



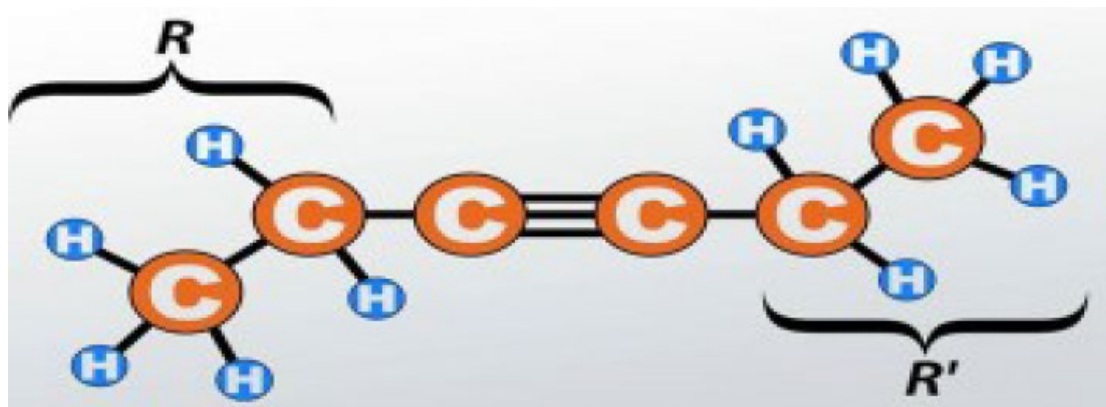
**The Islamic University**

**Department of Pharmaceutical Chemistry**

**Title of the course: *Organic Chemistry I***

**Level: 1<sup>st</sup> Class, 2<sup>nd</sup> Semester**

## ***Alkynes***

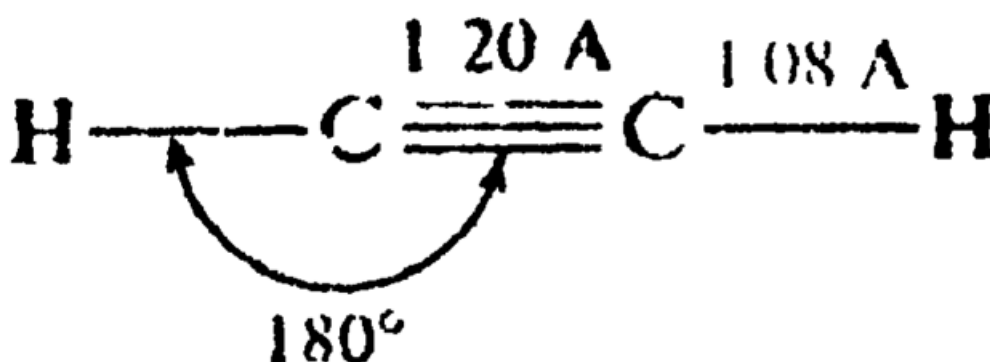


**Alkynes** are hydrocarbons that contain carbon–carbon triple bonds. Alkynes are also called **acetylenes** because they are derivatives of acetylene, the simplest alkyne.



acetylene

ethyne



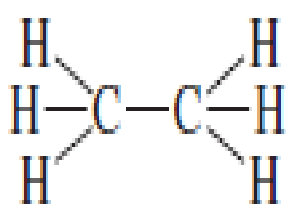
The carbon atoms of acetylene are connected by  $\sigma + \pi + \pi$  triple bond. Both carbon atoms are **sp**-hybridized, and each is bonded to a hydrogen by  $\sigma$  bond. The two  $\pi$  bonds are perpendicular to each other and are shown.

