# ALKYNE

## Introduction :

A triple bond gives an alkyne four fewer hydrogen atoms than the corresponding alkane. Therefore, the triple bond contribute two degree of unsaturation (DU).

Alkynes are not as common in nature as alkenes, but some plants do use alkynes to protect themselves against disease or predators. Acetylene is by far the most important commercial alkyne. Acetylene is an important industrial feedstock, but its largest use is as the fuel for the oxyacetylene welding torch.

## Structure and bonding in Alkynes

(a) Alkynes are hydrocarbons that contain carbon-carbon triple bond.

(b) Alkynes are also called acetylenes because they are derivatives of acetylene

(c) The general formula is : $C_nH_{2n-2}$. (one triple bond)

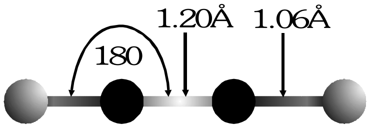
(d) In alkyne $C \equiv C$ bond length is 1.20 Å

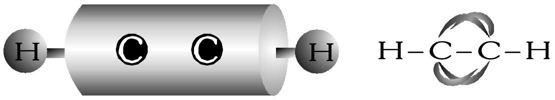
(e) Its bond energy is 192 kcal. mol–1

(f) The hybridization of carbon atoms having triple bond ($C \equiv C$) in alkynes is sp.

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

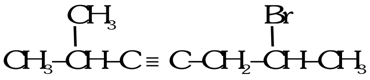
(h) Two π bonds result form overlap of the two remaining unhybridized p orbitals on each carbon atom.these orbitals overlap at **right angles** (90 ) to each other, forming one π bond with electron density above and below the C-C sigma bond, and the other with electron density in front and in back of the sigma bond. This result in a cylindrical π electron cloud around σ bonded structure.



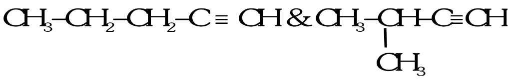
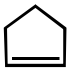


**Note** : Any type of stereoisomerism does not arise in acetylenic bond due to linearity of $C \equiv C$ bond.

## IUPAC Nomenclature of Alkynes :

| SN. | Compound | Name |
|---|---|---|
| 1. | $CH \equiv CH$ | Ethyne |
| 2. | $CH_3 - C \equiv CH$ | Propyne |
| 3. | $HC \equiv C - CH_2 - CH_3$ | But-1-yne |
| 4. | $CH_3-C \equiv C - CH_3$ | But-2-yne |
| 5. |  $CH_3-\underset{\displaystyle CH_3}{CH}-C\equiv C-CH_2-\underset{\displaystyle Br}{CH}-CH_3$ | 6-Bromo-2-methylhept-3-yne |

## Isomerism in Alkynes

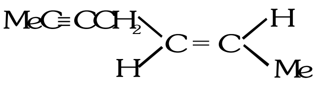
| Type | Categary | Examples |
|---|---|---|
| Structural Isomerism | (i) Chain isomerism |  $CH_3-CH_2-CH_2-C\equiv CH \;\&\; CH_3-\underset{\displaystyle CH_3}{CH}-C\equiv CH$ |
| | (ii) Positional isomerism | $CH_3-CH_2-CH_2-C \equiv CH$ & $CH_3-CH_2-C\equiv C-CH_3$ |
| | (iii) Functional group isomerism | $CH_3-CH_2-C\equiv C-CH_3$ & $CH_3-CH=C=CH-CH_3$ &  |

**Ex.** Cis-trans isomerism is not possible in alkynes because of :-

**Sol.** 180 bond-angle at the carbon-carbon triple bond.

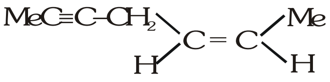
**Ex.** Draw the geometrical isomers of hept-2-en-5-yne ?

**Sol.**



(trans)

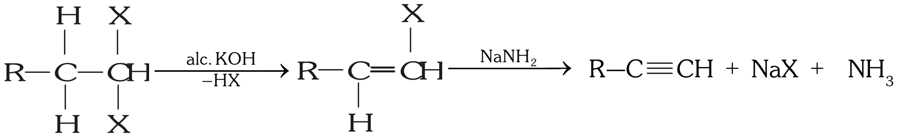
,



(Cis)

## ❑ General Methods of Preparation :

**1. From Gem dihalides ( by dehydrohalogenation)** : Dehydrohalogenation agents are : $NaNH_2$ (Sodamide) or Alc. KOH or ROH + RONa.



$$R-\underset{H}{\overset{H}{C}}-\underset{X}{\overset{X}{C}}H \xrightarrow[-HX]{alc.\,KOH} R-\underset{H}{C}=\overset{X}{C}H \xrightarrow{NaNH_2} R-C\equiv CH + NaX + NH_3$$

(Stable by resonance)

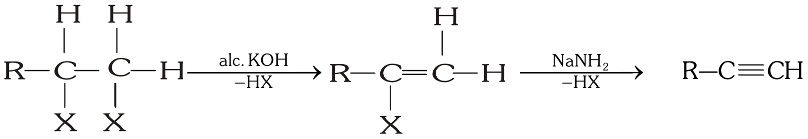
(Vinyl halide)

(a) Due to stability of vinyl halide by resonance there is partial double bond in which elimination does not take place by alc. KOH so stronger base $NaNH_2$ is used.

(b) Basic strength : $\overset{\ominus}{N}H_2$ is stronger base then $RO^{\ominus}$

(c) Trans elimination takes place in forming of alkynes.

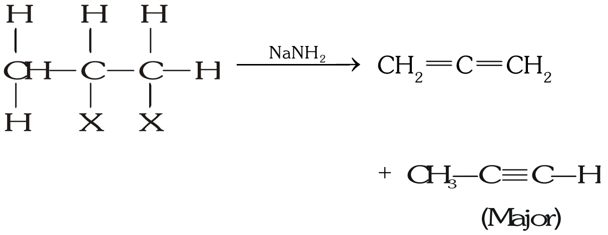
**2. From Vicinal dihalides (by dehydrohalogenation) :**



$$R-\underset{X}{\overset{H}{C}}-\underset{X}{\overset{H}{C}}-H \xrightarrow[-HX]{alc.\,KOH} R-\underset{X}{C}=\overset{H}{C}-H \xrightarrow[-HX]{NaNH_2} R-C\equiv CH$$

(a) Elimination of Vic. dihalides gives also alkadiene (1, 2 and 1, 3 alkadienes) but the major product is alkyne.

Example :

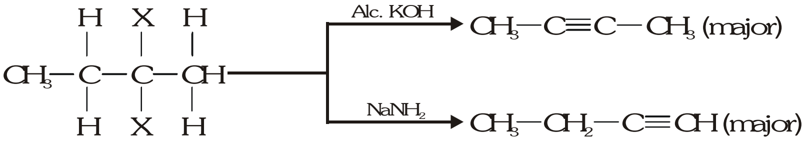


$$\underset{H}{\overset{H}{C}}H-\underset{X}{\overset{H}{C}}-\underset{X}{\overset{H}{C}}-H \xrightarrow{NaNH_2} CH_2=C=CH_2 + CH_3-C\equiv C-H$$

(Major)

(b) Non terminal gem dihalide gives 2-Alkyne in presence of alc. KOH while gives 1-alkyne in presence of $NaNH_2$.

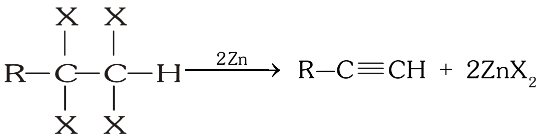
Example :



$$CH_3-\underset{H}{\overset{H}{C}}-\underset{X}{\overset{X}{C}}-\underset{H}{\overset{H}{C}}H \xrightarrow{Alc.\,KOH} CH_3-C\equiv C-CH_3 \text{ (major)}$$

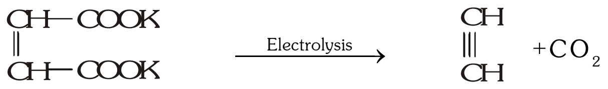
$$CH_3-\underset{H}{\overset{H}{C}}-\underset{X}{\overset{X}{C}}-\underset{H}{\overset{H}{C}}H \xrightarrow{NaNH_2} CH_3-CH_2-C\equiv CH \text{ (major)}$$

**3. Dehalogenation of tetrahalo alkane** : By heating 1, 1, 2, 2 - tetra halo alkane with Zn dust.



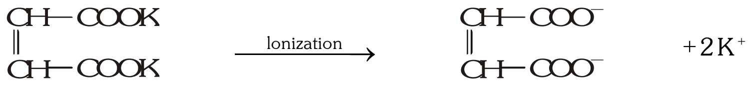
$$R-\underset{X}{\overset{X}{C}}-\underset{X}{\overset{X}{C}}-H \xrightarrow{2Zn} R-C\equiv CH + 2ZnX_2$$

4. **From Kolbe's electrolysis** : By the electrolysis of aqueous solution of sodium or potassium fumarate or maleate, acetylene is formed at anode.



