## ALKYNES : [$C_nH_{2n-2}$] Section - 3

Alkynes form a homologous series, represented by a general formula : $C_nH_{2n-2}$. These have one $C\equiv C$ bond or one can say that two carbon atoms (adjacent) in alkynes show sp type of hybridisation. The important members of alkynes are: Ethyne ($CH\equiv CH$), Propyne ($CH_3C\equiv CH$), 1-Butyne ($CH_3CH_2C\equiv CH$) and its isomer, 2-Butyne ($CH_3C\equiv CCH_3$).

Generally, alkynes are also represented as :

| | | | |
|---|---|---|---|
| **1.** | Terminal alkynes | $RC\equiv CH$ | |
| **2.** | Non-terminal alkynes | $RC\equiv CR, RC\equiv CR'$ | (where R : alkyl radical) |

### Preparation of Alkynes :

### 1. Dehydrohalogenation of Dihalides : (Gem and Vicinal)

$$CH_2=CH_2 \xrightarrow{Br_2} CH_2BrCH_2Br \xrightarrow[KOH,\ \Delta]{alc} CH_2=CHBr \xrightarrow{NaNH_2} CH\equiv CH$$

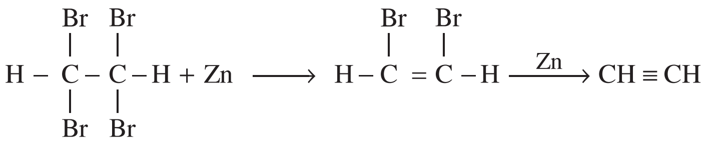
Vicinal dihalide

$$CH_3CHBr_2 \xrightarrow{NaNH_2} CH\equiv CH$$

Gem dihalides

If alcoholic KOH is used, vinylic halides are formed, as it is unable to remove vinylic hydrogen. So $NaNH_2$ (Sodamide) is used to produce alkynes.

### 2. Dehalogenation of Tetrahalides :



$$H-\underset{Br}{\overset{Br}{C}}-\underset{Br}{\overset{Br}{C}}-H + Zn \longrightarrow H-\overset{Br}{C}=\overset{Br}{C}-H \xrightarrow{Zn} CH\equiv CH$$

### 3. By dehalogenation of haloform :

Trihaloderivative of methane is known as haloform ($CHX_3$).
Chloroform and Iodoform on heating with silver powder undergo dehalogenation to form ethyne.
Trihaloalkane ($R-CX_3$) on heating with silver powder also undergo dehalogenation to form symmetrical internal alkyne.

$$CH\boxed{-\ Cl_3 + 6\,Ag + Cl_3 -}CH \xrightarrow{\Delta} HC\equiv CH + 6\,AgCl$$

Chloroform Ethyne

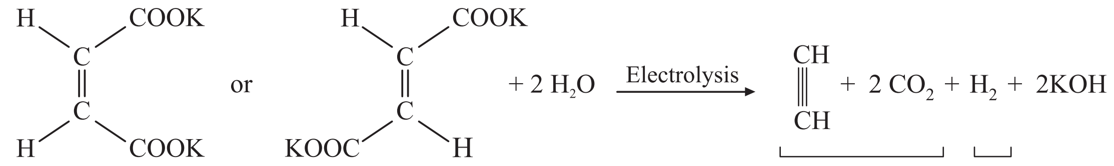
$$CH\boxed{-\ I_3 + 6\,Ag + I_3 -}CH \xrightarrow{\Delta} HC\equiv CH + 6\,AgI$$

Iodoform Ethyne

$$CH_3-CCl_3 + 6\,Ag + Cl_3C-CH_3 \xrightarrow{\Delta} CH_3-C\equiv C-CH_3 + 6\,AgCl$$

### 4. Kolbe's electrolytic reaction :

Acetylene can be prepared by electrolysis of a concentrated solution of sodium or potassium salt of Maleic acid or Fumaric acid.



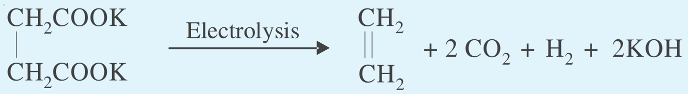
Potassium maleate (*cis*-isomer)

Potassium fumarate (*trans*-isomer)

(at Anode) (at Cathode)

This reaction is called Kolbe's electrolytic reaction.

