\Box 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 $: C_n H_{2n-2}$. (one triple bond)
- (d) In alkyne $C \equiv C$ bond length is 1.20 E
- (e) Its bond energy is 192 kcal. mol-1
- (f) The hybridization of carbon atoms having triple bond (C = 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
	ĊH, Br	
5.	CH ₂ -CH-C≡ C-CH ₂ -CH-CH ₃	6-Bromo-2-methylhept-3-yne

□ Isomerism in Alkynes

Туре	Categary	Examples	
	(i) Chain isomerism	CH₃-CH₂-C≡ CH&CH₃-CH-C≣CH I CH₃	
Structural	(ii) Positional isomerism	$CH_3 - CH_2 - CH_2 - C \equiv CH \& CH_3 - CH_2 - C \equiv C - CH_3$	
Isomerism	(iii) Functional group isomerism	CH ₃ -CH ₂ -C=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 ?

General Methods of Preparation :

1. From Gem dihalides (by dehydrohalogenation) : Dehydrohalogenation agents are : NaNH₂ (Sodamide) or Alc. KOH or ROH + RONa.

$$\begin{array}{cccc} H & X & X \\ R - C - C H & \xrightarrow{alc. KOH} & R - C = C \\ H & X & H \\ H & X & H \end{array} R - C = C H + NaX + NH_{3} \\ (Stable by resonance) \end{array}$$

(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 NaNH₂ is used.
- (b) Basic strength : ${}^{1}_{NH_2}$ is stronger base then RO¹
- (c) Trans elimination takes place in forming of alkynes.
- 2. From Vicinal dihalides (by dehydrohalogenation) :

$$\begin{array}{c} H & H \\ | & | \\ R - \underbrace{C}_{-} \underbrace{C}_{-} H \xrightarrow{\text{alc. KOH}}_{-HX} R - \underbrace{C}_{-} = \underbrace{C}_{-} H \xrightarrow{NaNH_2}_{-HX} R - C \equiv CH \\ X & X & X & X \end{array}$$

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

Example : $\begin{array}{cccc} H & H & H \\ | & | & | \\ CH - C - C - C - H & \xrightarrow{\text{NaNH}_2} & CH_2 = C = CH_2 \\ | & | & | \\ H & X & X & \\ & + & CH_3 - C \equiv C - H \\ & (Major) \end{array}$

(b) Non terminal gem dihalide gives 2-Alkyne in presence of alc. KOH while gives 1-alkyne in presence of NaNH₂.

Example :
$$CH_3 - C - C - CH_4$$
 (major)
H X H
Example : $CH_3 - C - C - CH_4$ (major)
H X H
H X H

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

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

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

$$\begin{array}{ccc} CH \\ \parallel \\ CH - COOK \end{array} \xrightarrow{Electrolysis} & \begin{array}{c} CH \\ \parallel \\ CH \end{array} + CO_2 \end{array}$$

 $Mechanism \ : \\$

$$\begin{array}{ccc} CH-COOK \\ \parallel \\ CH-COOK \end{array} \xrightarrow{lonization} \begin{array}{c} CH-COO^{-} \\ \parallel \\ CH-COO^{-} \end{array} + 2K^{+} \end{array}$$

at anode (Alkyl and CO_2 gas is formed)

(Oxygen free radical)

$$\begin{array}{ccc} & & & & \\ & & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\$$

at cathode (KOH and $\rm H_{2}$ gas is formed)

$$\begin{array}{rcl} 2\mathrm{K}^{\scriptscriptstyle +} + 2\mathrm{e}^{-} & \longrightarrow 2\mathrm{K} \\ 2\mathrm{K} &+ & 2\mathrm{H_2O} & \longrightarrow 2\mathrm{KOH} + \mathrm{H_2}^{\uparrow} \end{array}$$

