## **HYDROCARBONS**

Organic compounds composed of only carbon and hydrogen

Saturated Hydrocarbon (Al Kanes)

Represented by  $C_nH_{2n+2}$  (n = no of C-atoms) Called paraffins (parum = little; affinis = affinity) Bond angle is 109.5° or 109°28'

General methods of Preparation of Alkanes

1. Decarboxylation of carboxylic acids (Laboratory preparation)

An alkane is prepared by heating strongly the anhydrous sodium or potassium salt of a carboxylic acid with sodalime (NaOH + CaO).

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

$$\begin{array}{c} CH_{3}CH_{2}COONa + NaOH \xrightarrow{\Delta} CH_{3}CH_{3} + Na_{2}CO_{3} \\ Sodiumpropionate \end{array} \xrightarrow{Ethane} CH_{3}CH_{3} + Na_{2}CO_{3} \\ \end{array}$$

Note :

- (i) The alkane prepared contains one carbon atom less than that of the original acid.
- (ii) CaO increases the porosity of the mixture and acts as a dehydrating agent and catalyst.
- 2. Sabatier-Senderen's Reaction

Alkane may be obtained by the catalytic hydrogenation of alkenes or alkynes is presence Ni catalyst at  $200^{\circ}C - 300^{\circ}C$ .

$$\begin{array}{c} \mathbf{R} - \mathbf{CH} = \mathbf{CH}_2 + \mathbf{H}_2 \xrightarrow{\mathrm{Ni}} \mathbf{R} - \mathbf{CH}_2 \mathbf{CH}_3 \\ \text{Alkene} \end{array}$$

$$CH_{3}C \equiv CH + 2H_{2} \xrightarrow{\text{Ni}/\Delta} CH_{3}CH_{2}CH_{3}$$
  
Propyne Propane

Note :

- (i) Platinum or Palladium or Raney nickel may also be used as catalyst at ordinary temperature.
- (ii) Methane cannot be prepared by this method.

### 3. By the Reduction of Alkyl Halides :

Alkyl halides are directly reduced by either of the following reducing agent to form alkanes.

- (a)  $Zn/Cu + (C_2H_5OH)$
- (b) Zn + HCl
- (c)  $Zn + Acetic acid (CH_3COOH)$
- (d) LiAlH<sub>4</sub>

- (e) Red phosphorous and hydrogen iodide
- (f)  $H_2$  + nickel or palladium or platinum

$$\begin{array}{c} RX + 2H \xrightarrow{Zn+Cu} RH + HX \\ \hline Ethanol \\ halide \end{array}$$

4. Wurtz Reaction :

An ehterial solution of alkyl halide when treated with sodium metal forms alkane.

$$R - X + 2Na + X - R \xrightarrow{dry Ether} R - R + 2NaBr$$

$$H_3C-Br + 2Na + BrCH_3 \xrightarrow{dry \text{ ether}} CH_3CH_3 + 2NaBr$$
  
Methyl Bromide

Note :

(i) Wrutz Reaction is useful only for the preparation of symmetrical alkanes containing even number of carbon atoms.

(ii) When a mixture of two different alkyl halides are used a mixture of three alkanes are obtained.

- (iii) Methane cannot be prepared.
- (iv) This reaction fails with tertiary alkyl halides.
- 5. Clemmensen's Reduction :

Carbonyl compounds like aldehydes and ketones are reduced by amalgamated zinc and conc. HCl to produce the corresponding alkanes having the same number of carbon atoms.

$$\begin{array}{c} R \\ R \\ R \\ \end{array} \xrightarrow{ Zn-Hg+HCl} \\ R \\ \end{array} \xrightarrow{ R'} \\ CH_{3}COCH_{3} \\ \xrightarrow{ Zn-Hg+HCl} \\ Acetone \\ \end{array} \xrightarrow{ CH_{3}CH_{2}CH_{3} \\ Propane \\ \end{array}$$

6. Wolf-Kishner Reduction :

Carbonyl compounds can be reduced to hydrocarbons in presence of excess of hydrazine or semicarbazide and sodium alkoxide on heating.



7. Kolbe Reaction (Electrolytic Method) :

An alkane is prepared by the electrolysis of a concentrated aqueous solution of sodium or potassium salt of a saturated monocarboxylic acid using platinum electrodes.

$$2\text{RCOOK} + 2\text{H}_2\text{O} \xrightarrow{\text{Electrolysis}} \mathbf{R} \xrightarrow{-\mathbf{R}}_{444} \xrightarrow{2}_{442} \xrightarrow{2}_{443} + \underbrace{2\text{KQH}}_{\text{Solution Cathode}} + \underbrace{2\text{KQH}}_{\text{Solution Cathode}} \xrightarrow{\mathbf{R}}_{\mathbf{R}} \xrightarrow{\mathbf{R}}_{444} \xrightarrow{2}_{443} \xrightarrow{\mathbf{R}}_{\mathbf{R}} \xrightarrow{\mathbf{R}} \xrightarrow{\mathbf{R}}_{\mathbf{R}} \xrightarrow{\mathbf{R}}_{\mathbf{R}} \xrightarrow{\mathbf{R}} \xrightarrow{\mathbf$$

$$2CH_{3}COOK + 2H_{2}O \xrightarrow{\text{Electrolysis}} CH_{3}CH_{3} + 2CO_{2} + 2KOH + H_{2}$$
  
Ehtane

8. Frank Land Method :

The alkyl halide is heated with zinc in inert solvent.