The chemistry of **the carbon–carbon triple bond** is similar to that of the double bond. In this chapter, we see that alkynes undergo most of the same reactions as alkenes, especially the additions and the oxidations. We also consider reactions that are specific to alkynes: some that depend on the unique

characteristics of the triple bond, and others that depend on the unusual acidity of the acetylenic bond. A **triple bond** gives an alkyne four fewer hydrogens than the corresponding alkane. Its molecular formula is like that of a molecule with two double bonds:

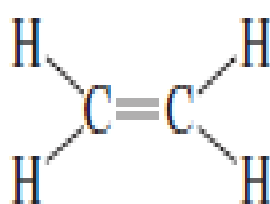


Therefore, the triple bond contributes two elements of unsaturation .



ethane,  $\text{C}_2\text{H}_6$

0 eu,  $\text{C}_n\text{H}_{2n+2}$



ethene,  $\text{C}_2\text{H}_4$

1 eu,  $\text{C}_n\text{H}_{2n}$



ethyne,  $\text{C}_2\text{H}_2$

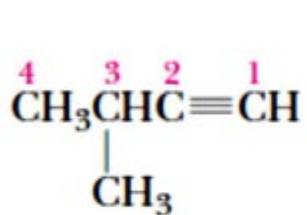
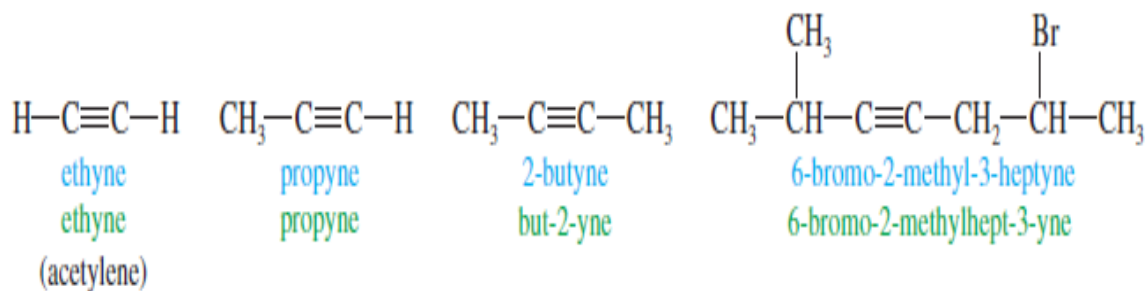
2 eu,  $\text{C}_n\text{H}_{2n-2}$

## Names The IUPAC

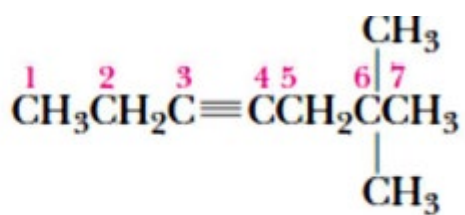
In naming **alkynes** the usual IUPAC rules are exactly the same as for the naming of alkenes, except that the ending **-yne** replaces **-ene**.

1. The parent structure is the longest continuous chain that contains the triple bond.
2. We number the longest carbon chain that contains the triple bond from the end that gives the triply bonded carbons the lower set of numbers.

3. We indicate the location of the triple bond by the number of the first carbon of the triple bond.



3-Methyl-1-butyne



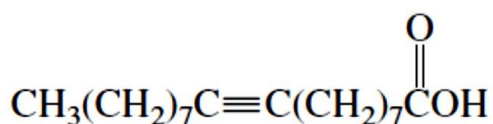
6,6-Dimethyl-3-heptyne

## Physical properties of Alkynes

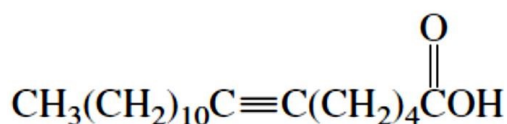
1. Being compounds of low polarity, the **alkynes** have physical properties that are essentially the same as those of the alkanes and alkenes.
2. They are insoluble in water but quite soluble in the usual organic solvents of low polarity: ligroin, ether, benzene, carbon tetrachloride.
3. They are less dense than water.
4. **Their boiling points show the usual increase with increasing carbon number**, and the usual effects of chain-branching; they are very nearly the same as the boiling points of alkanes or alkenes with the same carbon skeletons.

## Alkynes in Natural

More than 1000 natural products contain **carbon-carbon triple bonds**. Many, such as stearolic acid and tariric acid, are fatty acids—carboxylic acids with unbranched chains of 12–20 carbon atoms—or are derived from them.

