dienes
  - b) **Conjugated dienes**
  - c) Non- conjugated dienes
  - d) Simple dienes
9. A molecule in which more than one single separates two double bonds are called as
- a) Coordinate double bonds.
  - b) Conjugated double bonds.
  - c) **Isolated double bonds**
  - d) Cumulative Double Bonds
10. Which addition product is preferred at low temperature
- a) **1,2-Addition product**
  - b) 1,4- addition product
  - c) Both of the above
  - d) None of the above
11. State Markonikovs rule with example.
12. What happens when HBr reacts with propene in presence of peroxide.
13. What product is obtained when hydrogen halide is lost from alkyl halide.
14. What is Peroxide effect?
15. What are alkenes why do we call them olefins?
16. Define Saytzeffs rule.
17. Differentiate between Markonikovs and Anti markonikovs rule.
18. Explain hybridization of alkenes.
19. Discuss why alkenes are less reactive towards a majority of the organic reagent.

20. Discuss transition states of halogenation.
21. What are alkanes? Give their chemical reactivity.
22. Explain Wurtz reaction?
23. What is Corey-House Reaction?
24. Write about nomenclature of alkanes with examples

## MARKS QUESTION (5 or 10 Marks)

1. Discuss the molecular orbital structure of 1,3-butadiene.
2. How is 1,3-butadiene prepared
3. What happens when 1,3-butadiene reacts with bromine in carbon tetrachloride?
4. What happens when 1,3-butadiene is treated with HBr?
5. Write a note on Diels-Alder reaction
6. Write a note on stability of Conjugated dienes
7. Give important chemical reactions of Conjugated dienes.
8. Give the mechanism for the reaction of 1,3-butadiene with bromine
9. Give the method of preparation of conjugated dienes.
10. Explain in detail Conjugated dienes.. Explain the addition of HBr to propylene in accordance with
  - a) Markonikovs rule
  - b) AntiMarkonikovs rule
11. Why do alkenes undergo electrophilic addition reaction and not electrophilic substitution reaction.
12. Give the various chemical properties of alkenes.
13. Explain the mechanism by which alkyl halides undergo elimination reaction with suitable examples.
14. Write a detail note on Alkenes? Its preparation and reactions.
15. Explain in detail method of preparation of alkenes.
16. Describe the preparation of alkenes by E<sub>2</sub> mechanism.
17. Discuss why trans alkenes have higher boiling point but lower boiling point than cis isomer.
18. Describe the important method of preparation alkenes.

**19.** How alkanes are prepared by

- Wurtz reaction
- Corey-house reaction

**20.** Give suitable explanation of the followings

- The boiling point of isomeric alkanes decrease with increase in branching chain.
- As the molecular mass increase the boiling point of n-alkanes increase.
- N-alkanes with even number of carbon atom melts at higher temperature than those with odd number of carbon atoms.

**21.** Write a detail note on Chemical reactions of alkanes.

**22.** Give the nomenclature of alkanes for Branched chain with examples.

**23.** Explain in detail the free radical mechanism and hybridization of alkanes