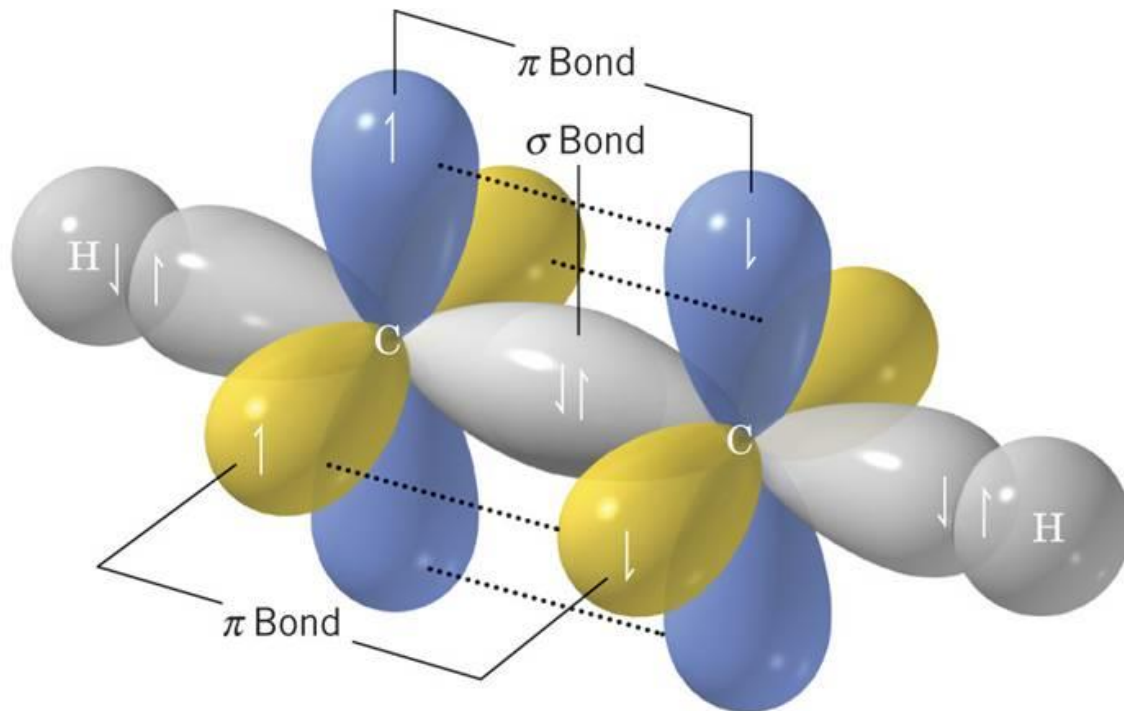


Alkyne



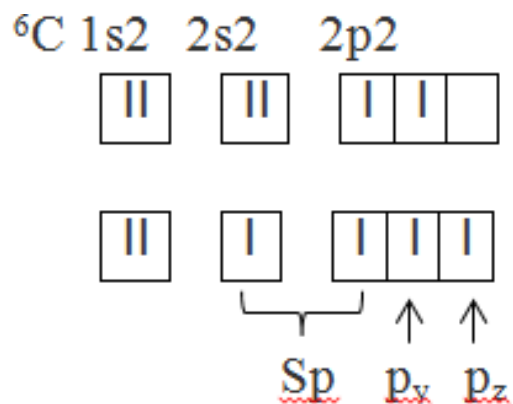
Org. Chem. - 1st Students

Dr. Munther A. M. Ali

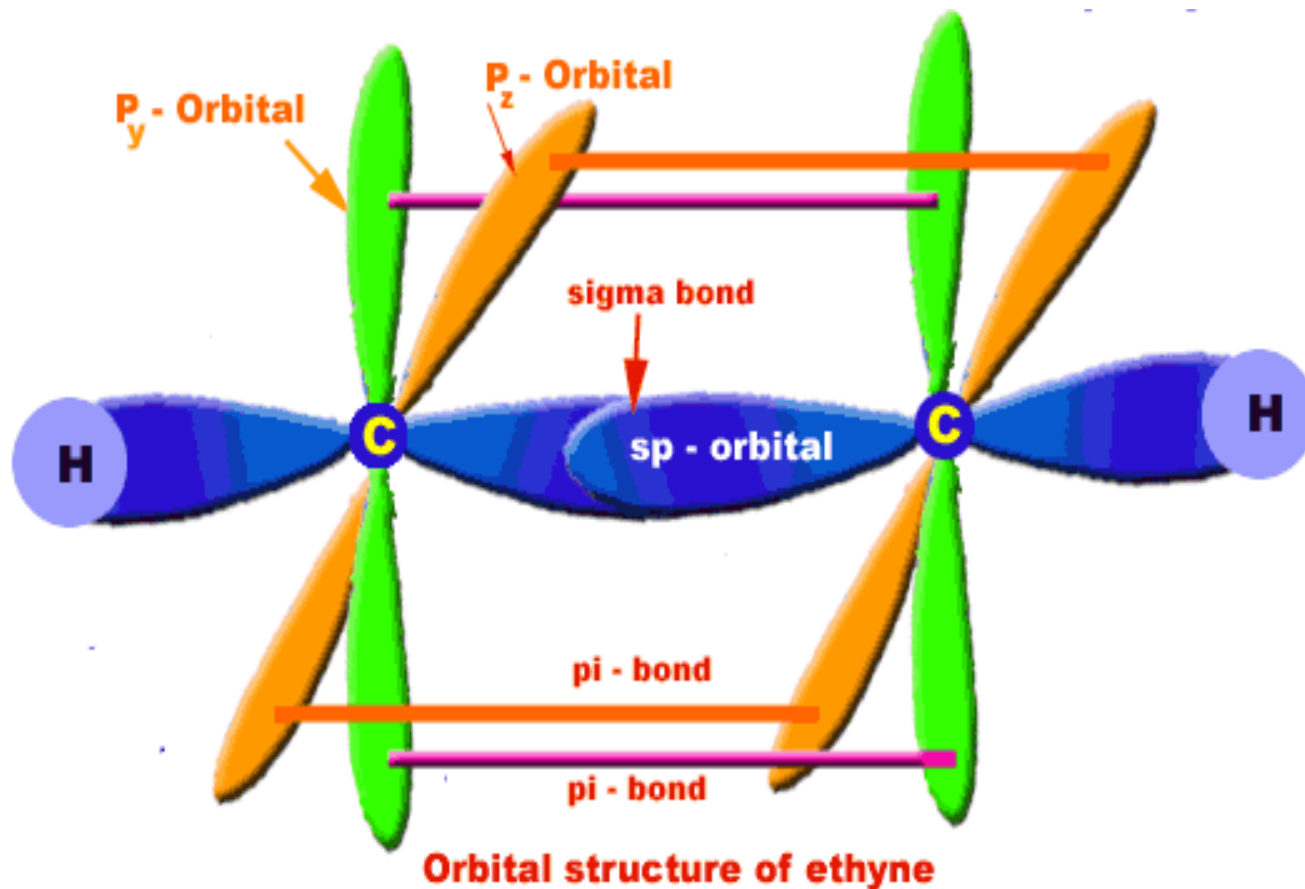
The functional group of alkynes is **carbon-carbon triple** bond, like double bond it is **unsaturated and