

Chemistry

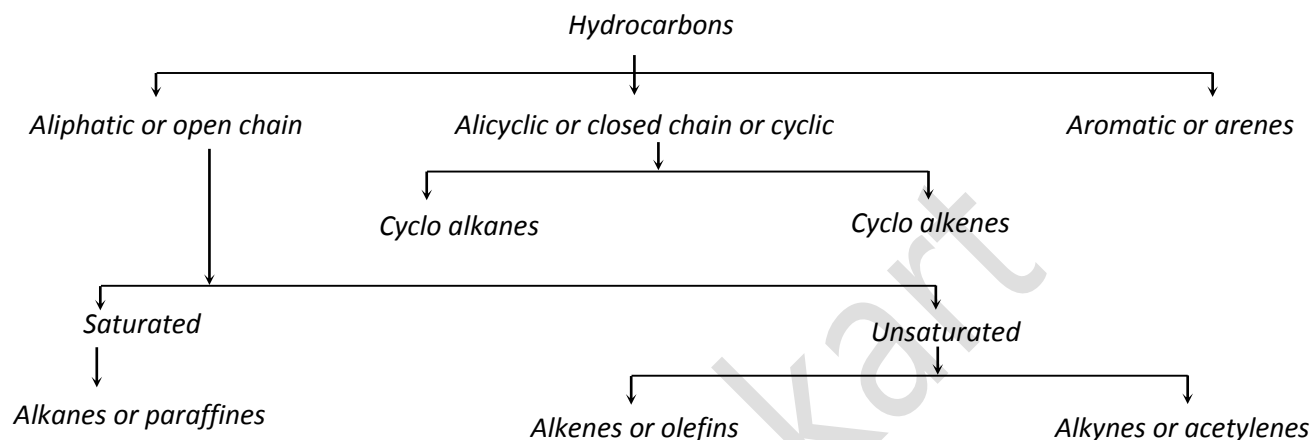
Aliphatic Hydrocarbons

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"Organic compounds composed of only carbon and hydrogen are called hydrocarbons. Hydrocarbons are obtained mainly from petroleum, natural gas or coal. Petroleum is a major source of aliphatic hydrocarbon. The important fuels like petrol, kerosene, coal gas, oil gas, compressed natural gas [CNG], LPG etc., all are hydrocarbon and their mixtures".



1. Sources of hydrocarbon.

Mineral oil or crude oil, petroleum [Petra → rock; oleum → oil] is the dark color oily liquid [do with offensive odour found at various depths in many regions below the surface of the earth. It is generally found under the rocks of earth's crust and often floats over salted water.

(1) Composition

- (i) **Alkanes:** found 30 to 70% contain up to 40 carbon atom. Alkanes are mostly straight chain but some are branched chain isomers.
- (ii) **Cycloalkanes:** Found 16 to 64% cycloalkanes present in petroleum are; cyclohexane, methyl cyclopentane etc. cycloalkanes rich oil is called asphaltic oil.
- (iii) **Aromatic hydrocarbon:** found 8 to 15% compound present in petroleum are; Benzene, Toluene, Xylene, Naphthalene etc.
- (iv) **Sulphur, nitrogen and oxygen compound:** Sulphur compound present in the extent of 6% and include mercaptans [R-SH] and sulphides [R-S-R]. The unpleasant smell of petroleum is due to sulphur compounds. Nitrogen compounds are alkyl pyridines, quinolines and pyrroles. Oxygen compounds present in petroleum are. Alcohols, Phenols and resins. Compounds like chlorophyll, haemin are also present in it.



(v) **Natural gas:** It is a mixture of Methane (80%), Ethane (13%), Propane (3%), Butane (1%), Vapors of low boiling pentanes and hexanes (0.5%) and Nitrogen (1.3%). L.P.G. Contain butanes and pentanes and used as cooking gas. It is highly inflammable. This contain, methane, nitrogen and ethane.

(vi) **C.N.G.:** The natural gas compressed at very high pressure is called compressed natural gas (CNG). Natural gas has octane rating of 130 it consists, mainly of methane and may contain, small amount of ethane and propane.

(2) Theories of origin of petroleum: Theories must explain the following characteristics associated with petroleum,

Its association with brine (sodium chloride solution). The presence of nitrogen and sulphur compounds in it. The presence of chlorophyll and haemin in it. Its optically active nature. Three important theories are as follows.

(i) **Mendeleeff's carbide theory or inorganic theory**

(a) Molten metals in hot earth's crust combine with coal deposits and formed carbides.

(b) Carbides reacted with steam or water under high temperature and pressure to form mixture of saturated and unsaturated hydrocarbons.

(c) The unsaturated hydrocarbon in presence of metal catalyst, high pressure and high temperature, undergoes reactions such as hydrogenation, isomerization and polymerization to form number of hydrocarbons.

Reactions: $Ca + 2C \rightarrow CaC_2$ (Calcium carbide); $Mg + 2C \rightarrow MgC_2$ (Magnesium carbide)

$4Al + 3C \rightarrow Al_4C_3$ (Aluminum carbide);

$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$

(Acetylene)

$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4$ (Methane); $C_2H_2 \xrightarrow{H_2} C_2H_4 \xrightarrow{H_2} C_2H_6$
(Ethane)

$3[CH \equiv CH] \xrightarrow{\text{Polymerisation}} C_6H_6$;
(Benzene)

$CH_3 - CH = CH - CH_3 \xrightarrow{\text{Isomerisation}} CH_3 - CH_2 - CH = CH_2$
(1-Butene)

Theory fails to account for, The presence of nitrogen and sulphur compounds. The presence of chlorophyll and haemin derivatives. The presence of optically active compounds.

(ii) **Engler's theory or organic theory:** Theory is supported by the following facts,

(a) The presence of brine with petroleum,

(b) The presence of optically active compounds,

(c) The presence of nitrogen and sulphur compounds

(d) The presence of fossils in the petroleum area.

The theory was further supported by the fact that when destructive distillation of fish oil and other animals fats under high temperature and pressure was carried out, a petroleum like liquid was obtained.



Theory fails to account for, The presence of chlorophyll in the petroleum. The presence of coal deposits found near the oil fields. The presence of resins in the oil.

(iii) **Modern theory:** This theory explain nearly all the facts about petroleum.

(a) The presence of chlorophyll and haemin in petroleum.

(b) The presence of coal deposits near oil fields suggesting its vegetable origin.

(c) The presence of nitrogen and sulphur compounds along with optically active compounds in petroleum.

(d) The presence of resins also suggests that oil must have been formed from vegetable substances.

(e) The presence of helium gas in natural gas suggests that radioactive substances must have helped in the decomposition of organic matter.

(3) **Mining of petroleum:** Petroleum deposits occurs at varying depth at different places ranging from 500 to 15000 feet. This is brought to the surface by artificial drilling.

(4) **Petroleum refining:** Separation of useful fractions by fractional distillation is called petroleum refining.

Fraction	Boiling range (°C)	Approximate composition	Uses
Uncondensed gases	Up to room temperature	$C_1 - C_4$	Fuel gases: refrigerants; production of carbon black, hydrogen; synthesis of organic chemicals.
Crude naphtha on refractionation yields,	30 – 150°	$C_5 - C_{10}$	
(i) Petroleum ether	30 – 70°	$C_5 - C_6$	Solvent
(ii) Petrol or gasoline	70 – 120°	$C_6 - C_8$	Motor fuel; dry-cleaning; petrol gas.
(iii) Benzene derivatives	120 – 150°	$C_8 - C_{10}$	Solvent; dry-cleaning
Kerosene oil	150 – 250°	$C_{11} - C_{16}$	Fuel; illuminant; oil gas
Heavy oil	250 – 400°	$C_{15} - C_{18}$	As fuel for diesel engines; converted to gasoline by cracking.
Refractionation gives,			
(i) Gas oil			
(ii) Fuel oil			
(iii) Diesel oil			



Residual oil on fractionation by vacuum distillation gives,	Above 400°	C ₁₇ – C ₄₀	
(i) Lubricating oil		C ₁₇ – C ₂₀	Lubrication
(ii) Paraffin wax		C ₂₀ – C ₃₀	Candles; boot polish; wax paper; etc.
(iii) Vaseline		C ₂₀ – C ₃₀	Toilets; ointments; lubrication.
(iv) Pitch		C ₃₀ – C ₄₀	Paints, road surfacing
Petroleum coke (on redistilling tar)			As fuel.

(5) Purification

(i) **Treatment with concentrated sulphuric acid:** The gasoline or kerosene oil fraction is shaken with sulphuric acid to remove aromatic compounds like thiophene and other sulphur compound with impart offensive odour to gasoline and kerosene and also make them corrosive.

(ii) **Doctor sweetening process:**
$$2RSH + Na_2PbO_2 + S \rightarrow RSSR + PbS + 2NaOH$$

Mercaptan Disulphides

(iii) **Treatment with adsorbents:** Various fractions are passed over adsorbents like alumina, silica or clay etc., when the undesirable compounds get adsorbed.

(6) Artificial method for manufacture of Petrol or gasoline

(i) Cracking, (ii) Synthesis

(i) **Cracking:** It is a process in which high boiling fractions consisting of higher hydrocarbons are heated strongly to decompose them into lower hydrocarbons with low boiling pts. Cracking is carried out in two different ways.

(a) **Liquid phase cracking:** In this process, the heavy oil or residual oil is cracked at a high temperature (475 – 530°C) under high pressure (7 to 70 atmospheric pressure). The high pressure keeps the reaction product in liquid state. The conversion is approximately 70% and the resulting petrol has the octane number in the range 65 to 70.

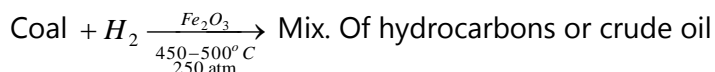
The cracking can be done in presence of some catalysts like silica, zinc oxide, titanium oxide, ferric oxide and alumina. The yields of petrol are generally higher when catalyst is used.

(b) **Vapor phase cracking:** In this process, kerosene oil or gas oil is cracked in vapor phase. The temperature is kept 600 – 800°C and the pressure is about 3.5 to 10.5 atmospheres. The cracking is facilitated by use of a suitable catalyst. The yields are about 70%.

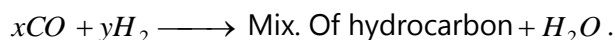
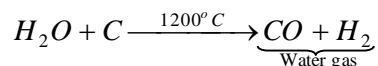


(ii) **Synthesis:** Two methods are applicable for synthesis.

(a) Bergius process: This method was invented by Bergius in Germany during First World War.



(b) Fischer- tropsh process: The overall yield of this method is slightly higher than Bergius process.



The best catalyst for this process is a mixture of cobalt (100 parts), thoria, (5 parts), magnesia (8 parts) and kieselguhr (200 parts).

2. Characteristics of hydrocarbons.

(1) **Knocking:** The metallic sound due to irregular burning of the fuel is termed as knocking.

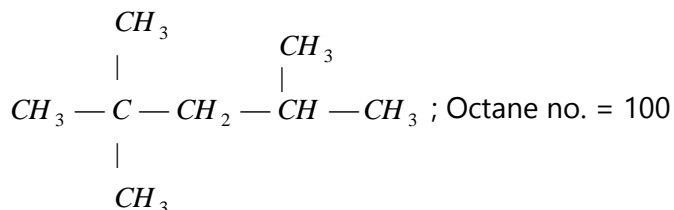
"The greater the compression greater will be efficiency of engine." The fuel which has minimum knocking property is always preferred.

The tendency to knock falls off in the following order: Straight chain alkanes > branched chain alkanes > olefins > cyclo alkanes > aromatic hydrocarbons.

(2) **Octane number:** It is used for measuring the knocking character of fuel used in petrol engine. The octane number of a given sample may be defined as the percentage by volume of iso-octane present in a mixture of iso-octane and heptane which has the same knocking performance as the fuel itself.



n-heptane; octane no. = 0



2, 2, 4-Trimethyl pentane or Iso-octane.



For example: a given sample has the knocking performance equivalent to a mixture containing 60% iso-octane and 40% heptane. The octane number of the gasoline is, therefore, 60.

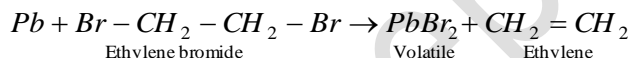
Presence of following types of compounds increases the octane number of gasoline.

- (i) In case of straight chain hydrocarbons octane number decreases with increase in the length of the chain.
- (ii) Branching of chain increases the value of octane number
- (iii) Introduction of double bond or triple bond increases the value of octane number.
- (iv) Cyclic alkanes have relatively higher value of octane number.
- (v) The octane number of aromatic hydrocarbons are exceptionally high
- (vi) By adding gasoline additives (eg TEL)

(3) **Antiknock compounds:** To reduce the knocking property or to improve the octane number of a fuel certain chemicals are added to it. These are called **antiknock compounds**. One such compound, which is extensively used, is tetraethyl lead (TEL). TEL is used in the form of following mixture,

TEL = 63%, Ethylene bromide = 26%, Ethylene chloride = 9% and a dye = 2%.

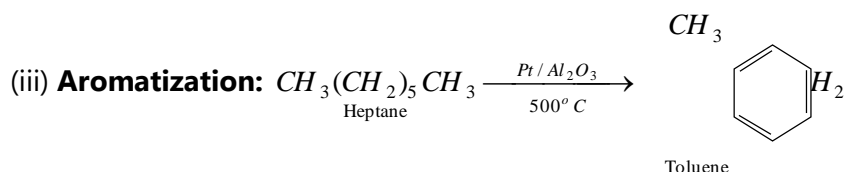
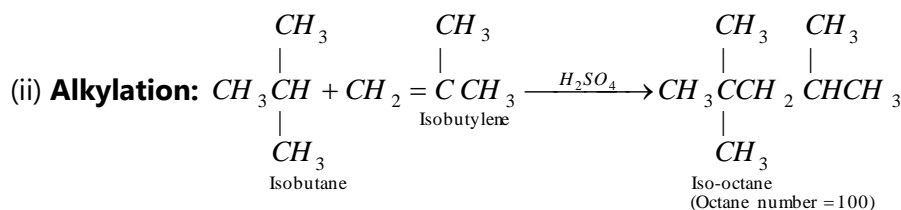
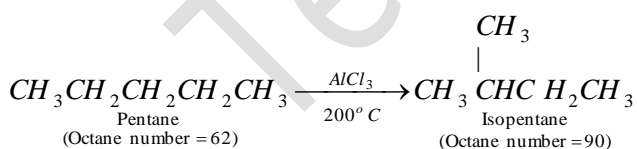
However, there is a disadvantage that the lead is deposited in the engine. To remove the free lead, the ethylene halides are added which combine with lead to form volatile lead halides.