- **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

$$CH \equiv \overset{\delta^{-}}{C} - \overset{\delta^{+}}{H} + \overset{\delta^{-}}{CH_{3}} - \overset{\delta^{+}}{Mg} - Br \longrightarrow \overset{C-MgBr}{H} + CH_{4} \xrightarrow{RI} \overset{Mg}{Mg} + R - C \equiv CH$$
$$R - C \equiv CH + CH_{3}Mg - Br \longrightarrow \overset{C-MgBr}{H} + CH_{4} \xrightarrow{R'I} R' - C \equiv C - R + \overset{Mg}{Mg}$$

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.

$$CaC_{2} + 2H_{2}O \longrightarrow CH \equiv CH + Ca(OH)_{2}$$
$$Ca^{+2} + \overset{1}{C} \equiv \overset{1}{C} + 2H^{+} + 2OH^{-} \longrightarrow CH \equiv CH + Ca(OH)_{2}$$

- (b) Manufacture : Acetylene is manufactured by heating methane or natural gas at 1500°C in an electric arc $2CH_4 \xrightarrow{Electric arc} CH \equiv CH + 3H_2$
- (c) Berthelot's process : Acetylene is synthesized by striking an electric arc between carbon electrodes in presence of hydrogen. $2C + H_2 \xrightarrow{1200^{\circ}C} CH \equiv CH$

(d) From haloform [CHI₃, CHCl₃] : 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.

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

D 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** f lelectrons : 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 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.
Evaluation - The evaluation is evaluated 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 scharacter 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

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

Relative acidic order H₂O > ROH > HC=CH > HNH₂ > CH₂=CH₂ > CH₃--CH₃

□ 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 $C \equiv C$, 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 :

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

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

Stability of intermediates :

\oplus		\oplus
R - CH = C - R	<	$R - CH_2 - CH - R$
(+) ve on more EN		more stable
atoms is less stable		

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

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

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

In presence of Lindlar's catalyst [Pd/CaCO3 + quinoline or Nickle boride] alkynes give cis – alkene

$$R-C \equiv C-R' \xrightarrow{\text{Lindlar's catalyst}} H^{2}C \equiv C < H^{2} \text{ (Stereo specific reaction)}$$

cis - alkene

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

$$R-C \equiv C-R' \qquad \xrightarrow{Na/NH_3} \qquad \begin{array}{c} R \\ H_2 \end{array} \qquad \begin{array}{c} R \\ H \end{array} C \equiv C \begin{pmatrix} H \\ R \\ H \end{pmatrix} (Stereo specific reaction)$$

trans-alkene

 $\label{eq:addition} \mbox{ of Halogens} : \mbox{ Reactivity order of Halogens} \qquad \mbox{ } Cl_2 > Br_2 > l_2$ (b) Alkynes react with Cl₂ or Br₂ in dark in presence of metal halide and form di and tetra halo derrivatives.

R—C≡CH	$\xrightarrow{2Cl_2}{FeCl_3}$	□ □ R−C−C−H
		άά

Mechanism :

 $Cl_2 + FeCl_3 \longrightarrow$

$$Cl^+ + FeCl_4^-$$



Reaction with dilute
$$Br_2$$
 or bromine water:
 $CH \equiv CH + Br_2$ H_2O $Br - CH = CH - Br$ $CH \equiv CH + Br_2$ H_2O $Br - CH = CH - Br$ $CH \equiv CH + Br_2$ H_2O $Br - CH = CH - Br$ $Br - CH = CH - Br_2$ $Br - CH = CH - Br$ $Br - Br_2$ Br_2 Br

ethanol → $CH \equiv CH + I_2$ CHI=CHI (addition reaction) $\xrightarrow{NH_3}$ $CH \equiv CH + I_{2}$ $I = C \equiv C = I + NH_4 I$ (substitution reaction) Di iodoacetylene

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

Reactivity order of
$$H - X$$
: $HI > HBr > HCl > HF$
 $R - C \equiv C - H$
 $\xrightarrow{H-X}$
 $R - C \equiv C - H$
 $\xrightarrow{H-X}$
 $R - C = C - H$
 $\xrightarrow{H-X}$
 $R - C = C - H$

(Gem dihalides major product)