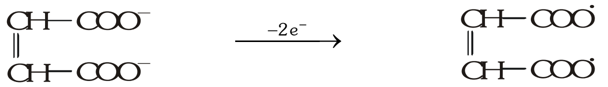
$$\begin{matrix}CH-COOK\\ \|\\ CH-COOK\end{matrix} \xrightarrow{\text{Electrolysis}} \begin{matrix}CH\\ |||\\ CH\end{matrix} + CO_2$$

**Mechanism** :



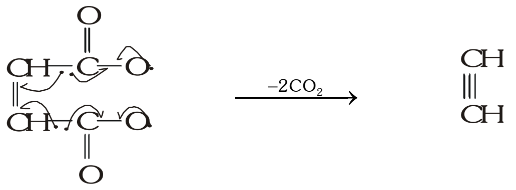
$$\begin{matrix}CH-COOK\\ \|\\ CH-COOK\end{matrix} \xrightarrow{\text{Ionization}} \begin{matrix}CH-COO^-\\ \|\\ CH-COO^-\end{matrix} \quad +2K^+$$

**at anode** (Alkyl and $CO_2$ gas is formed)



$$\begin{matrix}CH-COO^-\\ \|\\ CH-COO^-\end{matrix} \xrightarrow{-2e^-} \begin{matrix}CH-CO\dot{O}\\ \|\\ CH-CO\dot{O}\end{matrix}$$

(Oxygen free radical)



$$\begin{matrix}O\\ \|\\ CH-C-\dot{O}\\ \|\\ CH-C-\dot{O}\\ \|\\ O\end{matrix} \xrightarrow{-2CO_2} \begin{matrix}CH\\ |||\\ CH\end{matrix}$$

**at cathode** (KOH and $H_2$ gas is formed)

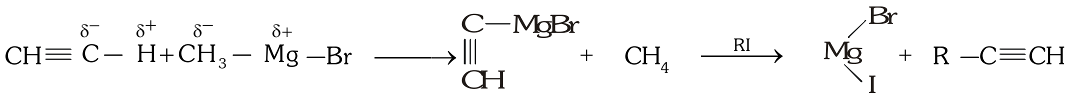
$2K^+ + 2e^- \longrightarrow 2K$

$2K + 2H_2O \longrightarrow 2KOH + H_2\uparrow$

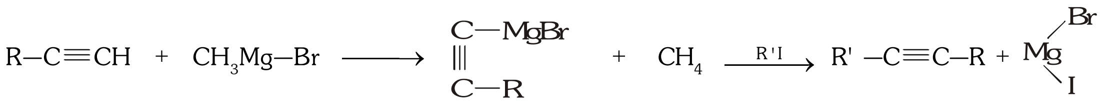
**Ex.** Is PH of solution changed in Kolbe's electrolysis.

**Sol.** The concentration of NaOH solution increased so pH of solution is increased with time.

5. **Preparation of higher alkynes by Grignard reagent** : By this method lower alkyne is converted in to higher alkyne



$$CH\equiv \overset{\delta-}{C}-\overset{\delta+}{H}+\overset{\delta-}{CH_3}-\overset{\delta+}{Mg}-Br \longrightarrow \begin{matrix}C-MgBr\\ |||\\ CH\end{matrix} + CH_4 \xrightarrow{RI} Mg\begin{matrix}Br\\ I\end{matrix} + R-C\equiv CH$$



$$R-C\equiv CH + CH_3Mg-Br \longrightarrow \begin{matrix}C-MgBr\\ |||\\ C-R\end{matrix} + CH_4 \xrightarrow{R'I} R'-C\equiv C-R + Mg\begin{matrix}Br\\ I\end{matrix}$$

6. **Preparation of Ethyne or Acetylene:**

(a) **From Metal carbide [ Laboratory method]** : Acetylene is prepared in the laboratory by the action of water on calcium carbide.

$CaC_2 + 2H_2O \longrightarrow CH\equiv CH + Ca(OH)_2$

$Ca^{+2} + \overset{\ominus}{C}\equiv\overset{\ominus}{C} + 2H^+ + 2OH^- \longrightarrow CH\equiv CH + Ca(OH)_2$

(b) **Manufacture** : Acetylene is manufactured by heating methane or natural gas at 1500°C in an electric arc

$$2CH_4 \xrightarrow{\text{Electric arc}} CH\equiv CH + 3H_2$$

(c) **Berthelot's process** : Acetylene is synthesized by striking an electric arc between carbon electrodes in presence of hydrogen. $2C + H_2 \xrightarrow{1200°C} CH\equiv CH$

(d) **From haloform [$CHI_3$, $CHCl_3$]** : Pure acetylene is obtained when iodoform or chloroform is heated with Silver powder

$$CHI_3 + 6Ag + I_3CH \longrightarrow CH{\equiv}CH + 6AgI$$

(e) **Partial oxidation of methane** : A recent method for manufacturing of acetylene is the controlled partial oxidation of methane at high temperature.

$$4CH_4 + 3O_2 \xrightarrow{1500°C} 2CH{\equiv}CH + 6H_2O$$

### ❑ Physical Properties :

(a) Alkynes are relatively nonopolar (w.r.t. alkyl halides and alcohols) and nearly insoluble in water (but they are more polar than alkenes and alkanes). They are quite soluble in most organic solvents, (acetone, ether, emthylene chloride, chloroform and alcohols).

(b) Acetylene, propyne, and the butynes are gases at room temperature, just like the corresponding alkanes and alkanes. In fact, the boiling points of alkynes are nearly the same as those of alkanes and alkenes with same number of carbon atoms.

### ❑ Chemical Properties :

The chemical properties of alkynes are due to two factors

(a) **Presence of $\pi$ electrons** : Due to presence of loosely bonded $\pi$ electrons, alkynes like alkenes, undergo easily electrophilic addition reaction.

Carbon-carbon triple bond is less reactive than the carbon-carbon double bond towards electrophilic addition reactions.

In addition to electrophilic additons, alkynes also undergo nucleophilic addition with nucleophiles

(b) **Presence of acidic hydrogen atom** : The hydrogen atom attached to the triple bonded carbon can be easily removed by a strong base and hence acetylene and 1-alkynes are considered as weak acids.

**Explanation** : The amounts of s-character in various types of C—H bonds is as-

| $\equiv C-H$ | $=C-H$ | $-C-H$ |
|---|---|---|
| 50% | 33% | 25% |

Since s electrons are closer to the nucleus than the p electrons, the electrons present in a bond having more s-character will be more closer to nucleus. Due to high s-character of the C—H bond in alkyne (s=50%) the electrons constituting this bond are more strongly held by the carbon nucleus, with the result the H present on CH can be easily removed as proton.

The acidic nature of the three types of –C–H bonds as

$$\underset{sp}{\equiv C-H} > \underset{sp^2}{=C-H} > \underset{sp^3}{-C-H}$$

Relative acidic order

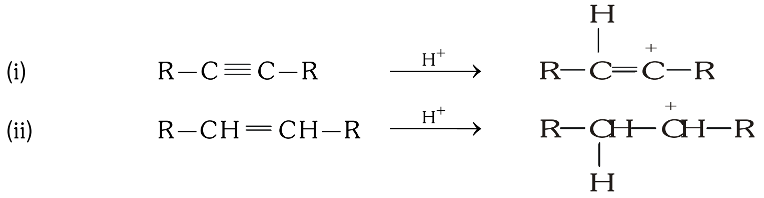
$$H_2O > ROH > HC{\equiv}CH > HNH_2 > CH_2{=}CH_2 > CH_3{-}CH_3$$

### ❑ Addition Reaction :

(1) **Electrophilic addition** : Addition reactions where the addition is initiated by electrophile (positive group).The characteristic reaction of alkynes is electrophilic addition but the reactivity of alkynes towards electrophilic addition is less than alkenes because in C≡C, the $\pi$ electrons are tightly held by carbon nuclei and so they are less easily available for reaction with electrophiles.

Reactivity order of hydrocarbons for electrophilic addition $\boxed{\text{Alkenes > Alkynes > Alkanes}}$.

**Another reasons is :** The intermediates when an electrophile attack on alkene and alkynes are :



(i) $R-C\equiv C-R \xrightarrow{H^+} R-\overset{\overset{H}{|}}{C}=\overset{+}{C}-R$

(ii) $R-CH=CH-R \xrightarrow{H^+} R-\underset{\underset{H}{|}}{CH}-\overset{+}{C}H-R$

**Stability of intermediates :**

$R-CH=\overset{\oplus}{C}-R$ < $R-CH_2-\overset{\oplus}{CH}-R$

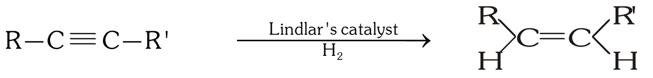
(+) ve on more EN atoms is less stable — more stable

So we can say that alkenes are more reactive towards electrophilic addition reaction.

