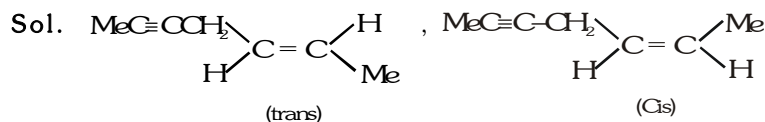


Ex. Cis-trans isomerism is not possible in alkynes because of :-

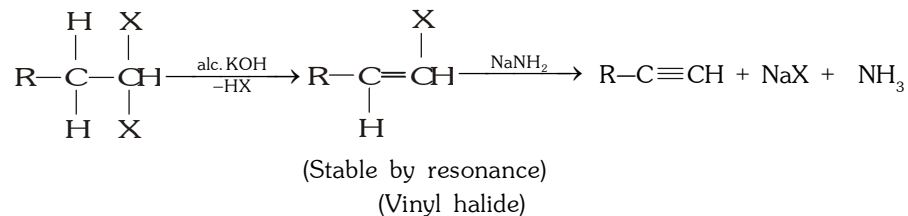
Sol. 180° bond-angle at the carbon-carbon triple bond.

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



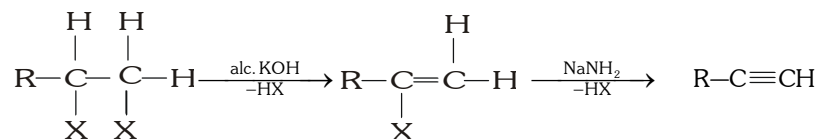
□ General Methods of Preparation :

- From Gem dihalides (by dehydrohalogenation) :** Dehydrohalogenation agents are : NaNH_2 (Sodamide) or Alc. KOH or $\text{ROH} + \text{RONa}$.

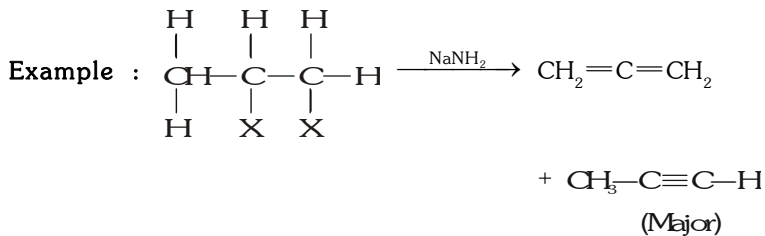


- Due to stability of vinyl halide by resonance there is partial double bond in which elimination does not take place by alc. KOH so stronger base NaNH_2 is used.
- Basic strength : NH_2^- is stronger base than RO^-
- Trans elimination takes place in forming of alkynes.

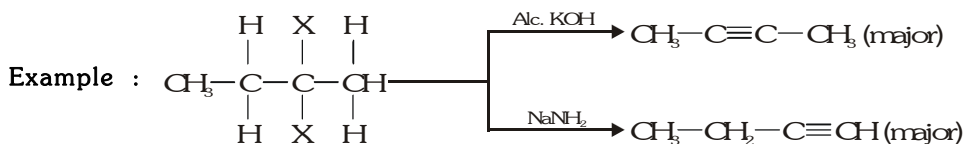
- From Vicinal dihalides (by dehydrohalogenation) :**



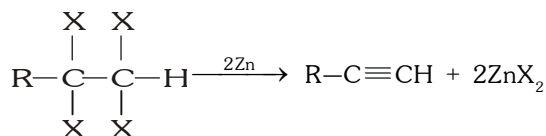
- Elimination of Vic. dihalides gives also alkadiene (1, 2 and 1, 3 alkadienes) but the major product is alkyne.



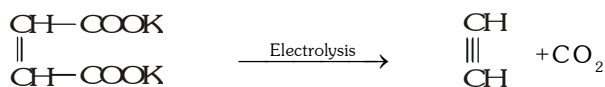
- Non terminal gem dihalide gives 2-Alkyne in presence of alc. KOH while gives 1-alkyne in presence of NaNH_2 .



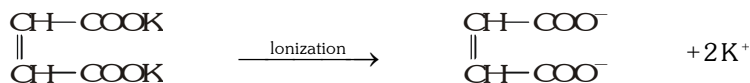
- Dehalogenation of tetrahalo alkane :** By heating 1, 1, 2, 2 - tetra halo alkane with Zn dust.



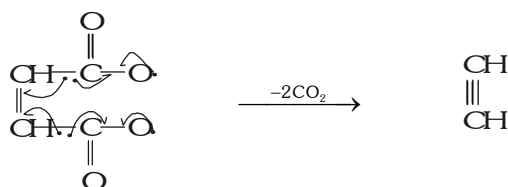
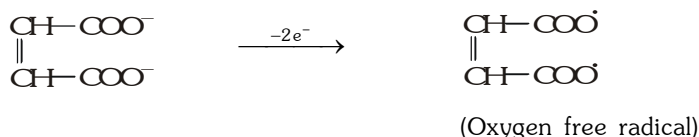
4. **From Kolbe's electrolysis :** By the electrolysis of aqueous solution of sodium or potassium fumarate or maleate, acetylene is formed at anode.



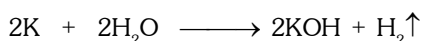
Mechanism :



at anode (Alkyl and CO_2 gas is formed)



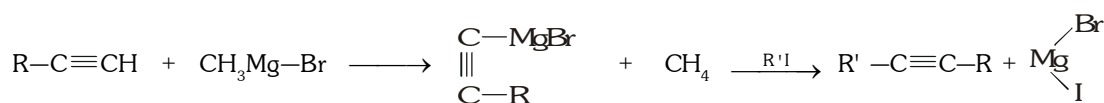
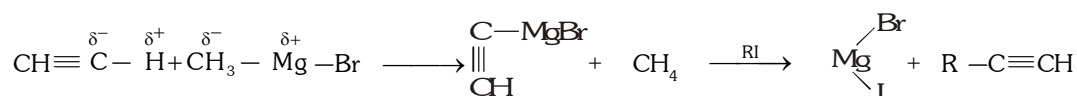
at cathode (KOH and H_2 gas is formed)



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

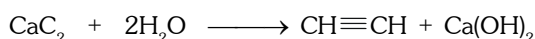
Sol. The concentration of NaOH solution increased so pH of solution is increased with time.