Mechanism :

$$R - C \equiv CH \qquad \xrightarrow{H^+}_{[H-X]} \rightarrow \qquad R - \stackrel{+}{C} = C - H$$

(Intermediate is carbocation)

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

Further

$$\stackrel{X}{\stackrel{|}{R-C=CH_2}} \xrightarrow{H^+}$$

$$\begin{array}{c} X \\ | \\ R - \underbrace{C}_{\oplus} - \underbrace{C}_{H_2} \\ H \end{array} + \\ H \end{array}$$

$$\begin{array}{c} X \\ H \\ R - C - C \\ H \\ H \\ H \end{array}$$

(only –I of X)

so



(Major Product)

(more stable

due to +M of X)

(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 H	HOCl >	> HOBr	>	HOI
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$$R - C \equiv C + HOC \longrightarrow R - C - C + C = O$$

Mechanism :

$$R-C \equiv CH \xrightarrow{Cl^{+}} R \xrightarrow{C} = CH \xrightarrow{C} R \xrightarrow{C} H \xrightarrow{C} H \xrightarrow{C} H$$

(Cyclic cation)



Further



so



Addition of BH_3 / THF or B_2H_6 (Hydroboration) : THF - Tetrahydrofurane is used as solvent. (e) $\begin{array}{cccc} 3R - C \equiv C - R & \stackrel{BH_3}{\xrightarrow{}} & (R - C = C -)_3 B \\ & & & | & | \\ & H & R \\ \end{array}$ Since BH₃ is not available as monomer so a solvent THF is used for the stability of BH₃.



Example :

$$CH_{3}-C \equiv C-CH_{3} \xrightarrow{BH_{3}} (CH_{3}-C=C-)_{3}B \xrightarrow{H_{2}O_{2}/OH} CH_{3}-CH=C-OH \longrightarrow CH_{3}-CH_{2}-C-CH_{3}$$

$$H CH_{3} \qquad CH_{3}-$$

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

$$R-C \equiv CH \xrightarrow{dil.H_2SO_4(1\%)}_{dil.H_3SO_4(40\%)} R-C-C-CH_3$$

Mechanism :

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



Example :
$$CH_3 - C \equiv C - CH_3 \xrightarrow{H^+/H_2O}_{H_3^{+2}} OH_3 - C = C - CH_3 \longrightarrow OH_3 - C - CH_2 - CH_3$$

2-butanone

(b) Addition of HCN : The addition of HCN in presence of barium cyanide to form vinyl cyanide. $CH \equiv CH + HCN \xrightarrow{Ba(CN)_2} CH_2 \equiv CHCN$

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

$$CH_2 = CHCN \xrightarrow{Polymerisation} (-CH_2 - CH_2)_n$$

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



When ethylidene acetate is heated it give acetaldehyde and acetic anhydride



(d) Addition of alcohols : In presence of BF₃ and HgO alkynes react with alcohols and form acetal and ketal

$$CH \equiv CH + CH_{3}OH \xrightarrow{BF_{3}} CH_{2} = CHOCH_{3} \xrightarrow{CH_{3}OH} CH_{3} - CH_{3}OH \xrightarrow{OCH_{3}OH} CH_{3} - CH_{3}OH \xrightarrow{OCH_{3}OH}$$

Methylal (acetal)

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

Ketal

Acetylene forms acetal while other alkynes form ketal.

(3) $_{3}$: In presence of AlCl₃ or HgCl₂ acetylene combines with AsCl₃ to yield Lewisite gas. It is four times poisonous than mustard gas.

$$CH \equiv CH + CI - AsCl_2 \longrightarrow OH - O$$

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.

