

Thi-Qar University

College of science

Chemistry Department

Organic Chemistry

Second stage

Lecture 8

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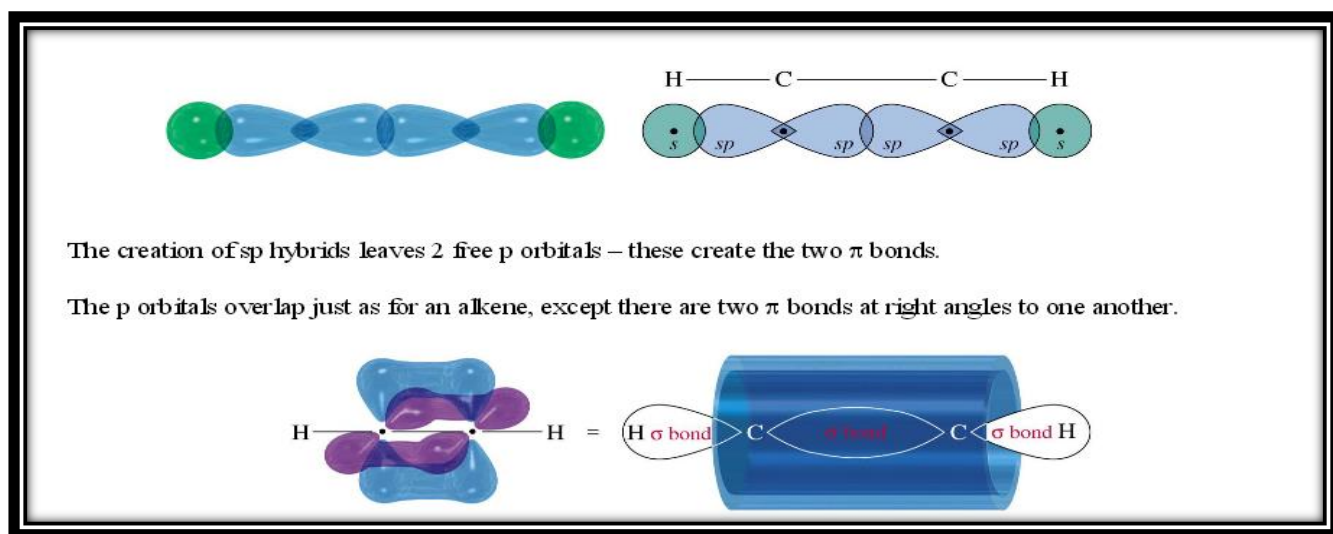
Alkynes

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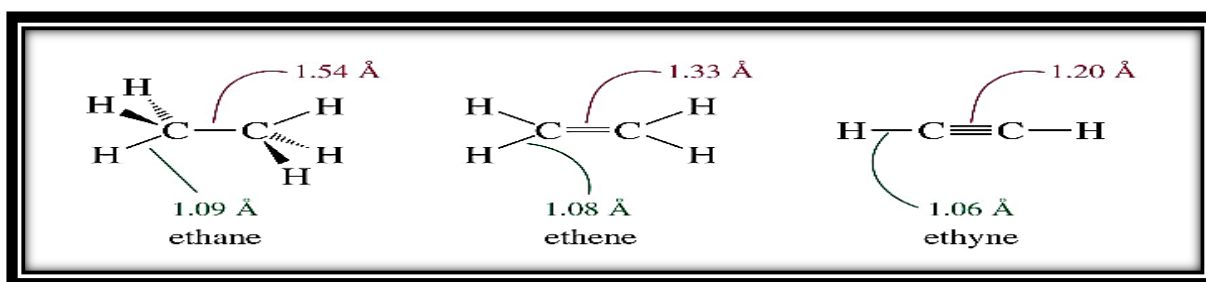
Alkynes or Acetylenes are compounds that contain a carbon –carbon triple bond.

Electronic Structure of Alkynes

The triple bond consists of one σ bond and two π bonds. Each carbon is bonded to two other atoms, and there are no nonbonding electrons. Carbon requires two hybrid orbitals to bond to the atoms, thus *sp* hybrids are used. The *sp* orbitals are linear and oriented at 180° . The C-C bond is formed from *sp*-*sp* overlap. The C-H bond is formed from *sp*-*s* overlap.



The C-C bond length for ethyne is 1.20\AA which is shorter than ethane (1.54\AA) and ethene (1.33\AA). The C-H bond length in ethyne is 1.06\AA which is also shorter than in ethane (1.09\AA) or ethene (1.08\AA). This is because the C-H bond contains more s character ($sp^3 \rightarrow sp^2 \rightarrow sp$) which gives stronger bonds.