highly reactive** toward a wide variety of reagents.

Structure of acetylene:

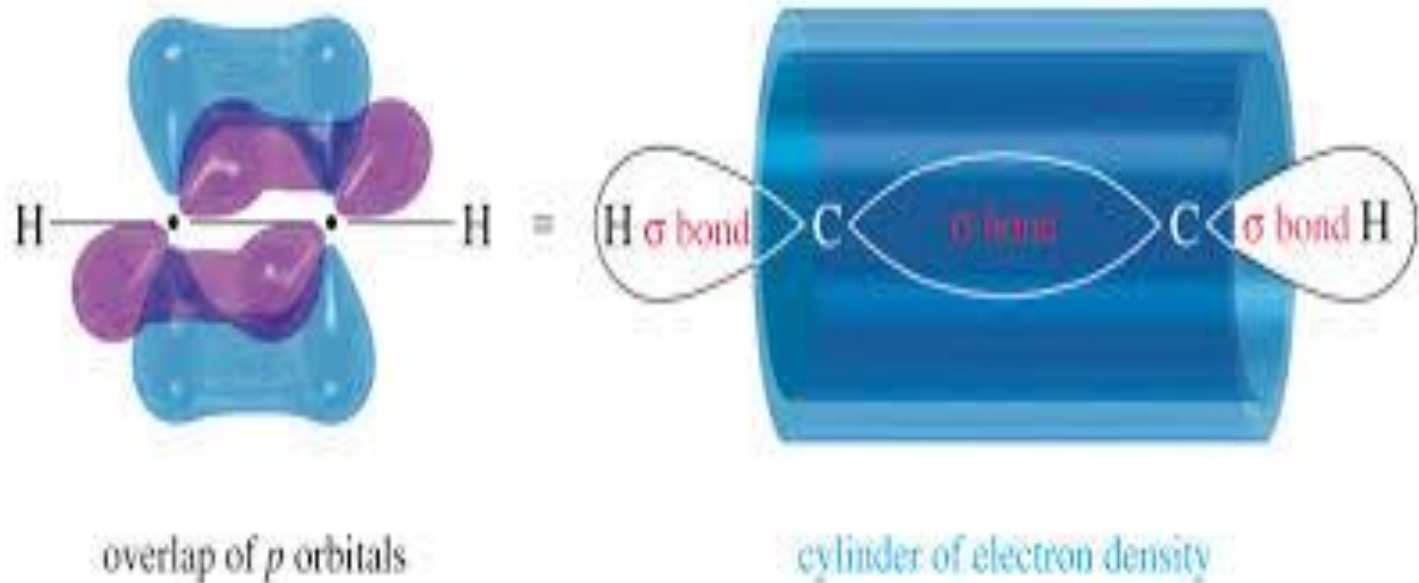
The **simplest member** of alkyne family is acetylene C_2H_2 .



sp hybridization, linear molecule with angle 180° .
There are two sp orbitals and two p for each carbon atom.



