HYDROCARBONS

ALKYNE

GENERAL INTRODUCTION

A triple bond gives an alkyne four fewer hydrogen atoms then the corresponding alkane. Therefore, the triple bond contributes two degrees 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 alkane. Acetylene is an important industrial feedstock, but its largest use is as the fuel the oxyacetylene welding torch.

STRUCTURE AND BONDING IN ALKYNES

- (a) Alkynes are also 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 from overlap of the two remaining unhybridized p orbits on each carbon atom. these orbitals overlap at **right angles** (90°) to each other, forming one π bond with electron density above and below th4e C-C sigma bond, and the other with electron density in format 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

S.No.	Compound	Name
1.	$CH \equiv CH$	Ethyne
2.	$CH_2 - C \equiv H$	Propyne
3.	$HC \equiv C - CH_2 - CH_3$	But-1-yne
4.	$CH_3 - C \equiv C - CH_3$	But-2-yne
5.	$\begin{array}{c} CH_{3} & Br \\ \\ CH_{3} - CH - C & C - CH_{2} - CH - CH_{3} \end{array}$	6-Bromo-2methylhept-3-yne

ISOMERISM IN ALKYNES

Туре	Category	Examples
(i)	Chain isomerism Structural	$CH_3 - CH_2 - CH_2 - C \equiv CH \&$
		$CH_3 - CH - C CH_{CH_3}$
(ii)	Positional Isomerism	$CH_3 - CH_2 - CH_2 - C \equiv CH \& CH_3 - C$
		\equiv C- CH ₃
(iii)	Functional group isomerism	$CH_3 - CH_2 - C \equiv C - CH_3 \& CH_3 - C = C$
		$= CH - CH_3$ &

METHOD OF PREPARATION

- (1) Dehydrohalogenation
 - (a) From Gem Dihalides

$$R \xrightarrow[H]{} X \\ R \xrightarrow[H]{} X \\ R \xrightarrow[H]{} X \\ R \xrightarrow[H]{} X \\ KOH + C_2H_5OH \rightarrow C_2H_5 \stackrel{\Theta}{} \xrightarrow[\Phi]{} \Theta \\ \Theta \\ H \xrightarrow{} X \\ R \xrightarrow{} C = C - H$$

Chemistry



(b) From Vicinal Dihalides



The elimination of one molecule of hydrogen halide yields vinyl halide which is very unreactive. Under mild conditions, the dehydrohalogenation stops at vinylic halide stage but more vigorous conditions – like the use of a stronger base like amide ion (NH_2^-) – are required for alkyne formation.

(c) From Tetra haloalkanes (Dehalogenation)