However, use of TEL in petrol is facing a serious problem of Lead pollution, to avoid this a new compound cyclopenta dienyl manganese carbonyl (called as AK-33-X) is used in developed countries as antiknocking compound.

(4) Other methods of improving octane number of gasoline

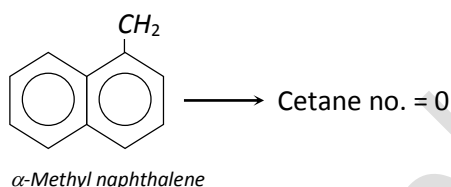
(i) **Isomerization** [Reforming]: By passing gasoline over AlCl_3 at 200°C .



The octane no. of petrol can thus be improved.

- By increasing the proportion of branched chain or cyclic alkanes.
- By addition of aromatic hydrocarbons (BTX)
- By addition of methanol or ethanol.
- By addition of tetraethyl lead $(C_2H_5)_4Pb$

(5) **Cetane number:** It is used for grading the diesel oils.



The cetane number of a diesel oil is the percentage of cetane (hexadecane) by volume in a mixture of cetane and α -methyl naphthalene which has the same ignition property as the fuel oil

(6) **Flash point:** The lowest temperature at which an oil gives sufficient vapors to form an explosive mixture with air is referred to as flash point of the oil.

The flash point in India is fixed at $44^\circ C$, in France it is fixed at $35^\circ C$, and in England at $22.8^\circ C$. The flash point of an oil is usually determined by means of "**Abel's apparatus**".

Chemists have prepared some hydrocarbons with octane number even less than zero (e.g., n-nonane has octane number -45) as well as hydrocarbon with octane number greater than 100 (e.g., 2, 2, 3 trimethylbutane. has octane number of 124).

(7) **Petrochemicals:** All such chemicals which are derived from petroleum or natural gas called petrochemicals. Some chemicals which are obtained from petroleum are:

Hydrocarbons	Compounds derived
Methane	Methyl chloride, chloroform, methanol, formaldehyde, formic acid, freon, hydrogen for synthesis of ammonia.
Ethane	Ethyl chloride, ethyl bromide, acetic acid, acetaldehyde, ethylene, ethyl acetate, nitroethane, acetic anhydride.



Ethylene	Ethanol, ethylene oxide, glycol, vinyl chloride, glyoxal, polyethene, styrene, butadiene, acetic acid.
Propane	Propanol, propionic acid, isopropyl ether, acetone, nitromethane, nitroethane, nitropropane.
Propylene	Glycerol, allyl alcohol, isopropyl alcohol, acrolein, nitroglycerine, dodecylbenzene, cumene, bakelite.
Hexane	Benzene, DDT, gammexane.
Heptane	Toluene
Cycloalkanes	Benzene, toluene, xylenes, adipic acid.
Benzene	Ethyl benzene, styrene, phenol, BHC (insecticide), adipic acid, nylon, cyclohexane, ABS detergents.
Toluene	Benzoic acid, TNT benzaldehyde, saccharin, chloramine-T, benzyl chloride, benzal chloride.

3. Alkanes [Paraffines].

"Alkanes are saturated hydrocarbon containing only carbon-carbon single bond in their molecules."

Alkanes are less reactive so called paraffins; because under normal conditions alkanes do not react with acids, bases, oxidizing agents and reducing agent.

General formula: C_nH_{2n+2}

Examples are: CH_4 (Methane), C_2H_6 (Ethane), C_3H_8 (Propane)

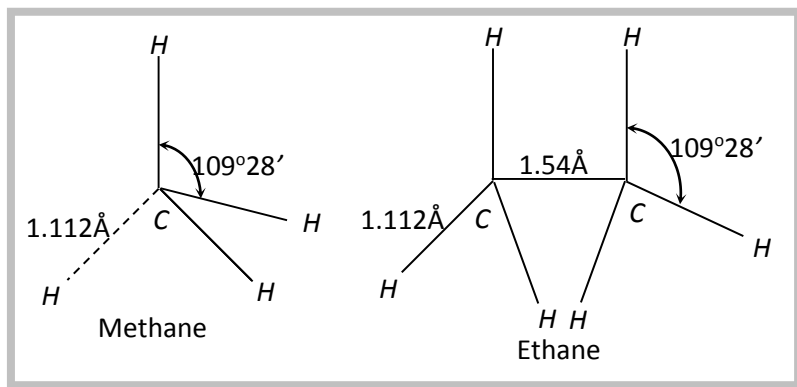
(1) Structure:

(i) Every carbon atom is sp^3 hybridized.

(ii) The bond length between carbon-carbon and carbon-hydrogen are 1.54\AA and 1.112\AA respectively.

(iii) Bond angle in alkanes are tetrahedral angles having a value of 109.5° ($109^\circ.28'$).

(iv) Alkanes have 3-D, rather than planer structure.



- (v) $C - C$ bond dissociation energy is 83 kcal/mol .
 (vi) $C - H$ bond dissociation energy is 99 kcal/mol .

(2) **Isomerism:** Only chain and structural Isomerism found.

No. of carbon atom in molecule \propto no. of chain Isomers

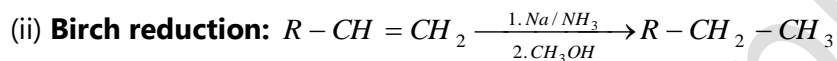
Alkanes :	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}	$C_{10}H_{22}$
No. of possible Isomer :	2	3	5	9	18	75

(3) General Methods of preparation

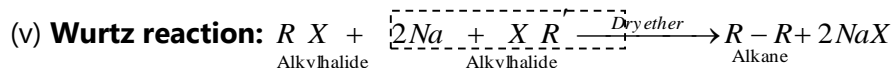
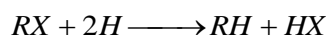
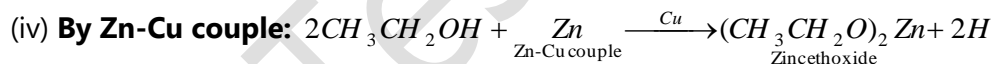
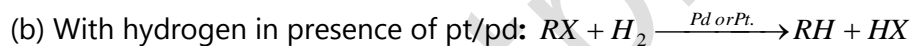
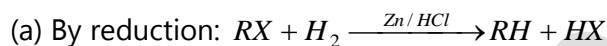
(i) **By catalytic hydrogenation of alkenes and alkynes** (Sabateir and sanderen's reaction)



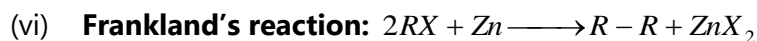
Note: Methane is not prepared by this method



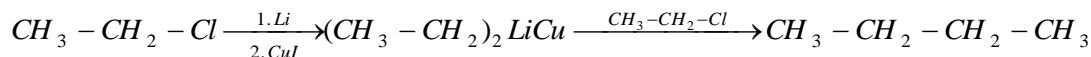
(iii) **From alkyl halide**



Note: $R - Br$ or RI preferred in this reaction. The net result in this reaction is the formation of even no. of carbon atoms in molecules.

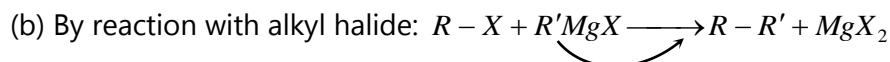
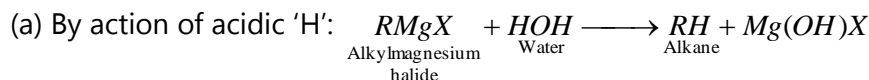


(vii) **Corey-house synthesis**



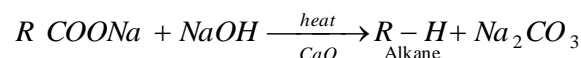
Note: Reaction is suitable for odd number of Alkanes.

(viii) **From Grignard reagent**

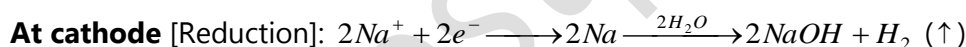
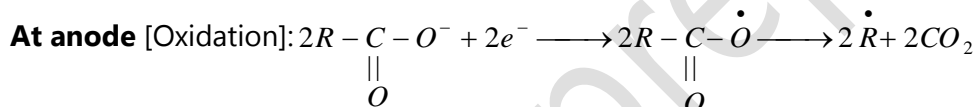
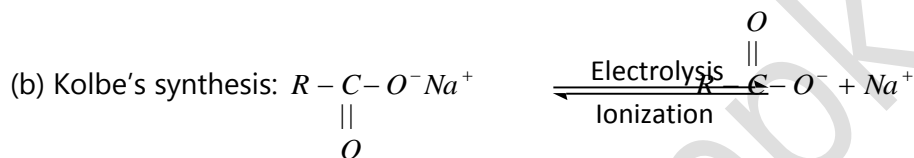


(ix) **From carboxylic acids**

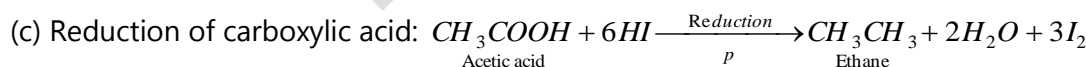
(a) Laboratory method [Decarboxylation reaction or Duma reaction]



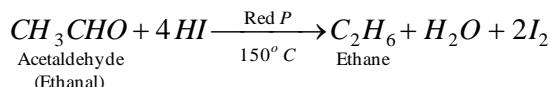
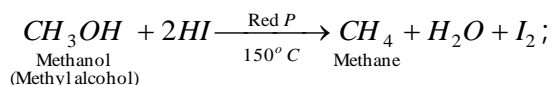
Note: NaOH and CaO is in the ratio of 3: 1.

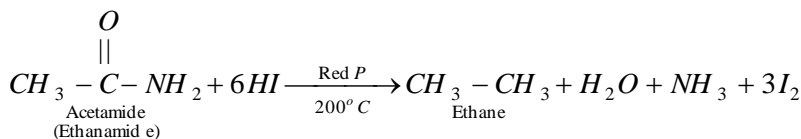


Note: Both ionic and free radical mechanism are involved in this reaction.



(x) **By reduction of alcohols, aldehydes, ketones or acid derivatives**




$$\underset{\substack{\text{Acetone} \\ \text{(Propanone)}}}{CH_3COCH_3} + 2H_2 \xrightarrow[HCl]{Zn-Hg} \underset{\text{Propane}}{CH_3CH_2CH_3} + H_2O$$

Wolff-kishner reduction:

$$\begin{array}{ccc}
 R & & R \\
 \diagup & & \diagup \\
 C=O & \xrightarrow[-H_2O]{H_2NNH_2} & C=NNH_2 \\
 \diagdown & & \diagdown \\
 R' & & R'
 \end{array}
 \xrightarrow[180^\circ C]{C_2H_5ONa}
 \begin{array}{ccc}
 R & & \\
 \diagup & & \diagup \\
 CH_2 & & \\
 \diagdown & & \diagdown \\
 R' & &
 \end{array}$$
$$R-\underset{\text{Alkene}}{\text{CH}}=\text{CH}_2 \xrightarrow{\text{B}_2\text{H}_6} (R-\underset{\text{Trialkyl borane}}{\text{CH}_2}-\text{CH}_2)_3\text{B} \xrightarrow{\text{CH}_3\text{COOH}} R-\underset{\text{Alkane}}{\text{CH}_2}-\text{CH}_3$$
$$6[R-CH=CH_2] \xrightarrow{2B_2H_6} [2R-CH_2-CH_2]_3B \xrightarrow[NaOH]{AgNO_3, 25^\circ C} 3[RCH_2CH_2-CH_2CH_2R]$$

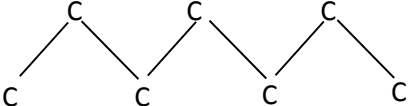
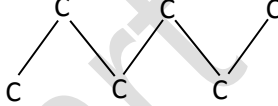
Alkanes	State
$C_1 - C_4$	Gaseous state
$C_5 - C_{17}$	Liquid state [Except neo pentane] [gas]

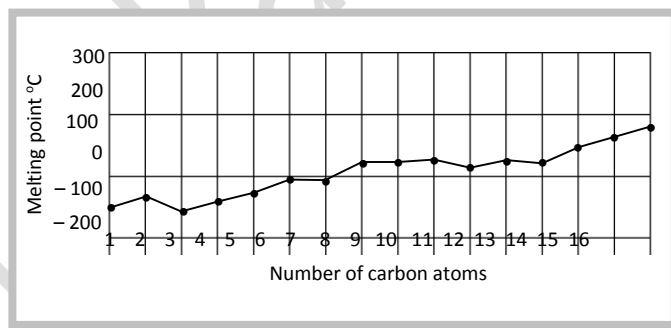
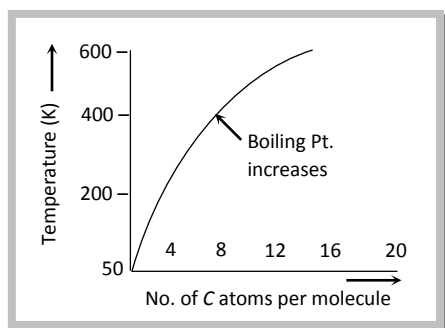
C_{18} & above Solid like waxes

(ii) **Density:** Alkanes are lighter than water.

