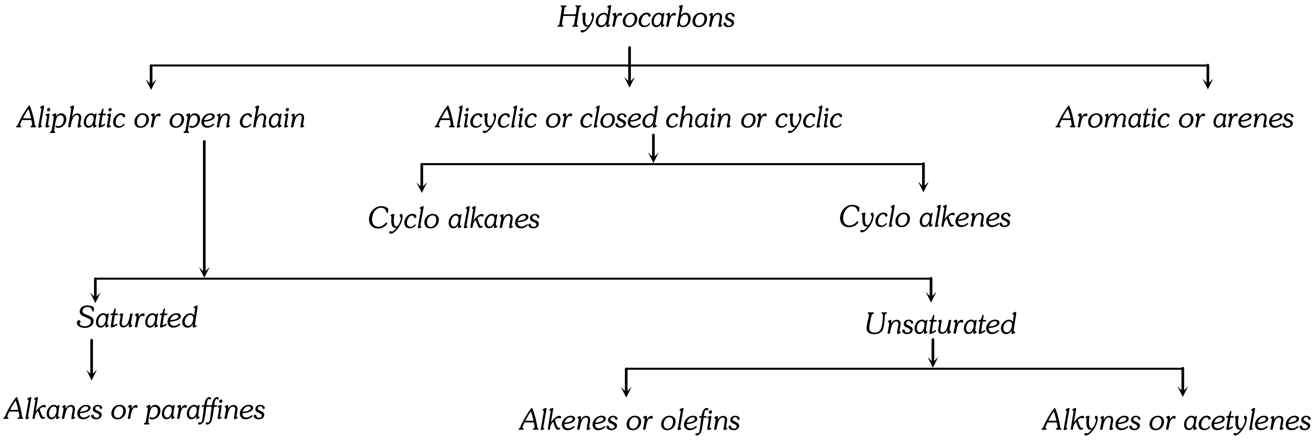
Aliphatic Hydrocarbons Part 1

"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".



Sources of hydrocarbon.

Mineral oil or crude oil, petroleum [Petra → rock; oleum → oil] is the dark colour 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 upto 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 asphattic 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%), Vapours 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, isomerisation and polymerisation to form number of hydrocarbons.

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

$4Al + 3C \rightarrow Al_4C_3$ (Aluminium 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) ; $C_2H_2 \xrightarrow{H_2} C_2H_4 \xrightarrow{H_2} \underset{\text{(Ethane)}}{C_2H_6}$

$3[CH \equiv CH] \xrightarrow{\text{Polymerisation}} \underset{\text{(Benzene)}}{C_6H_6}$; $CH_3 - CH = CH - CH_3 \xrightarrow{\text{Isomerisation}} \underset{\text{(1-Butene)}}{CH_3 - CH_2 - CH = CH_2}$

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	**Upto 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; drycleaning; petrol gas.**
(iii) Benzene derivatives	**120 – 150°**	$C_8 - C_{10}$	**Solvent; drycleaning**
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*** **:** $2\underset{\text{Mercaptan}}{RSH}+Na_2PbO_2+S\rightarrow \underset{\text{Disulphides}}{RSSR}+PbS+2NaOH$

(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) *Vapour phase cracking :* In this process, kerosene oil or gas oil is cracked in vapour 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.

Coal $+H_2 \xrightarrow[\substack{450-500^\circ C \\ 250\text{ atm}}]{Fe_2O_3}$ Mix. Of hydrocarbons or crude oil

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

$$H_2O + C \xrightarrow{1200^\circ C} \underbrace{CO + H_2}_{\text{Water gas}}$$

$$xCO + yH_2 \longrightarrow \text{Mix. Of hydrocarbon } + H_2O\,.$$

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

Characteristics of hydrocarbons.

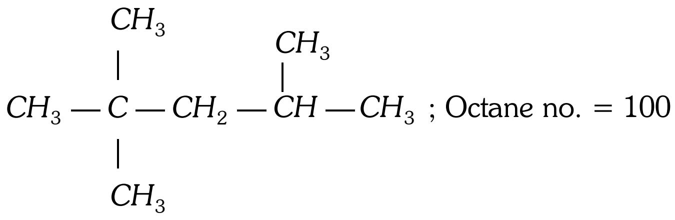
(1) **Knocking :** The metallic sound due to irregular burning of the fuel is termed as knocking.

"*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.

$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$ *n*-heptane; octane no. = 0



$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_2 - \overset{\overset{CH_3}{|}}{CH} - CH_3 \text{ ; Octane no.} = 100$$

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%.

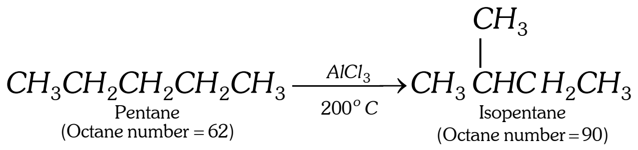
However, there is a disadvantage that the lead is deposited in the engine. To remove the free lead, the ethylene halides are added which combine with lead to form volatile lead halides.

$$Pb + \underset{\text{Ethylene bromide}}{Br - CH_2 - CH_2 - Br} \rightarrow \underset{\text{Volatile}}{PbBr_2} + \underset{\text{Ethylene}}{CH_2 = CH_2}$$

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.

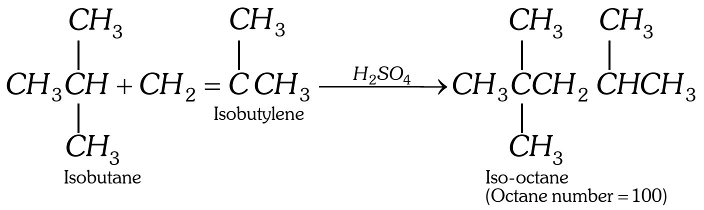
(4) Other methods of improving octane number of gasoline

(i) ***Isomerisation*** [Reforming] : By passing gasoline over $AlCl_3$ at $200^\circ C$.



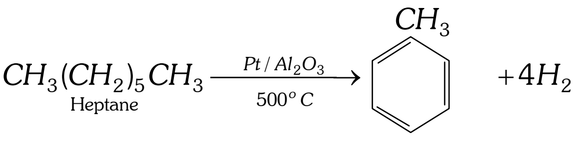
$$\underset{\substack{\text{Pentane}\\(\text{Octane number}=62)}}{CH_3CH_2CH_2CH_2CH_3} \xrightarrow[200^\circ C]{AlCl_3} \underset{\substack{\text{Isopentane}\\(\text{Octane number}=90)}}{CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2CH_3}$$

(ii) ***Alkylation*** **:**



$$\underset{\text{Isobutane}}{CH_3\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}H} + \underset{\text{Isobutylene}}{CH_2 = \overset{\overset{\displaystyle CH_3}{|}}{C}CH_3} \xrightarrow{H_2SO_4} \underset{\substack{\text{Iso-octane}\\(\text{Octane number}=100)}}{CH_3\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_3}$$

(iii) ***Aromatisation*** **:**



$$\underset{\text{Heptane}}{CH_3(CH_2)_5CH_3} \xrightarrow[500^\circ C]{Pt/Al_2O_3} \text{Toluene} + 4H_2$$

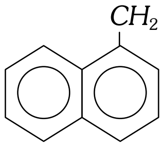
Toluene

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 additon of tetraethyl lead $(C_2H_5)_4Pb$

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

$CH_3-(CH_2)_{14}-CH_3$ Cetane → cetane no. = 100



⟶ Cetane no. = 0

α-Methyl naphthalene

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 vapours 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^oC, in France it is fixed at 35°C, and in England at 22.8°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 trimethyl-butane. 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.**

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, oxidising agents and reducing agent.

General formula : C_nH_{2n+2}

Examples are : $\underset{\text{Methane}}{CH_4}$, $\underset{\text{Ethane}}{C_2H_6}$, $\underset{\text{Propane}}{C_3H_8}$

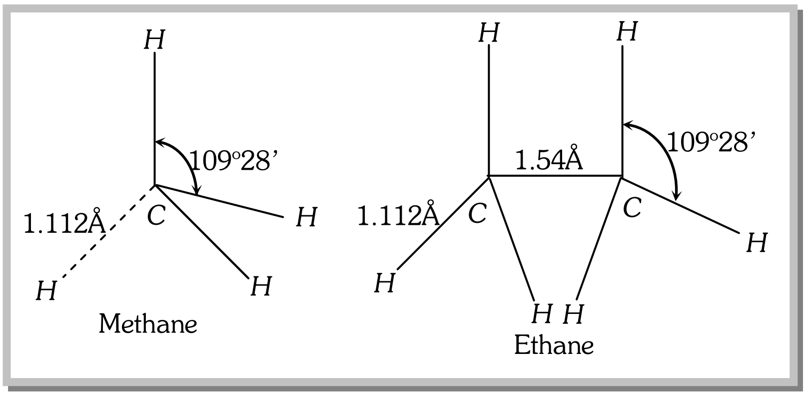
(1) Structure : (i) Every carbon atom is sp^3 hybridized.

