HYDROCARBON

ALKANE

1. Structure and Bonding

- (a) Alkanes are saturated hydrocarbons.
- (b) These are represented by general Formula (G.F.) C_nH_{2n+2}
- (c) In Ethane C C bond length is 1.54 ${\rm \AA}$
- (d) The hybridization of (C C) carbon is sp^3
- (e) These are also known as paraffin's.

2. Preparation of alkane

2.1. Wurtz Reaction :

This method is used for preparation of higher alkanes from 1° or 2° alkyl halides. In this method two moles of alkyl halides are treated with 'Na' metal in dry ether.

$$R - X + 2Na + R - X \xrightarrow{Na} R - R + 2Na - X.$$

 $CH_3 - CH - CH_3$

 $CH_3 - CH - CH_3$

Br (I)

Que. Write the structure of products when structure Ist and IInd undergo Wurtz reaction $CH_3 - CH - CH_3 + CH_3 - CH - CH_2 - Br$

 CH_3

$$\begin{array}{c} (II)\\ CH_{3} - CH - CH_{3}\\ |\\ CH_{2} - CH - CH_{3}\\ |\\ CH_{2} - CH - CH_{3}\\ |\\ CH_{2} - CH_{3}\\ |\\ CH_{2} - CH_{3}\\ |\\ CH_{3} - CH_{3}\\ |$$

(a)

2.2. By Corey House alkane synthesis :

(b)

It is used for the preparation of pure alkane having odd number of carbon atom.

CH₂

$$\begin{array}{c} R-X \\ (1^{\circ}, 2^{\circ}, 3^{\circ}) \xrightarrow{2Li} \overset{\bigotimes}{R} \overset{\bigoplus}{Li} + LiX \xrightarrow{CuX} Lithiumdialkyl cuprate \\ (Gilman's reagent) \xrightarrow{(1^{\circ}>2^{0})} \overset{R'-X}{\longrightarrow} R - R' \\ \end{array}$$

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$$\begin{array}{c} R-R' \\ R-R' \\ \overset{H_{3}}{\longrightarrow} 2 \\ CH_{3} \xrightarrow{(1^{\circ}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_$$

2.3. Reduction of alkyl halides :

(i) By Zn/HCI

 $R - X + Zn/HCI \longrightarrow RH + X^{\Theta}$ Reaction is proceed as
Purest form of methane can be obtained as :

$$CH_{3}I \xrightarrow{Zn-Cu(couple)} CH_{4}$$

 $Zn \longrightarrow Zn^{2+} + 2e^{-}$

(ii) Frankland reaction

 $R - X + Zn + R - X \xrightarrow{Ether} R - R + ZnX_{2}$



CH – CH₃

I CH₃

2.4. Preparation of Alkane from acid :

(i) Decarboxylation of sodium salt of acid :

It is removal of CO_2 . This reaction is used to desend the series and proceeds via carbanion intermediate.

Reagent \rightarrow Sodalime [mixture of NaOH + CaO] RCOONa + NaOH $\xrightarrow{CaO}_{\Delta}$ RH + Na₂CO₃

- Note: 1. This method is used to get alkane corresponds to alkyl part of acid.
 - 2. That acid will decarboxylate more readily which give more stable carbanion.
 - 3. Among the keto acid, it is β -keto acid which undergoes decarboxylation more readily because it proceeds via six membered cyclic transition state and syn elimination reaction.

$$\begin{array}{c} O & O \\ II & II \\ CH_3 - C - CH_2 - C - OH \xrightarrow{\Delta} CH_3 - C - CH_3 + CO_2 \end{array}$$

(ii) Kolbe's electrolytic method :

In this method two moles of Na/K - salt of fatty acids is used. During the electrolysis hydrogen gas is liberated at cathode because disharge potential of hydrogen is less than of that metal, while alkane is liberated at anode and this alkane will be dimer of alkyl part of acid.

$$\begin{array}{c} \begin{array}{c} Cathode \\ & \bigcirc \end{array} 2K^{\oplus} \xrightarrow{2e} 2K \xrightarrow{2H_2O} H_2 \uparrow + 2KOH \\ \end{array} \\ 2RCOONa/K \\ \hline \\ \hline \\ Anode \\ \oplus \end{array} 2RCOO^{-} \xrightarrow{\ominus 2e^{-}} 2R^{\bullet} \quad (\mathring{R} + \mathring{R} \longrightarrow R-R) \end{array}$$

(iii) Reduction of carboxylic acid :

On passing carboxylic acid in sealed tube containing HI/P at 200°C. We get alkane corresponding to acid.

