Alkynes.

These are the acyclic hydrocarbons which contain carbon-carbon triple bond are called alkynes. General formula is C_nH_{2n-2}. Ex. Ethyne $CH \equiv CH$; Propyne $CH_3 - C \equiv CH$

(1) **Structure**

(i) Hybridization in alkynes is sp.

(ii) Bond angle in alkynes is 180^o.

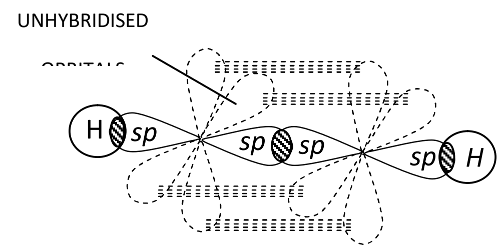
(iii) Geometry of carbon is linear.

(iv) $C - C$ Triple bond length is $120\ \AA$

(v) $C - H$ Bond length is $108\ \AA$

(vi) $C - C$ Triple bond energy is $190\ Kcal/mol$.

(vii) $C - H$ Bond energy is $102.38\ Kcal/mol$.



Acetylene

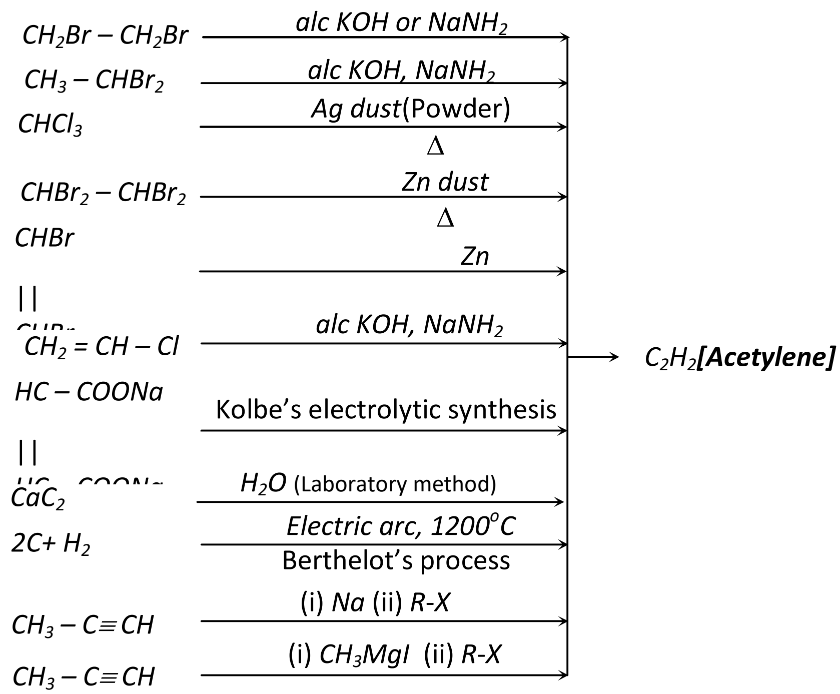
(2) **Isomerism**

(i) **Chain Isomerism:** $\underset{\text{1-Pentyne}}{CH_3CH_2CH_2C \equiv CH}$; $\underset{\text{3-Methyl-1-butyne}}{\overset{CH_3}{\underset{CH_3}{CH}} - C \equiv CH}$

(ii) **Position isomerism:** $\underset{\text{1-pentyne}}{CH_3CH_2CH_2C \equiv CH}$; $\underset{\text{2-pentyne}}{CH_3CH_2C \equiv CCH_3}$

(iii) **Functional isomerism:** $\underset{\text{Propyne}}{CH_3 - C \equiv CH}$; $\underset{\text{1, 2-propadiene (Allene)}}{CH_2 = C = CH_2}$

(3) **General methods of preparation**



Note: In reaction with gem dihalide, Alc. KOH is not used for elimination in 2^{nd} step.

In reaction with vicinal dihalide, if the reactant is 2-butylene chloride then product is 2-butyne as major product.