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

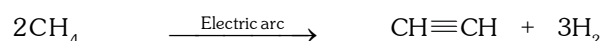


6. **Preparation of Ethyne or Acetylene:**

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

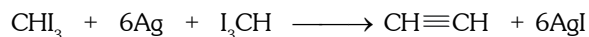


- (b) **Manufacture :** Acetylene is manufactured by heating methane or natural gas at 1500°C in an electric arc

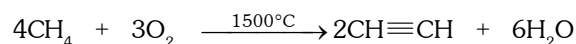


- (c) **Berthelot's process :** Acetylene is synthesized by striking an electric arc between carbon electrodes in presence of hydrogen.
- $$2\text{C} + \text{H}_2 \xrightarrow{1200^\circ\text{C}} \text{CH}\equiv\text{CH}$$

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



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



Physical Properties :

- (a) Alkynes are relatively nonpolar (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, ethylene chloride, chloroform and alcohols).
- (b) Acetylene, propyne, and the butynes are gases at room temperature, just like the corresponding alkanes and alkenes. 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 π electrons** : Due to presence of loosely bonded π 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 additions, alkynes also undergo nucleophilic addition with nucleophiles

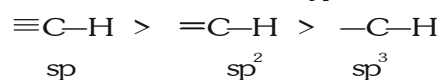
- (b) **Presence of acidic hydrogen atom** : The hydrogen atom attached to the triple bonded carbon can be easily removed by a strong base and hence acetylene and 1-alkynes are considered as weak acids.

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

$\equiv\text{C}-\text{H}$	$=\text{C}-\text{H}$	$-\text{C}-\text{H}$
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



Relative acidic order

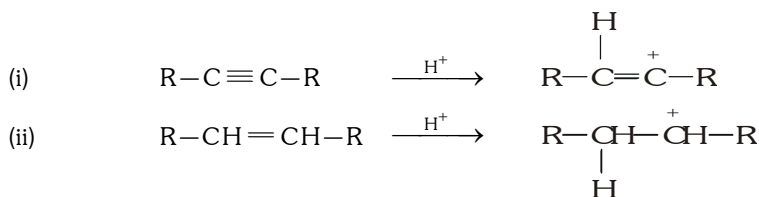


Addition Reaction :

- (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 $\text{C}\equiv\text{C}$, the π 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 Alkenes > Alkynes > Alkanes.

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

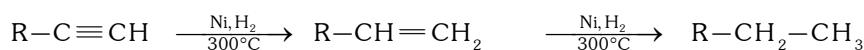


Stability of intermediates :

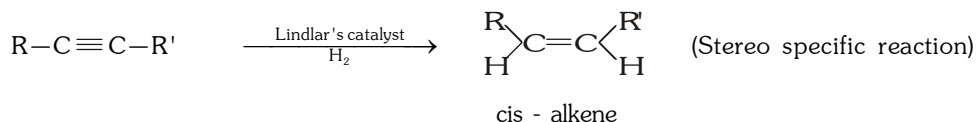


So we can say that alkenes are more reactive towards electrophilic addition reaction.

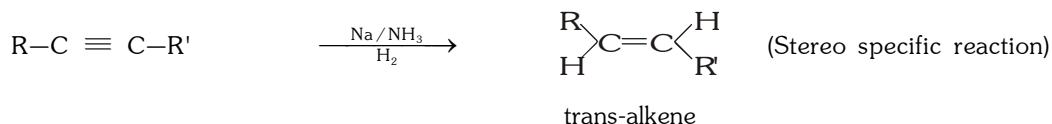
(a) Addition of hydrogen : Alkynes reacts with hydrogen in presence of a catalyst. In presence of Pt., Pd or Ni alkynes give alkanes with H_2



In presence of Lindlar's catalyst [$\text{Pd}/\text{CaCO}_3 + \text{quinoline}$ or Nickel boride] alkynes give cis - alkene

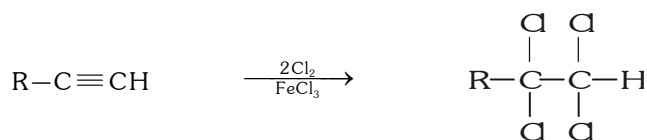


In presence of Na/NH_3 alkynes give trans-alkene. **(Birch Reduction)**

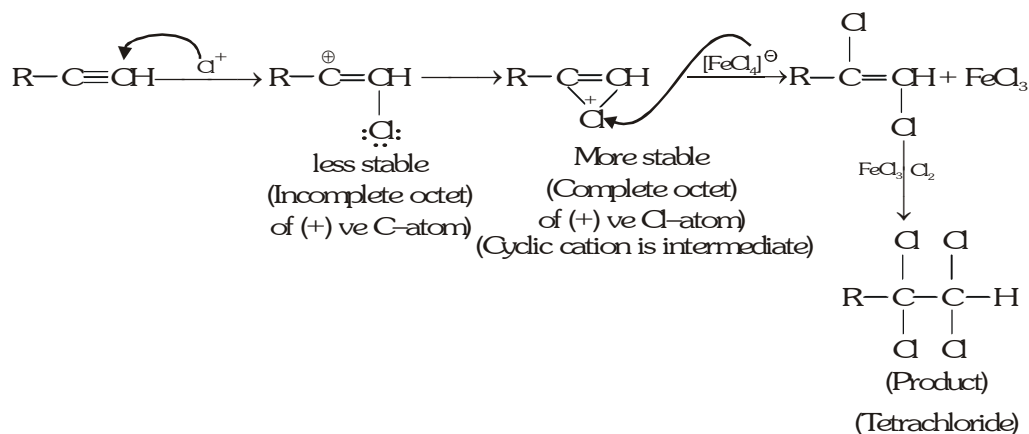
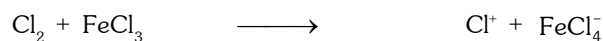


(b) Addition of Halogens : Reactivity order of Halogens $\text{Cl}_2 > \text{Br}_2 > \text{I}_2$

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

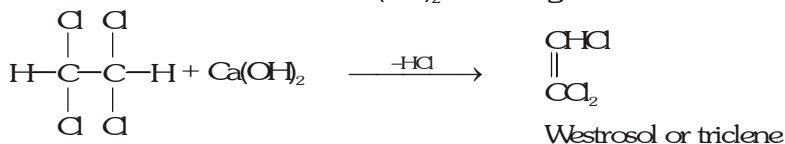


Mechanism :



Acetylene tetrachloride is also called as westron.

