



UNSATURATED HYDROCARBONS ALKYNES

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LEARNING OBJECTIVES

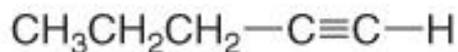
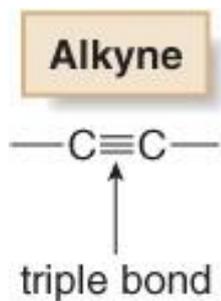
Chapter three discusses the following topics and the student by the end of this chapter will:

- Know the definition, structure, hybridization and bonding of Alkynes.
- Know the Nomenclature Of Alkynes (common and IUPAC).
- Know the physical properties of Alkynes.
- Know the general methods used for preparation of Alkynes.
- Know the addition reactions of Alkynes.
- Terminal and Internal Alkynes.
- Substituted groups from Alkynes; (Ethynyl)
- Acidity of terminal Alkynes.
- Bond Formation in Acetylene
- The comparative chart of bond length in aliphatic hydrocarbons

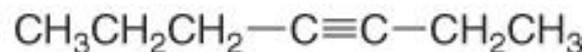


ALKYNES: MOLECULAR AND STRUCTURAL FORMULAE

- The alkynes Are the third class of simple hydrocarbons that contain at least one triple-bond between two carbon atoms.
- The general chemical formula of alkynes $C_n H_{2n-2}$
- The alkyne triple bond is composed of **one σ and two 2π covalent bonds**, the triple bond can be terminal or internal.



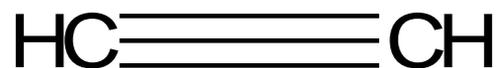
terminal alkyne



internal alkyne



The simplest alkyne, **ethyne** (also known as **acetylene**), has two carbon atoms and the molecular formula of C_2H_2 . The structural formula for ethyne is:

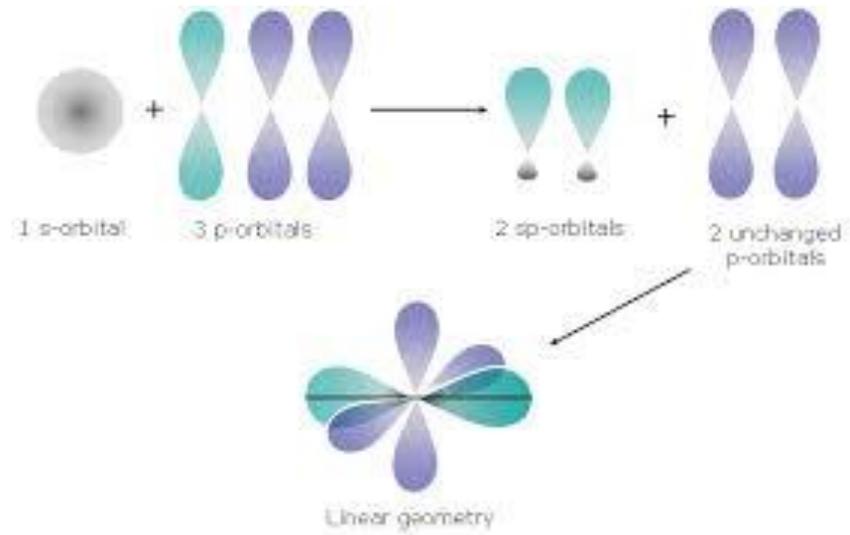
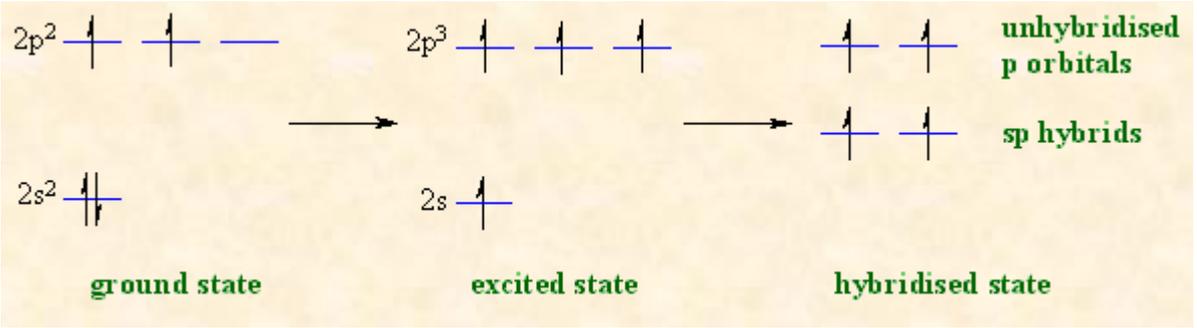


