SCHOOL OF ARTS AND SCIENCE

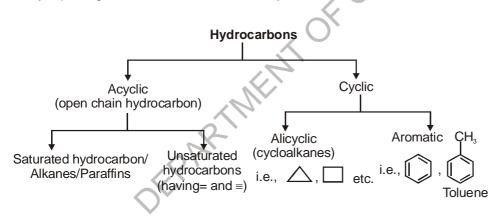
DEPARTMENT OF CHEMISTRY

Hydrocarbons

Classification, isomerism, IUPAC nomenclature, general methods of preparation, properties and reactions. **Alkanes** - Conformations : Sawhorse and Newman projections (of ethane); Mechanism of halogenation of alkanes. **Alkenes** - Geometrical isomerism; Mechanism of electrophilic addition: addition of hydrogen, halogens, water, hydrogen halides (Markownikoff's and peroxide effect); Ozonolysis, oxidation, and polymerization. **Alkynes** - Acidic character; Addition of hydrogen, halogens, water and hydrogen halides; Polymerization. **Aromatic hydrocarbons** - Nomenclature, benzene - structure and aromaticity; Mechanism of electrophilic substitution: halogenation, nitration, Friedel – Craft's alkylation and acylation, directive influence of functional group in mono-substituted benzene.

HYDROCARBONS AND THEIR CLASSIFICATIONS

Compounds of only Carbon and Hydrogen are called hydrocarbons. They are parent organic compounds and all other organic compounds have been derived by replacing one or more H atoms from hydrocarbon.



ALKANES

Methods of Preparation :

- I. Reactions where number of carbon atoms are increased
 - 1. Wurtz Reaction

 $2R - X + 2Na \xrightarrow{dry ether} R - R + NaX$

Here other metals in the finely divided state may also be used such as Cu, Ag etc.

- (i) Methane cannot be prepared by this method.
- (ii) Only symmetrical alkane can be prepared by this method in good yield.

2. Corey-House Synthesis:

 $\mathsf{R} \textbf{-} \mathsf{X} + \mathsf{L} \textbf{i} \longrightarrow \mathsf{R} \mathsf{L} \textbf{i} + \mathsf{L} \textbf{i} \mathsf{X}$

 $RLi + CuI \longrightarrow R_2LiCu$

- (a) $R_2LiCu + 2R X \longrightarrow 2R R + LiX + CuX$
- (b) $R_2LiCu + 2R' X \longrightarrow 2R R' + LiX + CuX$ etc.

It can be used for preparing both symmetrical and unsymmetrical alkanes.

3. Kolbe's Electrolytic Decarboxylation

2RCOONa (aq) $\xrightarrow{\text{electrolytic}}$ R - R + 2NaOH + 2CO₂ + H₂

Mechanism:

RCOONa → RCOO⁻ + Na⁺

2H,0 ____ 2H⁺ + 2OH⁻

Anodic Reaction

2RCOO⁻ → 2RCOO[•] + 2e⁻

Cathodic Reaction

2H⁺ + 2e⁻ → H,

- (i) Methane cannot be prepared by this method
- (ii) Unsymmetrical hydrocarbon (alkane) cannot be prepared

II. Reactions where number of carbon atoms are retained

1. Sabatier - Sanderen's Reduction

2. Reduction of Alkyl Halides

(a)
$$R - X + Zn \xrightarrow{HCI} R - H + HX$$

Zn – Cu and $C_{\rm 2}H_{\rm 5}OH~$ or Na and alcohol can also be used

(b) $4R-X + LiAIH_4 \longrightarrow 4RH + LiX+AIX_3$

This is a nucleophilic substitution reaction with the nucleophilic H⁻ coming from LiAIH_a.

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- (c) $R X + (n C_4 H_9)_3 SnH \longrightarrow R H + (n C_4 H_9)_3 SnX.$
- 3. Reduction of Alcohols, Aldehydes, Ketones and Carboxylic Acids with HI/Red P.

(a) ROH + 2HI
$$\xrightarrow{\text{Red P}}$$
 R - H + I₂ + H₂O

(b)
$$\begin{array}{c} R \\ H \end{array} \xrightarrow{C} C = O + 4HI \xrightarrow{\text{Red P}} R - CH_3 + H_2O + 2I_2 \\ R_1 \\ R_2 \end{array} \xrightarrow{C} C = O + 4HI \xrightarrow{\text{Red P}} R_1 - CH_2 - R_2 + H_2O + 2I_2 \\ R_2 \\ \end{array}$$

(c)
$$R \xrightarrow{-C} + 6HI \xrightarrow{\text{Red P}} R - CH_3 + 2H_2O + 3I_2$$

 $H \xrightarrow{-} + 6HI \xrightarrow{-150^{\circ}C} R - CH_3 + 2H_2O + 3I_2$

(d) Clemmensen's Reduction

$$CH_{3} - \bigcup_{O}^{C-H+4H} \xrightarrow{Zn-Hg/HCI} CH_{3} - CH_{3} + H_{2}O$$

$$R_{1} - \bigcup_{O}^{C-R_{2}} + 4H \xrightarrow{Zn-Hg/HCI} H_{2}O + R_{1} - CH_{2} - R_{2}$$

Clemmensen's reduction should not be used when the carbonyl compound has a basic end in it.

