

Chemistry

Aliphatic Hydrocarbons

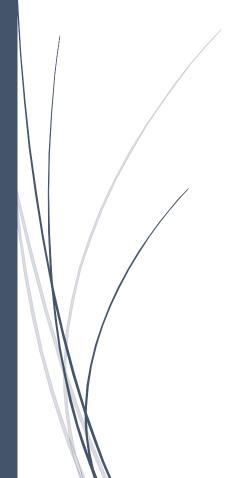




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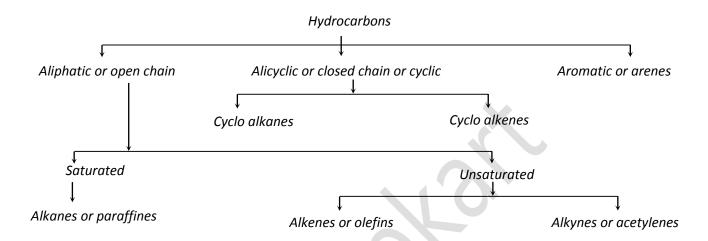








"Organic compounds composed of only carbon and hydrogen are called hydrocarbons. Hydrocarbons are obtained mainly from petroleum, natural gas or coal. Petroleum is a major source of aliphatic hydrocarbon. The important fuels like petrol, kerosene, coal gas, oil gas, compressed natural gas [CNG], LPG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



1. Sources of hydrocarbon.

Mineral oil or crude oil, petroleum [Petra \rightarrow rock; oleum \rightarrow 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 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%), 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)
$$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4 \text{ (Methane)}; \quad C_2H_2 \xrightarrow{H_2} C_2H_4 \xrightarrow{H_2} C_2H_6 \text{ (Ethane)}$$
 $3[CH \equiv CH] \xrightarrow{\text{Polymerisation}} C_6H_6$; (Benzene) ; $CH_3 - CH = CH - CH_3 \xrightarrow{\text{Isomerisation}} CH_3 - CH_2 - CH_2 = CH_2$

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.











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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	Above 400°	C ₁₇ – C ₄₀	
fractionation by vacuum			
distillation gives,			
(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			As fuel.
(on redistilling tar)			

(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: $2RSH + Na_2PbO_2 + S \rightarrow RSSR + PbS + 2NaOH$ 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 $(475 530^{\circ}\text{C})$ 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 $600 - 800^{\circ}$ 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%.











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- (ii) Synthesis: Two methods are applicable for synthesis.
- (a) Bergius process: This method was invented by Bergius in Germany during First World War.

Coal
$$+H_2 \xrightarrow{Fe_2O_3 \atop 450-500^{\circ}C}$$
 Mix. Of hydrocarbons or crude oil

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

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

$$xCO + yH_2 \longrightarrow Mix. Of hydrocarbon + H_2O$$
.

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

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.

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

$$CH_3$$

$$CH_3 - C - CH_2 - CH - CH_3$$
; Octane no. = 100
$$CH_3$$

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















For example: a given sample has the knocking performance equivalent to a mixture containing 60% isooctane 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.

$$Pb + Br - CH_2 - CH_2 - Br \rightarrow PbBr_2 + CH_2 = CH_2$$
 Ethylene bromide Volatile Ethylene

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 $200^{\circ} C$.

CH
$$_3$$
 CH $_2$ CH $_2$ CH $_3$ CH $_3$ CHC $_3$ CHC $_4$ CH $_3$ Isopentane (Octane number = 62)

CH $_3$ CH $_4$ CH $_3$ CH $_3$ CH $_3$ CH $_4$ CH $_3$ CH $_4$ CH $_3$ CH $_4$ CH $_4$ CH $_5$ Isobutylene CH $_3$ Isobutane

CH $_3$ CH $_4$ CH $_4$ CH $_5$ CH $_3$ CH $_4$ CH $_5$ CH













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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.

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

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° C, 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 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.











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rerywhere	
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].

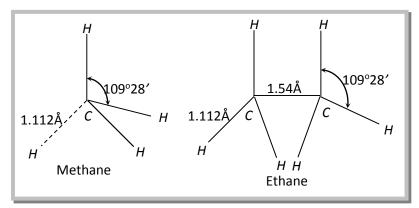
"Alkanes are saturated hydrocarbon containing only carbon-carbon single bond in their molecules." Alkanes are less reactive so called paraffins; because under normal conditions alkanes do not react with acids, bases, oxidizing agents and reducing agent.

General formula: $C_n H_{2n+2}$

Examples are: CH_4 , C_2H_6 , C_3H_8 Propane

(1) Structure:

- (i) Every carbon atom is $\mathit{sp}^{\,3}$ hybridized.
- (ii) The bond length between carbon-carbon and carbon-hydrogen are $1.54 \mbox{\normalfont\AA}$ and $1.112 \mbox{\normalfont\AA}$ respectively.
- (iii) Bond angle in alkanes are tetrahedral angles having a value of $109.5^{\circ}(109^{\circ}.28')$.
- (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 ∞ no. of chain Isomers

Alkanes:

$$C_4 H_{10}$$

$$C_5H$$

$$C_6 H_{14}$$

$$C_5H_{12}$$
 C_6H_{14} C_7H_{16} C_8H_{18}

$$C_{8}H_{18}$$

$$C_{10}H_{22}$$

No. of possible Isomer:

75

- (3) General Methods of preparation
- (i) By catalytic hydrogenation of alkenes and alkynes (Sabateir and sanderen's reaction)

$$C_n H_{2n} + H_2 \xrightarrow{Ni} C_n H_{2n+2}$$
Alkane
Alkane

$$\begin{array}{cccc} C_n H_{2n} + H_2 & \xrightarrow{Ni} & C_n H_{2n+2} & ; & & C_n H_{2n-2} + 2H_2 & \xrightarrow{Ni} & C_n H_{2n+2} \\ \text{Alkane} & & & & \text{Alkyne} & & & \text{Alkane} \end{array}$$

Note: Methane is not prepared by this method

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

- (iii) From alkyl halide
- (a) By reduction: $RX + H_2 \xrightarrow{Z_{II}/HCI} RH + HX$
- (b) With hydrogen in presence of pt/pd: $RX + H_2 \xrightarrow{Pd \ orPt.} RH + HX$
- (c) With HI in presence of Red phosphorus: $RBr + 2HI \longrightarrow RH + HBr + I_2$

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

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

(v) Wurtz reaction:
$$RX + 2Na + XR - Dryether$$
 $R - R + 2NaX$ Alkyhalide

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.