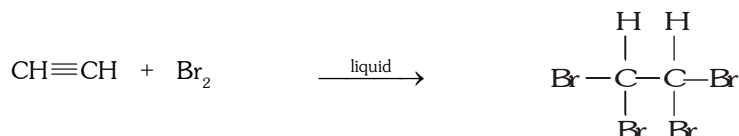
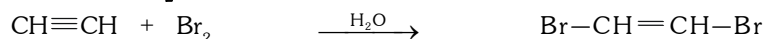
When westron is treated with $\text{Ca}(\text{OH})_2$ then we get westrosol



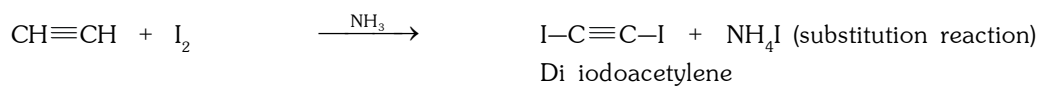
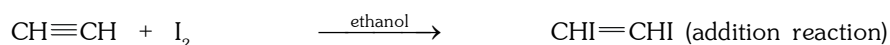
Westrosol or trichloroethylene

Both westron and westrosol are used as solvents in cloth industries

Reaction with dilute Br_2 or bromine water:

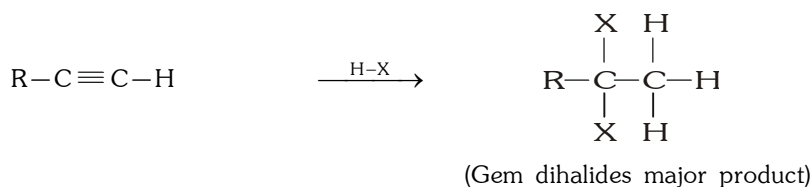


Reaction with Iodine :

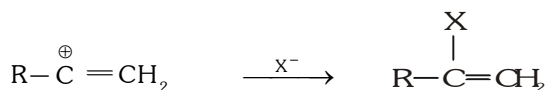
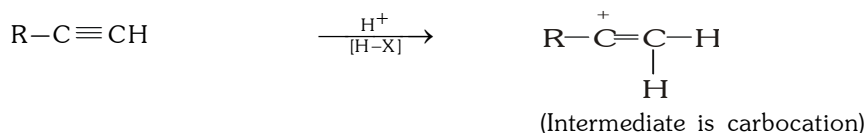


(c) **Addition of halogen acids ($\text{H} - \text{X}$) :** Addition according to Markowni-Koff's Rule.

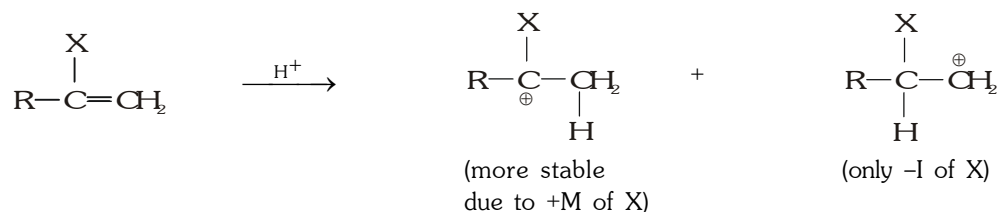
Reactivity order of $\text{H} - \text{X}$: $\boxed{\text{HI} > \text{HBr} > \text{HCl} > \text{HF}}$



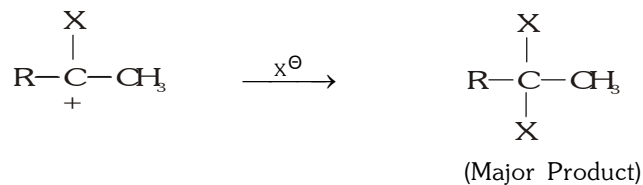
Mechanism :



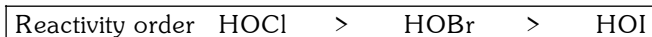
Further



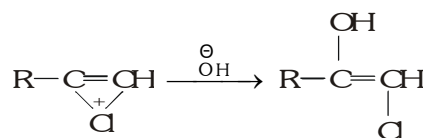
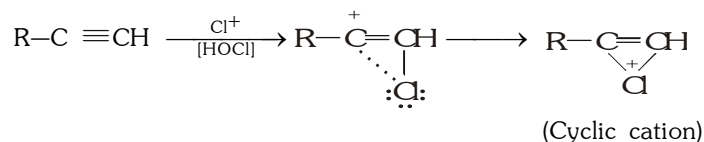
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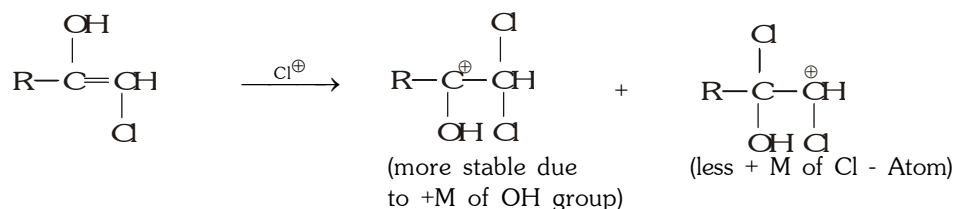
- (d) **Addition of HOX** : Alkynes react with hypohalous acids according to markownikoff's rule and form gem diol, which are unstable, lose a molecule of water and form halo aldehyde or halo ketones.



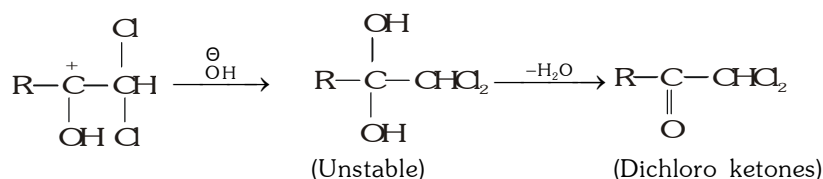
Mechanism :