**(a) Addition of hydrogen :** Alkynes reacts with hydrogen in presence of a catalyst.In presence of Pt., Pd or Ni alkynes give alkanes with $H_2$

$$R-C\equiv CH \xrightarrow[300°C]{Ni,H_2} R-CH=CH_2 \xrightarrow[300°C]{Ni,H_2} R-CH_2-CH_3$$

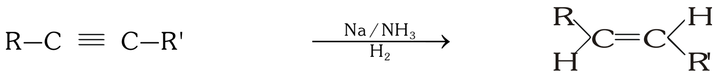
In presence of Lindlar's catalyst $[Pd/CaCO_3+$ quinoline or Nickle boride] alkynes give cis – alkene



(Stereo specific reaction)

cis - alkene

In presence of $Na/NH_3$ alkynes give trans-alkene. **(Birch Re-cuction)**

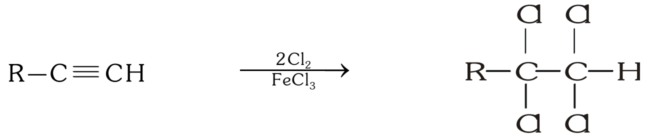


(Stereo specific reaction)

trans-alkene

**(b) Addition of Halogens :** Reactivity order of Halogens **$Cl_2 > Br_2 > I_2$**

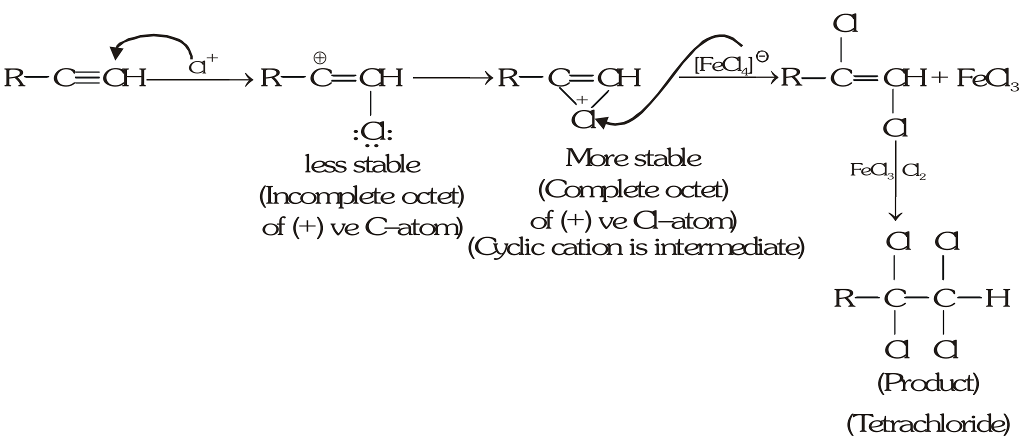
Alkynes react with $Cl_2$ or $Br_2$ in dark in presence of metal halide and form di and tetra halo derrivatives.



$$R-C\equiv CH \xrightarrow[FeCl_3]{2Cl_2} R-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-H$$

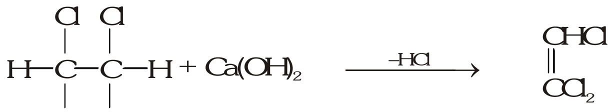
**Mechanism :**

$$Cl_2 + FeCl_3 \longrightarrow Cl^+ + FeCl_4^-$$



Acetylene tetrachloride is also called as westron.

When westron is treated with $Ca(OH)_2$ then we get westrosol



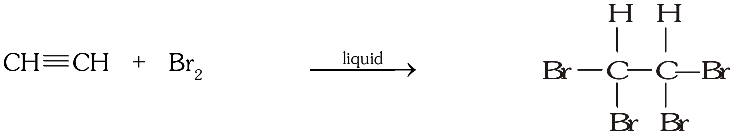
$$H-\underset{Cl}{\overset{Cl}{C}}-\underset{Cl}{\overset{Cl}{C}}-H + Ca(OH)_2 \xrightarrow{-HCl} CHCl{=}CCl_2$$

Westrosol or triclene

Both westron and westrosol are used as solvents in cloth industries

**Reaction with dilute $Br_2$ or bromine water:**

$$CH{\equiv}CH + Br_2 \xrightarrow{H_2O} Br-CH{=}CH-Br$$



$$CH{\equiv}CH + Br_2 \xrightarrow{\text{liquid}} Br-\underset{Br}{\overset{H}{C}}-\underset{Br}{\overset{H}{C}}-Br$$

**Reaction with Iodine :**

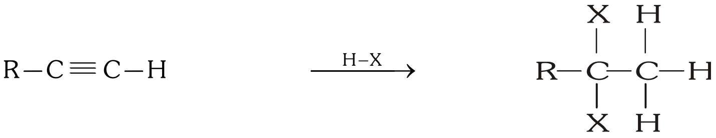
$$CH{\equiv}CH + I_2 \xrightarrow{\text{ethanol}} CHI{=}CHI \text{ (addition reaction)}$$

$$CH{\equiv}CH + I_2 \xrightarrow{NH_3} I-C{\equiv}C-I + NH_4I \text{ (substitution reaction)}$$

Di iodoacetylene

**(c) Addition of halogen acids (H – X) :** Addition according to Markowni-Koff's Rule.

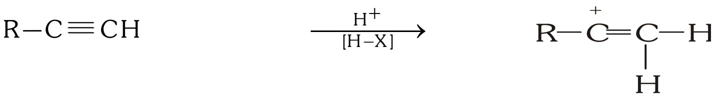
Reactivity order of H – X : $\boxed{HI > HBr > HCl > HF}$



$$R-C{\equiv}C-H \xrightarrow{H-X} R-\underset{X}{\overset{X}{C}}-\underset{H}{\overset{H}{C}}-H$$

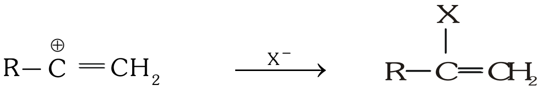
(Gem dihalides major product)

**Mechanism :**



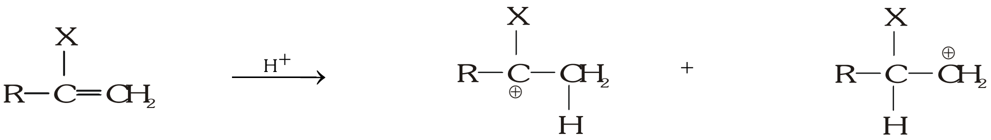
$$R-C{\equiv}CH \xrightarrow[{[H-X]}]{H^+} R-\overset{+}{C}{=}\underset{H}{C}-H$$

(Intermediate is carbocation)



$$R-\overset{\oplus}{C}{=}CH_2 \xrightarrow{X^-} R-\overset{X}{C}{=}CH_2$$

Further

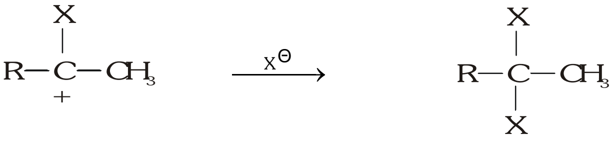


$$R-\overset{X}{C}{=}CH_2 \xrightarrow{H^+} R-\underset{\oplus}{\overset{X}{C}}-\underset{H}{CH_2} + R-\underset{H}{\overset{X}{C}}-\overset{\oplus}{CH_2}$$

(more stable due to +M of X)

(only –I of X)

so



$$R-\underset{+}{\overset{X}{C}}-CH_3 \xrightarrow{X^{\ominus}} R-\underset{X}{\overset{X}{C}}-CH_3$$

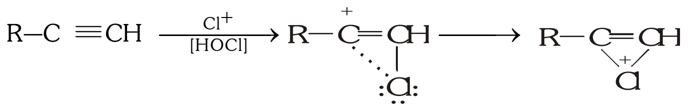
(Major Product)

(d) **Addition of HOX** : Alkynes react with hypohalous acids according to markownikoff's rule and form gem diol, which are unstable, lose a molecule of water and form halo aldehyde or halo ketones.

