Reaction List - Ch 13 Reactions of Alkynes

Formation of alkynes by substitution

alkyne must be deprotonated, then treated with an alkyl halide alkyl halide must be 1°, or E2 will interfere internal alkynes must be formed in 4 steps from acetylene

HC=CH
$$\frac{1. \text{ NaH or NaNH}_2}{2. \qquad \text{Br}:} \qquad alkyne$$

Formation of alkynes by elimination

vicinal or geminal dihalides can be used a much stronger base is needed for elimination of the vinyl halide if a terminal alkyne is formed, three equivalents of base and a second step of water are needed

Reduction of alkynes to alkanes

$$\xrightarrow{\text{H}_2}$$
 $\xrightarrow{\text{Pd/C}}$ alkane

Reduction of alkynes to cis alkenes

Lindlar catalyst contains Pd/BaSO₄, quinoline and/or lead acetate only way to make the cis alkene exclusively

Reduction of alkynes to trans alkenes

only way to make trans alkene exclusively

$$\frac{\text{Na}}{\text{NH}_3} \qquad \text{trans alkene}$$

Addition of HX to an alkyne

halogen goes to the more substituted side of an internal alkyne both halogens are added to the same carbon

Addition of X₂ to an alkyne

Br₂ and Cl₂ may be used different result depending on 1 or 2 equivalents used anti addition is observed

Acid and mercury catalyzed hydration of an alkyne

OH goes to more substituted side of an internal alkyne enol tautomerizes to a ketone

Hydroboration-oxidation of an alkyne

terminal alkynes require a sterically hindered borane such as disiamyl borane or dicyclohexyl borane OH goes to the less substituted side

OH goes to the less substituted side enol tautomerizes to a ketone or aldehydeC=O the OH (then C=O)

Permanganate oxidation of an alkyne

$$= \underbrace{\begin{array}{c} 2 \text{ eq KMnO}_4 \\ \text{H}_2\text{O} \end{array}}_{\text{HO}: \text{OH}} \underbrace{\begin{array}{c} \text{O:} \\ \text{O:} \\ \text{O:} \end{array}}_{\text{O:}} diketone$$

Oxidative cleavage of an alkyne