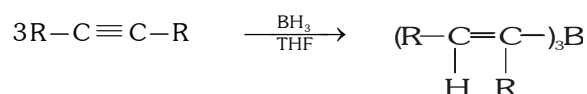
Further



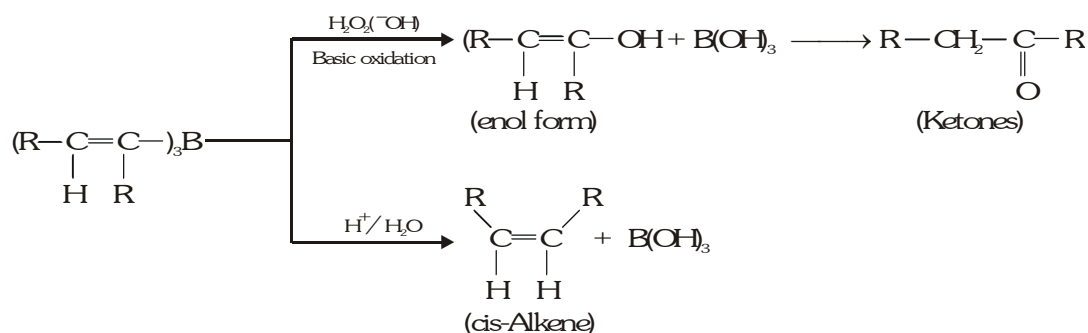
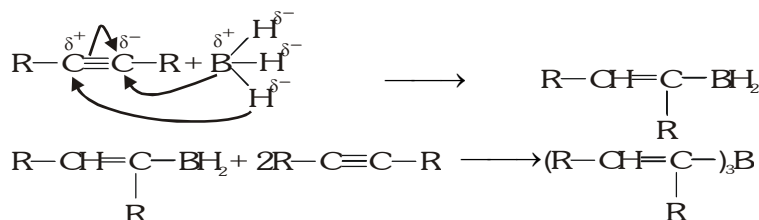
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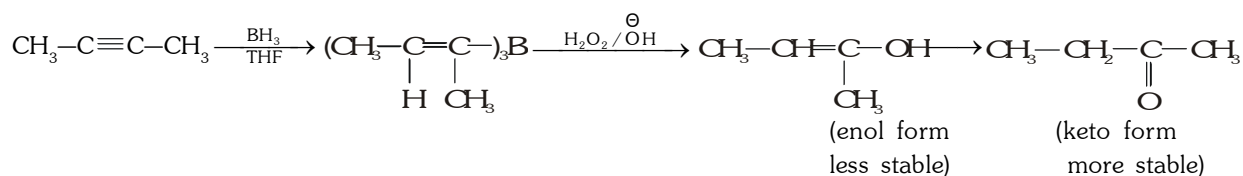
- (e) **Addition of BH₃ / THF or B₂H₆ (Hydroboration)** : THF - Tetrahydrofurane is used as solvent.



Since BH₃ is not available as monomer so a solvent THF is used for the stability of BH₃.

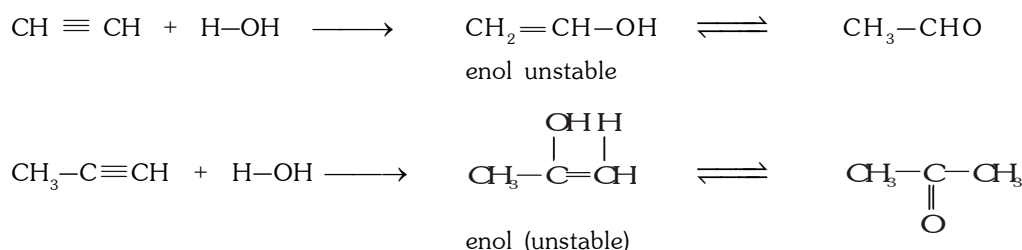


Example :

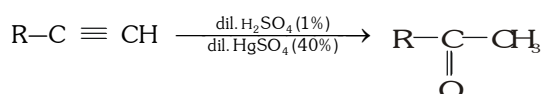


(2) **Nucleophilic addition reaction :** In these reactions some heavy metal cation like Hg^{+2} , Pb^{+2} , Ba^{+2} are used. These cation attracts the π e^- of alkynes and decrease the e^- density and hence a nucleophile can attack an alkynes.

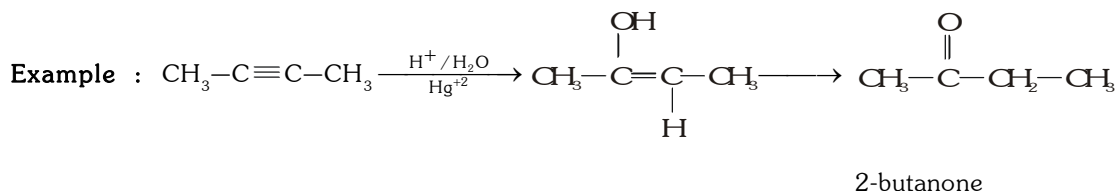
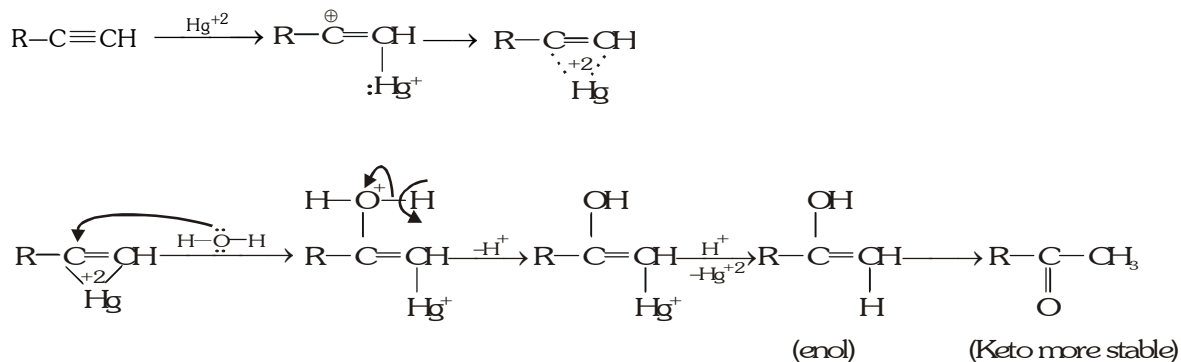
(a) **Addition of dil. H_2SO_4 (Hydration) :** The addition of water takes place in the presence of Hg^{+2} and H_2SO_4 [1% HgSO_4 +40% H_2SO_4]. In this reaction carbonyl compounds are obtained .



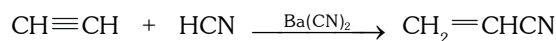
A structure in which $-\text{OH}$ group is attached to double bond carbon is called as enol (ene + - ol). This reaction is used for preparation of aldehyde and ketone.



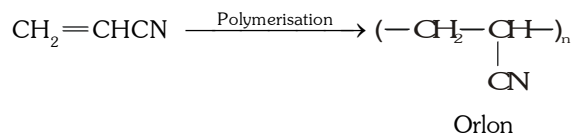
Mechanism :



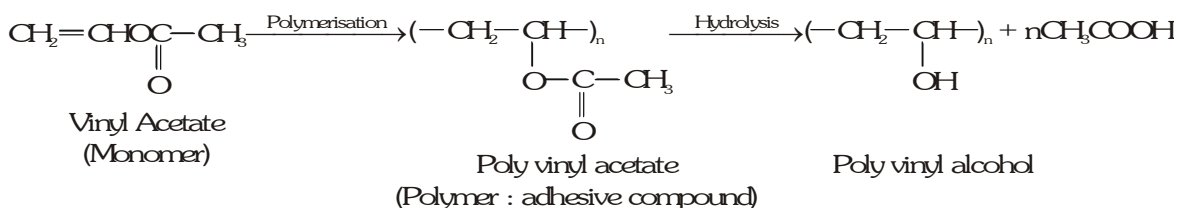
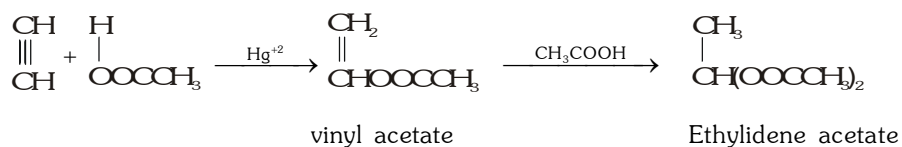
(b) **Addition of HCN :** The addition of HCN in presence of barium cyanide to form vinyl cyanide.