***Note :*** On electrolysis of aqueous solution of Potassium succinate, we get Ethylene ($C_2H_4$) as a product at anode.



$$\begin{array}{c} CH_2COOK \\ | \\ CH_2COOK \end{array} \xrightarrow{\text{Electrolysis}} \begin{array}{c} CH_2 \\ || \\ CH_2 \end{array} + 2\,CO_2 + H_2 + 2KOH$$

### 5. From Graphite :

$$2C(s) + H_2(g) \xrightarrow[1000^\circ C]{\text{Electric arc}} CH \equiv CH$$

(*Only acetylene can be formed*)

### 6. From calcium carbide :

$$CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2$$

(*Only acetylene can be formed*)

***Note :*** **(i)** Calcium carbide is formed as follows :

$$CaCO_3 \xrightarrow[\Delta]{2000^\circ C} CaO + CO_2$$

$$CaO + C \xrightarrow{2500^\circ C} CaC_2 + CO\uparrow$$

**(ii)** Carbides of Na, K, Ca, Mg, Ba are considered to be ionic and give acetylene with $H_2O$.

**(iii)** However, carbides of Cu and Ag are covalent and hence do not give acetylene with $H_2O$.

### 7. Higher alkynes from Lower alkynes :

$$\underset{\text{excess}}{CH \equiv CH} \xrightarrow[1.0\text{ eq.}]{NaNH_2,\ \text{liq. } NH_3} CH \equiv CNa \xrightarrow{R'X} CH \equiv C - R'$$

(Terminal alkynes)

$$CH \equiv CH \xrightarrow[2.0\text{ eq.}]{NaNH_2,\ \text{liq. } NH_3} Na - C \equiv C - Na \xrightarrow[\text{excess}]{R'X} R' - C \equiv C - R'$$

(Non-terminal Alkynes)

$$R - C \equiv CH \xrightarrow[1.0\text{ eq}]{NaNH_2,\ \text{liq. } NH_3} R - C \equiv C - Na \xrightarrow{R'X} R - C \equiv C - R'$$

(Non-terminal Alkynes)

***Note :*** R′ can only be 1° and 2° alkyl or cycloalkyl groups only.

## Physical Properties of Alkynes:

1. **Physical state :** The first three members of this family (Ethyne, Propyne and Butyne) are colourless gases, the next eight are liquids while the higher ones are solids.

2. **Smell :** All the alkynes are odourless. However acetylene has garlic smell due to the presence of phosphine as impurity.

3. **Melting and boiling points :** The boiling points and melting points of alkynes are slightly higher than those of the corresponding alkenes and alkanes. This is probably due to the reason that because of the presence of a triple bond, alkynes have linear structures and hence their molecules can be more closely packed in the crystal lattice as compared to those of corresponding alkenes and alkanes.

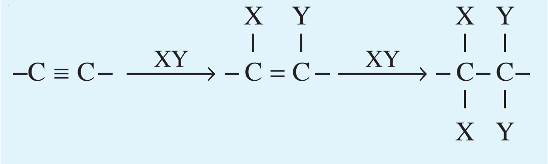
| Hydrocarbon | Ethane | Ethene | Ethyne |
|---|---|---|---|
| M.P. (K) | 101 | 104 | 191 |
| B.P. (K) | 184.5 | 171 | 198 |

4. **Solubility :** Alkynes like alkanes and alkenes being non-polar are insoluble in water but readily dissolve in organic solvents such as petroleum ether, benzene, carbon tetrachloride etc.

5. **Density :** Densities of alkynes increase as the molecular size increases. However, they are all lighter than water since their densities lie in the range 0.69 – 0.77 g/cm$^3$.

## Reactions of Alkynes :

### 1. Electrophillic Addition Reactions :



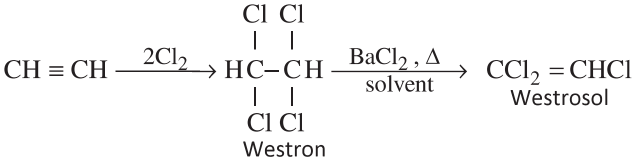
$$-C\equiv C- \xrightarrow{XY} -\overset{X}{\overset{|}{C}}=\overset{Y}{\overset{|}{C}}- \xrightarrow{XY} -\underset{X}{\underset{|}{\overset{X}{\overset{|}{C}}}}-\underset{Y}{\underset{|}{\overset{Y}{\overset{|}{C}}}}-$$