Ex- R-COOH + 6HI
$$\xrightarrow{\text{Red P}}$$
 R-CH₃ + 2H₂O + 3I₂

3. Physical properties of alkane

Alkane molecules are held together by weak Vander waal force which depends upon surface area. On increasing molecular mass surface area increases hence Vander waal forces also increased and thus physical properties are increased

$$\begin{array}{lll} \mathsf{C}_{_1}-\mathsf{C}_{_4} & \Rightarrow & \text{gas} \\ \mathsf{C}_{_5}-\mathsf{C}_{_{17}} & \Rightarrow & \text{liquid} \\ \mathsf{C}_{_{18}}\ldots\ldots & \Rightarrow & \text{solid} \end{array}$$

Note : 1. On increasing branching surface area tends to be spherical i.e.Vander waal interaction reduced and hence boiling point decreased.

2. Melting point of alkane having even number of carbon atoms is higher than neighbouring alkanes having odd number of carbon atom. Because in even number of alkanes two ends are facing towards opposite side hence there will be minimum intermolecular repulsion as a result they fit better into crystal lattice.

3. Density of alkane increases with molecular mass and then acquires a constant value 0.8 gm/cc³. Thus also it is clear that alkane is lighter than water.

4. Chemical reactions of alkane

4.1. Halogenation :

Reagents :- UV light / hv/ high temp ($250^{\circ}-400^{\circ}$ C) / Peroxide + X₂ (Cl₂ + Br₂)

General reaction :-

 $R - H + X_2 \xrightarrow{UV \text{ light or } 250^\circ - 400^\circ} R - X + HX$

Mechanism :- Free radical substitution this reaction is chain reaction which is completed in following three steps.

(i) Chain initiation step : It is homolytic clevage of chlorine molecule to give chlorine free radical .It is an endothermic step.

$$X_2 \xrightarrow{UV \text{ or temp.}} 250^\circ - 400^\circ C \xrightarrow{i} 2X$$

(ii) Chain propagation step - The step in which reactant and product, both are having free radical. It is longest step.

$$X + R - H \longrightarrow R + HX$$
; [rds] First propagation step
 $R + X - X \longrightarrow R - X + X$ Secod propagation step

(iii) Chain Termination step - It is the step in which any two free radicals combine to give a product without free radical. It is always exothermic step.

$$\begin{array}{c} \dot{X} + \dot{X} \longrightarrow X_{2} \\ \dot{R} + \dot{R} \longrightarrow R - R \\ \dot{R} + \dot{X} \longrightarrow R - R \\ \dot{R} + \dot{X} \longrightarrow R - X \\ \hline Remark: \\ \hline (i) Other halogenating reagent is \\ (a) Chlorination SO_2Cl_/ Peroxide \\ \hline (b) Bromination SO_2 Br_{2} / Peroxide \\ \hline (b) Bromination SO_2 Br_{2} / Peroxide \\ \hline Mechanism for (a) \\ RO - OR \longrightarrow 2 \cdot OR \\ \cdot OR + SO_{2}Cl_{2} \longrightarrow ROCl + 'SO_{2}Cl \\ \cdot SO_{2}Cl \longrightarrow \cdot Cl + SO_{2} \\ RH + \cdot Cl \longrightarrow R^{*} + HCl \\ \hline (ii) Methane reacts with excess of chlorine in diffused sunlight to give the final product as \\ CH_{4} + Cl_{2} \xrightarrow{hv} CH_{3}Cl + HCl \\ CH_{3}Cl + Cl_{2} \xrightarrow{hv} CH_{2}Cl_{2} + HCl \\ CH_{2}Cl_{2} + Cl_{2} \xrightarrow{hv} CH_{2}Cl_{2} + HCl \\ CHCl_{3} + Cl_{2} \xrightarrow{hv} CCl_{4} + HCl \\ \hline (cHCl_{3} + Cl_{2} \xrightarrow{hv} CCl_{4} + HCl \\ \hline (carbon tetrachloride] \\ \hline (iii) Reactivity of H = 3^{\circ}H > 2^{\circ}H > 1^{\circ} H \\ \hline (iv) In a chain reaction following reagents are involved : \\ \hline (a) Initiators : They initiate the chain reaction, Initiators are peroxide (R_{2}O_{2}), Perester's etc. \\ \hline (b) Inhibitors : A substance that slows down or stops the reaction is known as inhibitors For example O_{2} is a good inhibitor. \\ \hline \end{array}$$

 $R + O_2 \longrightarrow R - O - O + R \longrightarrow R - O - O - R$

all reactive alkyl free radicals are consumed so reaction stops for a period of time.

down or stops the reaction is known as inhibitors

Halogenation of higher alkane :



Factors affecting the relative yields :

(i) Probability factor : This factor is based on the number of each kind of H atom in the molecule.
(ii) Reactivity of hydrogen : The order of reactivity is 3° > 2° > 1° the relative rate per hydrogen atom is found to be

4.2. Catalytic Hydrogenation :

Alkenes, Alkynes, polyenes or polyynes can be hydrogenated by using catalysts Ni at 200⁰C & Pt/Pd at room temperature.

All Carbon–Carbon π bonds(C=C, C=C) get hydrogenated. The reaction can't be stopped at any intermediate stage.