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

Alkyne + CO + H2O
$$\underline{Ni(CO)_4}$$
Olefinic acidAlkyne + CO + R-OH $\underline{Ni(CO)_4}$ Olefinic ester $\begin{array}{c} CH\\ \parallel\\ \Pi\\ CH\end{array}$ + CO + H2O $\underline{Ni(CO)_4}$ $\begin{array}{c} CH_2\\ H2OOH\\ CHOOH\end{array}$ $\begin{array}{c} CH\\ H2\\ CHOOH\end{array}$ $\begin{array}{c} CH_2\\ H2OOH\\ CHOOH\end{array}$ $\begin{array}{c} CH\\ H2\\ CHOOH\end{array}$ $\begin{array}{c} CH_2\\ CHOOH\\ CHOOH\end{array}$ $\begin{array}{c} CH\\ H2\\ CHOOH\end{array}$ $\begin{array}{c} CH_2\\ CHOOH\\ CHOOH\end{array}$ $\begin{array}{c} CH\\ H2\\ CHOOH\end{array}$ $\begin{array}{c} CH_2\\ CHOOH\end{array}$ $\begin{array}{c} CH\\ H2\\ CHOOH\end{array}$ $\begin{array}{c} CH_2\\ CHOOH\end{array}$ $\begin{array}{c} CH\\ H2\\ CHOOH\end{array}$ $\begin{array}{c} CH_2\\ CHOOH\end{array}$ $\begin{array}{c} CH\\ CH\\ CH\end{array}$ $\begin{array}{c} CH_2\\ CHOOH\end{array}$ $\begin{array}{c} CH\\ CH\end{array}$ $\begin{array}{c} CH\\ CH$ $\begin{array}{c} CH\\ CH\end{array}$ $\begin{array}{c} CH\\ CH\end{array}$ $\begin{array}{c} CH\\ CH\end{array}$ $\begin{array}{c} CH\\ CH$ $\begin{array}{c} CH\\ CH\end{array}$ $\begin{array}{c} CH\\$

□ Oxidation reactions :

(a) Combustion :

$$\begin{array}{rcl} C_{n}H_{2n\cdot2} &+& \displaystyle\frac{3n-1}{2}O_{2} & \longrightarrow & nCO_{2} + (n-1)H_{2}O + Heat \\ \\ 2HC \equiv CH + 5O_{2} & \longrightarrow & 4CO_{2} + 2H_{2}O + 312 \text{ K.cal} \end{array}$$

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.

$$\begin{array}{c} CH\\ \parallel\\ CH\\ H\end{array} + 4[O] & \xrightarrow{alk.KMnO_4} & COOH\\ H\\ Acetylene & Oxalic acid\\ CH_3-C\equiv CH + 4[O] & \xrightarrow{alk.KMnO_4} & CH_3-COOH + HCOOH\\ \end{array}$$

(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.

$$R - C \equiv C - R' + 2[O] \longrightarrow R - C - C - R \xrightarrow{H_2O + [O]} RCOOH + R'COOH = C - C - R' \xrightarrow{H_2O + [O]} RCOOH = R'COOH = R'COOH$$

$$\begin{array}{cccc} CH \\ \parallel \\ CH \\ CH \end{array} + 2[O] & \longrightarrow & CHO \\ HO \\ Glyoxal \\ CH_3 - C \equiv CH + 2[O] & \longrightarrow & CH_3 - C \equiv O \xrightarrow{H_2O+[O]} & CH_3COOH + HCOOH \\ & GHO \end{array}$$

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.

$$\begin{array}{cccc} CH_{3}-C-OH+HO-C-CH_{3} & \longrightarrow & CH_{3}-C-C-CH_{3} \\ \parallel & \parallel & \\ O & O \end{array}$$

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



(e) Oxidation with ozone (O_3) : In the ozonolysis both sp-C-atoms are converted into -C-C-group.



In this reaction H_2O_2 is oxidant which oxidise $\begin{array}{cc} R-C-C-R \\ \parallel & \parallel \\ O & O \end{array}$

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 :
$$CH_3 - C \equiv CH$$

(i) O_3
(ii) H_2O
(ii) O_3
(ii) H_2O
(ii) O_3
(ii) H_2O/Zn
(ii)

□ 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

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.