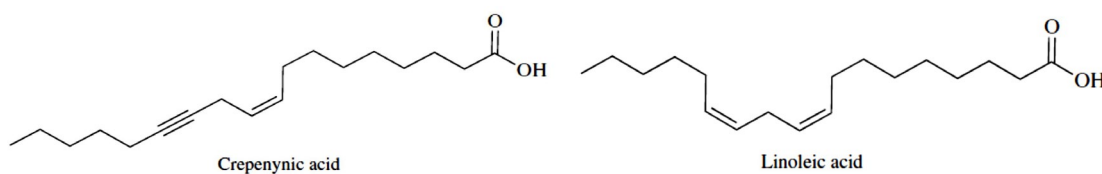


Stearolic acid



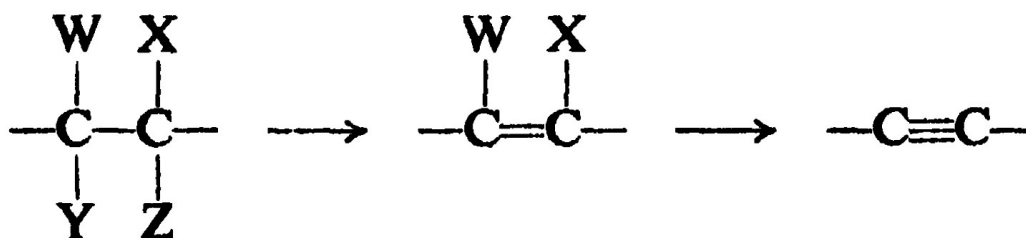
Tariric acid

A major biosynthetic route to **acetylenic fatty acids** in certain **flowering plants** involves oxidation of analogous compounds with carbon-carbon double bonds, and is catalyzed by enzymes of the desaturase class known as acetyleneases. **Crepenynic acid**, which is formed by oxidation of the fatty acid **linoleic acid**, is one example.

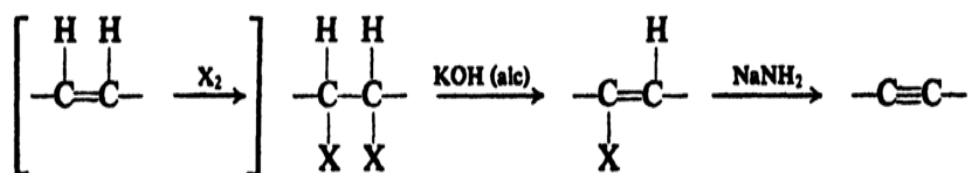


## Preparation of Alkynes

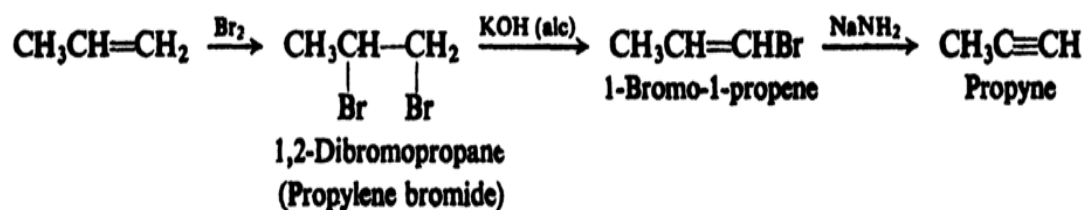
A **carbon-carbon triple bond** is formed in the same way as a double bond: **elimination** of atoms or groups **from two adjacent carbons**. The groups eliminated and the reagents used are



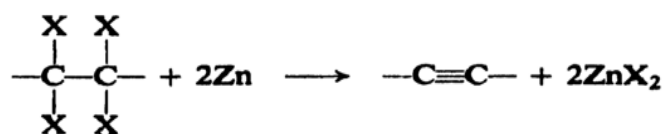
1. Dehydrohalogenation of alkyl dihalides: (*Elimination of 2HX*)



