

CHAPTER FOUR: ALKYNES

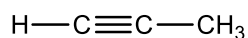
- Alkynes are hydrocarbons that contain carbon – carbon triple bond.
- They have a general formula of C_nH_{2n-2}

Nomenclature

- The IUPAC nomenclature for alkynes is similar to that for alkenes.
- Find the longest continuous chain of carbon atoms that includes the triple bond and change the -ane ending of the parent alkane to -yne.
- The chain is numbered from the end closest to the triple bond, and the position of the triple bond is designated by its lower numbered carbon atom.
- Substituents are given numbers to indicate their locations.



Ethyne /Acetylene

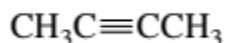


Propyne



1-Butyne

But-1-yne



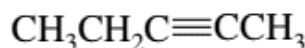
2-Butyne

But-2-yne



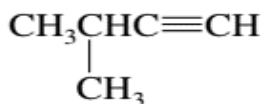
1-Pentyne

Pent-1-yne



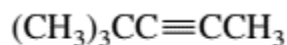
2-Pentyne

Pent-2-yne

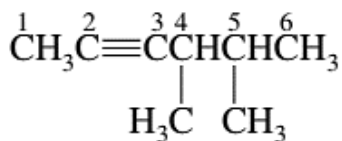


3-Methyl-1-butyne

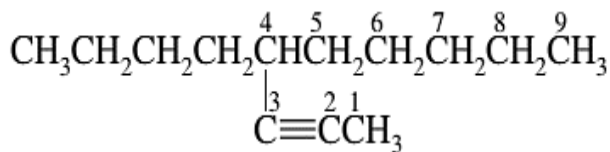
3-Methylbut-1-yne



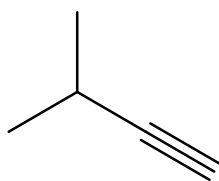
4,4-Dimethyl-2-pentyne



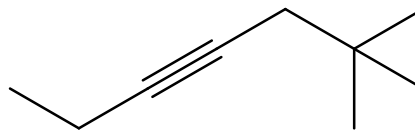
4,5-dimethylhex-2-yne



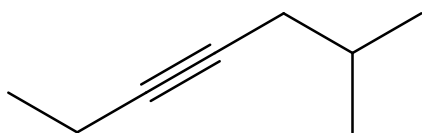
4-Butylnon-2-yne



3-methylbut-1-yne



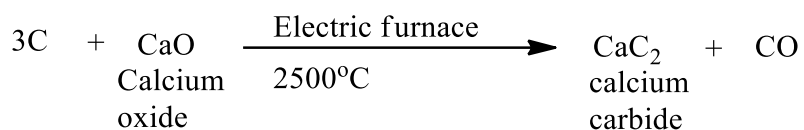
6,6-dimethylhept-3-yne



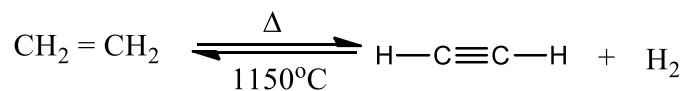
6-methylhept-3-yne

Preparation of Alkynes

1. Addition of water to calcium carbide

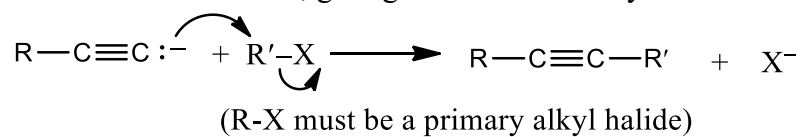


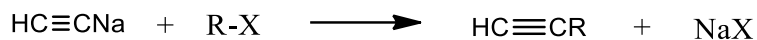
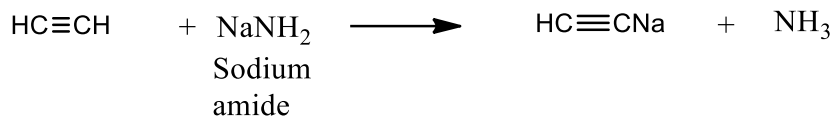
2. Dehydrogenation of ethene