 $RX + Zn + XR \longrightarrow R - R + ZnX_2$ 

$$\begin{array}{c} C_2H_5Br + Zn + BrC_2H_5 \longrightarrow C_4H_{10} + ZnBr_2\\ Ethyl & Butane\\ bromide \end{array}$$

9. By the reduction of alcohols, aldehydes, Ketones and Carboxylic acids, by red phosophorus and HI

$$R - OH + 2HI \xrightarrow{\text{Red P}} RH + I_2 + H_2O$$

$$R - CHO + 4HI \xrightarrow{\text{Red P}} RCH_3 + 2I_2 + H_2O$$

$$CH_3COCH_3 + 4HI \xrightarrow{\text{Red P}} 250^{\circ}C \rightarrow CH_3CH_2CH_3 + 2I_2 + H_2O$$

$$R - COOH + 6HI \xrightarrow{\text{Red P}} R - CH_3 + 3I_2 + 2H_2O$$

10. By the Decomposition of Grignard Reagents :

A Grignard reagent can be decomposed by active hydrogencontaining compound to produce alkane.

$$RMgX + HOH \xrightarrow{Ether} R - H + Mg(OH)X$$

$$RMgX + R' - OH \xrightarrow{Ether} R - H + Mg(OR')X$$

11. Corey-House Alkane Synthesis :

Symmetrical as well as unsymmetrical alkanes can be prepared by the action of alkyl halides with an etherial solution of lithium dialkyl cuperate (LiR<sub>2</sub>Cu)

$$RX + 2Li \xrightarrow{Ether} 2RLi + LiX$$

$$2RLi + CuI \longrightarrow LiR_{2}Cu + LiI$$
Lithium
dialkyl Cuprate

$$\text{LiR}_2\text{Cu} + \text{R'Br} \longrightarrow \begin{array}{c} \text{R} - \text{R'} + \text{R} - \text{Cu} + \text{LiBr} \\ \text{Alkane} \end{array}$$

Note :  $\mathbf{R}$ ' should be mainly  $1^{\circ}$ .

Examples :

$$CH_{3}Br + 2Li \xrightarrow{Ether} CH_{3}Li + LiBr$$

$$2CH_{3}Li + CuI \longrightarrow Li (CH_{3})_{2} Cu + LiI$$

$$Li (CH_{3})_{2} Cu + C_{2}H_{5}Br \longrightarrow C_{2}H_{5} - CH_{3} + CH_{3}Cu + LiBr$$
Propane

12. Hydroboration of Alkenes :

Diborane  $(B_2H_6)$  reacts with alkenes to form trialkyl-boranes which on treatment with acetic acid or propionic acid yields corresponding alkane.

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

13. By Cycloalkane :

Cycloalkanes can be reduced to alkanes by cleavage of C - C bond which minimises the strain.



14. Hydrolysis of Metal Carbides :

$$Al_4C_3 \xrightarrow{H_2O} Al(OH)_3 + CH_4$$

$$\operatorname{Be}_2 C \xrightarrow{\operatorname{H}_2 O} \operatorname{Be}(OH)_2 + CH_4$$

N.B. :

This method is applied only for methane.

### PROPERTIES

A. Physical Properties

First four members are gases, next 13 members are colourless liquids and rest are solids.

The alkanes are insoluble in water but soluble in organic solvents like ether, carbon tetrachloride, benzene etc.

The density and boiling points increase with the increase of molecular weights. The boiling points of isomeric branched chain alkanes, are generally lower than those of straight chain alkanes.

## B. Chemical Properties

Alkanes are generally stable and chemically inert. The C - H and C - C bonds in alkanes are almost non-polar, attacking reagents find no reaction sites to which they could be attacked.

Under suitable conditions the alkanes undergo two types of reactions

- (a) Free radical substitution Reaction
- (b) Thermal; and Catalytic Reaction

### (a) Substitution reaction

1. Halogenation :

In presence of diffused sunlight or in ultra violet light or at relatively high temperature  $(300^{\circ}C - 500^{\circ}C)$  the Hatoms (1°, 2°, 3° H) of alkanes are replaced by equal number of halogen atoms yielding a mixture of halogenated alkanes.

(i) Chlorination : (Free Radical Substitution)

$$\begin{array}{c} CH_4 + Cl_2 & \xrightarrow{UV-light} & CH_3Cl + HCl \\ Excess & & & CH_3Cl + HCl \\ Chloromethane \\ (Methylchloride) \end{array}$$

$$CH_{3}Cl + Cl_{2} \xrightarrow{UV-light} CH_{2}Cl_{2} + HCl_{Dichloromethane}$$

$$CH_{2}Cl_{2} + Cl_{2} \xrightarrow{UV-light} Or \Delta \xrightarrow{CHCl_{3} + HCl} CHCl_{3} + HCl Trichloromethane (Chloroform)$$

$$CHCl_{3} + Cl_{2} \xrightarrow{UV-light} or \Delta \xrightarrow{CCl_{4}} + HCl$$
Carbon tetrachloride
(Pyrene)

Note : Methyl Chloride is the major product if an excess of methane is used.