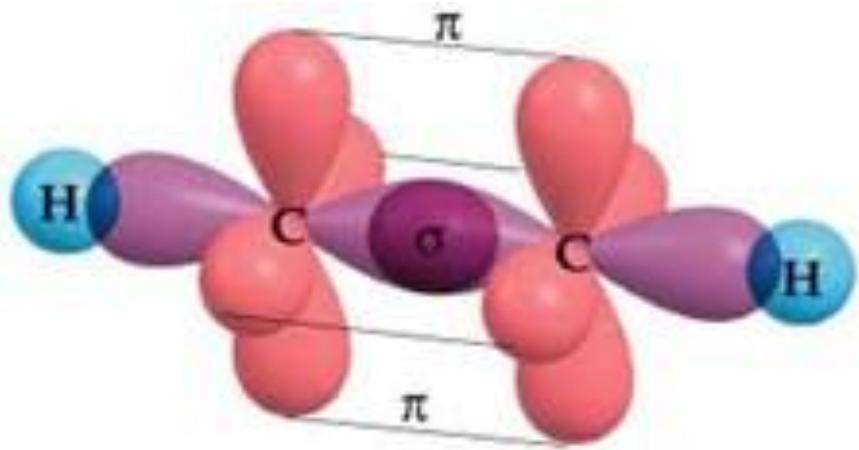
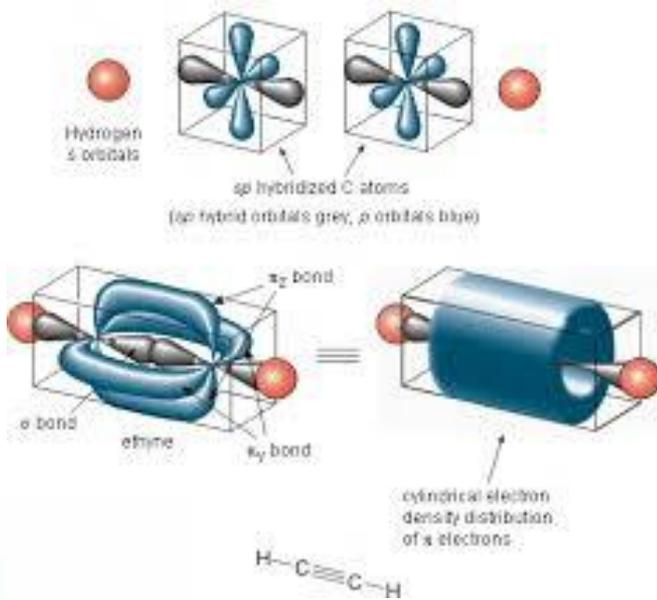
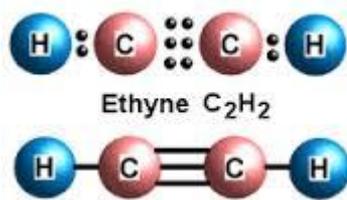
- Acetylene, the simplest alkyne is produced industrially from methane and steam at high temperature.
- Our study of alkynes provides an introduction to organic synthesis, the preparation of organic molecules from simpler organic molecules



HYBRIDIZATION OF ALKYNES

- This involves the mixing of one s- and one p-orbital forming two sp-hybrid orbitals of equivalent energy.
- Carbon-carbon triple bond result from sp orbital on each C forming a sigma bond and unhybridized px and py orbitals forming a π bond
- The two sp-hybrid orbitals are oriented in a linear arrangement and bond angle is 180° to minimize the repulsion between them.
- The bond is shorter and stronger than single or double





Geometry (shape) of ethyne molecule is **linear** in which bond angles are 180°



SUMMARY

- **sp** hybridization occurs when a C has 2 sigma bonds only
- **sp** hybridized orbital has 50% s and 50% p character
- The 2 **sp** hybrids point in opposite directions at 180° to each other
- Each **sp** hybrid is involved in a (σ) sigma bond
- The remaining **p** orbitals form the 2pi bonds
- The triple bond is one (σ) bond and two pi (Π) bonds.