(iii) **Solubility:** Insoluble in water, soluble in organic solvents, solubility $\propto \frac{1}{\text{Molecular mass}}$

(iv) **Boiling pts and Melting pts:** Melting pt. and boiling pts. $\propto \text{Molecular mass} \propto \frac{1}{\text{No. of branches}}$

Alkane :	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}
M.P. (K) :	85.9	138	143.3	179	182.5	216.2
						
	Odd no. of Carbons			Even no. of carbons		



Note: Melting points of even > Odd no. of carbon atoms, this is because, the alkanes with even number of carbon atoms have more symmetrical structure and result in closer packing in the crystal structure as compared to alkanes with odd number of carbon atoms.

(5) Chemical properties

(i) Substitution reactions of Alkanes

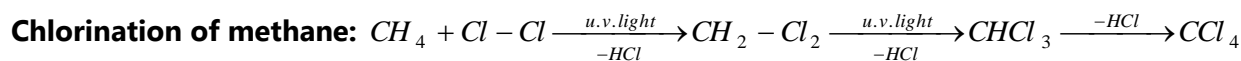
(a) Halogenation: $R-H + X-X \longrightarrow R-X + HX$

The reactivity of halogen is: $F_2 > Cl_2 > Br_2 > I_2$

Note: Fluorine can react in dark Cl_2, Br_2 require light energy. I_2 does not show any reaction at room temperature, but on heating it shows iodination.

Iodination of methane is done in presence of oxidizing agent such as $HNO_3 / HIO_3 / HgO$ which neutralizes HI .



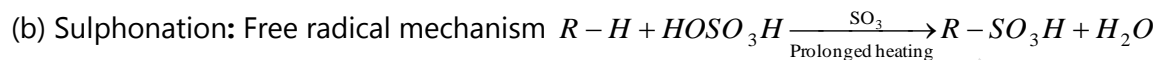


(ii) **Reaction based on free radical mechanism**



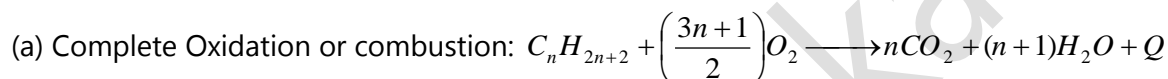
Nitrating mixture: (i) (Con. HNO_3 + Con. H_2SO_4) at $250^\circ C$

(ii) (HNO_3 vapour at $400^\circ - 500^\circ C$).



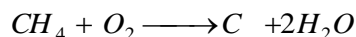
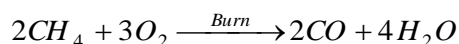
Note: Lower alkanes particularly methane, ethane, do not give this reaction.

(iii) **Oxidation**



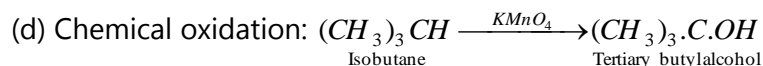
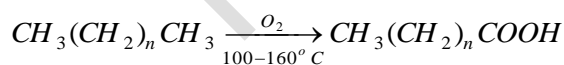
Note: This is exothermic reaction.

(b) Incomplete combustion or oxidation

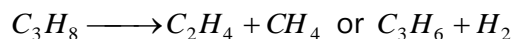
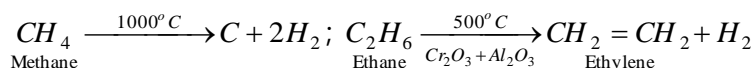


This is the industrial method for the manufacture of methyl alcohol.

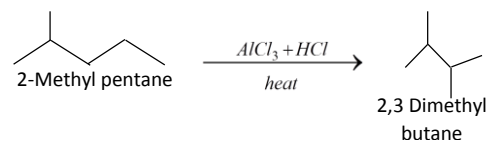
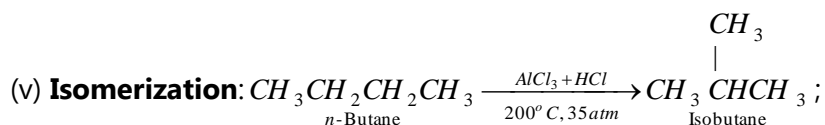
Note: Higher alkanes are oxidized to fatty acids in presence of manganese stearate.



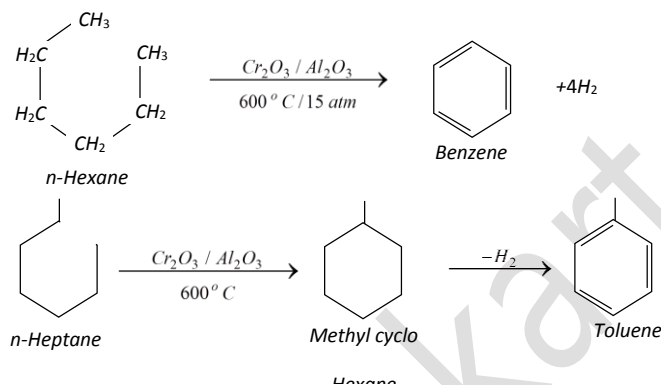
(iv) **Thermal decomposition or cracking or pyrolysis or fragmentation**



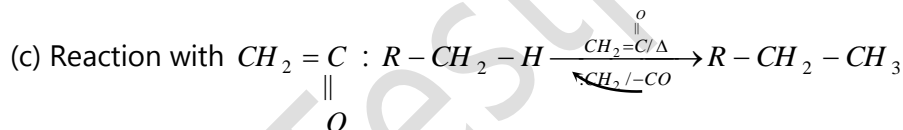
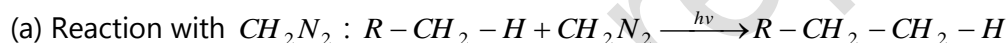
Note: This reaction is of great importance to petroleum industry.



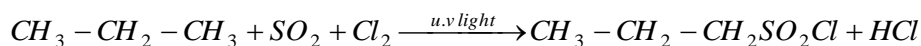
(vi) **Aromatization:**



(vii) **Step up reaction**

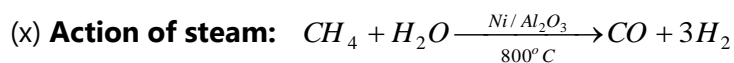


(ix) **Chloro sulphonation/Reaction with $SO_2 + Cl_2$**



This reaction is known as reed's reaction.

Note: This is used in the commercial formation of detergent.

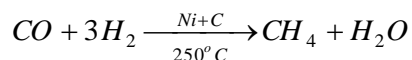


4. Individual members of alkanes.

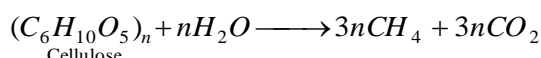
(1) **Methane:** Known as **marsh gas**.

(i) **Industrial method of preparation:** Methane gas is obtained on a large scale from natural gas by liquefaction. It can also be obtained by the application of following methods,

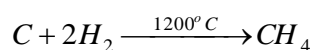
(a) From carbon monoxide: A mixture of carbon monoxide and hydrogen is passed over a catalyst containing nickel and carbon at 250°C when methane is formed.



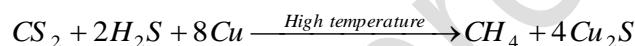
(b) Bacterial decomposition of cellulose material present in sewage water: This method is being used in England for production of methane.



(c) Synthesis: By striking an electric arc between carbon electrodes in an atmosphere of hydrogen at 1200°C , methane is formed.



By passing a mixture of hydrogen sulphide and carbon disulphide vapor through red hot copper, methane is formed.



(ii) **Physical properties**

(a) It is a colorless, odorless, tasteless and non-poisonous gas.

(b) It is lighter than air. Its density at NTP is 0.71 g/L.

(c) It is slightly soluble in water but is fairly soluble in ether, alcohol and acetone.

(d) Its melting point is -182.5°C and boiling point is -161.5°C .



(iii) Uses

- (a) In the manufacture of compounds like methyl alcohol, formaldehyde, methyl chloride, chloroform, carbon tetrachloride, etc.
- (b) In the manufacture of hydrogen, used for making ammonia.
- (c) In the preparation of carbon black which is used for making printing ink, black paints and as a filler in rubber vulcanization.
- (d) As a fuel and illuminant.

(2) Ethane

(i) Methods of preparation

- (a) Laboratory method of preparation:
$$\underset{\text{Ethyl iodide}}{C_2H_5I} + 2H \xrightarrow[C_2H_5OH]{Zn-Cu \text{ couple}} \underset{\text{Ethane}}{C_2H_6} + HI$$
- (b) Industrial method of preparation:
$$\underset{\substack{\text{Ethylene} \\ \text{(ethene)}}}{CH_2 = CH_2} + H_2 \xrightarrow[300^\circ C]{Ni} \underset{\text{Ethane}}{CH_3 - CH_3}$$

(iii) Physical properties

- (a) It is a colorless, odorless, tasteless and non-poisonous gas.
- (b) It is very slightly soluble in water but fairly soluble in alcohol, acetone, ether, etc.
- (c) Its density at NTP is 1.34 g/L
- (d) It boils at $-89^\circ C$. Its melting point is $-172^\circ C$.

(ii) Uses

- (a) As a fuel. (b) For making hexachloroethane which is an artificial camphor.

(3) Interconversion of Alkanes

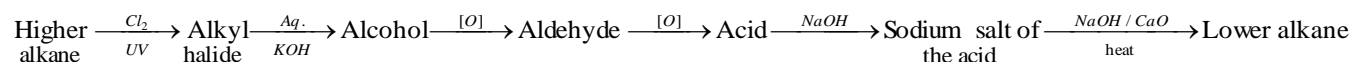
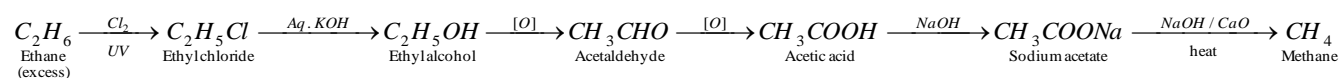
Ascent of alkane series,

- (i) **Methane to ethane:**
$$\underset{\text{Methane}}{CH_4} \xrightarrow[UV]{Cl_2} CH_3Cl \xrightarrow[\text{Heat with Na in ether}]{\text{Wurtz reaction}} \underset{\text{Ethane}}{CH_3 - CH_3}$$
- (ii) **Butane from ethane:**
$$\underset{\substack{\text{Ethane} \\ \text{(excess)}}}{C_2H_6} \xrightarrow[UV]{Cl_2} C_2H_5Cl \xrightarrow[\text{Heat with Na in ether}]{\text{Wurtz reaction}} C_2H_5 - C_2H_5 \underset{\text{Butane}}{}$$



Descent of alkane series: Use of decarboxylation reaction is made. It is a multistep conversion.

Ethane to methane



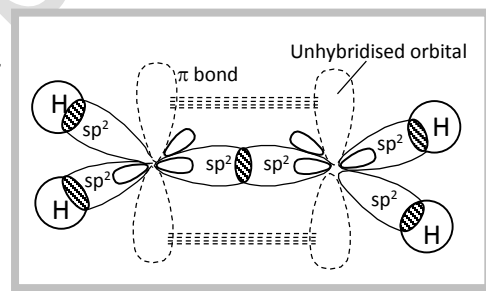
5. Alkenes.

These are the acyclic hydrocarbon in which carbon-carbon contain double bond. These are also known as olefins, because lower alkene react with halogens to form oily substances. General formula is C_nH_{2n} .

Ex: Ethene C_2H_4 , Propene C_3H_6 , Butene C_4H_8

(1) Structure

- Hybridization of unsaturated 'C' atom is sp^2
- Geometry of unsaturated 'c' atom is trigonal planer
- $C-H$ Bond length is 1.34 Å
- $C=C$ Bond energy is 143.1 K cal/mol
- $C-H$ Bond length is 1.10 Å
- $C=C$ Bond energy is 108 Kcal/mol



(2) Isomerism

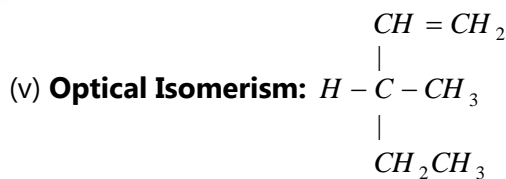
- Chain Isomerism:** $CH_3-CH_2-CH=CH_2$ and $(CH_3)_2-C=CH_2$
- Position Isomerism:** $CH_2=CH-CH_2-CH_3$ and $CH_3-CH=CH-CH_3$
- Functional Isomerism:** [Ring chain] $CH_3-CH_2-CH=CH_2$ and CH_2-CH_2

1-butene

$\begin{array}{c} | \quad | \\ CH_2-CH_2 \\ \text{Cyclobutene} \end{array}$

- Geometrical Isomerism:** CH_3-C-H and CH_3-C-H

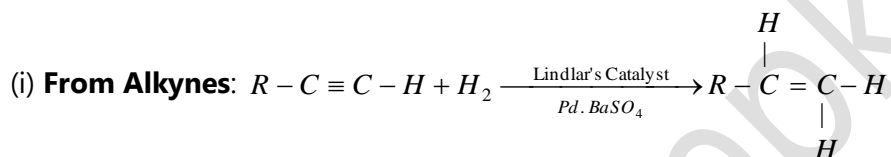




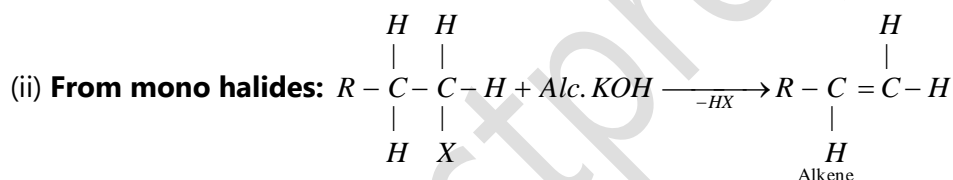
Note: Cumulated polythene having even no. of double bonds. Which has $=C$ system at both end can exhibit optical isomerism but cannot exhibit geometrical isomerism.