**(a) Addition of Hydrogen :**

$$CH\equiv CH \xrightarrow[Pt/573\,K]{H_2} CH_2=CH_2 \xrightarrow[Pt/573\,K]{H_2} CH_3-CH_3$$

*Read hydrogenation of alkynes in the preparation of alkenes.*

**(b) Addition of Halogens : (X = Cl, Br, I)**

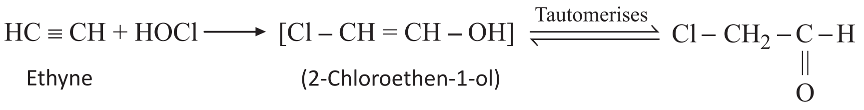


$$CH\equiv CH \xrightarrow{2Cl_2} \underset{\text{Westron}}{HC(Cl_2)-CH(Cl_2)} \xrightarrow[\text{solvent}]{BaCl_2,\ \Delta} \underset{\text{Westrosol}}{CCl_2=CHCl}$$

**(c) Addition of Halogen acids : (HX)**

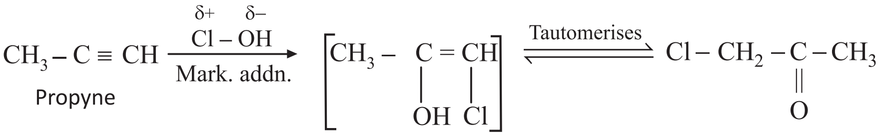
$$CH\equiv CH + HBr \longrightarrow CH_2=CHBr \xrightarrow{HBr} CH_3-CHBr_2 \quad (\text{Markovnikov's rule})$$

### (d) Addition of Hypohalous acid (HOX) :



$$\underset{\text{Ethyne}}{HC\equiv CH} + HOCl \longrightarrow \underset{\text{(2-Chloroethen-1-ol)}}{[Cl-CH=CH-OH]} \xrightleftharpoons{\text{Tautomerises}} Cl-CH_2-\underset{\underset{O}{\|}}{C}-H$$

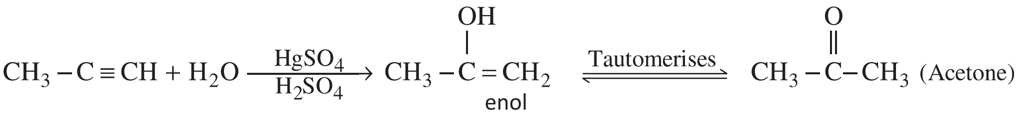
Similarly,



$$\underset{\text{Propyne}}{CH_3-C\equiv CH} \xrightarrow[\text{Mark. addn.}]{\overset{\delta+\ \ \delta-}{Cl-OH}} \left[CH_3-\underset{OH}{\underset{|}{C}}=\underset{Cl}{\underset{|}{CH}}\right] \xrightleftharpoons{\text{Tautomerises}} Cl-CH_2-\underset{\underset{O}{\|}}{C}-CH_3$$

### (e) Addition of water ($H_2O$) in presence of acid :

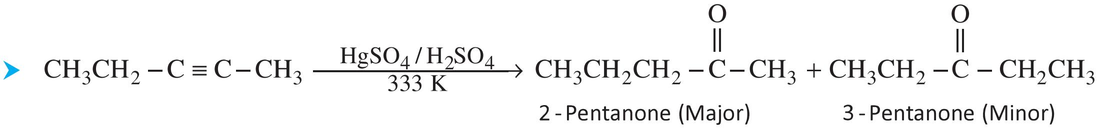
$$CH\equiv CH + H_2O \xrightarrow[H_2SO_4]{HgSO_4} \underset{\text{enol}}{CH_2=CHOH} \xrightleftharpoons{\text{Tautomerises}} CH_3-CHO\ \text{(Acetaldehyde)}$$



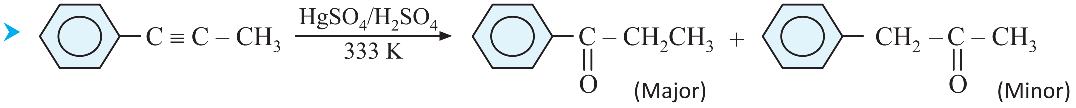
$$CH_3-C\equiv CH + H_2O \xrightarrow[H_2SO_4]{HgSO_4} \underset{\text{enol}}{CH_3-\overset{\overset{OH}{|}}{C}=CH_2} \xrightleftharpoons{\text{Tautomerises}} CH_3-\overset{\overset{O}{\|}}{C}-CH_3\ \text{(Acetone)}$$

***Note :*** The addition of water to alkynes also follows Markovnikov's rule. The hydrogen atom becomes attached to the carbon atom with the greater number of hydrogen atoms. Therefore, when higher terminal alkynes are hydrated, ketones, rather than aldehydes are formed.