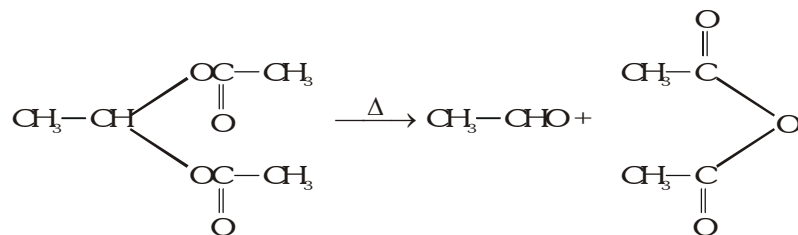
The vinyl cyanide is used for making polymers such as orlon and Buna-N rubber.



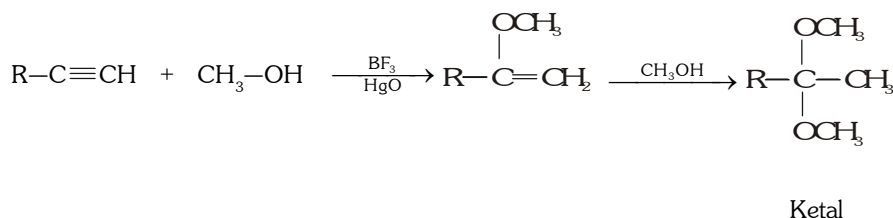
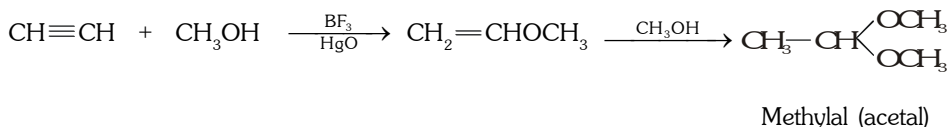
- (c) **Addition of acetic acid** : Acetylene combines with acetic acid in presence of mercuric sulphate. It first forms vinyl acetate and then ethylidene acetate.



When ethylidene acetate is heated it gives acetaldehyde and acetic anhydride

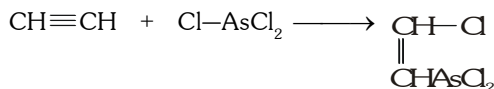


- (d) **Addition of alcohols** : In presence of BF_3 and HgO alkynes react with alcohols and form acetal and ketal



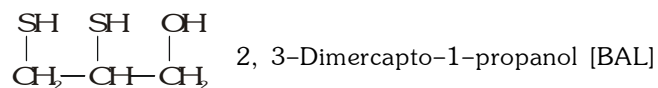
Acetylene forms acetal while other alkynes form ketal.

- (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.

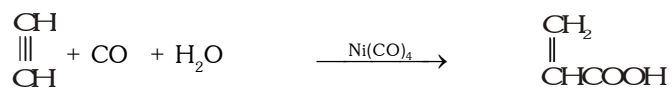
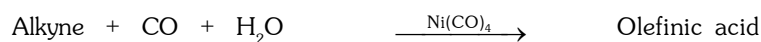


2-Chlorovinyl dichloro arsine (Lewisite gas)

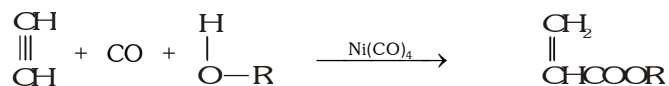
The action of Lewisite may be checked by its antidote BAL (British Anti Lewisite). BAL combines with the Lewisite to form a cyclic non toxic compound.



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



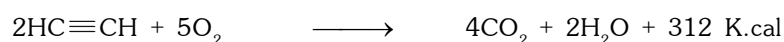
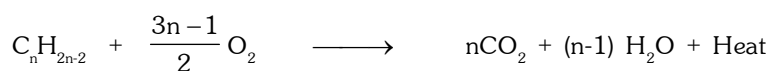
Acrylic acid



Alkyl acrylate

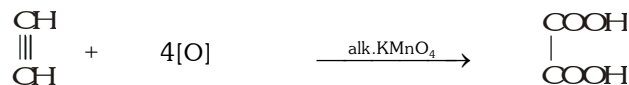
□ **Oxidation reactions :**

(a) **Combustion :**



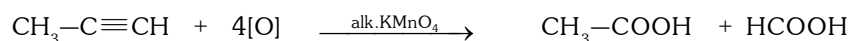
The combustion of acetylene is used for welding and cutting of metals in which oxy-acetylene flame having high temp (3000°C) is produced.

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

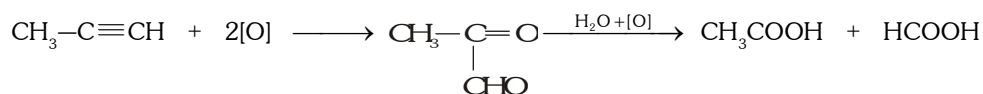
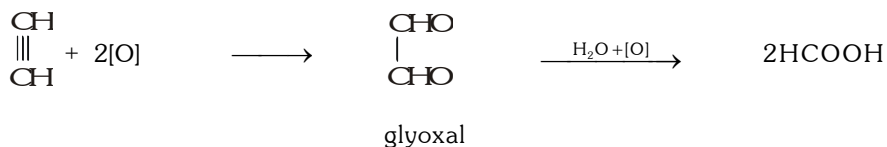
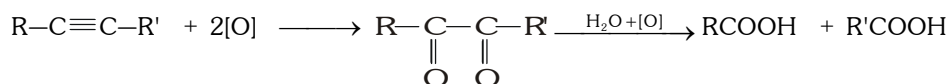


Acetylene

Oxalic acid

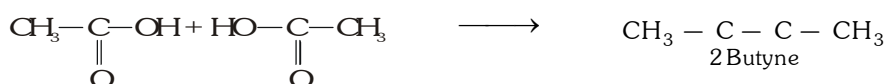


(c) **Oxidation with acidic KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$:** In presence of acidic KMnO_4 or acidic $\text{K}_2\text{Cr}_2\text{O}_7$. Alkynes are oxidised to monocarboxylic acids.