$$\begin{array}{cccc} X & X & & X \\ R - \overset{\ \ }{\underset{\ \ }} & R - C \equiv C - H & \overset{\ \ \ }{\underset{\ \ }} & \overset{\ \ }{\underset{\ \ }} & R - C \equiv C - H & \overset{\ \ \ }{\underset{\ \ }} & \overset{\ \ }{\underset{\ \ }} & R - C \equiv C - H & \overset{\ \ \ }{\underset{\ \ }} & \overset{\ \ }{\underset{\ \ }} & R - C \equiv C - H & \overset{\ \ \ }{\underset{\ \ }} & \overset{\ \ }{\underset{\ \ }} & R - C \equiv C - H & \overset{\ \ \ }{\underset{\ \ }} & \overset{\ \ \ }{\underset{\ \ }} & R - C \equiv C - H & \overset{\ \ \ \ }{\underset{\ \ }} & \overset{\ \ \ }{\underset{\ \ }} & R - C \equiv C - H & \overset{\ \ \ \ }{\underset{\ \ }} & \overset{\ \ \ }{\underset{\ \ }} & R - C \equiv C - H & \overset{\ \ \ \ }{\underset{\ \ }} & \overset{\ \ \ }{\underset{\ \ }} & R - C \equiv C - H & \overset{\ \ \ \ }{\underset{\ \ }} & \overset{\ \ \ }{\underset{\ \ }} & R - C \equiv C - H & \overset{\ \ \ \ \ }{\underset{\ \ }} & \overset{\ \ \ }{\underset{\ \ }} & R - C \equiv C - H & \overset{\ \ \ \ \ }{\underset{\ \ }} & \overset{\ \ \ }{} & H = C = C - H & \overset{\ \ \ \ \ }{\underset{\ \ }} & \overset{\ \ \ }{\underset{\ \ }} & H = C = C - H & \overset{\ \ \ \ \ }{\underset{\ \ }} & \overset{\ \ \ \ }{\underset{\ \ }} & \overset{\ \ \ }{\underset{\ \ }} & \overset{\ \ \ }{\underset{\ \ }} & H = C = C - H & \overset{\ \ \ \ \ }{\underset{\ \ }} & \overset{\ \ \ \ }{\underset{\ \ }} & \overset{\ \ \ }{} & \overset{\ \ \ }{\underset{\ \ }} & \overset{\ \ \ }{\atop \ }} & \overset{\ \ \ }{\atop \ \ } & \overset{\ \ \ }{\atop \ }} & \overset{\ \ \ }{\atop \ }} & \overset{\ \ \ }{\ \ }} & \overset{\ \ \ }{\ \ } & \overset{\ \ \ }{\ \ }} & \overset{\ \ \ }{\ \ }} & \overset{\ \ \ }{\ \ } & \overset{\ \ \ }{\ \ }} & \overset{\ \ \ }{\ \ } & \overset{\ \ \ }{\ \ }} & \overset{\ \ \ }{\ \ }} & \overset{\ \ \ }{\ \ }} & \overset{\ \ \ }{\ \ } & \overset{\ \ \ }{\ \ }} & \overset{\ \ \ }{\ \ } & \overset{\ \ \ }{\ \ }} & \overset{\ \ \ }{\ \ } & \overset{\ \ \ }{\ \ }} & \overset{\ \ \ }{\ \ } & \overset{\ \ \ }} & \overset{\ \ }{\ \ } & \overset{\ \ }}$$

In the above reaction it is necessary that the four halogen atoms must be attached at vicinal carbons.

If they are attached at the two ends then the product alkene is obtained.

(2) From Kolbe's Synthesis



Potassium Maleate

At Anode



At Cathode

$$2K^{+} + 2e^{-} \rightarrow 2K^{\bullet}$$
$$2K^{\bullet} + 2H_{2}O \rightarrow 2KOH + H_{2}$$

(3) From Alkynes: (To form higher Alkyne)

(i) With Na: When acetylene or 1-alkyne react with Na in presence of liq. NH₃ then an intermediate compound sodium acetylide or sodium alkyne is formed which gives higher alkyne with alkyl halide.

$$2H - C \equiv C - H + 2Na \xrightarrow{\lim_{q.NH_3}} 2H - C \equiv \overline{CN} a \xrightarrow{X-R} H - C \equiv C - R$$
$$H - C \equiv C - H \xrightarrow{\Theta} H = C \equiv C - R$$
$$H - C \equiv C - H \xrightarrow{\Theta} H = C \equiv C - R$$
$$H = H = C \equiv C - R$$
$$H = H = C = C - R$$
$$H = C \equiv C - R + MgX_2$$

 $2R - C \equiv C - H + 2Na \xrightarrow{liq.NH_3} 2R - C \equiv \overline{C} \overset{+}{N}a \xrightarrow{R'-X} R - C \equiv C - R' + NaX$

(ii) With Grimard reagent: When acetylene or 1–alkyne react with GR then alkane and unsaturated GR is formed which further react with alkyl halide and form higher alkyne.

Class-XI

$$H - C \equiv CH + RMgX \xrightarrow[-RH]{-RH} HC \equiv C MgX \xrightarrow[-MgX_2]{-MgX_2} H - C \equiv C - R$$

Acetylene
$$R - C \equiv C - H + R Mg X \xrightarrow[-RH]{-RH} R - C \equiv C MgX \xrightarrow[-R'-X]{-X} R - C \equiv C - R'$$

(4) Preparation of Ethyne of Acetylene

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

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

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

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

$$2CH_4 \xrightarrow{Electricarc} CH \equiv CH + 3H_2$$

- (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

 $CHI_3 + 6Ag + I_3CH \rightarrow CH \equiv CH + 6AgI$

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

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

PHYSICAL PROPERTIES

(a) Alkynes are colourless, odourless and tasteless.