(ii) The bond length between carbon-carbon and carbon-hydrogen are $1.54\mathring{A}$ and $1.112\mathring{A}$ respectively.

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

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

(v) $C-C$ bond dissociation energy is $83\, k\, cal/mol$.



(vi) $C-H$ bond dissociation energy is $99k\, cal/mol$.

(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)

$$\underset{\text{Alkene}}{C_nH_{2n}} + H_2 \xrightarrow[\text{heat}]{Ni} \underset{\text{Alkane}}{C_nH_{2n+2}} \;;\quad \underset{Alkyne}{C_nH_{2n-2}} + 2H_2 \xrightarrow[\text{heat}]{Ni} \underset{\text{Alkane}}{C_nH_{2n+2}}$$

Note : ✸Methane is not prepared by this method

(ii) ***Birch reduction*** : $R-CH=CH_2 \xrightarrow[2.CH_3OH]{1.Na/NH_3} R-CH_2-CH_3$

(iii) ***From alkyl halide***

(a) *By reduction* : $RX + H_2 \xrightarrow{Zn/HCl} RH + HX$

(b) *With hydrogen in presence of pt/pd* : $RX + H_2 \xrightarrow{Pd\, or Pt.} RH + HX$

(c) *With HI in presence of Red phosphorus* : $RBr + 2HI \xrightarrow{\quad} RH + HBr + I_2$

Purpose of Red P is to remove I

(iv) ***By Zn-Cu couple*** : $2CH_3CH_2OH + \underset{\text{Zn-Cu couple}}{Zn} \xrightarrow{Cu} \underset{\text{Zinc ethoxide}}{(CH_3CH_2O)_2Zn} + 2H$

$$RX + 2H \longrightarrow RH + HX$$

(v) ***Wurtz reaction*** : $\underset{\text{Alkyl halide}}{R}\boxed{X + 2Na + X}\underset{\text{Alkyl halide}}{R'} \xrightarrow{Dry\, ether} \underset{\text{Alkane}}{R-R} + 2NaX$

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.

(vi) ***Frankland's reaction*** : $2RX + Zn \longrightarrow R-R + ZnX_2$

(vii) ***Corey-house synthesis***

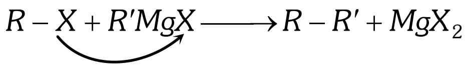
$$CH_3-CH_2-Cl \xrightarrow[2.CuI]{1.Li} (CH_3-CH_2)_2LiCu \xrightarrow{CH_3-CH_2-Cl} CH_3-CH_2-CH_2-CH_3$$

Note : ✹ Reaction is suitable for odd number of Alkanes.

(viii) *From Grignard reagent*

(a) *By action of acidic 'H'* : $\underset{\text{Alkyl magnesium halide}}{RMgX} + \underset{\text{Water}}{HOH} \longrightarrow \underset{\text{Alkane}}{RH} + Mg(OH)X$

(b) *By reaction with alkyl halide* :



$R-X + R'MgX \longrightarrow R-R' + MgX_2$

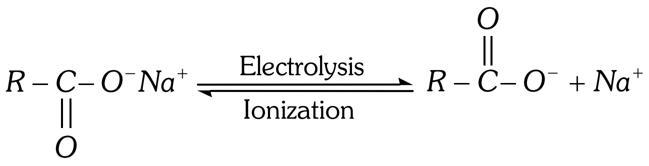
(ix) *From carboxylic acids*

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

$$R\,COONa + NaOH \xrightarrow[CaO]{heat} \underset{\text{Alkane}}{R-H} + Na_2CO_3$$

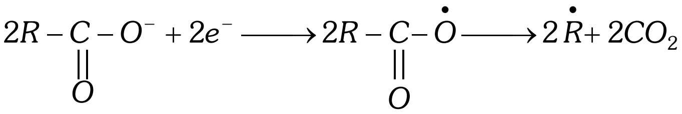
Note : ✹ $NaOH$ and CaO is in the ratio of 3 : 1.

(b) *Kolbe's synthesis* :



$$R-\underset{\underset{O}{||}}{C}-O^-Na^+ \underset{\text{Ionization}}{\overset{\text{Electrolysis}}{\rightleftharpoons}} R-\overset{\overset{O}{||}}{C}-O^- + Na^+$$

At anode [Oxidation] :



$$2R-\underset{\underset{O}{||}}{C}-O^- + 2e^- \longrightarrow 2R-\underset{\underset{O}{||}}{C}-\dot{O} \longrightarrow 2\dot{R} + 2CO_2$$

$$2\dot{R} \longrightarrow R-R \text{ (alkane)}$$

At cathode [Reduction] : $2Na^+ + 2e^- \longrightarrow 2Na \xrightarrow{2H_2O} 2NaOH + H_2\ (\uparrow)$

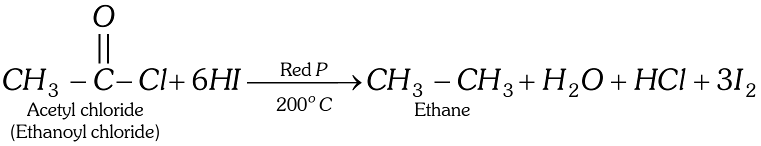
Note : ✹ Both ionic and free radical mechanism are involved in this reaction.

(c) *Reduction of carboxylic acid* : $\underset{\text{Acetic acid}}{CH_3COOH} + 6HI \xrightarrow[p]{Reduction} \underset{\text{Ethane}}{CH_3CH_3} + 2H_2O + 3I_2$

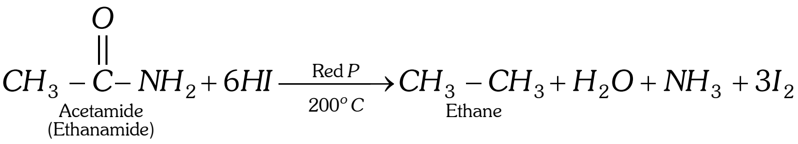
(x) *By reduction of alcohols, aldehyde, ketones or acid derivatives*

$\underset{\substack{\text{Methanol}\\\text{(Methyl alcohol)}}}{CH_3OH} + 2HI \xrightarrow[150^\circ C]{Red\,P} \underset{\text{Methane}}{CH_4} + H_2O + I_2$; $\underset{\substack{\text{Acetaldehyde}\\\text{(Ethanal)}}}{CH_3CHO} + 4HI \xrightarrow[150^\circ C]{Red\,P} \underset{\text{Ethane}}{C_2H_6} + H_2O + 2I_2$

$\underset{\substack{\text{Acetone}\\\text{(Propanone)}}}{CH_3COCH_3} + 4HI \xrightarrow[150^\circ C]{Red\,P} \underset{\text{Propane}}{CH_3CH_2CH_3} + H_2O + 2I_2$;



$$\underset{\substack{\text{Acetyl chloride}\\\text{(Ethanoyl chloride)}}}{CH_3-\overset{\overset{O}{||}}{C}-Cl} + 6HI \xrightarrow[200^\circ C]{Red\,P} \underset{\text{Ethane}}{CH_3-CH_3} + H_2O + HCl + 3I_2$$



$$\underset{\substack{\text{Acetamide}\\\text{(Ethanamide)}}}{CH_3-\overset{\overset{O}{||}}{C}-NH_2} + 6HI \xrightarrow[200^\circ C]{Red\,P} \underset{\text{Ethane}}{CH_3-CH_3} + H_2O + NH_3 + 3I_2$$

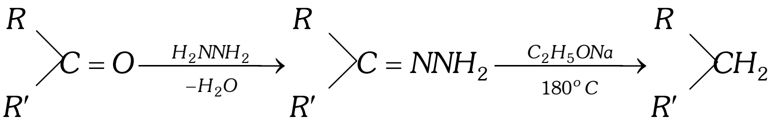
Note : ✹ Aldehyde and ketones when reduced with amalgamated zinc and conc. HCl also yield alkanes.