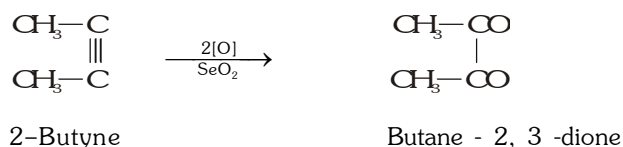
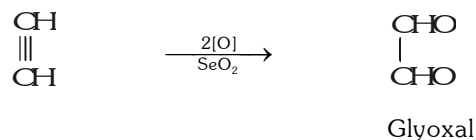


Ex. An alkyne on oxidation with acidic KMnO_4 , only acetic acid is obtained what is given alkynes ?

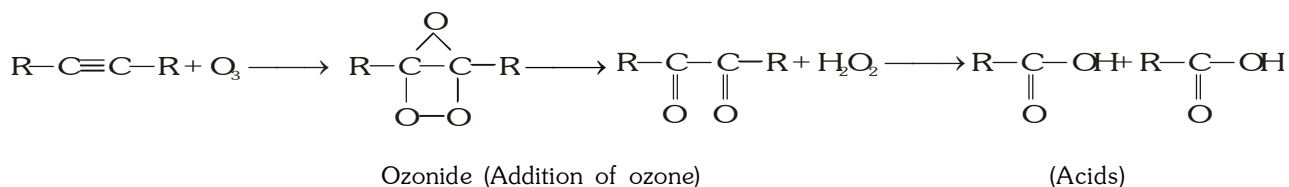
Sol. In Oxidation of alkynes two moles of mono carboxylic acids are obtained.



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

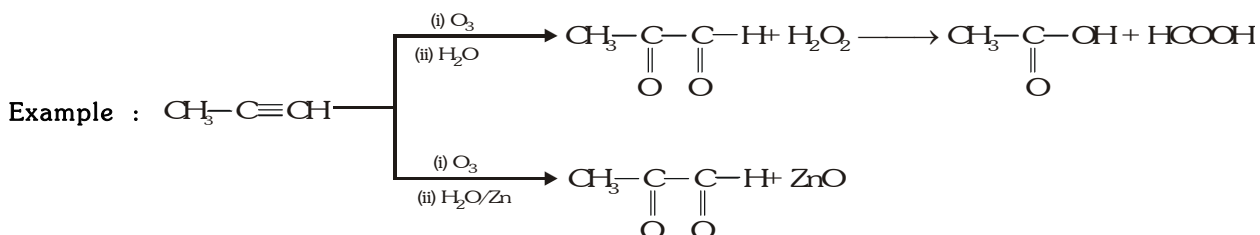


(e) **Oxidation with ozone (O₃)** : In the ozonolysis both sp-C-atoms are converted into $\begin{array}{c} \text{C}-\text{C} \\ || \quad || \\ \text{O} \quad \text{O} \end{array}$ group.



In this reaction H₂O₂ is oxidant which oxidise $\text{R}-\begin{array}{c} \text{O} \quad \text{O} \\ || \quad || \\ \text{C} \quad \text{C} \end{array}-\text{R}$ into acids.

But if we use some amount of Zn as reductant with H₂O then it reduce H₂O₂ so oxidation does not take place

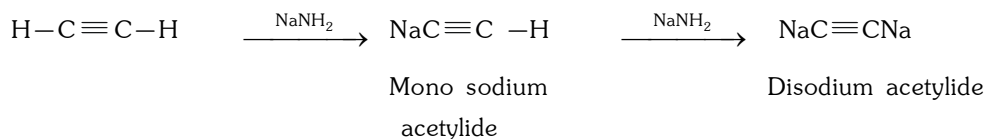
$$\text{H}_2\text{O}_2 + \text{Zn} \longrightarrow \text{ZnO} + \text{H}_2\text{O}$$


□ Substitution Reaction : (Formation of metallic derivatives)

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

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

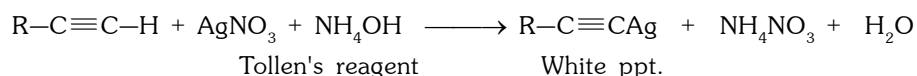
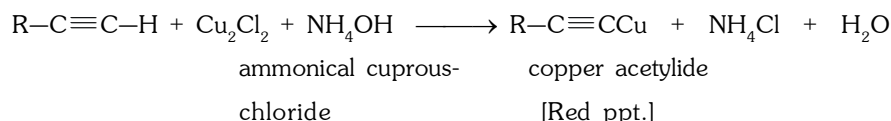


Dry alkynides are generally unstable and explosive. These are easily converted in to original alkynes when heated with dilute acids.



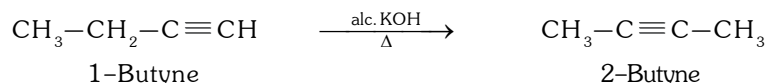
This reaction can be used for the purification, separation and identification of 1-alkynes.

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

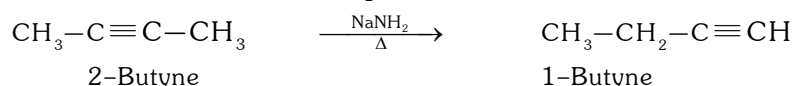


These reactions are used for detecting the presence of acetylenic hydrogen. These are test for distinguish alkenes and alkynes or 1-alkynes and 2-alkynes.

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



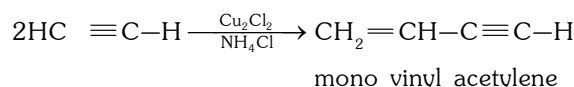
When alkyne -2 is heated with NaNH_2 alkyne -1 is obtained



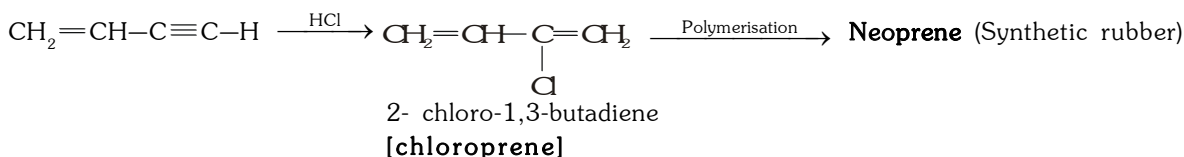
- **Polymerisation** :

- (a) **Linear polymerisation** :

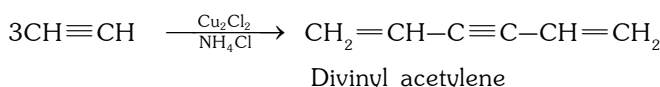
Dimerisation : When two molecules of acetylene passed through a solution of Cu_2Cl_2 and NH_4Cl a vinyl acetylene is obtained.