Overlapping between sp orbitals gives σ bond
Overlapping between p orbitals gives π bond



π cloud forms a cylindrical sheath

Total strength of bond $\text{C}\equiv\text{C}$; 198 kcal, $\text{C}=\text{C}$; 163 kcal, $\text{C}-\text{C}$ 88 kcal

Higher alkynes. Nomenclature

The alkynes are named according to two systems.

Common, they are considered to be derived from **acetylene** by replacement of one or both hydrogen atoms by **alkyl** groups.



Ethylacetylene

1-Butyne



Dimethylacetylene

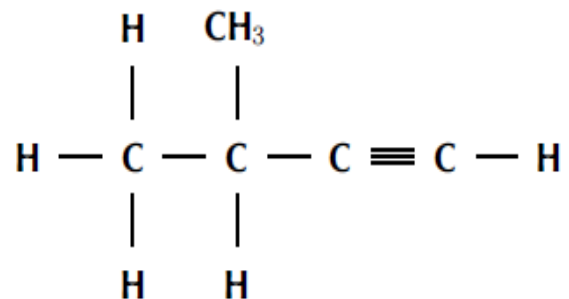
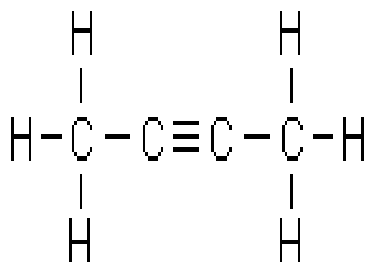
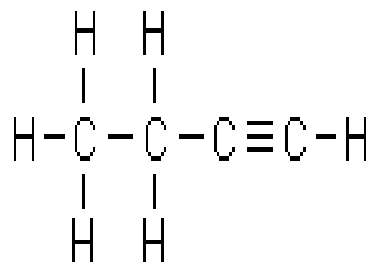
2-Butyne

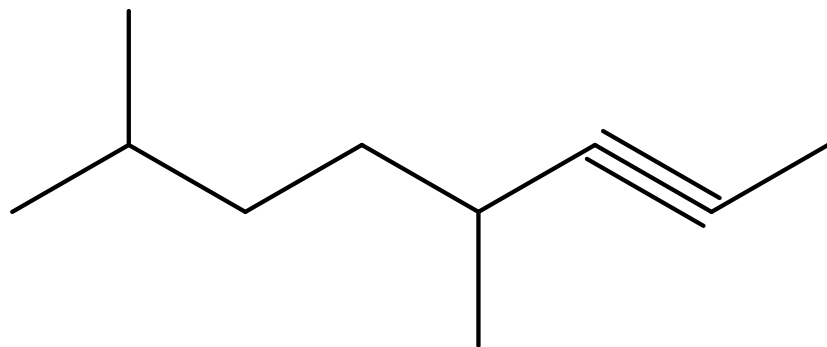


Methylisopropylacetylene

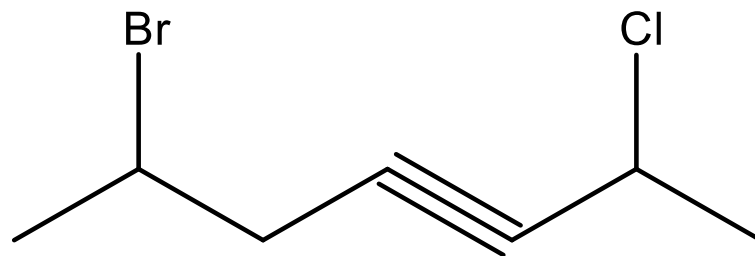
4-Methyl-2-pentyne

IUPAC, The rules are exactly the same as for the naming of **alkenes**, except that the ending **-yne** replaces **-ene**.