Clemmensen reduction : $\underset{\substack{\text{Acetaldehyde}\\\text{(Ethanal)}}}{CH_3CHO} + 2H_2 \xrightarrow[HCl]{Zn-Hg} \underset{\text{Ethane}}{CH_3-CH_3} + H_2O$

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

Note : ✹ Aldehydes and ketones ($>C=O$) can be reduced to hydrocarbon in presence of excess of hydrazine and sodium alkoxide on heating.

Wolff-kishner reduction :



$$\begin{matrix}R\\R'\end{matrix}\!\!>C=O \xrightarrow[-H_2O]{H_2NNH_2} \begin{matrix}R\\R'\end{matrix}\!\!>C=NNH_2 \xrightarrow[180^\circ C]{C_2H_5ONa} \begin{matrix}R\\R'\end{matrix}\!\!>CH_2$$

(xi) ***Hydroboration of alkenes***

(a) *On treatment with acetic acid*

$$\underset{\text{Alkene}}{R-CH=CH_2} \xrightarrow{B_2H_6} \underset{\text{Trialkyl borane}}{(R-CH_2-CH_2)_3B} \xrightarrow{CH_3COOH} \underset{\text{Alkane}}{R-CH_2-CH_3}$$

(b) *Coupling of alkyl boranes by means of silver nitrate*

$$6[R-CH=CH_2] \xrightarrow{2B_2H_6} [2R-CH_2-CH_2-]_3B \xrightarrow[NaOH]{AgNO_3\ 25^\circ C} 3[RCH_2CH_2-CH_2CH_2R]$$

(4) Physical Properties

(i) ***Physical state* :** Alkanes are colourless, odourless and tasteless.

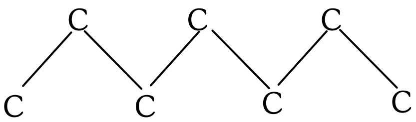
Alkanes	*State*
C_1-C_4	Gaseous state
C_5-C_{17}	Liquid state [Except neo pentane] [gas]
C_{18} & above	Solid like waxes

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

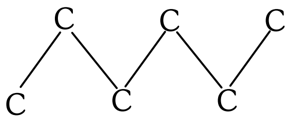
(iii) ***Solubility* :** Insoluble in water, soluble in organic solvents, solubility $\propto \dfrac{1}{\text{Molecular mass}}$

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

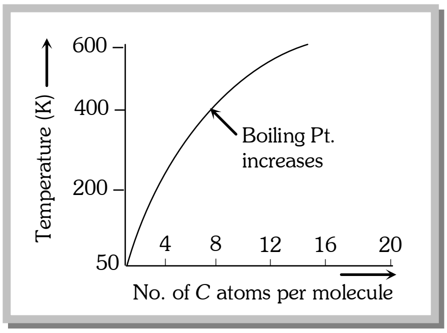
Alkane :	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}
M.P. (K) :	85.9	138	143.3	179	182.5	216.2

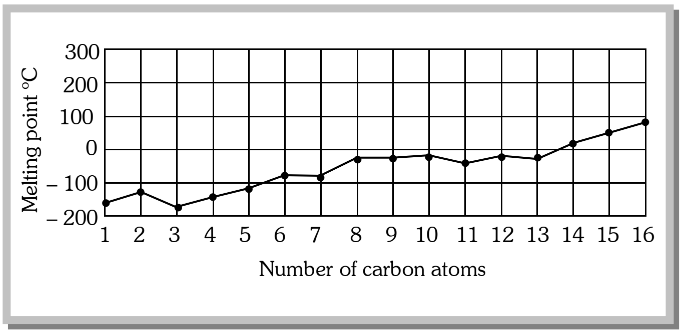


Odd no. of Carbons



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 doesnot show any reaction at room temperature, but on heating it shows iodination.

✹ Iodination of methane is done in presence of oxidising agent such as $HNO_3/HIO_3/HgO$ which neutralises HI.

✹ **Chlorination of methane :**

$$CH_4 + Cl-Cl \xrightarrow[-HCl]{u.v.light} CH_2-Cl_2 \xrightarrow[-HCl]{u.v.light} CHCl_3 \xrightarrow{-HCl} CCl_4$$

(ii) *Reaction based on free radical mechanism*

(a) *Nitration* : $\underset{\text{Alkane}}{R-H} + HONO_2 \xrightarrow[temp.]{High} \underset{\text{Nitroalkane}}{R-NO_2} + H_2O$

Nitrating mixture : (i) $(Con.HNO_3 + Con.H_2SO_4)$ at 250^oC

(ii) (HNO_3 vapour at $400^o - 500^oC$).

(b) *Sulphonation* : Free radical mechanism $R-H+HOSO_3H \xrightarrow[\text{Prolonged heating}]{SO_3} R-SO_3H+H_2O$

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

(iii) *Oxidation*

(a) *Complete Oxidation or combustion* : $C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)H_2O + Q$

Note : ✹ This is exothermic reaction.

(b) *Incomplete combustion or oxidation*

$$2CH_4 + 3O_2 \xrightarrow{Burn} 2CO + 4H_2O$$

$$CH_4 + O_2 \longrightarrow C + 2H_2O$$

(c) *Catalytic Oxidation* : $CH_4 + [O] \xrightarrow[100\,atm/200^oC]{Cu-tube} CH_3OH$

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

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

$$CH_3(CH_2)_nCH_3 \xrightarrow[100-160^oC]{O_2} CH_3(CH_2)_nCOOH$$

(d) *Chemical oxidation* : $\underset{\text{Isobutane}}{(CH_3)_3CH} \xrightarrow{KMnO_4} \underset{\text{Tertiary butyl alcohol}}{(CH_3)_3.C.OH}$

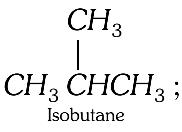
(iv) *Thermal decomposition or cracking or pyrolysis or fragmentation*

$$\underset{\text{Methane}}{CH_4} \xrightarrow{1000^{o}C} C + 2H_2 ;\ \underset{\text{Ethane}}{C_2H_6} \xrightarrow[Cr_2O_3 + Al_2O_3]{500^{o}C} \underset{\text{Ethylene}}{CH_2 = CH_2} + H_2$$

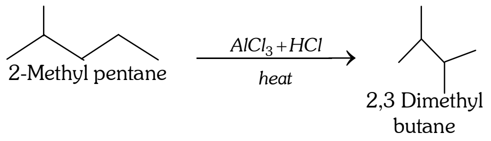
$$C_3H_8 \longrightarrow C_2H_4 + CH_4 \text{ or } C_3H_6 + H_2$$

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

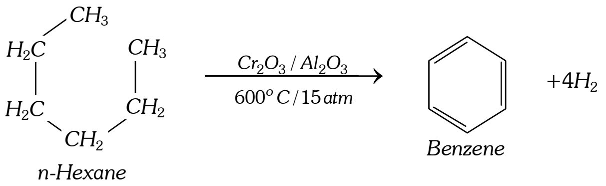
(v) ***Isomerisation*** :

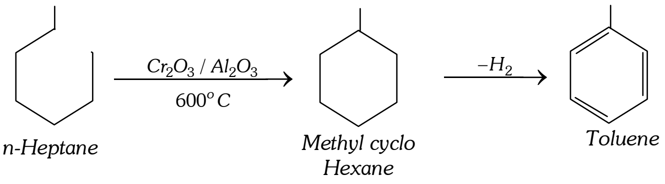


$$\underset{n\text{-Butane}}{CH_3CH_2CH_2CH_3} \xrightarrow[200^{o}C,\,35atm]{AlCl_3 + HCl} \underset{\text{Isobutane}}{CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_3}\ ;$$



(vi) ***Aromatisation :***



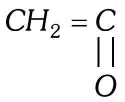


(vii) ***Step up reaction***

(a) *Reaction with* CH_2N_2 : $R - CH_2 - H + CH_2N_2 \xrightarrow{h\nu} R - CH_2 - CH_2 - H$

(b) *Reaction with* $CHCl_3 / NaOH$: $R - CH_2 - H \xrightarrow[:CCl_2]{CHCl_3 / OH^-} R - CH_2 - CHCl_2$

(c) *Reaction with*



$CH_2 = \underset{\underset{\displaystyle O}{||}}{C}$: $R - CH_2 - H \xrightarrow[:CH_2 / -CO]{CH_2 = \overset{\overset{O}{||}}{C} / \Delta} R - CH_2 - CH_3$

(viii) ***HCN formation :*** $2CH_4 \xrightarrow{N_2 / \text{electric arc}} 2HCN + 3H_2$ or $CH_4 + NH_3 \xrightarrow[700^{o}C]{Al_2O_3} HCN + 3H_2$

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

$$CH_3 - CH_2 - CH_3 + SO_2 + Cl_2 \xrightarrow{u.v\ light} CH_3 - CH_2 - CH_2SO_2Cl + HCl$$

This reaction is known as reed's reaction.