Cumulated polythene having odd no. of double bonds which have $=C$ system at both end can exhibit geometrical isomerism but cannot exhibit optical isomerism.

(3) Preparation methods



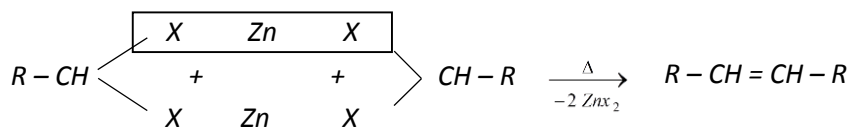
Note: Poison's catalyst such as $BaSO_4, CaCO_3$ are used to stop the reaction after the formation of alkene.



Note: If we use alc. $NaOH$ in place of KOH then trans product is formed in majority because of its stability. According to saytzeff rule.

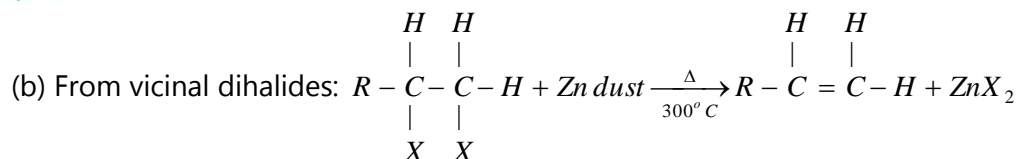
(iii) From dihalides

(a) From Gem dihalides

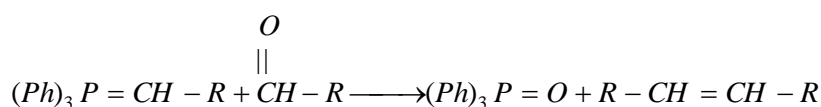
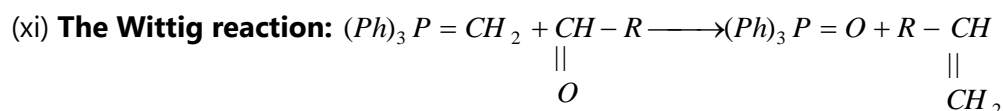
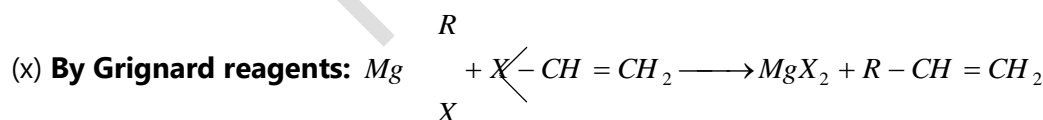
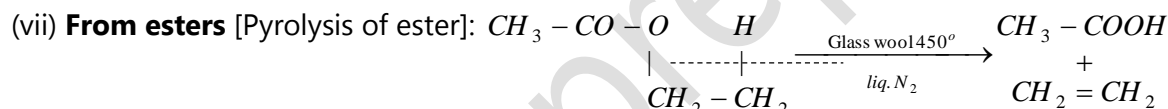
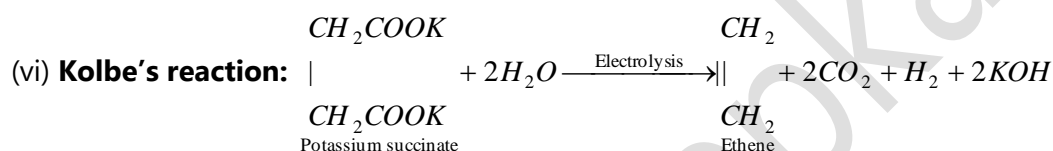
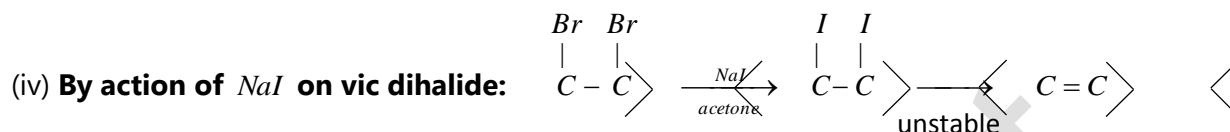
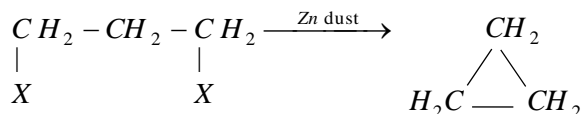


Note: If we take two different types of gemdihalides then we get three different types of alkenes. Above reaction is used in the formation of symmetrical alkenes only.

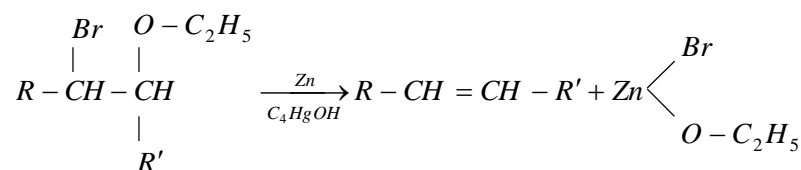




Note: Alkene is not formed from 1, 3 dihalides. Cycloalkanes are formed by dehalogenation of it.



(xii) **From β bromo ether** [Boord synthesis]



(4) Physical Properties

(i) Alkenes are colorless and odorless.

(ii) These are insoluble in water and soluble in organic solvents.

(iii) Physical state

$\text{C}_1 - \text{C}_4 \longrightarrow$ Gas

$\text{C}_5 - \text{C}_{16} \longrightarrow$ Liquid

$> \text{C}_{16} \longrightarrow$ Solid wax

(iv) B.P. and M.P. decreases with increasing branches in alkene.

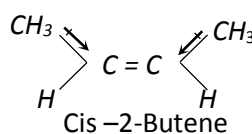
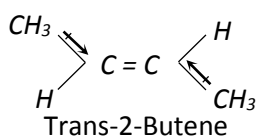
(v) The melting points of cis isomers are lower than trans isomers because cis isomer is less symmetrical than trans. Thus trans packs more tightly in the crystal lattice and hence has a higher melting point.

(vi) The boiling points of cis isomers are higher than trans isomers because cis-alkenes has greater polarity (Dipole moment) than trans one.

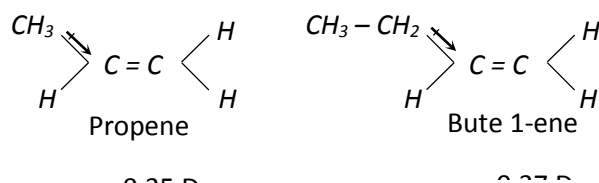
(vii) These are lighter than water.

(viii) **Dipole moment:** Alkenes are weakly polar. The, π -electrons of the double bond. Can be easily polarized. Therefore, their dipole moments are higher than those of alkanes.

The symmetrical trans alkenes are non-polar and hence have zero dipole moments in these alkene the dipole moment of individual bonds are equal in opposite direction. Therefore these get cancelled resulting zero dipole moment for the molecule.

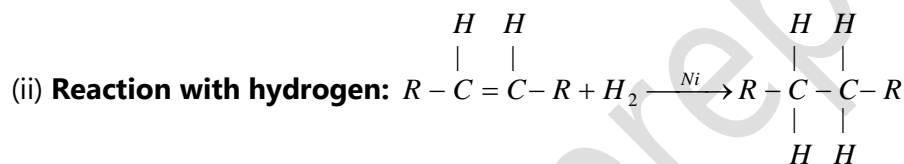
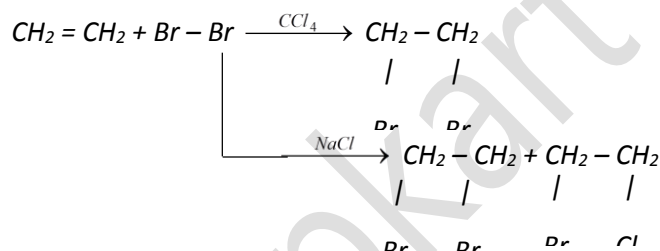


Thus symmetrical and unsymmetrical cis alkene are polar and hence have finite dipole moments



(5) Chemical properties

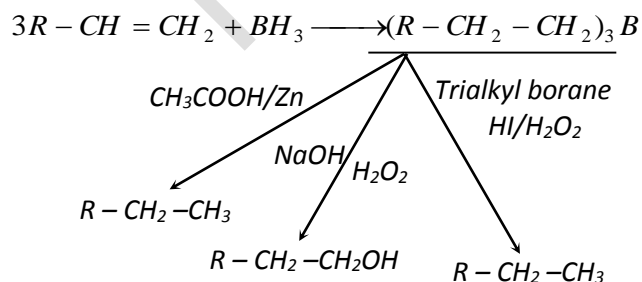
(i) **Francis experiment:** According to Francis electrophile first attacks on olefinic bond.



(iii) **Reduction of alkene via hydroboration:** Alkene can be converted into alkane by protolysis



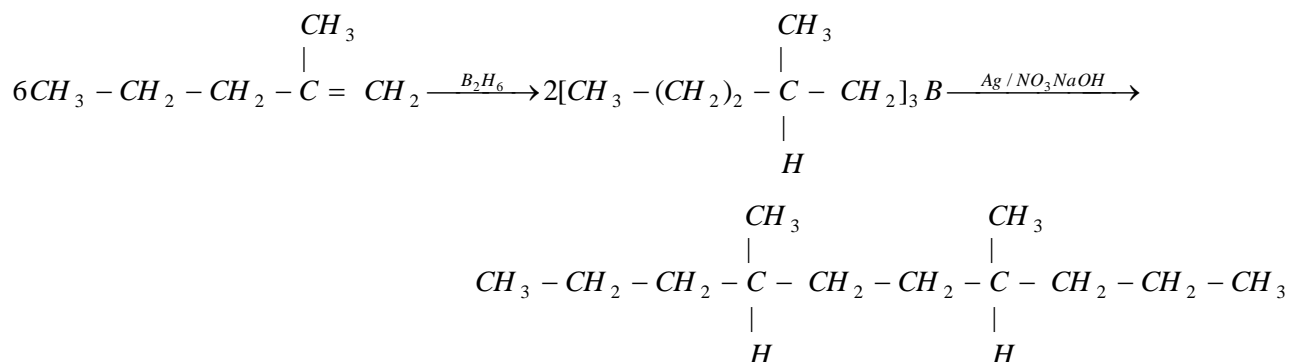
Hydroboration: Alkene give addition reaction with diborane which called hydroboration. In this reaction formed trialkylborane, which is very important and used for synthesis of different organic compound



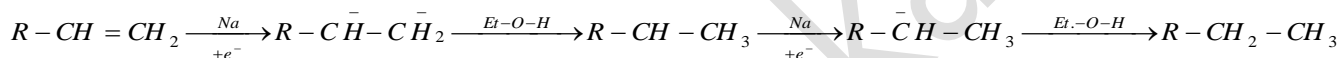
The overall result of the above reaction appears to be antimarkownikoff's addition of water to a double bond.



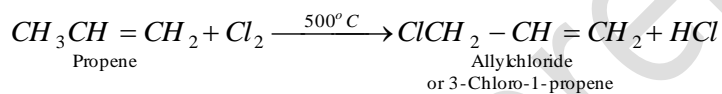
(iv) **By treatment with $\text{AgNO}_3 + \text{NaOH}$:** This reaction gives coupling



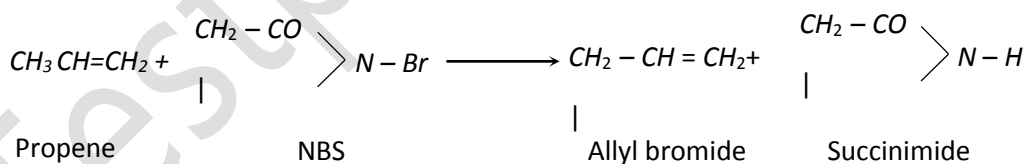
(v) **Birch reduction:** This reaction is believed to proceed via anionic free radical mechanism.



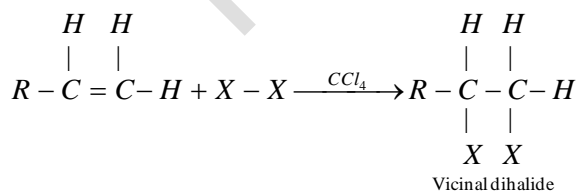
(vi) **Halogenation**



Note: If NBS [N-bromo succinimide] is a reagent used for the specific purpose of brominating alkenes at the allylic position.



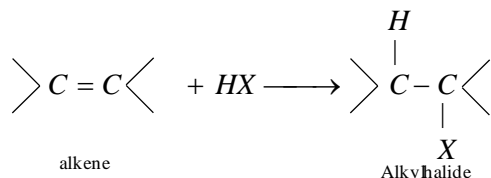
In presence of polar medium alkene form vicinal dihalide with halogen.