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.

$$\begin{array}{ccc} CH_{3} & -CH_{2} & -C \equiv CH & \xrightarrow{\text{alc.KOH}} & CH_{3} & -C \equiv C - CH_{3} \\ 1 - Butyne & 2 - Butyne \end{array}$$

When alkyne -2 is heated with $\mathrm{NaNH}_{\mathrm{2}}$ alkyne -1 is obtained

$$\begin{array}{ccc} CH_{3} \longrightarrow C \equiv C \longrightarrow CH_{3} & \xrightarrow{NaNH_{2}} & CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{2} \longrightarrow C \equiv CH \\ \hline 2 - Butyne & 1 - Butyne \end{array}$$

D 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.

$$2HC \equiv C - H \xrightarrow{Cu_2Cl_2} CH_2 = CH - C \equiv C - H$$

When vinyl acetylene react with HCl then chloroprene is obtained.

$$CH_2 = CH - C \equiv C - H \xrightarrow{HCl} CH_2 = CH - C = CH_2 \xrightarrow{Polymerisation} Neoprene (Synthetic rubber)$$

$$CH_2 = CH - C \equiv C - H \xrightarrow{HCl} CH_2 \xrightarrow{Q} O$$

$$CH_2 = CH - C = CH_2 \xrightarrow{Polymerisation} Neoprene (Synthetic rubber)$$

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$$CH_2 = CH - C = CH_2 \xrightarrow{Polymerisation} N$$

Trimerisation : 3 molecules of acetylene.

$$3CH \equiv CH \xrightarrow{Cu_2Cl_2} CH_2 = CH - C \equiv C - CH = CH_2$$

Divinyl acetylene

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

$$3CH \equiv CH \xrightarrow{\text{Redhot}} \bigcirc \\Benzene$$

$$3 CH_{3}-C \equiv CH \xrightarrow{\text{Redhot}} H_{3}C \xrightarrow{\text{CH}_{3}} (H_{3} \xrightarrow{\text{CH}_{3}}$$

Hexa methyl benzene



Other reactions of acetylene :

1,3,5,7-cyclooctatetraene

NH → 2HCN Electric spark NH_3 HC≡CH High temp. QΗ H Pyrole HON Red hot Fe Pyridine CH $\begin{array}{c} CH = CH & \xrightarrow{CH_2N_2} \\ CH_2 & \xrightarrow{-N_2} \end{array}$ CH_2N_2,Δ ЭH $-N_2$ Bicyclo (1,1,0) butane Cyclo propene CH,N, $\begin{array}{c} CH_2-CH_2\\ | & \|\\ CH_2 & N \end{array}$ cold ether solution СН Pyrazoline ah-ah IIIIII Ah ah Al₂O₃, 400°C Thiophene

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

 $CH \equiv CH + HCHO _Cu \rightarrow HC \equiv CCH_2 - OH _HCHO \rightarrow CH_2 - C \equiv C - CH_2$ propargyl alcohol (vii) Reaction with NaOCl : (Substitution reaction) $H - C \equiv C - H + NaOCl \xrightarrow{0^{\circ}C} H - C \equiv C - Cl + NaOH$ $H - C \equiv C - Cl + NaOCl \xrightarrow{0^{\circ}C} Cl - Cl + NaOH$ 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	Reagent	Observation	Reaction	Remarks
Group				
	(1) Bayer's Reagent alk.dil.Cold KMnO ₄	Pink Colour disappears	$CH_2 = CH_2 + H_2O + O \xrightarrow{alk.KMnO_4} OH_2 - OH_2 OH OH$	Hydroxylation
- C = C -	(2) Br ₂ /H ₂ O	Red Colour decolourises	$\begin{array}{c} & CH_2 - CH_2 \\ Br_2 + CH_2 = CH_2 \longrightarrow \begin{array}{c} Br & Br \\ Br & Br \end{array} \\ White ppt \end{array}$	Bromination
	(3) O ₃ (ozone)	Acid Formed	$R-C=C-R' \xrightarrow{O_3} RCOOH+R'COOH$	Ozonolysis

$\hfill\square$ \hfill Laboratory test of terminal alkynes :