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

(x) ***Action of steam :*** $CH_4 + H_2O \xrightarrow[800^{o}C]{Ni / Al_2O_3} CO + 3H_2$

Individual members of alkanes.

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

(i) ***Industrial method of preparation*** **:** Mathane 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 carbonmonoxide and hydrogen is passed over a catalyst containing nickel and carbon at $250^{o}C$ when methane is formed.

$$CO + 3H_2 \xrightarrow[250^{o}C]{Ni+C} CH_4 + H_2O$$

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

$$\underset{\text{Cellulose}}{(C_6H_{10}O_5)_n} + nH_2O \longrightarrow 3nCH_4 + 3nCO_2$$

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

$$C + 2H_2 \xrightarrow{1200^{o}C} CH_4$$

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

$$CS_2 + 2H_2S + 8Cu \xrightarrow{\text{High temperature}} CH_4 + 4Cu_2S$$

(ii) ***Physical properties***

(a) It is a colourless, odourless, 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 $-182.5^{o}C$ and boiling point is $-161.5^{o}C$.

(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 vulcanisation.

(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 :* $\underset{\substack{\text{Ethylene}\\ \text{(ethene)}}}{CH_2 = CH_2} + H_2 \xrightarrow[300^{o}C]{Ni} \underset{\text{Ethane}}{CH_3 - CH_3}$

(iii) ***Physical properties***

(a) It is a colourless, odourless, 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°C. Its melting point is –172°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 :*** $\underset{\text{Methane}}{CH_4} \xrightarrow[UV]{Cl_2} CH_3Cl \xrightarrow[\text{Heat with } Na \text{ in ether}]{\text{Wurtz reaction}} \underset{\text{Ethane}}{CH_3-CH_3}$

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

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

Ethane to methane

$$\underset{\substack{\text{Ethane}\\\text{(excess)}}}{C_2H_6} \xrightarrow[UV]{Cl_2} \underset{\text{Ethyl chloride}}{C_2H_5Cl} \xrightarrow{Aq.\,KOH} \underset{\text{Ethyl alcohol}}{C_2H_5OH} \xrightarrow{[O]} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{[O]} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{NaOH} \underset{\text{Sodium acetate}}{CH_3COONa} \xrightarrow[\text{heat}]{NaOH\,/\,CaO} \underset{\text{Methane}}{CH_4}$$

$$\underset{\text{alkane}}{\text{Higher}} \xrightarrow[UV]{Cl_2} \underset{\text{halide}}{\text{Alkyl}} \xrightarrow[KOH]{Aq.} \text{Alcohol} \xrightarrow{[O]} \text{Aldehyde} \xrightarrow{[O]} \text{Acid} \xrightarrow{NaOH} \underset{\text{the acid}}{\text{Sodium salt of}} \xrightarrow[\text{heat}]{NaOH\,/\,CaO} \text{Lower alkane}$$

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

(i) Hybridisation of unsaturated 'C' atom is sp^2

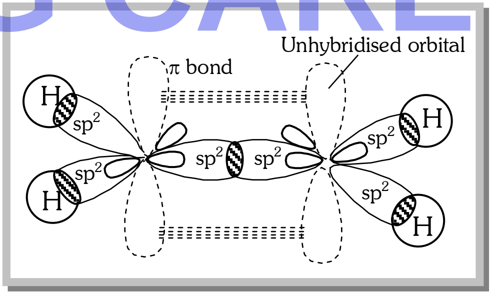
(ii) Geometry of unsaturated 'c' atom is trigonal planer

(iii) $C-H$ bond length is 1.34 Å

(iv) $C=C$ bond energy is 143.1 $K\,cal/mol$

(v) $C-H$ bond length is 1.10 Å

(vi) $C=C$ bond energy is 108 $Kcal/mol$

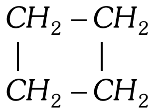


(2) Isomerism

(i) ***Chain Isomerism :*** $CH_3-CH_2-CH=CH_2$ and $(CH_3)_2-C=CH_2$

(ii) ***Position Isomerism*** **:** $CH_2=CH-CH_2-CH_3$ and $CH_3-CH=CH-CH_3$

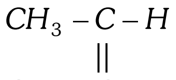
(iii) ***Functional Isomerism :*** [Ring chain] $\underset{1-butene}{CH_3-CH_2-CH=CH_2}$ and



$$\begin{array}{c} CH_2-CH_2 \\ |\qquad\ \ | \\ CH_2-CH_2 \end{array}$$

Cyclo butene

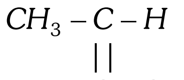
(iv) ***Geometrical Isomerism :***



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

cis–2–butene

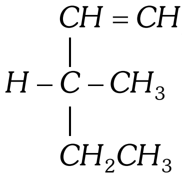
and



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

Trans–2–butene

(v) ***Optical Isomerism :***



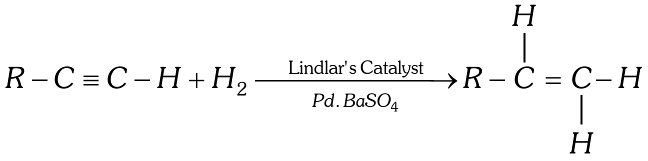
$$\begin{array}{c} CH=CH_2 \\ | \\ H-C-CH_3 \\ | \\ CH_2CH_3 \end{array}$$

Note : ✹ Cumulated polythene having even no. of double bonds. Which has $=C\langle^{a}_{b}$ system at the both end can exhibit optical isomerism but cannot exhibit geometrical isomerism.

✹ Cumulated polythene having odd no. of double bonds which have $=C\langle^{a}_{b}$ system at both end can exhibit geometrical isomerism but cannot exhibit optical isomerism.

(3) **Preparation methods**

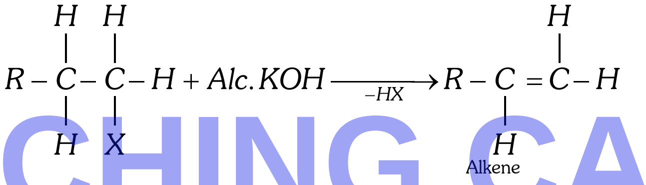
(i) ***From Alkynes :***



$$R-C\equiv C-H+H_2\xrightarrow[Pd.BaSO_4]{\text{Lindlar's Catalyst}}R-\overset{\overset{H}{|}}{C}=\underset{\underset{H}{|}}{C}-H$$

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

(ii) ***From mono halides*** **:**

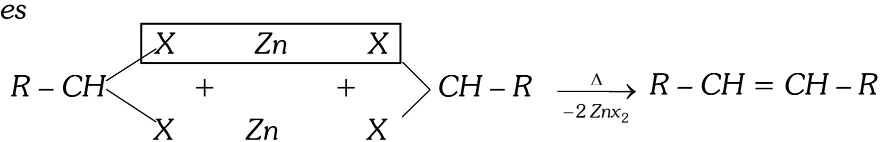


$$R-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C}}-H+Alc.KOH\xrightarrow[-HX]{}\underset{\text{Alkene}}{R-\underset{\underset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-H}$$

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*

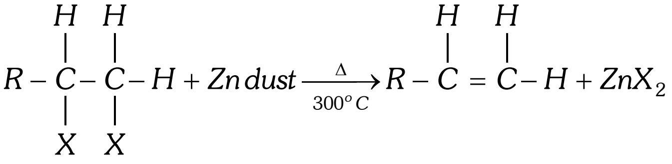


$$R-CH\left\langle\begin{matrix}\boxed{X\quad Zn\quad X}\\ +\qquad\quad +\\ X\quad Zn\quad X\end{matrix}\right\rangle CH-R\xrightarrow[-2\,Znx_2]{\Delta}R-CH=CH-R$$

Note : ✹ If we take two different types of gemdihalides then we get three different types of alkenes .

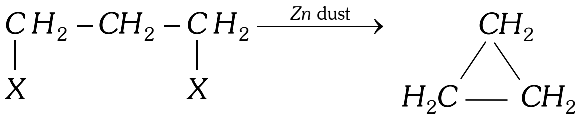
✹Above reaction is used in the formation of symmetrical alkenes only.

