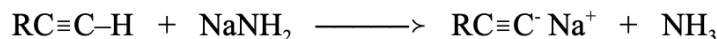
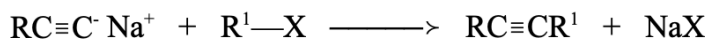


## Summary of Reactions of Alkynes.

- 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,  $t\text{-C}_4\text{H}_9\text{C}\equiv\text{CH}$  is 3,3-dimethyl-1-butyne)
  - B. trivial: substituted acetylene (eg,  $t\text{-C}_4\text{H}_9\text{C}\equiv\text{CH}$  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.  $\text{C}_{\text{sp}}\text{-H}$  bonds are quite short and relatively polarized so that the Hs are relatively acidic
        - i.  $\text{p}K_{\text{a}}$  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:



- b. metal acetylides are nucleophiles and participate in  $\text{S}_{\text{N}}2$  reactions:



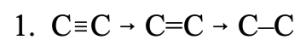
- i.  $\text{R}^1\text{-X}$  must be methyl or  $1^\circ$  otherwise elimination predominates

- 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  $\text{BaSO}_4$  + quinoline) 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  $\text{NH}_3$

- i. anti-addition stereochemistry yields 1-alkenes from terminal alkynes and (*E*)-alkenes from internal alkynes
  - 2. double hydrogenation: addition of 2 mol of H<sub>2</sub> to yield alkanes
    - a. noble metal catalyst + excess H<sub>2</sub>
  - 3. electrophilic additions (all by very similar mechanisms)
    - a. hydrohalogenation: addition of HX to yield haloalkenes
      - i. Markovnikov
      - ii. antiMarkovnikov in presence of peroxides, light or heat
    - b. double hydrohalogenation: addition of 2 HX to yield geminal dihaloalkanes
      - i. Markovnikov
    - c. hydration: addition of H<sub>2</sub>O to yield aldehydes and ketones
      - i. Markovnikov
        - I. 50:50 H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O; Hg<sup>+2</sup> 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. antiMarkovnikov
        - I. Borohydration-oxidation
    - d. dihalogenation: addition of X<sub>2</sub> to yield dihaloalkenes
      - i. halonium ion intermediate
      - ii. anti-addition stereochemistry
    - e. double dihalogenation: addition of 2 X<sub>2</sub> 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



B. Eliminations

