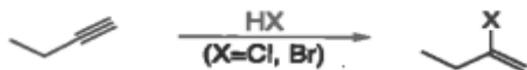




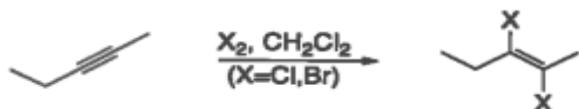
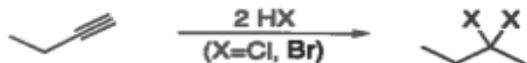
CHEM 2400/2410

Alkyne Reactions Summary Sheet

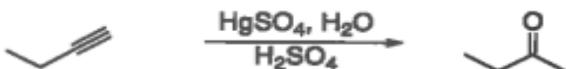
M. Pauly



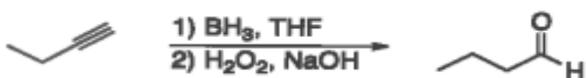
- > vinyl-carbocation-like intermediate
- > halogen adds to more substituted position – Markovnikov's rule
- > *trans* addition of H–X favored
- > form geminal dihalide with two equivalents of HX



- > vinyl-carbocation-like intermediate
- > *trans* addition of X–X favored
- > form tetrahalide with two equivalents of X₂



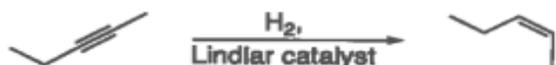
- > vinyl-carbocation intermediate initially
- > alcohol added to the more substituted position (if possible)
- > enol intermediate tautomerizes to ketone products



- > boron, then alcohol, added to less substituted position (if possible)
- > use (Sia)₂BH with terminal alkyne for better efficiency
- > aldehyde product with terminal alkyne - through enol intermediate
- > ketone product with internal alkyne - through enol intermediate



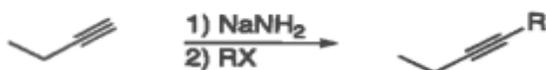
- > triple bond is cleaved, each carbon becomes a carboxylic acid
- > terminal alkynes will form CO₂ and a carboxylic acid,



- > alkene and alkyne hydrogenated by Pd/C, H₂
- > only alkyne hydrogenated with Lindlar catalyst, alkene not affected
- > *cis* addition of H–H to form *cis*-alkene product



- > only alkyne reduced, double bond not affected
- > *trans* addition of H to form *trans*-alkene product



- > other strong bases may be used
- > acetylide anion intermediate first
- > anion attacks R–X in S_N2 manner
- > R–X may be a primary alkyl bromide or iodide (not 2° or 3°)

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