However, if the unsymmetrical alkyne is nonterminal, a mixture of two isomeric ketones is obtained in which the methyl ketone predominates. In case of benzene ring, phenyl ketones is major product.



$$CH_3CH_2-C\equiv C-CH_3 \xrightarrow[333\ K]{HgSO_4/H_2SO_4} \underset{\text{2-Pentanone (Major)}}{CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-CH_3} + \underset{\text{3-Pentanone (Minor)}}{CH_3CH_2-\overset{\overset{O}{\|}}{C}-CH_2CH_3}$$



### (f) Addition of HCN :

$CH\equiv CH + HCN \longrightarrow CH_2=CHCN$ (Vinyl cyanide also known as acrylonitrile)

***Note :*** Acrylonitrile is used in manufacture of BuNa-N rubber and Orlon fibre.

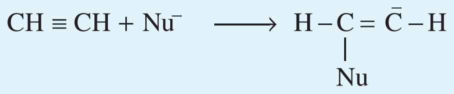
### (g) Addition of Acetic acid ($CH_3COOH$) :

$$CH\equiv CH + CH_3COOH \xrightarrow{Hg^{2+}} \underset{\text{Vinyl acetate}}{H_2C=HC-OAc} \xrightarrow{CH_3COOH} \underset{\text{Ethylidine acetate}}{CH_3-CH(OAc)_2}$$

### (h) Addition of Arsenic trichloride ($AsCl_3$) :

$$CH\equiv CH + ClAsCl_2 \longrightarrow \underset{\text{(Lewisite, a poisonous gas)}}{ClHC=CHAsCl_2}$$

## 2. Nucleophillic Addition reaction:



$$CH \equiv CH + Nu^{-} \longrightarrow H-\underset{\underset{Nu}{|}}{C}=\bar{C}-H$$

(Vinylic carbanion)

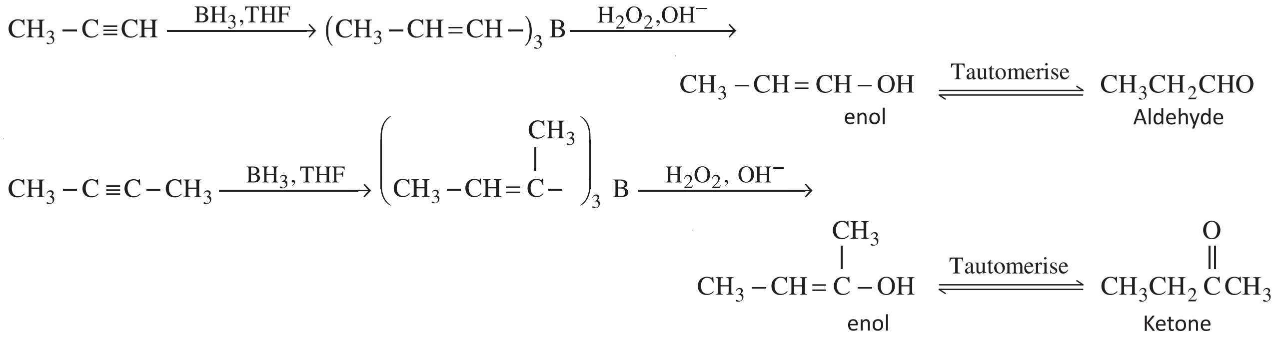
Vinylic Carbanion is formed which is more stable than vinylic carbonium ion.

### Addition of Methanol :

$$\underset{\text{Acetylene}}{HC \equiv CH} + CH_3OH \xrightarrow[433\text{–}473\ K]{CH_3O^{-}K^{+}} \underset{\text{Methyl vinyl ether}}{CH_2=CH-OCH_3}$$

Methyl vinyl ether is used for making polyvinyl ether plastics.

