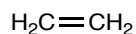
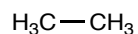


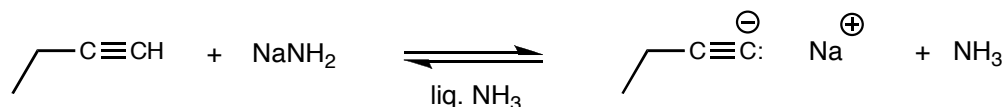
Acidity of Terminal Alkynes

- Do you recall the pK_a 's of the following species?



- Can you explain *why* the hydrocarbons have such different pK_a 's?

- Calculate the equilibrium constant of the following reaction:

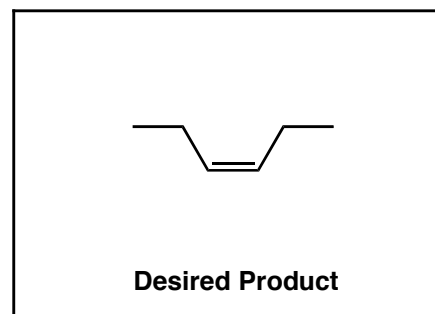


- The resulting species, often called an **acetylide anion**, is an excellent nucleophile for S_N2 reactions. (It has a Lewis structure that resembles that of what other good S_N2 nucleophile?) This might be a good way to make **carbon-carbon bonds**. . . do you recall the other ways of making carbon-carbon bonds?

Reading: Section 14.7

Organic Synthesis Using Alkynes

- Provide a synthetic route to the following product from starting materials that contain **no more than 2 carbons**:



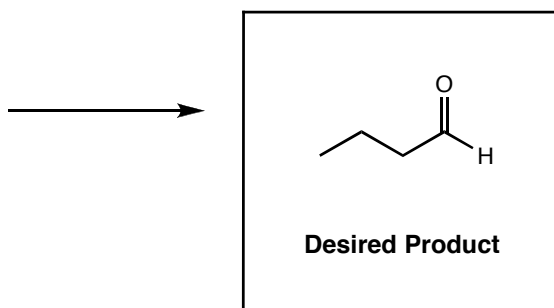
Reading: Section 14.8

Sample Synthesis Problem (from old exam)

- You should be able to find at least *three* completely different synthetic routes for the following problem!

Show all reagents and intermediates for the multi-step synthesis below. You may use **any** organic or inorganic reagents in your synthesis, but you must begin with the indicated starting material. You do not need to show any mechanisms. The correct answer will require fewer than 5 steps.

Starting Material:



More than One Alkene In a Molecule

- Molecules with 2 C=C bonds are **dienes**. Draw the structures of the following dienes:

1,4-cyclohexadiene

1,3-cyclohexadiene

1,3-butadiene

1,2-butadiene

- Molecules with 3 C=C bonds are **trienes**. Draw the structure of 1,3,5-cyclooctatriene.

Reading: Chapter 15 (introduction)

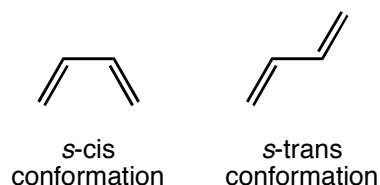
Cumulated π -Bonds: Allenes

- How close together can two C=C double bonds be in a single molecule?
- When two C=C bonds **share a single carbon atom**, they are called **cumulated** double bonds. The simplest compound that contains cumulated double bonds is **allene**, C₃H₄. Draw the structure of allene and determine the geometry and hybridization of each atom.
- Show the σ - and π -orbitals of allene. Is the entire molecule planar?
- Draw the structure of 1,2-cyclohexadiene. This molecule can **not** be prepared as a stable compound. Can you explain why?

Reading: Section 15.1

Conjugated π -Bonds: 1,3-Dienes

- When two double bonds are on *adjacent* carbons they are said to be **conjugated**. Draw some examples of conjugated dienes. Why are these compounds often called 1,3-dienes?
- Conformational analysis of rotation around the *single* bond in 1,3-butadiene shows that it has *two* stable conformations, both of which are (nearly) *planar*. Why are these conformations particularly stable? Which one is more stable, and why?

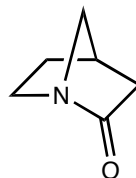
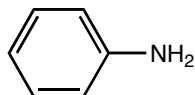
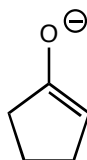
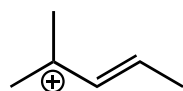
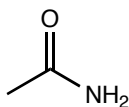
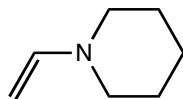


- Draw the π -molecular orbitals (MOs) for 1,3-butadiene. Can you explain why the *planar* conformations of butadiene are preferred?

Reading: Section 15.1

Multiple Conjugated *p*-Orbitals

- When a lone pair, vacant *p*-orbital, or radical (unpaired electron) is *adjacent* to a π -bond, the orbital in question can become *conjugated* with the π -bond. For each of the following structures, count *how many p-orbitals* are conjugated together, and count the total *number of π -electrons* in the conjugated system. Be sure to consider the appropriate hybridization for each atom in the conjugated system!



Reading: Section 15.6

When There's A Choice, Choose Conjugation

- **Conjugated π -systems are always more stable than comparable non-conjugated π -systems.** There are two reasons why this is true:

- In general: Overlap of molecular orbitals (moderate effect)

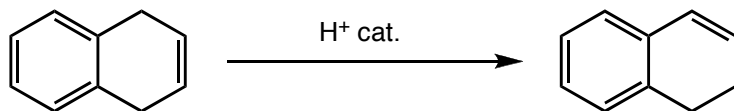
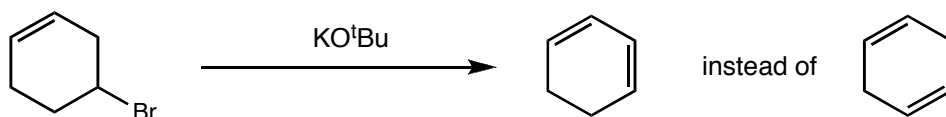
Example: 1,3-hexadiene

- For charged species: Delocalization of charge (large effect)

Example: allyl cation

- Thus, as a general rule, reactions will tend to favor conjugated products (and conjugated transition states) in order to maximize stability:

- Provide curved-arrow mechanisms for the following reactions and explain why the observed product is favored:

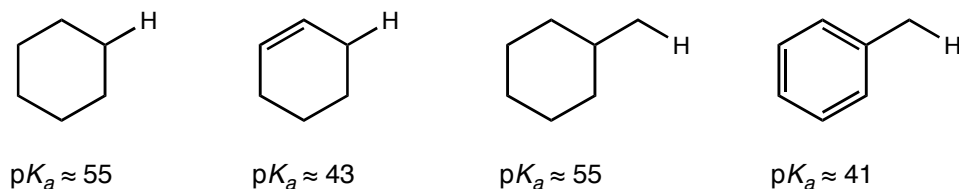


Reading: Section 15.6

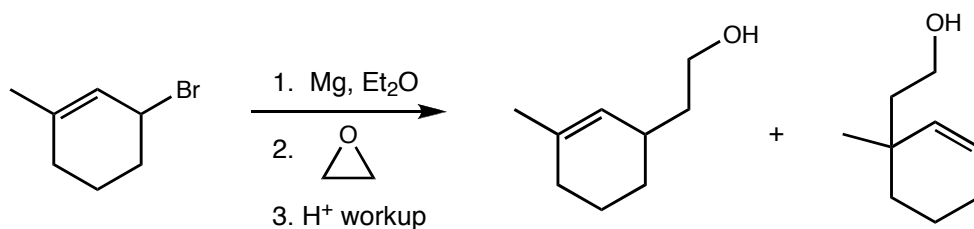
Allylic and Benzylic Carbanions: C–H Acidity and Allylic Grignard Rearrangements

- Draw the structure of the *allyl anion* and the *benzyl anion*. What makes these carbanions more stable than typical carbanions?

- Explain the pK_a values of the indicated C–H bonds in the following hydrocarbons:



- Explain why *two* products are observed from the following reaction sequence:



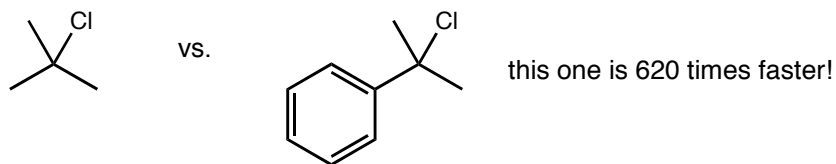
What can we say about allylic and benzylic reactivity?

Reading: Section 17.3

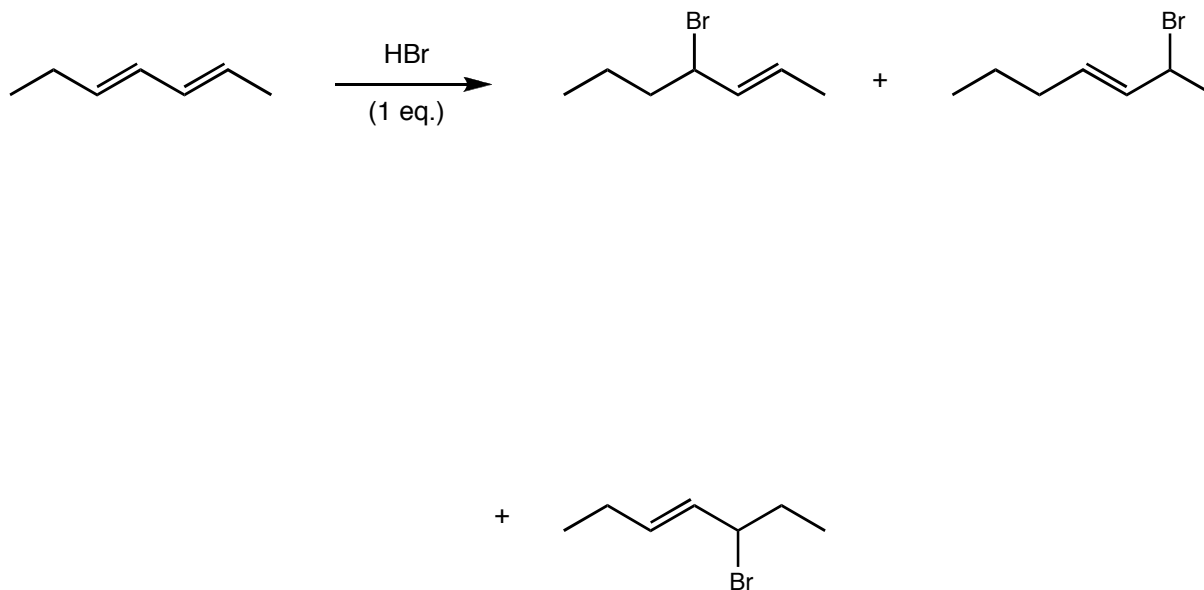
Allylic and Benzylic Carbocations: S_N1 Reactions and HX Addition

Explain the following observations:

- Replacing a methyl group in *t*-butyl chloride with a phenyl group increases the rate of S_N1 substitution by a factor of 620:



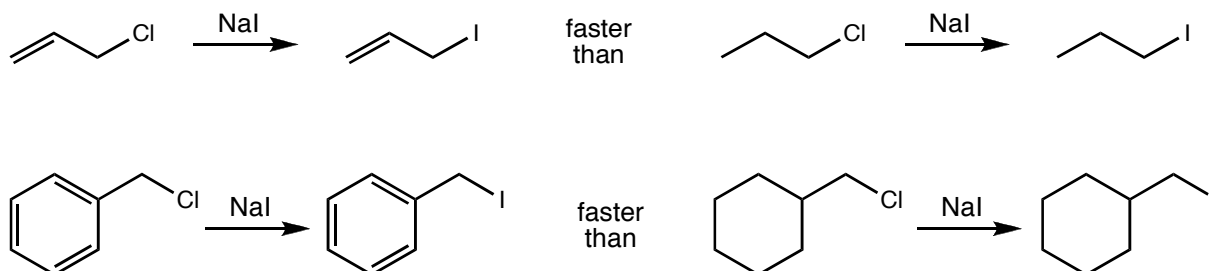
- Addition of HBr to the following diene results in the formation of **three** different products:



Reading: Sections 15.4 and 17.1

Allylic and Benzylic Alkyl Halides: S_N2 Reactions

- The following reactions are S_N2 reactions—there's no free carbocation—yet the reactions are accelerated if the alkyl halide is allylic or benzylic. Explain.

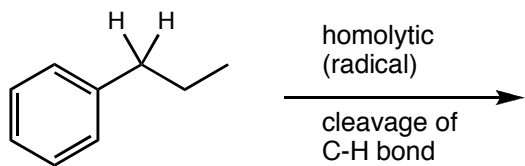


- This is a classic example of how conjugation (stabilization) in the **transition state** results in a faster reaction.