Preparation of higher alkynes (by metal acetylide)

Acetylene gives salt with $NaNH_2$ or $AgNO_3$ (ammonical) which react with alkyl halide give higher alkyne.

$$CH_3I + Na - C \equiv C - Na + I - CH_3 \longrightarrow \underset{\text{Butyne}}{CH_3 - C \equiv C - CH_3}$$

$$2CH \equiv CH \xrightarrow[NaNH_2]{} Na - C \equiv C - Na \xrightarrow[2CH_3I]{} \underset{Butyne}{CH_3 - C \equiv C - CH_3}$$

$$CH_3 - C \equiv CH + CH_3 - Mg - X \longrightarrow CH_3 - C \equiv C - Mg - X + CH_4 \xrightarrow{R-X} \underset{\text{Alkyne}}{CH_3 - C \equiv C - R} + MgX_2$$

(4) **Physical properties**

(i) Acetylene is a colorless gas. It has a garlic odour. The odour is due to presence of impurities. However, pure acetylene has pleasant odour.

(ii) It is insoluble in water but highly soluble in acetone and alcohol. Acetylene is transported under high pressure in acetone soaked on porous material packed in steel cylinders.

(iii) Its boiling point is $-80^{o}C$.

(iv) It is lighter than air. It is somewhat poisonous in nature.

(v) It burns with luminous flame and forms explosive mixture with air.

(5) **Chemical reactivity of alkynes**: $C \equiv C$ is less reactive than the carbon-carbon double bond towards electrophilic addition reaction. This is because in alkyne carbon has more has S-character than more strongly will be the attraction for π electrons. Alkyne also undergo nucleophilic addition with electron rich reagents. Ex. Addition of water, cyanide, carboxylic acid, alcohols. Nucleophilic addition can be explained on the basis that alkynes form vinylic carbanion which is more stable than alkyl carbanion formed by alkene

$$-C \equiv C- + Nu^{-} \longrightarrow -\underset{|}{\overset{Nu}{C}} = \overset{\ominus}{C}- \qquad -C = C- + Nu^{-} \longrightarrow -\underset{|}{\overset{Nu}{C}} - \overset{\ominus}{C}-$$

Vinylic carbanion (alkyl carbanion)

(More stable) (less stable)

(i) **Acidity of alkynes**: Acetylene and other terminal alkynes (1- alkynes) are weakly acidic in character

Ex. $CH \equiv CH + NaNH_2 \longrightarrow H - C \equiv \overline{C}\,Na^{+} + \frac{1}{2}H_2$ (Monosodium acetylide)

The acetylenic hydrogen of alkynes can be replaced by copper (I) and silver (I) ions. They react with ammonical solutions of cuprous chloride and silver nitrate to form the corresponding copper and silver alkynides.

$CH \equiv CH + 2[Cu(NH_3)_2]Cl \longrightarrow Cu - C \equiv C - Cu + 2NH_4Cl + 2NH_3$ Dicopper acetylide (Red ppt)

$CH \equiv CH + 2[Ag(NH_3)_2]NO_3 \longrightarrow AgC \equiv C - Ag + 2NH_4NO_3 + 2NH_3$ Disilver acetylide (white ppt)

This reaction can be used to distinguish between 2-alkynes and 1-alkynes. 1-alkynes will give this test while 2-alkynes, will not give this test.

$$\underset{\text{1-propyne}}{CH_3 - C \equiv CH} + 2[Ag(NH_3)_2]NO_3 \longrightarrow CH_3 - C \equiv C - Ag$$

$CH_3 - C \equiv C - CH_3 + 2[Ag(NH_3)_2]NO_3 \longrightarrow$ No reaction

Explanation for the acidic character: It explained by sp hybridization. We know that an electron in $s-$orbital is more tightly held than in a p-orbital. In sp hybridization s-character is more (50%) as compared to sp^2 (33%) or sp^3 (25%), due to large s-character the carbon atom is quite electronegative.