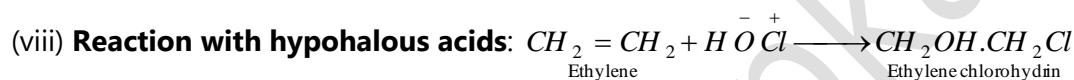
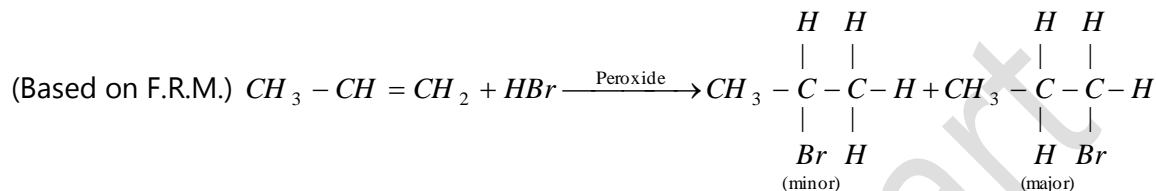
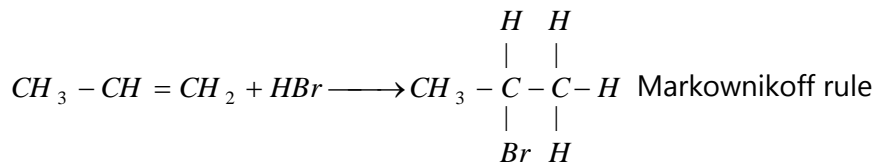
Reactivity of halogen is $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

(vii) **Reaction with HX** [Hydrohalogenation]

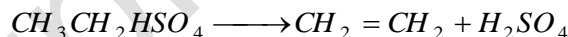
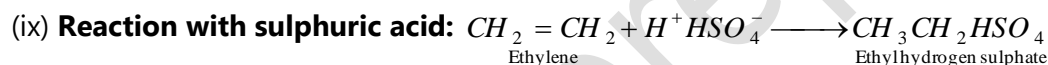




According to markownikoff's rule and kharasch effect.

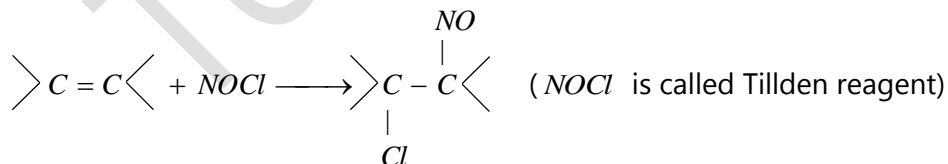


Note: In case of unsymmetrical alkenes markownikoff rule is followed.

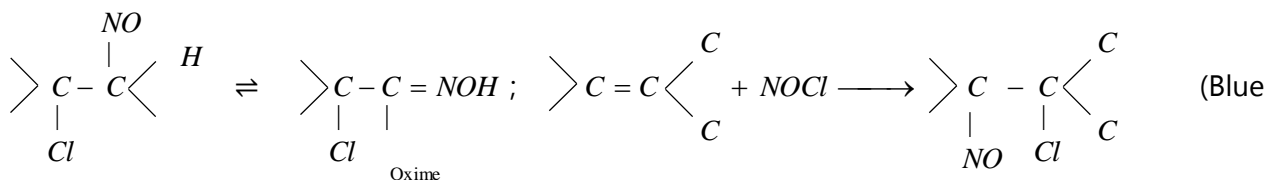


Note: This reaction is used in the separation of alkene from a gaseous mixture of alkanes and alkenes.

(x) Reaction with nitrosyl chloride



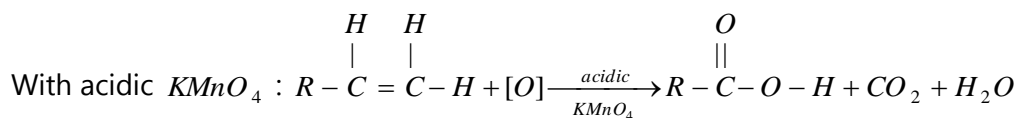
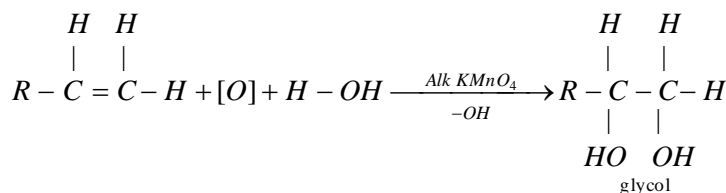
Note: If hydrogen is attached to the carbon atom of product, the product changes to more stable oxime.



color)

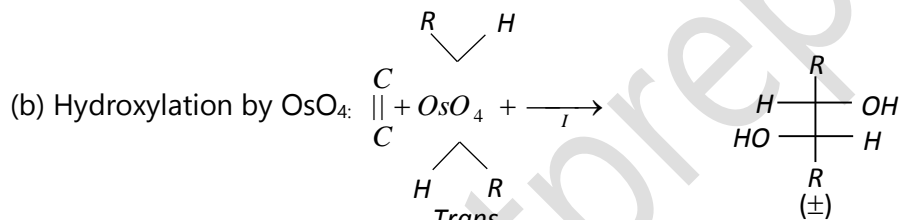
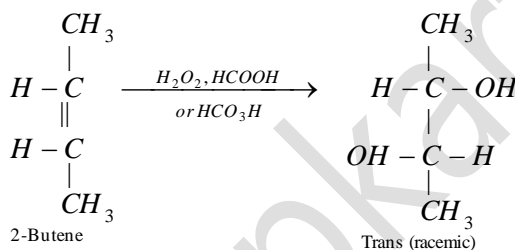


(xi) **Oxidation:** With alkaline $KMnO_4$ [Bayer's reagent]: This reaction is used as a test of unsaturation.

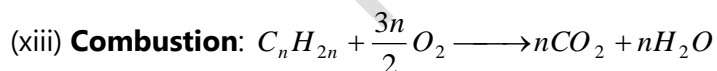
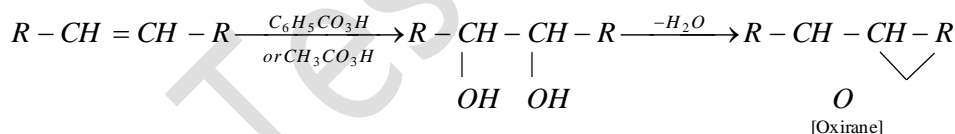


(xii) **Hydroxylation**

(a) Using per oxy acid:

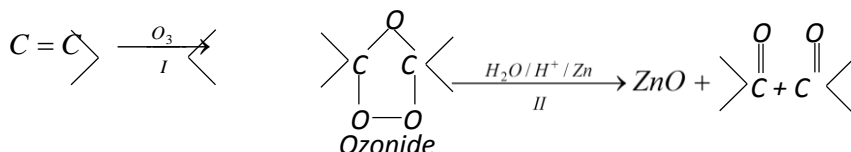


Note: If per benzoic acid or peroxy acetic acid is used then oxirane are formed.



They burn with luminous flame and form explosive mixture with air or oxygen.

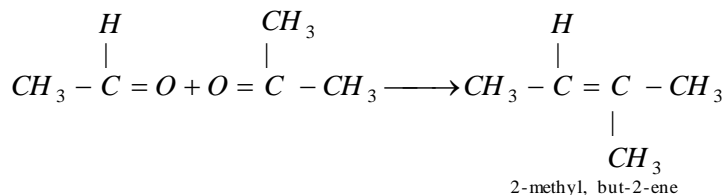
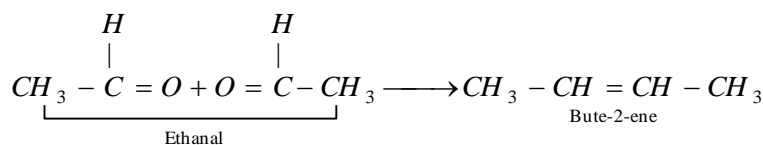
(xiv) **Ozonolysis**



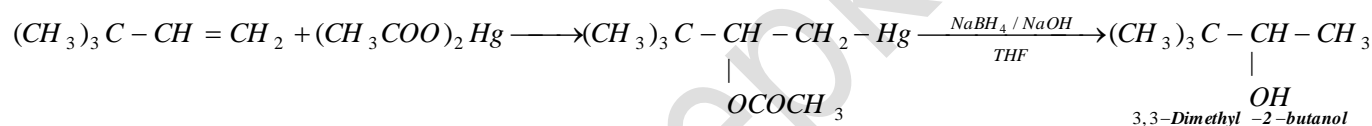
Application of Ozonolysis: This process is quite useful to locate the position of double bond in an alkene molecule. The double bond is obtained by joining the carbon atoms. of the two carbonyl compounds.



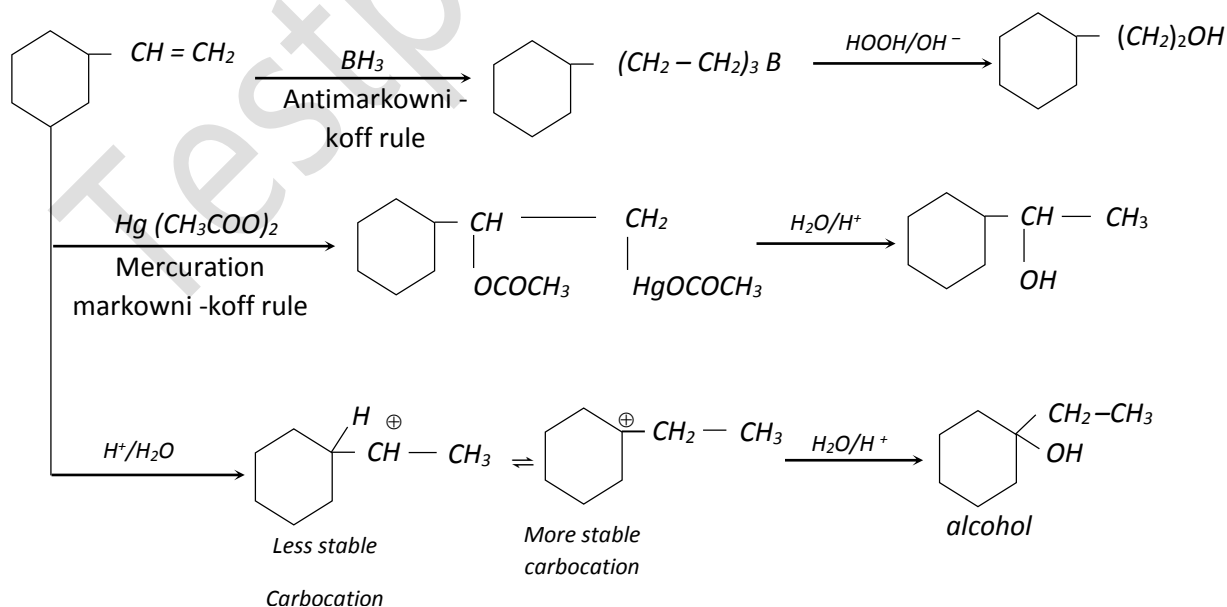
Ex.



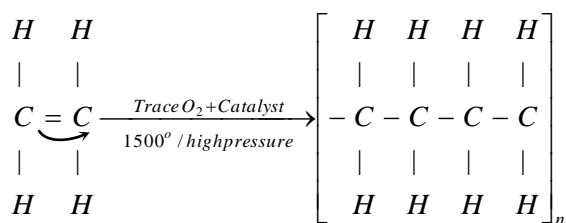
(xv) **Oxy – mercuration demercuration:** With mercuric acetate (in THF), followed by reduction with $\text{NaBH}_4 / \text{NaOH}$ is also an example of hydration of alkene according to markownikoff's rule.



Ex.



(xx) **Polymerization**



Note: If in polymerization zeigler- natta catalyst $[(R)_3Al + TiCl_4]$ is used then polymerization is known as zeigler-natta polymerization.



(xxi) **Isomerization:** $CH_3 - CH_2 - CH_2 - CH = CH_2$



The mechanism proceeds via carbocation.

(xxii) **Addition of HNO_3 :** $CH_2 = CH_2 + HO - NO_2 \longrightarrow CH_2OH.CH_2NO_2$
Ethene 2-Nitroethanol

(xxiii) **Addition of Acetyl chloride:** $CH_2 = CH_2 + CH_3COCl \longrightarrow CH_2ClCH_2COCH_3$
Ethene 4-Chlorobutanone-2

(6) **Uses**

(i) For the manufacture of polythene – a plastic material; (ii) For artificial ripening of fruits; (iii) As a general anesthetic; (iv) As a starting material for a large number of compounds such as glycol, ethyl halides, ethyl alcohol, ethylene oxide, etc.; (v) For making poisonous mustard gas (War gas); (vi) For making ethylene-oxygen flame.

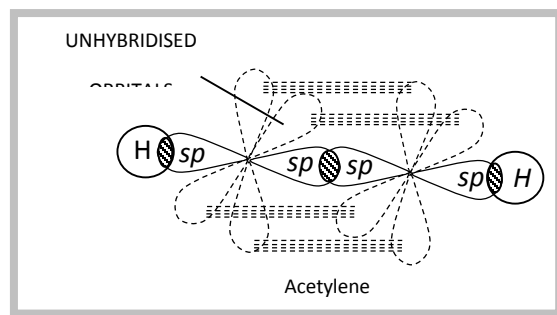


6. Alkynes.

These are the acyclic hydrocarbons which contain carbon-carbon triple bond are called alkynes. General formula is C_nH_{2n-2} . Ex. Ethyne $CH \equiv CH$; Propyne $CH_3 - C \equiv CH$

(1) Structure

- (i) Hybridization in alkynes is sp .
- (ii) Bond angle in alkynes is 180° .
- (iii) Geometry of carbon is linear.
- (iv) $C - C$ Triple bond length is 120 \AA
- (v) $C - H$ Bond length is 108 \AA
- (vi) $C - C$ Triple bond energy is 190 Kcal/mol .
- (vii) $C - H$ Bond energy is 102.38 Kcal/mol .