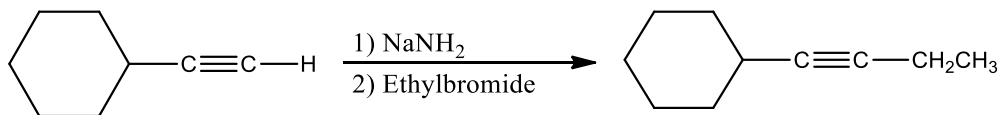
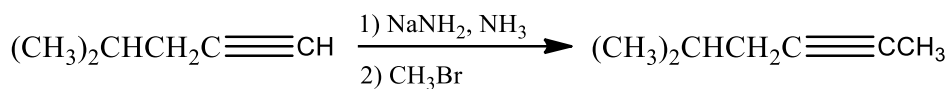
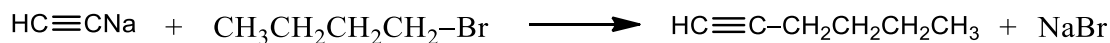
3. Alkylation of acetylene (ethyne) and terminal alkynes

- An acetylide ion is a strong base and powerful nucleophile. It can displace a halide ion from a suitable substrate, giving a substituted acetylene.



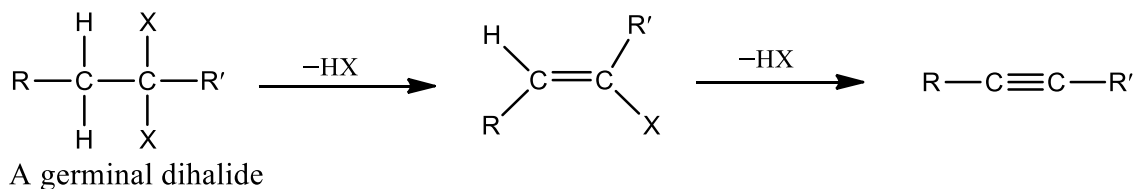
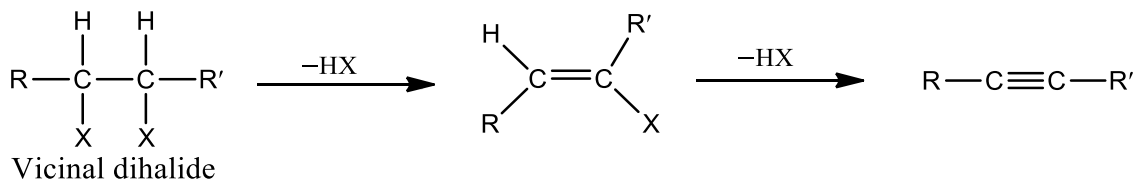


e.g

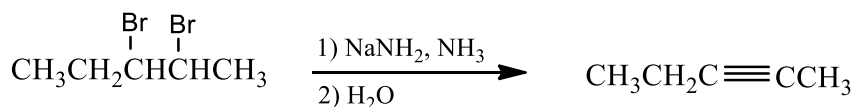


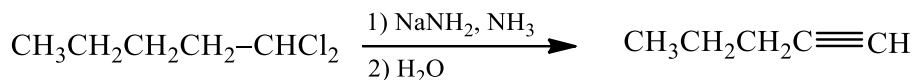
4. Elimination Reactions

- In some cases, we can generate a carbon – carbon triple bond by eliminating two molecules of HX from a dihalide.
- Dehydrohalogenation of a geminal or vicinal dihalides gives a vinyl halide. Under strongly basic conditions, a second dehydrohalogenation may occur to form an alkyne.



e.g.,



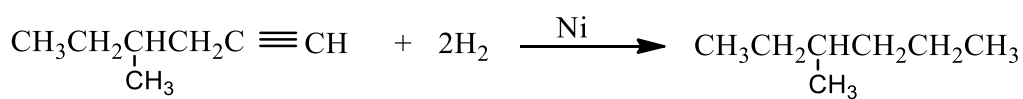
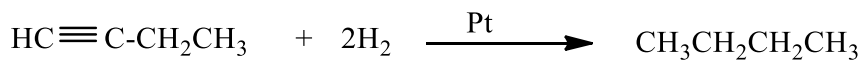
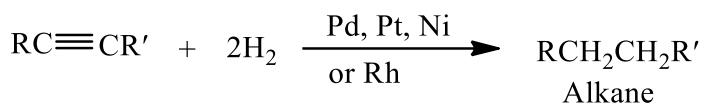