(ii) **Reaction with formaldehyde**

$$HC \equiv CH + 2CH_2O \longrightarrow \underset{OH}{\underset{|}{CH_2}} - C \equiv C - \underset{OH}{\underset{|}{CH_2}} \xrightarrow{Li/NH_3} CH_2 - CH = CH - CH_2OH$$ [Trans-product]

(6) **Chemical properties of acetylene**

CH≡CH **Acetylene**	$\longrightarrow$	**Benzene :** By passing acetylene through red hot tube, $3C_2H_2 \rightarrow C_6H_6$
	$\longrightarrow$	**Pyrrole :** By heating with $NH_3, 2C_2H_2 + NH_3 \rightarrow C_4H_5N + H_2$
	$\longrightarrow$	**Thiophene :** By heating with S or $H_2S, 2C_2H_2 + S \rightarrow C_4H_4S$
	$\longrightarrow$	**Acetaldehyde :** By passing acetylene through 40% H_2SO_4 and 1% $HgSO_4$ at 80^oC, $CH \equiv CH + H_2O \rightarrow CH_3CHO$ or by heating ethylidene acetate, $\underset{\text{[Kucherov's reaction]}}{CH \equiv CH + 2CH_3COOH} \xrightarrow[80^oC]{Hg^{2+}} \underset{\text{Ethylidene acetate}}{CH_3CH(OOCCH_3)_2} \rightarrow CH_3CHO + \begin{matrix} CH_3CO \\ \quad O \\ CH_3CO \end{matrix}$ Acetaldehyde so prepared may be used for the preparation of :

<table>
<tr><td></td><td></td><td>❑ Ethyl alcohol : By reduction with H_2 in presence of Ni at $140^o C$,
$CH_3CHO + H_2 \rightarrow CH_3CH_2OH$

❑ Acetic acid : By oxidation in presence of manganese acetate or platinum wire at $70^o C$,

$CH_3CHO + O \rightarrow CH_3COOH$

❑ Ethyl acetate : By esterification of acetic acid and alcohol or by condensation of acetaldehyde in presence of aluminum ethoxide, $2CH_3CHO \xrightarrow{Al(OC_2H_5)_3} CH_3COOC_2H_5$</td></tr>
<tr><td></td><td>$\longrightarrow$</td><td>Westron and Westrosol : Used as solvents,

$$\begin{array}{c} CH \\ ||| \\ CH \end{array} + Cl_2 \longrightarrow \underset{\text{(Westron)}}{\begin{array}{c} CHCl_2 \\ | \\ CHCl_2 \end{array}} \xrightarrow[KOH]{Alc.} \underset{\text{(Westrosol)}}{\begin{array}{c} CHCl \\ || \\ CCl_2 \end{array}}$$</td></tr>
<tr><td></td><td>$\longrightarrow$</td><td>Lewsite : A poisonous gas used during wars,

$$\begin{array}{c} CH \\ ||| \\ CH \end{array} + ClAsCl_2 \xrightarrow{AlCl_3} \underset{\text{Lewisite}}{\begin{array}{c} CHCl \\ || \\ CHAsCl_2 \end{array}}$$ $\longrightarrow$ Cadet and Busen reaction</td></tr>
<tr><td></td><td>$\longrightarrow$</td><td>Vinyl acetate : By reacting with acetic acid in presence of Hg^{2+},

$CH \equiv CH + CH_3COOH \xrightarrow{Hg^{2+}} CH_2 = CHOOCCH_3$

Vinyl acetate is used in paints</td></tr>
<tr><td></td><td>$\longrightarrow$</td><td>Vinyl chloride : By reacting with HCl in presence of Hg^{2+} at $60^o C$,

$CH \equiv CH + HCl \xrightarrow[60^o C]{Hg^{2+}} CH_2 = CHCl$

Vinyl chloride is used for the manufacture of PVC plastic.</td></tr>
<tr><td></td><td>$\longrightarrow$</td><td>Vinyl cyanide : By reacting with HCN in presence of $Ba(CN)_2$,

$CH \equiv CH + HCN \xrightarrow{Ba(CN)_2} CH_2 = CHCN$

It is employed for making orlon and buna-N rubber.</td></tr>
<tr><td></td><td>$\longrightarrow$</td><td>Chloroprene: See polymerization reactions.</td></tr>
<tr><td></td><td>$\longrightarrow$</td><td>Cuprene: See polymerization reactions.</td></tr>
<tr><td></td><td>$\longrightarrow$</td><td>Hexachloro ethane: C_2Cl_6 -used as artificial camphor.</td></tr>
</table>