(ii) Bromination : Bromine reacts with alkanes in a similar manner but less vigorously.

(iii) Iodination : The reaction between iodine and alkane is reversible. Iodination can be done in the presence of an oxidising agent such as  $HIO_3$  (or  $HNO_3$ ) which removes the hydroiodic acid (HI).

$$CH_4 + I_2 \ddagger \uparrow \dagger CH_3I + HI$$
  
$$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$$

(iv) Fluorination : Fluorine reacts with alkanes at ordinary temperature explosively. So fluorination can be done by diluting fluorine with an inert gas or indirectly.

$$2C_2H_5Br + HgF_2 \longrightarrow 2C_2H_5F + HgBr_2$$

2. Nitration : A mixture of an alkane and nitric acid vapours is heated at 400°C − 500°C, one hydrogen atom of the alkane is replaced by a nitro group. This reaction is also free radical substitution.

$$\begin{array}{c} R - H + HO - NO_2 \longrightarrow R - NO_2 + H_2O \\ \text{Nitric Acid} & \text{Nitroalkane} \end{array}$$

$$\begin{array}{c} CH_4 + HNO_3 \\ (VapourphaseNitration) & \xrightarrow{400^{\circ}C - 500^{\circ}C} \\ CH_3 - NO_2 + H_2O \\ Nitromethane \end{array}$$

N.B. : This temperature  $(400^{\circ}C - 500^{\circ}C)$  is sufficient to break C–H as well as C–C bond homolytically and thus mixture of products are obtained.

$$CH_{3}CH_{3} + HONO_{2} \xrightarrow{400^{\circ}C - 500^{\circ}C} CH_{3}CH_{2}NO_{2} + CH_{3}NO_{2} + H_{2}O$$
Nitroethane Nitromethane

3. Sulphonation : Sulphonation is carried out with fuming  $H_2SO_4$ .

$$R-H+ HO-SO_{3}H \xrightarrow{\Delta} R-SO_{3}H + H_{2}O$$
  

$$\xrightarrow{\text{Fuming}} Alkane Sulphonic Acid$$

Note :  $R = C_6 H_{13}$  or larger alkyl group

- 4. Oxidation :
  - (i) Complete Combustion :

In the presence of excess oxygen alkane burn to form carbon dioxide water.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + 212.8 \text{ Kcal/mole}$$
  
Methane

Note: 
$$C_nH_{2n+2} + \frac{3n+1}{2}O_2 \xrightarrow{\text{Flame}} nCO_2 + (n+1)H_2O + \text{Heat}$$

$$2CH_3CH_3 + 7O_2 \longrightarrow 4CO_2 + 6H_2O + 745.6$$
 Kcal/mole

(ii) Incomplete Combustion :

$$2CH_4 + 3O_2 \longrightarrow 2CO + 4H_2O$$
$$CH_4 + O_2 \longrightarrow \begin{array}{c} C \\ Carbon \\ black \end{array} + 2H_2O$$

(iii) Catalytic Oxidation :

I. 
$$CH_4 + O_2 \xrightarrow{Cu-tube}{200^\circ,100 \text{ atm.}} 2CH_3OH$$
  
Methyl alcohol

II. Alkane having  $3^{\circ}$  H on oxidation with KMnO<sub>4</sub> gives  $3^{\circ}$ -alcohol.

$$\begin{array}{cccc} & & & & & & & & \\ CH_3 - \begin{array}{c} & & & & & \\ &$$

III. Higher alkane on oxidation with manganese acetate gives carboxylic acids.

 $R-CH_{3} \xrightarrow{(CH_{3}COO)_{2}Mn} R-COOH$ 

IV. 
$$CH_4 + O_2 \xrightarrow{MO_2O_3} HCHO + H_2O$$

5. Isomerisation : Normal alkanes are converted to their branched chain isomers in the presence of aluminium chloride and HCl at 25°C.

$$CH_{3} - CH_{2} - CH_{2} - CH_{3} \xrightarrow[HCl]{AlCl_{3}} CH_{3} - CH - CH_{3}$$

$$Isobu tane (2-Methylpropane)$$

6. Prolysis (Cracking) : Decomposition of higher alkane into amixture of lower alkanes, alkenes and hydrogen on heating at high temperature in the absence of air.

$$3CH_3CH_3 \xrightarrow{500^{\circ}C} 2CH_2 = CH_2 + 2CH_4 + H_2$$
  
Ethylene Methane

N.B. : In the presence of finely divided silica-alumina as catalyst, this reaction can be carried atless high temperature. This is called catalytic cracking.

7. Aromatisation:

$$CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}CH_{3} \xrightarrow{Cr_{2}O_{3} + Al_{2}O_{3}}{600^{\circ}C, 10 \text{ atm}} + 4H_{2}$$

$$CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{3} \xrightarrow{Pt-Al_{2}O_{3}}{600^{\circ}C, 10 \text{ atm}} + 4H_{2}$$

8. 
$$CH_4 + H_2O \xrightarrow{\text{Ni on alu min a}} 1000^{\circ}C \xrightarrow{\text{Synthesis gas}} Synthesis gas$$

9. 
$$2CH_4 \xrightarrow{1500^{\circ}C} 2HC \equiv CH + 3H_2$$
  
Acetylene

10. 
$$CH_3CH_3 \xrightarrow{Al_2O_3 + Cr_2O_3}{500^{\circ}C - 600^{\circ}C} \rightarrow CH_2 = CH_2 + H_2 \uparrow Ethylene$$

11. Reaction with Alkenes

$$CH_{3} - CH_{3} + CH_{2} = C - CH_{3} \longrightarrow CH_{3} - CH_{2} - CH_{2} - CH_{3} - CH_{3}$$

Uses :

 $C_1$  to  $C_4$  alkanes are used as domestic fuels.