Note: (i) Aromatic π bonds are stable at room temperature but can be hydrogenated at high temperature.
 (ii) It can be concluded that the hydrogenation product of an alkene or alkyne or any unsaturated compound is always a saturated compound.

(iii) The no. of moles of H₂ consumed by 1 mole of compound is equal to the no. of π bonds.

(iv) During catalytic hydrogenation *carbon skeleton* does not change.

Application : This reaction gives an information about molecule that the molecule is saturated or unsaturated.

General reaction :

(a)
$$R - CH = CH - R + H_2 \xrightarrow{Ni} R - CH_2 - CH_2 - R$$

(b) $R - C = C - R + 2H_2 \xrightarrow{Ni/Pt/Pd} R - CH_2 - CH_2 - R$
 $\downarrow H_2$
 $R - CH = CH - R \xrightarrow{H_2} R - CH_2 - CH_2 - R$
(Not isolated)
(c) $CH_2 = CH - CH = CH_2 \xrightarrow{2H_2/Ni} CH_3 - CH_2 - CH_2 - CH_3$
(d) $\downarrow CH = CH_2 \xrightarrow{H_2/Ni}_{room temperature} \downarrow CH_2 - CH_3$

 H_2/Ni

4.3. Nitration of alkane :

It takes place in vapour phase and gives a mixture of nitroderivatives due to cracking.

$$\begin{array}{l} \mathsf{RH} + \mathsf{HNO}_3 & \xrightarrow{400^\circ \mathsf{C}} & \mathsf{RNO}_2 + \mathsf{H}_2\mathsf{O} \\ \mathsf{CH}_4 + \mathsf{HNO}_3 & \xrightarrow{\Delta} & \mathsf{CH}_3\mathsf{NO}_2 + \mathsf{H}_2\mathsf{O} \\ \mathsf{CH}_3 - \mathsf{CH}_2 - \mathsf{CH}_3 + \mathsf{HNO}_3 & \xrightarrow{\Delta} & \mathsf{CH}_3 - \mathsf{CH}_2 - \mathsf{CH}_2 - \mathsf{NO}_2 + \overset{\mathsf{CH}_3 - \mathsf{CH}_2 - \mathsf{CH}_3 + \mathsf{CH}_3 - \mathsf{CH}_2 - \mathsf{NO}_2 + \mathsf{CH}_3\mathsf{NO}_2 \\ \mathsf{I}_{\mathsf{NO}_2} \end{array}$$

Note : Nitration of propane gives a mixture of four nitroderivatives as it as two types of replaceable H-atom (1° and 2°) and also it undergoes cracking at high temperature.

4.4. Sulphonation of alkane :

Lower alkanes do not undergo sulphonation easily but higher members (from hexane onward) are sulphonated slowly when treated with fuming acid (oleum) at around 400°C

 $RH + H_2SO_4 \xrightarrow[Prolonged heating]{SO_3} R-SO_3H + H_2O$

- **Note :** 1. Lower members like propane, butane and pentane etc. react with SO₃ in vapour phase to give corresponding sulphonic acid.
 - Decreasing order of sulphonation of alkane 3° > 2° > 1° H–atom
 - 3. It s follows free radical mechanism as

$$H_2SO_4 \xrightarrow{\Delta} HO^{\bullet} + {}^{\bullet}SO_3H$$

$$RH + OH \longrightarrow R + H_0$$

4.5. Combustion of Alkane

$$C_{x}H_{y} + \left(x + \frac{y}{4}\right)O_{2} \longrightarrow x CO_{2} + \frac{y}{2}H_{2}O + \Delta; \qquad C_{3}H_{8} + \left(3 + \frac{8}{4}\right)O_{2} \longrightarrow 3 CO_{2} + \frac{8}{2}H_{2}O$$

Hydrocarbon + sufficient supply of $O_2 \Rightarrow CO_2 + H_2O + \Delta$ Hydrocarbon + insufficient supply of $O_2 \Rightarrow CO + H_2O$ or C (black)

Que. How many atoms of oxygen are needed for complete combustion of 2.2 g of propane ?

Ans.
$$C_3H_8 + 5O_2 \longrightarrow 3 CO_2 + 4H_2O_2$$

44 gm of C₃H₈ needs = 5 moles of Oxygen = 5 × N_A molecule of Oxygen = 5 × 2 × N_A atom 2.2 gm of C₃H₈ needs = $\frac{5 \times 2 \times 2.2 \times N_A}{44} = 0.5 \times N_A$ atoms of Oxygen

Note : 1. Heat of combustion α higher homologues

Ex-
$$C_{3}H_{8} > C_{2}H_{6} > CH_{4}$$

2. Heat of combustion
$$\propto \frac{1}{\text{Branching of alkane (in isomers)}}$$

Ex- CH₃ - CH₂ - CH₂ - CH₂ - CH₃ > CH₃ - CH - CH₂ - CH₃ > CH₃ - CH₂ - CH₂ - CH₃
 $\begin{array}{c} CH_3 \\ I \\ CH_3 \end{array}$
3. Heat of combustion $\propto \frac{1}{\text{circular planet}}$

3. Heat of compustion \propto sizeofring(cycloalkane)

On increasing the size of ring from three to six stability of ring increases and hence heat of combustion (its value) decreases per CH_2 group.