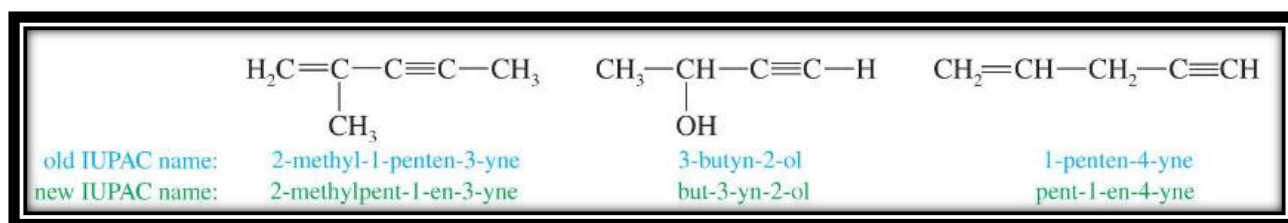


Nomenclature: Alkynes

1. count the number of carbons in the longest chain including the **triple** bonds
2. use the meth, eth, prop... root word followed by the **-yne** suffix
3. to determine which carbon is the first carbon, make the triple bond the lowest number possible
4. the number of the carbon where the triple bond is located is written before the root word
5. side chains and substitutions are written in alphabetical order
6. if there are more than one triple bond each bond position is noted with a number preceding the root name and a prefix; di, tri... is inserted before the -yne suffix, -diyne or -triyne are examples

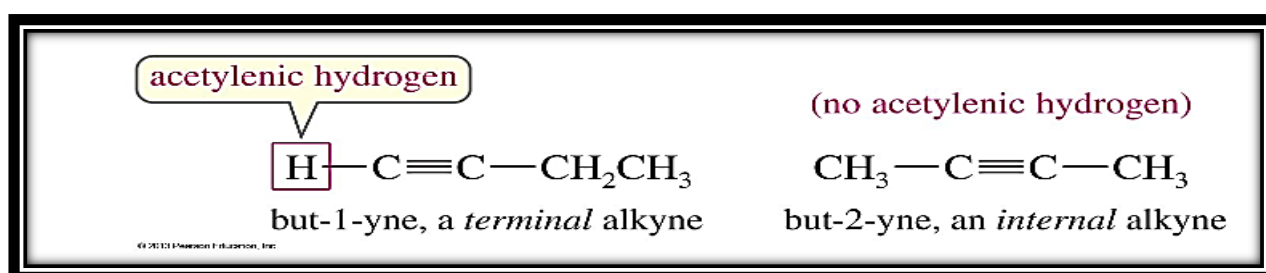
| | | | |
|----------|----------|------------------|---------------|
| | | | |
| 1-butyne | 2-butyne | 3-fluor-1-butyne | 1,4-hexadiyne |

| | | | | |
|-----------------|--|---|--|---|
| | $\text{H}-\text{C}\equiv\text{C}-\text{H}$ | $\text{CH}_3-\text{C}\equiv\text{C}-\text{H}$ | $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3$ | $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}-\text{C}\equiv\text{C}-\text{CH}_2-\text{CH}-\text{CH}_3 \\ \quad \quad \\ \text{Br} \end{array}$ |
| old IUPAC name: | ethyne | propyne | 2-butyne | 6-bromo-2-methyl-3-heptyne |
| new IUPAC name: | ethyne | propyne | but-2-yne | 6-bromo-2-methylhept-3-yne |



Terminal and Internal Alkynes.

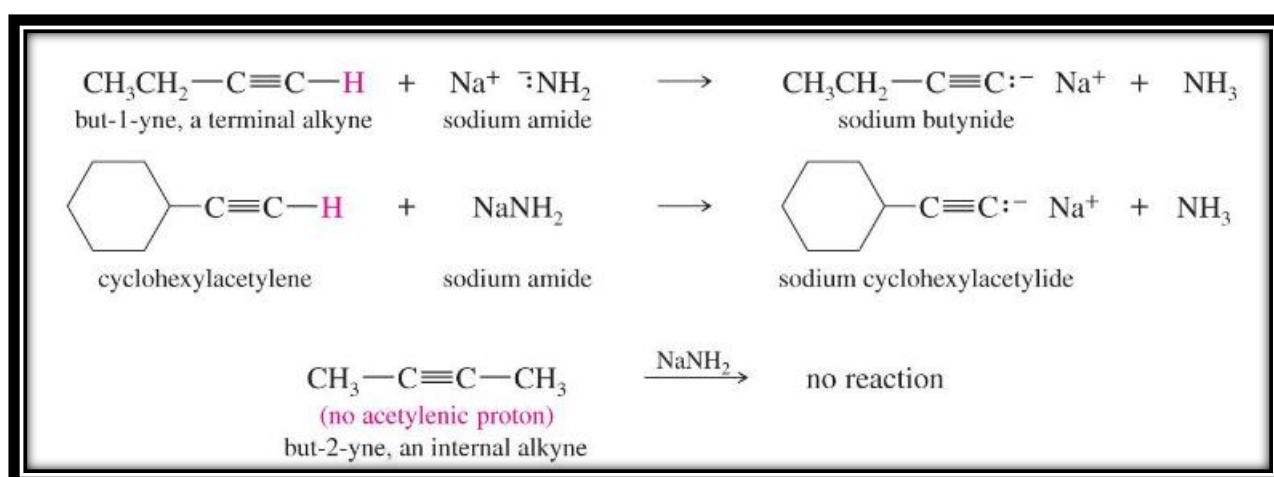
The position of the triple bond can alter the reactivity of the alkyne. Compounds with triple bonds at the end of a molecule are called terminal alkynes. (Terminal C-H groups are called acetylenic hydrogens).



If the triple bond is flanked by alkyl groups on both sides it is an internal alkyne.