In the manufacture of fuels.

Gasoline (petrol) is a mixture of alkanes alkenes and aromatic hydrocarbons. The quality of gasoline is determined by the amount of iso-octane (2, 2, 4-trimethyl pentane) present in it.

Methane is used in the manufacture of carbon black used in printer's ink, black paints etc.

## ALKENE

H - C - C or H - C - H bond angle in ethylene is  $120^{\circ}$ .

C = C bond distance in ethylene is 1.34 Å

Alkenes are generally very active and due to the presence of pie-bond they exhibit addition reactions.

$$120^{\circ}$$
  $\overset{H}{\underset{H}{\overset{\bullet}}}C$   $\overbrace{1.34\mathring{A}}^{\overset{\bullet}}C$   $\overset{H}{\underset{H}{\overset{\bullet}}}H$ 

Generally represented by the general formula  $C_nH_{2n}$ .

### Preparation

1. By the dehydration of alcohols :

$$CH_{3}CH_{2}OH \xrightarrow{Conc.H_{2}SO_{4}}{160^{\circ}C-180^{\circ}C} CH_{2} = CH_{2} + H_{2}O$$

$$\xrightarrow{Syrupy Phosphoric acid}{\Delta} CH_{2} = CH_{2} + H_{2}O$$

$$\xrightarrow{Al_{2}O_{3}}{350^{\circ}-400^{\circ}C} CH_{2} = CH_{2} + H_{2}O$$

Note :

- (i) Here conc.  $H_2SO_4$  acts as a dehyderating agent as well as catalyst.
- (ii) The ease of dehydration of alcohols is

Tertiary alcohol > Secondary alcohol > Primary alcohol



Note : Saytzeff's Rule :

During the dehydration of unsymmetrical alcohols the hydrogen atom is preferentially eliminated from that carbon atom which contains lesser number of hydrogen atoms (Dehydrohalogenation)

2. By the Removal of Hydrogen Halides from Alkyl Halides :

$$R - CH_2CH_2X \xrightarrow{Alc.KOH} R - CH = CH_2 + KX + H_2O$$
  
Alkyl halide

### MECHANISM



For unsymmetrical alkyl halide.

$$CH_{3}CHBrCH_{2}CH_{3} \xrightarrow{Alc. KOH} CH_{3}CHBrCH_{2}CH_{3} \xrightarrow{Alc. KOH} CH_{2} = CHCH_{2}CH_{3}$$

 $CH_2 = CH - CH_2 - CH_3$  and it is Hoffmann's product. Ease of reactivity is R - I > R - Br > R - Cl

3. By Kolbe's Electrolytic Method : When concentrated aqueous solution sodium or potasium salt of vicinal saturated dicarboxylic acid is electrolysed, the alkene and  $CO_2$  liberate at anode where as alkali and  $H_2$  at cathode.

$$R - CHCOOK$$

$$| \qquad \hat{\ddagger} \uparrow^{\uparrow} R - CH = CH - R' + 2CO_2$$

$$R' - CHCOOK$$

4. By the Partial Hydrogenation of Alkynes :

$$R - C \equiv C - R' + H_2 \xrightarrow[]{Pd-CaCO_3} R - CH = CH - R'$$
  
Quinoline  
or, Ni<sub>2</sub>-B(P-2)

Note :

(i) Lindlar's Catalyst : Finely divided palladium or platinum deactivated by poisons like  $BaSO_4$ ,  $CaCO_3$  or quinoline. Partial reduction with Lindlar's catalyst gives cis alkene

- (ii) P-2 Catalyst = Nickel boride also gives cis-alkene.
- (iii) Birch Reduction : Partial hydrogenation with Na and liquid  $NH_3$  produces trans alkene.

$$R - C = C - R + [H] \xrightarrow{Na/Liq.NH_3} \stackrel{R}{\underset{H}{\longrightarrow}} C = C \stackrel{H}{\underset{R}{\swarrow}} R$$

(iv)  $B_2H_6$  followed by treatment with  $CH_3COOH$  will give cis-alkene

4. By the dehalogenation of vicinal di-halides with Zn-dust in alcohol or NaI in acetone

$$\begin{array}{ccc} R - CH - CH - R' & \xrightarrow{Zn-dust} & R - CH = CH - R' + ZnBr_2 \\ Br & Br & \\ & \\ & & \\$$

7. By Dehydrogenation of Alkanes :

$$CH_3 - CH_2 - CH_2 - CH_3 \xrightarrow{Cr_2O_3 \cdot Al_2O_3} CH_3 - CH = CH - CH_3 + H_2$$
  
n-Butane But-2-ene

### Properties

At room temperature,  $C_2 - C_4 \rightarrow$  Gases

 $C_5 - C_{13} \rightarrow Liquids$ 

 $C_{13}$  Onwards  $\rightarrow$  Solids

Gaseous alkenes are colourless and odourless. Only ethylene has a sweet smell.