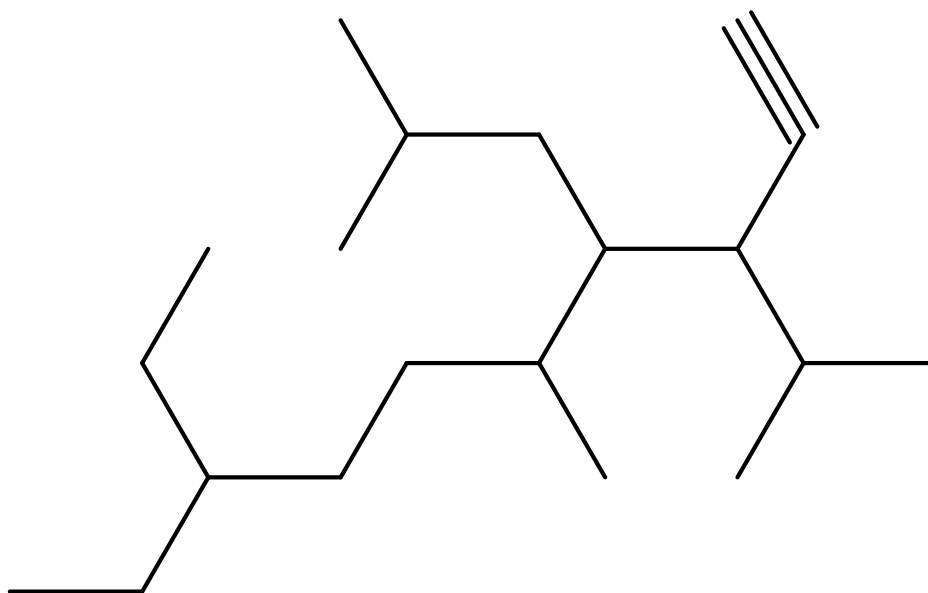




4,7-dimethyl-2-octyne



6-bromo-2-chloro-3-heptyne



4-isobutyl-8-ethyl-5-methyl-3-isopropyl-1-decyne

Physical properties of alkynes

- They are insoluble in water but quite soluble in the usual organic solvents of low polarity: ligroin, ether, benzene, carbon tetrachloride.
- They are less dense than water.
- Their boiling points show the usual increase with increasing carbon number.

1-hexyne b.p. = 77°C , 1-heptyne b.p. = 100°C

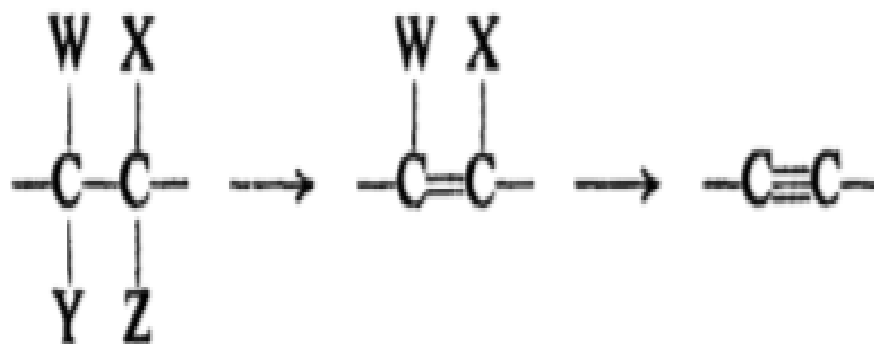
- The boiling points show the usual decrease with increasing chain-branching

2-Pentyne b.p.= 55°C , 3-methyl-1-butyne b.p. = 29°C

Preparation of alkynes

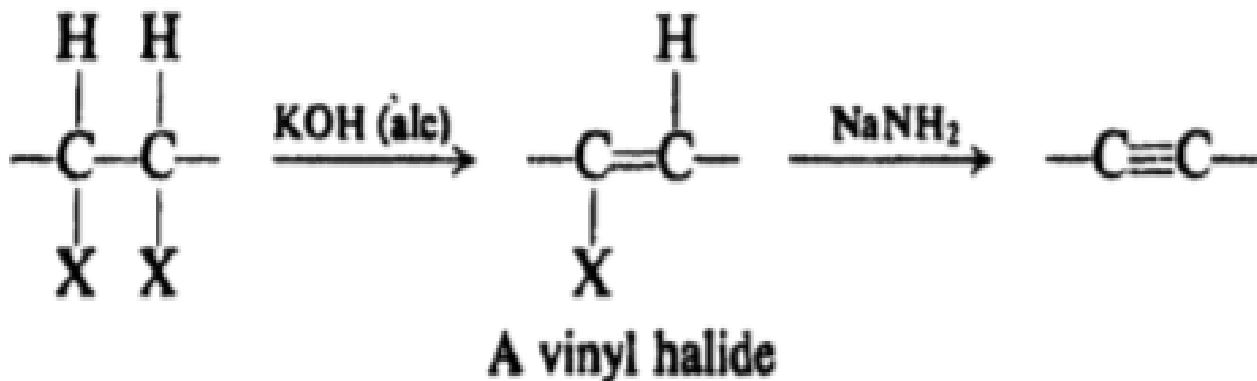
A carbon-carbon **triple bond** is formed in the same way as a **double bond**: **elimination of atoms or groups from two adjacent carbons**. The groups eliminated and the reagents used are essentially the same as in the preparations of alkenes.

There are two processes, **generation of $C\equiv C$** , or **increasing the molecular weight of the molecule that already contains a triple bond**.



1. Dehydrohalogenation of alkyl dihalides.

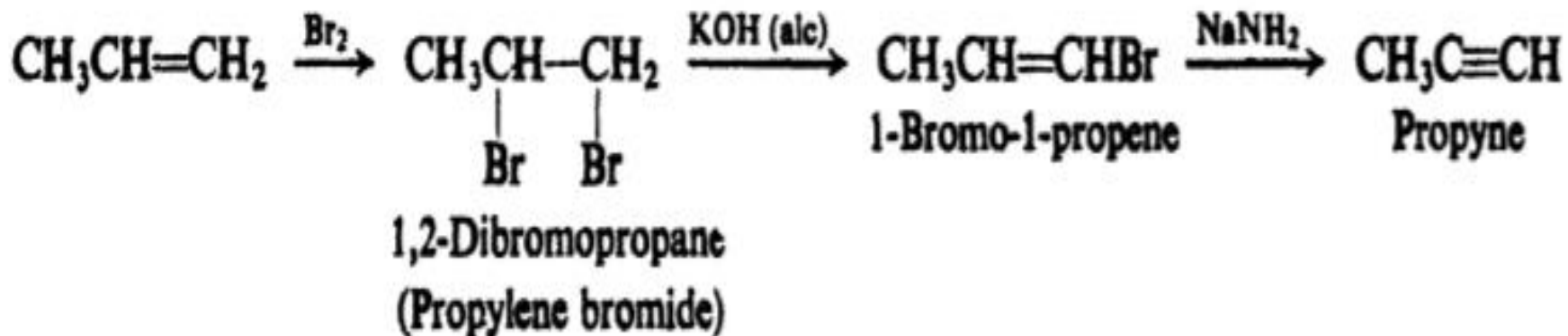
Dehydrohalogenation can generally be carried out in two stages,