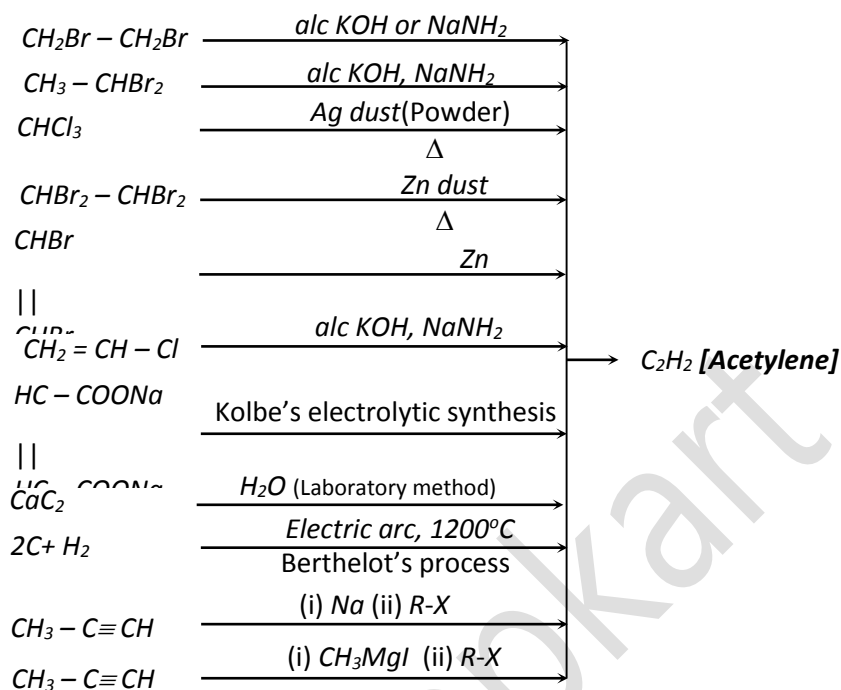


(2) Isomerism

- (i) **Chain Isomerism:** $CH_3CH_2CH_2C \equiv CH$ (1-Pentyne); $CH_3CH_2C \equiv CH$ (3-Methyl-1-butyne)
- (ii) **Position isomerism:** $CH_3CH_2CH_2C \equiv CH$ (1-pentyne); $CH_3CH_2C \equiv CCH_3$ (2-pentyne)
- (iii) **Functional isomerism:** $CH_3 - C \equiv CH$ (Propyne); $CH_2 = C = CH_2$ (1,2-propadiene (Allene))



(3) General methods of preparation

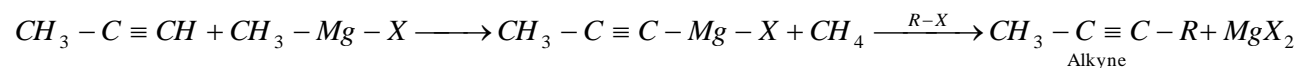
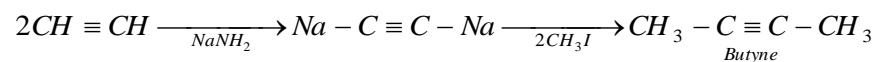


Note: In reaction with gem dihalide, Alc. KOH is not used for elimination in 2nd step.

In reaction with vicinal dihalide, if the reactant is 2-butylene chloride then product is 2-butyne as major product.

Preparation of higher alkynes (by metal acetylide)

Acetylene gives salt with $NaNH_2$ or $AgNO_3$ (ammonical) which react with alkyl halide give higher alkyne.



(4) Physical properties

(i) Acetylene is a colorless gas. It has a garlic odour. The odour is due to presence of impurities. However, pure acetylene has pleasant odour.

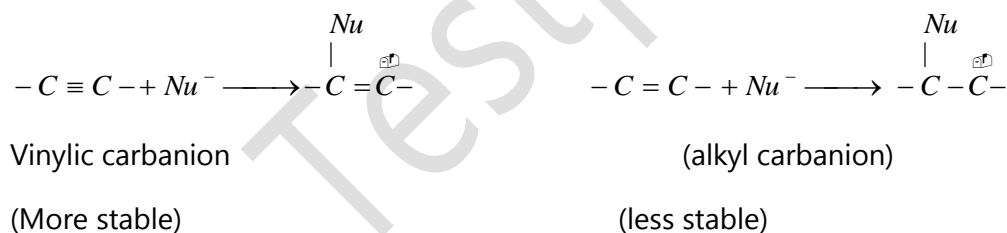
(ii) It is insoluble in water but highly soluble in acetone and alcohol. Acetylene is transported under high pressure in acetone soaked on porous material packed in steel cylinders.

(iii) Its boiling point is $-80^{\circ}C$.

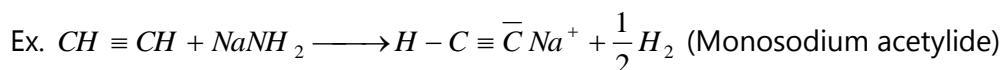
(iv) It is lighter than air. It is somewhat poisonous in nature.

(v) It burns with luminous flame and forms explosive mixture with air.

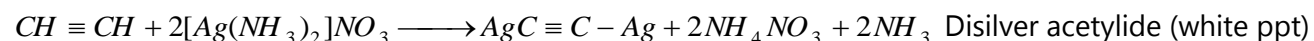
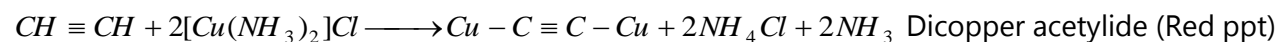
(5) **Chemical reactivity of alkynes:** $C \equiv C$ is less reactive than the carbon-carbon double bond towards electrophilic addition reaction. This is because in alkyne carbon has more s-character than more strongly will be the attraction for π electrons. Alkyne also undergo nucleophilic addition with electron rich reagents. Ex. Addition of water, cyanide, carboxylic acid, alcohols. Nucleophilic addition can be explained on the basis that alkynes form vinylic carbanion which is more stable than alkyl carbanion formed by alkene



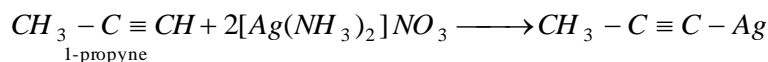
(i) **Acidity of alkynes:** Acetylene and other terminal alkynes (1- alkynes) are weakly acidic in character



The acetylenic hydrogen of alkynes can be replaced by copper (I) and silver (I) ions. They react with ammoniacal solutions of cuprous chloride and silver nitrate to form the corresponding copper and silver alkynides.

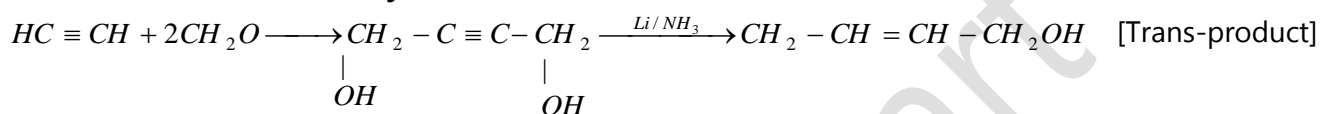


This reaction can be used to distinguish between 2-alkynes and 1-alkynes. 1-alkynes will give this test while 2-alkynes, will not give this test.



Explanation for the acidic character: It explained by sp hybridization. We know that an electron in s -orbital is more tightly held than in a p -orbital. In sp hybridization s -character is more (50%) as compared to sp^2 (33%) or sp^3 (25%), due to large s -character the carbon atom is quite electronegative.

(ii) Reaction with formaldehyde



(6) Chemical properties of acetylene

CH₃CH₂CH₃ Acetylene	→	Benzene : By passing acetylene through red hot tube, $3C_2H_2 \rightarrow C_6H_6$
	→	Pyrrole : By heating with NH_3 , $2C_2H_2 + NH_3 \rightarrow C_4H_5N + H_2$
	→	Thiophene : By heating with S or H_2S , $2C_2H_2 + S \rightarrow C_4H_4S$
	→	Acetaldehyde : By passing acetylene through 40% H_2SO_4 and 1% $HgSO_4$ at $80^\circ C$, $CH \equiv CH + H_2O \rightarrow CH_3CHO$ or by heating ethylidene acetate, $CH \equiv CH + 2CH_3COOH \xrightarrow[80^\circ C]{Hg^{2+}} \underset{\text{Ethylideneacetate}}{CH_3CH(OOCCH_3)_2} \rightarrow CH_3CHO + \begin{matrix} CH_3CO \\ >O \\ CH_3CO \end{matrix}$ [Kucherov's reaction] Acetaldehyde so prepared may be used for the preparation of : <input type="checkbox"/> Ethyl alcohol : By reduction with H_2 in presence of Ni at $140^\circ C$, $CH_3CHO + H_2 \rightarrow CH_3CH_2OH$ <input type="checkbox"/> Acetic acid : By oxidation in presence of manganese acetate or platinum wire at $70^\circ C$, $CH_3CHO + O \rightarrow CH_3COOH$ <input type="checkbox"/> Ethyl acetate : By esterification of acetic acid and alcohol or by condensation of acetaldehyde in presence of aluminum ethoxide, $2CH_3CHO \xrightarrow{Al(OC_2H_5)_3} CH_3COOC_2H_5$
	→	Westron and Westrosol : Used as solvents, $\begin{array}{ccc} CH & CHCl_2 & CHCl \\ + Cl_2 \longrightarrow & \xrightarrow[KOH]{Alc.} & \\ CH & CHCl_2 & CCl_2 \\ & \text{(Westron)} & \text{(Westrosol)} \end{array}$
	→	Lewisite : A poisonous gas used during wars, $\begin{array}{ccc} CH & CHCl & \\ + ClAsCl_2 \xrightarrow{AlCl_3} & & \longrightarrow \text{Cadet and Busen reaction} \\ CH & CHAsCl_2 & \\ & \text{Lewisite} & \end{array}$

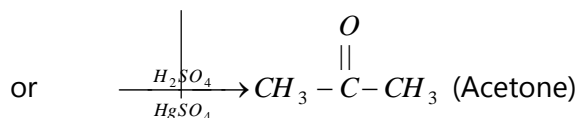
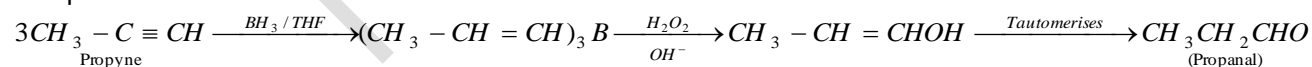


→	Vinyl acetate : By reacting with acetic acid in presence of Hg^{2+} , $CH \equiv CH + CH_3COOH \xrightarrow{Hg^{2+}} CH_2 = CHOCCH_3$ Vinyl acetate is used in paints
→	Vinyl chloride : By reacting with HCl in presence of Hg^{2+} at $60^\circ C$, $CH \equiv CH + HCl \xrightarrow[60^\circ C]{Hg^{2+}} CH_2 = CHCl$ Vinyl chloride is used for the manufacture of PVC plastic.
→	Vinyl cyanide : By reacting with HCN in presence of $Ba(CN)_2$, $CH \equiv CH + HCN \xrightarrow{Ba(CN)_2} CH_2 = CHCN$ It is employed for making orlon and buna-N rubber.
→	Chloroprene : See polymerization reactions.
→	Cuprene : See polymerization reactions.
→	Hexachloro ethane : C_2Cl_6 -used as artificial camphor.
→	Ethylene : $C_2H_2 + H_2 \xrightarrow[Catalyst]{Lindlar's} C_2H_4$ (Cis)
→	Ethane : $C_2H_2 + 2H_2 \xrightarrow[300]{Ni} C_2H_6$
→	Higher alkynes : $HC \equiv CNa + XR \xrightarrow{\text{Sod. acetylide}} HC \equiv C - R$
→	Glyoxal : By oxidation with O_3 or SeO_2 .
→	Oxalic acid : By oxidation with alk. $KMnO_4$ $\begin{array}{ccc} CH & & COOH \\ & + 4O \longrightarrow & \\ CH & & COOH \end{array}$

Consequently the electron pair of $H - C \equiv$ bond get displaced more towards the carbon atom and helps in the release of H^+ ion.

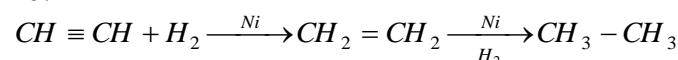
$R - C \equiv C \cdots \cdots H$ (Cleavage of bond is easy)

Oxidative-Hydroboration: Alkynes react with BH_3 (in THF) and finally converted into carbonyl compounds.



Thus it is useful for preparing aldehyde from terminal alkyne.

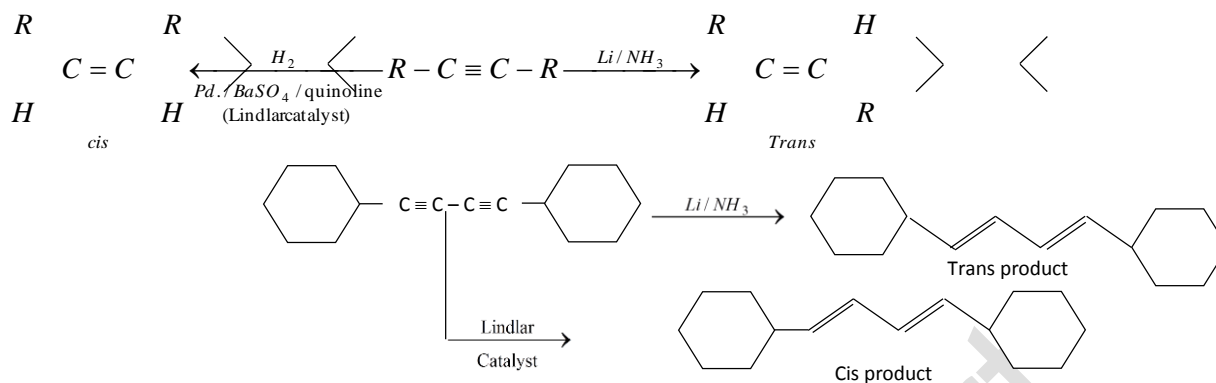
Reduction of Alkyne: Alkynes add on hydrogen in presence of suitable catalysts like finely divided Ni, Pd.



If the triple bond is not present at the end of the carbon chain of the molecule, the alkene formed may be cis and trans depending upon the choice of reducing agents.