## 3. Oxidative - Hydroboration:



$$CH_3-C\equiv CH \xrightarrow{BH_3,THF} (CH_3-CH=CH-)_3B \xrightarrow{H_2O_2,OH^{-}} \underset{\text{enol}}{CH_3-CH=CH-OH} \xrightleftharpoons{\text{Tautomerise}} \underset{\text{Aldehyde}}{CH_3CH_2CHO}$$

$$CH_3-C\equiv C-CH_3 \xrightarrow{BH_3,\ THF} \left(CH_3-CH=\overset{\overset{CH_3}{|}}{C}-\right)_3 B \xrightarrow{H_2O_2,\ OH^{-}} \underset{\text{enol}}{CH_3-CH=\overset{\overset{CH_3}{|}}{C}-OH} \xrightleftharpoons{\text{Tautomerise}} \underset{\text{Ketone}}{CH_3CH_2\overset{\overset{O}{\|}}{C}CH_3}$$

## 4. Acetylide Formation :

$$CH \equiv CH \xrightarrow[\text{ammonical}]{AgNO_3} Ag-C\equiv C-Ag$$

Silver Acetylide (white ppt.)

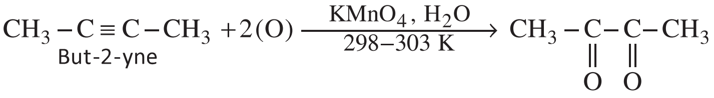
***Note :*** This reaction shows the acidity of terminal alkynes and serves as a test for terminal alkynes.

$$CH \equiv CH \xrightarrow[\text{amm.}]{CuCl_2} Cu-C\equiv C-Cu$$

Copper Acetylide (Red ppt.)

## 5. Oxidation of Alkynes :

### (a) Oxidation in Neutral $KMnO_4$ :

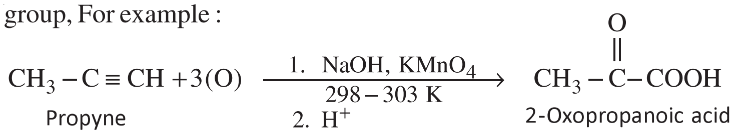


$$\underset{\text{But-2-yne}}{CH_3-C\equiv C-CH_3} + 2(O) \xrightarrow[298\text{–}303\ K]{KMnO_4,\ H_2O} CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3$$

(Butane-2, 3-dione)

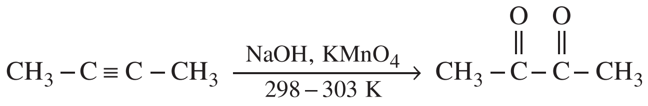
### (b) Oxidation with cold dilute alkaline $KMnO_4$ :

Alkynes are readily oxidised by cold dilute alkaline $KMnO_4$ solution to give dicarbonyl compounds. In case of terminal alkynes, $\equiv CH$ part is oxidised to $-COOH$ group while in case of non-terminal alkynes, $\equiv CR$ part is oxidised to $R-\underset{|}{C}=O$ group, For example :



$$CH_3-C\equiv CH+3(O)\xrightarrow[298-303\text{ K}\quad 2.\ H^+]{1.\ NaOH,\ KMnO_4}CH_3-\overset{\overset{O}{\|}}{C}-COOH$$

Propyne 2-Oxopropanoic acid



$$CH_3-C\equiv C-CH_3\xrightarrow[298-303\text{ K}]{NaOH,\ KMnO_4}CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3$$

Acetylene, however, under these conditions gives oxalic acid probably due to further oxidation of the initially formed glyoxal.

$$\underset{\text{Acetylene}}{HC\equiv CH+2(O)}\xrightarrow[298\text{–}303\text{ K}]{KMnO_4,\ NaOH}\underset{\text{Glyoxal}}{[OHC-CHO]}\xrightarrow[H^+]{+2(O)}\underset{\text{Oxalic acid}}{HOOC-COOH}$$

During this reaction, the pink colour of the $KMnO_4$ solution is discharged and a brown precipitate of manganese dioxide is obtained. This reaction is, therefore, used as a test for unsaturation under the name Baeyer's test.

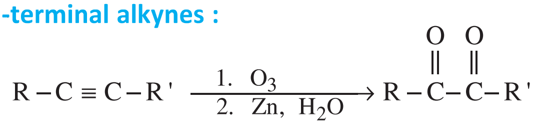
### (c) Oxidation by acidic $KMnO_4$ (hot) :

$$R-C\equiv C-R'\xrightarrow[H^+,\text{ heat}]{KMnO_4}R-COOH+R'COOH$$

Note that it is similar to the oxidation of alkenes.