4.6. Controlled oxidation :

Alkanes on heating with a regulated supply of dioxygen or air at high pressure and in the presence of suitable catalyst give a variety of oxidation products.

(i)
$$2CH_4 + O_2 \xrightarrow{Cu/523K/100atm} 2CH_3OH \text{ (methanol)}$$

(ii) $CH_4 + O_2 \xrightarrow{Mo_2O_3} A HCHO + H_2O$
methanal
(iii) $2CH_3CH_3 + 3O_2 \xrightarrow{(CH_3COO)_2Mn} 2CH_3COOH + 2H_2O$
Ethanoic acid

4.7. Isomerization of alkane :

n–Alkanes on heating in the presence of anhydrous aluminium chloride and hydrogen chloride gas isomerise to branched chain alkanes.

$$\begin{array}{c} CH_{3}(CH_{2})_{4}CH_{3} \\ n-Hexane \end{array} \xrightarrow{Anhy. AlCl_{3}/HCl} & CH_{3}-CH_{-}(CH_{2})_{2}-CH_{3} \\ I \\ CH_{3} \\ 2-methyl \ pentane \end{array} + \begin{array}{c} CH_{3}-CH_{2}-CH_{-}CH_{2}-CH_{3} \\ I \\ CH_{3} \\ 3-methyl \ pentane \end{array}$$

4.8. Aromatization of alkane :

n-alkanes having six or more carbon atoms on heating to 773 K at 10-20 atmospheric pressure in the presence of oxides of vanadium, molybdnum or chromium supported over alumina get dehydrogenated and cyclised to benzene and its homologues. This reaction is known as aromatization or reforming. CH₃



Que. Toluene (C_2H_2) is methyl derivative of benzene. Which alkane do you suggest for preparation of toluene?

Ans. n – Heptane

4.9. Reaction with steam

Methane reacts with steam at 1273 K in the presence of nickel catalyst to form carbon monoxide and dihydrogen.

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

4.10. Cracking of alkane

$$C_{6}H_{14} \xrightarrow{773 \text{ K}} C_{6}H_{12} + H_{2}$$

$$C_{4}H_{8} + C_{2}H_{6}$$

$$C_{3}H_{6} + C_{2}H_{4} + CH_{4}$$

ALKENE

1. Structure and Bonding :

(A) Alkenes are unsaturated hydrocarbons having at least one double bond. Alkenes are also known as olefins.

- (B) These are represented by general Formula $C_n H_{2n}$ (one double bond).
- (C) In Ethene C = C bond length is 1.34 \AA
- (D) Its bond energy is 146 kcal.mol⁻¹
- (E) The hybridization of (C = C) carbon is sp²
- (F) The πe^{-} cloud is present above and below the plane of σ bonded skeleton.

- (G) These are also known as olefins since ethene, the first member of the homologous series forms oily liquid substance when treated with halogens.
- (H) Compounds may exist as conjugated polyenes or as cumulated polyenes or as isolated polyenes



Note : Bond angle a > b since repulsion due to π electrons (double bond - single bond repulsion > single bond - single bond repulsion according to VSEPR theory.

2. Stability of Alkenes :

Overall relative stabilities of Alkenes

The greater the number of attached alkyl groups (i.e., the highly substituted the carbon atoms of the double bond), the greater is the alkene's stability. This order of stabilities can be given in general terms as follows.

Relative stabilities of alkenes



Note- 1. More and More alkylated double bonded alkene will be more stable.

2. The way of measuring stability of alkene is the determination of heat of hydrogenation. It is applicable only those isomeric alkene which gives same product after hydrogenation.

Stability $\infty \frac{1}{1}$

 $\frac{1}{1}$ Heat of Hydrogenation

i.e. more stable the alkene less will be heat of hydrogenation.

3. Preparation of Alkene :

3.1. Dehydro-halogenation of alkyl halide :

It is removal of H–X from alkyl halide where this reaction is said to be β -elimination reaction.

Reagent (i) Hot alcoholic solution of KOH (EtO⁻ / EtOH) (ii) NaNH₂ (iii) t-BuO⁻ K⁺ in t-BuOH

$$\begin{array}{c|c} & | & | \\ -C - C - & + & \text{KOH} \end{array} \xrightarrow{alcohol} & -C = C - + & \text{KX} + & \text{H}_2O \\ & | & | \\ H & X \end{array}$$

Remark : (i) Here β – H is eliminated by base hence called β elimination (follows Saytzeff rule). i.e. (Highly substituted alkene is major product). It also involves an anti elimination of HX.