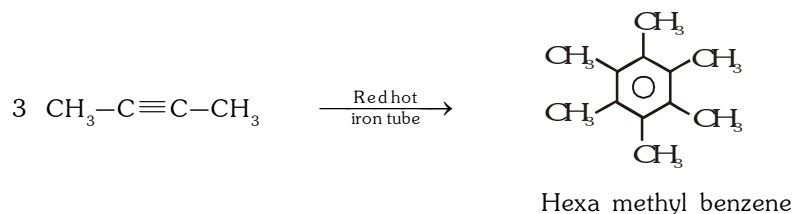
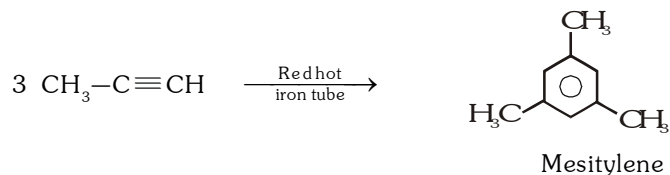
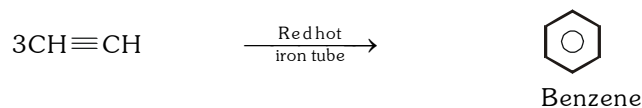
When vinyl acetylene react with HCl then chloroprene is obtained.

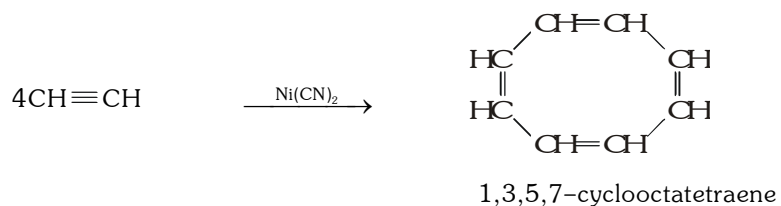
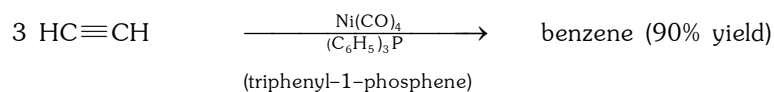


Trimerisation : 3 molecules of acetylene.

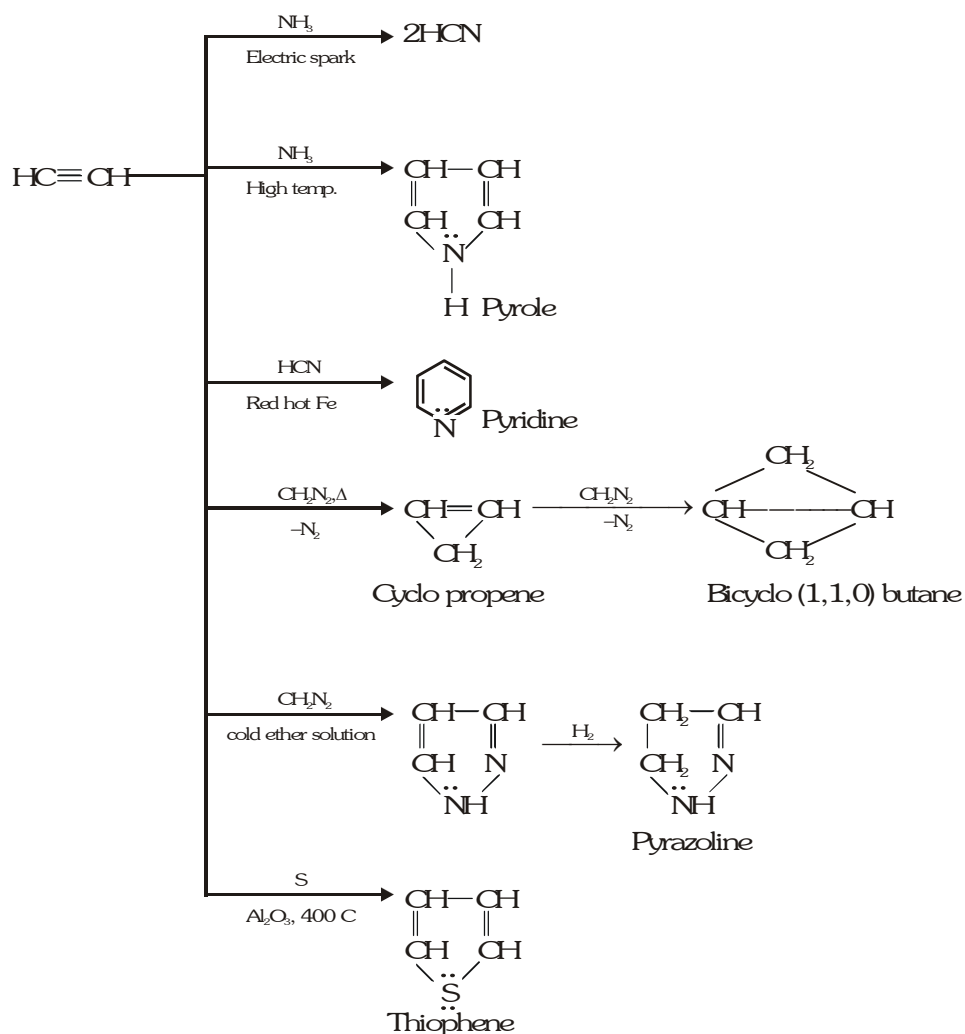


- (b) **Cyclic polymerisation** : When alkyne is passed through red hot metallic tube, cyclic polymerisation takes place with the formation of aromatic compound

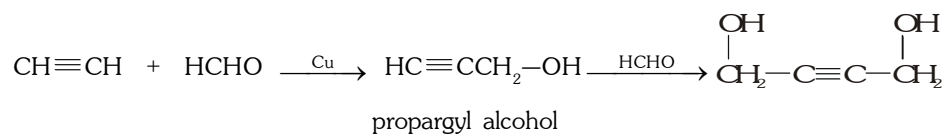




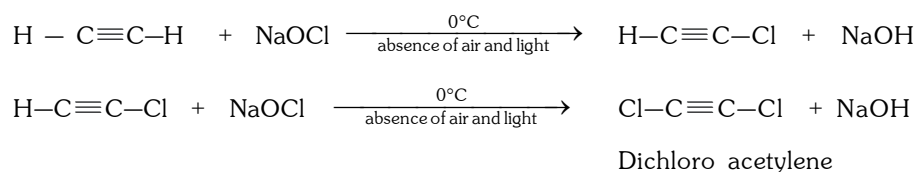
Other reactions of acetylene :



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



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



❑ **Uses of Acetylene :**

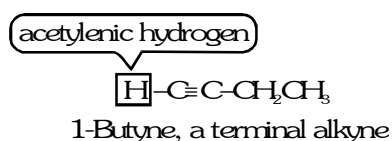
- (i) Oxyacetylene flame used in welding and cutting
- (ii) Acetylene is used as an illuminant
- (iii) Acetylene is used for artificial ripening of fruits
- (iv) Used for manufacture of acetaldehyde, acetic acid, ethyl alcohol, westron, westrosol, PVC, PVA, Chloroprene, butadiene, Lewisite etc.
- (v) It is used as a general anaesthetic.