	$\longrightarrow$	**Ethylene :** $C_2H_2 + H_2 \xrightarrow[Catalyst]{Lindlar's} C_2H_4$ (Cis)
	$\longrightarrow$	**Ethane :** $C_2H_2 + 2H_2 \xrightarrow[300]{Ni} C_2H_6$
	$\longrightarrow$	**Higher alkynes :** $\underset{\text{Sod. acetylide}}{HC \equiv CNa} + XR \longrightarrow HC \equiv C - R$
	$\longrightarrow$	**Glyoxal:** By oxidation with O_3 or SeO_2.
	$\longrightarrow$	**Oxalic acid:** By oxidation with alk. $KMnO_4$ $CH \equiv CH + 4O \longrightarrow COOH - COOH$

Consequently the electron pair of $H - C \equiv$ bond get displaced more towards the carbon atom and helps in the release of H^+ ion.

$R - C \equiv C .... H$ (Cleavage of bond is easy)

Oxidative–Hydroboration: Alkynes react with BH_3 (in THF) and finally converted into carbonyl compounds.

$$\underset{\text{Propyne}}{3CH_3 - C \equiv CH} \xrightarrow{BH_3 / THF} (CH_3 - CH = CH)_3 B \xrightarrow[OH^-]{H_2O_2} CH_3 - CH = CHOH \xrightarrow{Tautomeris es} \underset{\text{(Propanal)}}{CH_3CH_2CHO}$$

or $\xrightarrow[HgSO_4]{H_2SO_4} CH_3 - \overset{O}{\overset{||}{C}} - CH_3$ (Acetone)

Thus it is useful for preparing aldehyde from terminal alkyne.

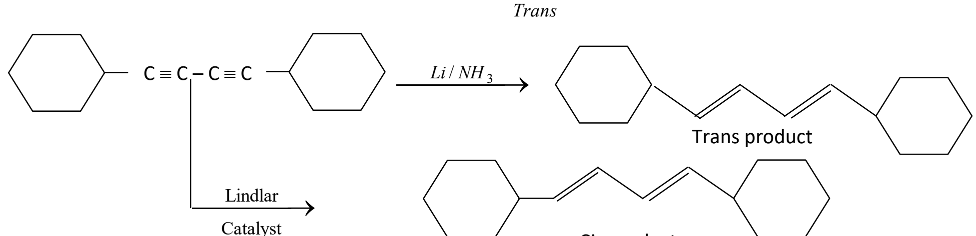
Reduction of Alkyne: Alkynes add on hydrogen in presence of suitable catalysts like finely divided Ni, Pd.

$$CH \equiv CH + H_2 \xrightarrow{Ni} CH_2 = CH_2 \xrightarrow[H_2]{Ni} CH_3 - CH_3$$

If the triple bond is not present at the end of the carbon chain of the molecule, the alkene formed may be cis and trans depending upon the choice of reducing agents.

With Na / NH_3 or Li / NH_3 in (liquid ammonia) trans alkene is almost an exclusive product while catalytic reduction at alkyne affords mainly cis alkenes.

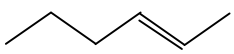
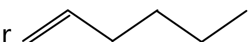
$$\underset{cis}{(R)(H)C = C(R)(H)} \xleftarrow[\text{Pd./}BaSO_4\text{/quinoline (Lindlarcatalyst)}]{H_2} R - C \equiv C - R \xrightarrow{Li / NH_3} \underset{Trans}{(R)(H)C = C(H)(R)}$$

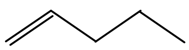
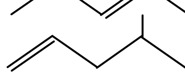
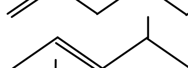


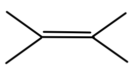
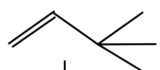
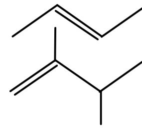
Degree of unsaturation: The number of degree of unsaturation in a hydrocarbon is given by $\frac{2n_1 + 2 - n_2}{2}$, Where n_1 is the number of carbon atoms; n_2 is the number of hydrogen atoms.