- Frankland's reaction: $2RX + Zn \longrightarrow R R + ZnX$,
- (vii) Corey-house synthesis

$$CH_3 - CH_2 - Cl \xrightarrow{1.Li} (CH_3 - CH_2)_2 LiCu \xrightarrow{CH_3 - CH_2 - Cl} CH_3 - CH_2 - CH_2 - CH_3$$











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Note: Reaction is suitable for odd number of Alkanes.

(viii) From Grignard reagent

(a) By action of acidic 'H':
$$RMgX + HOH \longrightarrow RH + Mg(OH)X$$

(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]

$$R \ COONa + NaOH \xrightarrow{heat} R - H + Na_2CO_3$$

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

(b) Kolbe's synthesis:
$$R - C - O^- Na^+$$
 | Electrolysis $C - O^- + Na^+$ | Ionization

At anode [Oxidation]:
$$2R - C - O^- + 2e^- \longrightarrow 2R - C - O \longrightarrow 2R + 2CO_2$$

$$2R \longrightarrow R - R$$
 (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:
$$CH_3COOH + 6HI \xrightarrow{\text{Reduction}} CH_3CH_3 + 2H_2O + 3I_2$$
Acetic acid

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

$$\begin{array}{c} CH_3OH + 2HI \xrightarrow{\text{Red }P} CH_4 + H_2O + I_2 \,; \\ \text{Methanol (Methyl alcohol)} \end{array} \xrightarrow{\text{Red }P} C_2H_6 + H_2O + 2I_2 \,; \\ \text{Methanol (Methyl alcohol)} \end{array} \xrightarrow{\text{Red }P} C_2H_6 + H_2O + 2I_2 \,; \\ \text{Acctaldehyde (Ethanal)}$$









$$\begin{array}{c} CH_{3}COCH_{3}+4HI \xrightarrow{\text{Red }P} CH_{3}CH_{2}CH_{3}+H_{2}O+2I_{2}; \\ \text{Acetone} \\ \text{(Propanone)} \end{array}$$

$$\begin{array}{c} O \\ || \\ CH_{3}-C-CI+6HI \xrightarrow{\text{Red }P} CH_{3}-CH_{3}+H_{2}O+HCI+3I_{2} \\ \text{Acetyl chloride} \\ \text{(Ethanoyl chloride)} \end{array}$$

$$\begin{array}{c} O \\ || \\ CH_{3}-C-NH_{2}+6HI \xrightarrow{\text{Red }P} CH_{3}-CH_{3}+H_{2}O+NH_{3}+3I_{2} \\ \text{Acetamide} \\ \text{(Ethanamid e)} \end{array}$$

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

Clemmensen reduction:
$$CH_3CHO + 2H_2 \xrightarrow{Zn-Hg} CH_3 - CH_3 + H_2O$$

Acetaldehyde (Ethanal)

$$CH_{3}COCH_{3} + 2H_{2} \xrightarrow{Zn-Hg} CH_{3}CH_{2}CH_{3} + H_{2}O$$
Acetone (Propanone)

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:
$$R$$
 $C = O \xrightarrow{H_2NNH_2} R$ $C = NNH_2 \xrightarrow{C_2H_5ONa} R$ CH_2

- (xi) Hydroboration of alkenes
- (a) On treatment with acetic acid

$$R-CH = CH_2 \xrightarrow{B_2H_6} (R-CH_2-CH_2)_3 B \xrightarrow{CH_3COOH} R-CH_2-CH_3$$
Alkane
Alkane

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

$$6[R - CH = CH_{2}] \xrightarrow{2B_{2}H_{6}} [2R - CH_{2} - CH_{2} - CH_{2} -]_{3}B \xrightarrow{AgNO_{3} \ 25^{o} \ C} 3[RCH_{2}CH_{2} - CH_{2}CH_{2}R]$$

- (4) Physical Properties
- (i) **Physical state:** Alkanes are colorless, odorless and tasteless.

Alkanes State

 $C_1 - C_4$ Gaseous state

 $C_5 - C_{17}$ Liquid state [Except neo pentane] [gas]











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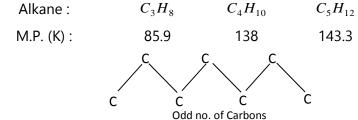
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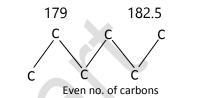




 C_{18} & above Solid like waxes

- (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. ∞ Molecular mass $\infty \frac{1}{\text{No. of branches}}$



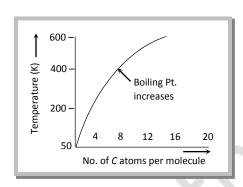


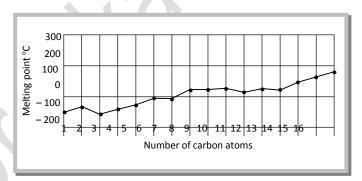
 $C_7 H_{16}$

 $C_{8}H_{18}$

216.2

 $C_6 H_{14}$





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.











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Chlorination of methane: $CH_4 + Cl - Cl \xrightarrow{u.v.light} CH_2 - Cl_2 \xrightarrow{u.v.light} CHCl_3 \xrightarrow{-HCl} CCl_4$

(ii) Reaction based on free radical mechanism

(a) Nitration:
$$R - H + HONO_2 \xrightarrow{High} R - NO_2 + H_2O$$

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

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

(b) Sulphonation: Free radical mechanism
$$R - H + HOSO_3H \xrightarrow{SO_3} R - SO_3H + H_2O$$

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

(iii) Oxidation

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

Note: This is exothermic reaction.