All the alkenes are soluble in organic solvents like ether, benzene, etc.

The densities and boiling points increase with the increase of molecular weights. Their b.p. and m.p. are higher than corresponding alkanes. Cis-isomer has a higher boiling point than trans-isomer due to higher polarity whereas trans alkene has higher melting point than cis alkene.

### Chemical :

Following types of reactions are given by alkenes

- 1. Addition Reaction (Electrophillic & radical addition)
- 2. Oxidation
- 3. Ozonolysis
- 4. Isomerisation
  - 5. Substitution at  $\alpha$  carbon
  - 6. Polymerisation

### 1. Addition Reaction

(a) Addition of HX(HCl, HBr and HI)

Electrophilic addition reaction.

Product of formation takes place according to Markovnikov's rule.

$$CH_3 - C = CH_2 + HI \longrightarrow CH_3 - \begin{array}{c} I \\ CH_3 \\ CH_3 \end{array} - \begin{array}{c} CH_3 \\ CH_3 \end{array}$$

Note : Monosubstituted and disubstituted alkenes whose  $\alpha$  – carbon is 4° give addition reaction through rearrangement.

$$CH_{3} - CH_{3} - CH_{2} - CH = CH_{2} + HBr \longrightarrow CH_{3} - CH_{3} -$$

Mechanism :

$$CH_{3} - C - CH = CH_{2} + H^{+} \xrightarrow{slow} CH_{3} - C - CH - CH_{3}$$

$$CH_{3} - C - CH - CH_{3} \xrightarrow{CH_{3}} H^{-} CH_{3} \xrightarrow{H^{-}} CH_{3} \xrightarrow{H^{-}} CH_{3} - CH_{3} \xrightarrow{H^{-}} CH_{3}$$

Product according to Anit Markownikoff's rule. (Free radical addition)

$$CH_3CH = CH_2 + HBr \xrightarrow{(C_6H_5COO)_2} CH_3CH_2CH_2Br$$

(b) Addition Reaction of Water : (Catalysed by acid) (Electrophillic addition)

$$R - CH = CH_2 + HOH \xrightarrow{H_2SO_4} R - CH - CH_3$$

Mechanism is exactly same as that of previous reaction.

(c) Addition Reaction of Conc. 
$$H_2SO_4 \begin{bmatrix} O \\ H - O - S - O - H \\ \| \\ O \end{bmatrix}$$
 (Electrophillic addition)

$$R - CH = CH_2 \xrightarrow[]{Conc.H_2SO_4} R - CH - CH_3$$

$$R - CH - CH_3$$

$$Alkyl hydrogen Sulphate$$

 $\begin{array}{c} OSO_{3}H & OH \\ | \\ R - CH - CH_{3} + HOH \longrightarrow R - CH - CH_{3} + H_{2}SO_{4} \end{array}$ 

(d) Addition of Hydrogen (Hydrogenation) :

$$R - CH = CH_2 \xrightarrow{\text{Ni,Pt or Pd}} R - CH_2CH_3$$

(e) Addition of Halogens : (Electrophillic addition)

$$R - CH = CH_{2} + Br_{2} \xrightarrow[\text{CCl}_{4}]{} CH_{2}Br - CH_{2}Br$$
Brown 
$$(Inert \text{ solvent}) \xrightarrow[\text{Colourless}]{} Ethylene \text{ bromide } (colourless)$$
(Test for Unsaturation)

This reaction proceeds via cyclic intermediate that's why their no chance of rearrangement and it is anti addition.

(f) Addition of hypohalous acids :

$$CH_2 = CH_2 + HOCl \longrightarrow CH_2OHCH_2Cl$$
  
Ethylene Chlorohydrin

Follow electrophillic addition via cyclic intermediati as in previous reaction.

(g) Hydroboronation oxidation :

$$6CH_3 - CH = CH_2 + B_2H_6 \longrightarrow 2(CH_3CH_2CH_2)_3 B$$

$$(CH_3CH_2CH_2)_3B+3H_2O_2 \xrightarrow{OH^-} 3CH_3CH_2CH_2CH_2OH+H_3BO_3$$

Overall result of above reaction is anti Markonikoff addition of  $H_2O$  with Syn Stereochemistry.

(h) Oxy-Mercuration demercuration :

$$(CH_3)_3 C-CH = CH_2 \xrightarrow{(CH_3COO)_2 Hg/H_2O}_{THF} (CH_3)_3 C-CH-CH_2 \cdot HgOOCCH_3$$
  
3,3-Dimethylbut-1-ene  

$$(CH_3)_3 C-CH-CH_2 \cdot HgOOCCH_3$$
  

$$OH \qquad \downarrow NaBH_4, NaOH$$
  

$$(CH_3)_3 C-CH-CH_3$$
  

$$OH$$
  
3,3-Dimethyl-2-bu tanol

Overall result of above reaction is Markonikoff's addition of  $H_2O$  without rearrangement chance and with anti stereochemistry.