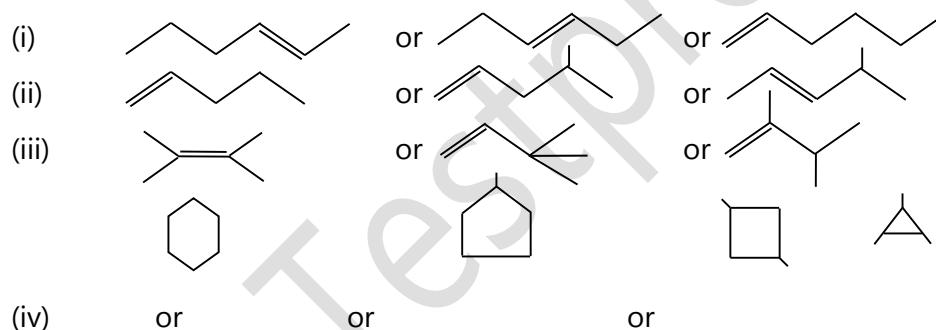
With Na / NH_3 or Li / NH_3 in (liquid ammonia) trans alkene is almost an exclusive product while catalytic reduction at alkyne affords mainly cis alkenes.



Degree of unsaturation: The number of degree of unsaturation in a hydrocarbon is given by $\frac{2n_1 + 2 - n_2}{2}$, Where n_1 is the number of carbon atoms; n_2 is the number of hydrogen atoms.

For example in C_6H_{12} , the degree of unsaturation is $= \frac{2 \times 6 + 2 - 12}{2} = 1$

So, C_6H_{12} with 1° of unsaturation can have different arrangements.



Other examples have the following degree of unsaturation.

- (i) $C_6H_6 \rightarrow 4^\circ$ (ii) $C_5H_8 \rightarrow 2^\circ$ (iii) $C_7H_{10} \rightarrow 3^\circ$ (iv) $C_8H_{12} \rightarrow 3^\circ$ (v) $C_{10}H_{16} \rightarrow 3^\circ$ (vi) $C_{12}H_{10} \rightarrow 8^\circ$
 (vii) C_3H_3Cl (like C_3H_6) $\rightarrow 1^\circ$ (viii) C_3H_4O (like C_3H_4) $\rightarrow 2^\circ$ (ix) C_4H_5N (like C_4H_4) $\rightarrow 3^\circ$
 (x) C_5H_9Cl (like C_5H_{10}) $\rightarrow 1^\circ$



Test of unsaturation

(a) Baeyer's reagent: It is 1% $KMnO_4$ solution containing sodium carbonate. It has pink color. An aqueous solution of the compound, a few drops of Baeyer's reagent are added, the pink color of the solution disappears. The decolourisation of pink color indicates the presence of unsaturation in the compound.

Note: Alkene without any hydrogen atom on the carbon forming the double bond

$$\begin{array}{ccc} R & & R \\ & \backslash & / \\ & C = C & \\ & / & \backslash \\ R & & R \end{array} \quad \text{don't show}$$

this test.

(b) Bromine- carbon tetrachloride test: The compound is dissolved in carbon tetrachloride or chloroform and then a few drops of 5% bromine solution in carbon tetrachloride are added to it, the color of bromine disappears. It indicates the presence of unsaturation.

Note: This test also fails in the case of alkene of the

$$\begin{array}{ccc} R & & R \\ & \backslash & / \\ & C = C & \\ & / & \backslash \\ R & & R \end{array} \quad \text{don't show}$$

(7) Uses

(i) Acetylene is used as an illuminant.

(ii) It is used for the production of oxy-acetylene flame. The temperature of the flame is above $3000^\circ C$. is employed for cutting and welding of metals.

(iii) Acetylene is used for artificial ripening of fruits.

(iv) It is used as a general anesthetic under the name naracylene.

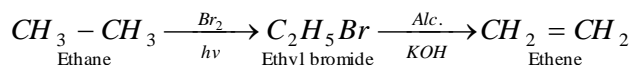
(v) Acetylene has synthetic applications. It serves as a starting material for the manufacture of a large variety of substances.

(vi) On electrical decomposition acetylene produces finely divided carbon and hydrogen. Hydrogen is used in airships. $C_2H_2 \longrightarrow 2C + H_2$

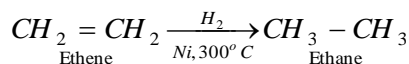


(8) Interconversion

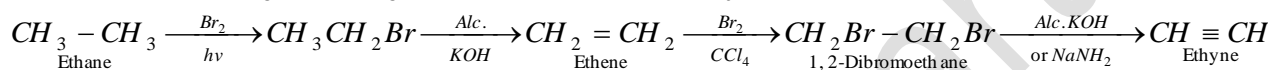
(i) Conversion of ethane into ethene: (Alkane into alkene)



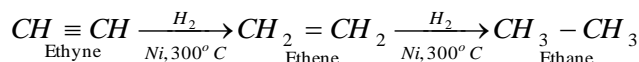
(ii) Ethene into ethane: (Alkene into alkane)



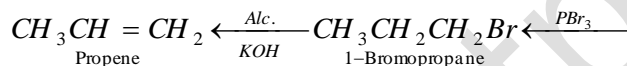
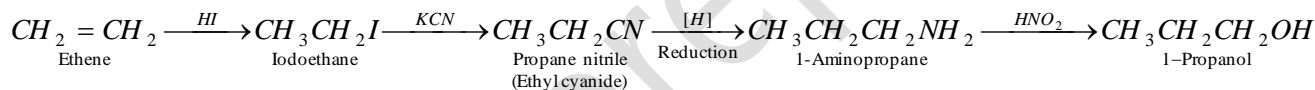
(iii) Ethane into ethyne (acetylene): i.e., alkane into alkyne



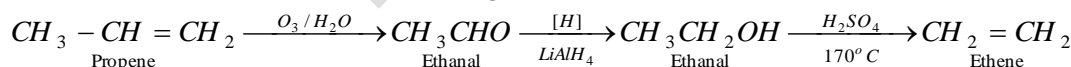
(iv) Ethyne into ethane: (Alkyne into alkane)



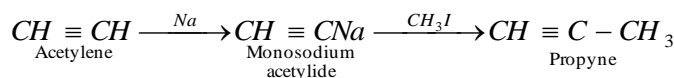
(v) Ethene into propene: Ascending in alkene series



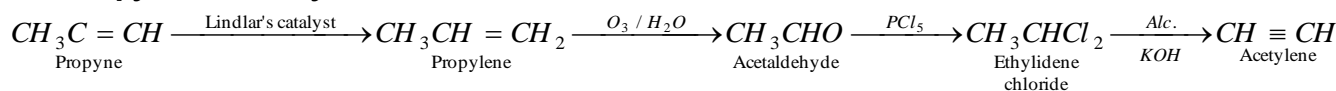
(vi) Propene into ethene: Descending an alkene series



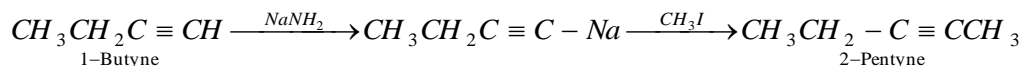
(vii) Acetylene into propyne (methyl acetylene): (Ascent)



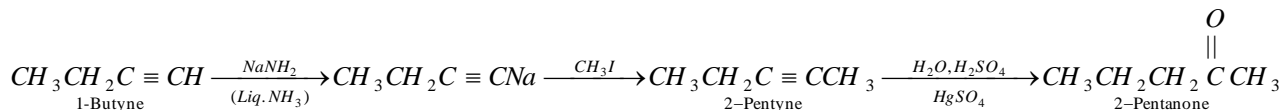
(viii) Propyne into acetylene: (Descent)



(ix) **1-Butyne into 2-pentyne:** (Ascent)

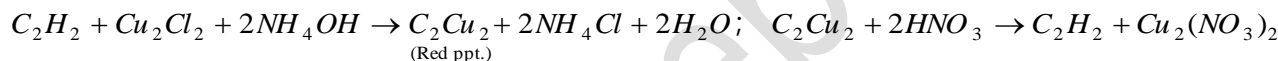


(x) **1-Butyne into 2-pentanone:** (Not more than three steps)

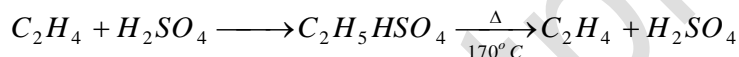


6. Separation of alkane, alkene and alkyne.

The gaseous mixture is passed through ammoniacal cuprous chloride solution. The alkyne (acetylene) reacts with Cu_2Cl_2 and forms a red precipitate. It is filtered. The alkyne or acetylene is recovered by decomposition of the precipitate with an acid.



The remaining gaseous mixture is passed through concentrated H_2SO_4 . Alkene is absorbed. The Hydrogen sulphate derivatives is heated at $170^\circ C$.



The methane or ethane is left behind.

7. 3.8 Distinction between alkanes, alkenes and alkynes.

Property	Alkane (Ethane)	Alkene (Ethene)	Alkyne (Ethyne)
Molecular formula	$C_nH_{2n+2}(C_2H_6)$	$C_nH_{2n}(C_2H_4)$	$C_nH_{2n-2}(C_2H_2)$
Nature	Saturated	Unsaturated	Unsaturated
	Single bond between carbon atoms. Each carbon atom is sp^3 -hybridized C – C	Double bond between two carbon atoms. Both carbon atoms are sp^2 -hybridized C = C	Triple bond between two carbon atoms both carbon atoms are sp -hybridized – C \equiv C –



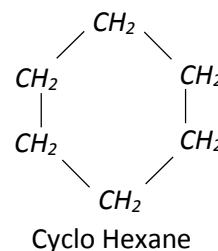
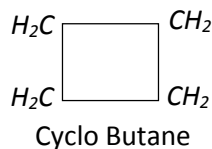
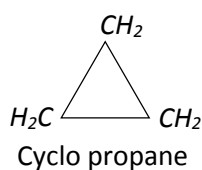
	Bond length 1.54 Å Bond energy : 83 Kcal mol ⁻¹	1.34 Å 146 Kcal mol ⁻¹	1.20 Å 200 Kcal mol ⁻¹
Burning	Burns with nonluminous flame $C_2H_6 + 7/2O_2 \rightarrow 2CO_2 + 3H_2O$	Burns with luminous flame $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$	Burns with smoky flame $C_2H_2 + 5/2O_2 \rightarrow 2CO_2 + H_2O$
Reaction with H ₂	–	Forms alkane	Forms alkene and alkane
		$C_nH_{2n} + H_2 \xrightarrow[300^\circ C]{Ni} C_nH_{2n+2}$ Alkane $C_2H_4 + H_2 \rightarrow C_2H_6$	$C_nH_{2n} + H_2 \xrightarrow[300^\circ C]{Ni} C_nH_{2n+2}$ Alkane $C_nH_{2n-2} + H_2 \xrightarrow[300^\circ C]{Ni} C_nH_{2n}$ Alkene
Reaction with conc. H ₂ SO ₄ and hydrolysis	–	Addition $C_2H_4 + H_2SO_4 \rightarrow C_2H_5HSO_4$ $\xrightarrow{H_2O} C_2H_5OH$	Addition $C_2H_2 \rightarrow CH_3CH(HSO_4)_2$ $\xrightarrow{Alcohol} CH_3CHO$ Aldehyde
Br ₂ /CCl ₄	–	Decolorizes Dibromo derivative, $C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$	Decolorizes Tetrabromo derivative, $C_2H_2Br_4$
Baeyer's reagent (Alk. KMnO ₄)	–	Decolorizes Glycol is formed $\begin{array}{ccc} CH_2 & & CH_2OH \\ & + H_2O + O \rightarrow & \\ CH_2 & & CH_2OH \end{array}$	Decolorizes Oxalic acid is formed $\begin{array}{ccc} CH & & COOH \\ & + 4O \rightarrow & \\ CH & & COOH \end{array}$
Ammonical Cu ₂ Cl ₂	–	–	Red precipitate $\begin{array}{ccc} CH & & CCu \\ & + Cu_2Cl_2 + 2NH_4OH \rightarrow & \\ CH & & CCu \\ & & (Red) \end{array}$ $+ 2NH_4Cl + 2H_2O$
Ammonical silver nitrate	–	–	White precipitate $\begin{array}{ccc} CH & & C - Ag \\ & + 2AgNO_3 + 2NH_4OH \rightarrow & \\ CH & & C - Ag \end{array}$ $+ 2NH_4Cl + 2H_2O$



8. Cycloalkane.

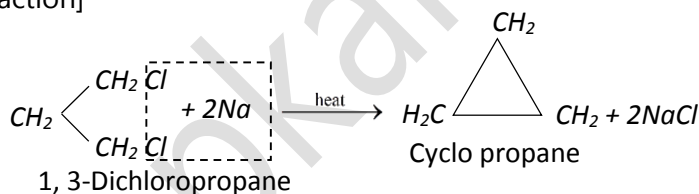
They are carbocyclic hydrocarbons in which carbon atoms are joined by single covalent bonds to form a ring. They have general formula C_nH_{2n} .

For Ex.



(1) Methods of preparation

(i) From dihalogen compounds [Freund reaction]

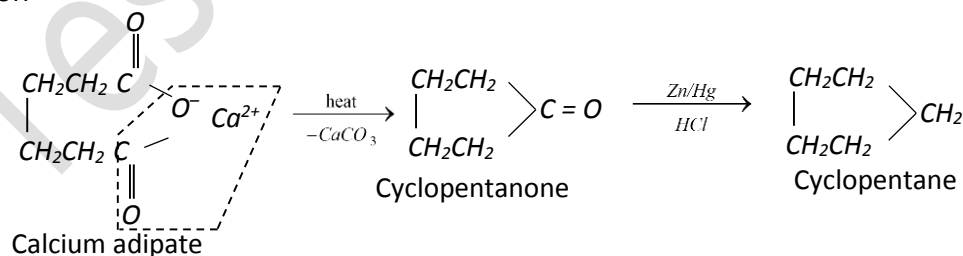


Note: It is useful in preparation of three to six membered ring.