Acidity of Alkynes.

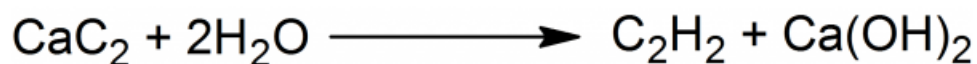
Terminal alkynes are acidic, the end hydrogen can be removed as a proton by a strong base.



Synthesis of Alkynes.

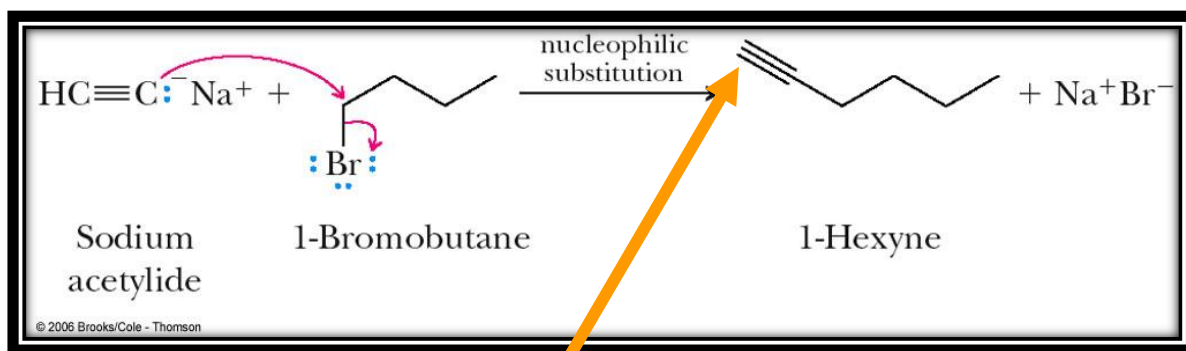
Preparation of acetylene

Preparation of acetylene from calcium carbide and water

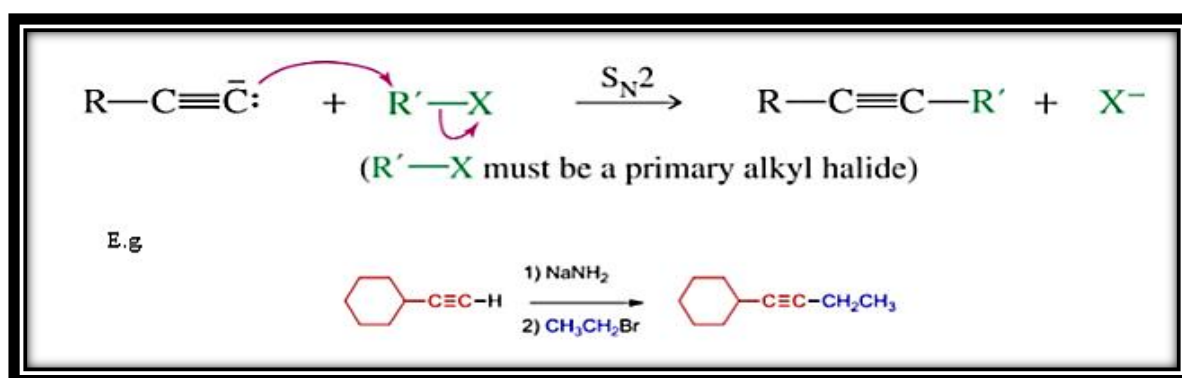


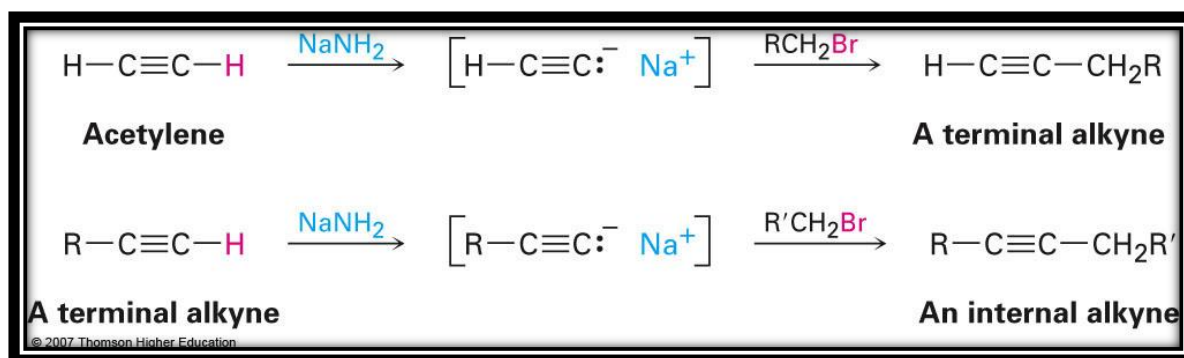
Preparation of acetylene from calcium carbide and water

The carbanions produced are called acetylides, and are strong nucleophile.