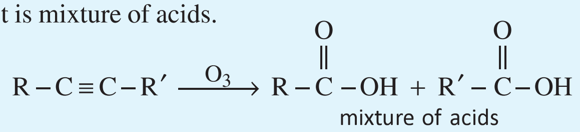
## 6. Ozonolysis :

### (a) For non-terminal alkynes :



$$R-C\equiv C-R'\xrightarrow[2.\ Zn,\ H_2O]{1.\ O_3}R-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-R'$$

***Note :*** If, Zn or Pb is not used, then the product is mixture of acids.

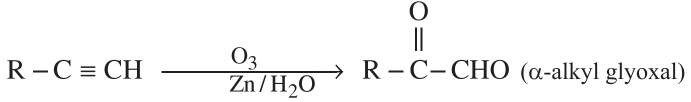


$$R-C\equiv C-R'\xrightarrow{O_3}R-\overset{\overset{O}{\|}}{C}-OH+R'-\overset{\overset{O}{\|}}{C}-OH$$

mixture of acids

### (b) For terminal alkynes :

$$H-C\equiv CH\xrightarrow[Zn/H_2O]{O_3}OHC-CHO\quad\text{(Glyoxal)}$$

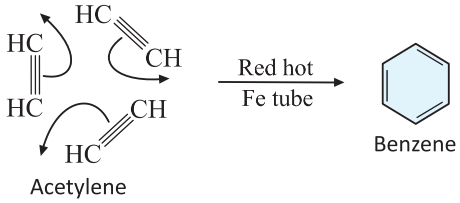


$$R-C\equiv CH\xrightarrow[Zn/H_2O]{O_3}R-\overset{\overset{O}{\|}}{C}-CHO\quad(\alpha\text{-alkyl glyoxal})$$

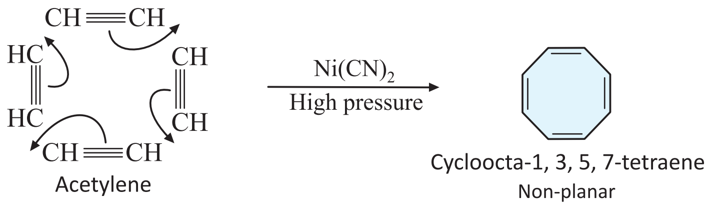
## 7. Polymerization Reactions of Alkynes :

Like alkenes, alkynes also undergo polymerization reactions. For example,

(a) When acetylene is passed through red hot iron tube, it trimerises to give benzene.



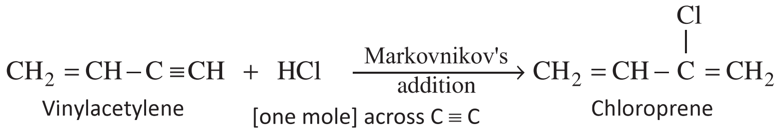
**(b)** In presence of nickel cyanide as catalyst and under high pressure, four molecules of acetylene combine to form a tetramer called cycloocta-1, 3, 5, 7-tetraene.



**(c)** However, in presence of $CuCl/NH_4Cl$, acetylene first gives vinylacetylene and then divinylacetylene. Thus,

$$\underset{\text{Acetylene}}{2HC \equiv CH} \xrightarrow{CuCl/NH_4Cl} \underset{\text{Vinylacetylene}}{HC \equiv C-CH=CH_2} \xrightarrow[CuCl/NH_4Cl]{HC\equiv CH} \underset{\text{Divinylacetylene}}{H_2C=CH-C\equiv C-CH=CH_2}$$

Vinylacetylene is widely used in the manufacture of chloroprene which is the starting material for the synthetic rubber neoprene.



$$\underset{\text{Vinylacetylene}}{CH_2=CH-C\equiv CH} + HCl \xrightarrow[\text{addition}]{\text{Markovnikov's}} \underset{\text{Chloroprene}}{CH_2=CH-\overset{\overset{\large Cl}{|}}{C}=CH_2}$$

[one mole] across C ≡ C

**(d)** Under suitable conditions, polymerization of acetylene produces the linear polymer polyacetylene. It is a high molecular weight conjugated polyene containing the repeating unit $(-CH=CH-CH=CH-)_n$. Under proper conditions, this material conducts electricity. Since polyacetylenes have much higher conductance than metal conductors, these can be used to prepare lighter and cheaper batteries.