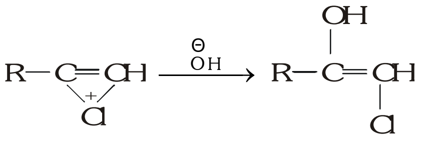
Reactivity order HOCl > HOBr > HOI

$$R-C\equiv CH + HOCl \longrightarrow R-\underset{\underset{O}{\|}}{C}-CHCl_2$$

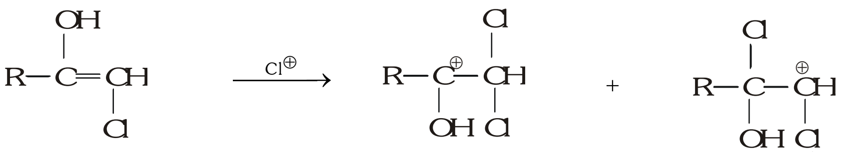
**Mechanism** :



(Cyclic cation)



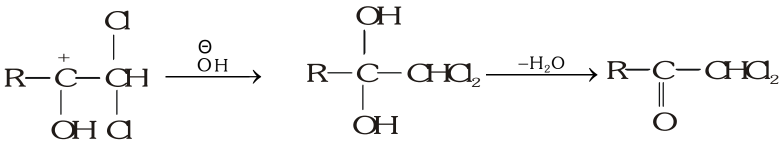
Further



(more stable due to +M of OH group)

(less + M of Cl - Atom)

so

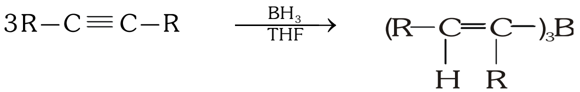


$$R-\overset{+}{C}(OH)-CH(Cl)Cl \xrightarrow{\overset{\ominus}{O}H} R-C(OH)_2-CHCl_2 \xrightarrow{-H_2O} R-\underset{\underset{O}{\|}}{C}-CHCl_2$$

(Unstable)

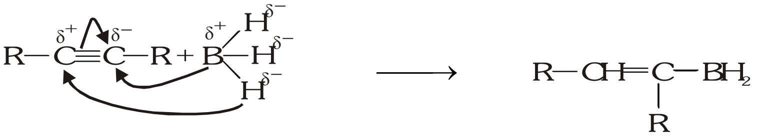
(Dichloro ketones)

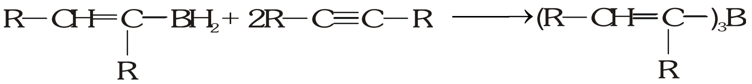
(e) **Addition of $BH_3$ / THF or $B_2H_6$ (Hydroboration)** : THF - Tetrahydrofurane is used as solvent.



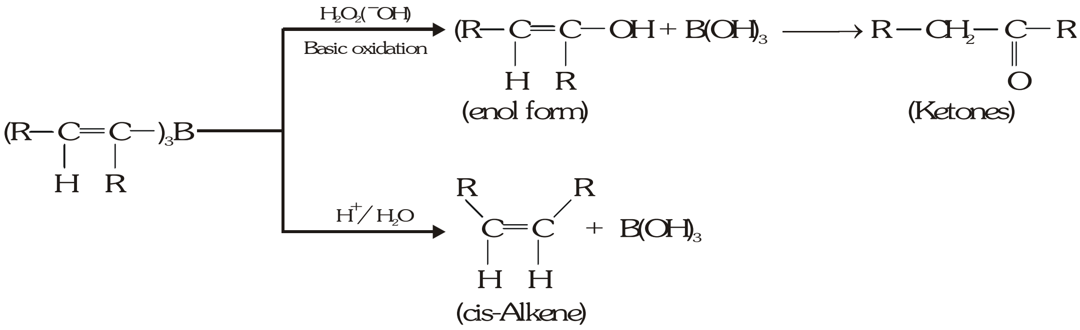
$$3R-C\equiv C-R \xrightarrow[THF]{BH_3} (R-\underset{H}{C}=\underset{R}{C}-)_3B$$

Since $BH_3$ is not available as monomer so a solvent THF is used for the stability of $BH_3$.





$$R-CH=\underset{R}{C}-BH_2 + 2R-C\equiv C-R \longrightarrow (R-CH=\underset{R}{C}-)_3B$$

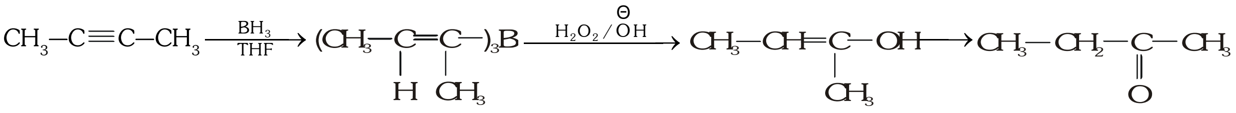


(enol form)

(Ketones)

(cis-Alkene)

**Example :**



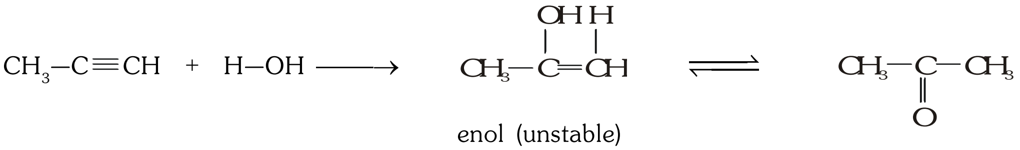
$$CH_3-C\equiv C-CH_3 \xrightarrow[THF]{BH_3} (CH_3-\underset{H}{C}=\underset{CH_3}{C}-)_3B \xrightarrow{H_2O_2/\overset{\ominus}{O}H} CH_3-CH=\underset{CH_3}{C}-OH \longrightarrow CH_3-CH_2-\underset{\underset{O}{\|}}{C}-CH_3$$

(enol form less stable) (keto form more stable)

(2) **Nucleophilic addition reaction** : In these reactions some heavy metal cation like $Hg^{+2}$, $Pb^{+2}$, $Ba^{+2}$ are used. These cation attracts the $\pi^-$ $e^-$ of alkynes and decrease the $e^-$ density and hence a nucleophile can attack an alkynes.

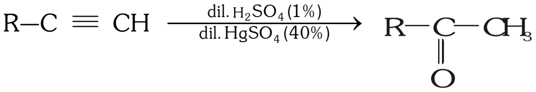
(a) **Addition of dil. $H_2SO_4$ (Hydration)** : The addition of water takes place in the presence of $Hg^{+2}$ and $H_2SO_4$ [1% $HgSO_4$+40% $H_2SO_4$]. In this reaction carbonyl compounds are obtained .

$$CH \equiv CH + H-OH \longrightarrow \underset{\text{enol unstable}}{CH_2=CH-OH} \rightleftharpoons CH_3-CHO$$



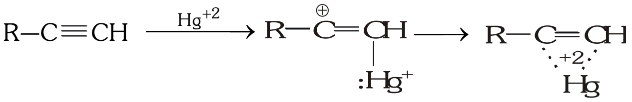
$$CH_3-C\equiv CH + H-OH \longrightarrow \underset{\text{enol (unstable)}}{CH_3-\overset{OH}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}H} \rightleftharpoons CH_3-\underset{\underset{O}{\|}}{C}-CH_3$$

A structure in which –OH group is attached to double bond carbon is called as enol (ene + – ol).
This reaction is used for preparation of aldehyde and ketone.

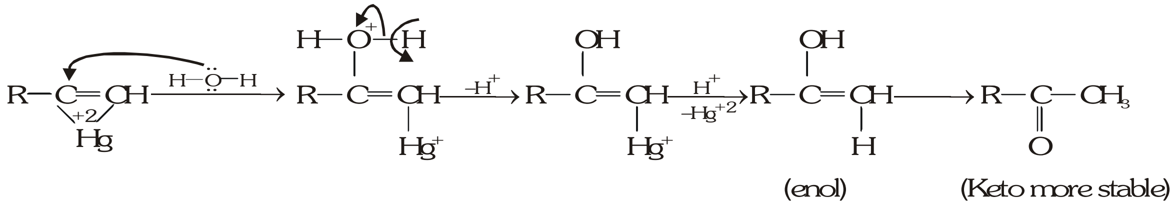


$$R-C \equiv CH \xrightarrow[\text{dil. }HgSO_4\,(40\%)]{\text{dil. }H_2SO_4\,(1\%)} R-\underset{\underset{O}{\|}}{C}-CH_3$$

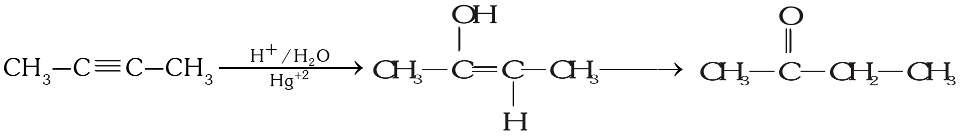
**Mechanism :**



$$R-C\equiv CH \xrightarrow{Hg^{+2}} R-\overset{\oplus}{\underset{:Hg^+}{C}}=CH \longrightarrow \underset{Hg}{\underset{\cdot\cdot+2\cdot\cdot}{R-C=CH}}$$



$$\underset{Hg}{\underset{+2}{R-C=CH}} \xrightarrow{H-\ddot{O}-H} R-\overset{H-\overset{+}{O}-H}{\overset{|}{C}}=\underset{Hg^+}{CH} \xrightarrow{-H^+} R-\overset{OH}{\overset{|}{C}}=\underset{Hg^+}{CH} \xrightarrow[-Hg^{+2}]{H^+} \underset{\text{(enol)}}{R-\overset{OH}{\overset{|}{C}}=\underset{H}{CH}} \longrightarrow \underset{\text{(Keto more stable)}}{R-\underset{\underset{O}{\|}}{C}-CH_3}$$