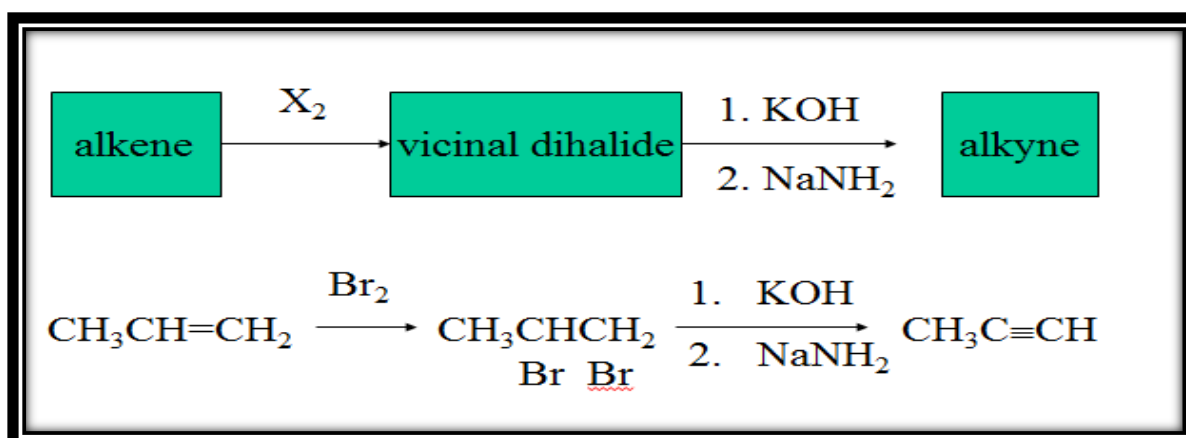
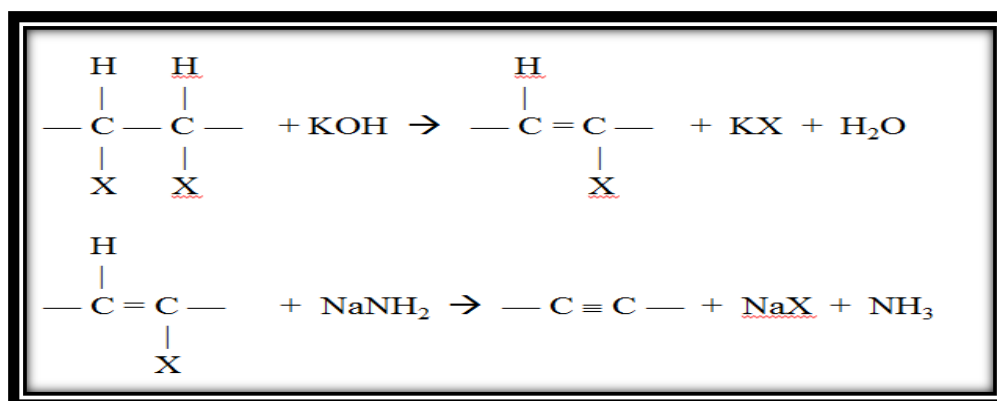
Note that we still have an acidic hydrogen and, thus, can react with another alkyl group in this way to make RCCR'



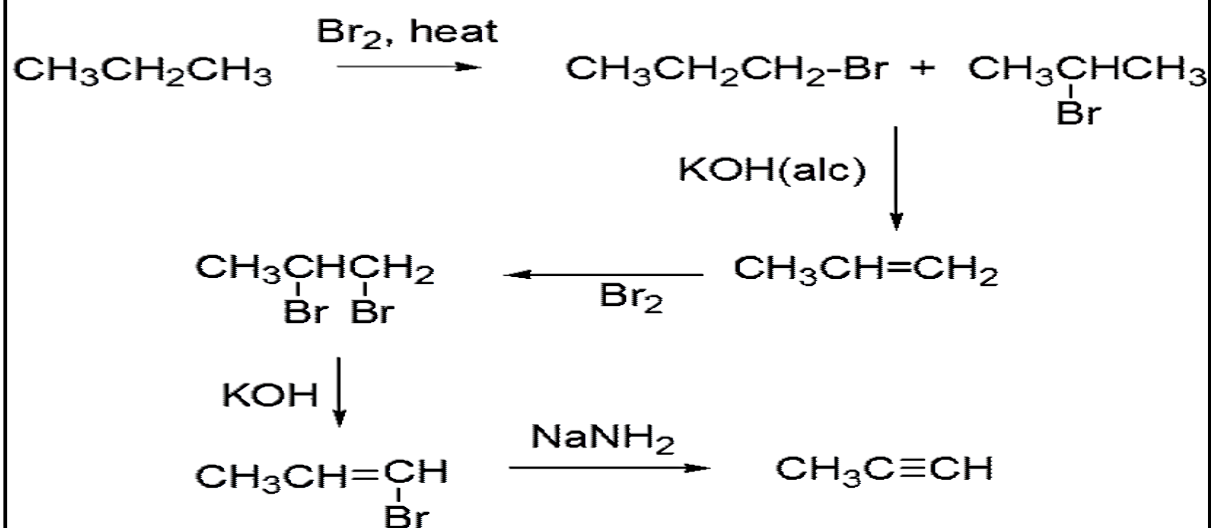


Synthesis of Alkynes via Elimination.

In the same way that alkenes are produced by elimination of H - X, alkynes can be produced by elimination of 2 moles of H -X from a germinal or vicinal dihalide.