(b) *From vicinal dihalides :*



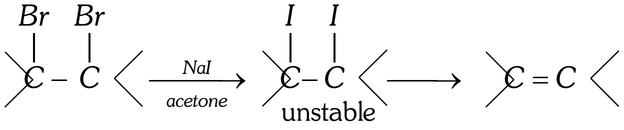
$$R-\underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C}}-H+Zn\,dust\xrightarrow[300^{\circ}C]{\Delta}R-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-H+ZnX_2$$

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



$$\underset{\underset{X}{|}}{CH_2}-CH_2-\underset{\underset{X}{|}}{CH_2}\xrightarrow{Zn\text{ dust}}$$

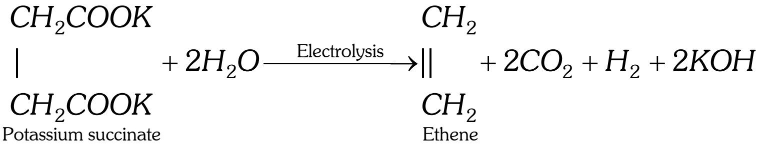
(iv) ***By action of*** *NaI* ***on vic dihalide :***



$$>\overset{\overset{Br}{|}}{C}-\overset{\overset{Br}{|}}{C}<\xrightarrow[acetone]{NaI}\underset{\text{unstable}}{>\overset{\overset{I}{|}}{C}-\overset{\overset{I}{|}}{C}<}\longrightarrow\ >C=C<$$

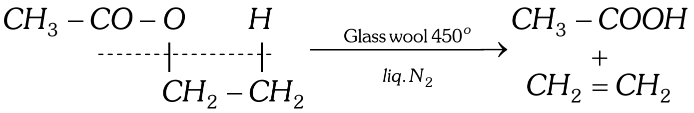
(v) ***From alcohols*** [Laboratory method] **:** $\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[443\,K]{H_2SO_4\ or\ H_3PO_4} \underset{\text{Ethene}}{CH_2 = CH_2} + H_2O$

(vi) ***Kolbe's reaction* :**



$$\underset{\text{Potassium succinate}}{\begin{array}{l} CH_2COOK \\ | \\ CH_2COOK \end{array}} + 2H_2O \xrightarrow{\text{Electrolysis}} \underset{\text{Ethene}}{\begin{array}{c} CH_2 \\ || \\ CH_2 \end{array}} + 2CO_2 + H_2 + 2KOH$$

(vii) ***From esters*** [Pyrolysis of ester] **:**

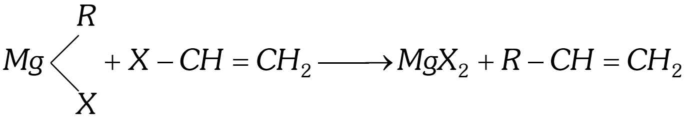


$$\begin{array}{l} CH_3 - CO - O \quad\quad H \\ \quad\quad\quad CH_2 - CH_2 \end{array} \xrightarrow[liq.\,N_2]{\text{Glass wool }450^o} \begin{array}{c} CH_3 - COOH \\ + \\ CH_2 = CH_2 \end{array}$$

(viii) ***Pyrolysis of quaternary ammonium compounds* :** $\underset{\textbf{Tetraethyl ammonium hydroxide}}{(C_2H_5)_4\overset{+}{N}\overset{-}{O}H} \xrightarrow{heat} \underset{\textbf{Triethylamine (Tert. amine)}}{(C_2H_5)_3N} + \underset{\textbf{Ethene}}{C_2H_4} + H_2O$

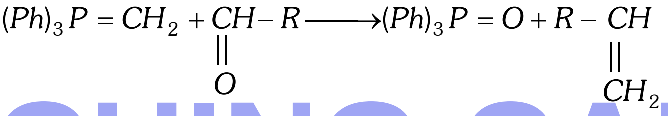
(ix) ***Action of copper alkyl on vinyl chloride* :** $\underset{\text{Vinyl chloride}}{H_2C = CHCl} \xrightarrow{CuR_2} H_2C = CHR$

(x) ***By Grignard reagents* :**

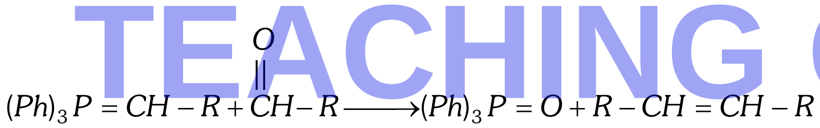


$$Mg\begin{array}{l} R \\ X \end{array} + X - CH = CH_2 \longrightarrow MgX_2 + R - CH = CH_2$$

(xi) ***The wittig reaction* :**

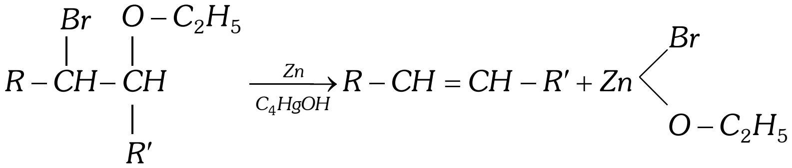


$$(Ph)_3P = CH_2 + \begin{array}{c} CH - R \\ || \\ O \end{array} \longrightarrow (Ph)_3P = O + \begin{array}{c} R - CH \\ || \\ CH_2 \end{array}$$



$$(Ph)_3P = CH - R + \begin{array}{c} O \\ || \\ CH - R \end{array} \longrightarrow (Ph)_3P = O + R - CH = CH - R$$

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



$$\begin{array}{c} Br \quad O - C_2H_5 \\ | \quad\quad | \\ R - CH - CH \\ \quad\quad | \\ \quad\quad R' \end{array} \xrightarrow[C_4HgOH]{Zn} R - CH = CH - R' + Zn\begin{array}{l} Br \\ O - C_2H_5 \end{array}$$

(4) Physical Properties

(i) Alkenes are colourless and odourless.

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

(iii) Physical state

$C_1 - C_4 \longrightarrow$ gas

$C_5 - C_{16} \longrightarrow$ liquid

$> C_{16} \longrightarrow$ solid wax

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

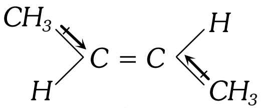
(v) The melting points of cis isomers are lower than trans isomers because cis isomer is less symmetrical than trans. Thus trans packs more tightly in the crystal lattice and hence has a higher melting point.

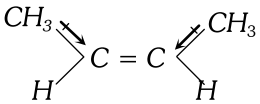
(vi) The boiling points of cis isomers are higher than trans isomers because cis-alkenes has greater polarity (Dipole moment) than trans one.

(vii) These are lighter than water.

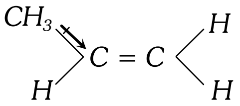
(viii) ***Dipole moment* :** Alkenes are weakly polar. The, π-electron's of the double bond. Canbe easily polarized. Therefore, their dipole moments are higher than those of alkanes.

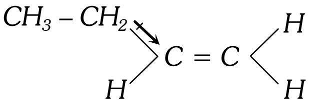
The symmetrical trans alkenes are non polar and hence have zero dipole moments in these alkene the dipole moment of individual bonds are equal in opposite direction. Therefore these get cancelled resulting zero dipole moment for the molecule.