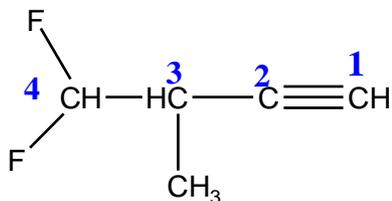
IUPAC NOMENCLATURE OF ALKYNES

- Find the longest chain containing both atoms of the triple bond; this gives the root name.
- Add the ending *-yne* to the root name.
- Number the chain, starting at the end closest to the triple bond.
- Give branches or other substituents names and numbers to locate their positions.
- Indicate the number of identical groups by prefixes di, tri, tetra, etc.
- Place the position numbers and names of the substituent groups in alphabetical order, before the root name. In alphabetizing ignore prefixes like *tert.*, di, tri, etc. but include iso and cyclo.
- Double** and **triple** bonds are considered to **have equal priority**: thus in a molecule with both a double and triple bond, whichever is close to the end of the chain determines the direction of numbering.
- In case where double and triple bonds would have the **same position number**, the **double bond takes the lower number**.
- In writing the final name **“ene” comes before “yne”** regardless which takes the lower number (i.e. alphabetical order).

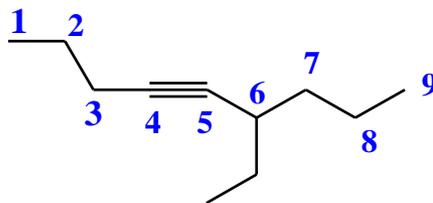


EXAMPLES

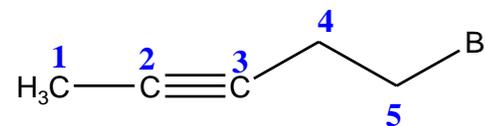
IUPAC NAMES OF ALKYNES



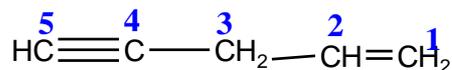
4,4-Difluoro-3-methyl-1-butyne



6-Ethyl-4-nonyne

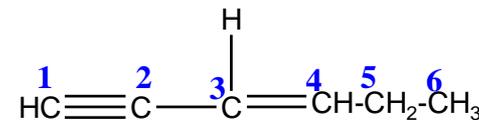


5-Bromo-2-pentyne
Not 1-Bromo-3-pentyne



Pent-1-en-4-yne

double and triple bonds have the same position number
thus ene take lower number



Hex-3-en-1-yne

(triple bond closer to the end of chain)
Note: An "e" is dropped from "ene"
due to it is followed by a vowel

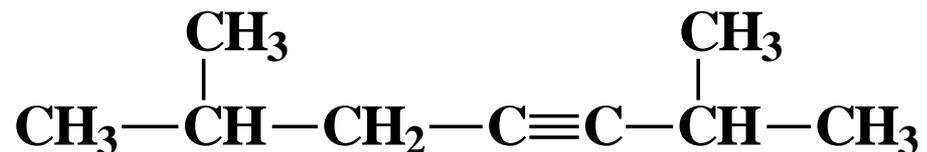


COMMON NOMENCLATURE OF ALKYNES

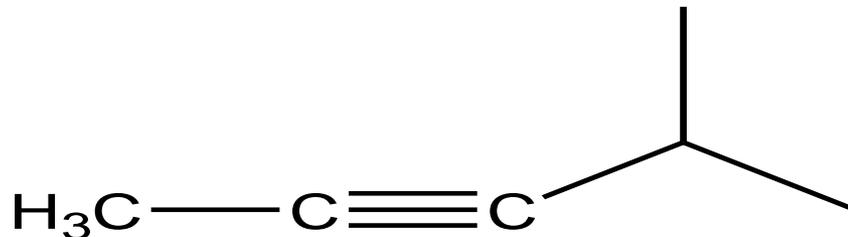
- The simplest alkyne its common name is **acetylene**
- Therefore the common names of alkynes are derived from acetylene (e.g. Methyl acetylene)
- **Examples:**



Common : Methyl acetylene



Common : Isobutyisopropylacetylene



Common: Isopropylmethylacetylene



PHYSICAL PROPERTIES

◉ physical states

Up to 4 carbons, gas at room temperature.

◉ Solubility

Nonpolar, insoluble in water.

Soluble in most organic solvents.