Ex-1.
$$CH_3 \xrightarrow[]{H_3} CH_3 - C = CH_2 + KBr + H_2O$$

 $\downarrow CH_3 \xrightarrow[]{CH_3} CH_3 - C = CH_2 + KBr + H_2O$

Ex-2.
$$\begin{array}{c} \overset{\beta}{\mathsf{CH}}_{3} - \overset{\alpha}{\underset{\mathsf{CH}}{\mathsf{CH}}}_{3} - \overset{\beta}{\underset{\mathsf{CH}}{\mathsf{CH}}}_{3} - \overset{\mathsf{CH}}{\underset{\mathsf{CH}}{\mathsf{CH}}}_{3} - \overset{\mathsf{CH}}{\underset{\mathsf{CH}}{\mathsf{H}}}_{3} - \overset{\mathsf{CH}}{\underset{\mathsf{CH}}{\mathsf{H}}}_{3} - \overset{\mathsf{CH}}{\underset{\mathsf{CH}}{\mathsf{H}}}_{3} - \overset{\mathsf{CH}}{\underset{\mathsf{CH}}{\mathsf{H}}}_{3} + \overset{\mathsf{CH}}{\underset{\mathsf{CH}}{\mathsf{H}}}_{2} = \overset{\mathsf{CH}}{\underset{\mathsf{(minor)}}{\mathsf{H}}}_{1} - \overset{\mathsf{CH}}{\underset{\mathsf{(minor)}}{\mathsf{H}}}_{1} + \overset{\mathsf{CH}}{\underset{\mathsf{(minor)}}{\mathsf{H}}}_{2} = \overset{\mathsf{CH}}{\underset{\mathsf{(minor)}}{\mathsf{H}}}_{1} - \overset{\mathsf{CH}}{\underset{\mathsf{(minor)}}{\mathsf{H}}}_{3} - \overset{\mathsf{CH}}{\underset{\mathsf{(minor)}}{\mathsf{H}}}_{2} = \overset{\mathsf{CH}}{\underset{\mathsf{(minor)}}{\mathsf{H}}}_{2} = \overset{\mathsf{CH}}{\underset{\mathsf{(minor)}}{\mathsf{H}}}_{2} - \overset{\mathsf{CH}}{\underset{\mathsf{(minor)}}{\mathsf{H}}}_{2} - \overset{\mathsf{CH}}{\underset{\mathsf{(minor)}}{\mathsf{H}}}_{2} = \overset{\mathsf{CH}}{\underset{\mathsf{(minor)}}{\mathsf{H}}}_{2} - \overset{\mathsf{CH}}{\underset{\mathsf{(minor)}}{\mathsf{(minor)}}}_{2} - \overset{\mathsf{CH}}{\underset{\mathsf{(minor)}}{\mathsf{(minor)}}}_{2} - \overset{\mathsf{(minor)}}{\mathsf{(minor)}}_{2} - \overset{\mathsf{CH}}{{\mathsf{(minor)}}}_{2} - \overset{\mathsf{(minor)}}{\mathsf{(minor)}}_{2} - \overset{\mathsf{(minor)}}{\mathsf{(minor)}}_{2} - \overset{\mathsf{(minor)}}{\mathsf{(minor)}}_{2} - \overset{\mathsf{(minor)}}{\mathsf{(minor)}}_{2} - \overset{\mathsf{(minor)}}{\mathsf{(minor)}}_{2} - \overset{\mathsf{(minor)}}{\mathsf{(minor)}}_{2} - \overset{\mathsf{(minor)}}{\mathsf{(minor)}}_{2$$

3.2. By Dehydration of alcohols

Reagents: (i) $H_2SO_4 / 160^{\circ}C$ (ii) H_3PO_4 / Δ (iii) P_2O_5 / Δ (iv) $AI_2O_3 / 350^{\circ}C$ undergo loss of water molecule and form alkenes $RCH_2CH_2OH \xrightarrow{P_2O_5 \text{ or conc. } H_2SO_4 \text{ or } AI_2O_3}{\Delta} \Rightarrow R - CH = CH_2 + H_2O$

3.3. Dehalogenation of dihalo-alkane :

It is removal of X_2 from dihalo alkane.

Reagent: NaI in acetone or zinc in presence of acetic acid or ethanol or Zn/Δ **Dihalides are of two types :**

(A) Vicinal dihalide or Alkylene dihalides

Rr

General Reaction :

$$\begin{array}{c|c} & & \\ -C - C - C - \\ & \\ Br \end{array} \xrightarrow{\begin{subarray}{c} NaI/Acetone \\ or Zn, CH_3COOH \end{array} } C=C < \\ \end{array}$$

(B) Gem-dihalide or Alkylidene halides

Ex: CH₃—CHCl₂ (ethylidene chloride)

When gem dihalide is heated with Zinc dust at 300°C then higher alkenes are formed, which is based on free radical mechanism.