### 2. OXIDATION

- (a) Addition of Oxygen :  $R - CH = CH_2 + {}_{2}^{1}O_2 \xrightarrow{Ag} R - CH - CH_2 \xrightarrow{H_2O/H^*} R - CH - CH_2$ oxirane  $R - CH - CH_2 \xrightarrow{H_2O/H^*} R - CH - CH_2 \xrightarrow{H_2O/H^*} R - CH - CH_2$
- (b) Reductive ozonolysis :

$$> C = C < +O_3 \xrightarrow{CCl_4} > C \xrightarrow{O} \xrightarrow{C} C > \xrightarrow{Zn/H_2O} > C = O + O = C < Carbonyl Compounds$$

Note Zn-dust is added to prevent the oxidation of aldehyde into carboxylic group by  $H_2O_2$ 

(c) Oxidative Ozonolysis :

$$CH_3 - CH = \underset{\substack{| \\ CH_3}}{CH_3} - CH_3 \xrightarrow{1.0_3}{2.H_2O} CH_3 - C - OH + CH_3 - \overset{O}{C} - CH_3$$

(d) Hydroxylation :

$$R - CH = CH - R' \xrightarrow{Hydroxyllating} R - CH = CH - R' \xrightarrow{Hydroxyllating} R - CH - CH - R$$

Hydroxylating agent

1. Cold dilute alkaline  $KMnO_4$ 

2. 
$$OsO_4/H_2O_2$$
  
 $O$   
 $B$   
 $B$   
 $R - C - O - OH / H_3O^+$ 

(e) Wacker Process :

$$CH_3 - CH_2 - \overset{2}{C}H = \overset{1}{C}H_2 \xrightarrow{PdCl_2 / HOH} CH_3 - CH_2 - \overset{O}{C}H_3 - CH_2 - \overset{O}{C}H_3$$

(f) Oxidation with hot basic  $KMnO_4$ .

In this reaction =  $CH_2$  part gets oxidised to  $CO_2$  and  $H_2O_2$  = CHR part gets oxidised to RCOOH and =  $CR_2$  part gets oxidised  $\frac{R}{R} \ge C = O$ 

$$CH_3 - CH = CH - CH_3 \xrightarrow{KMnO_4 / OH^- / \Delta} CH_3COOH + CH_3COOH$$

(g) Combustion :

$$C_{n}H_{2n} + \frac{3n}{2}O_{2} \longrightarrow nCO_{2} + nH_{2}O$$
$$C_{2}H_{4} + 3O_{2} \longrightarrow 2CO_{2} + 2H_{2}O$$

#### 3.SUBSTITUTION AT - CARBON

(a) Allyllic oxidation :

$$CH_3 - CH = CH_2 \xrightarrow{SeO_2} CH_2 - CH = CH_2$$
  
Allyl alcohol

$$CH_3 - CH_2 - CH - CH = CH_2 \xrightarrow{SeO_2} CH_3 - CH_2 - CH_2 - CH_2 = CH_2$$

(b) Allylic halogenation :

$$CH_3 - CH = CH_2 \xrightarrow[]{NBS/CCl_4} or X_2/\Delta \xrightarrow[]{NBS/CCl_4} CH_2 - CH = CH_2$$
  
Allyl bromide

Uses

Ethylene is used in the preparation of polythene and also used in the manufacture of synthetic rubber, ethylene di chloride and mustard gas.

Ethene is used for artificial ripening of fruits.

Ethene is used as a general anaesthetic.

## ALKYNES

General formula  $-C_nH_{2n-2}$ The C – H bonds are formed by the overlapping of sp hybrid orbital of one carbon atom and s-orbital of

 $H \xrightarrow{1.06 \text{\AA}} C \xrightarrow{180^{\circ}} C \longrightarrow H$ hydrogen atom  $C \equiv C$  distance is 1.20Å and C – H bond length is 1.08Å

H - C - C bond angle is  $180^{\circ}$ 

General Methods of Preparation of Alkynes

By the reaction of calcikum carbide with water : 1.

$$C C + 2HOH \xrightarrow{\text{Room Temp.}} H - C \equiv -H + Ca (OH)_2$$
  
Acetylene

Calcium carbide

2. Dehydrohalogenation of Vicinal Dihalides

$$R - C - C - C - H - H \xrightarrow{(i) \text{ Alc.KOH } / \Delta} R - C = H + 2HBr$$
  
Br H

$$R - C - C - C - H \xrightarrow{NaNH_2 / \Delta} R - C \equiv C - H + 2HBr$$
  
Br H

3. Dehalogenation of Tetrahalides :

$$\begin{array}{ccc} X & X \\ | & | \\ R - C - C - C - R + 2Zn & \xrightarrow{Alcohol} & R - C \equiv C - R + 2ZnX_2 \\ | & | \\ X & X \\ Tetrahalide \end{array}$$

4. Reaction of sodium acetylides with primary alkyl halides :

 $H-C \equiv C-Na+CH_3Br \longrightarrow CH_3-C \equiv CH+NaBr$ 

5. Kolbe's Method :

CHCOONa  $\begin{array}{c} +2H_2O, Current \\ CHCOONa \\ Sodium Salt of \\ maleic acid or \\ fumaric acid \end{array} HC \equiv CH + 2CO_2 + 2NaOH + H_2$ 

6. By heating Iodoform with Silver

$$CHI_3 + 6Ag + I_3CH \longrightarrow CH = CH + 6AgI$$

### Properties

A. PHYSICAL

The first three members are gases. The next 8 members are liquids and the rests are<br/>Alkynes are slightly soluble in water but dissolves in organic solvents like acetone,solids.<br/>benzen,

ethanol.