◉ Boiling point

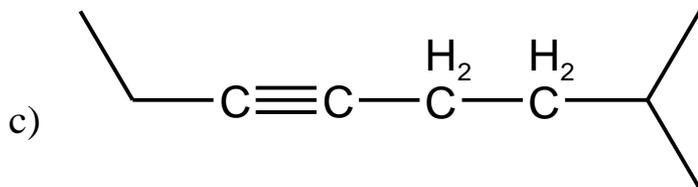
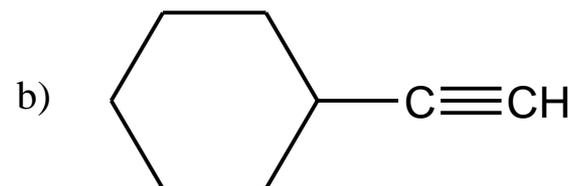
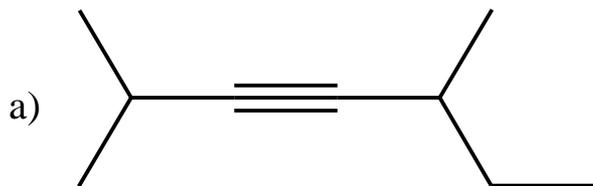
Boiling points similar to alkane of same size and **increase** with **molecular weight**.

Branching reduces the boiling point of alkynes



□ acidity

Terminal alkynes, $R-C\equiv C-H$, are more acidic than other hydrocarbons.

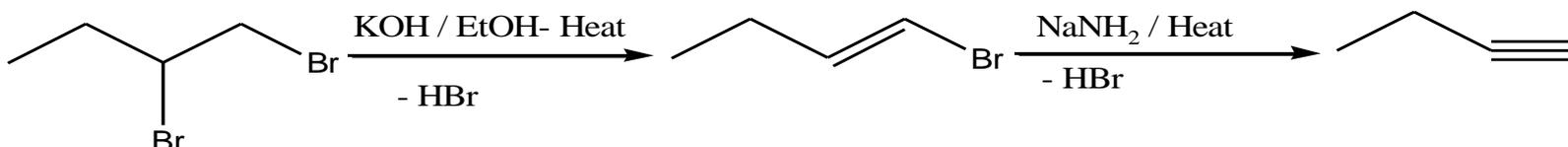
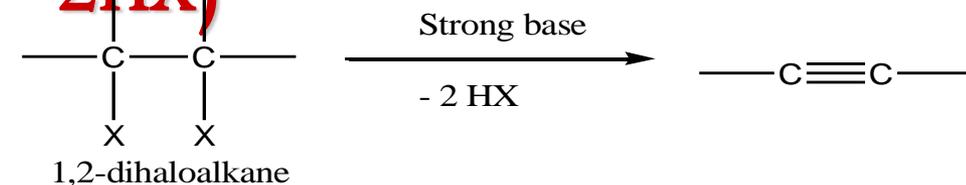




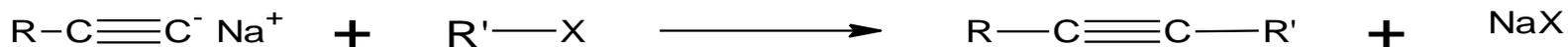
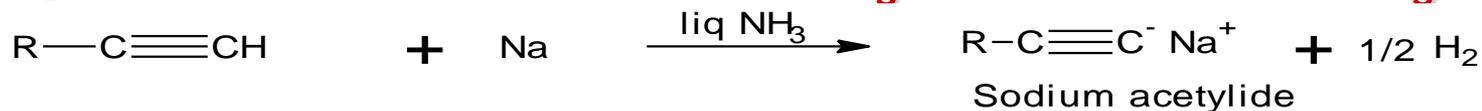
PREPARATION OF ALKYNES

1. Dehydrohalogenation of dihaloalkanes (-

2HX)