Trans-2-Butene
μ = 0


Cis –2-Butene
μ = 0.25 D

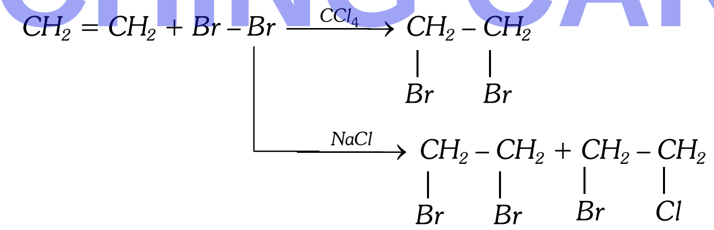
Thus symmetrical and unsymmetricals cis alkene are polar and hence have finite dipole moments


Propene
μ = 0.35 D


Bute 1-ene
μ = 0.37 D

(5) Chemical properties

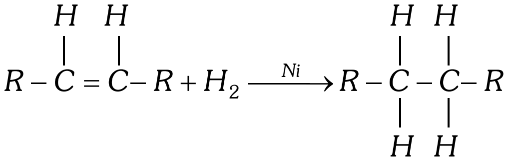
(i) ***Francis experiment* :** According to Francis electrophile first attacks on olefinic bond.



$$CH_2 = CH_2 + Br - Br \xrightarrow{CCl_4} \underset{Br}{CH_2} - \underset{Br}{CH_2}$$

$$\xrightarrow{NaCl} \underset{Br}{CH_2} - \underset{Br}{CH_2} + \underset{Br}{CH_2} - \underset{Cl}{CH_2}$$

(ii) ***Reaction with hydrogen* :**

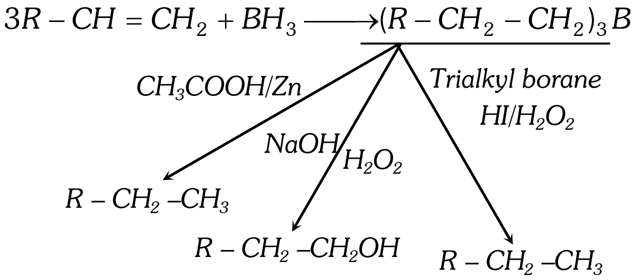


$$R - \overset{H}{C} = \overset{H}{C} - R + H_2 \xrightarrow{Ni} R - \underset{H}{\overset{H}{C}} - \underset{H}{\overset{H}{C}} - R$$

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

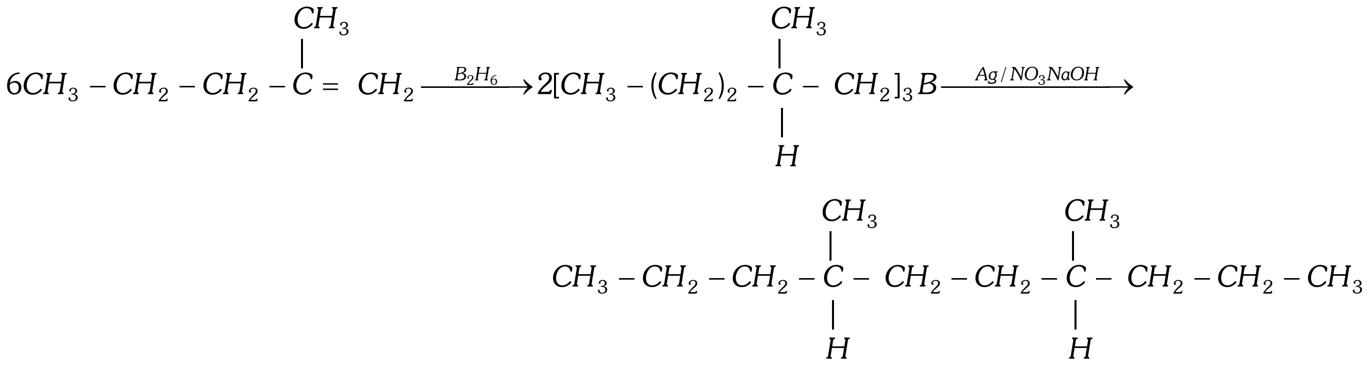
$$RCH = CH_2 \xrightarrow{H-BH_2} (R - CH_2 - CH_2)_3 B \xrightarrow{H^+/H_2O} R - CH_2 - CH_3$$

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 $AgNO_3$ + NaOH :*** This reaction gives coupling



$$6CH_3-CH_2-CH_2-\overset{\overset{CH_3}{|}}{C}=CH_2 \xrightarrow{B_2H_6} 2[CH_3-(CH_2)_2-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2]_3B \xrightarrow{Ag/NO_3NaOH}$$

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

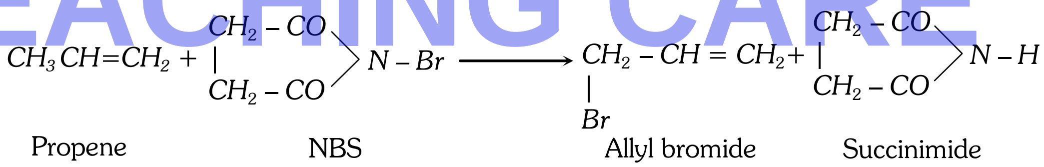
(v) ***Birch reduction :*** This reaction is believed to proceed via anionic free radical mechanism.

$$R-CH=CH_2 \xrightarrow[+e^-]{Na} R-C\overset{-}{H}-\overset{-}{C}H_2 \xrightarrow{Et-O-H} R-CH-CH_3 \xrightarrow[+e^-]{Na} R-\overset{-}{C}H-CH_3 \xrightarrow{Et.-O-H} R-CH_2-CH_3$$

(vi) ***Halogenation***

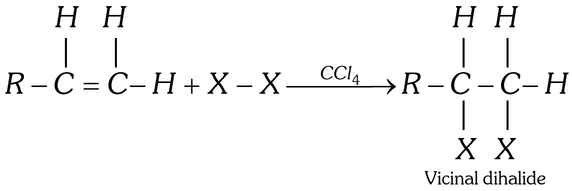
$$\underset{\text{Propene}}{CH_3CH=CH_2}+Cl_2 \xrightarrow{500^oC} \underset{\substack{\text{Allyl chloride}\\ \text{or 3-Chloro-1-propene}}}{ClCH_2-CH=CH_2}+HCl$$

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



$$CH_3CH{=}CH_2 + \left.\begin{matrix}CH_2-CO\\|\\CH_2-CO\end{matrix}\right\rangle N-Br \longrightarrow \underset{\underset{Br}{|}}{CH_2}-CH=CH_2+\left.\begin{matrix}CH_2-CO\\|\\CH_2-CO\end{matrix}\right\rangle N-H$$

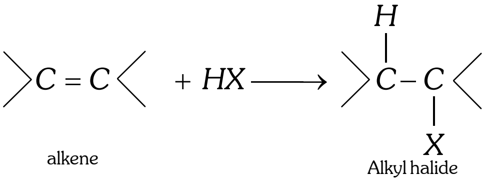
✸ In presence of polar medium alkene form vicinal dihalide with halogen.



$$R-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-H+X-X \xrightarrow{CCl_4} R-\underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C}}-H$$

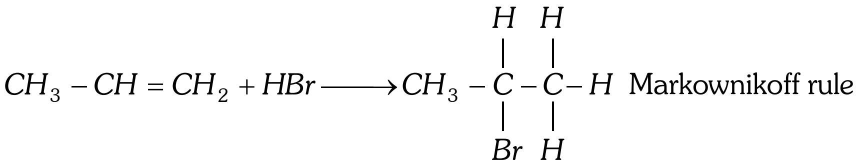
Reactivity of halogen is $F_2 > Cl_2 > Br_2 > I_2$

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



$$>C=C< \;+ HX \longrightarrow\; >\underset{}{\overset{\overset{H}{|}}{C}}-\underset{\underset{X}{|}}{C}<$$

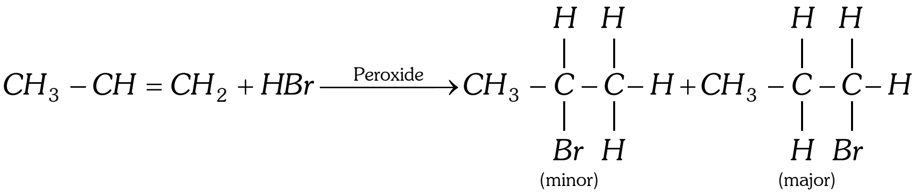
According to markownikoff's rule and kharasch effect.



$$CH_3-CH=CH_2+HBr\longrightarrow CH_3-\underset{Br}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$$

Markownikoff rule

(Based on F.R.M.)



$$CH_3-CH=CH_2+HBr\xrightarrow{\text{Peroxide}}\underset{\text{(minor)}}{CH_3-\underset{Br}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H}+\underset{\text{(major)}}{CH_3-\underset{H}{\overset{H}{C}}-\underset{Br}{\overset{H}{C}}-H}$$

(viii) **Reaction with hypohalous acids :** $\underset{\text{Ethylene}}{CH_2=CH_2}+H\overset{-}{O}\overset{+}{Cl}\longrightarrow\underset{\text{Ethylene chlorohydrin}}{CH_2OH.CH_2Cl}$

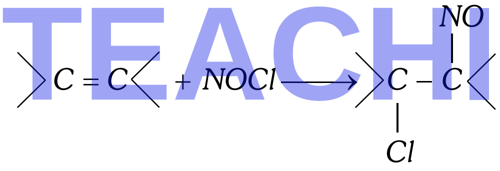
Note : ✸ In case of unsymmetrical alkenes markownikoff rule is followed.

