

Alkynes II

Reading: Wade chapter 9, sections 9-8 – 9-10

Study Problems: 9-32, 9-33, 9-34, 9-37, 9-38, 9-39

Key Concepts and Skills:

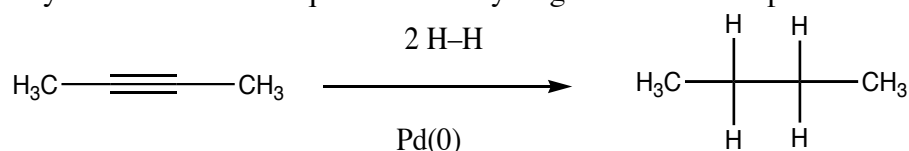
- Propose effective single- and multistep syntheses of alkynes
- Predict the products of additions, oxidations, reductions, and cleavages of alkynes, including regiochemistry and stereochemistry.

Lecture Topics:

I. Reduction of Alkynes

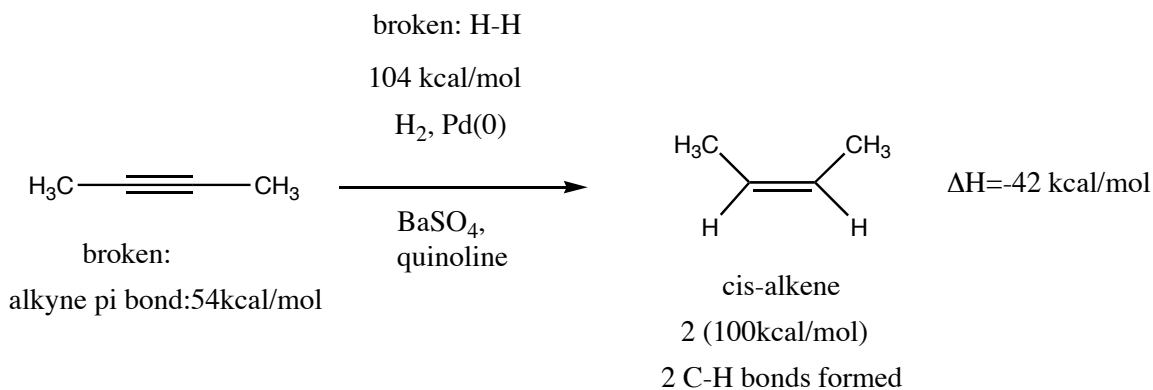
a. Hydrogenation

Treatment of an alkyne with hydrogen over palladium results in complete reduction to the alkane, via syn addition of two equivalents of hydrogen across the triple bond:



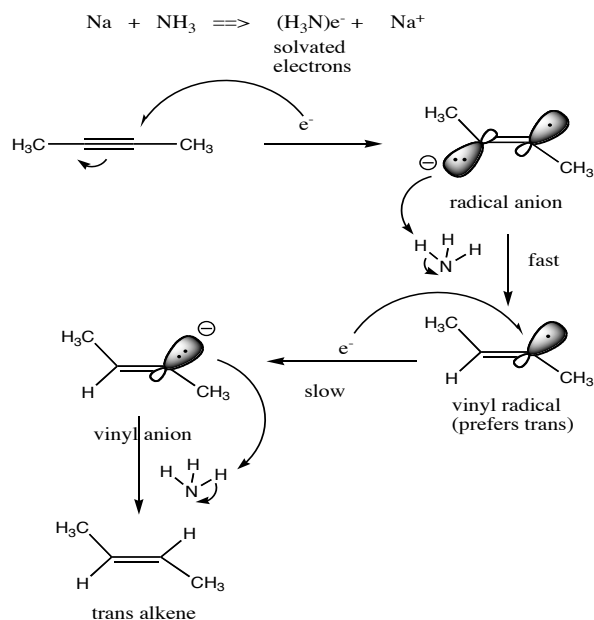
b. Lindlar reduction.