❑ **Laboratory Test for alkynes :**

Functional Group	Reagent	Observation	Reaction	Remarks
- C \equiv C -	(1) Bayer's Reagent alk.dil.Cold KMnO ₄	Pink Colour disappears	$\text{CH}_2=\text{CH}_2 + \text{H}_2\text{O} + \text{O} \xrightarrow{\text{alk. KMnO}_4}$ $\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \quad \\ \text{OH} \quad \text{OH} \end{array}$	Hydroxylation
	(2) Br ₂ /H ₂ O	Red Colour decolourises	$\text{Br}_2 + \text{CH}_2=\text{CH}_2 \longrightarrow$ $\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \quad \\ \text{Br} \quad \text{Br} \\ \text{White ppt} \end{array}$	Bromination
	(3) O ₃ (ozone)	Acid Formed	$\text{R}-\text{C}\equiv\text{C}-\text{R}' \xrightarrow{\text{O}_3} \text{RCOOH} + \text{R}'\text{COOH}$	Ozonolysis

❑ **Laboratory test of terminal alkynes :**

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

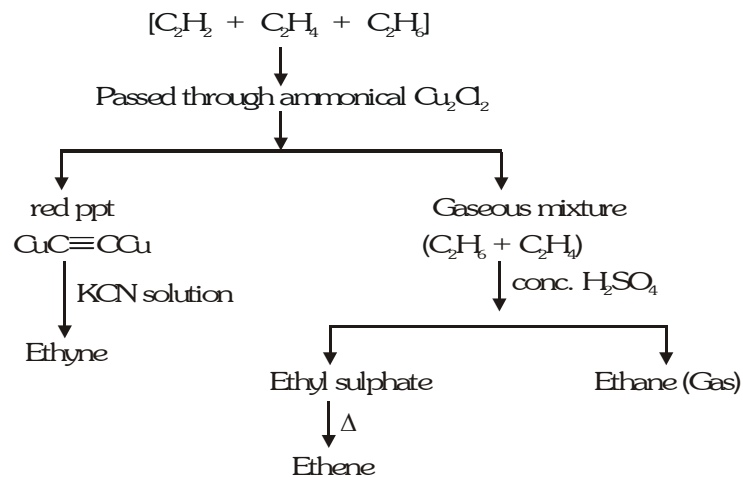


Functional Group	Reagent	Observation	Reaction
R-C \equiv C-H	(1) Cuprous chloride + NH ₄ OH	Red ppt.	$\text{R}-\text{C}\equiv\text{CH} + \text{CuCl} \xrightarrow{\text{NH}_4\text{OH}}$ $\text{R}-\text{C}\equiv\text{C}\text{Cu} \downarrow (\text{red})$
	(2) AgNO ₃ +NH ₄ OH	White ppt.	$\text{R}-\text{C}\equiv\text{CH} + \text{Ag}^+ \rightarrow \text{R}-\text{C}\equiv\text{C}\text{Ag} \downarrow (\text{white})$
	(3) Na in ether	Colourless gas	$\text{HC}\equiv\text{CH} + 2\text{Na} \rightarrow \text{Na}-\text{C}\equiv\text{C}-\text{Na} + \text{H}_2 \uparrow$

- (i) Decolourization of Br₂ in CCl₄ solution.
- (ii) Decolourisation of 1% alkaline KMnO₄ solution.
- (iii) 1- alkynes give white ppt. with ammonical AgNO₃ 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 dehydrohalogenation

Ex. Acetylene when treated with dilute HCl at $60^\circ C$ (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. $CH_3-C \equiv CH + H_2O \longrightarrow CH_3-\underset{\substack{| \\ OH}}{C}=CH_2 \rightleftharpoons CH_3-\underset{\substack{|| \\ O}}{C}-CH_3$

Ex. Alkaline $KMnO_4$, oxidizes acetylene to -

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

Ans.(C)

Sol. $H-C \equiv C-H + 4[O] \rightarrow \begin{array}{c} COOH \\ | \\ COOH \end{array}$

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. $HC \equiv CH \xrightarrow[(ii) H_2O/Zn]{(i) O_3} \begin{array}{c} H-C-C-H \\ || \quad || \\ O \quad O \\ \text{Glyoxal} \end{array}$

Ex. Propyne on reaction with aqueous chlorine gives -

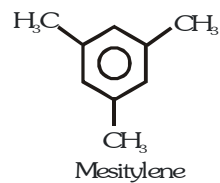
- (A) 1, 1, 2, 2-Tetrachloropropane (B) 1, 2-Dichloropropene
(C) 1, 1-Dichloropropanone (D) 2, 2-Dichloropropanone **Ans.**(C)

Sol. $CH_3-C \equiv CH + 2HOCl \rightarrow \left[\begin{array}{c} OH \\ | \\ CH_3-C-CHCl_2 \\ | \\ OH \end{array} \right] \xrightarrow{-H_2O} CH_3-\overset{\substack{O \\ ||}}{C}-CHCl_2$

Ex. Mesitylene can be obtained by polymerization of -

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

Sol. Propyne on trimerization yields mesitylene $3\text{CH}_3\text{C} \equiv \text{CH} \rightarrow$



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

- (A) $\text{CH}_3\text{CH}(\text{OOCCH}_3)_2$ (B) $\text{CH}_2 = \text{CH}(\text{OOCCH}_3)$
 (C) $(\text{CH}_3\text{COO})\text{CH}_2 - \text{CH}_2(\text{OOCCH}_3)$ (D) None of these

Ans.(A)

Sol. $\text{H}-\text{C} \equiv \text{C}-\text{H} + 2\text{CH}_3\text{COOH} \longrightarrow \text{CH}_3 - \text{CH}(\text{OCOCH}_3)_2$

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