(b) Incomplete combustion or oxidation

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

$$CH_4 + O_2 \xrightarrow{C} +2H_2O$$

(c) Catalytic Oxidation:
$$CH_4 + [O] \xrightarrow{Cu-tube} CH_3OH$$

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

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

$$CH_3(CH_2)_n CH_3 \xrightarrow[100-160^{\circ}C]{O_2} CH_3(CH_2)_n COOH$$

(d) Chemical oxidation:
$$(CH_3)_3 CH \xrightarrow{KMnO_4} (CH_3)_3 .C.OH$$

Isobutane

Tertiary butylalcohol

(iv) Thermal decomposition or cracking or pyrolysis or fragmentation

$$\begin{array}{c} CH_4 \xrightarrow{\quad 1000^{\circ}C \quad} C + 2H_2; \ C_2H_6 \xrightarrow{\quad 500^{\circ}C \quad} CH_2 = CH_2 + H_2 \\ \text{Methane} \end{array}$$
 Ethylene

$$C_3H_8 \longrightarrow C_2H_4 + CH_4$$
 or $C_3H_6 + H_2$











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

(v) **Isomerization**:
$$CH_3CH_2CH_2CH_3 \xrightarrow{AlCl_3+HCl} CH_3 \xrightarrow{AlCl_3+HCl} CH_3 CHCH_3$$
; Isobutane 2.3 Dimethy butane

(vi) Aromatization:

(vii) Step up reaction

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

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

(c) Reaction with
$$CH_2 = C$$
: $R - CH_2 - H \xrightarrow{CH_2 = C/\Delta} R - CH_2 - CH_3$

$$O$$

(viii) **HCN formation:**
$$2CH_4 \xrightarrow{N_2/electric arc} 2HCN + 3H_2$$
 or $CH_4 + NH_3 \xrightarrow{Al_2O_3} HCN + 3H_2$

(ix) Chloro sulphonation/Reaction with SO₂+Cl₂

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

This reaction is known as reed's reaction.

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

(x) Action of steam:
$$CH_4 + H_2O \xrightarrow{Ni/Al_2O_3} CO + 3H_2$$











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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 $250^{\circ}C$ when methane is formed.

$$CO + 3H_2 \xrightarrow{Ni+C} CH_4 + H_2O$$

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

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

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

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

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

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

- (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 $-182.5^{\circ}C$ and boiling point is $-161.5^{\circ}C$.















(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: $C_2H_5I + 2H \xrightarrow{Zn-Cu\ couple} C_2H_6 + HI$ Ethyliodide C_2H_5OH

(b) Industrial method of preparation: $CH_2 = CH_2 + H_2 \xrightarrow{Ni} CH_3 - CH_3$ Ethylene (ethene)

(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°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:** $CH_4 \xrightarrow{Cl_2} CH_3Cl \xrightarrow{\text{Wurtzreaction}} CH_3 - CH_3$ Heat with $Na \text{ in ether} \longrightarrow CH_3 - CH_3$

(ii) Butane from ethane: $C_2H_6 \xrightarrow[\text{excess}]{Cl_1} UV \xrightarrow[\text{Ethyl chloride}]{Cl_2} C_2H_5Cl \xrightarrow[\text{Heat with Na in ether}]{\text{Wurtzreaction}} C_2H_5 - C_2H_5$ Butane











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Descent of alkane series: Use of decarboxylation reaction is made. It is a multistep conversion. **Ethane to methane**

$$C_{2}H_{6} \xrightarrow{Cl_{2}} C_{2}H_{5}Cl \xrightarrow{Aq.KOH} C_{2}H_{5}OH \xrightarrow{[O]} CH_{3}CHO \xrightarrow{[O]} CH_{3}COOH \xrightarrow{NaOH} CH_{3}COONa \xrightarrow{NaOH/CaO} CH_{4}COONa CH_{4}COONA$$

$$\begin{array}{ccc} \text{Higher} & \xrightarrow{Cl_2} & \text{Alkyl} & \xrightarrow{Aq_-} & \text{Alcohol} & \xrightarrow{[O]} & \text{Aldehyde} & \xrightarrow{[O]} & \text{Acid} & \xrightarrow{NaOH} & \text{Sodium salt of} & \xrightarrow{NaOH / CaO} & \text{Lower alkane} \\ & \text{alkane} & & \text{the acid} & & & \text{heat} \end{array}$$

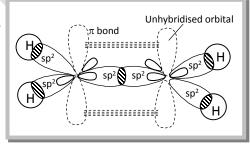
5. Alkenes.

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

- (i) Hybridization of unsaturated 'C' atom is sp²
- (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 $CH_3 CH = CH CH_3$
- (iv) Geometrical Isomerism: CH_3-C-H and CH_3-C-H \parallel CH_3-C-H $H-C-CH_3$ CIS-2-butene Trans-2-butene











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system at the both end can exhibit Note: Cumulated polythene having even no. of double bonds. Which has = C

optical isomerism but cannot exhibit geometrical isomerism.

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

(3) Preparation methods

(i) From Alkynes:
$$R - C \equiv C - H + H_2 \xrightarrow{\text{Lindlar's Catalyst}} R - C = C - H$$

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:
$$R-C-C-H+Alc.KOH \xrightarrow{-HX} R-C=C-H$$

 $H X$

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

$$R-CH \xrightarrow{X} Zn \qquad X \\ + \qquad + \qquad + \\ X \qquad Zn \qquad X \\ R-CH=CH-R$$

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.











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(b) From vicinal dihalides:
$$R-C-C-H+Zn\,dust\xrightarrow{\Delta} R-C=C-H+ZnX_2$$
 X

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

$$\begin{array}{ccc}
C H_2 - CH_2 - C H_2 & \xrightarrow{Zn \text{ dust}} \\
 & | & & \\
X & & X
\end{array}$$

$$H_2C \stackrel{CH_2}{\longrightarrow} CH_2$$

(iv) By action of
$$\it NaI$$
 on vic dihalide:

(v) **From alcohols** [Laboratory method]:
$$CH_3CH_2OH \xrightarrow{H_2SO_4 \ or \ H_3PO_4} CH_2 = CH_2 + H_2O$$
 Ethene

$$CH_{2}COOK \qquad CH_{2}$$
 (vi) **Kolbe's reaction:**
$$| + 2H_{2}O \xrightarrow{\text{Electrolysis}} | + 2CO_{2} + H_{2} + 2KOH$$

$$CH_{2}COOK \qquad CH_{2}$$
 Potassium succinate
$$CH_{2}COOK \qquad CH_{2}$$
 Ethene

(vii) From esters [Pyrolysis of ester]:
$$CH_3 - CO - O$$
 H $CH_2 - CH_2$ $CH_3 - COOH$ $CH_3 - COOH$ $CH_2 - CH_2$

(viii) Pyrolysis of quaternary ammonium compounds:
$$(C_2H_5)_4 \stackrel{+}{NOH} \xrightarrow{heat} (C_2H_5)_3 N + C_2H_4 + H_2O$$

Tetraethyl ammonium hydroxide

Triethylam ine (Tert. amine)

Triethylam ine (Tert. amine)

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

(x) By Grignard reagents:
$$Mg$$
 $+ X - CH = CH_2 \longrightarrow MgX_2 + R - CH = CH_2$

(xi) The Wittig reaction:
$$(Ph)_3 P = CH_2 + CH - R \longrightarrow (Ph)_3 P = O + R - CH$$
 $||$ $||$ CH_2

$$O$$

$$||$$

$$(Ph)_3 P = CH - R + CH - R \longrightarrow (Ph)_3 P = O + R - CH = CH - R$$













(xii) From β bromo ether [Boord synthesis]

$$Br \quad O - C_2 H_5$$

$$R - CH - CH$$

$$\downarrow \qquad \qquad \xrightarrow{C_4 HgOH} R - CH = CH - R' + Zn$$

$$\downarrow \qquad \qquad O - C_2 H_5$$

$$R'$$

(4) Physical Properties

- (i) Alkenes are colorless and odorless.
- (ii) These are insoluble in water and soluble in organic solvents.
- (iii) Physical state

$$C_1 - C_4 \longrightarrow \mathsf{Gas}$$
 $C_5 - C_{16} \longrightarrow \mathsf{Liquid}$
 $C_{16} \longrightarrow \mathsf{Solid} \mathsf{wax}$

- (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.

$$CH_3$$
 $C = C$
 CH_3
Trans-2-Butene

$$CH_3$$
 $C = C$
 H
Cis -2-Butene











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

$$CH_3$$
 $C = C$
 H
 $CH_3 - CH_2$
 $C = C$
 H
 $CH_3 - CH_2$
 $C = C$
 H
 $C = C$
 $C = C$
 $C = C$
 H
 $C = C$
 C

- (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

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

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

$$3R - CH = CH_2 + BH_3 \longrightarrow (R - CH_2 - CH_2)_3 B$$

$$CH_3COOH/Zn \qquad Trialkyl borane$$

$$HI/H_2O_2$$

$$R - CH_2 - CH_3$$

$$R - CH_2 - CH_2OH$$

$$R - CH_2 - CH_3$$

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











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(iv) By treatment with AgNO₃ + NaOH: This reaction gives coupling

$$CH_{3} \xrightarrow{CH_{2} - CH_{2} - C$$

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

$$R - CH = CH_2 \xrightarrow{Na} R - CH - CH_2 \xrightarrow{Et - O - H} R - CH - CH_3 \xrightarrow{Na} R - CH - CH_3 \xrightarrow{Et - O - H} R - CH_2 - CH_3 \xrightarrow{Et - O - H} R - CH_2 - CH_3 \xrightarrow{Et - O - H} R - CH_2 - CH_3 \xrightarrow{Et - O - H} R - CH_2 - CH_3 \xrightarrow{Et - O - H} R - CH_2 - CH_3 \xrightarrow{Et - O - H} R -$$

(vi) Halogenation

$$CH_{3}CH = CH_{2} + Cl_{2} \xrightarrow{500^{o}C} ClCH_{2} - CH = CH_{2} + HCl$$
 Allykhloride or 3-Chloro-1-propene

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

$$CH_{3} CH = CH_{2} + CO$$

$$N - Br \longrightarrow CH_{2} - CH = CH_{2} + CH_{2} - CO$$

$$N - H$$
Propene NBS Allyl bromide Succinimide

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

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

(vii) Reaction with HX [Hydrohalogenation]











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$$C = C \left\langle + HX \longrightarrow \right\rangle C - C \left\langle X \right\rangle$$
alkene
$$X = X$$
Alkyhalide

According to markownikoff's rule and kharasch effect.

$$CH_3 - CH = CH_2 + HBr \longrightarrow CH_3 - C - C - H$$
 Markownikoff rule $\begin{vmatrix} H & H \\ & | & | \\ & | & | \\ & Br & H \end{vmatrix}$

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

Ethylene Chlorohydin

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

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

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

(x) Reaction with nitrosyl chloride

$$C = C + NOCl \longrightarrow C - C$$
(NOCl is called Tillden reagent)

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

color)











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

$$\begin{array}{c|c} H & H & H & H \\ & | & | & | \\ R-C=C-H+[O]+H-OH \xrightarrow{Alk\ KMnO_4} R-C-C-C-H \\ & & | & | \\ & & HO & OH \\ & & glycol \\ \end{array}$$
 With acidic $KMnO_4: R-C=C-H+[O] \xrightarrow{acidic} R-C-O-H+CO_2+H_2O$

(xii) Hydroxylation

 $H - C \xrightarrow{H_2O_2, HCOOH} OH - C - OH$ $H - C \downarrow CH_3$ 2-Butene CH_3 $OH - C - H \downarrow CH_3$ CH_3 (a) Using per oxy acid:

(b) Hydroxylation by OsO_{4:}
$$|| + OsO_4| + \longrightarrow$$

$$C \longrightarrow H \longrightarrow H \longrightarrow H$$

$$Trans \longrightarrow H \longrightarrow R \longrightarrow H \longrightarrow H \longrightarrow H$$

$$(\pm)$$

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

$$R - CH = CH - R \xrightarrow{C_6H_5CO_3H} R - CH - CH - R \xrightarrow{-H_2O} R - CH - CH - R$$

$$OH OH OH$$

$$O$$
[Oxirane]

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

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

(xiv) Ozonolysis

$$C = C \longrightarrow 0_{3}$$

$$O \longrightarrow C$$

$$O \longrightarrow I$$

$$O \longrightarrow$$

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.











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Ex.

(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.

$$(CH_3)_3 C - CH = CH_2 + (CH_3COO)_2 Hg \xrightarrow{} (CH_3)_3 C - CH - CH_2 - Hg \xrightarrow{NaBH_4/NaOH} (CH_3)_3 C - CH - CH_3 - Hg \xrightarrow{} (CH_3)_3 C - CH_3 - Hg \xrightarrow{} (CH_3)_3 C$$

Ex.

$$CH = CH_2 \qquad BH_3 \qquad (CH_2 - CH_2)_3 B \qquad HOOH/OH^- \qquad (CH_2)_2OH$$

$$Roff rule \qquad CH \qquad CH_2 \qquad H_2O/H^+ \qquad CH \qquad CH_3$$

$$Mercuration \qquad OCOCH_3 \qquad HgOCOCH_3 \qquad OH$$

$$More stable \qquad CH_2 - CH_3 \qquad H_2O/H^+ \qquad OH$$

$$Less stable \qquad More stable \qquad Carbocation$$













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(xvi) **Epoxidation**

(a) By
$$O_2 / Ag$$
: $CH_2 = CH_2 + \frac{1}{2}O_2 \xrightarrow{Ag} CH_2 - CH_2$

0 11

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

$$CH_2 = CH_2 \longrightarrow CH_2 - CH_2$$

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

(xvii) Hydroboration

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

(Anti markownikoff's rule)

(xviii) **Hydroformylation:**
$$R-CH=CH_2+CO+H_2 \xrightarrow{CoH(CO)_4} R-C-C-C-H_1 \\ H C=O$$

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

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

$$|$$

$$COOH$$

(xix) Addition of formaldehyde

$$H_{2}C = O + H \longrightarrow [H_{2}C = OH \longleftrightarrow H_{2}C - OH] \xrightarrow{R-CH=CH_{2}} R - CH - CH_{2} - CH_{2} - OH \xrightarrow{HOH} R - CH - CH_{2} - CH_{2} - OH \xrightarrow{HOH} CH_{2} - CH_{2} - OH \xrightarrow{HOH} CH_{2} - CH_{2} - OH \xrightarrow{HOH} OH OH$$











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(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:
$$CH_3 - CH_2 - CH_2 - CH = CH_2$$

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

The mechanism proceeds via carbocation.

(xxii) Addition of HNO₃:
$$CH_2 = CH_2 + HO - NO_2 \longrightarrow CH_2OH.CH_2NO_2$$

Ethene

(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.











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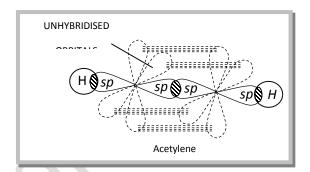


6. Alkynes.

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:
$$CH_3CH_2CH_2C \equiv CH$$
; $CH_3 = CH_3$ $CH_3 = CH_3$ $CH_3 = CH_3$

(ii) **Position isomerism:**
$$CH_3CH_2CH_2C \equiv CH$$
; $CH_3CH_2C \equiv CCH_3$

(iii) Functional isomerism:
$$CH_3 - C \equiv CH$$
; $CH_2 = C = CH_2$
Propyne 1, 2-propadiene (Allene)









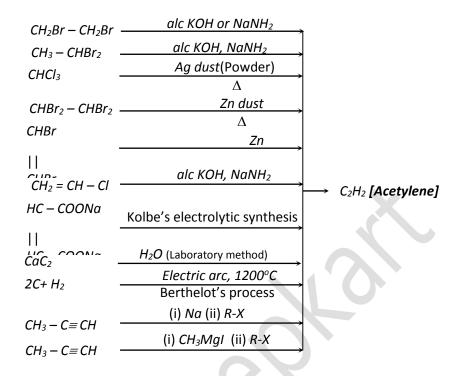


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(3) General methods of preparation



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.

$$CH_{3}I + Na - C \equiv C - Na + I - CH_{3} \longrightarrow CH_{3} - C \equiv C - CH_{3}$$

$$2CH \equiv CH \xrightarrow{NaNH_{2}} Na - C \equiv C - Na \xrightarrow{2CH_{3}I} CH_{3} - C \equiv C - CH_{3}$$

$$CH_{3} - C \equiv CH + CH_{3} - Mg - X \longrightarrow CH_{3} - C \equiv C - Mg - X + CH_{4} \xrightarrow{R-X} CH_{3} - C \equiv C - R + MgX_{2}$$

$$Alkyne$$











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(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° 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 has 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 Ex. $CH \equiv CH + NaNH_2 \longrightarrow H - C \equiv C Na^+ + \frac{1}{2}H_2$ (Monosodium acetylide)

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

$$CH \equiv CH + 2[Cu(NH_3)_2]Cl \longrightarrow Cu - C \equiv C - Cu + 2NH_4Cl + 2NH_3$$
 Dicopper acetylide (Red ppt)
 $CH \equiv CH + 2[Ag(NH_3)_2]NO_3 \longrightarrow AgC \equiv C - Ag + 2NH_4NO_3 + 2NH_3$ Disilver acetylide (white ppt)











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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.

$$CH_3 - C \equiv CH + 2[Ag(NH_3)_2]NO_3 \longrightarrow CH_3 - C \equiv C - Ag$$
1-propyne

$$CH_3 - C \equiv C - CH_3 + 2[Ag(NH_3)_2]NO_3 \longrightarrow$$
 No reaction

Explanation for the acidic character: It explained by sp hybridization. We know that an electron in sorbital 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

$$HC \equiv CH + 2CH_2O \longrightarrow CH_2 - C \equiv C - CH_2 \xrightarrow{Li/NH_3} CH_2 - CH = CH - CH_2OH$$
 [Trans-product]
$$| OH \qquad OH$$

(6) Chemical properties of acetylene

		Benzene : By passing acetylene through red hot tube, $3C_2H_2 \rightarrow C_6H_6$		
	\longrightarrow	Pyrrole : By heating with $NH_3, 2C_2H_2 + NH_3 \rightarrow C_4H_5N + H_2$		
CH≡CH	\longrightarrow	Thiophene: By heating with S or $H_2S, 2C_2H_2 + S \rightarrow C_4H_4S$		
Acetylene		Acetaldehyde: By passing acetylene through 40% H_2SO_4 and 1% H_8SO_4 at $80^{\circ}C$,		
		$CH \equiv CH + H_2O \rightarrow CH_3CHO$ or by heating ethylidene acetate,		
		$CH \equiv CH + 2CH_{3}COOH \xrightarrow{Hg^{2+}} CH_{3}CH(OOCCH_{3})_{2} \rightarrow CH_{3}CHO + CH_{3}CO$ [Kucherov's reaction] $CH_{3}CO \rightarrow CH_{3}CHO + CH_{3}CO$		
		Acetaldehyde so prepared may be used for the preparation of :		
		\square Ethyl alcohol: By reduction with H_2 in presence of Ni at $140^{o}C$,		
		$CH_3CHO + H_2 \rightarrow CH_3CH_2OH$		
		☐ Acetic acid: By oxidation in presence of manganese acetate or platinum wire at		
		$70^{\circ}C$,		
		$CH_3CHO + O \rightarrow CH_3COOH$		
		□ 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,		
		CH CHCl ₂ CHCl		
		$ + Cl_2 \longrightarrow \frac{Alc.}{KOH} \rightarrow $		
		CH CHCl ₂ CCl ₂ (Westron) (Westrosol)		
_		Lewsite: A poisonous gas used during wars,		
		CH CHCl		
		$ + ClAsCl_2 \xrightarrow{AlCl_3} \longrightarrow Cadet and Busen reaction$		
		CH CHAsCl ₂ Lewisite		











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verywhere	
	Vinyl acetate : By reacting with acetic acid in presence of Hg^{2+} ,
	$CH \equiv CH + CH_3COOH \xrightarrow{Hg^{2+}} CH_2 = CHOOCCH_3$
	Vinyl acetate is used in paints
	Vinyl chloride : By reacting with HCl in presence of Hg^{2+} at $60^{\circ}C$,
	$CH \equiv CH + HCl \xrightarrow{Hg^{2+}} CH_2 = CHCl$
	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: $C_2H_2 + H_2 \xrightarrow{Lindlar's} C_2H_4$ (Cis)
	Ethane : $C_2H_2 + 2H_2 \xrightarrow{Ni} C_2H_6$
	Higher alkynes: $HC \equiv CNa + XR \longrightarrow HC \equiv C - R$ Sod. acetylide
	Glyoxal: By oxidation with O_3 or SeO_2 .
	Oxalic acid: By oxidation with alk. KMnO ₄
	СН СООН
	+40>
	СН СООН

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

 $R - C \equiv C....H$ (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.

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

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.











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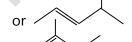
With Na/NH_3 or Li/NH_3 in (liquid ammonia) trans alkene is almost an exclusive product while catalytic reduction at alkyne affords mainly cis alkenes.

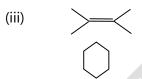
Degree of unsaturation: The number of degree of unsaturation in a hydrocarbon is given by

 $\frac{2n_1+2-n_2}{2}$, Where n_1 is the number of carbon atoms; n_2 is the number of hydrogen atoms.

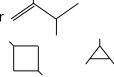
For example in C_6H_{12} , the degree of unsaturation is $=\frac{2\times 6+2-12}{2}=1$

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









(iv) or or

Other examples have the following degree of unsaturation.

or

(i)
$$C_6H_6 \to 4^o$$
 (ii) $C_5H_8 \to 2^o$ (iii) $C_7H_{10} \to 3^o$ (iv) $C_8H_{12} \to 3^o$ (v) $C_{10}H_{16} \to 3^o$ (vi) $C_{12}H_{10} \to 8^o$

$$\text{(vii)} \ \ C_3H_3Cl \ \ \text{(like} \ \ C_3H_6) \rightarrow 1^o \ \ \text{(viii)} \ \ C_3H_4O \ \ \text{(like} \ \ C_3H_4) \rightarrow 2^o \ \ \text{(ix)} \ \ C_4H_5N \ \ \text{(like} \ \ C_4H_4) \rightarrow 3^o$$

(x)
$$C_5H_9Cl$$
 (like C_5H_{10}) $\rightarrow 1^o$









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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 C = C don't show R

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 C = C

- (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° 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. $C_2H_2 \longrightarrow 2C + H_2$











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(8) Interconversion

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

$$CH_3 - CH_3 \xrightarrow{Br_2} C_2H_5Br \xrightarrow{Alc.} CH_2 = CH_2$$

Ethane Ethane Ethyl bromide Ethene

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

$$CH_{2} = CH_{2} \xrightarrow[Ni,300^{\circ}C]{H_{2}} CH_{3} - CH_{3}$$
Ethane

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

$$CH_{3} - CH_{3} \xrightarrow{Br_{2}} CH_{3}CH_{2}Br \xrightarrow{Alc.} CH_{2} = CH_{2} \xrightarrow{Br_{2}} CH_{2}Br - CH_{2}Br \xrightarrow{Alc.KOH} CH_{2}Br \xrightarrow{Alc.KOH}$$

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

$$CH \equiv CH \xrightarrow[\text{Ethyne}]{H_2} CH \xrightarrow[\text{Ethene}]{H_2} CH \xrightarrow[\text{Ethene}]{H_2} CH \xrightarrow[\text{Sthane}]{H_2} CH \xrightarrow[\text{Ethane}]{H_2}$$

(v) Ethene into propene: Ascending in alkene series

$$CH_{2} = CH_{2} \xrightarrow{HI} CH_{3}CH_{2}I \xrightarrow{KCN} CH_{3}CH_{2}CN \xrightarrow{[H]} CH_{3}CH_{2}CH_{2}NH_{2} \xrightarrow{HNO_{2}} CH_{3}CH_{2}CH_{2}OH$$
Ethene
Propane nitrile (Ethyl cyanide)
$$(Ethyl cyanide)$$
Propane nitrile (Ethyl cyanide)

$$CH_{3}CH = CH_{2} \leftarrow \frac{Alc.}{KOH} - CH_{3}CH_{2}CH_{2}Br \leftarrow \frac{PBr_{3}}{1-Bromopropane}$$

$$\text{Or } CH_2 = CH_2 \xrightarrow{HI} CH_3 CH_2 I \xrightarrow{CH_3I/Na} CH_3 CH_2 CH_3 \xrightarrow{Cl_2} CH_3 CH_2 CH_2 CI \xrightarrow{Alc.} CH_3 CH_2 CH_2 CI \xrightarrow{ROH} CH_3 CH_2 CH_2 CI \xrightarrow{ROH} CH_3 CH_2 CH_3 CH_2 CI \xrightarrow{ROH} CH_3 CH_2 CI \xrightarrow{ROH} CH_3 CH_2 CI \xrightarrow{ROH} CH_3 CH_2 CI \xrightarrow{ROH} CH_3 CI \xrightarrow{ROH} CI \xrightarrow{ROH}$$

(vi) **Propene into ethene:** Descending an alkene series

$$CH_{3} - CH = CH_{2} \xrightarrow{O_{3}/H_{2}O} CH_{3}CHO \xrightarrow{[H]} CH_{3}CH_{2}OH \xrightarrow{H_{2}SO_{4}} CH_{2} = CH_{2}$$
Ethanal Ethanal Ethanal Ethanal

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

$$CH \equiv CH \xrightarrow{Na} CH \equiv CNa \xrightarrow{CH_3I} CH \equiv C - CH_3$$
Acetylene
Acetylide
Acetylide
Acetylide

(viii) **Propyne into acetylene:** (Descent)

$$CH_{3}C = CH \xrightarrow{\text{Lindlar's catalyst}} CH_{3}CH = CH_{2} \xrightarrow{O_{3}/H_{2}O} CH_{3}CHO \xrightarrow{PCl_{5}} CH_{3}CHCl_{2} \xrightarrow{Alc.} CHO \xrightarrow{\text{KOH}} CHCl_{2} \xrightarrow{\text{KOH}} CHCl_{2} \xrightarrow{\text{KOH}} CHCl_{2} \xrightarrow{\text{CHO}} CHCl_{2} \xrightarrow{\text{C$$











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

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

$$CH_{3}CH_{2}C \equiv CH \xrightarrow{NaNH_{2}} CH_{3}CH_{2}C \equiv CNa \xrightarrow{CH_{3}I} CH_{3}CH_{2}C \equiv CCH_{3} \xrightarrow{H_{2}O,H_{2}SO_{4}} CH_{3}CH_{2}CH_{2}C CH_{3}$$

$$\xrightarrow{I-Butyne} CH_{3}CH_{2}C \equiv CCH_{3} \xrightarrow{H_{2}O,H_{2}SO_{4}} CH_{3}CH_{2}CH_{2}CCH_{3}$$

6. Separation of alkane, alkene and alkyne.

The gaseous mixture is passed through ammonical 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.

$$C_{2}H_{2} + Cu_{2}Cl_{2} + 2NH_{4}OH \rightarrow C_{2}Cu_{2} + 2NH_{4}Cl + 2H_{2}O; \quad C_{2}Cu_{2} + 2HNO_{3} \rightarrow C_{2}H_{2} + Cu_{2}(NO_{3})_{2} + Cu_{2}Cu_{2} + 2HNO_{3} \rightarrow C_{2}H_{2} + Cu_{2}(NO_{3})_{2} + Cu_{2}Cu_{2} + Cu_$$

The remaining gaseous mixture is passed through concentrated H_2SO_4 . Alkene is absorbed. The Hydrogen sulphate derivatives is heated at 170°C.

$$C_2H_4 + H_2SO_4 \longrightarrow C_2H_5HSO_4 \xrightarrow{\Delta} C_2H_4 + H_2SO_4$$

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 $-C \equiv C -$











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	Bond length 1.54 Å	1.34 Å	1.20 Å
	Bond energy : 83 Kcal mol ⁻	146 Kcal mol ⁻¹	200 Kcal mol ⁻¹
Burning	Burns with nonluminous	Burns with luminous flame	Burns with smoky flame
	flame $C_2H_6+7/2O_2 \rightarrow$ $2CO_2+3H_2O$	$C_2H_4+3O_2 \rightarrow 2CO_2+2H_2O$	$C_2H_2+5/2O_2 \rightarrow 2CO_2+H_2O$
Reaction with H_2	_	Forms alkane	Forms alkene and alkane
		$C_nH_{2n} + H_2 \xrightarrow[300^{\circ}C]{Ni} C_nH_{2n}$	$C_nH_{2n} + H_2 \xrightarrow[300^{\circ}C]{Ni} C_nH_{2n}$ Afkane
		$C_2H_4 + H_2 \rightarrow C_2H_6$	$C_nH_{2n-2} + H_2 \xrightarrow[300^{\circ}C]{Ni} C_nH_{2Alkene}$
Reaction with	_	Addition	Addition
conc. H ₂ SO ₄ and hydrolysis		$C_2H_4+H_2SO_4 \rightarrow C_2H_5HSO_4$	$C_2H_2 \rightarrow CH_3CH(HSO_4)_2$ AlcoH $6P \rightarrow$ Alder
, ,		$\xrightarrow{H_2O}$ C ₂ H ₅ OH	CH₃CHO
Br ₂ /CCl ₄	-	Decolorizes	Decolorizes
		Dibromo derivative,	Tetrabromo derivative,
		$C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$	C ₂ H ₂ Br ₄
Baeyer's	-	Decolorizes	Decolorizes
reagent (Alk.		Glycol is formed	Oxalic acid is formed
KMnO ₄)	16,	$\begin{array}{ccc} CH_2 & CH_2OH \\ & +H_2O+O \rightarrow \\ CH_2 & CH_2OH \end{array}$	$CH \qquad COOH$ $ + 4O \rightarrow $ $CH \qquad COOH$
Ammonical	-	_	Red precipitate
Cu_2Cl_2			$CH \qquad \qquad CCu \\ + Cu_2Cl_2 + 2NH_4OH \rightarrow \\ CH \qquad \qquad CCu \\ \qquad \qquad (Red)$
			+ 2NH ₄ Cl + 2H ₂ O
Ammonical	_	_	White precipitate
silver nitrate			$CH \qquad \qquad C-Ag \\ +2AgNO_3 +2NH_4OH \rightarrow \\ CH \qquad \qquad C-Ag$
			+ 2NH ₄ CI + 2H ₂ O











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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.

$$CH_2$$
 H_2C
 CH_2
Cyclo propane

$$H_2C$$
 CH_2
 CH_2
Cyclo Butane

(1) Methods of preparation

(i) From dihalogen compounds [Freund reaction]

$$CH_{2} \stackrel{C}{C}I \xrightarrow{heat} H_{2}C \xrightarrow{CH_{2} + 2NaC}CH_{2} + 2NaC}CH_{2} + 2NaC$$

$$CH_{2} \stackrel{C}{C}I \xrightarrow{heat} H_{2}C \xrightarrow{CH_{2} + 2NaC}CH_{2} + 2NaC$$

$$Cyclo propane$$

$$1, 3-Dichloropropane$$

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

$$CH_{2}CH_{2}C \longrightarrow C$$

$$CYclopentanone$$

$$Cyclopentane$$

$$Cyclopentane$$

$$Cyclopentane$$

$$Cyclopentane$$

(b) Diekmann Cyclization

$$CH_{2}C$$

$$COOC_{2}H_{5}$$

$$COOC_{2}H_{5}$$

$$COOC_{2}H_{5}$$

$$C_{2}H_{5}ONa$$

$$C_{2}H_{5}OH$$

$$CH_{2}C$$

$$CH_{2}$$

$$CH_{2}$$

$$CH_{2}$$

$$CH_{2}$$

$$CH_{2}$$

$$CH_{2}$$

$$CH_{2}$$

Preparation Classes







COOC₂H₅



39



COOH

$$CH_2$$
 CH_2
 H_2C
 CH_2
 H_2C
 CH_2
 H_2C
 CH_2
 CH_2
 CH_2
 CH_2
 CH_2
 CH_2
 CH_2
 CH_2
 CH_2
 $CYClopentane$
 $CYClopentanone$

(iii) From alkenes:
$$CH_3 - CH = CH_2 + CH_2I_2 \xrightarrow{Zn-Cu \text{ alloy}} CH_3 - CH - CH_2$$

CH 2

Methyl cyclopropane

(iv) From Aromatic compounds

 $+3H_2 \xrightarrow{Ni,200^{\circ}C}$
under pres sure

(2) Physical properties

(i) First two members are gases, next three members are liquids and higher ones are solids.

Benzene

- (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.







Cyclohexane







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

small ring

$$+ H_2 \longrightarrow \bigcirc$$

Spiro compound

Because small ring is more unstable than large ring Higher cycloalkanes do not give addition due to more stability.

(ii) Free radical substitution with Cl₂

$$CH_2 - CH_2 + Cl_2 \xrightarrow{hv} CH_2 - CH Cl + HCl$$

$$CH_2 \qquad CH_2$$
Cyclopropane Chlorocycbpropane

(iii) Addition reaction

$$\begin{array}{c} Br_2 \longrightarrow BrH_2C - CH_2 - CH_2Br \\ (CCI_4) \text{ dark} & 1, 3\text{-Dibromopropane} \\ HBr \longrightarrow CH_3 - CH_2 - CH_2Br \\ 1\text{-Bromopropane} \\ \hline (i) \text{ Conc. } H_2SO_4 \longrightarrow CH_3 - CH_2 - CH_2OH \\ \hline (ii) H_2O & 1\text{-Propanol} \\ \hline H_2, Ni \longrightarrow CH_3 - CH_2 - CH_3 \\ \hline 80^\circ C & Propane \\ \end{array}$$

(iv) Oxidation

$$\begin{array}{c|cccc} CH_2 & CH_2 & CH_2CH_2COOH \\ & & & & & & & & & \\ & & & & & & & \\ H_2C & & & & & & & \\ CH_2 & & & & & & & \\ CH_2 & & & & & & \\ Cyclohexane & & & & & & \\ \end{array}$$













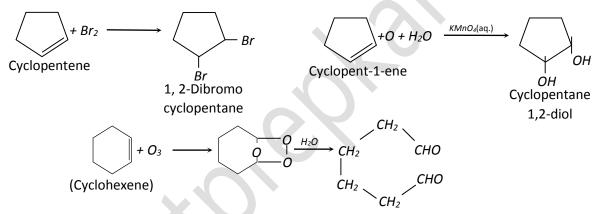


9. Cycloalkene.

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



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 $C_n H_{2n-2}$. The predominant member of this class is 1, 3-butadiene.











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- (1) Method of preparation
- (i) From acetylene: $2HC \equiv CH \xrightarrow{Cu_2Cl_2} HC \equiv C CH = CH_2 \xrightarrow{H_2} CH_2 = CH CH = CH_2$ Vinylacetylene $2HC \equiv CH CH = CH_2 \xrightarrow{NH_4Cl} HC \equiv C CH = CH_2 \xrightarrow{Pd/BaSO_4} CH_2 = CH CH = CH_2 \xrightarrow{NH_4Cl} HC \equiv CH_4 \xrightarrow{NH_4Cl} HC$
- Cl
- OH(iii) From 1,4-butanediol: $CH_2 CH_2 CH_2 CH_2 CH_2 - \frac{H_2SO_4}{heat} CH_2 = CH - CH = CH_2$
- (iv) From butane: $CH_3CH_2CH_2CH_3 \xrightarrow{Catalyst \\ 600^{\circ}C} CH_2 = CH CH = CH_2$ (Cr₂O₃ used as catalyst.)
- $H_2 = CH CH = CH_2 + CH_2 = CH_2$ 1, 3-Butadiene Ethene (v) From cyclohexene:
- (2) **Physical property:** 1, 3-butadiene is a gas.
- (3) Chemical properties
- (i) Addition of halogens:
- $CH_2 = CHCH = CH_2 + Br_2$ 1, 3-Butadiene

CH2BrCHBrCH=CH2 3,4-Dibromo-1-butene (1, 2-Addition) predominates (62%) in non-ionising solvent (hexane)

> CH₂BrCH=CH.CH₂Br 1,4-Dibromo-2-butene (1, 4-Addition) predominates (70%) in an ionising solvent (acetic acid)

Mechanism

Step I: The halogen molecule (Br_2) undergoes heterolytic fission.

$$Br_2 \longrightarrow Br^+_{\text{Bromonium Bromide}} + : Br^-_{\text{Bromonium Bromide}}$$

Step II: The bromonium ion attacks the double bond to give a resonance stabilized carbonium ion.

$$BrCH_{2} - \overset{+}{C}H - CH = CH_{2}(A)$$

$$Br^{+} + CH_{2} = CH - CH = CH_{2} \longrightarrow \qquad \updownarrow$$

$$BrCH_{2} - CH = CH - \overset{+}{C}H_{2}(B)$$











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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).

$$Br-CH_2-CH-CH=CH_2$$
 1, 2-product; $Br-CH_2-CH=CH-CH_2-Br$ 1, 4-product Br $CH_3CHBrCH=CH_2$

(ii) Addition of halogen acids:

$$CH_{3}CHBrCH=CH_{2}$$

$$(1, 2-Addition)$$

$$3-Bromo-1-butene$$

$$CH_{3}-CH=CH-CH_{2}Br$$

$$(1, 4-Addition)$$

$$1-Bromo-2-butene$$

$$(Major yield at high temp.)$$

(iii) Addition of water:

$$CH_{3}CHOHCH=CH_{2}$$

$$CH_{2}=CH-CH=CH_{2}+H_{2}O$$

$$CH_{3}CH=CHCH_{2}OH$$

$$2-Butenol-1$$

(iv) **Polymerization:**
$$nCH_2 = CHCH = CH_2 \xrightarrow{\text{Peroxide}} [-CH_2CH = CHCH_2 -]_n$$
_{1,3-Butadiene}

Diels-alder reaction:

$$CH_2$$
 $H-C$
 CH_2
 $H-C$
 CH_2
 $CYClohexene$
 CY

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;
$$CH_2 = C = CH_2$$
; ; C











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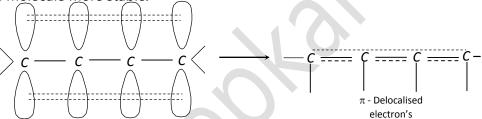




Mechanism (FMO)

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**:
$$CH_2 = CHCH = CH_2 + 2O_3 \xrightarrow{Zn/H_2O} 2HCHO + OHCCHO$$

$$CH_2 - O - CH - CH - CH_2$$

$$O \longrightarrow O \longrightarrow O \longrightarrow O$$
(Diozonide)











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