Φ Θ

- (b) Lower alkynes are partially soluble in H₂O. (It is due to its polarizability).
- (c) Higher alkynes are insoluble in water due to more % of covalent character.
- (d) Completely soluble in organic solvents.
- (e) Melting point and boiling point increases with molecular mass and decreases with number of branches.
- (f) Up to C₄ alkynes are gaseous C₅ C₁₁ are liquid, C₁₂ & above are solids.
- (g) Pure acetylene is odourless and impure acetylene has odour like garlic. It is due to impurities of Arsene (AsH₃) & Phosphine (PH₃).
- (h) Acetylene & 1-alkyne are acidic in nature. It is due to greater electronegativity of sp hybridized 'C'.
- (i) Acetylene has two acidic hydrogen atoms. It can neutralise two equivalents of base at the same time. So, it is also called as dibasic acid but the base should be very stronger as 'NH₂ or ⁻CH₃ etc.

CHEMICAL PROPERTIES

The chemical properties of alkyne are due to two factors:

Presence of π **electrons:** Due to presence of loosely bond 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 reaction.

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

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 I-alkynes are considered as weak acids.

Ex: The amounts of s-character in various types of C-H bods is as-

≡ C – H	= C – H	– C – H
50%	33%	25%

Since s electrons are closer to the nucleus than the p electrons, the electrons in a bond having more s-character will be 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 sp² sp³
Relative acidic order $H_2O > ROH > HC \equiv CH > HNH_2 > CH_2 = CH_2 > CH_3 - CH_3$

(1) Addition Reaction

Electrophilic Addition: Addition reactions where the addition is initiated electrophilic (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 for reaction with electrophiles.

Reactivity order of hydrocarbons for electrophilic addition

Alkenes > Alkynes > Alkanes.

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

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

Chemistry

(ii)
$$R-C \equiv CH-R \xrightarrow{H^+} R - CH - \overrightarrow{C}H - R$$

|
H

Stability of intermediates

$$\begin{array}{ll} \mathbf{R} - \mathbf{C}\mathbf{H} = \overset{\oplus}{\mathbf{C}} - \mathbf{R} & < & \mathbf{R} - \mathbf{C}\mathbf{H}_2 - \overset{\oplus}{\mathbf{C}}\mathbf{H} - \mathbf{R} \\ (+) \text{ve on more En} & & \text{More stable} \end{array}$$

Atoms are less stable

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

(a) ADDITION OF HYDROGEN Hydrogenation

$$\mathbf{R} - \mathbf{C} \equiv \mathbf{C} - \mathbf{H} + \mathbf{H}_2 \xrightarrow[\text{HighTemp.}]{Ni} \mathbf{R} - \underbrace{\mathbf{C}}_{l} = \underbrace{\mathbf{CH}}_{l} + \mathbf{H}_2 \xrightarrow[\text{HighTemp.}]{Ni} \mathbf{R} - \mathbf{CH}_2 - \mathbf{CH}_3$$

The above reaction is called as Sabatier Sanderson's reaction.

Hydrogenation in the presence of lindlar's Catalyst

Addition up to alkene takes place in cis manner.

(i)
$$H - VC \equiv C - H + H_2 \xrightarrow{Pd - BaSO_4} H = C + H_H$$

(ii)
$$CH_3 - C \equiv C - CH_3 + H_2 \xrightarrow{Pd - BaSO_4} CH_3 C = C H_3$$

Hydrogenation by Na + NH₃ (liq.)

Addition up to alkene takes place in trans manner

(i)
$$CH \equiv CH \xrightarrow{Na}_{NH(liq)} H \subset C = C H$$

(ii)
$$R - C \equiv C - R' \xrightarrow{Na/NH_3Liq} R \subset C = C \land R$$

Class-XI

Mechanism

$$Na \rightarrow \overset{\oplus}{N}a + e^{-}$$

$$R - C \stackrel{\oplus}{\searrow} C - R' + e^{-} \rightarrow R - \overset{\Theta}{C} = R'$$

$$\xrightarrow{\Theta}{-NH_2} \downarrow Liq. NH_3$$

$$R - C = C - R'$$

$$\downarrow Na \rightarrow \overset{\oplus}{N}a + e^{-}$$

$$R - \overset{\Theta}{C} = C - R'$$

$$\xrightarrow{\Theta}{H}$$

$$-NH_2 \downarrow Liq. NH_3$$

$$R - \overset{\Theta}{C} = C - R'$$

$$\xrightarrow{\Theta}{H}$$

$$-NH_2 \downarrow Liq. NH_3$$

(b) ADDTION OF BH_3 / THF OR B_2H_6 (HYDROBORATION):

THF – Tetrahydrofuran is used as solvent.

$$3R-C \equiv C - R \xrightarrow{BH_3} (R - C = C -)_3 B$$
$$| \qquad | \qquad H H$$

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

Chemistry

Ex.
$$CH_3 - C \equiv C - CH_3 \xrightarrow{BH} (CH_3 - C = C -)_3 B \xrightarrow{H_2O_2/OH} CH3 - CH = C - OH \rightarrow CH_3 - CH_2 C - CH_3 \downarrow H CH_3 CH_3 - CH_3 - CH_3 - CH_2 C - CH_3 - CH_3$$

(c) ADDITION OF HALOGENS (HALOGENATION)

In presence of Lewis acid as a catalyst alkyne form tetrahaloderivative with halogen.

$$R - C \equiv C - H + X - X \xrightarrow{FeX_3} R - C = C - H \xrightarrow{X_2} R - C = C - H \xrightarrow{X_2} R - C = C - H \xrightarrow{X_2} R - C = C - H$$

FeX₃ + X₂ \rightarrow FeX₄ + X⁺

$$R-C = C-H$$

$$+X \rightarrow \downarrow$$

$$R-C = C-H$$

$$\downarrow$$

$$X-X+FeX_3$$

$$X-X^+$$

$$R-C = C-H$$

$$\downarrow$$

$$X-X+FeX_3$$

$$X-X^+$$

$$R-C = C-H$$

$$\downarrow$$

$$X = X$$

$$R-C = C-H$$

$$\downarrow$$

$$X = X$$

$$R-C = C-H$$

$$X = X$$

$$X =$$

Reaction with dilute \mbox{Br}_2 or bromine water

Reaction with iodine

$$\begin{array}{ll} \text{CH} \equiv \text{CH} + \text{I}_2 & \xrightarrow{ethanol} & \text{CHI} = \text{CHI} \text{ (addition reaction)} \\ \text{CH} \equiv \text{CH} + \text{I}_2 & \xrightarrow{\text{NH}_2} & \text{I} - \text{C} \equiv \text{C} - \text{I} + \text{NH}_4 \text{I} \text{ (substitution reaction)} \\ & \text{Di diiodoacetylene} \end{array}$$

Chemistry

(d) ADDITION OF HALOGEN ACIDS (H-X) {HYDROHALOGENATION} Addition according to Marconi-KOff's Rule.

Reactivity order of H – X: HI > HBr > HCl > HF

$$R - C \equiv C - H \xrightarrow{H-X} R - \begin{bmatrix} X & H \\ I & I \\ C & - \begin{bmatrix} - & H \\ I \\ X & H \end{bmatrix} + H$$

(Gem dihalides major product)

Mechanism

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

(Intermediate is carbocation)

$$\mathbf{R} - \stackrel{\oplus}{\mathbf{C}} = \mathbf{C}\mathbf{H}_2 \xrightarrow{\mathbf{X}^-} \mathbf{R} - \stackrel{\mathbf{X}^-}{\mathbf{C}} = \mathbf{C}\mathbf{H}_2$$

Further

$$R - \overset{X}{C} = CH_2 \xrightarrow{H^+} \overset{R^+}{\longrightarrow} \begin{array}{c} X & X \\ | & & | \\ R - \overset{H^+}{C} = CH_2 & + R - \overset{| \\ C - C - C \\ \oplus \\ | & | \\ H \\ (morestabledueto + Mof X) \end{array}$$

So



(e) ADDITION OF HOX: Alkynes react with hypohalous acids according to markwonikoff's rule ant form gem diol, which are unstable, lose a molecule of water and form halo aldehyde or halo ketones.

Reactivity order HOCl > HOBr > HOl

$$R - C \equiv CH + HOCl \rightarrow R - C - CHCl_2$$

Class-XI

Mechanism

$$R - C \equiv CH + \xrightarrow[(HOCI]]{O^{+}} R - \stackrel{+}{C} = \stackrel{+}{C} H \rightarrow R - C = CH$$

$$::Cl: \qquad Cl$$

$$R - C = CH \xrightarrow[]{OH} R - C = CH$$

$$:Cl \qquad Cl$$

$$Cl \qquad Cl$$

Further



So



(2) Nucleophilic Addition Reaction

In these reactions some heavy metal cation like Hg⁺², Pb⁺², Ba⁺² is used. This cation attracts the $\pi^- e^-$ of alkynes and decrease the e^- density and hence a nucleophilic can attack an alkyne.

(a) ADDITION OF DIL. H₂SO₄ (HYDRATION): The addition of water takes place in the presence of Hg⁺² and H₂SO₄ [1% HgSO₄ + 40% H₂SO₄]. In this reaction carbonyl compounds are obtained.

 $CH \equiv CH + H - OH \rightarrow CH_2 = CH - OH \rightleftharpoons CH_3 - CHO$ enol unstable

A structure in which –OH group is attached to double bond carbon is called as enol (enol + – ol).

This reaction is used for preparation of aldehyde and ketone.

$$R - C \equiv CH \xrightarrow[dil H_2SO_4(1\%)]{dil HgSO_4(40\%)} \begin{array}{c} R - C - CH_3 \\ \parallel \\ 0 \end{array}$$

Mechanism

$$R - C \equiv CH \xrightarrow{Hg^{+2}} R - \bigcup_{\substack{| \\ :Hg^{+}}}^{\bigoplus} = CH \rightarrow R - C = CH$$



$$\rightarrow R - C - CH_3$$

(Keto more stable)

Ex.
$$CH_3 - C \equiv C - CH_3 \xrightarrow{H^+/H_2O}_{Hg^{+2}} CH_3 - \overset{OH}{\overset{I}{C}} = \underset{H}{C} - CH_3 \xrightarrow{O}_{2-but an one} CH_3 - \overset{OH}{\overset{I}{C}} - CH_2 - CH_3$$

(b) ADDITION OF HCN

Addition takes place in the presence of CuCl

$$\mathbf{H} - \mathbf{C} \equiv \mathbf{C} - \mathbf{H} + \mathbf{H} - \mathbf{CN} \xrightarrow{Cucl} \mathbf{CH}_2 = \mathbf{CH} - \mathbf{C} \equiv \mathbf{N}$$

(c) ADDITION OF ACETIC ACID: Acetate acetylene combines with acetic acid in presence of mercurocuprate.

It first forms vinyl acetate and then ethylidene acetate.

Chemistry

$$\begin{array}{c} \mathbf{CH}_{2} = \mathbf{CHOC} - \mathbf{CH}_{3} & \xrightarrow{\text{Polymerisation}} & (-\mathbf{CH}_{2} - \mathbf{CH}_{-})_{n} & \xrightarrow{\text{Hybrolysis}} \\ \\ \mathbf{Vinyl Acetate} & & \mathbf{O} - \mathbf{C} - \mathbf{CH}_{3} & & & \\ \\ (Monomer) & & & & & \\ \end{array}$$

Poly viny 1acetate (Polymer: adhesive compound)

$$(-CH_2) - CH_{-})_n + nCH_3COOH$$

 OH
Polyvinylalcohol

When ethylidene acetate is heated it gives acetaldehyde and acetic anhydride



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

$$CH \equiv CH + CH_{3}O \xrightarrow{BF_{3} \\ HgO} CH_{2} = CHOCH_{3} \xrightarrow{CH_{3}OH} CH_{3} - CH_{Methylal(acetal)} \xrightarrow{OCH_{3}} OCH_{3}$$

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

$$OCH_{3}$$

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

Acetylene forms acetal while other alkynes form ketal.

(3) Addition of AsCl₃

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.

$$CH \equiv CH + Cl - AsCl_2 \rightarrow \qquad CH - Cl \\ \parallel \\ CHAsCl_2 \end{cases}$$

2-Chlorovinyl dichlorvos arsine (Lewisite gas)

Chemistry

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

 $\stackrel{\rm SH}{\underset{}}$ $\stackrel{\rm SH}{\underset{}}$ $\stackrel{\rm OH}{\underset{}}$ 2,3-Dimercapto-1-propanol [BAL] $C\,H_2-\,C\,H-\,C\,H_2$

(4) Carbonylation

Reaction of alkynes with CO in presence of Ni (CO)₄

Alkyne + CO + H₂O $\xrightarrow{Ni(CO)_4}$ Olefinic acid Alkyne + CO + R - OH $\xrightarrow{Ni(CO)_4}$ Olefinic ester

$$\begin{array}{ccc} C H & & CH_{2} \\ \parallel & + CO + H_{2}O & \xrightarrow{Ni(CO)_{4}} & \parallel \\ C H & & CHCOOR \\ & & Acrylic acid \end{array}$$

$$\begin{array}{cccc} C H & H & CH_{2} \\ \parallel & + CO + H_{2}O & \parallel & \\ C H & O - & \xrightarrow{Ni(CO)_{4}} & CH_{2}O \\ & & CHCOOR \\ & & Acrylic acid \end{array}$$

- (5) Oxidation Reactions
- (a) COMBUSTION

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

 $2\text{HC} \equiv \text{CH} + 50_2 \longrightarrow 4\text{CO}_2 + 2\text{H}_2\text{O} + 312 \text{ K.cal}$

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

(b) OXIDATION WITH ALKALINE KMNO₄: Oxidation with alkaline KMnO₄ gives carboxylic acids.

CH
$$COOH$$

 $\parallel \\ C H + 4[0] \xrightarrow{alk. KMnO_4} COOH$
 $COOH$ $COOH$
 $COOH$

Chemistry

$$CH_3 - C \equiv CH + 4[0] \xrightarrow{alk. KMn_4} CH_3 - COOH + HCOOH$$

(c) OXIDATION WITH ACIDIC KMNO₄ OR K₂CR₂O₇: In presence of acidic KMnO₄ or acidic K₂Cr₂O₇. Alkynes are oxidised to monocarboxylic acids.

$$R - C \equiv C - R' + 2[0] \rightarrow R - C - C - R' \xrightarrow{H_2 O + [0]} RCOOH + R'COOH$$

 $\begin{array}{c} CH\\ III\\ CH\\ CH\\ +2[0] \end{array} \rightarrow \begin{array}{c} CH\\ III\\ CH\\ +2[0] \end{array} \xrightarrow{H_2O+[0]} 2HCOOH \end{array}$

CH₃ − C ≡ CH + 2[0] → CH₃-C=0
$$\xrightarrow{H_2O+[0]}$$
 CH₃COOH + HCOOH
|
CHO

(d) OXIDATION WITH SELENIUM DIOXIDE: Selenium dioxide alkynes to the tricarbonyl compounds.

(e) OXIDATION WITH OZONE (O₃): In the ozonolysis both sp-C-atoms are converted into -C - C - group.

$$\mathbf{R} \cdot \mathbf{C} \equiv \mathbf{C} \cdot \mathbf{R} = \mathbf{0}_3 \quad \rightarrow \quad \mathbf{R} - \begin{array}{c} \mathbf{O} \\ \mathbf{O} \\ \mathbf{O} \\ \mathbf{O} \\ \mathbf{O} \end{array} \xrightarrow{\mathbf{O}} \mathbf{R} \rightarrow \mathbf{R} - \begin{array}{c} \mathbf{C} - \mathbf{C} \\ \mathbf{C} \\ \mathbf{O} \\ \mathbf{O} \end{array} \xrightarrow{\mathbf{O}} \mathbf{R} \rightarrow \mathbf{R} - \begin{array}{c} \mathbf{C} \\ \mathbf{C} \\ \mathbf{C} \\ \mathbf{O} \\ \mathbf{O} \end{array} \xrightarrow{\mathbf{O}} \mathbf{R} \rightarrow \mathbf{R} - \begin{array}{c} \mathbf{C} \\ \mathbf{C} \\ \mathbf{C} \\ \mathbf{C} \end{array} \xrightarrow{\mathbf{O}} \mathbf{R} \rightarrow \mathbf{R} - \begin{array}{c} \mathbf{C} \\ \mathbf{C} \\ \mathbf{C} \\ \mathbf{C} \end{array} \xrightarrow{\mathbf{O}} \mathbf{R} \rightarrow \mathbf{R} - \begin{array}{c} \mathbf{C} \\ \mathbf{C} \\ \mathbf{C} \\ \mathbf{O} \end{array} \xrightarrow{\mathbf{O}} \mathbf{R} \rightarrow \mathbf{R} - \begin{array}{c} \mathbf{C} \\ \mathbf{C} \\ \mathbf{C} \\ \mathbf{C} \end{array} \xrightarrow{\mathbf{O}} \mathbf{R} \rightarrow \mathbf{R} - \begin{array}{c} \mathbf{C} \\ \mathbf{C} \\ \mathbf{C} \\ \mathbf{C} \end{array} \xrightarrow{\mathbf{O}} \mathbf{R} \rightarrow \mathbf{R} - \begin{array}{c} \mathbf{C} \\ \mathbf{C} \\ \mathbf{C} \\ \mathbf{C} \end{array} \xrightarrow{\mathbf{O}} \mathbf{R} \xrightarrow{\mathbf{O}} \xrightarrow{\mathbf{O}} \mathbf{R} \xrightarrow{\mathbf{O}} \mathbf{R} \xrightarrow{\mathbf{O}} \mathbf{R} \xrightarrow{\mathbf{O}} \overrightarrow{\mathbf{O}} \xrightarrow{\mathbf{O}} \overrightarrow{\mathbf{O}} \xrightarrow{\mathbf{O}} \mathbf{R} \xrightarrow{\mathbf{O}} \overrightarrow{\mathbf{O}} \xrightarrow{\mathbf{O}} \xrightarrow{\mathbf{O}} \overrightarrow{\mathbf{O}} \xrightarrow{\mathbf{O}} \xrightarrow{\mathbf{O}} \overrightarrow{\mathbf{O}} \overrightarrow{\mathbf{O}} \xrightarrow{\mathbf{O}} \overrightarrow{\mathbf{O}} \xrightarrow{\mathbf$$

Ozonide (Addition of ozone)

$$\begin{array}{c} \mathbf{R} - \mathbf{C} - \mathbf{O}\mathbf{H} + \mathbf{R} - \mathbf{C} - \mathbf{O}\mathbf{H} \\ \parallel \\ \mathbf{0} \\ \mathbf{0} \\ \mathbf{0} \end{array}$$
(Acids)

Chemistry

In this reaction H_2O_2 is oxidant which oxidase R - C - C - R into acids.

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

$$H_2O_2 + Zn \rightarrow ZnO + H_2O$$

(3) Substitution Reaction: (Formation of metallic derivatives)

Only 1-alkynes gives substitution reaction and show acidic characters $\equiv \tilde{C} - \tilde{H}$ 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 so diamide to form acetylides

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

Mono sodium Disodium acetylide
acetylide

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

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

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

(b) FORMATION OF COPPER AND SILVER ACETYLIDES: Copper and silver acetylides are obtained by passing 1-alkynes in the ammoniacal solution of cuprous chlorides and silver nitrate (Tollen's reagent) respectively.

$R - C \equiv C - H + Cu_2 Cl_2 + NH_4 OH -$	$\rightarrow R - C \equiv CCu + NH_4Cl + H_2O$
ammoniacal cuprous-	copper acetylide
chloride	[Red ppt.]
$R - C \equiv C - H + AgNO_3 + NH_4OH$	\rightarrow R - C \equiv CAg + NH ₄ NO ₃ + H ₂ O
Tollen's reagent	White ppt.

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.

(4) Reaction with NaOCl

Acidic hydrogen is substituted by 'Cl'

- (i) $H C \equiv C H \xrightarrow{\text{NaOCl}} Cl C \equiv C Cl$
- (ii) $R-C \equiv C-H \xrightarrow{\text{NaOCl}} R-C \equiv C-Cl$

Class-XI

Mechanism

$$R-C \equiv C-H \xrightarrow[]{NaOCl} R-C \equiv C \xrightarrow[]{Cl} \cap H \\ OH^- \rightarrow R-C \equiv C-Cl$$

(5) Other reactions of acetylene



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

 $CH \equiv CH + HCHO \xrightarrow{Cu} HC \equiv CCH_2 - OH \xrightarrow{HCHO} CH_2 - C \equiv C - CH_2$

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, Wistron, webtool, PVC, PVA, Chloroprene, butadiene, Lewisite etc.
- (v) It is used as a general anaesthetic.

(7) Polymerisation

Polymerisation Reactions: Alkyne mainly shows addition polymerisation reactions. **Dimerization and Cyclization**

- (a) **DIMERISATION:** Two mole acetylene reacts with Cu₂Cl₂ & NH₄Cl and forms vinyl acetylene.
- **Note**: If acetylene would be in excess then product would be divinyl acetylene and the reaction is called trimerization.

(b) TRIMERISATION: If three mole of acetylene is passed into red hot iron or Cu or quartz tube, then a cyclic trimer is formed which is called benzene.





mesitylene (having 3-1°, 3-2º & 3-3° carbons)

Important: Mesitylene can also be obtained from acetone by condensation polymerisation.

(c) **TETRAMERISATION:** According to the name four moles of acetylene are heated with nickel tetra cyanide, then acetylene forms a cyclic tetramer cyclol octa tetraene.



(8) Coupling

 (a) Alkyne form respective cuprous alkyne with ammoniacal cuprous chloride solution. When cuprous alkyne is reacted with potassium ferry cyanide [K₃Fe (CN)₆] they converted into conjugated dyne.

$$R - C \equiv CH + Cu (NH_3)_2Cl → R - C \equiv C. Cu$$

cuprous alkynide

$$2R - C \equiv C.Cu \quad \frac{O_2}{\Delta} \quad R - C \equiv C - C \equiv C - R$$

divne

(b) Coupling is also done easily by 1-alkyne in the presence of Cu₂Cl₂ (cuprous compound) and amine (i.e., pyridine + air) cuprous alkynide is formed (this coupling is known as oxidative coupling or glass coupling)

$$2R - C \equiv CH + \frac{1}{2}O_2 \xrightarrow{Cu_2Cl_2/NH_3} R - C \equiv C - C \equiv C - R + H_2O$$
$$2CH_3 - C \equiv CH \frac{1}{2}O_2 \xrightarrow{Cu_2Cl_2/NH_3} CH_3 - C \equiv C - C \equiv C - CH_3 + H_2O$$

(9) Isomerisation

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(a) When 1-alkyne is treated with alcoholic KOH 2-alkyne is formed.

$$\mathbf{R} - \mathbf{C}\mathbf{H}_{2} - \mathbf{C} \equiv \mathbf{C}\mathbf{H} \xrightarrow{\text{Alco.KOH}} \mathbf{R} - \mathbf{C} \equiv \mathbf{C} - \mathbf{C}\mathbf{H}_{3}$$

(b) When 2-alkyne is treated with iodamide then it is converted into 1-alkyne. $CH_3 - C \equiv C - CH_3 \xrightarrow{NaNH_2} CH_3 - CH_2 - C \equiv CNa \xrightarrow{+H_2O} CH_3 - CH_2 - C \equiv CH$