3.4. Electrolysis of Potassium succinate :

This reaction gives ethylene as follows

$$CH_2 - COOK \xrightarrow{Cathod} 2K^{\oplus} \xrightarrow{+2e} 2K$$

 $| \\ CH_2 - COOK \xrightarrow{Anode} CH_2COO^- (i) -2e^- CH_2 - CH_2$

succinate

4. Physical Properites of Alkene

- (i) From $C_2 C_4$ they are colourless, odourless gases, from $C_5 C_{17}$ they are colourless liquids, C_{18} onwards alkenes are solids.
- (ii) Alkenes are practically insoluble in water because they can not form hydrogen bonds with H₂O molecules. They dissolve freely in organic solvents like benzene, chloroform, CCl₄ petroleum ether, etc.
- 5. Chemical reactions of alkene Electrophilic addition Reaction : Reactivity of an Alkene:
 - (1) Presence of electron releasing groups (+m, +I) at C = C increases electrophilicity and reactivity.
 - (2) Presence of ERG stabilises the intermediate carbocation.
 - (3) More stable C^{\oplus} , more is reactivity.

Examples of Reactivity Orders :



CHEMISTRY FOR NEET



5.5. Addition of H₂O (Hydration Reaction)

(i) Acid-Catalyzed Hydration of Alkenes : Reagents : Dilute H_2SO_4 or H_3O^+

$$C = C + H_2O \xrightarrow{H^{\oplus}} - \begin{array}{c} - & | & | \\ - & - & - \\ & | & | \\ H & OH \end{array}$$

5.6. Ozonolysis :

Ozonolysis reaction is used to determine the position of C=C, C=C in a molecule. In this reaction Alkene, Alkyne and polyalkene on ozonolysis undergo oxidative cleavage. It is of two types.

(i) Reductive ozonolysis :

Reagents are : (1) O_3 (ozone) (2) Zn or $(CH_3)_2S$ and H_2O or CH_3COOH The products are carbonyl compounds (aldehydes or ketones).

(ii) Oxidative ozonolysis :

Reagents are : (1) O_3 (ozone) (2) H_2O_2 or H_2O The products are ketones and/or acids.

Note: (i) Ozonolysis does not interfere with other functional groups. (ii) At higher temperature, the aromatic double bonds can also undergo ozonolysis reaction.

General Reaction :

(i) Reductive ozonolysis

$$\begin{array}{c} R-CH \stackrel{+}{\underset{I}{=}} C - R \begin{pmatrix} (1) O_3 \\ (2) Zn/H_2O \end{pmatrix} \\ R - C = C - H \begin{pmatrix} (1) O_3 \\ (2) Zn/H_2O \end{pmatrix} \\ R - C = C - H \begin{pmatrix} (1) O_3 \\ (2) Zn/H_2O \end{pmatrix} \\ R - C - C - H + ZnO + H_2O \\ H \\ O O \end{array}$$

(ii) Oxidative ozonolysis

$$R-CH \stackrel{i}{=} C-R \xrightarrow{(1) O_3}{(2) H_2O_2} R-COOH + O=C-R + H_2O$$

$$R$$

$$R-C=C-H \xrightarrow{(1) O_3}{(2) H_2O_2} R-COOH + HCOOH$$

$$CO_2 + H_2O$$

Ex. (a)
$$CH_2=CH_2 \xrightarrow{(1)} O_3 \xrightarrow{(1)} CH_2=O + CH_2=O$$

(b) $CH_3-CH_2-CH=CH_2 \xrightarrow{(1)} O_3 \xrightarrow{(2)} CH_3-CH_2-CH=O + O=CH_2$
(c) $CH_2=CH-CH_2-CH=CH-CH_3 \xrightarrow{(1)} O_3 \xrightarrow{(2)} CH_2=O + O=CH-CH_2-CH=O + O=CH-CH_3$
(d) $(1) \xrightarrow{(1)} O_3 \xrightarrow{(2)} 2 OHC-CH_2-CHO (Propandial)$
(e) $- \xrightarrow{(1)} \xrightarrow{(1)} (2) \xrightarrow{(1)} O_3 \xrightarrow{(2)} O=CH-CH_2-C_1-CH_2-CH=O + O=CH_2$
(f) $\xrightarrow{(1)} -- \xrightarrow{(1)} O_3 \xrightarrow{(1)} O=C_1-C_1 = O (Ethanedial) or (glyoxal)$
(g) $\xrightarrow{(1)} CH = CH - CH_3 \xrightarrow{(i)} O \xrightarrow{(i)} O$

ALKYNE

1. Introduction

- (1) Alkynes are hydrocarbons that contain carbon-carbon triple bond.
- (2) Alkynes are also called acetylenes because they are derivatives of acetylene.
- (3) The general formula is : C_nH_{2n-2} . (one triple bond)
- (4) In alkyne C = C bond length is 1.20 Å
- (5) Its bond energy is 192 kcal. mol⁻¹
- (6) The hybridization of carbon atoms having triple bond ($C \equiv C$) in alkynes is sp

(7) Overlapping of these sp hybrid orbitals with each other and with 1–s of the hydrogen orbitals gives the sigma bond framework which is linear (180°) structure.

(8) Two π bonds result from overlap of the two remaining unhybridized p orbitals on each carbon atom.