B. CHEMICAL

Alkynes give two types of chemical reaction

1. Reaction due to acidic hydrogen and

2. Reaction due to  $\pi$ -bonds.

1. Reaction due to Acidic Hydrogen

(a) 
$$R - C \equiv C - H \xrightarrow{\text{NaNH}_2} R - C \equiv C^- \text{Na}^+ + \frac{1}{2}H_2$$

(i) 
$$CO_2(solid) \rightarrow R - C \equiv C - COOH$$
  
(ii)  $H_2O/H^+ \rightarrow R - C \equiv C - CH_2 - R'$   
(i)  $R - C \equiv CNa \xrightarrow{(i) R' - C - R''} R - C \equiv C - CH_2 - R'$   
(ii)  $H_2O/H^+ \rightarrow R - C \equiv C - CH_2 - R'$   
(ii)  $H_2O/H^+ \rightarrow R - C \equiv C - CH_2 - R'$   
(ii)  $H_2O/H^+ \rightarrow R - C \equiv C - CH_2 - R'$   
(ii)  $H_2O/H^+ \rightarrow R - C \equiv C - CH_2 - R'$   
(ii)  $H_2O/H^+ \rightarrow R - C \equiv C - CH_2 - R'$   
(ii)  $H_2O/H^+ \rightarrow R - C \equiv C - CH_2 - R'$   
(ii)  $H_2O/H^+ \rightarrow R - C \equiv C - CH_2 - R'$   
(b)  $R - C \equiv C - H \xrightarrow{(AgNO_3/N_4OH)} R - C \equiv C - CH_2 - R'$   
(b)  $R - C \equiv C - H \xrightarrow{(AgNO_3/N_4OH)} R - C \equiv C - Ag\psi$   
(c)  $AuCl/N_4OH \rightarrow R - C \equiv C - Ag\psi$   
(c)  $AuCl/N_4OH \rightarrow R - C \equiv C - Au\psi$   
(c)  $AuCl/N_4OH \rightarrow R - C \equiv C - Au\psi$   
(c)  $AuCl/N_4OH \rightarrow R - C \equiv C - Au\psi$   
(c)  $AuCl/N_4OH \rightarrow R - C \equiv C - Au\psi$ 

(c) Reaction with Grignard reagent and alkyl lithium :  

$$R - C \equiv C - H \xrightarrow{CH_{3}MgBr} R - C \equiv C - MgBr + CH_{4}$$

$$R - C \equiv C - H \xrightarrow{CH_{3}-Li} R - C \equiv C - Li + CH_{4}$$
Organolithium

2. Reaction due to -bonds (Addition Reaction of Alkynes) Alkynes generally gives electrophilic addition reaction and are less reactive than alkene for electrophilic addition reaction due to following reason

$$R - CH = CH_2 + H^+ \longrightarrow R - CH - CH_3$$
Alkene
(I)
Alkyl carbocation

$$R - C \equiv C - H + H^{+} \longrightarrow \begin{array}{c} R - \overset{+}{C} = CH_{2} \\ (II) \\ Vinyl \ carbocation \\ less \ stable \ than \ (I) \end{array}$$

They also give nucleophilic addition reactions with HOH, HCN, ROH, RCOOH etc.

I. Electrophilic Addition Reaction (a) Addition of HOX :

$$R-C \equiv C-H+HO-X \longrightarrow R- C = CH \xrightarrow{HO-X} R - C = CH \xrightarrow{HO-X} R - C = CH - CH - X$$

(b) Addition of HX :

$$R - C \equiv C - R + HX \longrightarrow \begin{array}{c} R \\ X \end{array} \xrightarrow{} C = C \begin{array}{c} X \\ R \end{array} \xrightarrow{} HX \\ R \xrightarrow{} R - CH_2 - \begin{array}{c} C \\ -R \\ \vdots \\ x \\ gem - dihalide \end{array}$$

Note : order of reactivity of HX is HI > HBr > HCl (c) Addition of  $X_2$  (Cl<sub>2</sub>, Br<sub>2</sub> and I<sub>2</sub>) :

$$R-C \equiv C-R+X_2 \xrightarrow{CCl_4} \underset{H}{\overset{R}{\longrightarrow}} C = C \xrightarrow{X} \underset{R}{\overset{X_2/CCl_4}{\longrightarrow}} \underset{X X}{\overset{R}{\longrightarrow}} R \xrightarrow{CCl_4} R \xrightarrow{R} \underset{I}{\overset{K}{\longrightarrow}} R$$

Note : The reactivity order of Halogen is  ${\rm Cl}_2 \! > \! {\rm Br}_2 \! > \! {\rm I}_2$ 

II. Nucleophilic Addition Reaction (a) Addition of water

$$R - C \equiv CH + HOH \xrightarrow{HgSO_4 / H_2SO_4} R - C \equiv CH_2$$

$$R - C \equiv CH_2$$

$$R - C = CH_3$$

(b) Addition of HCN :

$$R - C \equiv C - H + HCN \xrightarrow{Ba(CN)_2} R - \stackrel{CN}{C} = CH_2$$

(c) Addition of  $CH_3 - C - OH$ :

- 3. Other Reactions :
  - I. Oxidation of Alkynes (a) Baeyer's Test :

$$R - C \equiv C - R \xrightarrow{KMnO_4 / OH^- / HOH} R - C - C - R$$
  
Cold & dil 
$$R - C - C - R$$

(b) Oxiation by  $SeO_2$ :

II. Coupling Reaction (linear polymerisation)

 $H-C \equiv C-H+H-C \equiv C-H \xrightarrow{Cu_2Cl_2} H_2C = CH-C \equiv CH$ Vinylaccetylene

III. Isomerisation

(a) 
$$CH_3 - C \equiv C - CH_3 \xleftarrow{alc.KOH} CH_3 - CH_2 - C \equiv CH$$
  
 $\downarrow NaNH_2$   
 $CH_3 - CH_2 - C \equiv CNa$ 

IV. Oxidative ozonolysis

$$R - C \equiv C - R' \xrightarrow{O_3} R - C \xrightarrow{I} C - R' \xrightarrow{H_2O} R - C - C - R'$$

$$0 \xrightarrow{I} C - R' \xrightarrow{H_2O} R - C - C - R'$$

$$0 \xrightarrow{I} U \xrightarrow{I} U \xrightarrow{I} U$$

$$0 \xrightarrow{I} U \xrightarrow{I} U$$

$$H_2O_2$$

$$R - COOH + R'COOH$$

e.g. 
$$CH_3C \equiv C - H \xrightarrow{(i)O_3} CH_3COOH + [HCOOH]$$
  
Acetic Acid Formic Acid  
 $\downarrow [O]$   
 $CO_2 + H_2O$ 

V. Reductive ozonolysis

$$R - C = C - R' \xrightarrow{O_3} R - C \xrightarrow{I} C - R' \xrightarrow{H_2O + Zn} R - C - C - R'$$

$$CH_{3} - C \equiv CH \xrightarrow{O_{3}} CH_{3} - C \xrightarrow{P} CH_{3} - CH_{3} \xrightarrow{P} CH_{3} - COCHO$$
Propyne
$$CH_{3} - C \equiv CH \xrightarrow{O_{3}} CH_{3} - COCHO$$
Methyl glyoxal

Uses :

(a) It is used for the production of oxy-acetylene flame, which is employed for cutting welding of metals. it provides the temperature above 300°C.

(b) Acetylene on electrical decomposition produces finely divided carbon and hydrogen.

Hydrogen is used in air ships.  $C_2H_2 \rightarrow 2C + H_2$ 

(c) It is used for the preparation of Westron and Westrosol (solvents).

 $\begin{array}{c} CH \\ \parallel \\ CH \end{array} + Cl_2 \longrightarrow \begin{array}{c} CHCl_2 \\ \mid \\ CHCl_2 \\ (Western) \end{array} \xrightarrow{Alc.KOH} \begin{array}{c} CHCl \\ \parallel \\ CCl_2 \\ (Westrosol) \end{array}$ 

## AROMATIC HYDROCARBON

Methods of Preparation :

1. Hydrofroming or Catalytic reforming :

2. High Temperature Cracking :

$$H_2C = CH - CH = CH_2 + CH_2 = CH_2 \xrightarrow{\text{Metal Oxide}} O^{-2H_2} \xrightarrow{\text{Order}} O^{-2H_2} \xrightarrow{\text{Benzene}} O^{-2H_2} \xrightarrow{\text{Benzene}}$$

3. Laboratory Method :



4. From Chlorobenzene :



5. From Benzenediazonium Chloride :

a n d



6. From Phenol:



## CHEMICAL PROPERTIES

- A. Electrophilic Aromatic Substitution -
- 1. Nitration



2.







Friedal Craft's Reaction 3.



4. Halogneation :



Electrophile

- B. Addition Reaction
- 1. Addition of Hydrogen :



2. Addition of Halogens :



- 3. Oxidation Reaction :
  - (a) Ozonolysis :



(b) Vapour Phase Oxiation :





Other Reaction

1. Gattermann Koch Aldehyde Synthesis :



2. Gattermann Aldehyde Synthesis :



Uses of Benzene :

It is used as a solvent for oils and fats. As synthethic liquid by mixing with petrol. For the manufacture of toluene, nitrobenzene, acetophenone, etc.

# TOLUENE OR METHYL BENZENE

## **PREPARATION:**

1. From Benzene



2. Wurtz Fittig Reaction



## 3. Aromatisation Reaction



## 4. From Grignard Reagent



iodide



5. From Tolueic Acid



## Properties

Toluene gives three types of Reaction

(a) Side Chain Reaction

- (c) Reduction Reaction
- A. Side Chain Reaction 1. Chlorination

(b) Nuclear Chain Reaction



2. Side Chain Oxidation







- B. Reduction :
  - 1. Total Reduction



2. Birch Reduction :



- C. Nuclear Chain Reaction :
  - 1. Nitration :





2. Reaction with Halogen :



3. Friedal Craft's Reaction :



4. Sulphonation :