REACTION OF ALKYNES

1. Addition reactions

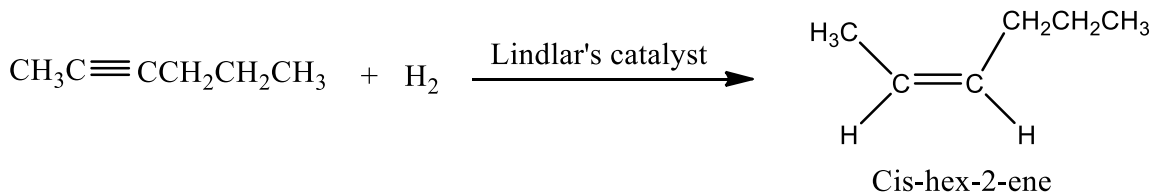
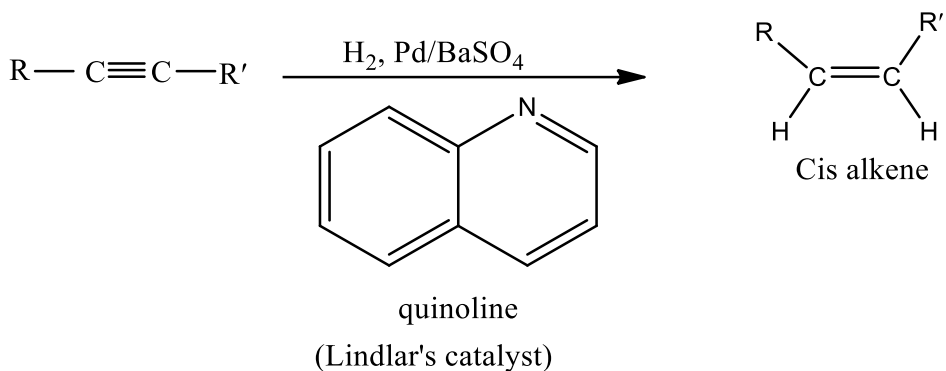
i) Hydrogenation

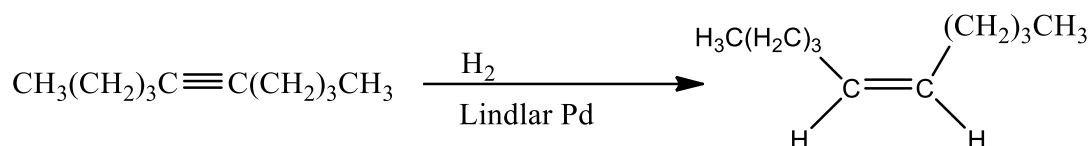
a) Using H₂ and an active metal (Pt, Rh, Pd, Ni)



