

BOOKS

- 1) Organic Chemistry Structure and Function, K. Peter C. Vollhardt, Neil Schore, 6th Edition
- 2) Organic Chemistry, T. W. Graham Solomons, Craig B. Fryhle
- 3) Organic Chemistry: A Short Course, H. Hart, L. E. Craine, D. J. Hart, C. M. Hadad,
- 4) Organic Chemistry: A Brief Course, R. C. Atkins, F.A. Carey

4. ALKYNES

4.1 Synthesis of Alkynes

4.1.1 Elimination of Dihaloalkanes

4.1.2 Elimination of Tetrahaloalkanes

4.1.3 Alkynes by Alkylation of Acetylene and Terminal Alkynes

4.2 Reactions of Alkynes

4.2.1 Combustion Reactions

4.2.2 Hydrogenation

4.2.3 Halogenation

4.2.4 Hydro halogenation

4.2.5 Anti Markovnikov Addition of HBr

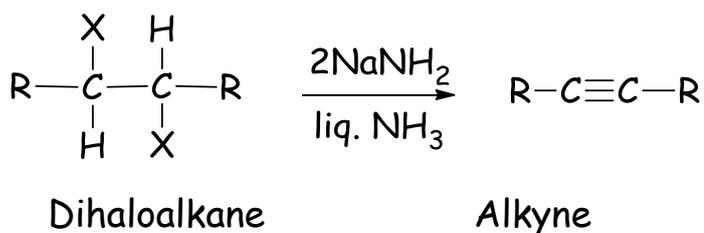
4.2.6 Hydration

Alkynes are organic molecules made of the functional group carbon-carbon triple bonds and molecular formula is C_nH_{2n-2} . Alkynes are unsaturated hydrocarbons. There are two types of alkynes: terminal and internal.

4.1 Synthesis of Alkynes

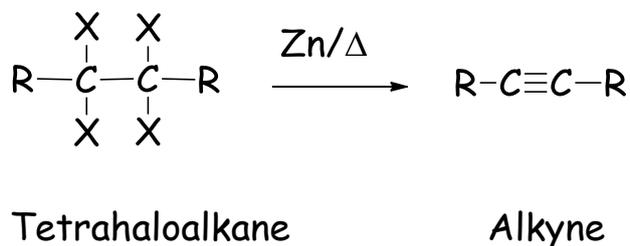
4.1.1. Elimination of Dihaloalkanes

One simple method for alkyne synthesis is by double elimination from a dihaloalkane. The majority of these reactions take place using sodium amide, $NaNH_2$ with high temperatures.



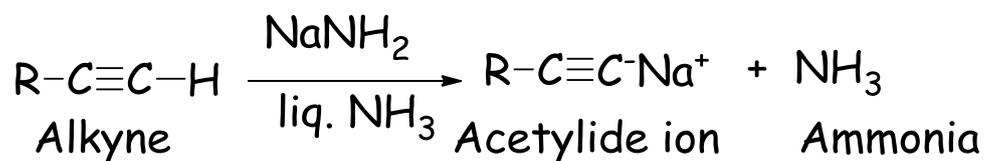
4.1.2 Elimination of Tetrahaloalkanes

A mechanism similar to above dehalogenation takes place with zinc metal.



4.1.3. Alkynes by Alkylation of Acetylene and Terminal Alkynes

Acetylide ions are strong nucleophiles and undergo nucleophilic substitution reactions with primary 1°alkyl halides to extend the chain.



4.2 Reactions of Alkynes

The principal reaction of the alkynes is addition to the triple bond to form alkanes. These addition reactions are analogous to those of the alkenes.

4.2.1 Combustion Reactions

Alkynes burn in presence of oxygen to produce carbon dioxide and heat.



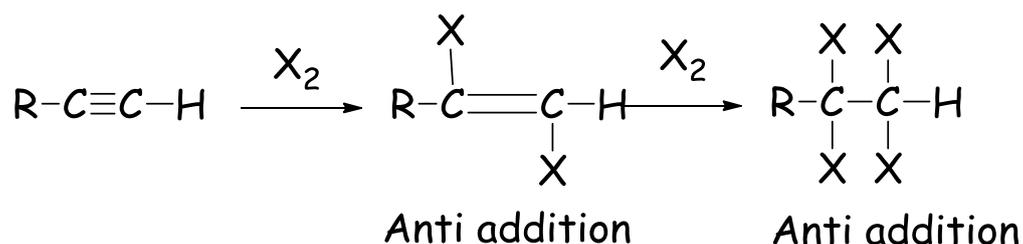
4.2.2 Hydrogenation

Alkynes undergo catalytic hydrogenation with the same catalysts used in alkene hydrogenation: platinum, palladium, or nickel. See the Section 3.4.4 (Hydrogenation of alkynes - reduction) for details.