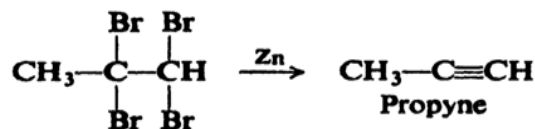
*Example:*



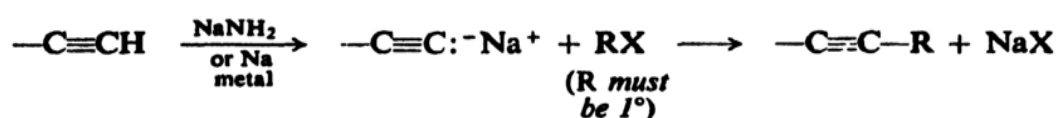
2. Dehalogenation of tetrahalides: (*Elimination of 2 X<sub>2</sub>*)



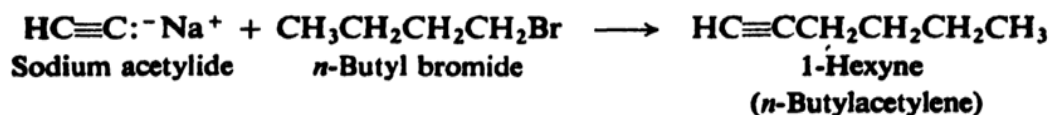
*Example:*



3. Reaction of sodium acetylides with primary alkyl halides



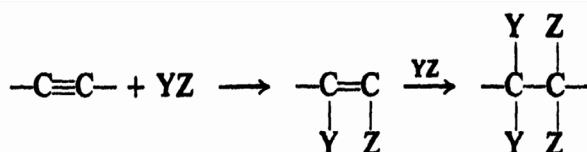
*Examples:*



## Reactions of Alkynes

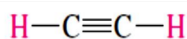
Alkynes undergo two types of reactions: **Addition Reactions** and **Reactions as Acids**

**Addition Reactions:** Just like alkenes, **alkynes** undergo **electrophilic addition**, and for the same reason: availability of the **loosely held  $\pi$  electrons**.

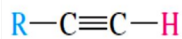


Addition of **hydrogen**, **halogens**, and **hydrogen halides** to alkynes is very much like addition to alkenes, except that here **two molecules** of reagent can be consumed for each triple bond.

**Reactions as Acids:** **Alkynes** undergo certain reactions that are due to the **acidity of a hydrogen atom** held by triply-bonded carbon.



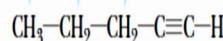
Acetylene



Monosubstituted or terminal alkyne

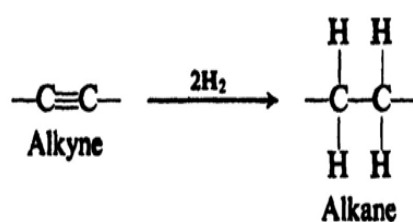


these hydrogens are much lower in acidity and are not deprotonated by  $\text{NaNH}_2$

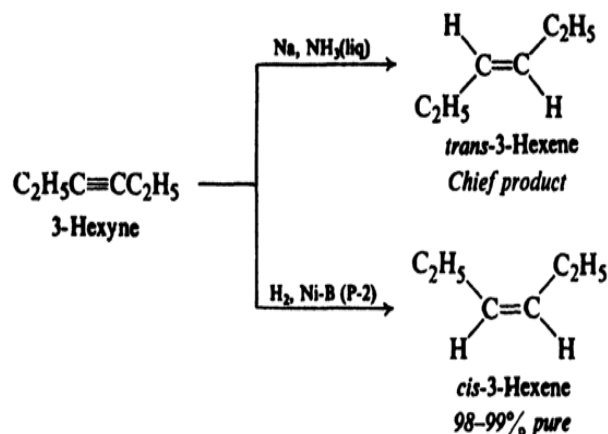
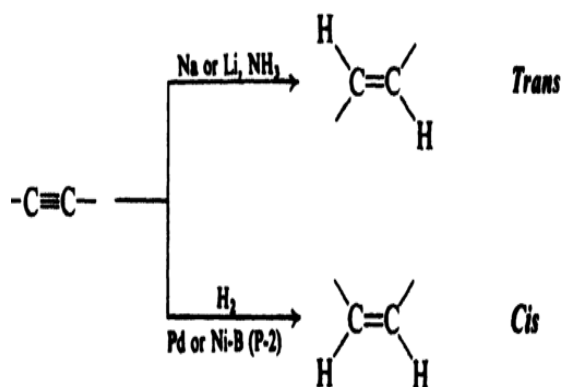
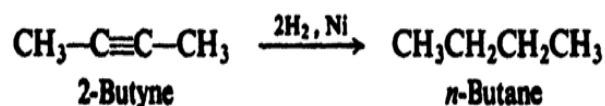