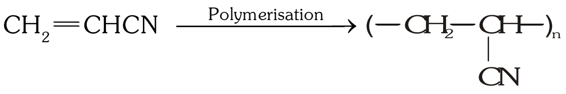
**Example** : $$CH_3-C\equiv C-CH_3 \xrightarrow[Hg^{+2}]{H^+/H_2O} CH_3-\overset{OH}{\overset{|}{C}}=\underset{H}{C}-CH_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$$

2-butanone

(b) **Addition of HCN** : The addition of HCN in presence of barium cyanide to form vinyl cyanide.

$$CH\equiv CH + HCN \xrightarrow{Ba(CN)_2} CH_2=CHCN$$

The vinyl cyanide is used for making polymers such as orlon and Buna-N rubber.



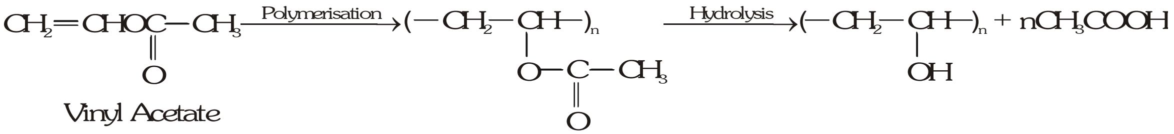
$$CH_2=CHCN \xrightarrow{\text{Polymerisation}} (-CH_2-\underset{CN}{CH}-)_n$$

Orlon

(c) **Addition of acetic acid :** Acetate acetylene combines with acetic acid in presence of murcuricsulphate. It first forms vinyl acetate and then ethylidene acetate.

$$\begin{matrix} CH \\ ||| \\ CH \end{matrix} + \begin{matrix} H \\ | \\ OOCCH_3 \end{matrix} \xrightarrow{Hg^{+2}} \begin{matrix} CH_2 \\ || \\ CHOOCCH_3 \end{matrix} \xrightarrow{CH_3COOH} \begin{matrix} CH_3 \\ | \\ CH(OOCCH_3)_2 \end{matrix}$$

vinyl acetate Ethylidene acetate



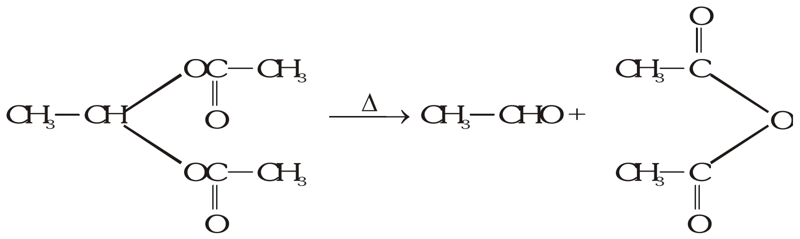
$$\underset{\underset{O}{||}}{CH_2{=}CHOC{-}CH_3} \xrightarrow{Polymerisation} (-CH_2-\underset{\underset{\underset{O}{||}}{O-C-CH_3}}{|}{CH}-)_n \xrightarrow{Hydrolysis} (-CH_2-\underset{OH}{\underset{|}{CH}}-)_n + nCH_3COOH$$

Vinyl Acetate (Monomer)

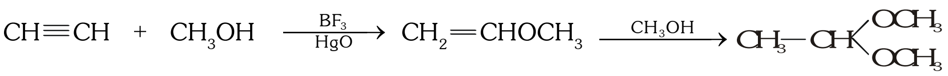
Poly vinyl acetate (Polymer : adhesive compound)

Poly vinyl alcohol

When ethylidene acetate is heated it give acetaldehyde and acetic anhydride

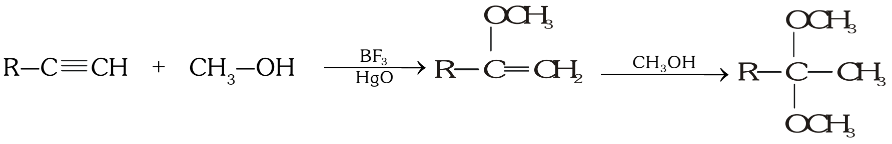


(d) **Addition of alcohols :** In presence of $BF_3$ and HgO alkynes react with alcohols and form acetal and ketal



$$CH{\equiv}CH + CH_3OH \xrightarrow[HgO]{BF_3} CH_2{=}CHOCH_3 \xrightarrow{CH_3OH} CH_3-CH\begin{matrix} OCH_3 \\ OCH_3 \end{matrix}$$

Methylal (acetal)

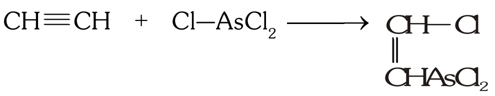


$$R-C{\equiv}CH + CH_3-OH \xrightarrow[HgO]{BF_3} R-\overset{\overset{OCH_3}{|}}{C}{=}CH_2 \xrightarrow{CH_3OH} R-\underset{\underset{OCH_3}{|}}{\overset{\overset{OCH_3}{|}}{C}}-CH_3$$

Ketal

Acetylene forms acetal while other alkynes form ketal.

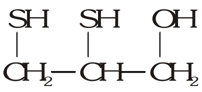
(3) **Addition of $AsCl_3$ :** In presence of $AlCl_3$ or $HgCl_2$ acetylene combines with $AsCl_3$ to yield Lewisite gas. It is four times poisonous than mustard gas.



$$CH{\equiv}CH + Cl-AsCl_2 \longrightarrow \begin{matrix} CH-Cl \\ || \\ CHAsCl_2 \end{matrix}$$

2-Chlorovinyl dichloro arsine (Lewisite gas)

The action of Lewsite may be checked by its antidote BAL (British Anti Lewisite). BAL combines with the Lewisite to form a cyclic non toxic compound.



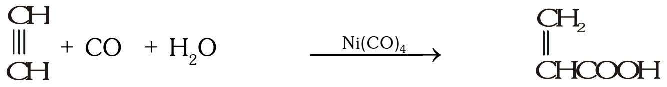
$$\overset{\overset{SH}{|}}{CH_2}-\overset{\overset{SH}{|}}{CH}-\overset{\overset{OH}{|}}{CH_2}$$

2, 3–Dimercapto–1–propanol [BAL]

(4) **Carbonylation** : Reaction of alkynes with CO in presence of $Ni(CO)_4$

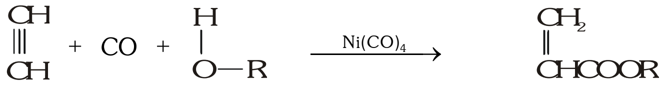
$$\text{Alkyne} + CO + H_2O \xrightarrow{Ni(CO)_4} \text{Olefinic acid}$$

$$\text{Alkyne} + CO + R\text{–}OH \xrightarrow{Ni(CO)_4} \text{Olefinic ester}$$



$$\begin{matrix}CH\\ |||\\ CH\end{matrix} + CO + H_2O \xrightarrow{Ni(CO)_4} \begin{matrix}CH_2\\ \|\\ CHCOOH\end{matrix}$$

Acrylic acid



$$\begin{matrix}CH\\ |||\\ CH\end{matrix} + CO + \begin{matrix}H\\ |\\ O\text{—}R\end{matrix} \xrightarrow{Ni(CO)_4} \begin{matrix}CH_2\\ \|\\ CHCOOR\end{matrix}$$

Alkyl acrylate

❑ Oxidation reactions :

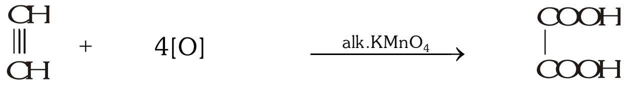
(a) **Combustion** :

$$C_nH_{2n-2} + \frac{3n-1}{2}O_2 \longrightarrow nCO_2 + (n\text{-}1)\ H_2O + \text{Heat}$$

$$2HC{\equiv}CH + 5O_2 \longrightarrow 4CO_2 + 2H_2O + 312\ \text{K.cal}$$

The combustion of acetylene is used for welding and cutting of metals in which oxy-acetylene flame having high temp (3000°C) is produced.

(b) **Oxidation with alkaline $KMnO_4$:** Oxidation with alkaline $KMnO_4$ gives carboxylic acids.

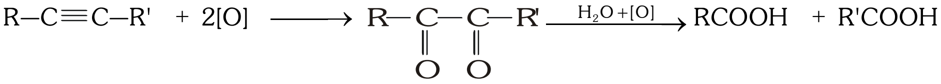


$$\begin{matrix}CH\\ |||\\ CH\end{matrix} + 4[O] \xrightarrow{alk.KMnO_4} \begin{matrix}COOH\\ |\\ COOH\end{matrix}$$

Acetylene Oxalic acid

$$CH_3\text{—}C{\equiv}CH + 4[O] \xrightarrow{alk.KMnO_4} CH_3\text{—}COOH + HCOOH$$

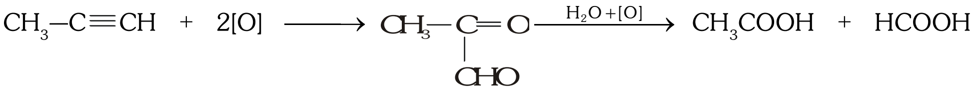
(c) **Oxidation with acidic $KMnO_4$ or $K_2Cr_2O_7$ :** In presence of acidic $KMnO_4$ or acidic $K_2Cr_2O_7$. Alkynes are oxidised to monocarboxylic acids.



$$R\text{—}C{\equiv}C\text{—}R' + 2[O] \longrightarrow R\text{—}\underset{\underset{O}{\|}}{C}\text{—}\underset{\underset{O}{\|}}{C}\text{—}R' \xrightarrow{H_2O+[O]} RCOOH + R'COOH$$

$$\begin{matrix}CH\\ |||\\ CH\end{matrix} + 2[O] \longrightarrow \begin{matrix}CHO\\ |\\ CHO\end{matrix} \xrightarrow{H_2O+[O]} 2HCOOH$$

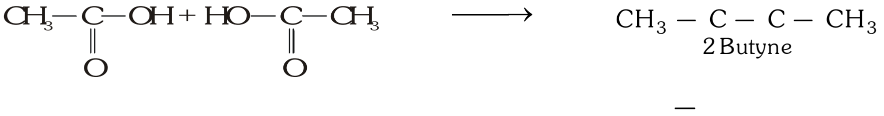
glyoxal



$$CH_3\text{—}C{\equiv}CH + 2[O] \longrightarrow CH_3\text{—}\underset{\underset{CHO}{|}}{C}{=}O \xrightarrow{H_2O+[O]} CH_3COOH + HCOOH$$

**Ex.** An alkyne on oxidation with acidic $KMnO_4$, only acetic acid is obtained what is given alkynes ?

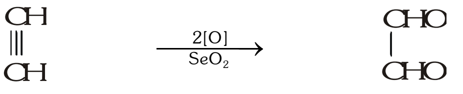
**Sol.** In Oxidation of alkynes two moles of mono carboxylic acids are obtained.



$$CH_3\text{—}\underset{\underset{O}{\|}}{C}\text{—}OH + HO\text{—}\underset{\underset{O}{\|}}{C}\text{—}CH_3 \longrightarrow CH_3 - C - C - CH_3$$

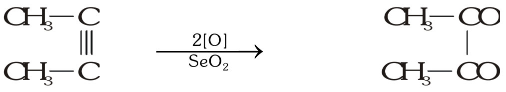
2 Butyne

(d) **Oxidation with selenium dioxide :** Selenium dioxide oxidises alkynes to the dicarbonyl compounds.



$$\begin{matrix}CH\\ |||\\ CH\end{matrix} \xrightarrow[SeO_2]{2[O]} \begin{matrix}CHO\\ |\\ CHO\end{matrix}$$

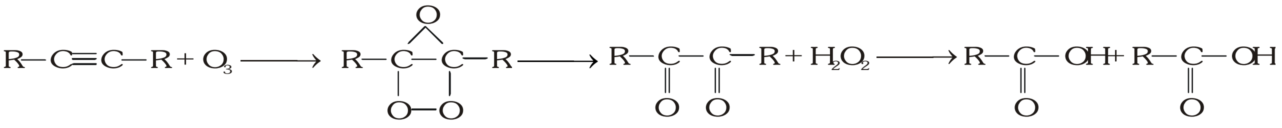
Glyoxal



$$\begin{matrix}CH_3-C\\ \quad\ |||\\ CH_3-C\end{matrix} \xrightarrow[SeO_2]{2[O]} \begin{matrix}CH_3-CO\\ \quad\ \ |\\ CH_3-CO\end{matrix}$$

2–Butyne Butane - 2, 3 -dione

(e) **Oxidation with ozone ($O_3$) :** In the ozonolysis both sp-C-atoms are converted into $-\underset{\overset{\|}{O}}{C}-\underset{\overset{\|}{O}}{C}-$group.



$$R-C\equiv C-R+O_3\longrightarrow R-\underset{O-O}{\overset{O}{C-C}}-R\longrightarrow R-\underset{\overset{\|}{O}}{C}-\underset{\overset{\|}{O}}{C}-R+H_2O_2\longrightarrow R-\underset{\overset{\|}{O}}{C}-OH+R-\underset{\overset{\|}{O}}{C}-OH$$

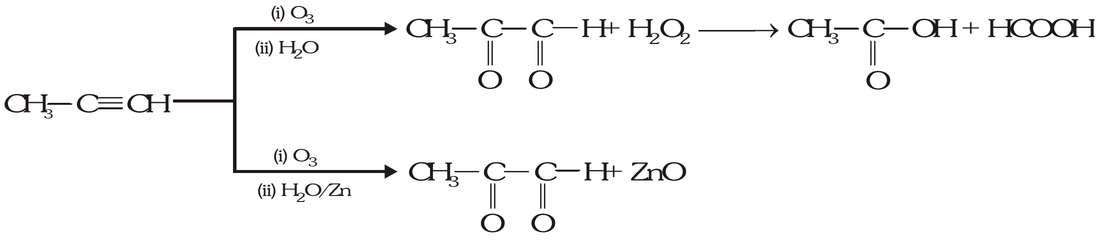
Ozonide (Addition of ozone) (Acids)

In this reaction $H_2O_2$ is oxidant which oxidise $R-\underset{\overset{\|}{O}}{C}-\underset{\overset{\|}{O}}{C}-R$ into acids.

But if we use some amount of Zn as reductant with $H_2O$ then it reduce $H_2O_2$ so oxidation does not take place

$H_2O_2 + Zn \longrightarrow ZnO + H_2O$

**Example :**



$$CH_3-C\equiv CH \xrightarrow[(ii)\ H_2O]{(i)\ O_3} CH_3-\underset{\overset{\|}{O}}{C}-\underset{\overset{\|}{O}}{C}-H+H_2O_2\longrightarrow CH_3-\underset{\overset{\|}{O}}{C}-OH+HCOOH$$

$$CH_3-C\equiv CH \xrightarrow[(ii)\ H_2O/Zn]{(i)\ O_3} CH_3-\underset{\overset{\|}{O}}{C}-\underset{\overset{\|}{O}}{C}-H+ZnO$$

❑ **Substitution Reaction : (Formation of metallic derivatives)**

Only 1-alkynes give substitution reaction and show acidic characters $\equiv\overset{\delta^-}{C}-\overset{+\delta}{H}$

Acetylene is dibasic acid where as propyne is monobasic means acetylene can give two $H^+$ where as propyne can give one $H^+$.

(a) **Formation of sodium acetylides :** Acetylene and 1-alkynes react with sodamide to form acetylides

$$H-C\equiv C-H \xrightarrow{NaNH_2} NaC\equiv C-H \xrightarrow{NaNH_2} NaC\equiv CNa$$

Mono sodium acetylide Disodium acetylide

Dry alkynides are generally unstable and explosive. These are easily converted in to original alkynes when heated with dilute acids.

$NaC\equiv CNa + 2HNO_3 \longrightarrow HC\equiv CH + 2NaNO_3$

This reaction can be used for the purification, seperation and identification of 1-alkynes.

(b) **Formation of copper and silver acetylides** : Copper and silver acetylides are obtained by passing 1-alkynes in the ammonical solution of cuprous chloride and silver nitrate (Tollen's reagent) respectivley.

$$\mathrm{R{-}C{\equiv}C{-}H} + \underset{\text{ammonical cuprous-chloride}}{\mathrm{Cu_2Cl_2 + NH_4OH}} \longrightarrow \underset{\substack{\text{copper acetylide}\\ \text{[Red ppt.]}}}{\mathrm{R{-}C{\equiv}CCu}} + \mathrm{NH_4Cl} + \mathrm{H_2O}$$

$$\mathrm{R{-}C{\equiv}C{-}H} + \underset{\text{Tollen's reagent}}{\mathrm{AgNO_3 + NH_4OH}} \longrightarrow \underset{\text{White ppt.}}{\mathrm{R{-}C{\equiv}CAg}} + \mathrm{NH_4NO_3} + \mathrm{H_2O}$$

These reactions are used for detecting the presence of acetylenic hydrogen.These are test for distinguish alkenes and alkynes or 1-alkynes and 2-alkynes.

❑ **Isomerisation** : When alkyne-1 is heated with alc. KOH alkyne-2 is obtained.

$$\underset{\text{1–Butyne}}{\mathrm{CH_3{-}CH_2{-}C{\equiv}CH}} \xrightarrow[\Delta]{\text{alc. KOH}} \underset{\text{2–Butyne}}{\mathrm{CH_3{-}C{\equiv}C{-}CH_3}}$$

When alkyne -2 is heated with $NaNH_2$ alkyne -1 is obtained

$$\underset{\text{2–Butyne}}{\mathrm{CH_3{-}C{\equiv}C{-}CH_3}} \xrightarrow[\Delta]{\mathrm{NaNH_2}} \underset{\text{1–Butyne}}{\mathrm{CH_3{-}CH_2{-}C{\equiv}CH}}$$

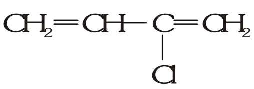
❑ **Polymerisation** :

(a) **Linear polymerisation** :

**Dimerisation** : When two molecules of acetylene passed through a solution of $Cu_2Cl_2$ and $NH_4Cl$ a vinyl acetylene is obtained.

$$\mathrm{2HC{\equiv}C{-}H} \xrightarrow[\mathrm{NH_4Cl}]{\mathrm{Cu_2Cl_2}} \underset{\text{mono vinyl acetylene}}{\mathrm{CH_2{=}CH{-}C{\equiv}C{-}H}}$$

When vinyl acetylene react with HCl then chloroprene is obtained.



$$\mathrm{CH_2{=}CH{-}C{\equiv}C{-}H} \xrightarrow{\mathrm{HCl}} \mathrm{CH_2{=}CH{-}\underset{\substack{|\\ Cl}}{C}{=}CH_2} \xrightarrow{\text{Polymerisation}} \textbf{Neoprene}\ \text{(Synthetic rubber)}$$

2- chloro-1,3-butadiene

**[chloroprene]**

**Trimerisation** : 3 molecules of acetylene.

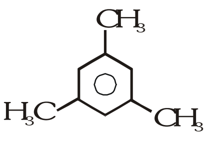
$$\mathrm{3CH{\equiv}CH} \xrightarrow[\mathrm{NH_4Cl}]{\mathrm{Cu_2Cl_2}} \underset{\text{Divinyl acetylene}}{\mathrm{CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2}}$$

(b) **Cyclic polymerisation** : When alkyne is passed through red hot metallic tube, cyclic polymerisation takes place with the formation of aromatic compound

$$\mathrm{3CH{\equiv}CH} \xrightarrow[\text{iron tube}]{\text{Red hot}}$$

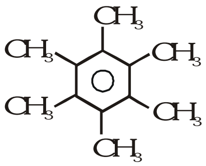
Benzene

$$\mathrm{3\ CH_3{-}C{\equiv}CH} \xrightarrow[\text{iron tube}]{\text{Red hot}}$$



Mesitylene

$$\mathrm{3\ CH_3{-}C{\equiv}C{-}CH_3} \xrightarrow[\text{iron tube}]{\text{Red hot}}$$

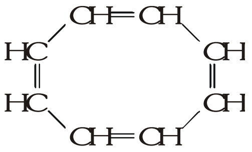


Hexa methyl benzene

$$3\ HC\equiv CH \xrightarrow[(C_6H_5)_3P]{Ni(CO)_4} \text{benzene (90\% yield)}$$

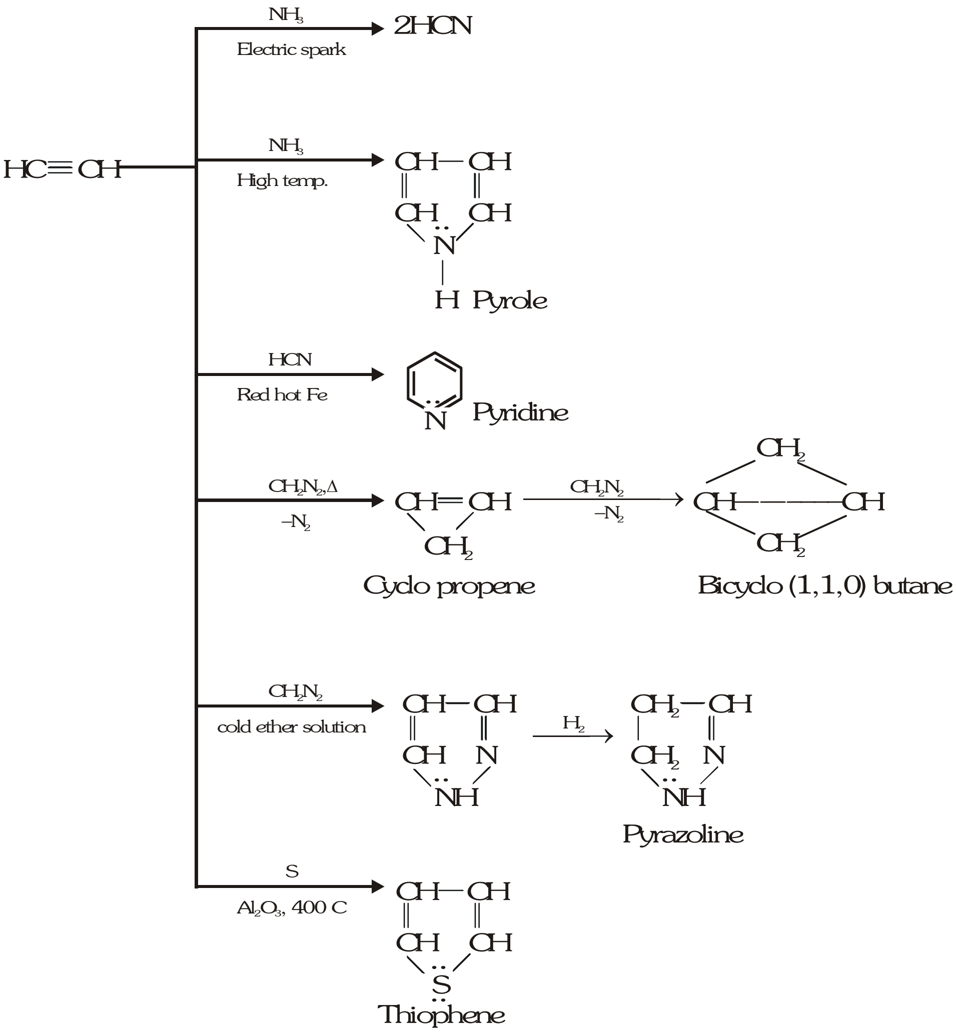
(triphenyl–1–phosphene)

$$4CH\equiv CH \xrightarrow{Ni(CN)_2}$$

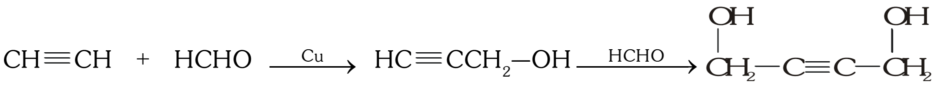


1,3,5,7–cyclooctatetraene

Other reactions of acetylene :



**(vi) Reaction with HCHO** : This reaction is called ethynylation.



$$CH\equiv CH + HCHO \xrightarrow{Cu} HC\equiv CCH_2{-}OH \xrightarrow{HCHO} \underset{\substack{|\\ \text{OH}}}{}\!\!\overset{\text{OH}}{\overset{|}{CH_2}}{-}C\equiv C{-}\overset{\text{OH}}{\overset{|}{CH_2}}$$

propargyl alcohol

**(vii) Reaction with NaOCl : (Substitution reaction)**

$$H - C\equiv C{-}H + NaOCl \xrightarrow[\text{absence of air and light}]{0°C} H{-}C\equiv C{-}Cl + NaOH$$

$$H{-}C\equiv C{-}Cl + NaOCl \xrightarrow[\text{absence of air and light}]{0°C} Cl{-}C\equiv C{-}Cl + NaOH$$

Dichloro acetylene

## ❑ Uses of Acetylene :

(i) Oxyacetylene flame used in welding and cutting

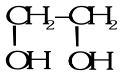
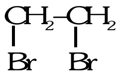
(ii) Acetylene is used as an illuminant

(iii) Acetylene is used for artificial ripenning of fruits

(iv) Used for manufacture of acetaldehyde, acetic acid, ethyl alcohol, westron, westrosol, PVC, PVA, Chloroprene, butadiene, Lewisite etc.

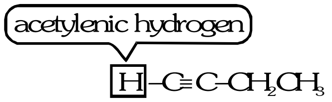
(v) It is used as a general anaesthetic.

## ❑ Laboratory Test for alkynes :

| Functional Group | Reagent | Observation | Reaction | Remarks |
|---|---|---|---|---|
| – C ≡ C – | (1) Bayer's Reagent<br>alk.dil.Cold $KMnO_4$ | Pink Colour disappears | $CH_2{=}CH_2+H_2O+O \xrightarrow{alk.KMnO_4}$  $\underset{OH}{CH_2}-\underset{OH}{CH_2}$ | Hydroxylation |
|  | (2) $Br_2/H_2O$ | Red Colour decolourises | $Br_2+CH_2{=}CH_2 \longrightarrow$  $\underset{Br}{CH_2}-\underset{Br}{CH_2}$<br>White ppt | Bromination |
|  | (3) $O_3$ (ozone) | Acid Formed | $R–C{\equiv}C–R' \xrightarrow{O_3} RCOOH+R'COOH$ | Ozonolysis |

## ❑ Laboratory test of terminal alkynes :

When triple bond comes at the end of a carbon chain. The alkyne is called a terminal alkyne.



1-Butyne, a terminal alkyne

| Functional Group | Reagent | Observation | Reaction |
|---|---|---|---|
| R–C≡C–H | (1) Cuprous chloride<br>+ $NH_4OH$ | Red ppt. | $R–C{\equiv}CH+CuCl \xrightarrow{NH_4OH} R–C{\equiv}C\,Cu\downarrow(red)$ |
|  | (2) $AgNO_3+NH_4OH$ | White ppt. | $R–C{\equiv}CH+Ag' \rightarrow R–C \equiv C\ Ag \downarrow$ (white) |
|  | (3) Na in ether | Colourless gas | $HC \equiv CH + 2Na \rightarrow Na – C \equiv C – Na + H_2 \uparrow$ |

(i) Decolourization of $Br_2$ in $CCl_4$ solution.

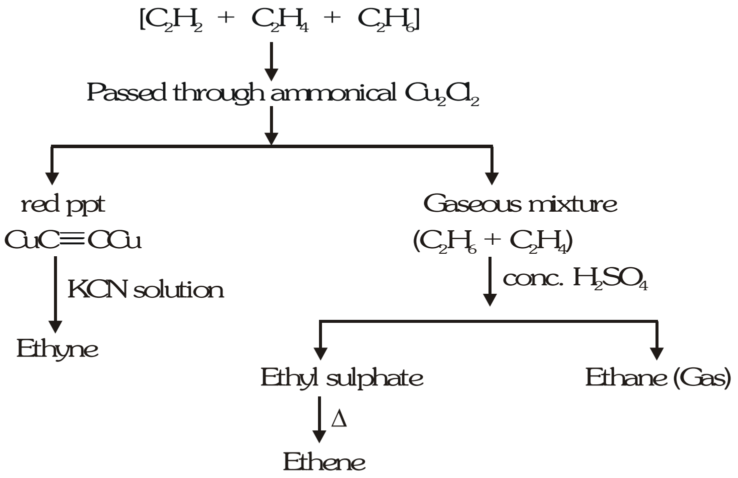
(ii) Decolourisation of 1% alkaline $KMnO_4$ solution.

(iii) 1- alkynes give white ppt. with ammonical $AgNO_3$ and red ppt with ammonical cuprous chloride solution.

**Note :** (i) and (ii) tests are used for determination of unsaturation (i.e, presence of double or triple bond in any compound)

(iii) Test is used for distinguish between alkenes and 1-alkynes or 1-alkyne and 2-alkyne.

### ❑ Seperation of ethane, ethene and ethyne :



# SOLVED EXAMPLES

**Ex.** $R-CH_2-CCl_2-R \xrightarrow{\text{Reagent}} R-C \equiv C-R$. The reagent is -

(A) Na (B) HCl in $H_2O$ (C) KOH in $C_2H_5OH$ (D) Zn in alcohol.

**Ans.**(C)

**Sol.** Alcoholic KOH brings about dehyrohalogenation

**Ex.** Acetylene when treated with dilute HCl at $60^0C$ (333 K) in presence of $HgCl_2$ produces -

(A) Methyl chloride (B) Vinyl chloride (C) Acetaldehyde (D) Formaldehyde

**Ans.**(B)

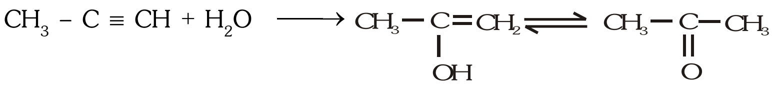
**Sol.** (B) $H-C \equiv C-H + HCl \xrightarrow[60^\circ]{HgCl_2} CH_2 = CH-Cl$

Vinyl chloride

**Ex.** When propyne is treated with aqueous $H_2SO_4$ in the presence of $HgSO_4$, the major product is -

(A) Acetaldehyde (B) Propanal (C) 2-Propanol (D) Propanone **Ans.**(D)

**Sol.**



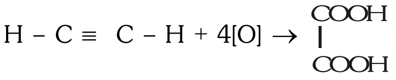
$$CH_3-C \equiv CH + H_2O \longrightarrow CH_3-\underset{\underset{OH}{|}}{C}=CH_2 \rightleftharpoons CH_3-\underset{\underset{O}{\|}}{C}-CH_3$$

**Ex.** Alkaline $KMnO_4$, oxidizes acetylene to -

(A) Acetic acid (B) Glyoxal (C) Oxalic acid (D) Ethylene glycol

**Ans.**(C)

**Sol.**



$$H-C \equiv C-H + 4[O] \rightarrow \begin{matrix} COOH \\ | \\ COOH \end{matrix}$$

**Ex.** Which of the following is most acidic -

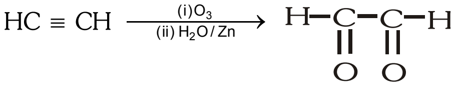
(A) Ethyne (B) Propyne (C) 1-Butyne (D) 2-Butyne **Ans.**(A)

**Sol.** Because ethyne gives most stable anion.

**Ex.** Ozonolysis of acetylene gives -

(A) Oxalic acid (B) Ethylene glycol (C) Glyoxal (D) $CH_3CHO$ **Ans.**(C)

**Sol.**



$$HC \equiv CH \xrightarrow[\text{(ii) } H_2O/Zn]{\text{(i)}O_3} H-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-H$$

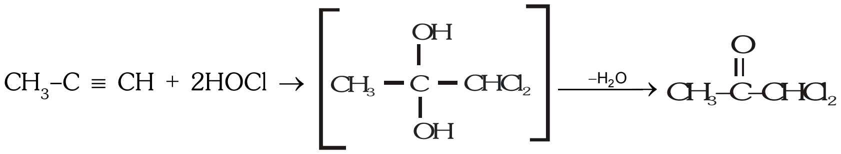
Glyoxal

**Ex.** Propyne on reaction with aqueous chlorine gives -

(A) 1, 1, 2, 2-Tetrachloropropane (B) 1, 2-Dichloropropene

(C) 1, 1-Dichloropropanone (D) 2, 2-Dichloropropanone **Ans.**(C)

**Sol.**

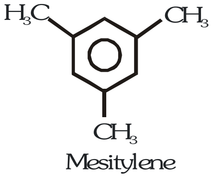


$$CH_3-C \equiv CH + 2HOCl \rightarrow \left[ CH_3-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}}-CHCl_2 \right] \xrightarrow{-H_2O} CH_3-\overset{\overset{O}{\|}}{C}-CHCl_2$$

**Ex.** Mesitylene can be obtained by polymerization of -

(A) Ethyne (B) Ethene (C) Propene (D) Propyne **Ans.**(D)

**Sol.** Propyne on trimerization yields mesitylene $3CH_3C \equiv CH \rightarrow$



**Ex.** Excess of $CH_3COOH$ is reacted with $CH \equiv CH$ in presence of $Hg^{2+}$, the product is -

(A) $CH_3CH(OOCCH_3)_2$ (B) $CH_2 = CH(OOCCH_3)$

(C) $(CH_3COO)CH_2-CH_2(OOCCH_3)$ (D) None of these

**Ans.**(A)

**Sol.** $H-C \equiv C-H + 2CH_3COOH \longrightarrow CH_3 - CH(OCOCH_3)_2$

Both the protons go to same carbon atom

**Ex.** A compound is treated with $NaNH_2$ to give sodium salt. Identify the compound -

(A) $C_2H_2$ (B) $C_6H_6$ (C) $C_2H_6$ (D) $C_2H_4$

**Ans.**(A)

**Sol.** Ethyne is acidic in character

$$H-C \equiv C-H + NaNH_2 \longrightarrow H - C \equiv C^-Na^+ + \frac{1}{2}H_2$$