

Chemistry 0310 - Organic Chemistry 1

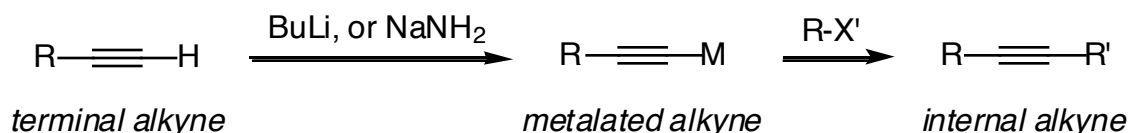
Chapter 13. Alkynes

Methods for preparation of alkynes:

- **Dehydrohalogenation** of vicinal dihalides with strong bases (NaNH_2). Vicinal dihalides can be obtained by dibromination of alkenes.

- **Dehydrohalogenation** of geminal dihalides with strong bases (NaNH_2). Geminal dihalides are obtained from ketones by treatment with PX_5 .

- A popular synthesis of alkynes applies **displacement reactions** ($\text{S}_{\text{N}}2$) of acetylides.



Reactions of alkynes:

- **Hg(II)-catalyzed hydration** provides ketones from terminal as well as internal alkynes.

- **Hydrogenation** (H_2 , catalyst) provides alkanes via twofold syn-addition of H_2 to the double bond. In the presence of poisoned catalysts (Lindlar, Ni_2B) the intermediate alkene can be isolated.

- Lindlar or Ni_2B hydrogenation of alkynes provides Z-alkenes via syn-addition.

- **Dissolving metal reduction** of alkynes with Li or Na in liquid amines provides E-alkenes via radical anions, radicals, and anions.

- **Addition of X_2** to alkynes occurs stepwise via (*E*)-1,2-dihaloalkenes to 1,1,2,2-tetrahaloalkanes. Addition of Br_2 in the absence of heat or light provides vicinal dibromides.

- **Addition of HX** to alkynes follows Markovnikov's rule to give vinyl halides and *geminal* dihaloalkanes.

- **Oxidative cleavage** of alkynes with O_3 or KMnO_4 results in carboxylic acids.