These orbitals overlap at **right angles** (90°) to each other, forming one π bond with electron density above and below the C–C sigma bond, and the other with electron density in front and in back of the sigma bond. This result in a cylindrical π electron cloud around σ bonded structure



Note : Any type of stereoisomerism does not arise in acetylenic bond due to linearity of $C \equiv C$ bond.

2. Methods of preparation :

2.1. By Double Dehydrohalogenation of Gem and Vicinal Dihalide : (A) Vicinal Dihalide :

$$\begin{array}{c} H & H \\ R - C & -C - R \\ Br & Br \end{array} + alc. KOH \xrightarrow{-HBr} R - C = C - R \xrightarrow{NaNH_2}{-HBr} R - C = C - R \\ Br & Br \\ alc.KOH \end{array}$$

 $\mathrm{NaNH}_{\mathrm{2}}$ is more basic than alc. KOH.

(B) Gem Dihalides :

$$\begin{array}{c} H & Br \\ R - C - C - R \\ H & Br \end{array} + alc. KOH \xrightarrow{-HBr} R - C = C - R \xrightarrow{NaNH_2}{-HBr} R - C = C - R \\ Br \\ H & Br \end{array}$$

2.2. From Tetrahaloalkanes (Dehalogenation) :

$$R \xrightarrow{X} A \xrightarrow{X} A \xrightarrow{Zn(dust)} R \xrightarrow{Zn(dust)} R \xrightarrow{X} A \xrightarrow{Zn(dust)} R \xrightarrow{Zn($$

2.4. From Kolbe's Synthesis :

At Cathode : $2H_2O + 2e^{\Theta} \longrightarrow H_2 + 2OH^{\Theta}$ $2OH^- + 2K^+ \longrightarrow 2KOH$

If R = H, product will be CH = CH; If R = CH₃, product will be CH₃ - C = C - CH₃.

2.5. Preparation of Acetylene :

It is first member of alkyne can be prepared by using any one of the following methods.

(a) In laboratory acetylene if prepared by hydrolysis of calcium carbide.

(b) It can also be prepared from $CHCI_3$ with Ag dust.

$$H - C \boxed{CI_3 + 6Ag + CI_3} - CH \xrightarrow{-6AgCl} H - C \equiv C - H$$

(c) $2CHI_3 + 6Ag \longrightarrow H - CC - H \equiv + 6AgI$

3. Physical Properties of Alkyne :

- (i) Alkynes are colourless, odourless and tasteless.
- (ii) Lower alkynes are partially soluble in H_2O . (It is due to its polarizability)
- (iii) Higher alkynes are insoluble in water due to more % of covalent character.
- (iv) Completely soluble in organic solvents.
- (v) Melting point and boiling point are directly proportional to molecular mass and inversely proportional to number of branches.
- (vi) Upto C_4 alkynes are gaseous, C_5 – C_{11} liquid, C_{12} & above are solids.
- (vii) Acetylene & 1-alkyne are acidic in nature. It is due to presence of active H.
- (viii) Order of Solubility, density, B.P., M.P. and Acidic nature : Alkyne > Alkene > Alkane * All terminal alkynes are acidic in nature.

4. Chemical Properties of Alkyne :

Electrophilic Addition to Alkynes :

4.1. Halogenation :

$$R - C \equiv C - R \xrightarrow{Br_2} (1 \text{ eq.}) \xrightarrow{R - C \equiv C - R} \xrightarrow{Br_1} Br_2 (1 \text{ eq.}) \xrightarrow{R - C - C - R} Br_1 \xrightarrow{Br_2} (1 \text{ eq.}) \xrightarrow{R - C - C - R} Br_1 \xrightarrow{Br_2} (1 \text{ eq.}) \xrightarrow{Br_1} Br_2 \xrightarrow{Br_2} (1 \text{ eq.}) \xrightarrow{Br_2} Br_2 \xrightarrow{Br_$$

4.2. Addition of HOX :

Alkynes + HOX
$$\longrightarrow \alpha, \alpha$$
-dihaloketone + α -haloketone
(90% major) (10% minor)
 $R - C = C - H \xrightarrow{HOX(leq.)} R - C = CH \xrightarrow{HOX} HOX \xrightarrow{OH} R - C - CHX_2$
 OH enol $(1 eq.)$ $R - C - CHX_2$
 OH $Gem-diol$
 $I = C - CH_2X$ $R - C - CHX_2$
 $0 = C - CH_2X$ $R - C - CHX_2$
 $0 = C$

Ex.
$$CH_3-C=CH \xrightarrow{Cl_2/H_2O} CH_3 - C = CH - CI \xrightarrow{HOCI} CH_3 - C - CHCI_2 \xrightarrow{-H_2O} CH_3 - C - CHCI_2$$

4.3. Addition of Hydrogen Halides (+ HX) :

$$R - C \equiv C - H \xrightarrow{HBr} (dark) \xrightarrow{R - C = C - H} \xrightarrow{HBr} R - \xrightarrow{Br}_{L} \xrightarrow{R - C = C - H} \xrightarrow{HBr} R - \xrightarrow{Br}_{L} \xrightarrow{R - C - CH_3} \xrightarrow{H}_{MK}$$

4.4. Addition of H₂O (Hydration Reaction) : (i) Mercuric ion catalyzed hydration :



AROMATIC HYDROCARBON

1. Introduction :

All organic compounds classify into two broad classes, aliphatic compounds and aromatic compounds. Aromatic compounds are those that resemble with benzene in chemical behaviour.

