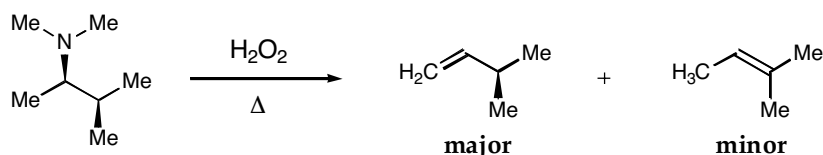


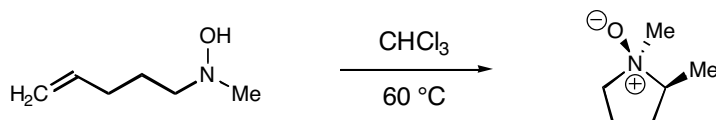
Problem Set 5

Due: Thursday, 11/6/03 at 4 PM

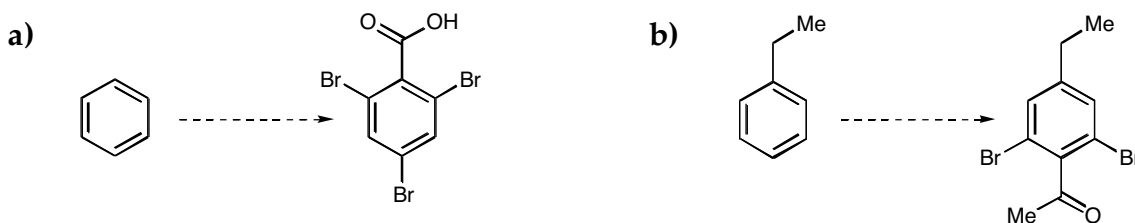
1. a) The Cope elimination generally provides the least substituted alkene product. Analyze the selectivity of the following reaction in the same way that we analyzed the selectivity of the Hofmann elimination in lecture. Provide an explanation for the observed selectivity.



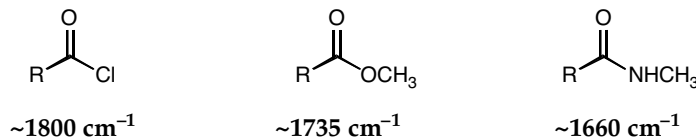
b) While the Cope elimination is a good way to convert an amine *N*-oxide to an alkene and a hydroxylamine, in some cases the *reverse* Cope elimination can be used to convert an alkene to an amine *N*-oxide. Using what you know about the mechanism for the Cope elimination, propose a mechanism for the following reverse Cope elimination.



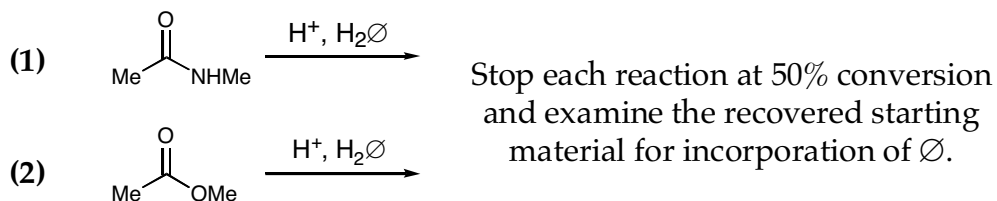
2. Provide a synthesis that will *selectively* generate each of the following molecules from the given starting material. Show all of the key intermediates and reagents.



3. As you know, carbonyl groups display characteristic IR resonances in the 1600–1800 cm^{-1} region. Different carbonyl groups display different stretching frequencies. In general, the stronger the $\text{C}=\text{O}$ bond, the higher the stretching frequency. Using what you know about resonance stabilization of carboxylic acid derivatives, explain the following trend in IR stretching frequencies.

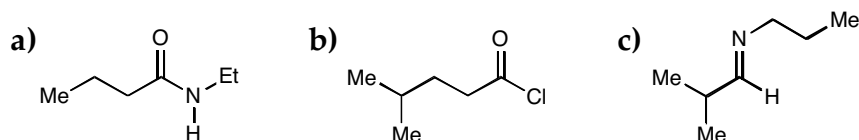
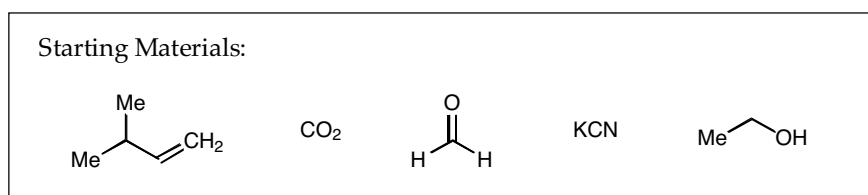


4. Consider the labeling experiments outlined below:



Under acidic hydrolysis conditions, would you expect more O incorporation into the amide (eq 1) or the ester (eq 2)? Your answer should include the mechanism for these reactions.

5. Provide syntheses of the following molecules. All of the carbon atoms should come from the given starting materials. You may use any common reagents.



6. Phosgene is a highly reactive acylating reagent that can be used to synthesize a large variety of carboxylic acid derivatives. Unfortunately, it is also a highly toxic gas that was once used as a chemical warfare agent. Triphosgene is now used in place of phosgene because it is an easy to handle solid. In the presence of catalytic chloride ion, triphosgene decomposes to form three equivalents of phosgene *in situ*. Provide a detailed mechanism for this decomposition process.