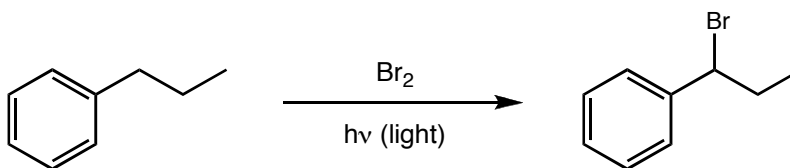
Reading: Section 17.4

Benzylic C–H Bonds: Bromination and Oxidation

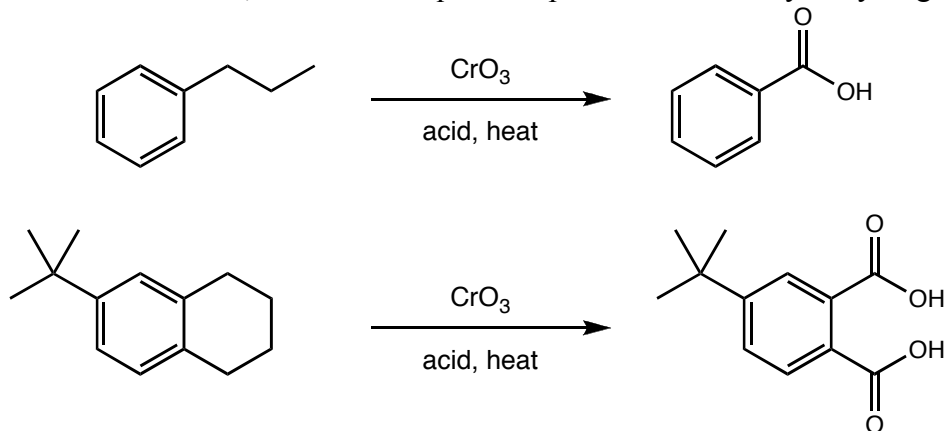
- The C–H bonds at a *benzylic* carbon are especially susceptible to radical (homolytic) dissociation. Why?



- Thus, one can carry out radical substitution *selectively* at the benzylic carbon. Propose a curved-arrow mechanism for the following reaction:



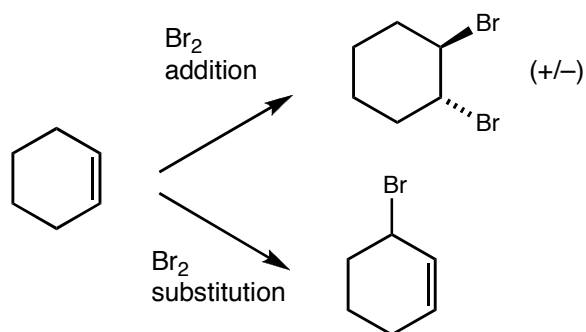
- In addition, strong oxidizing agents can **completely oxidize** any hydrocarbon sidechain of an aromatic ring to carboxylic acid (–COOH) groups. You need not worry about the mechanism, but it does require the presence of a benzylic hydrogen atom. For example:



Reading: Sections 17.2, 17.5

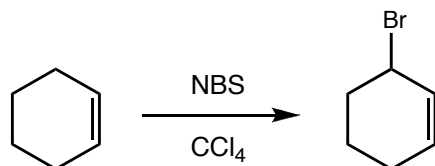
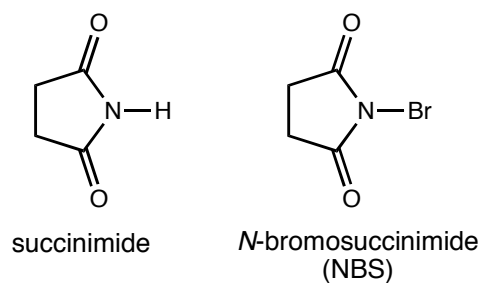
Allylic C–H Bonds: Bromine Addition vs. Substitution

- Allylic C–H bonds are similarly susceptible to radical cleavage. However, in the case of allylic compounds there are two possible reactions that can take place. Under what conditions would each of the following reactions be favored?



- Draw a curved-arrow mechanism for allylic bromination of cyclohexene.

- Allylic bromination can be carried out selectively using the brominating agent *N*-bromosuccinimide (NBS) in carbon tetrachloride solvent (CCl_4). (The mechanism is given in Loudon.) For example:



Reading: Section 17.2