Q/ Give the mechanism of dehydrohalogenation of 1,2-dichlorobutane.

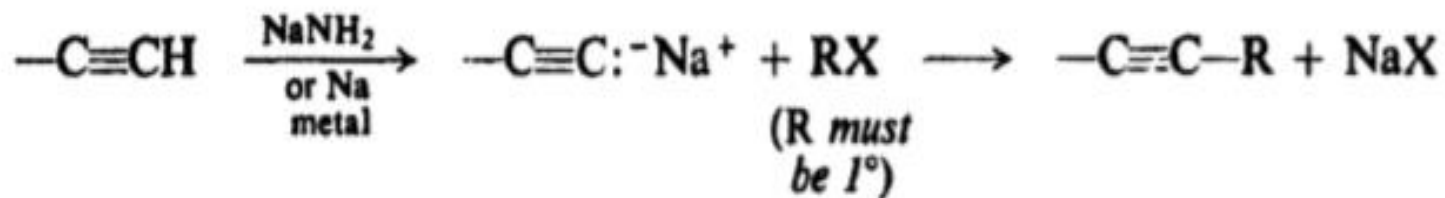
Q/ Starting with propylene, prepare propyne

Example:

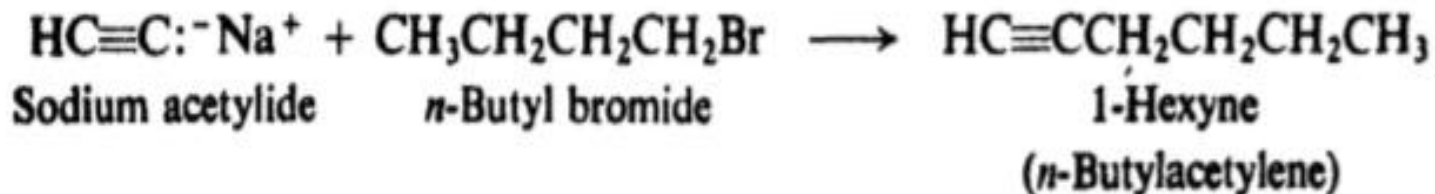


2. Reaction of sodium acetylides with primary alkyl halides.

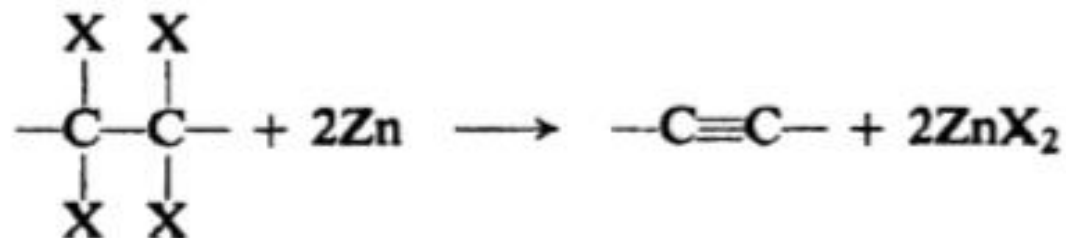
It is method of conversion of smaller alkynes into larger ones, using sodium amide or sodium metal to form metal acetylide which reacts with primary alkyl halide to give longer alkyne.



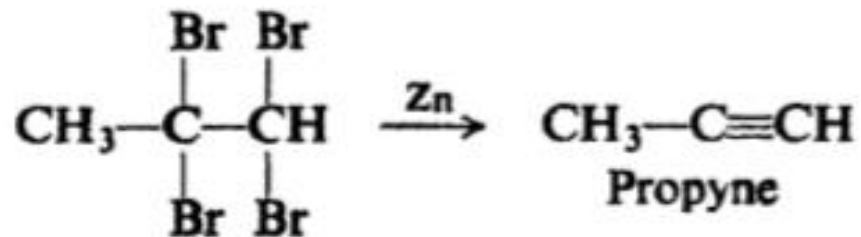
Examples:



3. Dehalogenation of tetrahalides.



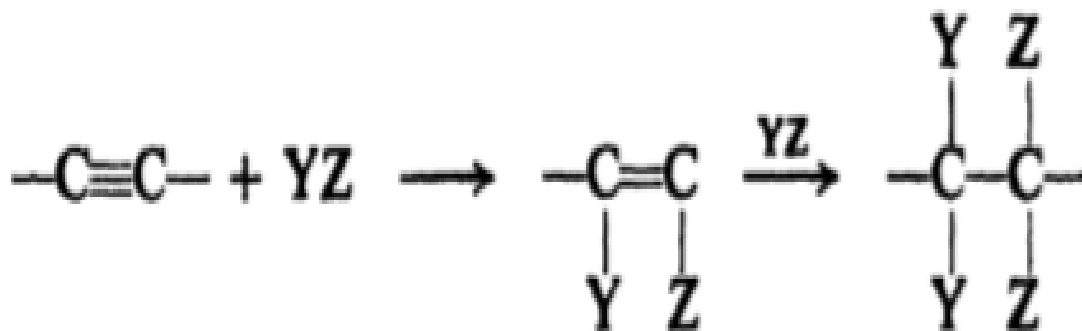
Example:



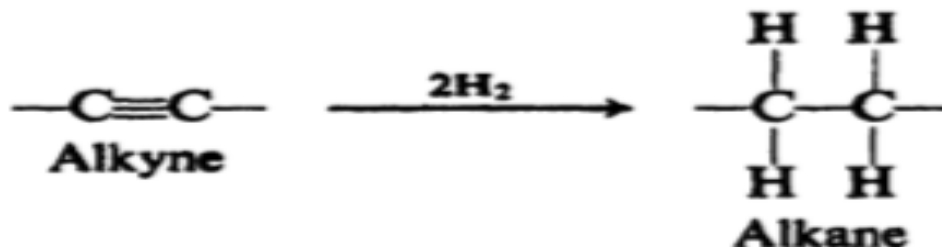
Reactions of alkynes

Like alkenes, alkynes undergo **electrophilic addition**. Addition of H_2 , X_2 and HX to alkynes includes reaction of **two** molecules of reagent with alkynes.

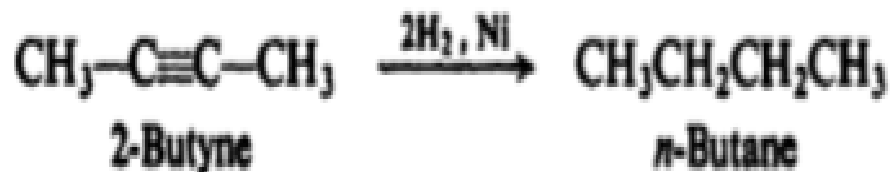
In general



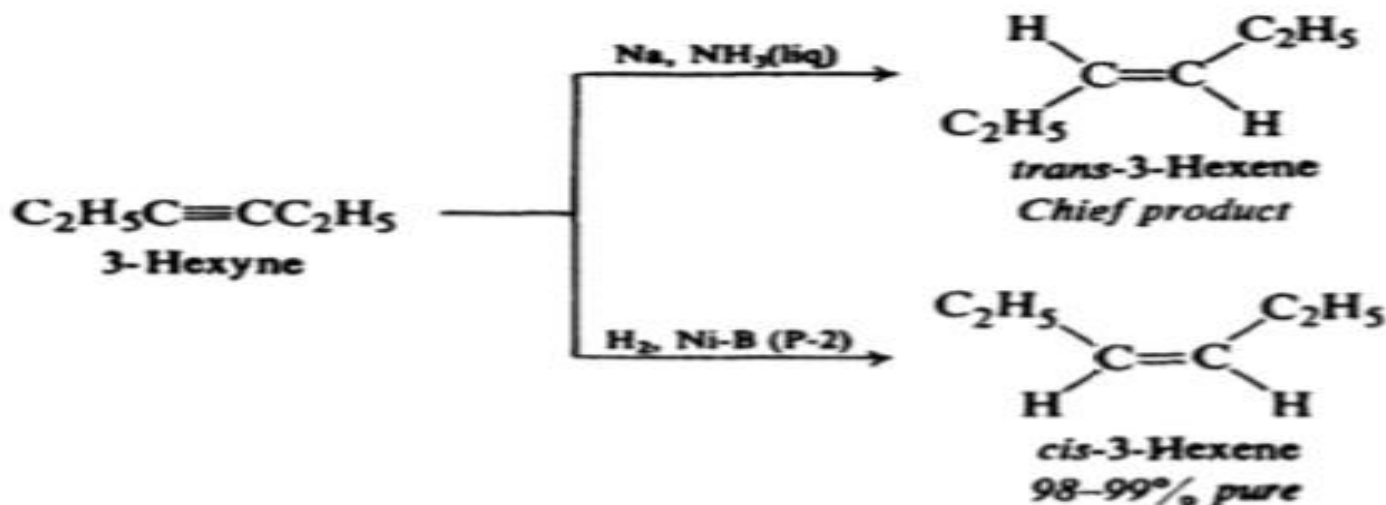
1. Addition of hydrogen.



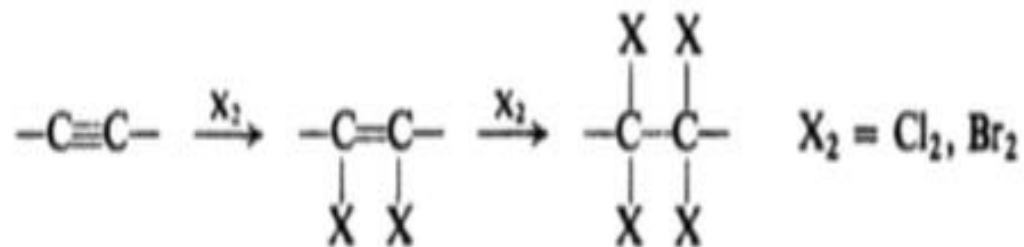
Examples:



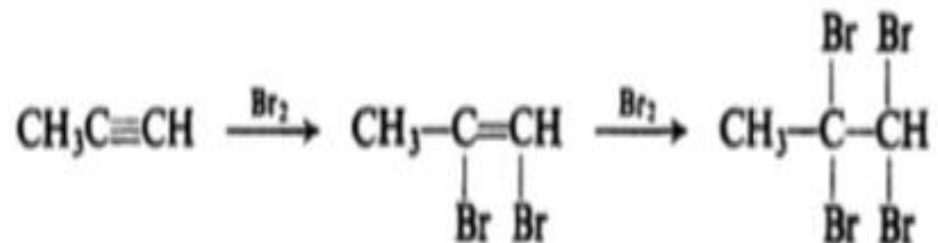
Using **Na, NH₃** (liquid) gives **trans-alkene**, whereas, using **H₂ over palladium (Lindlar catalyst)** gives **cis-alkene**.



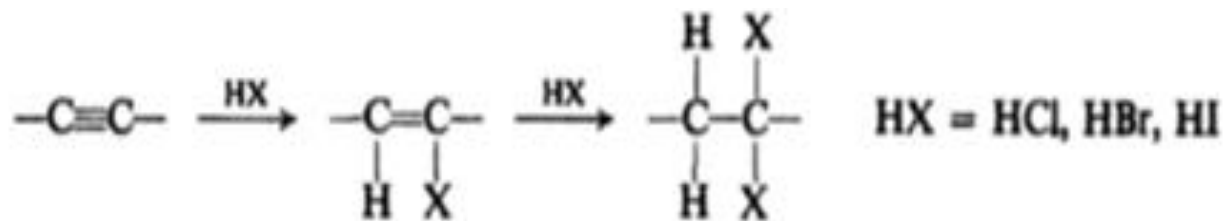
2. Addition of halogens.



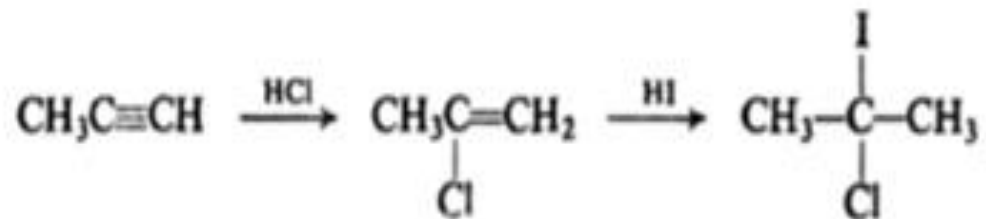
Example:



3. Addition of hydrogen halides.

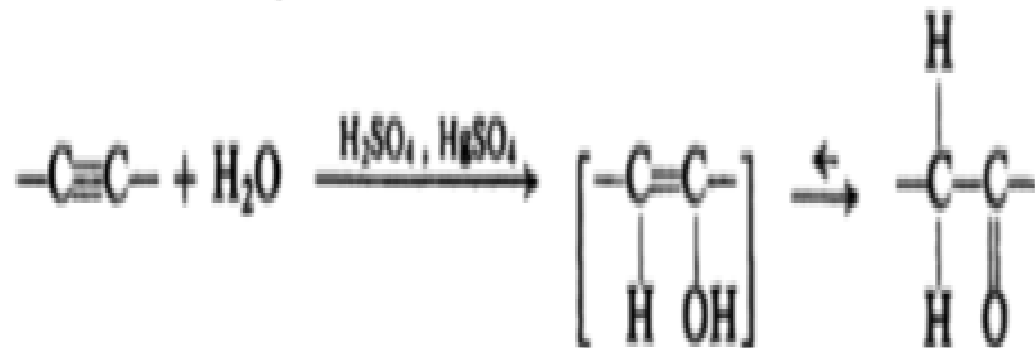


Example:



4. Addition of water. Hydration.

Addition of water to alkynes can occur in the presence of acid and HgSO_4 , when a molecule of water adds to the triple bond.

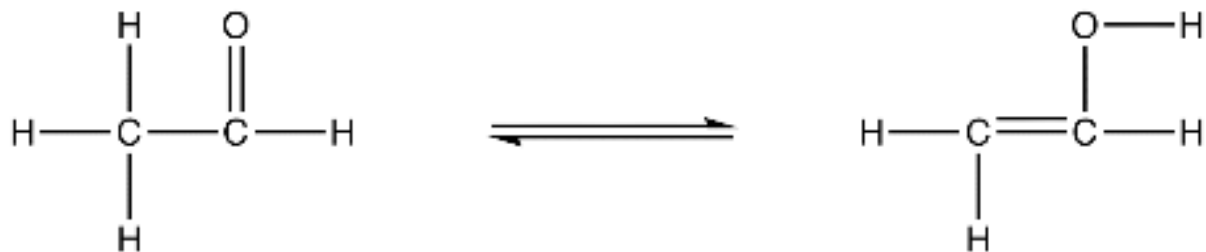


For the hydration of acetylene, we would expect addition of H and OH to the triple bond to yield the structure that we would call **vinyl alcohol** which converts to **acetaldehyde**.

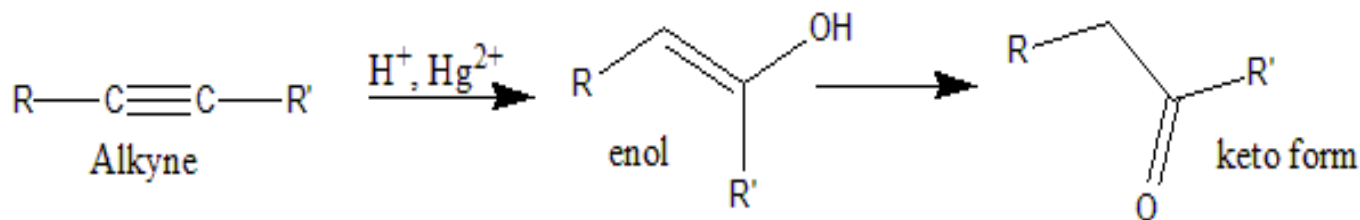
A structure with OH attached to doubly-bonded carbon is called an **enol** (**ene** for the carbon-carbon double bond, **-ol** for alcohol).

It is almost always true that when we try to make a compound with the **enol** structure, we obtain instead a compound with the **keto** structure (one that contains a C=O group).

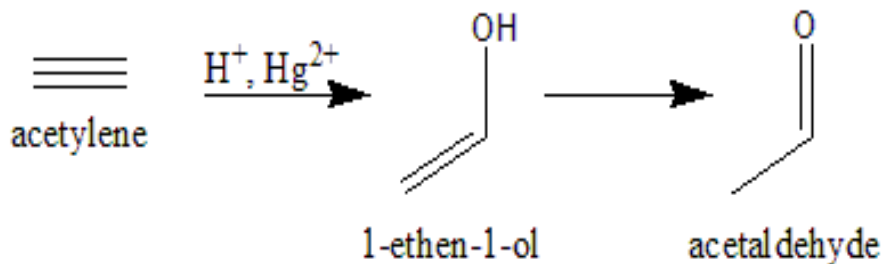
There is **equilibrium between the two structures**, but it generally lies very much in favor of the **keto form**. Thus, vinyl alcohol is formed initially by hydration of acetylene, but it is rapidly converted into an equilibrium mixture that is almost all **acetaldehyde**.



General Reaction:

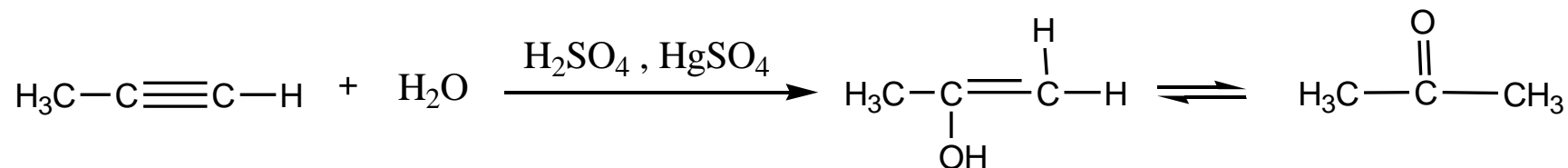


Example:



Compounds whose structures differ markedly in arrangement of atoms, but which exist in equilibrium, are called **tautomers**.

The most common kind of tautomerism involves structures that differ in the point of attachment of hydrogen.



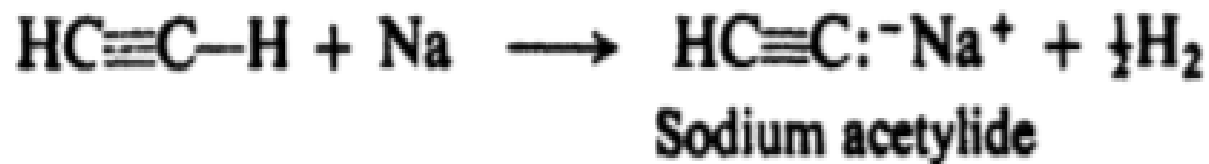
5- Formation of alkali metal acetylides

The hydrogen attached to triply-bonded carbon, as in acetylene or any alkyne with the triple bond at the end of the chain ($\text{RC}\equiv\text{C H}$), shows appreciable acidity.

The acidity is tendency of a compound to lose a hydrogen ion.

The acidity is generally shown by compounds in which hydrogen is attached to a rather electronegative atom (e.g., N, O, S, X).

Sodium reacts with acetylene to liberate hydrogen gas and form the compound **sodium acetylide**.



In the same way, **lithium amide** can react with acetylene to form **lithium acetylide**.