2. Reaction of sodium Acetylide with Primary





ELECTROPHILIC ADDITION REACTION

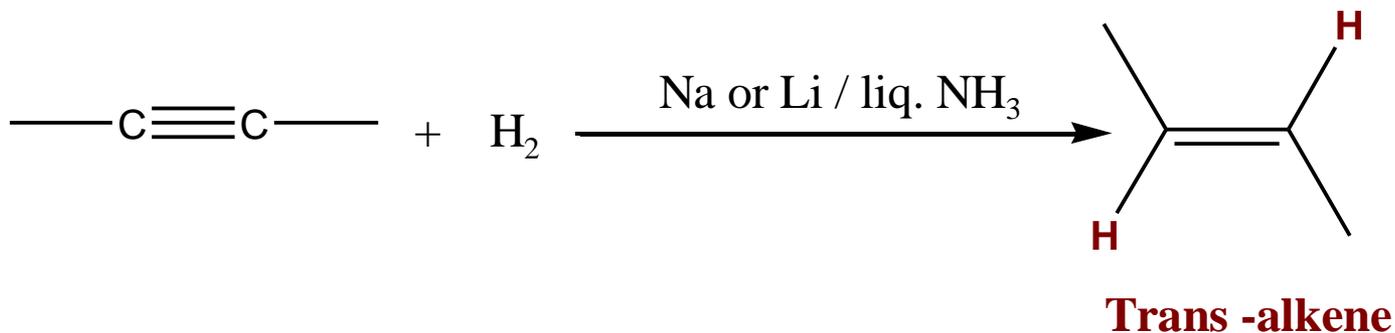
REACTIONS OF ALKYNES

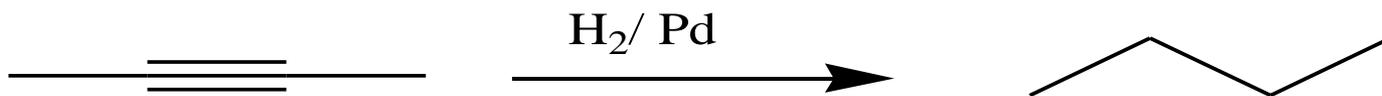
1. ADDITION OF HYDROGEN (HYDROGENATION)

- Alkynes can be partially reduced to *cis*-alkenes with H_2 in the presence of *poisoned catalysts*.