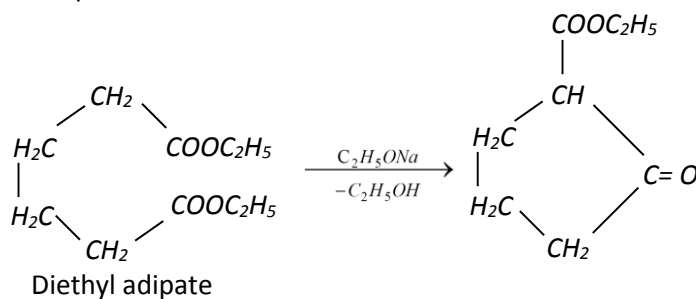
It is also known as intramolecular wurtz reaction.

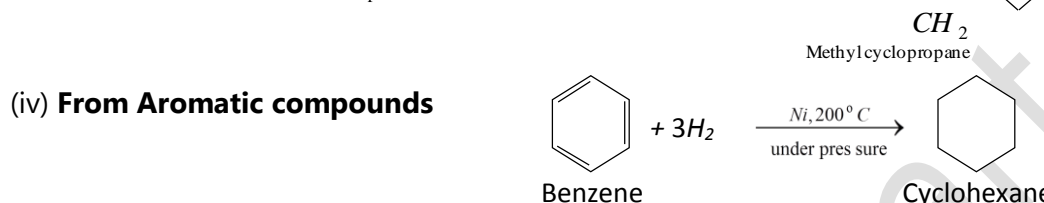
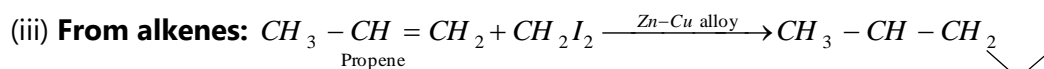
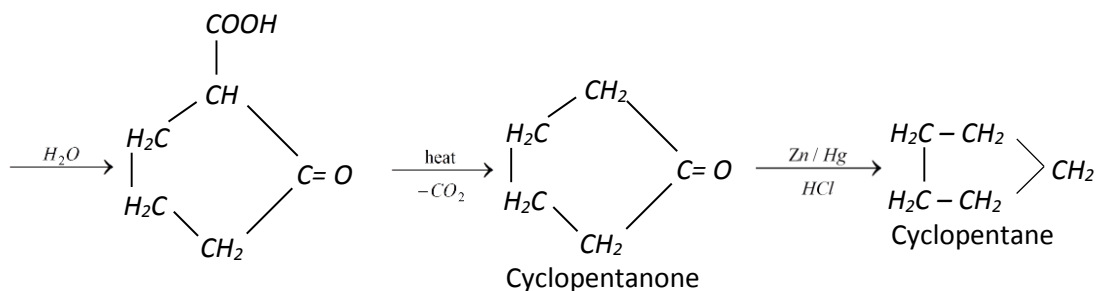
(ii) From calcium salts of dicarboxylic acids

(a) Clemmensen reduction



(b) Diekmann Cyclization





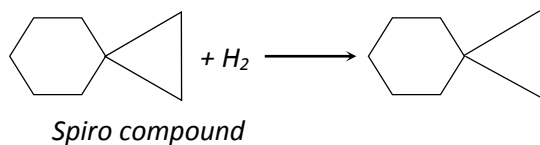
(2) Physical properties

- (i) First two members are gases, next three members are liquids and higher ones are solids.
- (ii) They are insoluble in water but soluble in alcohol and ether.
- (iii) Their boiling points show a gradual increase with increase of molecular mass. Their boiling points are higher than those of isomeric alkenes or corresponding alkanes.
- (iv) Their density increase gradually with increase of molecular mass.

(3) **Chemical properties:** Cycloalkanes behave both like alkenes and alkanes. All cycloalkanes undergo substitution reaction with halogen in the presence of light (like alkane). All cycloalkane (lower members) undergo addition reaction (ex. Addition of H_2 , HX , X_2). Further the tendency of forming addition compounds. Decreases with increase in size of ring cyclopropane > Cyclobutane > Cyclopentane. Relative ring opening of ring is explained by Baeyer strain theory.



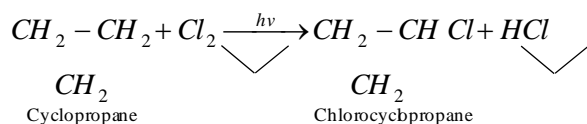
(i) **Addition in spiro cycloalkane:** If two cycloalkane fused with one another then addition take place in small ring



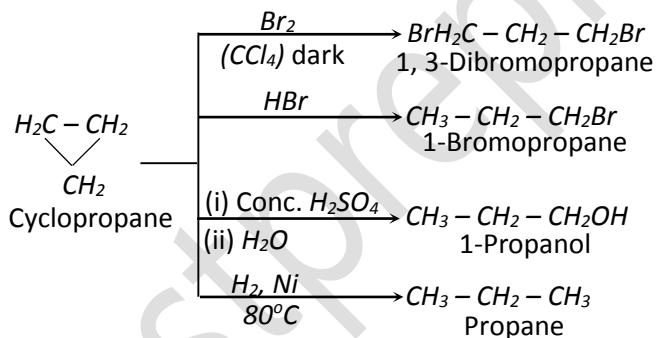
Because small ring is more unstable than large ring

Higher cycloalkanes do not give addition due to more stability.

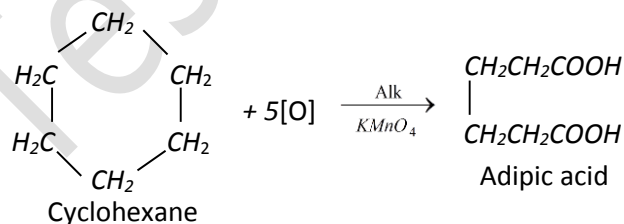
(ii) **Free radical substitution with Cl_2**



(iii) **Addition reaction**

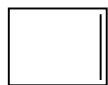


(iv) **Oxidation**



9. Cycloalkene.

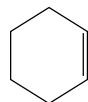
Carbocyclic compounds with double bonds in the ring are called cycloalkenes. Some of the common cycloalkenes are



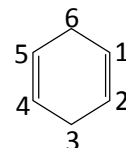
Cyclobutene



Cyclopenten

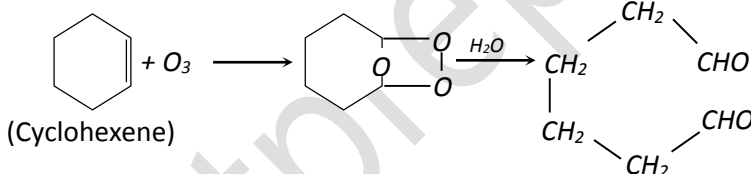
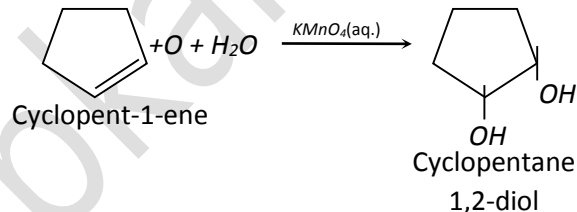
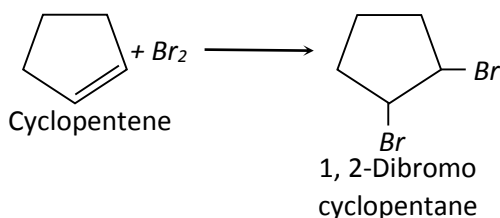


Cyclohexene



1, 4-Cyclohexadiene

Cycloalkenes can be easily obtained by Diels-Alder reaction. These compounds undergo the electrophilic addition reactions which are characteristic of alkenes, while the ring remains intact. Cycloalkenes decolorize the purple color of dilute cold $KMnO_4$ or red color of bromine in carbon tetrachloride.



10. Dienes.

These are hydrocarbon with two carbon-carbon double bonds. Dienes are of three types

(1) **Conjugated dienes:** Double bonds are separated by one single bond.

Ex: $CH_2 = CH - CH = CH_2$ (1, 3-butadiene)

(2) **Cumulative dienes:** Double bonds are adjacent to each other.

Ex: $CH_2 = C = CH_2$ Propadiene [allene]

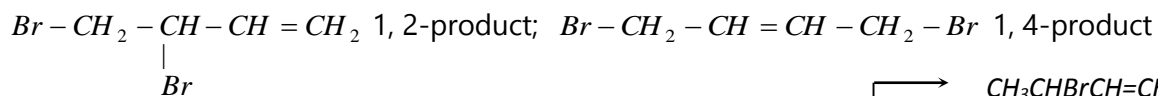
(3) **Isolated or Non-conjugated:** Double bonds are separated by more than one single bond.

Ex: $CH_2 = CH - CH_2 - CH = CH_2$ (1, 4 pentadiene)

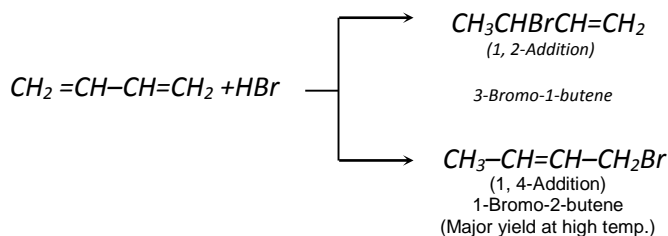
The general formula is C_nH_{2n-2} . The predominant member of this class is 1, 3-butadiene.



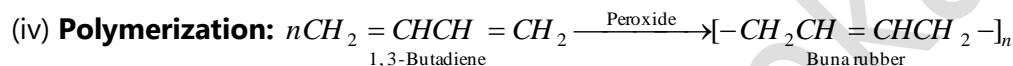
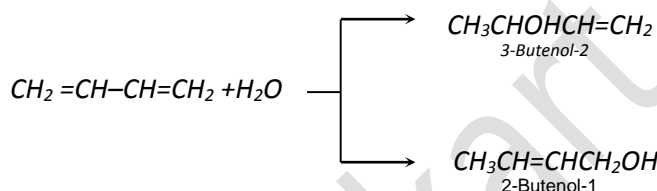
Step III: The bromide ion combines with (A) to form 3, 4-dibromo-1-butene (1, 2-addition). It combines with (B) to form 1, 4-dibromo-2-butene (1, 4-addition).



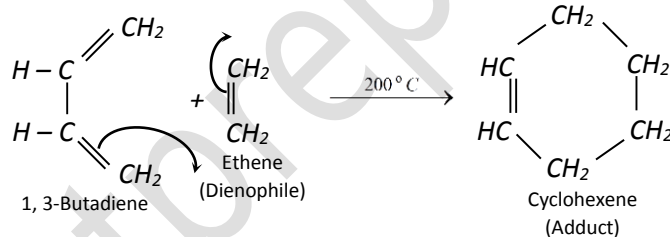
(ii) **Addition of halogen acids:**



(iii) **Addition of water:**



Diels-alder reaction:



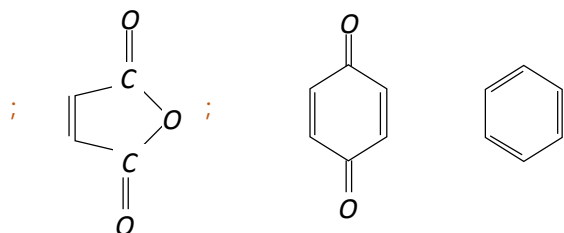
Note: Diene is known as Diene and alkene or alkyne is known as Dienophile.

If product is cyclohexene then dienophile is alkene or alkene derivative.

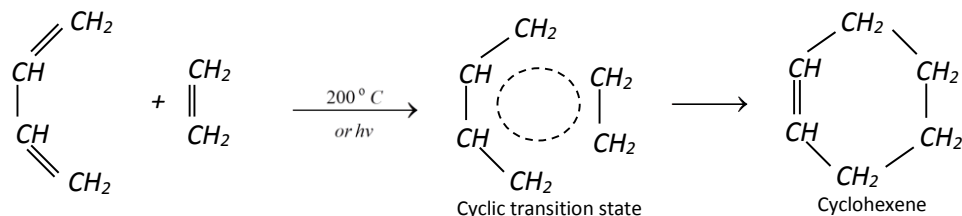
If product is 1, 4-cyclohexadiene then dienophile is alkyne or alkyne derivative.

Dienophiles of the reaction may be one of the following,

Alkenes; Alkynes; $\text{CH}_2=\text{C}=\text{CH}_2$;

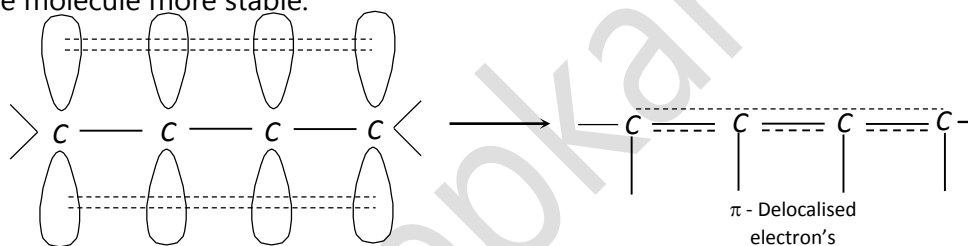


Mechanism (FMO)



Stability of conjugated dienes: It explained on the basis of delocalization of electron cloud between carbon atoms.

The four π electrons of 1,3-butadiene are delocalized over all the four atoms. This delocalization of the π electrons makes the molecule more stable.



(v) **Ozonolysis:** $\text{CH}_2=\text{CHCH}=\text{CH}_2 + 2\text{O}_3 \xrightarrow{\text{Zn}/\text{H}_2\text{O}} 2\text{HCHO} + \text{OHCCHO}$