## Acidic character of Alkynes :

### (a) Formation of alkali metal acetylides :

$$\underset{\substack{\text{Ethyne}\\\text{(Acetylene)}}}{2HC\equiv CH + 2Na} \xrightarrow{475°C} \underset{\text{Sodium acetylide}}{2HC\equiv C^-Na^+} + H_2$$

$$\underset{\text{(A terminal alkyne)}}{R-C\equiv CH} + NaNH_2 \xrightarrow[196\ K]{\text{Liq. }NH_3} \underset{\text{(An acetylide)}}{R-C\equiv C^-Na^+} + NH_3$$

During these reactions, the acetylenic hydrogen is removed as a proton to form stable carbanions (acetylide ions). Sodium acetylide is decomposed by water regenerating acetylene. This shows that water is a stronger acid than acetylene and thus displaces acetylene from sodium acetylide.

$$HC\equiv C^-Na^+ + H_2O \longrightarrow \underset{\text{Acetylene}}{HC\equiv CH} + NaOH$$

### (b) Formation of heavy metal acetylides :

$$\underset{\text{Ethyne}}{CH\equiv CH} + \underset{\text{Tollen's reagent}}{2\left[Ag(NH_3)_2\right]^+OH^-} \longrightarrow \underset{\substack{\text{Silver acetylide}\\\text{(White ppt.)}}}{AgC\equiv CAg} + 2H_2O + 4NH_3$$

$$R-C\equiv CH+\underset{\text{Tollen's reagent}}{\left[Ag\left(NH_3\right)_2\right]^+OH^-}\longrightarrow \underset{\substack{\text{Silver acetylide}\\ \text{(White ppt.)}}}{R-C\equiv C-Ag}+H_2O+2NH_3$$

$$\underset{\text{Ethyne}}{HC\equiv CH}+2\left[Cu\left(NH_3\right)_2\right]^+OH^-\longrightarrow \underset{\substack{\text{Copper acetylide}\\ \text{(Red ppt.)}}}{CuC\equiv C-Cu}+H_2O+4NH_3$$

Unlike alkali metal acetylides, silver and copper acetylides are not decomposed by water. They can, however, be decomposed with dilute mineral acids to regenerate the original alkynes.

$$\underset{\text{Silver acetylide}}{AgC\equiv CAg}+2HNO_3\longrightarrow \underset{\text{Acetylene}}{HC\equiv CH}+AgNO_3$$

$$\underset{\text{Copper acetylide}}{CuC{\equiv}CCu}+2HCl\longrightarrow \underset{\text{Acetylene}}{HC{\equiv}CH}+2CuCl$$

## (c) Formation of alkynyl Grignard reagents :

$$\underset{\text{Acetylene}}{HC\equiv CH}+\underset{\text{Grignard reagent}}{RMgX}\xrightarrow[\text{ether}]{\text{Dry}}\underset{\substack{\text{Acetylenic}\\ \text{Grignard reagent}}}{HC\equiv CMgX}+\underset{\text{Alkane}}{RH}$$

$$\underset{\text{Terminal alkyne}}{R'-C\equiv CH}+RMgX\xrightarrow[\text{ether}]{\text{Dry}}\underset{\substack{\text{Alkynyl}\\ \text{Grignard reagent}}}{R'-C\equiv CMgX}+RH$$

**Illustration - 7** *How would you convert acetylene to acetone ?*

**SOLUTION :**

$$HC\equiv CH\longrightarrow CH_3COCH_3$$

In such question, try to visualise formation of $CH_3COCH_3$. It is formed by hydration of $CH_3C\equiv CH$. So now convert $HC\equiv CH$ to $CH_3C\equiv CH$.

$$HC\equiv CH\xrightarrow[1.0\text{ eq}]{NaNH_2}HC\equiv\bar{C}-\overset{+}{Na}\xrightarrow{CH_3Br}HC\equiv C-CH_3\xrightarrow{H_2O/H^+/Hg^{2+}}\underset{\text{(via Tautomerism)}}{CH_3COCH_3}$$