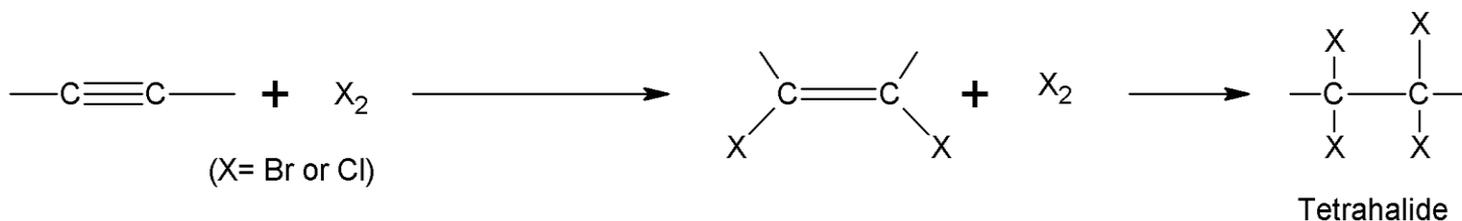


- Alkynes can be reduced to *trans*-alkenes using Na or Li in liquid NH_3

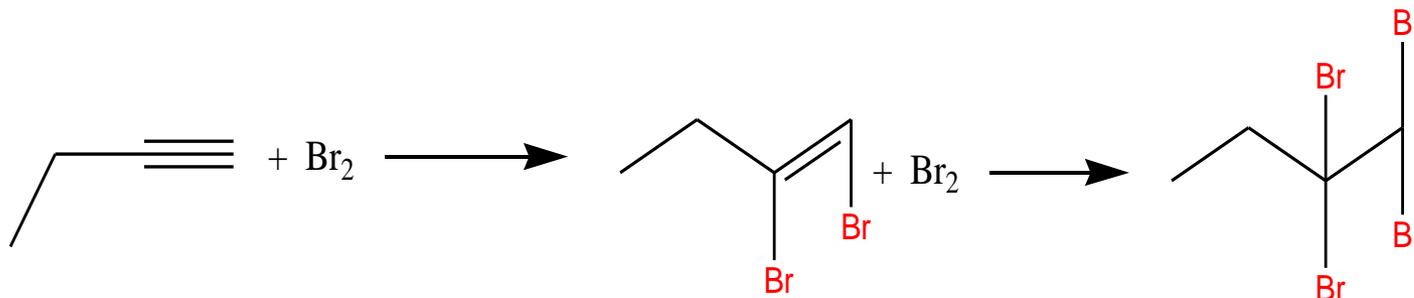




2. ADDITION OF HALOGEN (HALOGENATION)

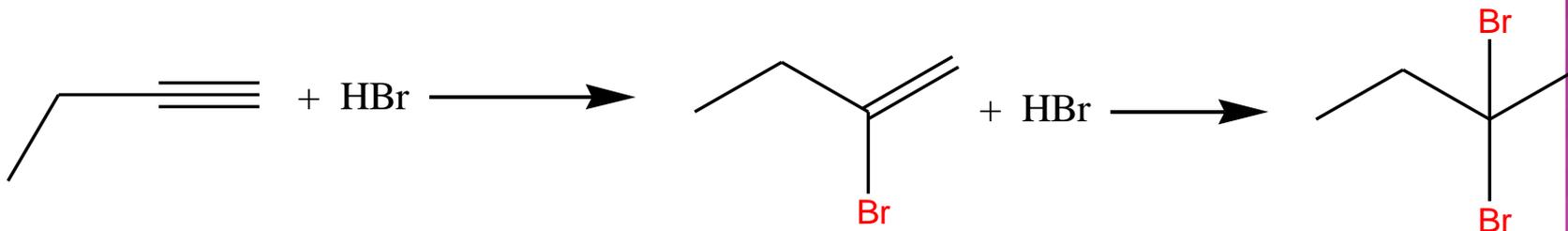
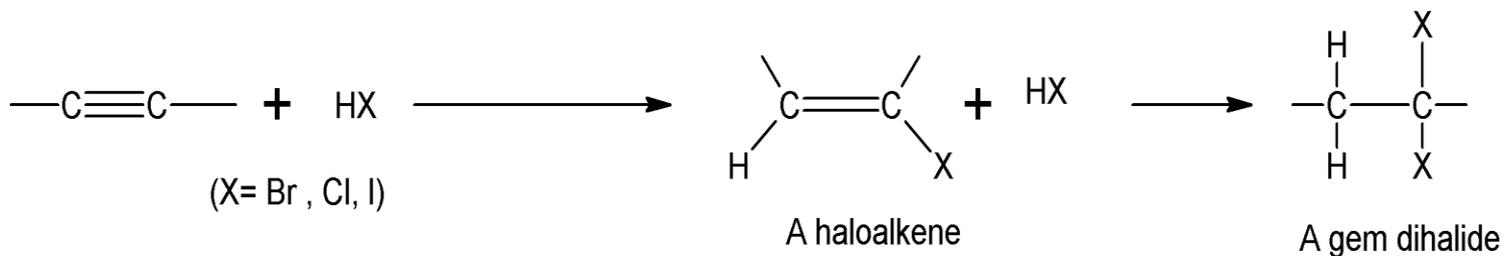