b) Using Lindlar Catalyst

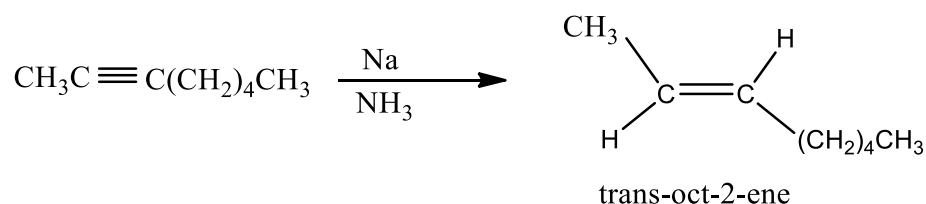
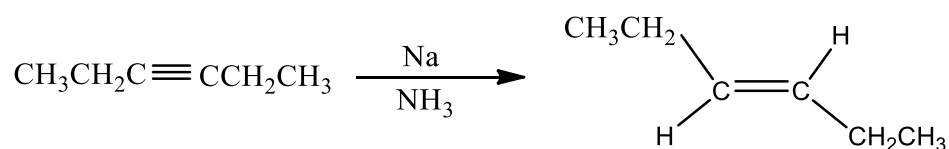
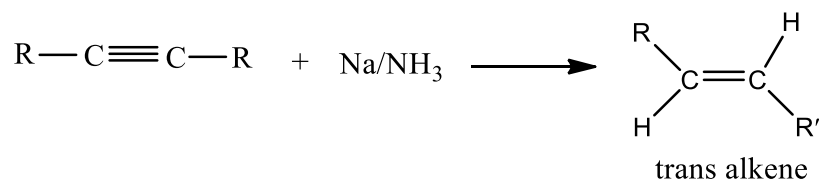
- Hydrogenation of an alkyne can be stopped at the alkene stage by using a “poisoned” (partially deactivated) catalyst made by treating a good catalyst with a compound that makes the catalyst less effective.
- Lindlar’s catalyst - poisoned palladium catalyst, composed of powdered BaSO₄ coated with palladium, poisoned with quinoline.
- In an internal alkyne, syn addition gives a cis product (Z).





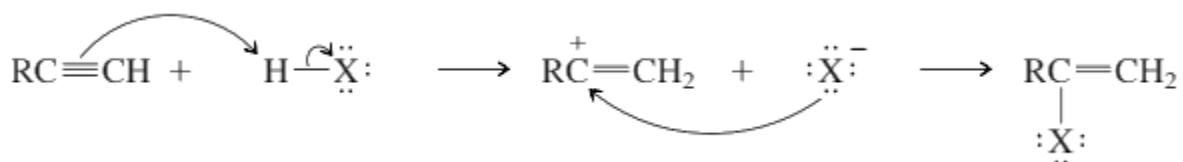
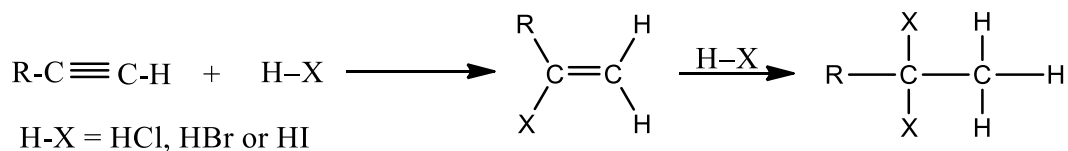
c) Metal – ammonia reduction to trans alkenes.

- A useful alternative to catalytic partial hydrogenation for converting alkynes to alkenes is reduction by a group 1 metal (Lithium, Sodium or Potassium) in liquid ammonia.

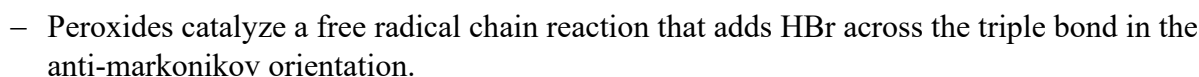
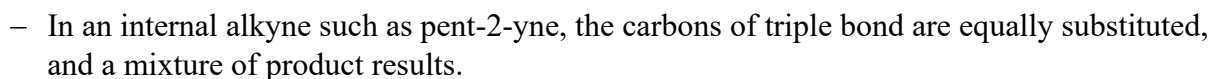


ii) Addition of hydrogen halides

- Follows markonikov's orientation.

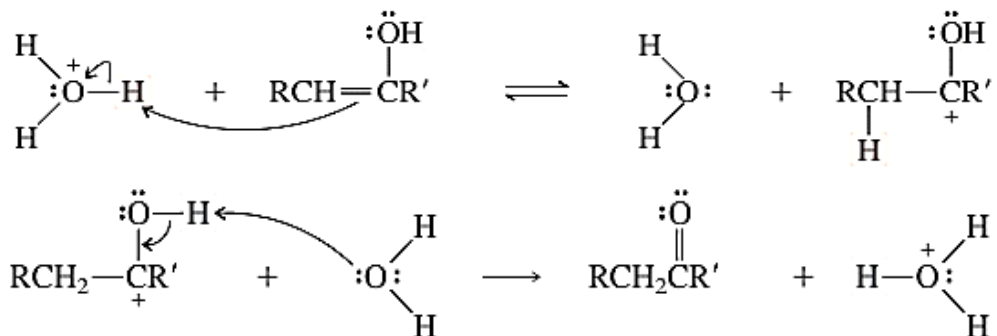


- The reaction of pent-1-yne with HBr gives the Markonikov product.