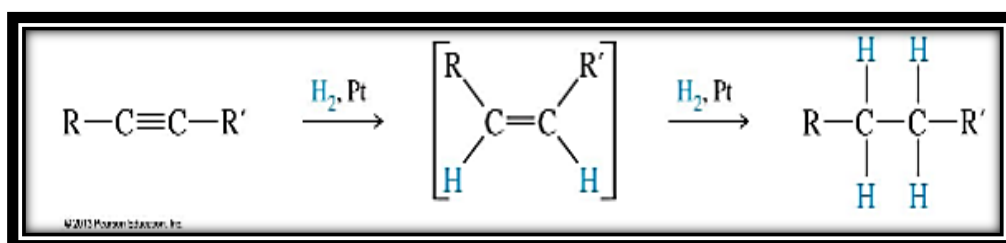
Synthesis of propyne from propane



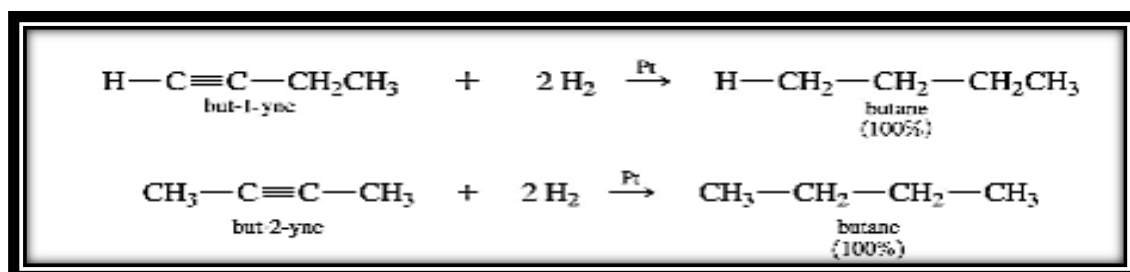
Reactions: alkyne

Addition of Hydrogen

Hydrogen in the presence of a catalyst will add twice to alkynes to generate alkane.

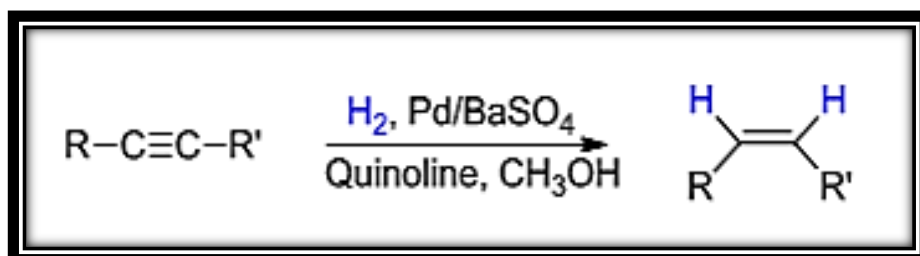


This reaction proceeds through a cis alkene intermediate, but cannot be stopped at this stage except with the use of a special catalysts.



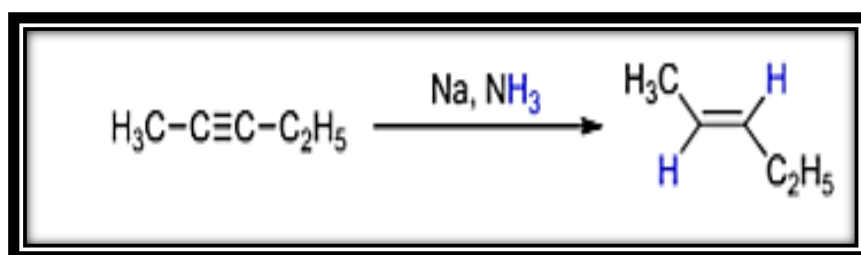
The special catalyst is : Lindlar's catalyst

This is a partially deactivated (poisoned) catalyst consisting of barium sulfate, palladium and quinoline .



Trans Alkenes

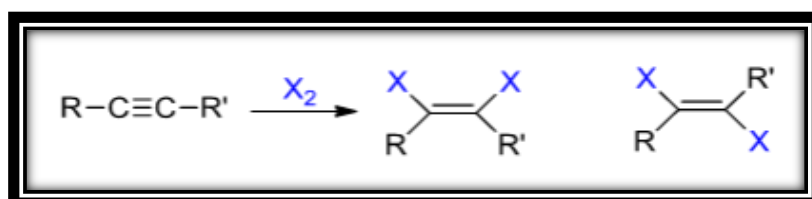
These can be produced by the action of sodium metal in liquid ammonia.