4.2.3 Halogenation

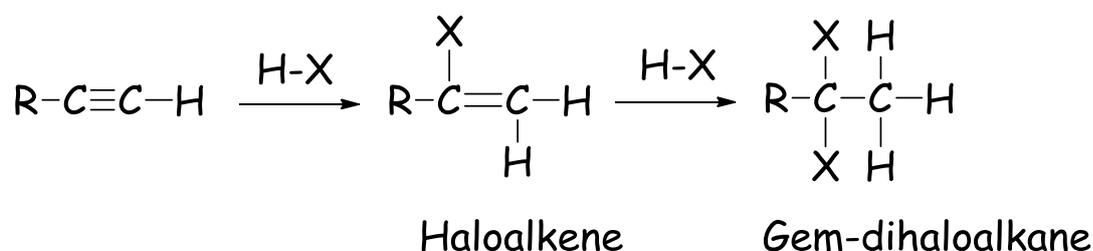
The addition of halogens to an alkyne proceeds in the same manner as halogen addition to alkenes. The halogen atoms add to an alkyne molecule, leading to the formation of the corresponding alkene, which undergoes further reaction to a tetrahaloalkane.

X :Cl, Br



4.2.4 Hydro halogenation

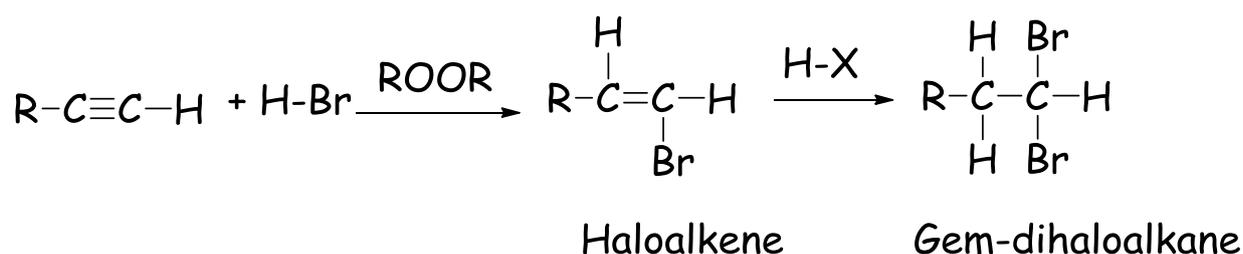
Hydrogen halides react with alkynes in the same manner as they do with alkenes. Both steps in the below addition follow the Markovnikov's rule.



HX: HCl, HBr or HI

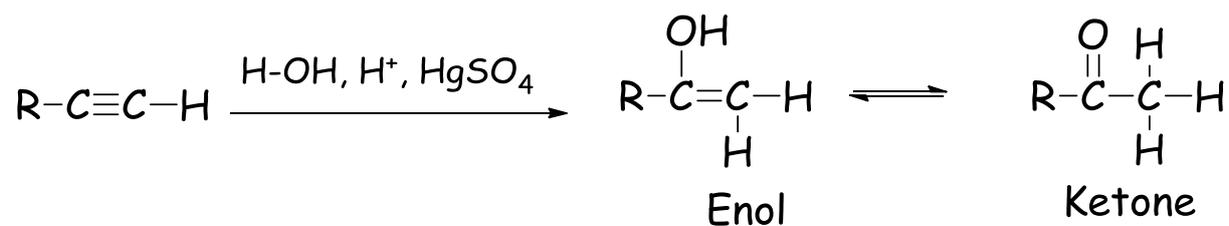
4.2.5 Anti Markovnikov Addition of HBr

The presence of the peroxides (radical mechanism) leads to the anti-Markovnikov addition. Br of the hydrogen bromide attaches to the less substituted 1-carbon of the terminal alkyne shown below and product form according to the anti-Markovnikov's rule.



4.2.6 Hydration

Hg (II) catalysed hydration of alkynes is similar to alkenes. With the addition of water, alkynes can be hydrated to form enols that spontaneously tautomerize to ketones. Reaction is catalysed by mercury ions and follows Markovnikov's rule.



Tautomerization is equilibrium between two tautomers, which differ by the migration of a proton and a π -bond. Keto-enol tautomerization normally favours the keto form ($\text{C}=\text{O}$).