Treatment of an alkyne with a poisoned palladium catalyst known as Lindlar's catalyst (Pd(0), BaSO₄, quinoline) leads to formation of cis alkenes through addition of one equivalent of H₂ across the triple bond. The cis alkene formed cannot undergo further addition because of its steric size relative to the alkyne; the poisoned palladium catalyst will not accept the bulky alkene as a ligand



c. Alkali-Metal/ ammonia reduction

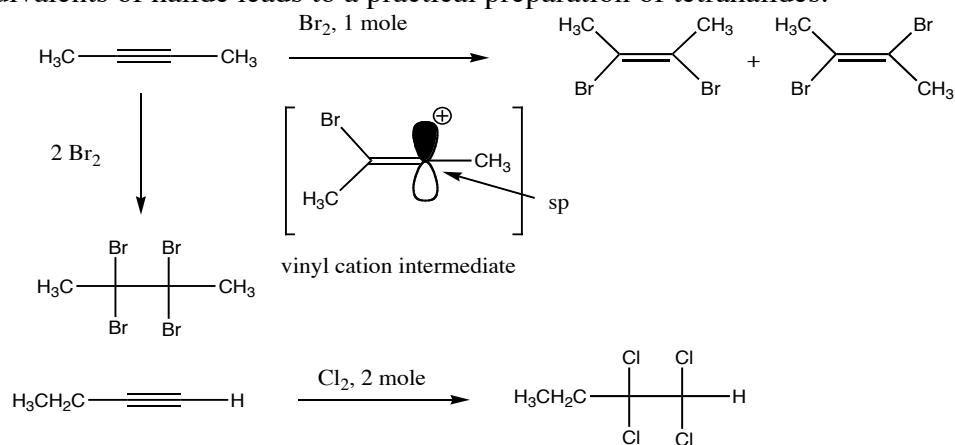
Alkynes are reduced to **trans alkenes** by treatment with lithium or sodium in ammonia. The alkali-metal ammonia complex is a deep blue solution of “solvated” electrons which add to the alkyne to give a radical anion and thence a vinyl radical after protonation. Note that the vinyl radical prefers the trans orientation of substituents at low temperatures, and thus trans stereochemistry is usually observed in the product alkenes.



II. Addition of X_2 and HX to alkynes

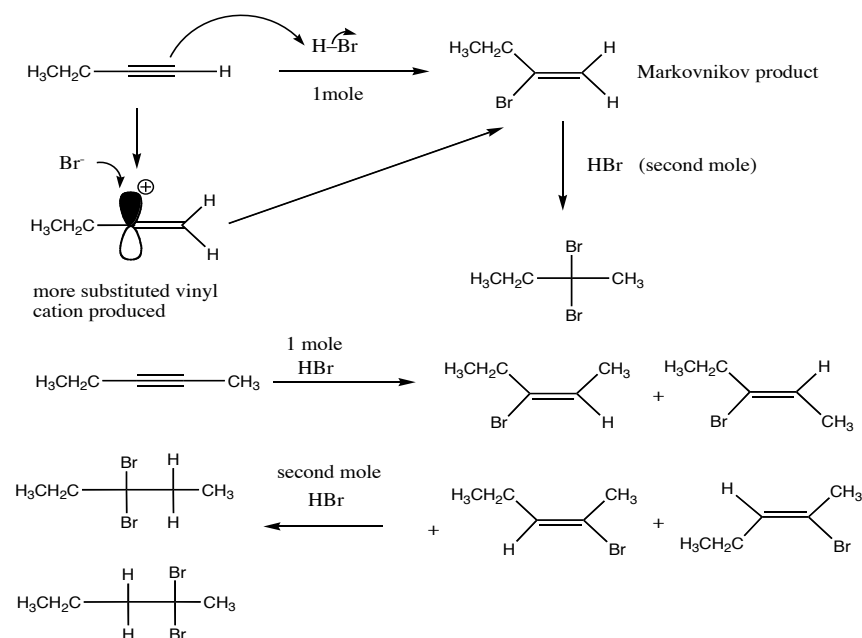
a. Addition of halogens, X_2

Addition of one equivalent of Br_2 or Cl_2 to an alkyne results in cis-trans mixtures of dihaloalkenes; a vinyl cation intermediate is postulated as giving rise to this result. Addition of two equivalents of halide leads to a practical preparation of tetrahalides:



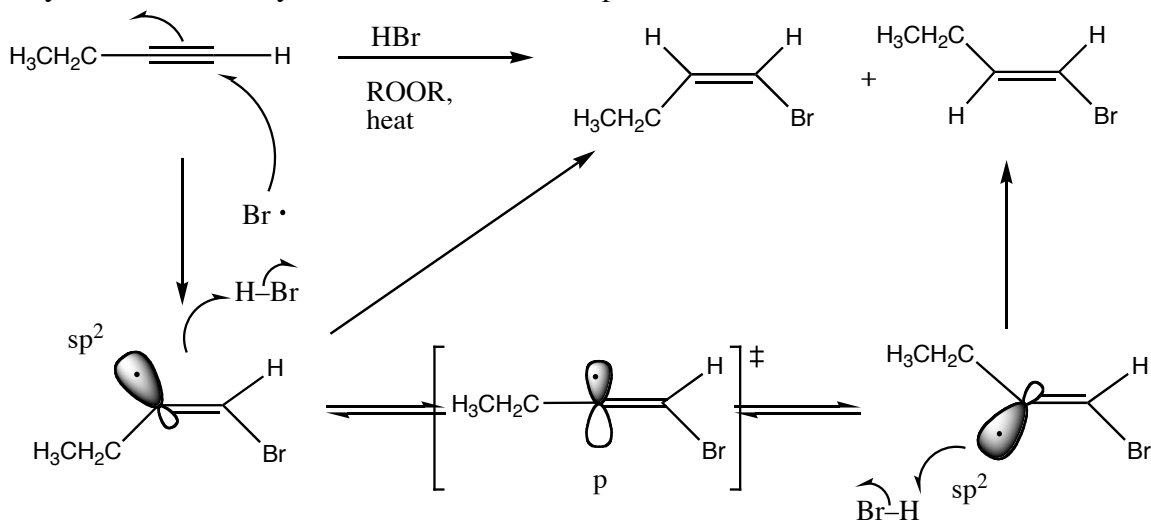
b. Addition of hydrogen halides, H-X

These additions follow Markovnikov's rule, with the halide ending up on the more substituted carbon atom. A vinyl cation intermediate is involved. Internal alkynes give cis/trans mixtures of vinyl halides. Addition of a second mole of H-X yields a dihaloalkane. Terminal alkynes give one vinyl halide and one dihaloalkane; internal alkynes can give four vinyl halides and two dihaloalkanes.



c. Anti-Markovnikov addition of H-X

Radical-promoted addition of HBr to alkynes results in formation of anti-Markovnikov vinyl bromides; a vinyl radical intermediate is postulated:

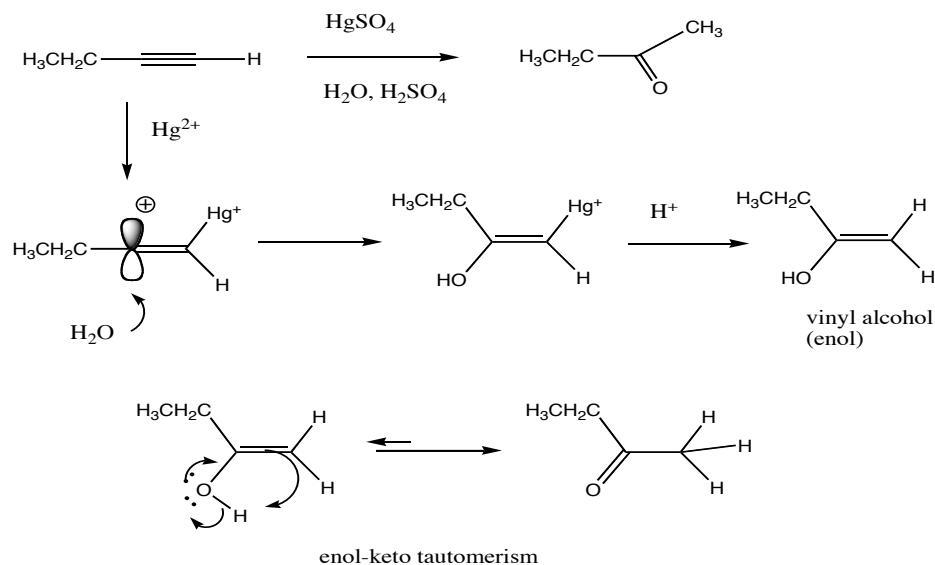


At elevated temperatures, the vinyl radical equilibrates so that a mixture of cis and trans vinyl bromides are obtained.