**Illustration - 8** *Identify A, B, C . . . . . . . . .*

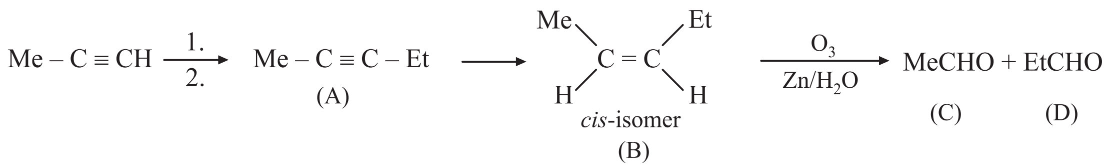
**(a)** $$Me-C\equiv CH\xrightarrow[2.\,EtBr]{1.\,NaNH_2}A\xrightarrow[\substack{Pd-BaSO_4\\ \text{quinoline}}]{H_2}B\xrightarrow[Zn/H_2O]{O_3}C+D$$

**(b)** $$\begin{tikzcd}
 & & B \\
HC\equiv C-CH_2Br \arrow[r, "Mg", "Et_2O"'] & A \arrow[ur, "H_2O"] \arrow[dr, "HC\equiv C-CH_2Br"'] & \\
 & & C
\end{tikzcd}$$

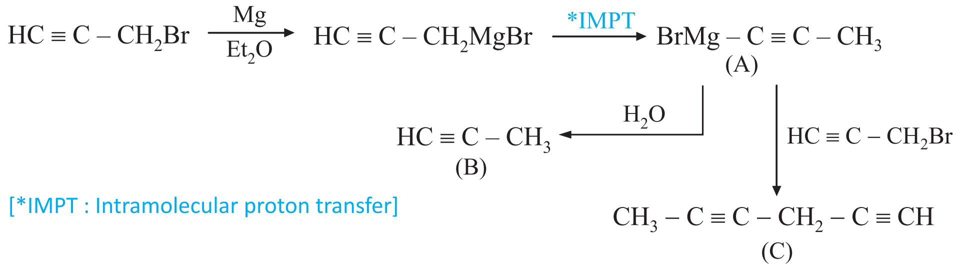
**(c)** $$HC{\equiv}CH\xrightarrow[2.\ EtBr\,(2.0\,eqv.)]{1.\ NaNH_2\,(2.0\,eqv.)}A\xrightarrow[NH_3]{H_2,\ Liq.Li}B\xrightarrow{Br_2/CCl_4}C$$

**SOLUTION :**

**(a)**

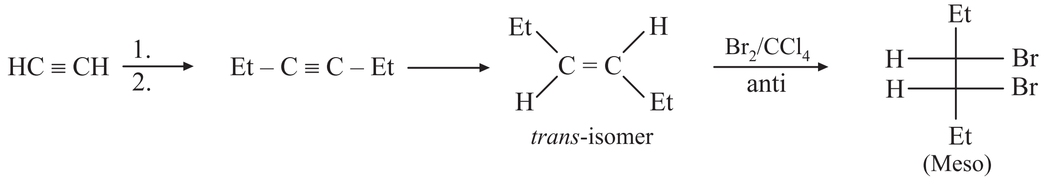


**(b)**



[*IMPT : Intramolecular proton transfer]

**(c)**



## IN-CHAPTER EXERCISE-C

**1.** Identify the product A, B. . . . .

**(i)** $CH_3CH_2C \equiv CCH_2CH_3 \xrightarrow[quinoline]{H_2, Pd / CaCO_3} A$

**(ii)** $C_6H_5 - C \equiv CH \xrightarrow[H_2SO_4 / Hg^{2+}]{H_2O} B$

**Choose the correct alternative. Only one choice is correct.**

**2.** *Silver acetylide when heated with HCl or* $HNO_3$ *gives* :

**(A)** $C_2H_2$ **(B)** $H_2$ **(C)** $C_2H_4$ **(D)** *None of these*

**3.** *The products obtained via oxymercuration* ($HgSO_4 + H_2SO_4$) *of* 1-*Butyne would be* :

**(A)** $CH_3 - CH_2 - CO - CH_3$ **(B)** $CH_3 - CH_2 - CH_2 - CHO$

**(C)** $CH_3 - CH_2 - CHO + HCHO$ **(D)** $CH_3CH_2COOH + HCOOH$

**4.** *Which is the most suitable reagent among the following to distinguish compound (III) from rest of the compounds ?*

I. $CH_3 - C \equiv C - CH_3$ II. $CH_3 - CH_2 - CH_2 - CH_3$

III. $CH_3 - CH_2 - C \equiv CH$ IV. $CH_3 - CH = CH_2$

**(A)** *Bromine in carbon tetrachloride* **(B)** *Bromine in acetic acid*

**(C)** *Alk.* $KMnO_4$ **(D)** *Ammonical* $Cu_2Cl_2$ *solution*