(ix) **Reaction with sulphuric acid :** $\underset{\text{Ethylene}}{CH_2=CH_2}+H^+HSO_4^-\longrightarrow\underset{\text{Ethyl hydrogen sulphate}}{CH_3CH_2HSO_4}$

$$CH_3CH_2HSO_4\longrightarrow CH_2=CH_2+H_2SO_4$$

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

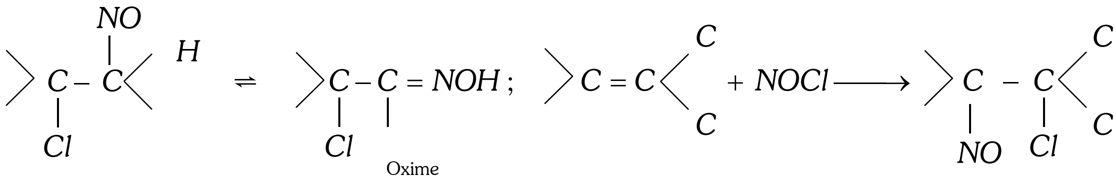
(x) **Reaction with nitrosyl chloride**



$$\rangle C=C\langle+NOCl\longrightarrow\rangle\underset{Cl}{C}-\overset{NO}{C}\langle$$

($NOCl$ is called Tillden reagent)

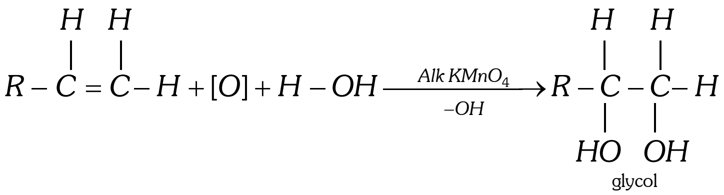
Note : ✸ If hydrogen is attached to the carbon atom of product, the product changes to more stable oxime.



$$\rangle\underset{Cl}{C}-\overset{NO}{C}\langle^{H}\rightleftharpoons\rangle\underset{Cl}{C}-\underset{\text{Oxime}}{\underset{|}{C}=NOH};\quad\rangle C=C\langle^{C}_{C}+NOCl\longrightarrow\rangle\underset{NO}{C}-\underset{Cl}{C}\langle^{C}_{C}$$

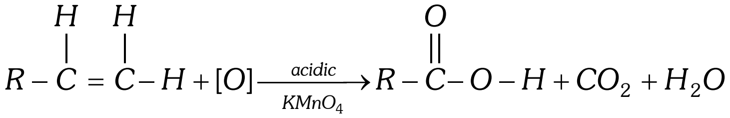
(Blue colour)

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



$$R-\overset{H}{C}=\overset{H}{C}-H+[O]+H-OH\xrightarrow[-OH]{Alk\,KMnO_4}\underset{\text{glycol}}{R-\underset{HO}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-H}$$

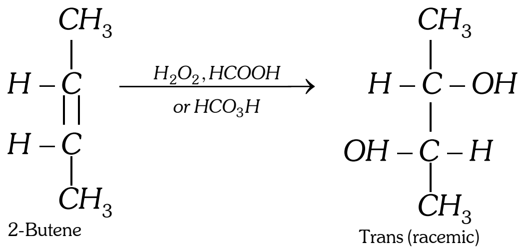
With acidic $KMnO_4$:



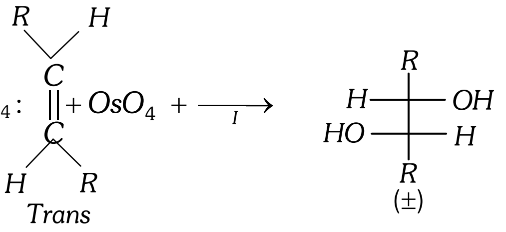
$$R-\overset{H}{C}=\overset{H}{C}-H+[O]\xrightarrow[KMnO_4]{acidic}R-\overset{O}{\overset{\|}{C}}-O-H+CO_2+H_2O$$

(xii) ***Hydroxylation***

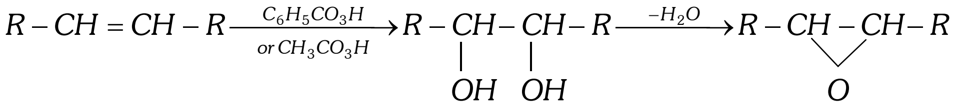
(a) Using per oxy acid :



(b) Hydroxylation by OsO_4:



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

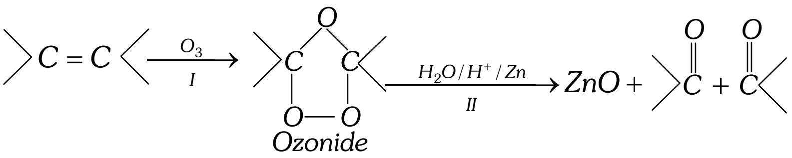


$$R-CH=CH-R \xrightarrow[\text{or } CH_3CO_3H]{C_6H_5CO_3H} R-\underset{OH}{CH}-\underset{OH}{CH}-R \xrightarrow{-H_2O} R-CH-CH-R$$

(xiii) ***Combustion*** : $C_nH_{2n} + \frac{3n}{2}O_2 \longrightarrow nCO_2 + nH_2O$

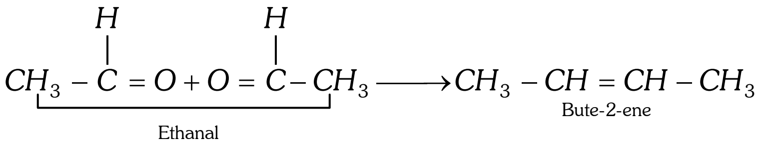
They burn with luminous flame and form explosive mixture with air or oxygen.

(xiv) ***Ozonolysis***

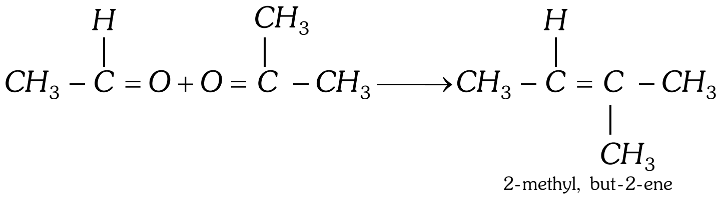


✹ Application of ozonolysis : This process is quite useful to locate the position of double bond in an alkene molecule. The double bond is obtained by Joining the carbon atoms. of the two carbonyl compounds.

Ex.

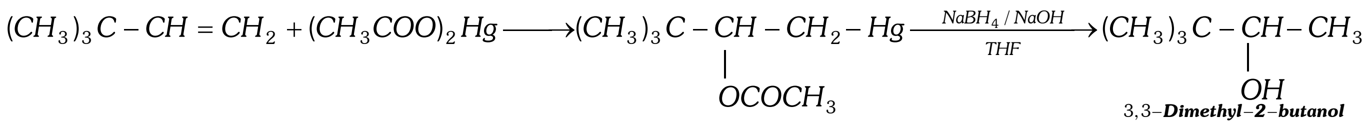


$$CH_3-\overset{H}{C}=O+O=\overset{H}{C}-CH_3 \longrightarrow CH_3-CH=CH-CH_3$$



$$CH_3-\overset{H}{C}=O+O=\overset{CH_3}{C}-CH_3 \longrightarrow CH_3-\overset{H}{C}=\underset{CH_3}{C}-CH_3$$

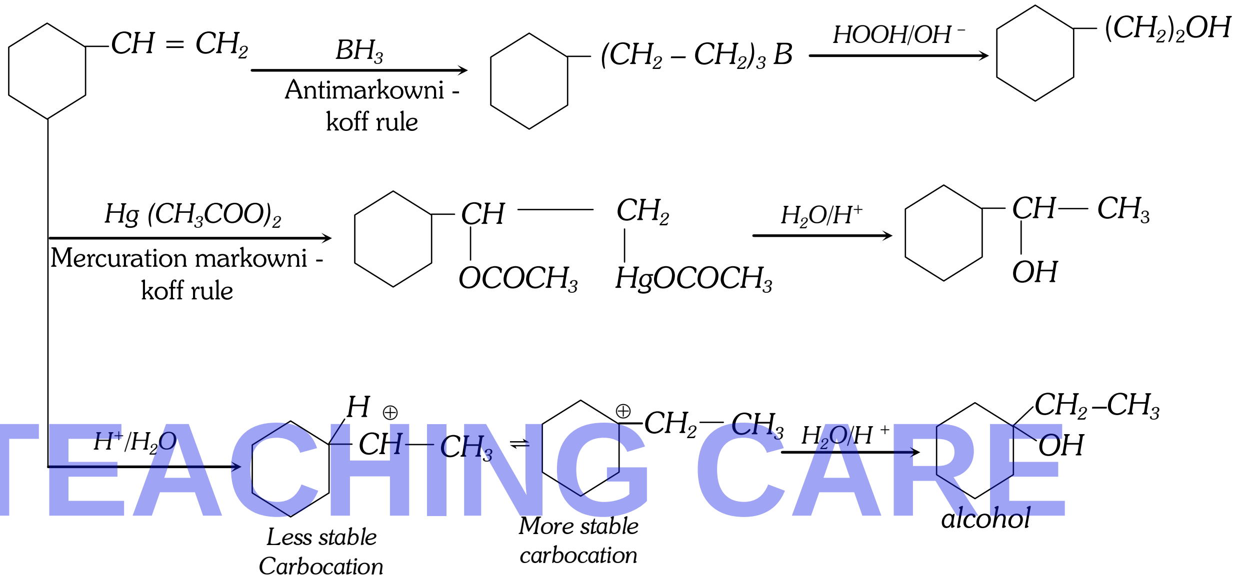
(xv) ***Oxy – mercuration demercuration*** : With mercuric acetate (in THF), followed by reduction with $NaBH_4 / NaOH$ is also an example of hydration of alkene according to markownikoff's rule.



$$(CH_3)_3C-CH=CH_2+(CH_3COO)_2Hg \longrightarrow (CH_3)_3C-\underset{OCOCH_3}{\underset{|}{CH}}-CH_2-Hg \xrightarrow[THF]{NaBH_4/NaOH} (CH_3)_3C-\underset{OH}{\underset{|}{CH}}-CH_3$$

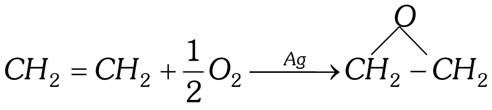
3, 3–**Dimethyl–2–butanol**

Ex.



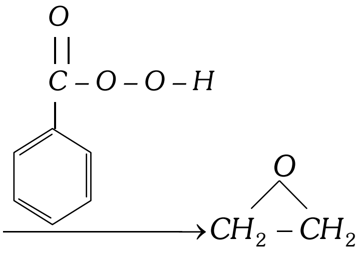
(xvi) ***Epoxidation***

(a) *By* O_2 / Ag :

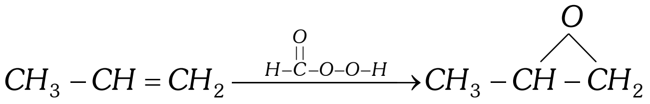


$$CH_2=CH_2+\frac{1}{2}O_2 \xrightarrow{Ag} \overset{O}{CH_2-CH_2}$$

(b) Epoxidation by performic acid or perbenzoic acid : $CH_2=CH_2$



$$CH_2=CH_2 \longrightarrow \overset{O}{CH_2-CH_2}$$



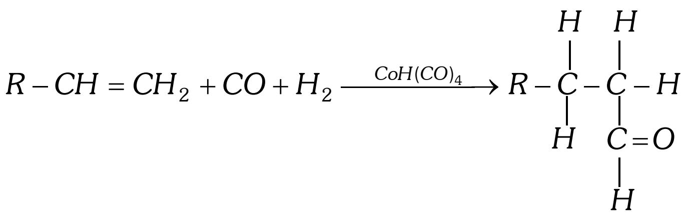
$$CH_3-CH=CH_2 \xrightarrow{H-\overset{O}{\overset{||}{C}}-O-O-H} CH_3-\overset{O}{CH-CH_2}$$

(xvii) ***Hydroboration***

$$3R-CH=CH_2+BH_3 \longrightarrow \underset{\text{Tri alkyl borane}}{(R-CH_2-CH_2)_3B} \xrightarrow{H_2O_2/OH^-} R-CH_2-CH_2-OH+B(OH)_3$$

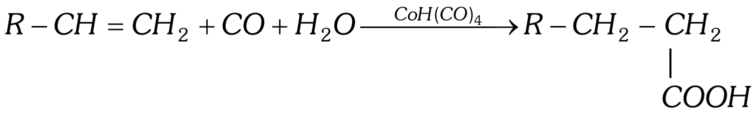
(Anti markownikoff's rule)

(xviii) **Hydroformylation :**



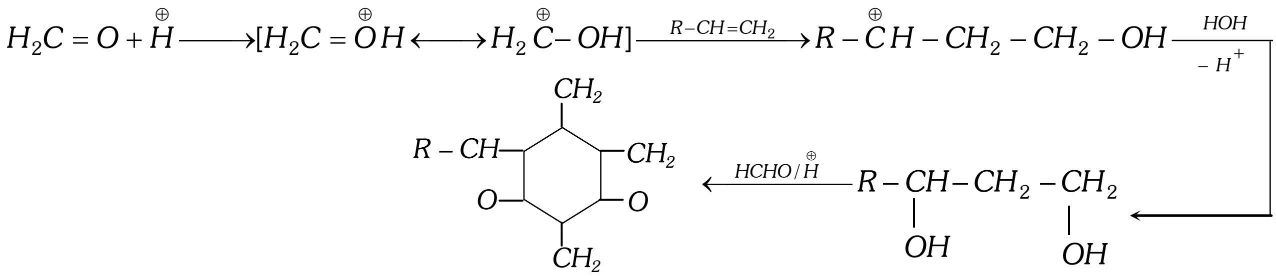
$$R-CH=CH_2+CO+H_2 \xrightarrow{CoH(CO)_4} R-\underset{H}{\overset{H}{C}}-\underset{\underset{H}{C=O}}{\overset{H}{C}}-H$$

Note : ✹ If $CO+H_2O$ is taken then respective acid is formed.

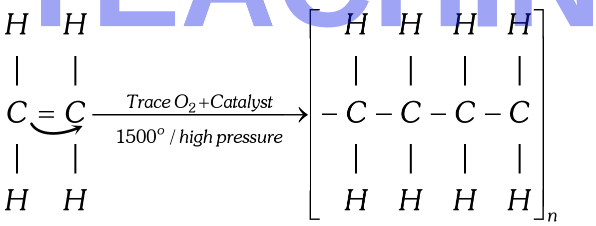


$$R-CH=CH_2+CO+H_2O \xrightarrow{CoH(CO)_4} R-CH_2-\underset{COOH}{CH_2}$$

(xix) **Addition of formaldehyde**



(xx) **Polymerisation**



$$\underset{H}{\overset{H}{C}}=\underset{H}{\overset{H}{C}} \xrightarrow[1500^o / \text{high pressure}]{\text{Trace } O_2+\text{Catalyst}} \left[-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}\right]_n$$

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

(xxi) **Isomerisation :** $CH_3-CH_2-CH_2-CH=CH_2 \xrightleftharpoons{AlCl_3} CH_3-CH_2-CH=CH-CH_3$

The mechanism proceeds via carbocation.

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

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

(6) Uses

(i) For the manufacture of polythene – a plastic material; (ii) For artificial ripening of fruits; (iii) As a general anaesthetic; (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.

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) Hybridisation in alkynes is sp.

(ii) Bond angle in alkynes is 180^o.

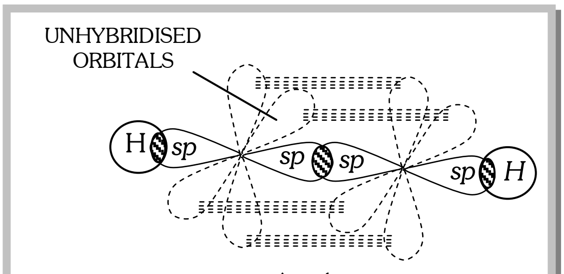
(iii) Geometry of carbon is linear.

(iv) $C - C$ triple bond length is $120 Å$

(v) $C - H$ bond length is $108 Å$

(vi) $C - C$ triple bond energy is $190\,Kcal/mol$.

(vii) $C - H$ bond energy is $102.38\,Kcal/mol$.



Acetylene