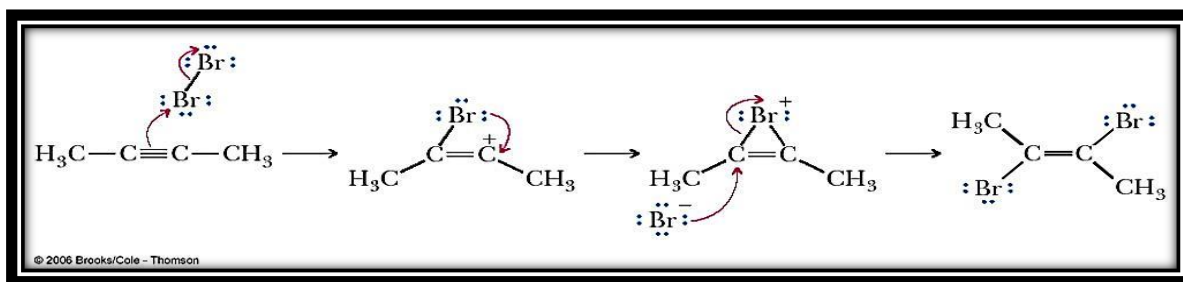


Addition of Halogens

Chlorine and bromine add in an analogous fashion as for alkenes.

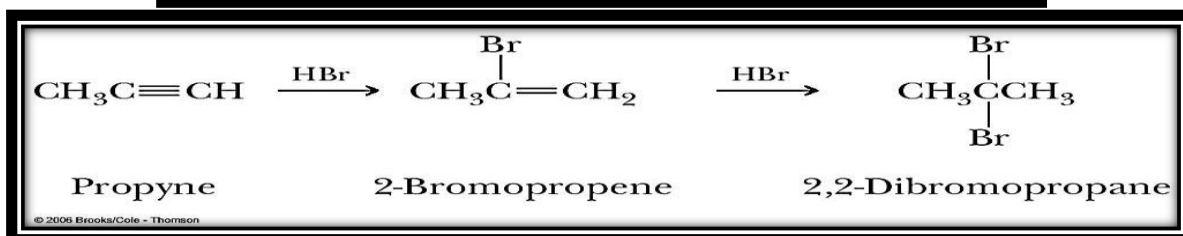
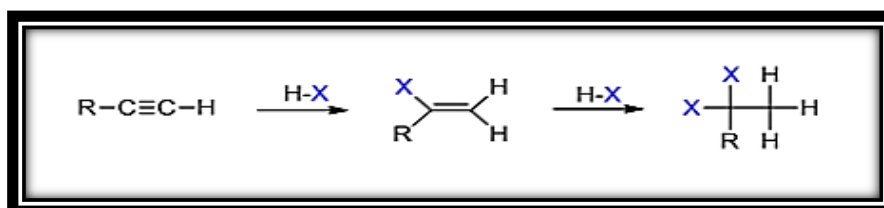
If only one mole of halogen is added then a dihaloalkene is produced, and a mixture of syn and anti addition is observed .



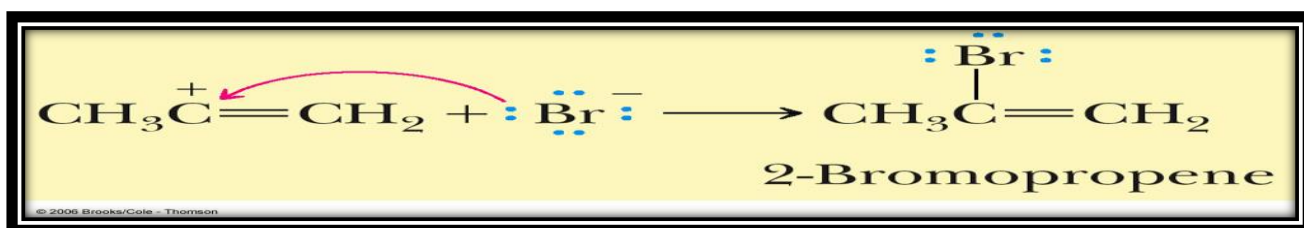
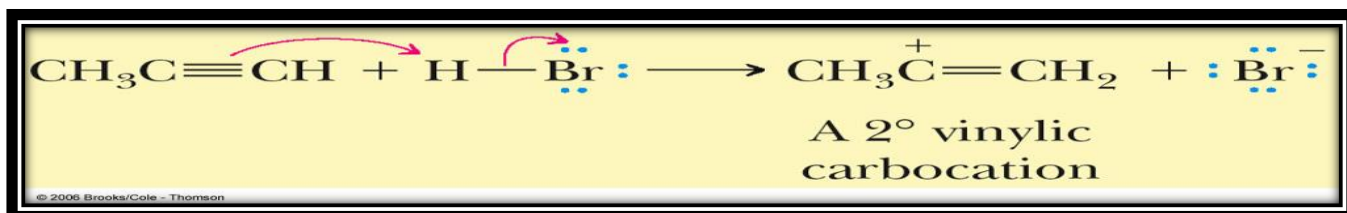


