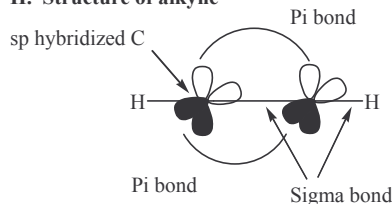


Summary of CH 13 Alkynes

I. Nomenclature

- Common name: acetylene
- IUPAC name: Alkane --> Alkyne
Alkane --> Alkenyne
Alkane --> Alkynol

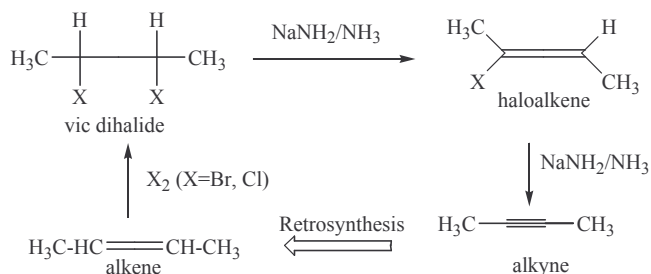
II. Structure of alkyne



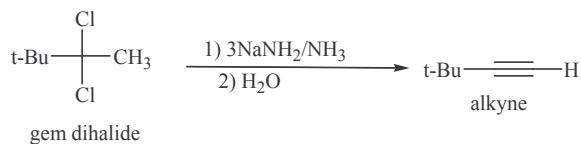
- $C\equiv C$ is viewed as consisting of one σ bond and two π bonds
- Linear geometry of $C\equiv C$ results from the two sp carbon atoms
- The terminal alkyne H is considerably acidic (pKa 25)
- Internal alkyne is more stable than terminal alkynes

III. Synthesis of alkynes by elimination reactions

- From vic dihalide

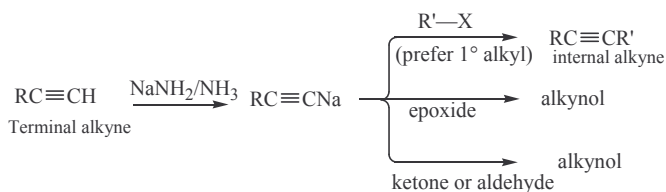


- Dehydrohalogenation requires strong bases and occurs in two steps of E2 reaction.
- Halogenation-dehydrohalogenation provides a synthesis of alkynes from alkenes.
- From gem dihalide



- Dehydrohalogenation requires strong bases and occurs in two steps of E2 reaction

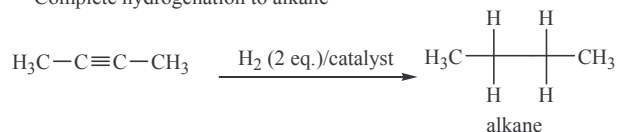
IV. Synthesis of alkynes by alkylation of terminal alkynes



- RC≡CNa acts as a nucleophile to react with electrophiles such as RX, epoxide, carbonyl compounds.

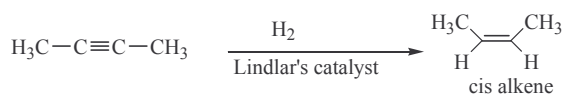
V. Reduction by catalytic hydrogenation

- Complete hydrogenation to alkane



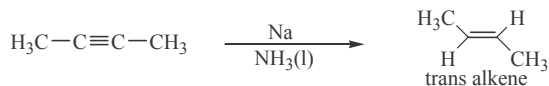
Catalysts: heterogeneous catalysts: Pt, Ni, Pd
homogenous catalyst: (Ph₃P)₃RhCl (Wilkinson's catalyst)

• Partial hydrogenation to cis alkene



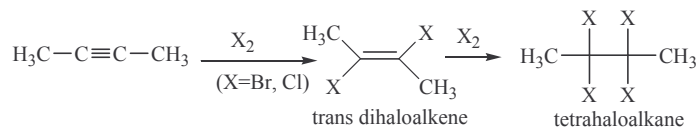
Lindlar's catalyst = 5% Pd-CaCO₃, Pb(CH₃CO₂)₂, quinoline,

VI. Reduction by dissolving metals



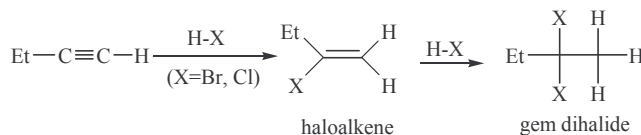
- Synthesis of trans alkenes from alkynes via a stepwise single electron transfer mechanism (complementary to partial catalytic hydrogenation)

VII. Addition of Br₂ or Cl₂

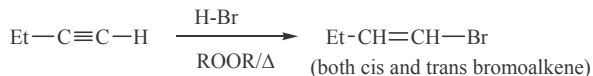


- Sequential addition of Br₂ or Cl₂ to C=C via a trans dihaloalkene intermediate.
- Partial addition to prepare trans dihaloalkenes from alkynes

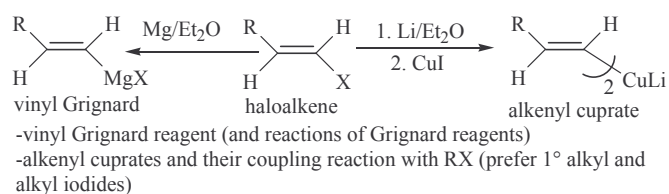
VIII. Addition of H-X



- Sequential addition of H-X to C=C via a haloalkene intermediate to yield a gem dihalide
- Partial addition to prepare haloalkenes from alkynes
- Regioselectivity: Markovnikov addition (i.e. more stable C⁺ intermediate)
- Anti Markovnikov addition can be accomplished via a radical mechanism

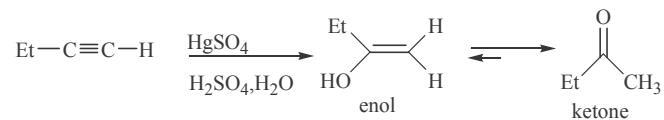


- Alkenyl organometallic reagents from haloalkenes



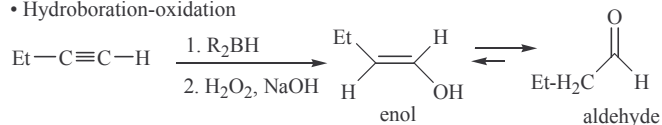
IX. Addition of H-OH

- Hg²⁺ - catalyzed hydration



- hydration of alkynes in H⁺/H₂O requires Hg²⁺ as catalyst
- regioselectivity: Markovnikov addition (i.e. more stable C⁺ intermediate)
- terminal alkynes give methyl ketones

- Hydroboration-oxidation



- regioselectivity: B adds to the less hindered C and hydroboration-oxidation sequence gives a net anti Markovnikov addition of H-OH
- terminal alkynes give aldehydes