only this hydrogen is acidic enough to be deprotonated by  $\text{NaNH}_2$

### 1. Addition of hydrogen:



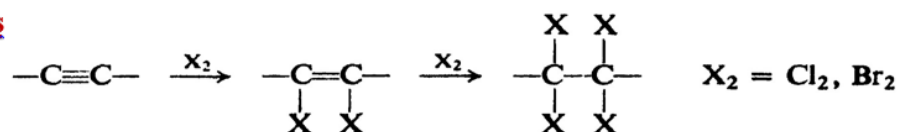
**Example:**



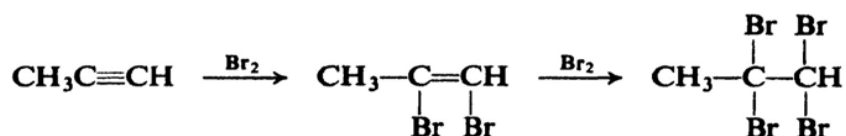


## Reactions of Alkynes

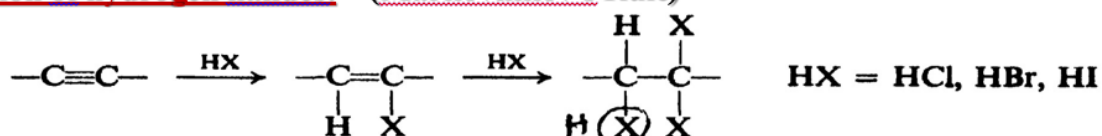
### 2. Addition of halogens



Example:

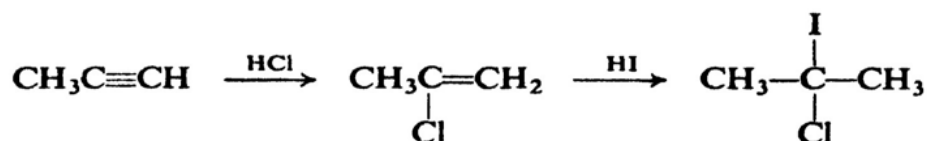


### 3. Addition of hydrogen halides: (Markovnikov's Rule)



Example:

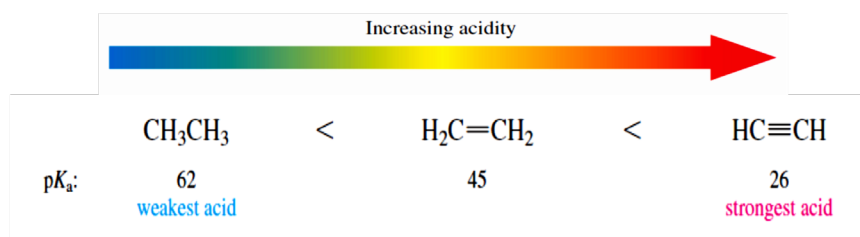
Example:



## Reactions of Alkynes

### Reactions as Acids

According to the *Lowry-Bronsted definition* of acids; **acidity is a measure of the tendency of a compound to lose a hydrogen ion**. The C-H bonds of hydrocarbons show little tendency to ionize, and alkanes, alkenes, and alkynes are all very weak acids. However, **acetylene and terminal alkynes are far stronger acids than other hydrocarbons**.



Thus, **acetylene and terminal alkynes** react with a strong base (such as alkali metals or NaNH<sub>2</sub>) to form alkali metal acetylides (page9).