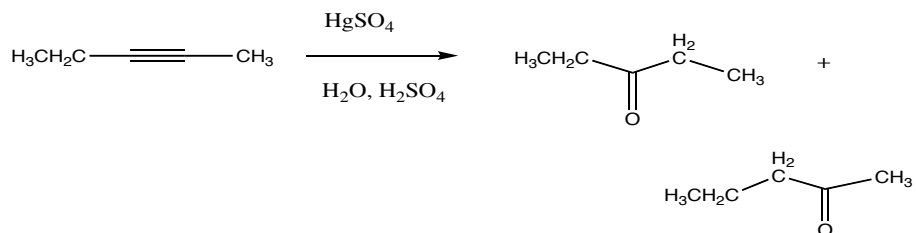
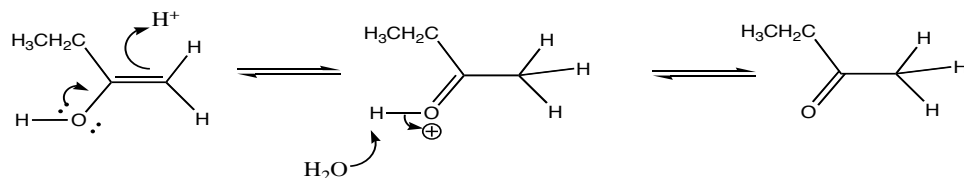
III. Hydration of alkynes

a. Oxymercuration/Markovnikov Hydration

Reaction of terminal alkynes with mercuric sulfate in the presence of aqueous acid results in the production of a vinyl alcohol (**enol**) intermediate that rapidly tautomerizes to a more stable carbonyl compound known as a ketone. The driving force for this isomerization is the formation of the more stable C=O (164kcal/mol) from the C=C (144 kcal/mol). Internal alkynes give regioisomeric ketone mixtures.

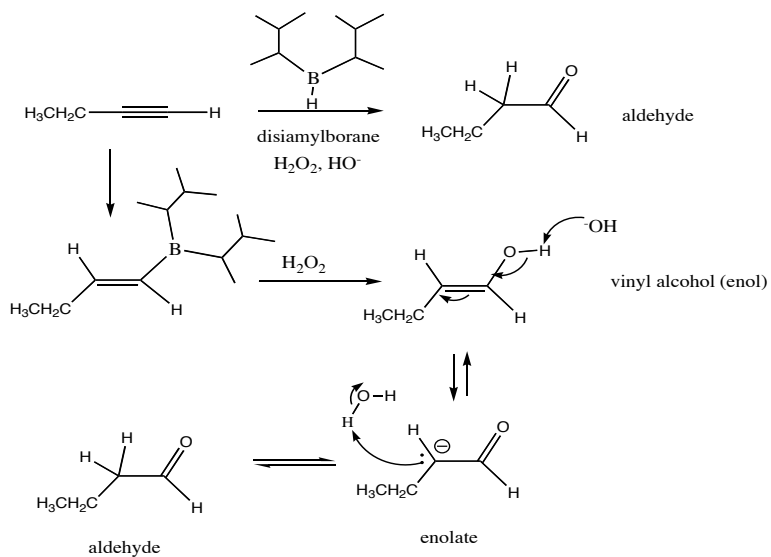


Acid-catalyzed Keto-enol tautomerism



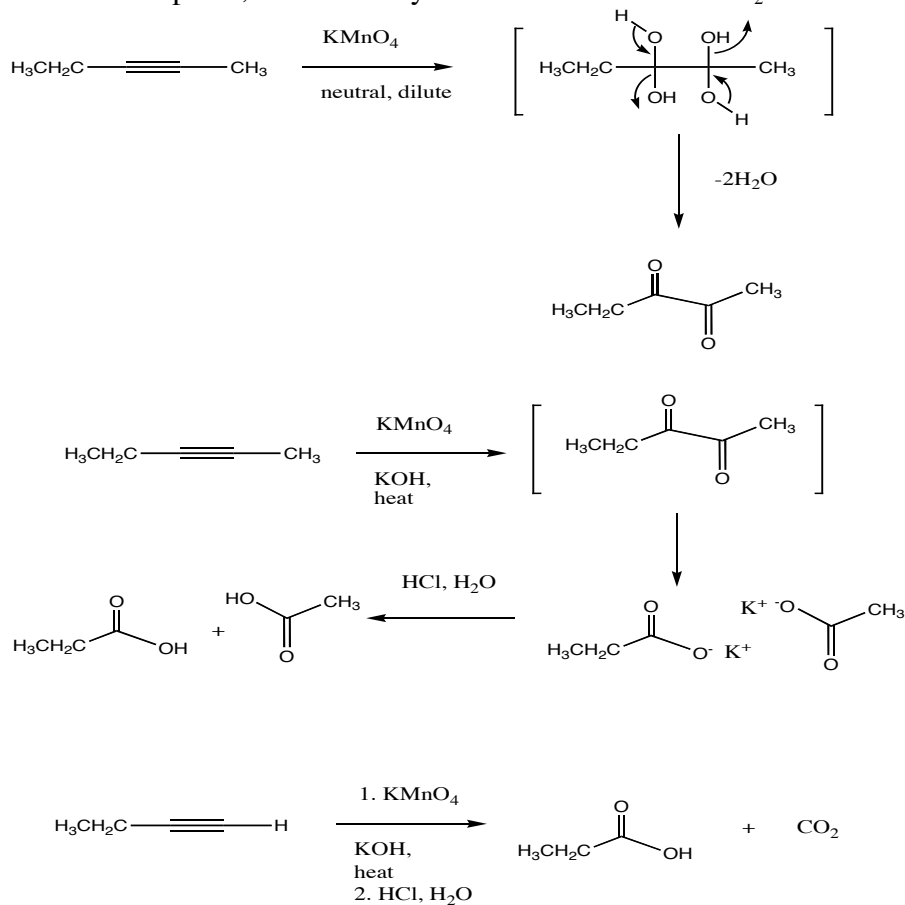
b. Anti-Markovnikov Hydration: Hydroboration of Alkynes