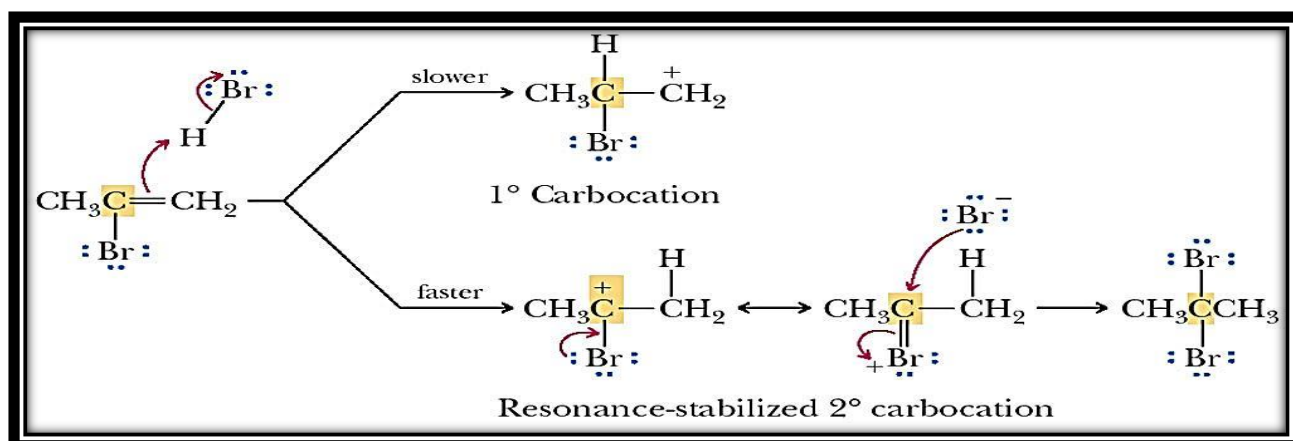
Addition of Hydrogen Halides

H-X can be added to alkynes just like to alkene.



Mechanism

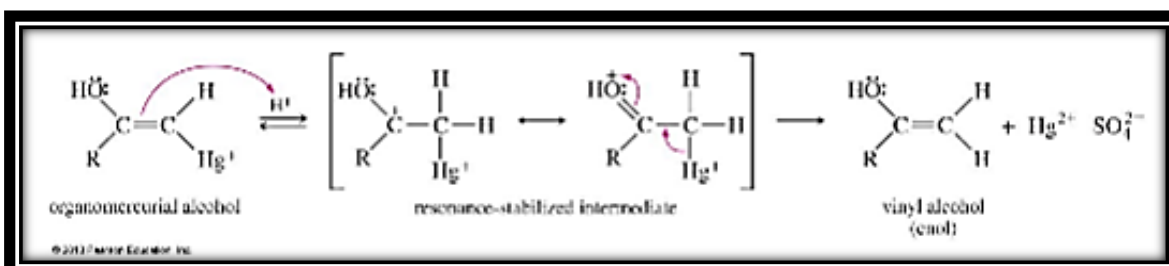
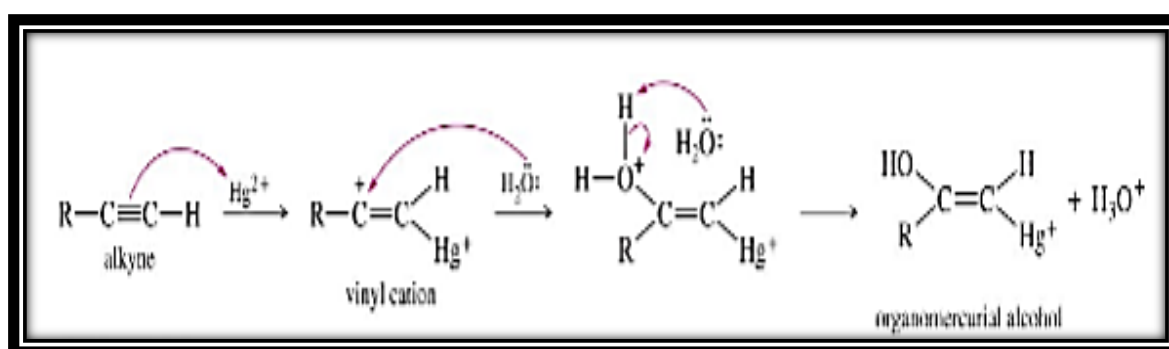
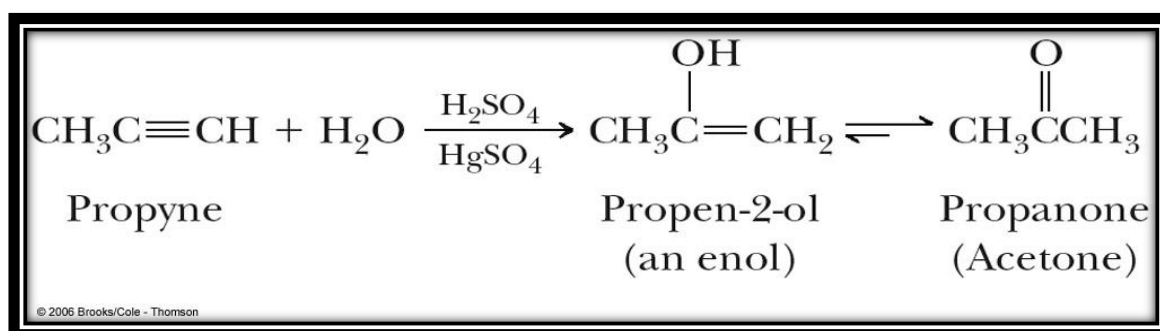


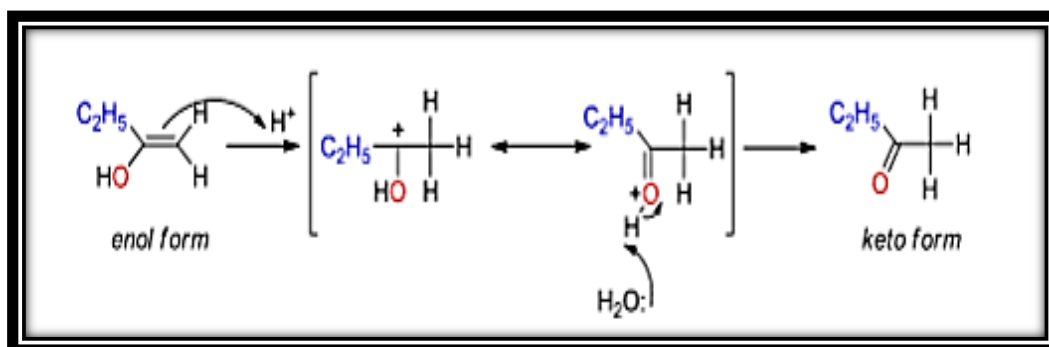


Hydration of Alkynes to Ketones and Aldehydes .

There are two different methods: Mercuric-ion catalyzed hydrations.

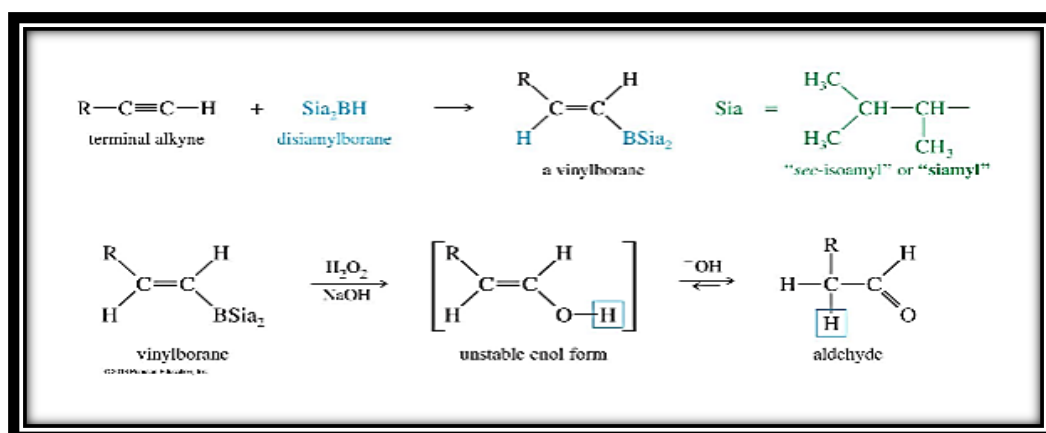
A mixture of mercuric sulfate and aqueous sulfuric acid is used to perform addition of water across the triple bond. The orientation is Markovnikov, and the initial products are enole .





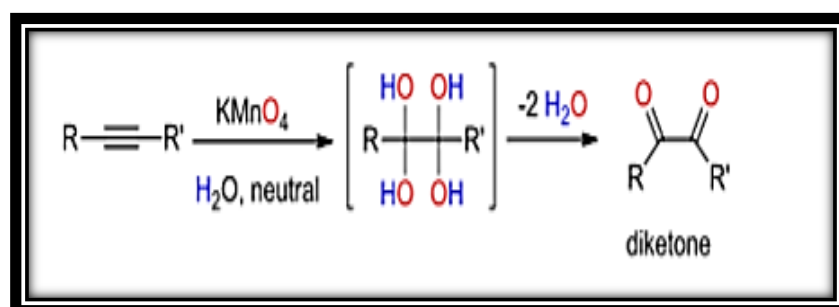
Hydroboration – Oxidation.

Terminal alkynes are converted into aldehyde.

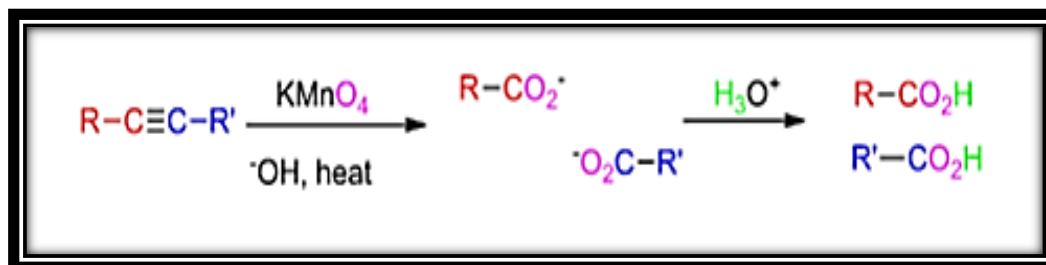


Oxidation of Alkynes.

Under mild (cold, neutral) conditions the reaction of potassium permanganate with an alkyne can generate a diketone.



If the mixture becomes too warm or basic, the oxidation proceeds further to generate two carboxylate anions, which on acidification generates two carboxylic acid .



Terminal alkynes are similarly cleaved to give a carboxylic acid and carbon dioxide



Ozonolysis

Ozonolysis of an alkyne followed by hydrolysis gives similar products to those obtained from permanganate oxidative cleavage , except terminal alkynes yield formic (methanoic) acid .