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

(acetylenic hydrogen) H-C≡C-CH2CH3 1-Butyne, a terminal alkyne

Functional Group	Reagent	Observation	Reaction
	(1) Cuprous chloride + NH ₄ OH	Red ppt.	R-C≡CH+CuCl <u>NH₁OH</u> R-C≡CCu√(red)
R–C≡C–H	(2) AgNO ₃ +NH ₄ OH	White ppt.	R-C=CH+Ag' → R -C = C Ag ↓ (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.	$R - CH_2 - CCl_2 - R - R - R - C \equiv C - R$. The reagent is -						
	(A) Na	(B) HCl in H ₂ O	(C) KOH in C_2H_5O	H (D) Zn in alcoho	ol.		
					Ans.(C)		
Sol.	Alcoholic KOH brings about dehyrohalogenation						
Ex.	Acetylene when treate	ed with dilute HCl at 60°C	(333 K) in presence of H	lgCl ₂ produces -			
	(A) Methyl chloride	(B) Vinyl chloride	(C) Acetaldehyde	(D) Formaldehy	ide (D)		
					Ans.(B)		
Sol.	$(B) H - C \equiv C - H + H$	$\text{Cl} \xrightarrow{\text{HgCl}_2} \text{CH}_2 = \text{CH} - 0$	Cl				
		Vinyl chloride					
Ex.	When propyne is trea	ted with aqueous H_2SO_4 in	the presence of $HgSO_4$,	, the major product is	5 -		
	(A) Acetaldehyde	(B) Propanal	(C) 2-Propanol	(D) Propanone	Ans.(D)		
Sol.	$CH_3 - C \equiv CH + H_2C$	$ \longrightarrow CH_3 - C = CH_2 = I $	\Rightarrow CH ₃ -C-CH ₃ \parallel O				
Ex.	Alkaline KMnO ₄ , oxid	izes acetylene to -					
	(A) Acetic acid	(B) Glyoxal	(C) Oxalic acid	(D) Ethylene gly	col		
					Ans.(C)		
Sol.	$H - C \equiv C - H + 4[C$)] → [COOH COOH					
Ex.	Which of the following	g 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 acetyler	ne gives -					
	(A) Oxalic acid	(B) Ethylene glycol	(C) Glyoxal	(D) CH ₃ CHO	Ans.(C)		
Sol.	$HC \equiv CH \frac{(i)O_3}{(ii) H_2O/Zn}$	→ H−C−C−H II II O O Gyoxal					
Ex.	Propyne on reaction v	with aqueous chlorine gives	; -				
	(A) 1, 1, 2, 2-Tetrach	loropropane	(B) 1, 2-Dichloropro	opene			
	(C) 1, 1-Dichloroprop	Danone	(D) 2, 2-Dichloropro	panone	Ans.(C)		
		Г он]	О				
Sol.	$CH_3 - C = CH + 2HO$	$Cl \rightarrow \begin{bmatrix} CH_3 - C - CHCl_2 \\ 0H \end{bmatrix}$	$\xrightarrow{-H_2O} CH_3 \xrightarrow{\parallel} C \xrightarrow{-C} CH_2O_2$				
Ex.	Mesitylene can be obtained by polymerization of -						
	(A) Ethyne	(B) Ethene	(C) Propene	(D) Propyne	Ans.(D)		

Propyne on trimerization yields mesitylene 3CH_3C = CH \rightarrow Sol.

Excess of CH_3COOH is reacted with $CH \equiv CH$ in presence of Hg^{2+} , the product is -Ex. (A) CH₃CH(OOCCH₃)₂ (B) $CH_2 = CH(OOCCH_3)$ (C) (CH₃COO)CH₂--CH₂(OOCCH₃) (D) None of these

 $H-C \equiv C-H + 2CH_3COOH \longrightarrow CH_3 - CH(OCOCH_3)_2$ Sol. Both the protons go to same carbon atom Ex. A compound is treated with NaNH2 to give sodium salt. Identify the compound -(A) $C_2 H_2$ (B) $C_6 H_6$ (C) C_2H_6 (D) $C_2 H_4$ Ans.(A)

Sol. Ethyne is acidic in character

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



Ans.(A)