Hydroboration of terminal alkynes is usually performed with a bulky borane to prevent addition of two molecules of borane across the triple bond. Disiamyl borane is usually used for this purpose. A vinyl alcohol (enol) intermediate is again formed, but because of the preference for addition of boron to the terminal carbon of alkynes, aldehydes are the carbonyl products obtained.



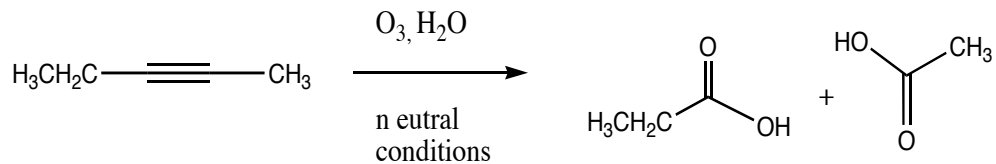
c. Permanganate Oxidation/Oxidative cleavage of alkynes

Treatment of alkynes with dilute permanganate under neutral conditions results in oxidation to 1,2-diketones. Under heating and basic conditions, oxidative cleavage to carboxylic acids takes place; terminal alkynes liberate a mole of CO_2 .



d. Ozonolysis of alkynes

When subjected to ozonolysis, alkynes give the same products as obtained from permanganate cleavage. The products of an ozonolytic or permanganate cleavage give important clues as to the structure of the parent alkyne.

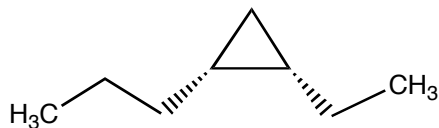


What is the structure of the unknown alkyne?

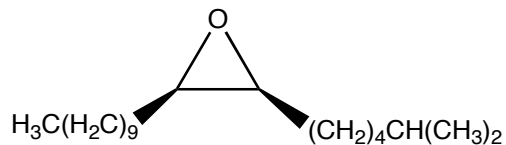


Additional Problems for practice:

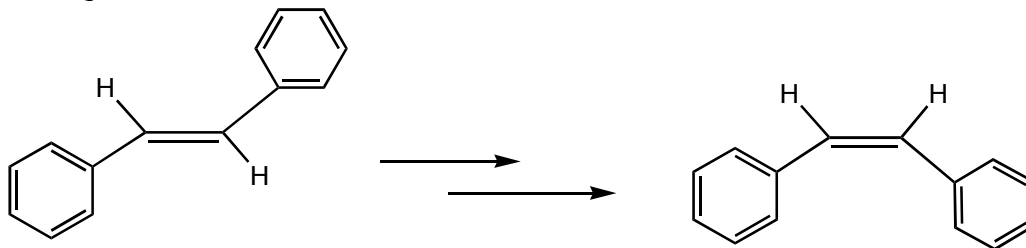
1. Design a synthesis of the following racemic cyclopropane starting from acetylene, organic compounds containing three or fewer carbons, and any inorganic reagents necessary. Note with a star each step that creates a chiral product, explain why each starred step affords a racemic mixture.



2. Outline a preparation of racemic disparlure from acetylene and any other compound containing not more than five carbon atoms. Note with a star each step that creates a chiral product, explain why each starred step affords a racemic mixture



3. Explain how you could accomplish the following isomerization in a three-step sequence:



4. Propose a structure for the unknown compound given the following data:

