ALKYNES

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.

Nomenclature and Isomerism

In the conventional nomenclature, alkynes receive names based on their relation to acetylene. However, in the IUPAC system, they are denoted as derivatives of the respective alkanes, where the suffix 'ane' is substituted with 'yne'. The positioning of the triple bond is designated by identifying the first carbon atom in the chain bonded to three other carbons. Below, the table presents examples of both the common and IUPAC names for various members within the alkyne series.

Value of n	Formula	Structure	Common name	IUPAC name
2	C_2H_2	$H-C\equiv CH$	Acetylene	Ethyne
3	C_3-H_4	$CH_3-C\equiv CH$	Methylacetylene	Propyne
4	C_4-H_6	$CH_3CH_2-C\equiv CH$	Ethylacetylene	But-1-yne
4	C_4-H_6	$CH_3-C\equiv C-CH_3$	Dimethylacetylene	But-2-yne

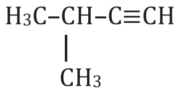
Alkynes are known for their ability to exhibit isomerism, a phenomenon where compounds with the same molecular formula have different structures.

For instance, ethyne (C_2H_2) and propyne (C_3H_4) each have only one possible structure. However, butyne (C_4H_6) presents two potential structures: but-1-yne and but-2-yne. These isomers differ in the position of the triple bond, classifying them as position isomers.

Furthermore, variations in the length of the alkyne chain while maintaining the same molecular formula can give rise to chain isomerism.

For instance, different arrangements of carbon atoms in the chain can lead to distinct structures.

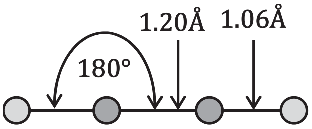
To illustrate, let's consider constructing the structure for the next homologue, which possesses the molecular formula C_5H_8. We aim to arrange five carbon atoms in a continuous chain or with a side chain to form the next alkyne compound.

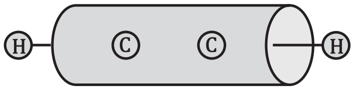
	Structure	IUPAC name
1.	$HC\equiv C-CH_2-CH_2-CH_3$	Pent–1–Yne
2.	$H_3C-C\equiv C-CH_2-CH_3$	Pent–2–yne
3.	 $H_3C-\underset{\substack{\vert\\ CH_3}}{CH}-C\equiv CH$	3–Methyl but–1–Yne

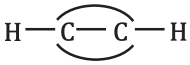
Structures I and II exhibit position isomerism, a type of isomerism where molecules with the same molecular formula differ in the position of functional groups or multiple bonds. On the other hand, structures I and III, as well as structures II and III, demonstrate chain isomerism. Chain isomerism occurs when compounds with the same molecular formula have different arrangements of carbon atoms in their carbon chains.

Structure of Triple Bond

(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 ≡ 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 ≡ 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 the 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 ≡ C bond.

Preparation

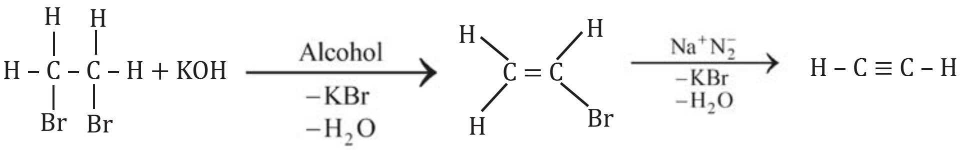
1. **Synthesis from Calcium Carbide:** At an industrial scale, ethyne is synthesized through a reaction involving calcium carbide and water. Calcium carbide, in turn, is produced by heating quicklime with coke. Quicklime is derived from limestone through a series of chemical reactions as outlined below:

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

$$CaO + 3C \rightarrow \underset{\substack{\text{Calcium}\\\text{carbide}}}{CaC_2} + CO$$

$$CaC_2 + 2H_2O \rightarrow CO(OH)_2 + C_2H_2$$

2. **Derived from Vicinal Dihalides:** When vicinal dihalides are subjected to treatment with alcoholic potassium hydroxide, they undergo a process known as dehydrohalogenation. This chemical reaction results in the elimination of one molecule of hydrogen halide, leading to the formation of an alkenyl halide. Further treatment of this alkenyl halide with sodamide facilitates the conversion into an alkyne compound.



$$H-\underset{Br}{\overset{H}{C}}-\underset{Br}{\overset{H}{C}}-H + KOH \xrightarrow[\substack{-KBr\\-H_2O}]{\text{Alcohol}} \underset{H}{\overset{H}{C}}=\underset{Br}{\overset{H}{C}} \xrightarrow[\substack{-KBr\\-H_2O}]{Na^+N_2^-} H-C \equiv C-H$$

3. **Obtained from Tri halogen Derivatives:**

$$R-CCl_3 \xrightarrow{\text{Ag Powder}} R-C \equiv C-R$$

Physical and Chemical Properties of Alkynes

Physical properties

(a) Alkynes are colourless, odourless and tasteless.

(b) Lower alkynes are partially soluble in H_2O. (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 C_4 alkynes are gaseous $C_5 - C_{11}$ are liquid, C_{12} & above are solids.

(g) Pure acetylene is odourless and impure acetylene has odour like garlic. It is due to impurities of Arsene (AsH_3) & Phosphine (PH_3).

(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 'NH_2 or $^-CH_3$ 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–

$\equiv C - H$	$= C - H$	$- C - H$
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

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

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).

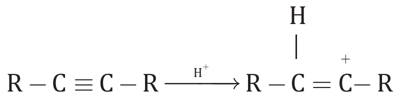
The characteristic reaction of alkynes is electrophilic addition but the reactivity of alkynes towards electrophilic addition is less than alkenes because in C ≡ C, the π electrons are tightly held by carbon nuclei and so they are less easily available for reaction for reaction with electrophiles.

Reactivity order of hydrocarbons for electrophilic addition

Alkenes > Alkynes > Alkanes.

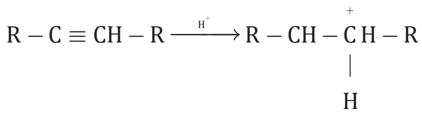
Another reason is: The intermediates when an electrophile attack on alkene and alkynes a are:

(i)



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

(ii)



$$R-C\equiv CH-R\xrightarrow{H^{+}}R-CH-\underset{\underset{H}{|}}{\overset{+}{C}}H-R$$

Stability of intermediates

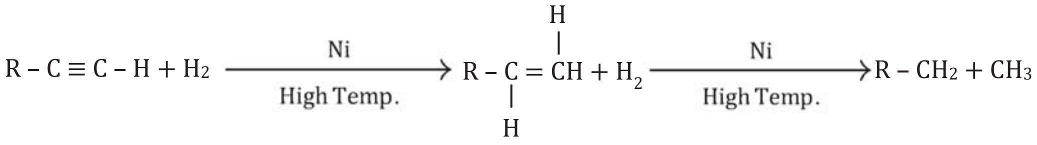
$$\underset{(+)\text{ve on more En}}{R-CH=\overset{\oplus}{C}-R} < \underset{\text{More stable}}{R-CH_2-\overset{\oplus}{C}H-R}$$

Atoms are less stable

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

(a) **Addition Of Hydrogen**

Hydrogenation

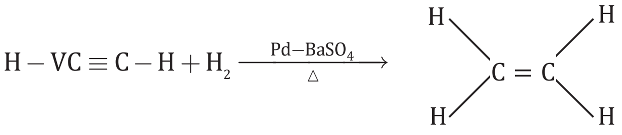


$$R-C\equiv C-H+H_2\xrightarrow[\text{High Temp.}]{Ni}R-\underset{\underset{H}{|}}{C}=\overset{\overset{H}{|}}{C}H+H_2\xrightarrow[\text{High Temp.}]{Ni}R-CH_2+CH_3$$

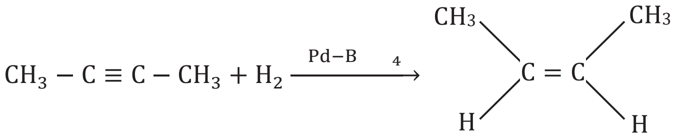
The above reaction is called as Sabatier Sanderson's reaction.

Hydrogenation in the presence of lindlar's Catalyst

Addition up to alkene takes place in cis manner.

(i) 

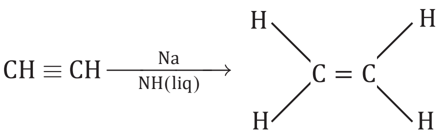
$H-VC\equiv C-H+H_2\xrightarrow[\triangle]{Pd-BaSO_4}$

(ii) 

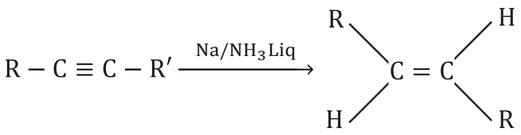
$CH_3-C\equiv C-CH_3+H_2\xrightarrow{Pd-B\quad 4}$

Hydrogenation by Na + NH_3 (liq.)

Addition up to alkene takes place in trans manner

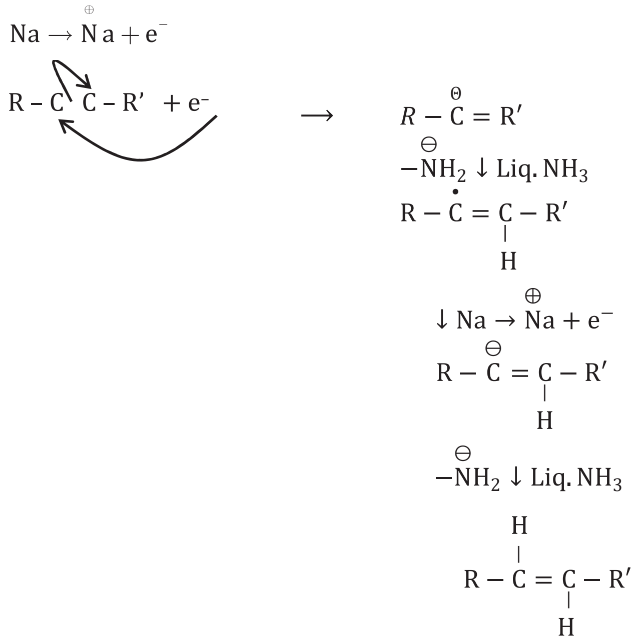
(i) 

$CH\equiv CH\xrightarrow[NH(liq)]{Na}$

(ii) 

$R-C\equiv C-R'\xrightarrow{Na/NH_3 Liq}$

Mechanism



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

$$R-C\quad C-R' + e^- \longrightarrow R-\overset{\Theta}{C}=R'$$

$$\overset{\ominus}{-NH_2}\downarrow \text{Liq. } NH_3$$

$$R-\overset{\bullet}{C}=\underset{\underset{H}{|}}{C}-R'$$

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

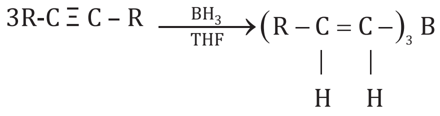
$$R-\overset{\ominus}{C}=\underset{\underset{H}{|}}{C}-R'$$

$$\overset{\ominus}{-NH_2}\downarrow \text{Liq. } NH_3$$

$$R-\overset{\overset{H}{|}}{C}=\underset{\underset{H}{|}}{C}-R'$$

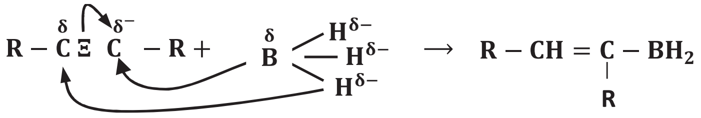
(b) **Addtion of BH_3 / THF Or B_2h_6 (Hydroboration)**

THF – Tetrahydrofuran is used as solvent.

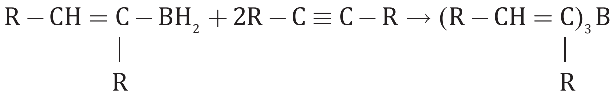


$$3R\text{-}C \equiv C-R \xrightarrow[THF]{BH_3} (R-\underset{\underset{H}{|}}{C}=\underset{\underset{H}{|}}{C}-)_3B$$

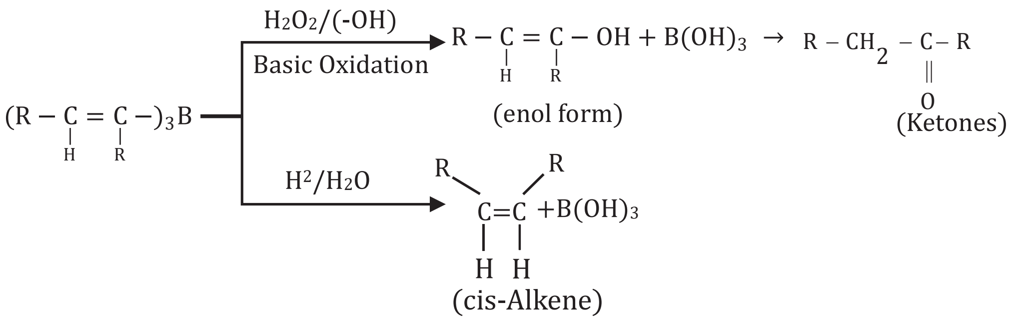
Since BH_3 is not available as monomer so a solvent THF is used for the stability of BH_3.



$$R-\overset{\delta}{C}\equiv\overset{\delta-}{C}-R + \overset{\delta}{B}\begin{matrix}H^{\delta-}\\H^{\delta-}\\H^{\delta-}\end{matrix} \longrightarrow R-CH=\underset{\underset{R}{|}}{C}-BH_2$$



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



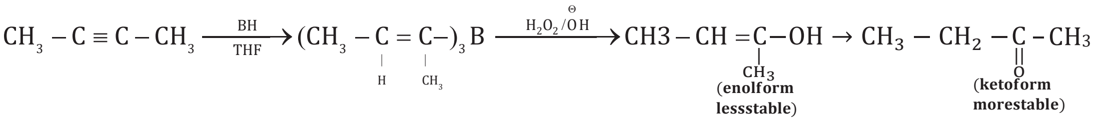
$$(R-\underset{\underset{H}{|}}{C}=\underset{\underset{R}{|}}{C}-)_3B \xrightarrow[\text{Basic Oxidation}]{H_2O_2/(\text{-}OH)} R-\underset{\underset{H}{|}}{C}=\underset{\underset{R}{|}}{C}-OH + B(OH)_3 \rightarrow R-CH_2-\underset{\underset{O}{\|}}{C}-R$$

(enol form) (Ketones)

$$(R-\underset{\underset{H}{|}}{C}=\underset{\underset{R}{|}}{C}-)_3B \xrightarrow{H^2/H_2O} \begin{matrix}R & & R\\ & C=C & \\ & |\quad | & \\ & H\quad H & \end{matrix} + B(OH)_3$$

(cis-Alkene)

Ex.



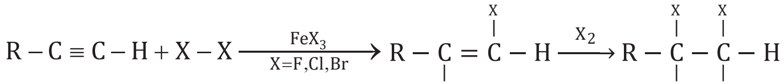
$$CH_3-C\equiv C-CH_3 \xrightarrow[THF]{BH} (CH_3-\underset{H}{C}=\underset{CH_3}{C}-)_3B \xrightarrow{H_2O_2/\overset{\ominus}{O}H} CH3-CH=\underset{CH_3}{C}-OH \rightarrow CH_3-CH_2-\underset{O}{\overset{}{C}}-CH3$$

(enolform lessstable)

(ketoform morestable)

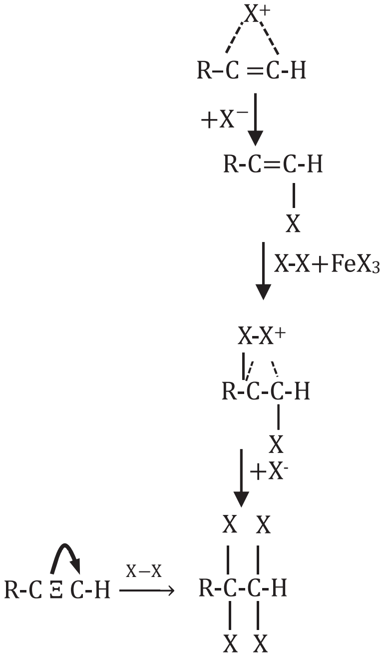
(C) Addition Of Halogens (Halogenation)

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



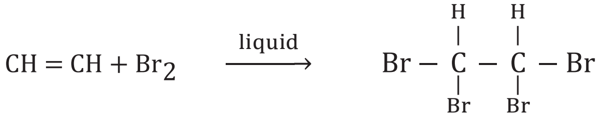
$$R-C\equiv C-H+X-X \xrightarrow[X=F,Cl,Br]{FeX_3} R-\underset{X}{C}=\overset{X}{C}-H \xrightarrow{X_2} R-\underset{X}{\overset{X}{C}}-\underset{X}{\overset{X}{C}}-H$$

$FeX_3 + X_2 \rightarrow \overset{-}{Fe}X_4 + X^+$



Reaction with dilute Br_2 or bromine water

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



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

Reaction with iodine

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

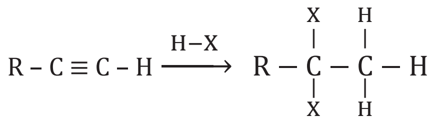
$CH \equiv CH + I_2 \xrightarrow{NH_2} I-C\equiv C-I + NH_4I$ (substitution reaction)

Di diiodoacetylene

(d) Addition of Halogen Acids (H-X) {Hydrohalogenation}

Addition according to Marconi-KOff's Rule.

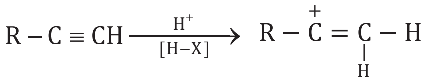
Reactivity order of H – X: HI > HBr > HCl > HF



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

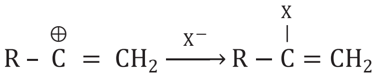
(Gem dihalides major product)

Mechanism



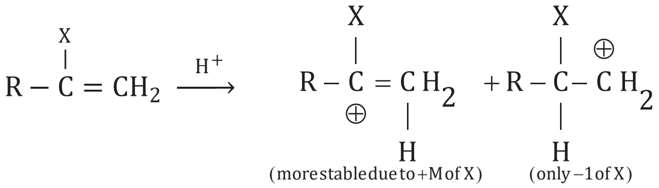
$$R-C\equiv CH \xrightarrow[{[H-X]}]{H^+} R-\overset{+}{C}=\underset{H}{C}-H$$

(Intermediate is carbocation)



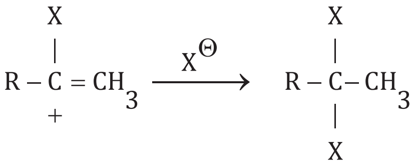
$$R-\overset{\oplus}{C}=CH_2 \xrightarrow{X^-} R-\overset{X}{C}=CH_2$$

Further



$$R-\overset{X}{C}=CH_2 \xrightarrow{H^+} \underset{\text{(more stable due to +M of X)}}{R-\overset{X}{\underset{\oplus}{C}}=\underset{H}{C}H_2} + \underset{\text{(only −I of X)}}{R-\overset{X}{\underset{H}{C}}-\overset{\oplus}{C}H_2}$$

So



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

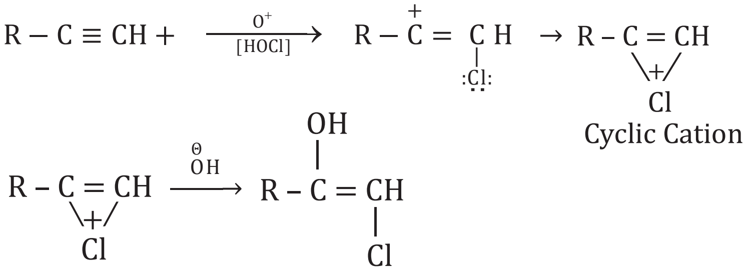
(Major product)

(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

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

Mechanism

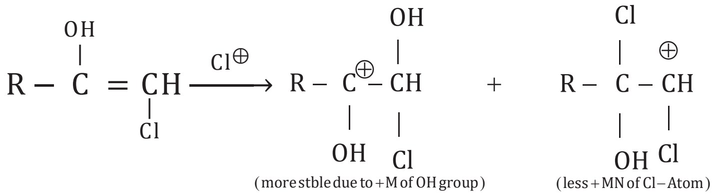


$$R-C\equiv CH + \xrightarrow[{[HOCl]}]{O^+} R-\overset{+}{C}=\underset{:\ddot{Cl}:}{C}H \rightarrow R-C=CH \;(\backslash + /\; Cl)$$

Cyclic Cation

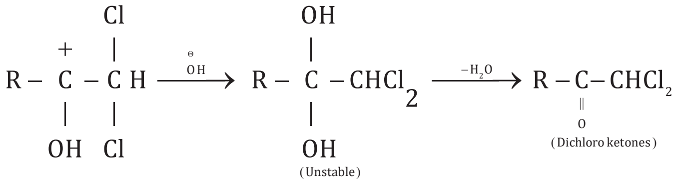
$$R-C=CH \;(\backslash + /\; Cl) \xrightarrow{\overset{\Theta}{O}H} R-\overset{OH}{C}=\underset{Cl}{C}H$$

Further



$$R-\overset{OH}{C}=\underset{Cl}{CH}\xrightarrow{Cl^{\oplus}}\underset{\text{(more stble due to +M of OH group)}}{R-\underset{OH}{\overset{\oplus}{C}}-\underset{Cl}{\overset{OH}{CH}}}+\underset{\text{(less +MN of Cl-Atom)}}{R-\underset{OH}{\overset{Cl}{C}}-\underset{Cl}{\overset{\oplus}{CH}}}$$

So



$$R-\underset{OH}{\overset{+}{C}}-\underset{Cl}{\overset{Cl}{C}}H\xrightarrow{\overset{\ominus}{O}H}\underset{\text{(Unstable)}}{R-\underset{OH}{\overset{OH}{C}}-CHCl_2}\xrightarrow{-H_2O}\underset{\text{(Dichloro ketones)}}{R-\underset{\underset{O}{\|}}{C}-CHCl_2}$$

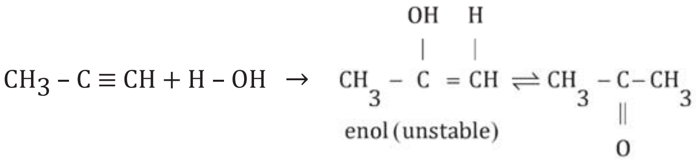
(2) Nucleophilic Addition Reaction

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

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

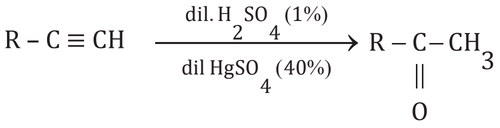
$$CH\equiv CH+H-OH\rightarrow CH_2=CH-OH\rightleftharpoons CH_3-CHO$$

enol unstable



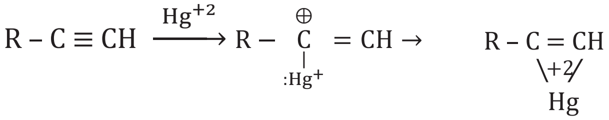
$$CH_3-C\equiv CH+H-OH\rightarrow\underset{\text{enol (unstable)}}{CH_3-\overset{OH}{C}=\overset{H}{CH}}\rightleftharpoons CH_3-\underset{\underset{O}{\|}}{C}-CH_3$$

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

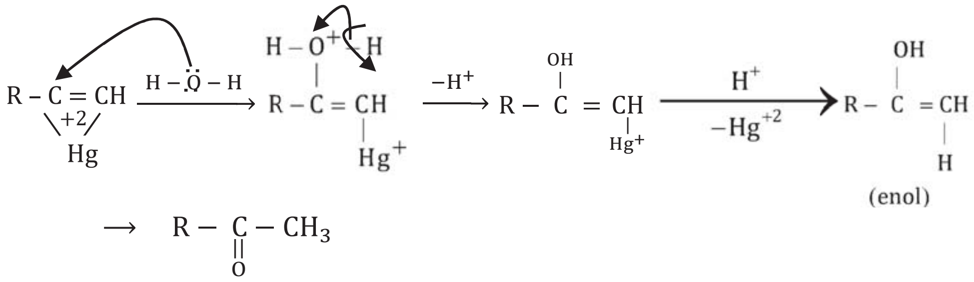


$$R-C\equiv CH\xrightarrow[\text{dil HgSO}_4\text{ (40\%)}]{\text{dil. H}_2\text{SO}_4\text{ (1\%)}}R-\underset{\underset{O}{\|}}{C}-CH_3$$

Mechanism



$$R-C\equiv CH\xrightarrow{Hg^{+2}}R-\underset{:Hg^{+}}{\overset{\oplus}{C}}=CH\rightarrow\underset{\underset{Hg}{\backslash +2 /}}{R-C=CH}$$



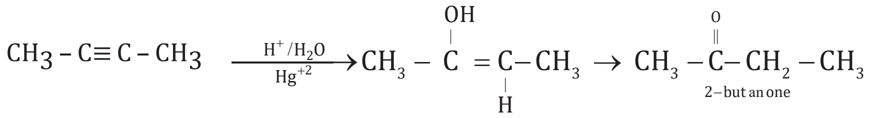
$$R-\underset{\underset{Hg}{\diagdown^{+2}\diagup}}{C}=CH \xrightarrow{H-\ddot{O}-H} R-\overset{\overset{H-O^{+}-H}{|}}{C}=\underset{\underset{Hg^{+}}{|}}{CH} \xrightarrow{-H^{+}} R-\overset{\overset{OH}{|}}{C}=\underset{\underset{Hg^{+}}{|}}{CH} \xrightarrow[-Hg^{+2}]{H^{+}} R-\overset{\overset{OH}{|}}{C}=\underset{\underset{H}{|}}{CH}$$

(enol)

$$\longrightarrow R-\underset{\underset{O}{\|}}{C}-CH_3$$

(Keto more stable)

Ex.



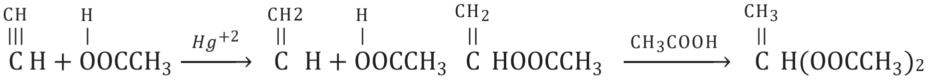
$$CH_3-C\equiv C-CH_3 \xrightarrow[Hg^{+2}]{H^{+}/H_2O} CH_3-\overset{\overset{OH}{|}}{C}=\underset{\underset{H}{|}}{C}-CH_3 \rightarrow \underset{2-\text{but an one}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3}$$

(b) **Addition of HCN**

Addition takes place in the presence of CuCl

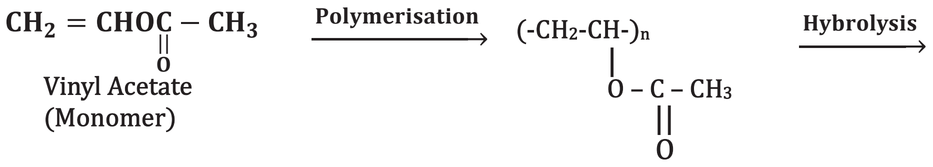
$$H-C\equiv C-H+H-CN \xrightarrow[770^{\circ}]{Cucl} CH_2=CH-C\equiv N$$

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



$$\begin{matrix}CH\\|||\\C\,H\end{matrix} + \begin{matrix}H\\|\\OOCCH_3\end{matrix} \xrightarrow{Hg^{+2}} \begin{matrix}CH_2\\||\\C\,H\end{matrix} + \begin{matrix}H\\|\\OOCCH_3\end{matrix}\;\; \begin{matrix}CH_2\\||\\C\;HOOCCH_3\end{matrix} \xrightarrow{CH_3COOH} \begin{matrix}CH_3\\||\\C\;H(OOCCH_3)_2\end{matrix}$$

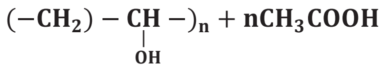
vinylacetate Ethylidene acetate



$$CH_2=CHO\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{\textbf{Polymerisation}} (\text{-}CH_2\text{-}\underset{\underset{O-\underset{\underset{O}{\|}}{C}-CH_3}{|}}{CH}\text{-})_n \xrightarrow{\textbf{Hybrolysis}}$$

Vinyl Acetate
(Monomer)

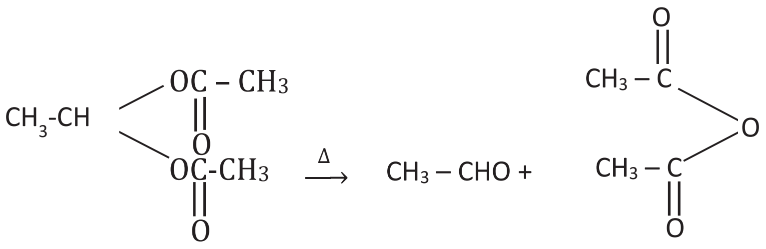
Poly viny 1acetate
(Polymer: adhesive compound)



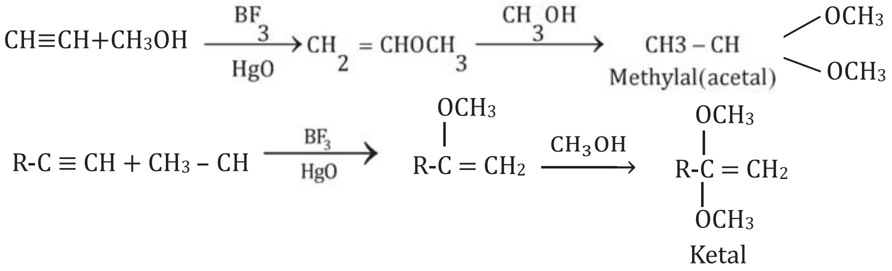
$$(-CH_2)-\underset{\underset{OH}{|}}{CH}-)_n + nCH_3COOH$$

Polyvinylalcohol

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



$$CH\equiv CH + CH_3OH \xrightarrow[HgO]{BF_3} CH_2=CHOCH_3 \xrightarrow{CH_3OH} CH_3-CH(OCH_3)_2$$

Methylal(acetal)

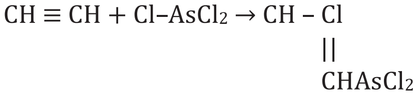
$$R\text{-}C\equiv CH + CH_3-CH \xrightarrow[HgO]{BF_3} R\text{-}\overset{OCH_3}{\overset{|}{C}}=CH_2 \xrightarrow{CH_3OH} R\text{-}\underset{\underset{OCH_3}{|}}{\overset{\overset{OCH_3}{|}}{C}}=CH_2$$

Ketal

Acetylene forms acetal while other alkynes form ketal.

(3) **Addition of $AsCl_3$**

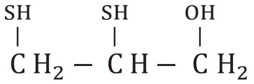
In presence of $AlCl_3$ or $HgCl_2$ acetylene combines with $AsCl_3$ to yield Lewisite gas. It is four times poisonous than mustard gas.



$$CH\equiv CH + Cl\text{–}AsCl_2 \rightarrow \begin{array}{c} CH-Cl \\ \| \\ CHAsCl_2 \end{array}$$

2-Chlorovinyl dichlorvos 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 nontoxic compound.



$$\underset{}{\overset{SH}{\overset{|}{C}}}H_2-\overset{SH}{\overset{|}{C}}H-\overset{OH}{\overset{|}{C}}H_2$$

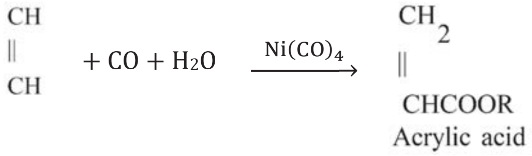
2,3-Dimercapto-1-propanol [BAL]

(4) **Carbonylation**

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

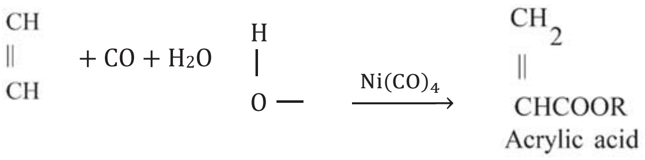
$$\text{Alkyne} + CO + H_2O \xrightarrow{Ni(CO)_4} \text{Olefinic acid}$$

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



$$\begin{array}{c} CH \\ \| \\ CH \end{array} + CO + H_2O \xrightarrow{Ni(CO)_4} \begin{array}{c} CH_2 \\ \| \\ CHCOOR \end{array}$$

Acrylic acid



$$\begin{array}{c} CH \\ \| \\ CH \end{array} + CO + H_2O \quad \begin{array}{c} H \\ | \\ O- \end{array} \xrightarrow{Ni(CO)_4} \begin{array}{c} CH_2 \\ \| \\ CHCOOR \end{array}$$

Acrylic acid

(5) Oxidation Reactions

(a) Combustion

$$C_nH_{2n-2} + \frac{3n-1}{2}O_2 \longrightarrow nCO_2 + (n-1)\,H_2O + \text{Heat}$$
$$2HC \equiv CH + 5O_2 \longrightarrow 4CO_2 + 2H_2O + 312\ \text{K.cal}$$

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

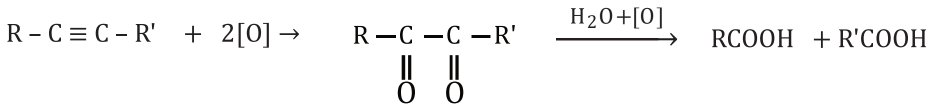
(b) Oxidation With Alkaline $KMnO_4$: Oxidation with alkaline $KMnO_4$ gives carboxylic acids.

$$CH \equiv CH + 4[O] \xrightarrow{\textbf{alk. KMnO}_4} COOH{-}COOH$$

Oxalic acid

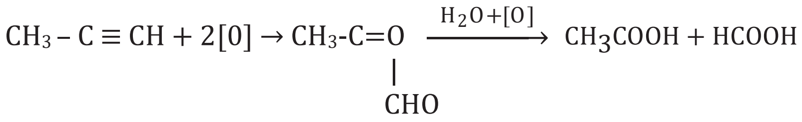
$$CH_3 - C \equiv CH\ + 4[O] \xrightarrow{\text{alk. KMnO}_4} CH_3 - COOH + HCOOH$$

(c) Oxidation With Acidic $KMNO_4$ OR $K_2CR_2O_7$: In presence of acidic $KMnO_4$ or acidic $K_2Cr_2O_7$. Alkynes are oxidised to monocarboxylic acids.



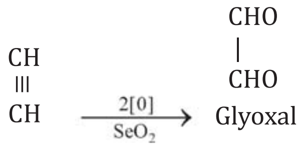
$$R - C \equiv C - R' + 2[O] \rightarrow R-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-R' \xrightarrow{H_2O+[O]} RCOOH + R'COOH$$

$$CH \equiv CH + 2[O] \rightarrow CH \equiv CH + 2[O] \xrightarrow{H_2O+[O]} 2HCOOH$$



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

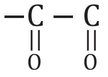
(d) Oxidation With Selenium Dioxide: Selenium dioxide alkynes to the tricarbonyl compounds.



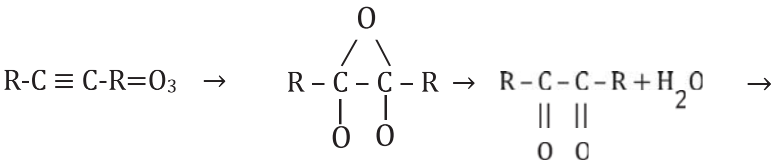
$$CH \equiv CH \xrightarrow[SeO_2]{2[O]} CHO{-}CHO$$

Glyoxal

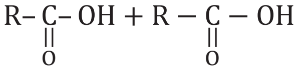
(e) Oxidation With Ozone (O_3): In the ozonolysis both sp-C-atoms are converted into



$$-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-\text{group.}$$



Ozonide (Addition of ozone)



$$R-\underset{O}{\underset{\|}{C}}-OH + R-\underset{O}{\underset{\|}{C}}-OH$$

(Acids)

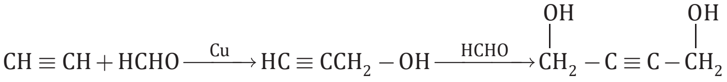
In this reaction H_2O_2 is oxidant which oxidase $R-\underset{O}{\underset{\|}{C}}-\underset{O}{\underset{\|}{C}}-R$ into acids.

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

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

(6) Reaction with HCHO

This reaction is called ethynylation.



$$CH\equiv CH + HCHO \xrightarrow{Cu} HC\equiv CCH_2-OH \xrightarrow{HCHO} \overset{OH}{\overset{|}{C}H_2}-C\equiv C-\overset{OH}{\overset{|}{C}H_2}$$

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.

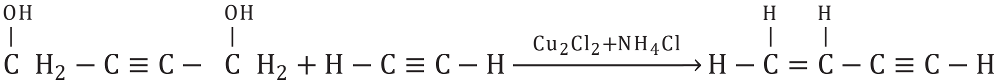
(7) Polymerisation

Polymerisation Reactions: Alkyne mainly shows addition polymerisation reactions.

Dimerization and Cyclization

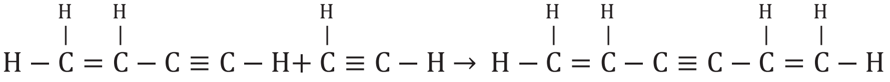
(a) **Dimerization:** Two mole acetylene reacts with Cu_2Cl_2 & NH_4Cl and forms vinyl acetylene.

Note: If acetylene would be in excess then product would be divinyl acetylene and the reaction is called trimerization.



$$\overset{OH}{\overset{|}{C}}\ H_2-C\equiv C-\overset{OH}{\overset{|}{C}}\ H_2 + H-C\equiv C-H \xrightarrow{Cu_2Cl_2+NH_4Cl} H-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-C\equiv C-H$$

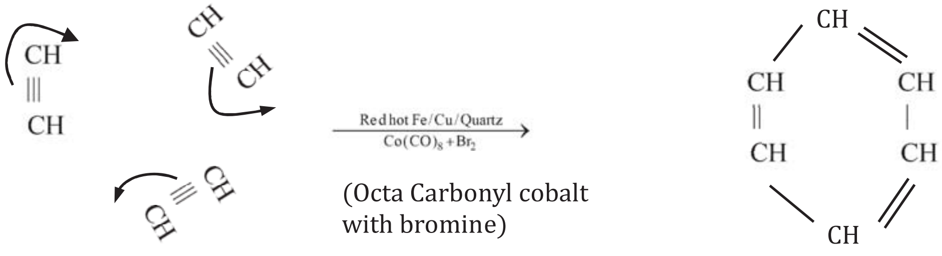
vinyl acetylene or buteonine



$$H-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-C\equiv C-H+\overset{H}{\overset{|}{C}}\equiv C-H \rightarrow H-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-C\equiv C-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-H$$

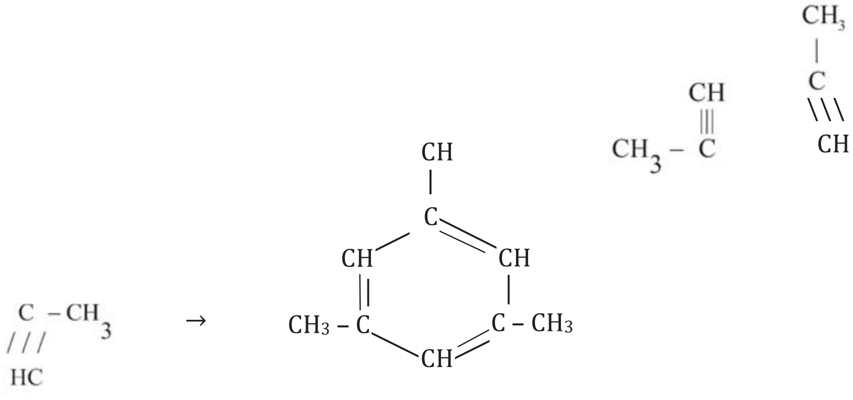
divinyl acetylene

(b) **Trimerization:** 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.



(Octa Carbonyl cobalt with bromine)

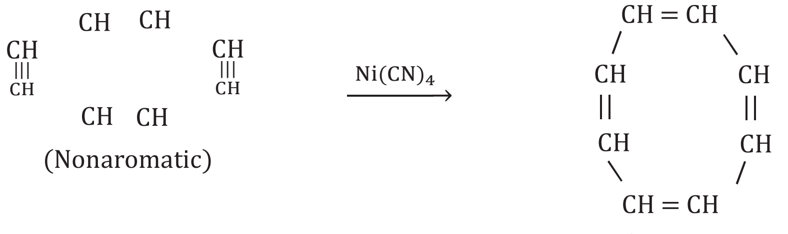
Benzene



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

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

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



(Nonaromatic)

Cyclooctatetraene

(8) Coupling

(a) Alkyne form respective cuprous alkyne with ammoniacal cuprous chloride solution. When cuprous alkyne is reacted with potassium ferry cyanide [$K_3Fe(CN)_6$] they converted into conjugated dyne.

$$R - C \equiv CH + Cu(NH_3)_2Cl \longrightarrow \underset{\text{cuprous alkynide}}{R - C \equiv C.Cu}$$

$$2R - C \equiv C.Cu \xrightarrow[\Delta]{O_2} \underset{\text{diyne}}{R - C \equiv C - C \equiv C - R}$$

(b) Coupling is also done easily by 1-alkyne in the presence of Cu_2Cl_2 (cuprous compound) and amine (i.e., pyridine + air) cuprous alkynide is formed (this coupling is known as oxidative coupling or glass coupling)

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

$$2CH_3-C\equiv CH\frac{1}{2}O_2\xrightarrow{Cu_2Cl_2/NH_3}\underset{\text{2,4-Hexadyne}}{CH_3-C\equiv C-C\equiv C-CH_3}+H_2O$$

(9) Isomerisation

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

$$\underset{\text{1-alkyne}}{R-CH_2-C\equiv CH}\xrightarrow[\triangle]{\text{Alco.KOH}}\underset{\text{2-Alklyne}}{R-C\equiv C-CH_3}$$

(b) When 2-alkyne is treated with iodamide then it is converted into 1-alkyne.

$$CH_3-C\equiv C-CH_3\xrightarrow[-NH_3]{NaNH_2}CH_3-CH_2-C\equiv CNa\xrightarrow[-NaOH]{+H_2O}CH_3-CH_2-C\equiv CH$$