(e) Wolf-Kishner's Reduction:

$$\begin{array}{c} \mathsf{R}_{1}-\mathsf{C}-\mathsf{H}+\mathsf{N}\mathsf{H}_{2}-\mathsf{N}\mathsf{H}_{2}\rightarrow\mathsf{R}-\mathsf{C}=\mathsf{N}-\mathsf{N}\mathsf{H}_{2}+\mathsf{H}_{2}\mathsf{O} & \underbrace{\mathsf{KOH}+\mathsf{Glycol}}{453\,\mathsf{k}-473\,\mathsf{k}} \; \mathsf{R}-\mathsf{C}\mathsf{H}_{3}+\mathsf{N}_{2} \\ \\ \mathsf{O} & \mathsf{H} & \mathsf{Hydrazone} \end{array}$$

$$\begin{array}{c} \mathsf{C}\mathsf{H}_{3}-\mathsf{C}-\mathsf{C}_{2}\mathsf{H}_{5}+\mathsf{N}\mathsf{H}_{2}-\mathsf{N}\mathsf{H}_{2} \\ \\ \mathsf{O} & & \mathsf{C}\mathsf{H}_{3} \\ \\ \mathsf{O} & & \mathsf{C}\mathsf{H}_{3} \\ \\ \mathsf{O} & & \mathsf{C}\mathsf{H}_{3} \\ \\ \mathsf{C}_{2}\mathsf{H}_{5} & \underbrace{\mathsf{C}}=\mathsf{N}-\mathsf{N}\mathsf{H}_{2}+\mathsf{H}_{2}\mathsf{O} & \underbrace{\mathsf{KOH}+\mathsf{Glycol}}{453\,\mathsf{K}-473\,\mathsf{K}} \; \mathsf{C}\mathsf{H}_{3}\mathsf{C}\mathsf{H}_{2}\mathsf{C}_{2}\mathsf{H}_{5}+\mathsf{N}_{2} \end{array}$$

This reaction should not be used when the carbonyl compound has an acidic end in it.

(a) Using Grignard's Reagent

$$R - X + Mg \xrightarrow{ether} RMgX$$

 $RMgX + H - OH \longrightarrow R - H + MgX(OH)$
 $+ H - NH_2 \longrightarrow R - H + MgX(NH_2)$
 $+ H - OR^1 \longrightarrow R - H + MgX(OR^1)$
 $^+H-O-C-R' \longrightarrow R-H + |MgX(O-C-R')$
 0

(b) Using Alkyl lithium compound

$$R^1 NH_2 + R-Li \longrightarrow (R^1 NH) Li + R - H.$$

III. Reaction where number of carbon atom are decreased

Sodalime Decarboxylation

 $\mathsf{RCOONa} + \mathsf{NaOH} \xrightarrow[630\,k]{\mathsf{CaO}} \mathsf{R} - \mathsf{H} + \mathsf{Na}_2\mathsf{CO}_3$

$$\begin{array}{c} \mathsf{CH}_{3} \\ \mathsf{CH}_{3} \end{array} \\ \mathsf{CH}_{-}\mathsf{CH}_{2} - \mathsf{COONa} + \mathsf{NaOH} \xrightarrow{\mathsf{CaO}}_{630 \text{ k}} \begin{array}{c} \mathsf{CH}_{3} \\ \mathsf{CH}_{3} \end{array} \\ \mathsf{CH}_{3} \end{array} \\ \mathsf{CH}_{-}\mathsf{CH}_{3} + \mathsf{Na}_{2} \operatorname{CO}_{3} \end{array}$$

4.

IV. Some other methods of preparation

- (1) Preparation of Methane from carbides
 - (a) $AI_4C_3 + 12H_2O \longrightarrow 4AI(OH)_3 + 3CH_4$
 - (b) $Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$
- (2) Methane from carbon monoxide

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

This is also called Sabatier Sanderen's reduction

Physical Properties

Boiling Point (B.P.)

B.P. increases with the increase of molecular mass. Among the isomers, straight chain alkane have higher b.p. than branched chain alkane.

Melting Point (M.P.)

The melting points do not show regular variation with increase in molecular size. The even number members have higher m.p. as compared to next alkanes with odd number of carbon atoms (ALTERATION EFFECT).

Solubility

They are soluble in non polar solvents but insoluble in polar solvents such as water.

Chemical Properties

Alkanes are generally inert towards acids, bases, oxidising and reducing agents but they give following reactions:

(1) Halogenation. Alkanes undergoes substitution reaction with halogen. Cl₂ and Br₂ only in presence of ultra violet light or high temperature (573 – 773K). But in presence of direct sunlight reaction is as

$$CH_{4} + 2CI_{2} \xrightarrow{\text{direct sunlight}} C + 4HCI$$

$$CH_{4} + CI_{2} \xrightarrow{\text{hv}} CH_{3}CI + HCI$$

$$CH_{3}CI + CI_{2} \xrightarrow{\text{hv}} CH_{2}CI_{2} + HCI$$

$$CH_{2}CI_{2} + CI_{2} \xrightarrow{\text{hv}} CHCI_{3} + HCI$$

$$CHCI_{3} + CI_{2} \xrightarrow{\text{hv}} CCI_{4} + HCI$$

Decreasing order of reactivity of halogens towards alkanes.

$$\mathsf{F}_2 > \mathsf{Cl}_2 > \mathsf{Br}_2 > \mathsf{I}_2$$

$$CH_3 - CH_2 - CH_3 + CI_2 \xrightarrow{298 \text{ K}} CH_3CH - CH_3 + CH_3CH_2CH_2 - CI$$

$$CH_{3} \xrightarrow[l]{CH_{3}} CH_{3} \xrightarrow[l]{CH_{3}} CH_{2} \xrightarrow{298 \text{ K}} (CH_{3})_{3}C - CI + (CH_{3})_{2}CHCH_{2}CI$$

$$CH_{3} \xrightarrow[l]{CH_{3}} CH_{3}$$

Similarly

$$CH_{3} - CH_{3} + Br_{2} \xrightarrow{298 \text{ K}} (CH_{3})_{3}C - Br + (CH_{3})_{2}CH - CH_{2}Br$$

$$H_{3} + CH_{3} + Br_{2} \xrightarrow{298 \text{ K}} (CH_{3})_{3}C - Br + (CH_{3})_{2}CH - CH_{2}Br$$

Note : The reaction with iodine is extremely slow and reversible

$$CH_4 + I_2 \implies CH_3I + HI$$

So iodination is carried out in presence of oxidising agent such as iodic acid or HNO₃.

 $HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$

(2) General mechanism : Halogenation of alkanes takes place in 3 steps :

(i) Chain initiation steps :
$$X \xrightarrow{-} X$$
 sunlight $X^{\bullet} + X^{\bullet}$

(ii) Propagation :

$$\mathsf{R} - \mathsf{H} + \mathsf{X}^{\bullet} \longrightarrow \mathsf{R}^{\bullet} + \mathsf{H}\mathsf{X}$$

$$\mathsf{R}^{\bullet} + \mathsf{X} - \mathsf{X} {\longrightarrow} \mathsf{R} \mathsf{X} + \mathsf{X}^{\bullet}$$

(iii) Termination

$$X^{\bullet} + X^{\bullet} \longrightarrow X - X$$
$$R^{\bullet} + R^{\bullet} \longrightarrow R - R$$
$$R^{\bullet} + X^{\bullet} \longrightarrow R - X$$

Among these three steps, propagation step is rate determing step.

The relative rates of abstraction of various types of hydrogen follow the order :

$$3^{\circ}C : 2^{\circ}C : 1^{\circ}C$$
Chlorination $\rightarrow 5 : 3.8 : 1$
Bromination $\rightarrow 1600 : 82 : 1$
Liquid phase \longrightarrow For higher alkanes – Fuming HNO₃, at 413 K
e.g., :
C₆H₁₃-H + HONO₂ \longrightarrow C₆H₁₃NO₂ + H₂O
Vapour phase \longrightarrow For lower alkanes – conc. HNO₃, at 670-750 K

e.g., :
$$CH_3 - H + HO_3NO_2 - CH_3NO_2 + H_2O_3$$

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(4) Oxidation : Alkanes undergo oxidation under special conditions to yield a variety of products.

(a)
$$2CH_4 + O_2 \xrightarrow{Cu} 2CH_3OH$$

(b)
$$CH_4 + O_2 \xrightarrow{MO_2O_3} HCHO + H_2O$$

(c)
$$2R - CH_3 + 3O_2 \xrightarrow{\text{Manganese acetate}} 2R - C - OH + 2H_2O$$

 $\xrightarrow{\text{Or}}_{Ag_2O}$

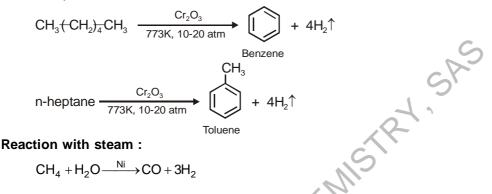
(3)

(5) **Isomerization :** In presence of Anhy. AICl₃ + HCl or AIBr₃ + HBr, straight chain alkanes, get converted in branched alkane.

$$CH_{3} - CH_{3} - CH_{3} - CH_{3} - CH_{3} \xrightarrow{AICl_{3} + HCl} CH_{3} - CH - CH_{3}$$

$$CH_{3} - CH_{3} - CH_{3}$$

2-methyl pentane 3-methyl pentane
 (6) Aromatization : Alkanes having minimum 6 or more carbons when heated at 773 K under high pressure (10-20 atm) in presence of Cr₂O₃, V₂O₃, Mo₂O₃ supported on Alumina gets converted into aromatic hydrocarbon.

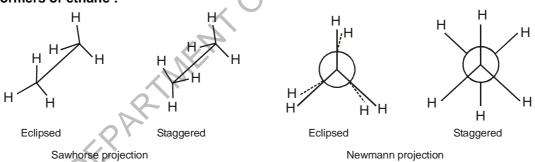


Conformations of Alkanes

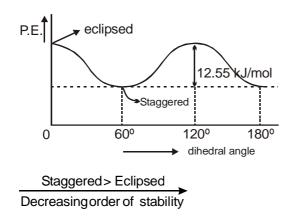
(7)

Conformations isomers/conformers are compounds which arises due to rotation around C–C. In fact C–C rotation is hindered by an energy barrier of **1 to 20 kJ × mol**⁻¹. There are infinite number of conformers possible. Out of infinite number of conformers extremes can be discussed as

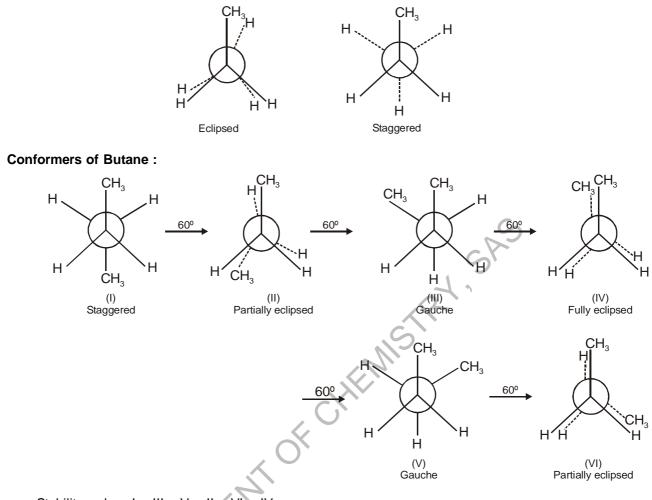




- (i) It may be noted that one extreme conformation of ethane can be converted into other extreme conformer by rotation of 60° about C–C bond.
- (ii) Conformers lying between two extreme are called **skew conformations**.



Conformers of propane :



Stability order : $I > III \approx V > II \approx VI > IV$

ALKENES

Alkene have the structural unit $\rangle C = C \langle \rangle$. The carbon atoms carrying the unsaturation are sp^2 hybridized with the *p* orbital laterally overlaping to form π -bonds. They have the general formula C_nH_{2n} . They are isomeric with cycloalkanes e.g. $-C_4H_8$

$$CH_3 - CH_2 - CH = CH_2$$

Butene
$$CH_2 - CH_2 - CH_2$$

Nomenclature :

The IUPAC rules for naming alkenes are similar in many respects to those for naming alkanes. Hence few solved examples are taken.

(i) $CH_{3}^{1} - CH_{3}^{2} = CH_{3}^{3} - CH_{2}^{4} - CH_{3}^{5}$ 2 - pentene

(ii)
$$CH_3 = CH_2 - CH_3 - CH_2 - CH_3 - CH_2 - CH_3 - CH_3 - CH_2 - CH_3 - CH$$

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5-Ethyl-2-methyl-2-octene

(iii) Alkene – H = Alkenyl

e.g., $CH_2 = CH$ – ethenyl (Vinyl group); $CH_2 = CH - CH_2$ – propenyl (Allyl group) *e.g.*, $CH_2 = CH - CI$ - Vinyl chloride; $CH_2 = CH$ – CH_2 –OH Allyl alcohol

Preparations of Alkenes

From Alcohols

By heating alcohol with H_2SO_4 or H_3PO_4 at 170°C.

$$CH_3 - CH_2 - OH \xrightarrow{95\% H_2SO_4} CH_2 = CH_2$$

Mechanism :

1st step :
$$H_2SO_4 \longrightarrow H^+ + HSO_4^-$$

2nd step : $CH_3 - CH_2 - OH + H^+ \iff CH_3 - CH_2 - OH_2$
3rd step : $CH_3 - CH_2 \stackrel{\textcircled{(+)}{\to}}{\to} OH_2 \rightarrow CH_3 - \stackrel{\textcircled{(+)}{C}}{\to} CH_2 + H_2O$
4th step : $CH_2 - CH_2^+ \rightarrow CH_2 = CH_2 + H_2SO_4$
HSO₄

Here the 3rd step i.e. formation of carbocation is rate determining step.

The ease of dehydration of alcohols depends on the stability of carbocations formed. Hence the order of reactivity of alcohols is ter-> sec-> pri-> $CH_3 - OH$ because the incipient carbonium ion stability is ter-> sec-> pri-> CH_3^+ .

Note : Since the carbocation stability is the primary criteria so the initally formed carbocation undergoes molecular rearrangement by either to give more stable carbocation.

Hydride shift or

Example (Hydride shift)

$$\begin{array}{ccc} CH_{3}-CH-CH-CH_{3} \xrightarrow[170^{\circ}C]{H_{2}SO_{4}} & CH_{3}-C=CH_{2}-CH_{3}+CH_{2}=C-CH_{2}-CH_{3}\\ CH_{3} & OH & CH_{3} & CH_{3}\\ (Major) & (Minor) \end{array}$$

Mechanism :

$$CH_{3} - CH - CH - CH_{3} + H + CH_{3} - CH - CH - CH_{2}$$

$$CH_{3} \cdot OH + CH_{3} + CH_{3} - CH - CH_{2}$$

$$CH_{3} - C - CH - CH_{3} + CH_{3} - C - CH - CH_{3} + CH_{3} - CH_{2} - CH_{3}$$

$$CH_{3} - C - CH - CH_{3} + CH_{3} - CH_{3} - CH_{3} + CH_$$

$$H - CH_{2} - CH_{2} - CH_{2} - CH_{3} - CH_{3}$$

(i) Dehydration of alcohols follow Saytzeff's rule.

Hence (B) product is maximum.

Saytzeff's Rule: It states that "During dehydration of alcohols and dehydrohalogenation of alkyl halides the product formed is preferentially the one in which maximum number of alkyl groups are attached to the doubly bonded carbon atoms.

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(ii) Dehydration by passing over alumina (Lewis Acid)

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

$$CH_{3} \xrightarrow{CH_{3}} CH - OH \xrightarrow{Al_{2}O_{3}}{250^{\circ}C} CH_{3} - CH = CH_{2}$$

$$(CH_{3})_{3} C - OH \xrightarrow{Al_{2}O_{3}}{250^{\circ}C} CH_{3} - C = CH_{2}$$

The experimental conditions change with the structure of alcohols pri - alcohols $\xrightarrow[180^{\circ}C]{}$ alkene sec - alcohols $\xrightarrow[475]{}$

pri - alcohols
$$\xrightarrow[180^{\circ}C]{180^{\circ}C}$$
 alkene
sec - alcohols $\xrightarrow[170^{\circ}C]{170^{\circ}C}$ alkene
e.g., $\bigcirc^{OH} \xrightarrow[170^{\circ}C]{170^{\circ}C}$ 1
ter - alcohols $\xrightarrow[20\% H_2SO_4]{170^{\circ}C}$ alkene
 $\stackrel{CH_2 - OH}{=} \xrightarrow[85^{\circ}C]{H^*/heat}$

I. Dehydrohalogenation of alkyl halides

1.
$$CH_3 - CH_2 - CH_2 - CH_2 - Br \xrightarrow{alc KOH} CH_3 - CH_2 - CH = CH_2$$

2.
$$\begin{array}{c} CH_{3} - CH_{2} - CH_{2} - CH_{3} - CH_{3} \xrightarrow{\text{alc KOH}} CH_{3} - CH = CH - CH_{3} + CH_{3} - CH_{2} - CH = CH_{2} \\ | \\ Br \end{array} \xrightarrow{\text{(Major)}} (Minor)$$

3.
$$\begin{array}{cccc} CH_3 & CH_3 & CH_2 \\ & & & | & | \\ H_3 - CH - CH - CH - CH_3 & \underline{alc \ KOH} \\ & & & | \\ Br & & (Minor) & CH_3 + (CH_3)_2 \ C = C(CH_3)_2 \\ & & & | \\ (Minor) & CH_3 & (Major) \end{array}$$

- (i) The base used may be strongly basic anions like OH^- , RO^- , $C_2H_5O^-$ $(CH_3)_3CO^-$ etc.)
- (ii) The group leaving (*i.e.*, halogen) is a good leaving group if it is the conjugate base of a strong acid. (*i.e.*, weakly basic halide ion).
- (iii) One may also use sulphonates.
- (iv) Dehydrohalogenation of 2° and 3° alkyl halides follow Saytzeff's Rule.

II. Exception to Saytzeff's Rule (Hofmann Rule)

When dehydrohalogenation is carried out with potassium, tertiary butoxide there is formation of less substituted alkene.

$$(CH_{3})_{3} CO^{-} + CH_{3}CH_{2} \overset{C}{C} - Br \xrightarrow{(CH_{3})_{3}COH}{75^{\circ}C} CH_{3} - CH = C \overset{CH_{3}}{CH_{3}} + \overset{CH_{3} - CH_{2} - C = CH_{2}}{(Minor)}$$

$$Dehalogenation Reactions$$

$$-\overset{I}{C} - \overset{I}{C} - + Zn \xrightarrow{alc}{KOH} - \overset{I}{C} = \overset{I}{C} - + ZnBr_{2}$$
Br Br VICINAL
$$2 R - CH \overset{Br}{H} + Zn \xrightarrow{alc}{KOH} R - CH = CH - R + 2ZnBr_{2}$$
GEMINAL

IV. By controlled hydrogenation of alkynes

(i)
$$CH_3 - C \equiv C - CH_3 + H_2$$
 $\xrightarrow{Pd/BaSO_4}$ $CH_3 - C = C \begin{pmatrix} CH_3 \\ H \end{pmatrix}$ C is - 2 - Butene

Here we may use small amounts of sulphur or quinoline also.

$$CH_{3} - C = C - CH_{3} \xrightarrow{\text{Na/LiqNH}_{3}} CH_{3} = C + CH_{3}$$

trans-2-Butene

V. By heating Quaternary Ammonium hydroxide

$$(C_2H_5)NOH \xrightarrow{+ - -} CH_2 = CH_2 + (C_2H_5)_3N + H_2O$$

VI. Kolbe's Electrolysis

$$\begin{array}{c} CH_2COONa \\ | \\ CH_2COONa \end{array} + 2H_2O \xrightarrow{electrolysis} CH_2 = CH_2 + 2CO_2 + 2NaOH + H_2 \end{array}$$

Sodium succinate

Mechanism is similar to preparation of alkanes.

III.

VII. Pyrolysis

$$CH_3CH_2CH_2CH_3 \xrightarrow{\Delta} CH_3-CH=CH_2 + CH_4$$

$$CH_3CH_2CH_2CH_2CH_2CH_3 \xrightarrow{\Lambda} CH_3CH=CH_2 + CH_3CH_2CH_3$$

VIII. By heating saturated hydrocarbon with SiO_2

$$C_6H_5 - CH_2 - CH_2 - C_6H_5 \xrightarrow{SiO_2} C_6H_5 - CH = CH - C_6H_5 + H_2$$

Physical Properties

Solubility

They are insoluble in water but soluble in organic solvents.

Boiling point

The boiling point of cis-alkenes is usually higher than corresponding trans-alkenes (More polarity).

Melting point

The melting point of trans-alkenes is usually greater than cis-alkene. (trans form is more symmetrical).

Chemical Properties

In alkenes C = C bond is made of stable σ -bond and reactive π -bond. As π -bond can easily be broken, alkenes undergo addition reactions.

$$c = c < + xy \longrightarrow c - c <$$

Being electron rich species they react with electrophiles in three ways.

1. Ionic Mechanism

$$C = C \left\langle \underbrace{E - Nu}_{F} \right\rangle C = C \left\langle \underbrace{E - Nu}_{F} \right\rangle C = C \left\langle \underbrace{E - C}_{F} \right\rangle C + Nu$$

2. Free Radical Mechanism

$$c = C \left\langle \underbrace{E - E}_{\substack{E \to E}} \right\rangle c - c \left\langle + \dot{E} \right\rangle c$$

3. Transition State

$$C = C + E - Nu \longrightarrow C - C$$

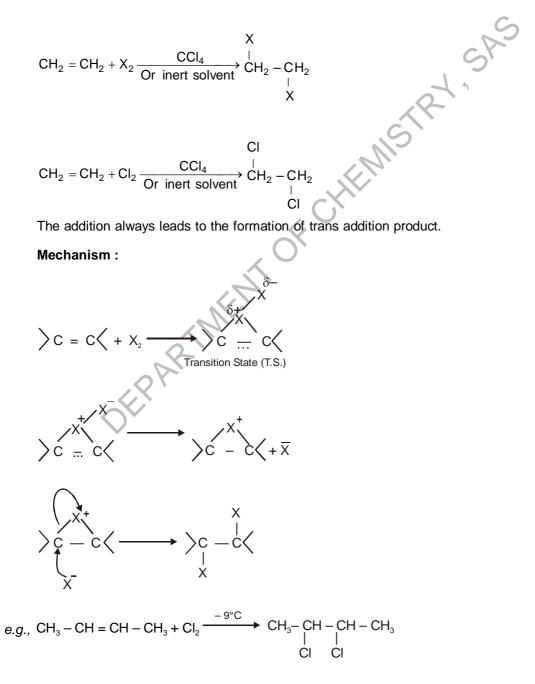
Reactions:

1. Hydrogenation :

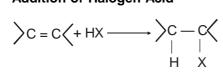
$$C = C \left(+ H_2 \xrightarrow{Pd \text{ or } Pd}_{or \text{ Ni} \Delta} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H + H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H} \right) C - C \left(H + H_2 \xrightarrow{Pd \text{ or } Pd}_{H} \right) C - C$$

The relative rates of hydrogenation is $CH_2 = CH_2 > RCH = CH_2 > R_2 C = CH_2 > RCH = CHR > R_2 C = CR_2$. This is due to the fact that as number of alkyl groups increase the steric hindrance increases and there by rate decreases.

2. Halogenation :



3. Addition of Halogen Acid



The reactivity order of halogen acid is HI > HBr > HCl

Mechanism :

$$R-CH=CH_{2}+HX \longrightarrow R-CH-CH_{2} \xrightarrow{\delta} (a) \qquad (a) \qquad R-CH-CH_{3}+\overline{X} \qquad (a) \qquad R-CH-CH_{3}+\overline{X} \qquad (b) \qquad R-CH_{2}-CH_{2}+\overline{X} \qquad (b) \qquad R-CH_{2}-CH_{2}+\overline{X}$$

Here the transition state cleaves to from the most stable carbocation hence (a) cleavage takes place and hence, $R - CH_3 + \overline{X}$ are formed

FMIS

i.e.,
$$R - CH - CH_3 + \overline{X} \longrightarrow R - CH - CH_3$$

|
X

Markownikoff's Rule may therefore be applied. It states that, "During the addition of unsymmetrical reagents to unsymmetrical alkenes, the negative part of the addendum goes to carbon of double bond with least number of atoms".

Example :

$$CH_{3}-CH=CH_{2}+HX \longrightarrow CH_{3}-CH-CH_{2}$$
(a)
$$CH_{3}-CH_{2}-CH_{2}-CH_{2}-CH_{2}+\bar{X}$$

$$CH_{3}-CH_{3}+\bar{X} \qquad CH_{3}-CH_{2}-CH_{2}+\bar{X}$$

$$B$$

Since A is more stable than B. Hence A is formed and we get

$$CH_{3} - CH - CH_{3} \xrightarrow{\bar{X}} CH_{3} - CH - CH_{3}$$

$$\downarrow X$$

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

$$H_{3} - CH_{3} - CH_{3} - CH_{3}$$

Kharasch - Mayo Effect

If the above reaction is carried out in the presence of some peroxide then addition takes place contrary to Markownikoff's Rule

 $CH_3 - CH = CH_2 + HBr \xrightarrow{Peroxide} CH_3 - CH_2 - CH_2 - Br$

Explanation

This can be explained on the basis of free radical formation

Step 1 : $R - O - O - R \longrightarrow 2R - O$

Step 2 : $R - \mathbf{0} + HBr \longrightarrow ROH + Br$

Step 3 : $CH_3 - CH = CH_2 + Br$ (B) is more stable than (A). $CH_3 - CH - CH_2^{\bullet}(A)$ Br 1° Carbon free radical $CH_3 - CH - CH_2 - Br (B)$ (B) Carbon free radical

(B) is more stable than (A). 2° Carbon free radical

Hence (B) is formed.

$$R - CH - CH_2 - Br + HBr \longrightarrow R - CH_2 - CH_2 - Br + Br$$

Note : Only HBr adds on by Anti Markownikoff's Rule (in presence of organic peroxide) not HCl or HI.

Addition of Hypohalous Acid 4.

$$\begin{array}{c} \begin{array}{c} \begin{array}{c} \\ \end{array} \\ C = C \left< + HOX \longrightarrow \right) \\ OH \\ CH_2 = CH_2 + HOCI \longrightarrow \begin{array}{c} CH_2 - CH_2 \\ OH \\ OH \\ CI \\ \end{array}$$

$$\begin{array}{c} CH_2 - CH = CH_2 + HOBr \longrightarrow CH_2 - CH - CH_2 \\ OH \\ H \\ Br \end{array}$$

5. Addition of Water

> This reaction also takes place via carbocation mechanism (Rearrangement possible). СН

$$(CH_3)_2 C = CH_2 + H_2 O \xrightarrow[10\%]{H^+} CH_3 - CH_3 - OH_3 - OH_3$$

6. Addition of cold and conc. H₂SO₄

Carbocation Mechanism Followed, (Rearrangement Possible)

$$R - CH = CH_{2} + H_{2}SO_{4} \longrightarrow R - CH - CH_{3} \xrightarrow[Heat]{Heat} R - CH - CH_{3}$$

7. Oxy-Mercuration - Demercuration

Synthesis of alcohols from alkenes is in accordance with Markownikoff's Rule (No carbocation formed)

$$R - CH = CH_2 \xrightarrow{i) Hg(OAc)_2/THF, H_2O} R - CH - CH_3$$

ii) NaBH₄/OH⁻ OH

8. Addition of Oxygen:

$$CH_{2} = CH_{2} + \frac{1}{2} O_{2} \xrightarrow{Ag} CH_{2} \xrightarrow{CH_{2}} CH_{2}$$

9. Ozonolysis:

$$\sum C = C \left\langle + O_{3} \xrightarrow{CCI_{4}} \right\rangle C = C \left\langle -\frac{Zn/H_{2}O}{-H_{2}O_{2}} \right\rangle 2 \sum C = O$$

Example :
$$CH_{3}CH = CH_{2} + O_{3} \xrightarrow{CCI_{4}} CH_{3} - CH \xrightarrow{CH} CH_{2} \xrightarrow{Zn/H_{2}O} CH_{3} - CHO + HCHO$$

$$O = O \xrightarrow{I} O = O \xrightarrow{CH_{3}O_{2}} CH_{3} - CHO + HCHO$$

$$\begin{array}{c} & & & \\ & &$$

Ozonalysis helps to locate the positions of double bonds in alkene.

10. Hydroboration Oxidation

$$R - CH = CH_2 + B_2H_6 \xrightarrow[]{0^{\circ}C} (R - CH_2 - CH_2)_3 - B \xrightarrow[]{H_2O_2} OH^- R - CH_2 - CH_2 - OH + H_3BO_3$$

(Product is Antimarkownikov product.)

11. Oxidation Reactions

(a) Reaction with Baeyer's Reagent (Cold dilute Alkaline KMnO₄, Hydroxylation)

$$C = C \langle + alk KMnO_4 \longrightarrow \rangle C - C \langle \\ | \\ OH OH \rangle$$

The addition is a syn addition to form vicinal dihydroxy compounds.

Note : Decolorization of Baeyer's reagent is also used as a test for unsaturation.

With hot KMnO₄ or acidic KMnO₄ (b)

$$CH_{2} = CH_{2} \xrightarrow{[0]}_{Hot KMnO_{4}} 2HCOOH \longrightarrow 2CO_{2} + 2H_{2}O$$

$$CH_{3} - CH = CH_{2} \xrightarrow{KMnO_{4}}_{H^{+}} CH_{3}COOH + CO_{2} + H_{2}O$$

$$(CH_{3})_{2} C = C(CH_{3})_{2} \xrightarrow{Hot}_{KMnO_{4}} 2 \xrightarrow{CH_{3}}_{CH_{2}} C = O$$

12. Substitution Reaction

 $\mathsf{CH}_3-\mathsf{CH}=\mathsf{CH}_2+\mathsf{Cl}_2 \xrightarrow{500-600^\circ\mathsf{C}} \mathsf{CI}-\mathsf{CH}_2-\mathsf{CH}=\mathsf{CH}_2+\mathsf{HCI}_2$

This type of reaction takes place at a carbon atom attached to double bond carbon. This is called allylic substitution.

SP

Mechanism

Step - 1 :
$$CI - CI \xrightarrow{500-600^{\circ}C} 2CI^{\circ}$$

Step - 2 : $CH_2 = CH - CH_3 \xrightarrow{+CI^{\circ}} HCI + CH_2 = CH - CH_2^{\circ}$
Step - 3 : $CH_2 = CH - CH_2^{\circ} + CI_2 \longrightarrow CH_2 = CH - CH_2 - CI + CI^{\circ}$
Wohl Zeigler Reaction

13. Wohl Zeigler Reaction

$$CH_3 - CH = CH_2 + Br_2 \xrightarrow{Low conc. of Br_2} CH_2 = CH - CH_2 - Br$$

The low concentration of Br_{2} is obtained from NBS

$$CH_{3} - CH = CH_{2} + CH_{2} - C$$

$$| CH_{2} - C$$

14. Addition of Carbenes

(i)
$$\overrightarrow{CH_2} - \overrightarrow{N} \equiv \overrightarrow{N} + \overrightarrow{CH_2} + \overrightarrow{N_2}$$

(ii)
$$CH_3 - CH = CH_2 + \ddot{C}H_2 \xrightarrow{hv} CH_3 - CH - CH_2$$

 $CH_2 \xrightarrow{hv} CH_3 - CH - CH_2$

15. Isomerization :

$$CH_{2} - CH_{2} - CH_{2} - CH = CH_{2} \xrightarrow{700 - 970 \text{ atm}} CH_{3} - CH_{2} - CH = CH - CH_{3}$$

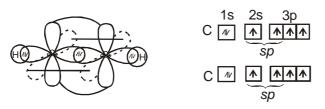
16. Polymerization :

$$CH_{2} = CH_{2} \xrightarrow{\text{Pressure}} (CH_{2} - CH_{2})_{n}$$

$$CF_{2} = CF_{2} \xrightarrow{\text{Trans}}_{O_{2}} (F_{2}C - CF_{2})_{n}$$

ALKYNES

Compounds containing the structural unit - C=C- are called Alkynes. Like the double bond it is unsaturated and highly reactive towards the reagent that double bonds react with and also towards others. The simplest member of the alkyne family is acetylene, C2H2.Each of the carbon atoms carrying the triple bond are sp hybridized.



Alkynes the compounds having general formula C_nH_{2n-2} where $n \ge 2$ it can be categorize by two ways.

- Terminal alkynes : Alkynes having triple bond at one end of the carbon attached to H 1. e.g. $CH_3-C \equiv C-H$, $CH_3 - CH_2-C \equiv CH$. Terminal hydrogen is acidic in nature.
- Non-terminal alkynes : Alkynes in which both triple bonded carbons are attached to alkyl group. 2.

Preparation of Alkynes

1. From Dehydrohalogenation of vicinal or geminal dihalides

$$CH_{2} - CH_{2} \xrightarrow{\text{alc. KOH}} CH \equiv CH + 2H_{2}O + KBr$$
Br
Br
Br
Br
R-CH-CH_{2} \xrightarrow{\text{alc. KOH}} R - C \equiv CH + 2H_{2}O + KBr
Br
Dehalogenation Reaction

2. Dehalogenation Reaction

(a)
$$\begin{pmatrix} X & X \\ | & | \\ -C - C - C \\ | & | \\ X & X \end{pmatrix} \xrightarrow{Zn \text{ dust}} -C = C + 2ZnX_2$$

(b)
$$2R - C \xrightarrow{X} X \xrightarrow{Zn \text{ dust}} R - C \equiv C - R + 3ZnX_2$$

3. Kolbe's Electrolytic Decarboxylation

$$R \xrightarrow{COOK} + 2H_2O \xrightarrow{Electrolysis} R - C \equiv C - R + 2KOH + CO_2 + H_2$$

$$R \xrightarrow{COOK} COOK$$
is or trans

cis or trans

4. Formation of Higher alkyne

NI - NII I

(i)
$$CH = CH \xrightarrow{\text{Na} NH_2} CH = \overline{C} \text{ N}_a^{\dagger} + \text{NH}_3$$

 $CH = \overline{C} \text{ N}_a^{\dagger} + CH_3 CI \longrightarrow CH = C - CH_3 + \text{Na}CI$

 $R-C \equiv CH + NaNH_2 \longrightarrow RC \equiv \overline{C}Na^{\dagger} + NH_3$ (ii) $R-C = \overline{C} \operatorname{Na}^{+} + R' X \longrightarrow R-C = C-R' + \operatorname{Na}X$

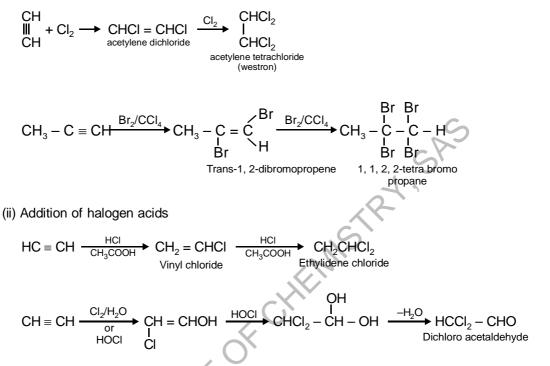
Chemical Properties

Alkynes undergo electrophilic addition generally but in the presence of salt of heavy metals which forms complexes with multiple bonds it undergo nucleophilic addition reaction.

1. Addition Reaction

A. Electrophilic addition reaction :

(i) Addition of halogen



B. Nucleophilic addition reaction

Because of greater electronegativity of *sp* hybridized C as compared to sp^2 hybridized carbons, Alkynes are more susceptible to nucleophilic addition reactions than alkenes. It is due to formation of some

sort of complex of heavy metal ion with π electrons like $\begin{bmatrix} -C \equiv C - \\ V \\ Hg^{2*} \end{bmatrix}$ and this results decrease in

electron density around triply bonded carbon atoms and this can be attacked by nucleophiles.

(i) Addition of H₂O or hydration of alkyne or Kucherov reaction

$$\begin{array}{c} \mathsf{CH} \\ \mathsf{III} \\ \mathsf{III} \\ \mathsf{CH} \end{array} + \mathsf{H}_2\mathsf{O} \xrightarrow{\mathsf{H}^+, \mathsf{Hg}^{2+}}_{333 \mathsf{K}} \\ \mathsf{H} - \mathsf{C} \\ \mathsf{C} \\ \mathsf{H} \\ \mathsf{CH} \end{array} \xrightarrow{\mathsf{OH}}_{\mathsf{Vinyl alcohol}} \\ \mathsf{H} \\ \mathsf{H} \\ \mathsf{H} \\ \mathsf{CH} \\ \mathsf{H} \\ \mathsf{CH} \\ \mathsf{H} \\$$

$$R - C \equiv C - H + H_2O \xrightarrow{H^*, Hg^{2*}} R - \stackrel{OH}{C} = CH_2 \xrightarrow{\text{tautomerise}} R - \stackrel{O}{C} = CH_3$$

Ketone

(ii) Addition of HCN

Similarly alkynes adds acids in presence of lewis acid catalyst or Hg²⁺ give vinyl ester.

$$HC \equiv C - H + H_3CCOOH \xrightarrow{Hg^{2+}/353 H} CH_3 - C - O - CH = CH_2$$

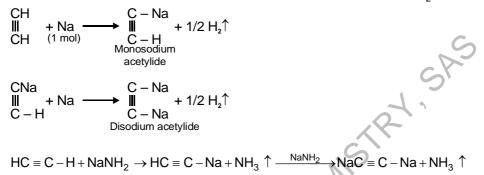
Vinyl ethanoate

$$R - C \equiv CH + CH_{3} - C - OH \xrightarrow{BF_{3}} CH_{3} - C - O - C = CH_{2}$$

a-alkyl vinyl ethanoate

2. Reaction of Acidic H Atom

(i) Alkynes having acidic H atom reacts with metals like Na, K, evolves H_2 gas.



(ii) **Reaction with Tollens reagent :** When alkyne reacts with tollens reagent (Ammonical AgNO₃ solution) at forms white precipitate of silver acetylide.

$$\begin{array}{c} C - H \\ \blacksquare \\ C - H \end{array} \xrightarrow{+ 2AgNO_3 + 2NH_4OH} \xrightarrow{- + 2NH_4CI + 2H_2O} \\ (Tollens reagent) \end{array} \xrightarrow{- + 2NH_4CI + 2H_2O} \begin{array}{c} C - Ag \\ \blacksquare \\ C - Ag \end{array} \xrightarrow{- + 2NH_4CI + 2H_2O} \\ (White precipitate) \end{array}$$

These acetylide are not decomposed by H₂O like acetylide of Na but by mineral acids like dil HNO₃.

$$\begin{array}{c} C - Ag \\ H \\ C - Ag \end{array}^{+} 2HNO_{3} \longrightarrow 2AgNO_{3} + \begin{array}{c} CH \\ H \\ CH \end{array}$$
$$R - C \equiv CH + Ag^{+} \rightarrow R - C \equiv C - Ag + H^{\oplus}$$

(iii) Reaction with Ammonical Cuprous Chloride :

$$\begin{array}{c} HC\\ HC\\ HC\\ HC \end{array} + Cu_2Cl_2 + 2NH_4OH \longrightarrow \begin{matrix} CCu\\ III\\ CCu\\ (red \ ppt)\\ copper \ acetylide \end{matrix} \downarrow + 2NH_4CI + 2H_2O$$

These reactions are used to distinguish terminal alkynes from other alkynes.

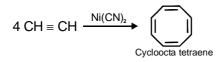
3. Polymerization Reaction

(i) When acetylene is passed in red hot cutube or retube. It converted into benzene.

$$3 \stackrel{\text{CH}}{=} \xrightarrow{773\text{K}} C_6 H_6$$

Similarly
$$CH_3 - C \equiv CH \xrightarrow{\text{red hot } Cu \text{ or } Fe \text{ tube}} H_3C \xrightarrow{CH_3} H_3C \xrightarrow$$

Chloroprene on polymerization gives polymer called neoprene; used as artificial rubber. (iii) Under high pressure and in presence $Ni(CN)_2$ acetylene tetramerises.



4. Reaction with S_8 , N_2 , NH_3 and HCN

Acetylene reacts with S_8 , N_2 , NH_3 and HCN to form different heterocyclic compounds.