If we used one mole(alkene) two molealkane



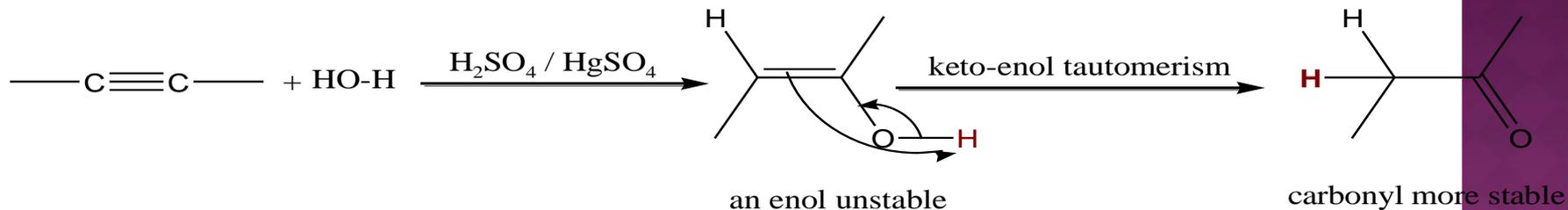


3. ADDITION OF HYDROGEN HALIDE

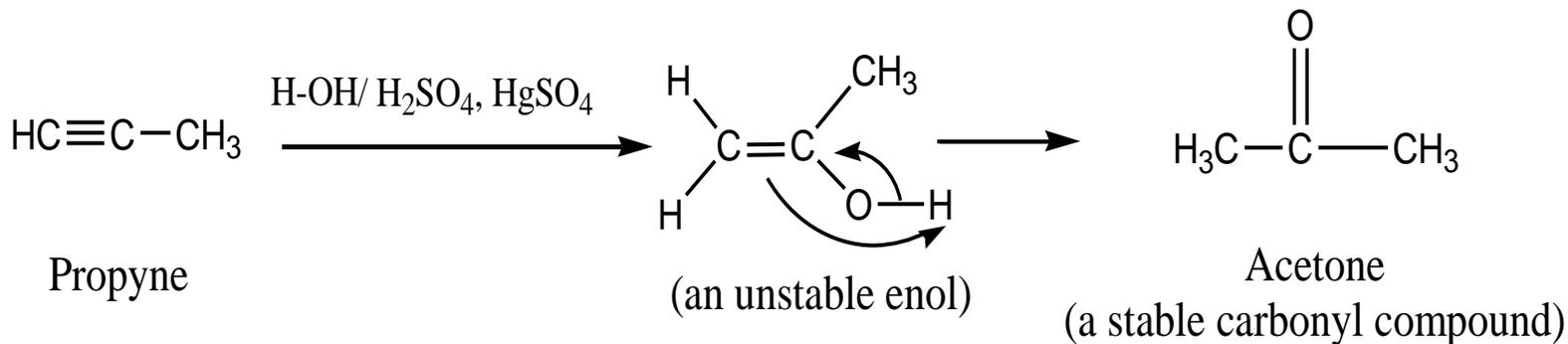
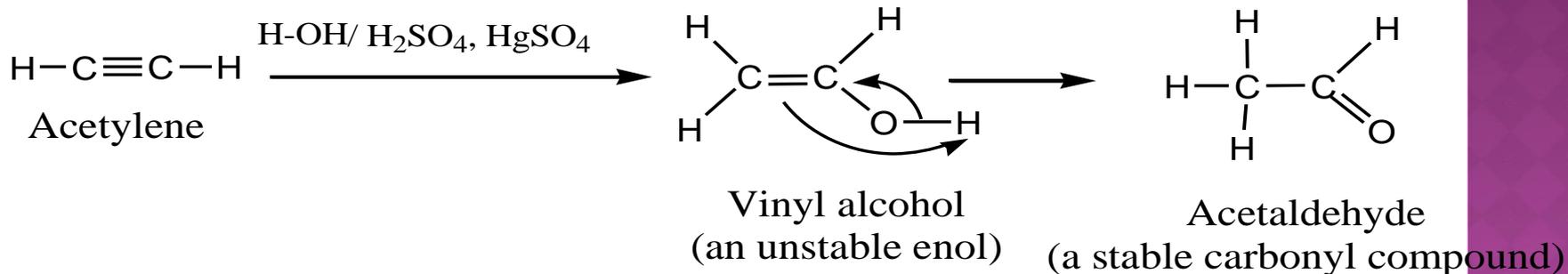




4. ADDITION OF WATER: HYDRATION



Specific example:





DIYNES, ENYNES AND TRIYENE

- A compound with two double bonds is a diyne
- An enyne has a double bond and triple bond
- A triene has three double bonds
- Systems with many $C=C$ can be referred to as "*polyenes*"
- A triyne has three triple bonds (alkyne)
- Number from chain that ends nearest a double or triple bond – double bonds preferred if both are present in the same relative position

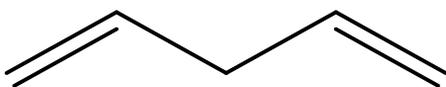


CLASSES OF DIENES

- ◉ Conjugated dienes are dienes which have at least two double bonds separated by a single carbon-carbon bond, and for this reason conjugated dienes are observed to have a special stability due to the overlap of electron orbitals. ($R-C=C-C=C-R$)
- ◉ Isolated dienes are The double bond units occur separately. The π systems are isolated from each other by sp^3 hybridized centers. ($R'-C=C-R-C=C-R'$)



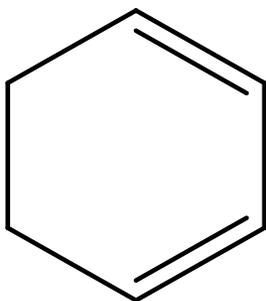
Cumulated dienes are The double bond units share a common sp hybridized C atom. The result is that cumulated dienes have reactivity more like simple alkynes. (*Allenenes*) ($R-C=C=C-R$)