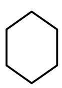
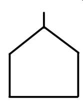
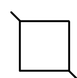
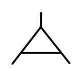
For example in C_6H_{12}, the degree of unsaturation is $= \frac{2 \times 6 + 2 - 12}{2} = 1$

So, C_6H_{12} with 1^o of unsaturation can have different arrangements.

(i)  or  or 

(ii)  or  or 

(iii)  or  or 

(iv)  or  or  or 

Other examples have the following degree of unsaturation.

(i) $C_6H_6 \rightarrow 4^o$ (ii) $C_5H_8 \rightarrow 2^o$ (iii) $C_7H_{10} \rightarrow 3^o$ (iv) $C_8H_{12} \rightarrow 3^o$ (v) $C_{10}H_{16} \rightarrow 3^o$ (vi) $C_{12}H_{10} \rightarrow 8^o$

(vii) C_3H_3Cl (like $C_3H_6) \rightarrow 1^o$ (viii) C_3H_4O (like $C_3H_4) \rightarrow 2^o$ (ix) C_4H_5N (like $C_4H_4) \rightarrow 3^o$

(x) C_5H_9Cl (like $C_5H_{10}) \rightarrow 1^o$

Test of unsaturation

(a) Baeyer's reagent**:** It is 1% $KMnO_4$ solution containing sodium carbonate. It has pink color. An aqueous solution of the compound, a few drops of Baeyer's reagent are added, the pink color of the solution disappears. The decolourisation of pink color indicates the presence of unsaturation in the compound.

Note: Alkene without any hydrogen atom on the carbon forming the double bond $\begin{matrix} R & & R \\ & C = C & \\ R & & R \end{matrix}$ don't show this test.

(b) Bromine- carbon tetrachloride test: The compound is dissolved in carbon tetrachloride or chloroform and then a few drops of 5% bromine solution in carbon tetrachloride are added to it, the color of bromine disappears. It indicates the presence of unsaturation.

Note: This test also fails in the case of alkene of the $\begin{matrix} R & & R \\ & C = C & \\ R & & R \end{matrix}$.

(7) **Uses**

(i) Acetylene is used as an illuminant.

(ii) It is used for the production of oxy-acetylene flame. The temperature of the flame is above $3000\,^{o}C$. is employed for cutting and welding of metals.

(iii) Acetylene is used for artificial ripening of fruits.

(iv) It is used as a general anesthetic under the name naracylene.

(v) Acetylene has synthetic applications. It serves as a starting material for the manufacture of a large variety of substances.

(vi) On electrical decomposition acetylene produces finely divided carbon and hydrogen. Hydrogen is used in airships. $C_2H_2 \longrightarrow 2C + H_2$

(8) **Interconversion**

(i) **Conversion of ethane into ethene:** (Alkane into alkene)

$$\underset{\text{Ethane}}{CH_3-CH_3}\xrightarrow[hv]{Br_2}\underset{\text{Ethyl bromide}}{C_2H_5Br}\xrightarrow[KOH]{Alc.}\underset{\text{Ethene}}{CH_2=CH_2}$$

(ii) **Ethene into ethane:** (Alkene into alkane)

$$\underset{\text{Ethene}}{CH_2=CH_2}\xrightarrow[Ni,300^oC]{H_2}\underset{\text{Ethane}}{CH_3-CH_3}$$

(iii) **Ethane into ethyne (acetylene):** i.e., alkane into alkyne

$$\underset{\text{Ethane}}{CH_3-CH_3}\xrightarrow[hv]{Br_2}CH_3CH_2Br\xrightarrow[KOH]{Alc.}\underset{\text{Ethene}}{CH_2=CH_2}\xrightarrow[CCl_4]{Br_2}\underset{\text{1, 2-Dibromoethane}}{CH_2Br-CH_2Br}\xrightarrow[\text{or } NaNH_2]{Alc.KOH}\underset{\text{Ethyne}}{CH\equiv CH}$$

(iv) **Ethyne into ethane:** (Alkyne into alkane)

$$\underset{\text{Ethyne}}{CH\equiv CH}\xrightarrow[Ni,300^oC]{H_2}\underset{\text{Ethene}}{CH_2=CH_2}\xrightarrow[Ni,300^oC]{H_2}\underset{\text{Ethane}}{CH_3-CH_3}$$

(v) **Ethene into propene: Ascending in alkene series**

$$\underset{\text{Ethene}}{CH_2=CH_2}\xrightarrow{HI}\underset{\text{Iodoethane}}{CH_3CH_2I}\xrightarrow{KCN}\underset{\substack{\text{Propane nitrile}\\\text{(Ethyl cyanide)}}}{CH_3CH_2CN}\xrightarrow[\text{Reduction}]{[H]}\underset{\text{1-Aminopropane}}{CH_3CH_2CH_2NH_2}\xrightarrow{HNO_2}\underset{\text{1-Propanol}}{CH_3CH_2CH_2OH}$$

$$\underset{\text{Propene}}{CH_3CH=CH_2}\xleftarrow[KOH]{Alc.}\underset{\text{1-Bromopropane}}{CH_3CH_2CH_2Br}\xleftarrow{PBr_3}$$

or

$$\underset{\text{Ethene}}{CH_2=CH_2}\xrightarrow{HI}\underset{\text{Iodoethane}}{CH_3CH_2I}\xrightarrow{Li(CH_3)_2Cu}\underset{\text{Propane}}{CH_3CH_2CH_3}\xrightarrow[hv]{Cl_2}\underset{\text{1-Chloro propane}}{CH_3CH_2CH_2Cl}\xrightarrow[KOH]{Alc.}\underset{\text{Propene}}{CH_3CH=CH_2}$$

or

$$CH_2=CH_2\xrightarrow{HI}CH_3CH_2I\xrightarrow{CH_3I/Na}\underset{\text{Propane}}{CH_3CH_2CH_3}\xrightarrow[hv]{Cl_2}\underset{\text{1-Chloro propane}}{CH_3CH_2CH_2Cl}\xrightarrow[KOH]{Alc.}\underset{\text{Propene}}{CH_3CH=CH_2}$$

(vi) **Propene into ethene:** Descending an alkene series

$$\underset{\text{Propene}}{CH_3-CH=CH_2}\xrightarrow{O_3/H_2O}\underset{\text{Ethanal}}{CH_3CHO}\xrightarrow[LiAlH_4]{[H]}\underset{\text{Ethanal}}{CH_3CH_2OH}\xrightarrow[170^oC]{H_2SO_4}\underset{\text{Ethene}}{CH_2=CH_2}$$

(vii) **Acetylene into propyne (methyl acetylene):** (Ascent)

$$\underset{\text{Acetylene}}{CH\equiv CH}\xrightarrow{Na}\underset{\substack{\text{Monosodium}\\\text{acetylide}}}{CH\equiv CNa}\xrightarrow{CH_3I}\underset{\text{Propyne}}{CH\equiv C-CH_3}$$

(viii) **Propyne into acetylene:** (Descent)

$$\underset{\text{Propyne}}{CH_3C = CH} \xrightarrow{\text{Lindlar's catalyst}} \underset{\text{Propylene}}{CH_3CH = CH_2} \xrightarrow{O_3 / H_2O} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{PCl_5} \underset{\text{Ethylidene chloride}}{CH_3CHCl_2} \xrightarrow[KOH]{Alc.} \underset{\text{Acetylene}}{CH \equiv CH}$$

(ix) **1-Butyne into 2-pentyne:** (Ascent)

$$\underset{1-\text{Butyne}}{CH_3CH_2C \equiv CH} \xrightarrow{NaNH_2} CH_3CH_2C \equiv C - Na \xrightarrow{CH_3I} \underset{2-\text{Pentyne}}{CH_3CH_2 - C \equiv CCH_3}$$

(x) **1-Butyne into 2-pentanone:** (Not more than three steps)

$$\underset{\text{1-Butyne}}{CH_3CH_2C \equiv CH} \xrightarrow[(Liq.NH_3)]{NaNH_2} CH_3CH_2C \equiv CNa \xrightarrow{CH_3I} \underset{2-\text{Pentyne}}{CH_3CH_2C \equiv CCH_3} \xrightarrow[HgSO_4]{H_2O, H_2SO_4} \underset{2-\text{Pentanone}}{CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}CH_3}$$