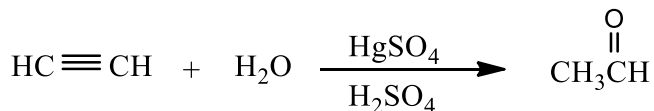


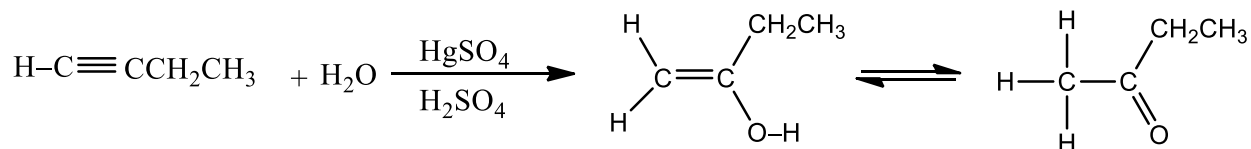
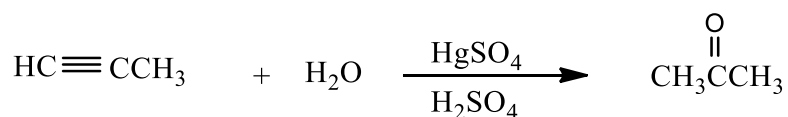
a) Acid-catalyzed addition of water

- Alkynes undergo acid-catalyzed addition of water across the triple bond in the presence of mercuric ion as a catalyst.
- A mixture of mercuric sulphate in aqueous sulfuric acid is commonly used as a reagent.
- Markonikov orientation.



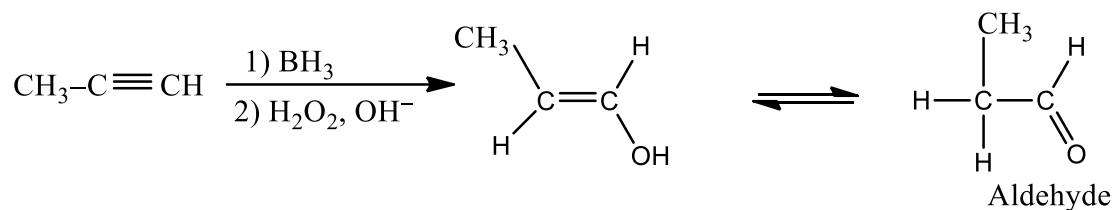
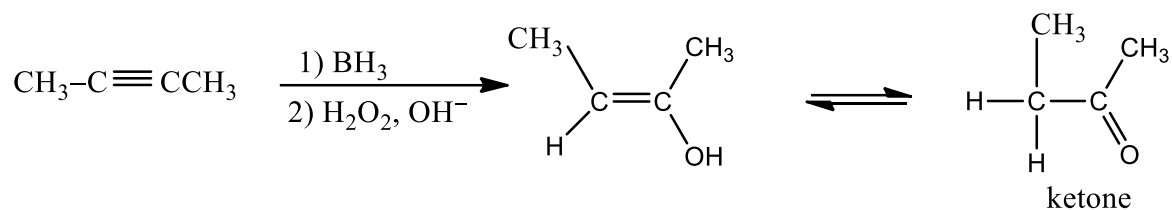
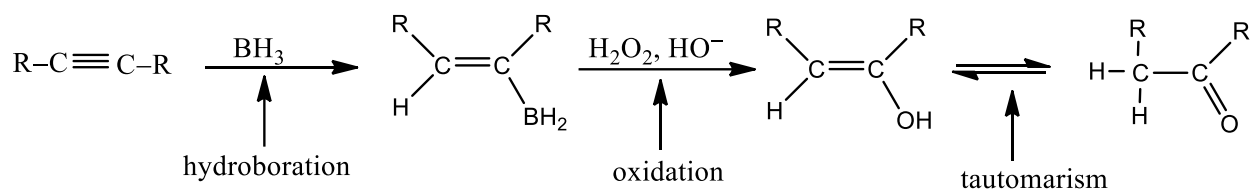
e.g





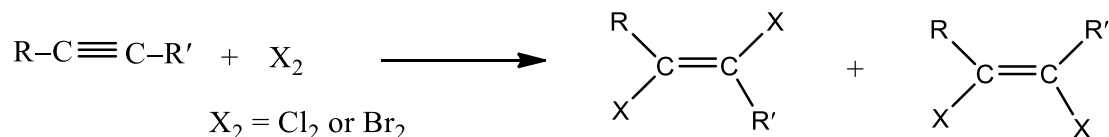
b) Hydroboration – Oxidation

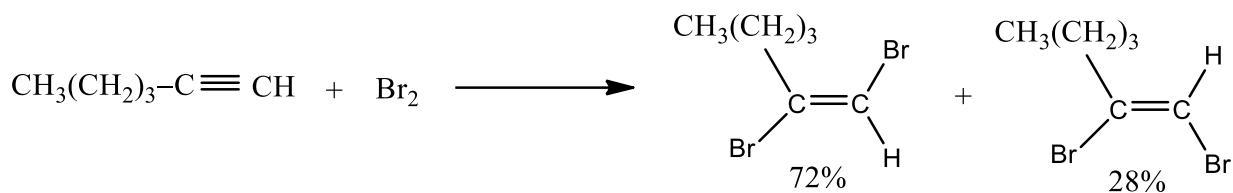
- Hydroboration-oxidation is a two-step reaction sequence that converts an alkyne to a carbonyl compound.
- Anti – markonikov addition.



iv) Addition of Halogens

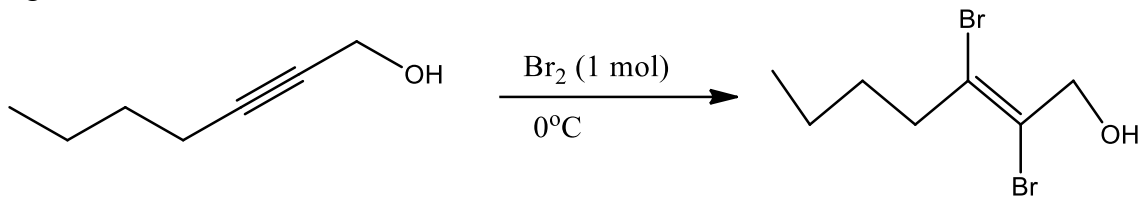
- Bromine and chlorine add to alkyne just as they add to alkenes.
- The addition may either be syn or anti, and the products are often mixture of cis and trans isomers.





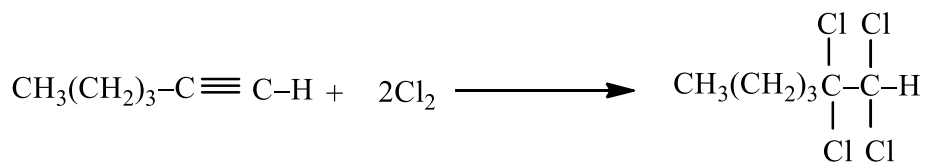
- It is usually possible to prepare a dihaloalkene by simply adding one molar equivalent of the halogen.

e.g



- Addition of one molar equivalent of chlorine or bromine to an alkyne generally results in anti-addition and yields a trans-dihaloalkene.
- If 2 moles of halogen add to 1 mole of an alkyne, a tetrahalide results.

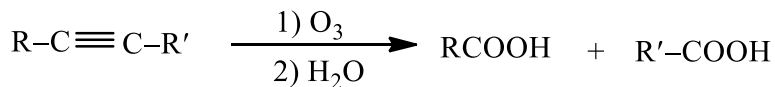
e.g



Oxidative Cleavage of Alkynes

Ozonolysis

- Ozonolysis of an alkyne followed by hydrolysis cleaves the triple bond and gives two carboxylic acids.



e.g