Proposed structure of benzene :







[Prism like structure proposed

Kekule benzene

Dewar's benzene by Albert Ladenberg]

* Benzene mostly represents by Kekule structure.

Comparison of Aromatic compounds with alkenes :

Benzene is not as reactive as alkenes. Alkene gives addition reaction while benzene gives substitution reaction.

$$H + Br_2 \longrightarrow H^H Br \Delta H^\circ = -29 \text{ kcal } (-121 \text{ kJ})$$

The analogous addition of bromine to benzene is endothermic because it requires the loss of aromatic stability. The addition is not seen under normal circumstances. The substitution of bromine in place of hydrogen atom gives an aromatic product. The substitution requires a Lewis acid catalyst to convert bromine into a stronger electrophile.





2. Aromatic Electrophilic Substitution (ArS_E2) Reactions in Benzene Ring

2.2 Effect of substituent groups in monosubstituted benzene :

(A) Ortho-para directing and activating groups :

All electron releasing groups (+m, +I) are ortho-para directing groups and activating towards electrophilic reactions.

(B) Ortho para directing but deactivating groups :

Halogens are deactivating but ortho-para directing groups.

Reactivity of benzene decreases by -I effect of halogens and ortho-para directing nature decided by +m effect of halogens.

(C) Meta directing and deactivating groups :

Mostly electron withdrawing groups (-m, -l) are meta directing groups and deactivating towards electrophilic reactions.

	Substituent groups	Reactivity (effect on rate)	Directing nature (effect on orientation)
1.	$-O^{-} > -NH_2 > -NHR$ > $-NR_2 > -OH$	Very strongly activating	Ortho-para directing
2.	0 0 ∥ ∥ –OR > – NH–C–R > –O–C–R	Strongly activating	Ortho-para directing
3.	–R, –Ar, –CH=CH ₂	Activating	Ortho-para directing
4.	–X(F, Cl,Br,I), –N=O, –CH ₂ X, –CHX ₂	Deactivating	Ortho-para directing
5.	O ∥ –CHO, –C–R, –COOH, –COOR, –COCI, –C≡N,–SO₃H	Strongly deactivating	Meta directing
6.	-NO ₂ , -NR ₃ , -SR ₂ , -CF ₃	Very strongly deactivating	Meta directing

2.4 Halogenation

• Bromine or chlorine itself is not sufficiently electrophilic to react with benzene so a strong Lewis acid such as FeBr₃ or AlCl₃ catalyzes the reaction.

• Iodination takes place in presence of oxidising agents like HNO₃ or HIO₃. Kinetic isotope effect is also observed in iodination reaction of benzene.

2.5 Nitration

• HNO_3 alone is a weak nitrating agent where as the mixture of concentrated HNO_3 and concentrated H_2SO_4 is strong nitrating mixture. In this mixture HNO_3 is act as base.

2.6 Sulphonation

Sulphur trioxide in sulphuric acid is used as the sulphonation agent.

2.7 Friedel Craft reaction

(a) Alkylation :

- Electrophile is carbocation.
- Alkylating agents are : RX + AlX₃ (lewis acid), Alkene in acidic medium and alcohol in acidic medium.

(b) Acylation :

• Electrophile is acylium ion.

• Acylation of benzene may be brought about with acid, acid chlorides or anhydrides in presence of Lewis acids.

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3. Benzene :

3.1 Preparation of Benzene

(1) By polymerisation of Acetylene :

$$3HC \equiv CH \xrightarrow{\text{Red hot iron tube}} Or, \text{ quartz tube}$$

(2) By decarboxylation of Benzoic acid : (mechanism S_E1)



(3) By catalytic reforming of n-Hexane :

$$CH_{3} - (CH_{2})_{4} - CH_{3} \xrightarrow{Pt, 873 \ K} \bigcup_{\text{cyclohexane}} \xrightarrow{Pt, 873 \ K} \bigcup_{\text{cyclohexane}} O(1)^{1/2} O(1)^{1/2$$

(4) By reduction of Benzene diazonium Chloride :

$$\bigcup^{N_2^+ \mathbb{C}I^-} + H_3 \mathbb{P}O_2 + H_2 \mathbb{O} \longrightarrow \bigcirc + N_2$$

(5) By reduction of Phenol :



(6) From Grignard reagent : MgCl



3.4 Chemical Reactions of Benzene :



Diketone also undergos the friedel craft reaction with benzene.