Summary of Reactions of Alkynes.

I. Structure and bonding
   A. sp-hybridization of carbons in triple bond
   B. 2 perpendicular \( \pi \) and 1 \( \sigma \) bonds
   C. relative stabilities
      1. disubstituted (interior or internal) > monosubstituted (terminal)

II. Nomenclature
   A. IUPAC system: alkyne (eg, \( t-C_2H_5C≡CH \) is 3,3-dimethyl-1-butyne)
   B. trivial: substituted acetylene (eg, \( t-C_4H_9C≡CH \) is \( t \)-butylacetylene)

III. Preparations of alkynes
   A. elimination reactions
      1. elimination of 2 HX from geminal, 1,1-dihaloalkanes: double dehydrohalogenation using very strong bases
         a. \( E_2 \) twice is usually mechanism
         b. must use strong base like \( \text{NaNH}_2 \)
         c. anti-elimination stereochemistry of \( E_2 \) is followed
         d. an intermediate haloalkene is generated; this alkene is the major product if bases weaker than \( \text{NaNH}_2 \) (eg, alkoxides) are used
      2. elimination of 2 HX from vicinal,1,2-dihaloalkanes: double dehydrohalogenation using very strong bases
         a. same comments as above
      3. alkylation of terminal alkynes
         a. \( C_{sp}^2-H \) bonds are quite short and relatively polarized so that the Hs are relatively acidic
            i. \( pK_a \) of acetylene is 26
            ii. terminal acetylenes can be deprotonated by very strong bases (eg, \( \text{NaNH}_2 \)) to form their conjugate bases which are called metal acetylides:

\[
\text{RC≡C} - \text{H} + \text{NaNH}_2 \rightarrow \text{RC≡C} - \text{Na}^+ + \text{NH}_3
\]

b. metal acetylides are nucleophiles and participate in \( S_N2 \) reactions:

\[
\text{RC≡C} - \text{Na}^+ + \text{R}^1-X \rightarrow \text{RC≡CR}^1 + \text{NaX}
\]

   i. \( \text{R}^1-X \) must be methyl or \(^1^\circ\) otherwise elimination predominates

IV. Reactions of alkynes
   A. addition reactions
      1. hydrogenation: addition of 1 mol \( \text{H}_2 \) to yield alkenes
         a. Lindlar's catalyst (\( \text{Pd on BaSO}_4 + \text{quoline} \)) and \( \text{H}_2 \)
            i. syn-addition stereochemistry yields 1-alkenes from terminal alkynes and (\( Z \))-alkenes from internal alkynes
         b. dissolving metal reduction: \( \text{Na in liquid NH}_3 \)
i. anti-addition stereochemistry yields 1-alkenes from terminal alkynes and (E)-alkenes from internal alkynes

2. double hydrogenation: addition of 2 mol of H₂ to yield alkanes
   a. noble metal catalyst + excess H₂

3. electrophilic additions (all by very similar mechanisms)
   a. hydrohalogenation: addition of HX to yield haloalkenes
      i. Markovnikov
      ii. anti-Markovnikov in presence of peroxides, light or heat
   b. double hydrohalogenation: addition of 2 HX to yield geminal dihaloalkanes
      i. Markovnikov
   c. hydration: addition of H₂O to yield aldehydes and ketones
      i. Markovnikov
         I. 50:50 H₂SO₄:H₂O₂, Hg²⁺ usually is added
         II. Mechanism is tricky, as it involves a rearrangement of the enol product to a thermodynamically more stable carbonyl-containing product
         III. Process is called tautomerization
      ii. anti-Markovnikov
         I. Borohydration-oxidation
   d. dihalogenation: addition of X₂ to yield dihaloalkanes
      i. halonium ion intermediate
      ii. anti-addition stereochemistry
   e. double dihalogenation: addition of 2 X₂ to yield tetrahaloalkanes
      i. halonium ion intermediate
      ii. anti-addition stereochemistry
      iii. mechanism is dihalogenation twice

4. electrophilic cleavage reactions
   a. ozonolysis: addition of ≥ O to yield formic acid and/or carboxylic acids

5. nucleophilic addition reactions
   a. conjugate bases of terminal alkynes are nucleophiles; see III. A. 3. above

V. Synthesis strategies: interconversions of single, double and triple bonds
   A. Additions
      1. C≡C → C≡C → C≡C
   B. Eliminations
      1. C≡C → C≡C