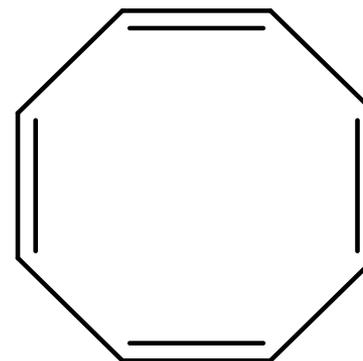
1,4-Pentadiene (non conjugated)



1,3-Hexadiene (conjugated)



1,3- Cyclohexadiene (conjugated)

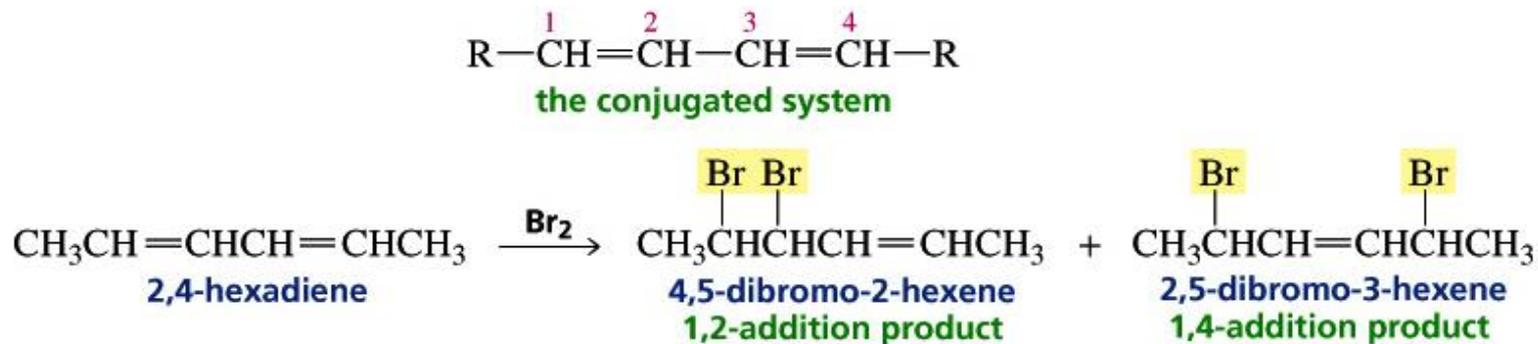


1,3,5,7-Cyclooctatetraene (conjugated)



ELECTROPHILIC ADDITION REACTIONS OF CONJUGATED DIENES

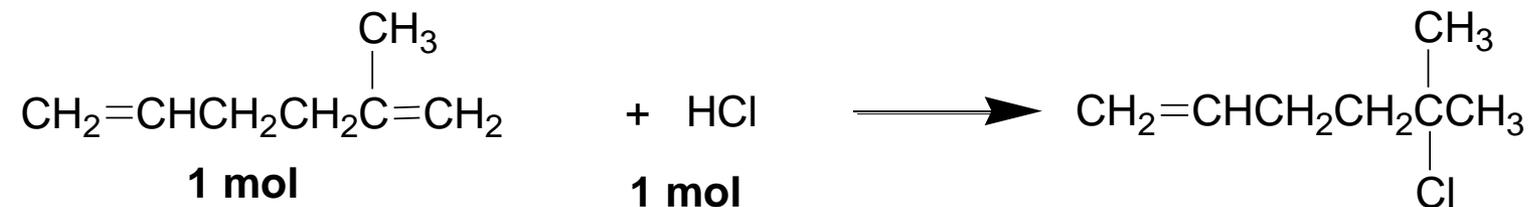
Conjugated dienes can give both 1,2- and 1,4- addition products + Markovnikov's Rule is followed





ELECTROPHILIC ADDITION REACTIONS OF ISOLATED DIENES

◉ Markovnikov's Rule is followed

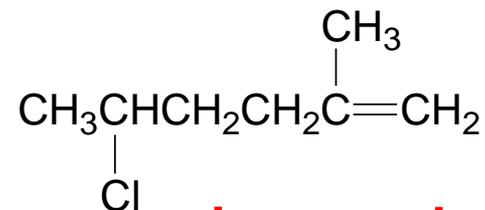


2-methyl-1,5-hexadiene

5-chloro-5-methyl-1-hexene

major product

+



minor product

5-chloro-2-methyl-1-hexene



Thank You for your kind
attention !

Questions?