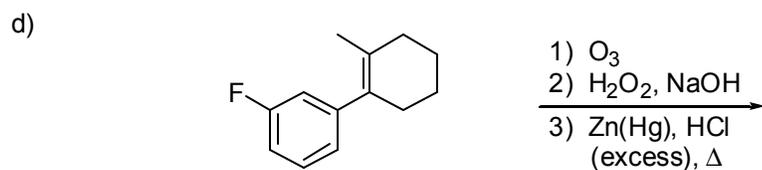
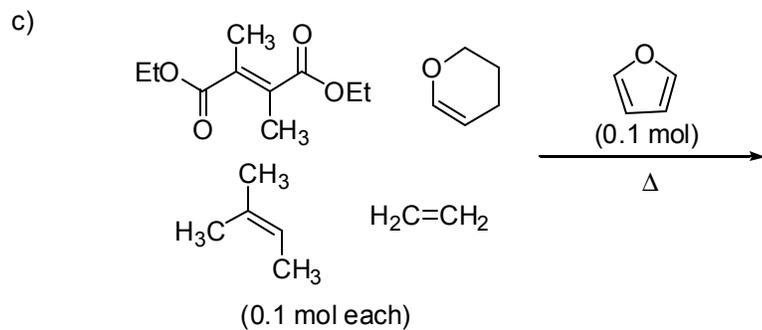
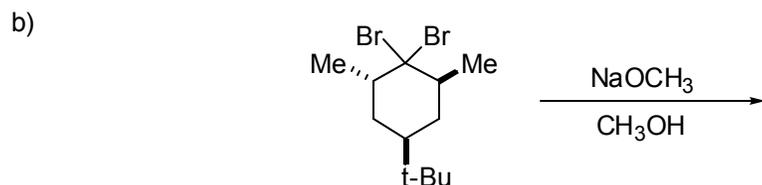
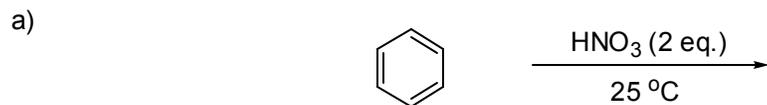
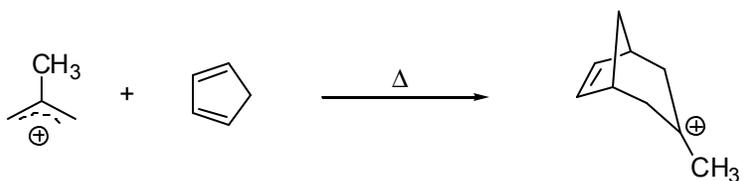


Section Problem Set
Bonding, MO Theory, Aromatic Substitution, and More

Problem 1 (parts a-d original, part e based on Kirby's *Stereoelectronic Effects*). Predict the major product for each of the following reactions. Beware of trick questions designed to embarrass you and break your spirit.



Problem 2 (based on material in *Frontier Orbitals and Organic Chemical Reactions* by I. Fleming). Taste the rainbow of fruit flavor in the following cycloaddition reaction:



Solution

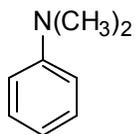
- Classify the reaction as [m+n]
- By combining unhybridized p atomic orbitals on each molecule, build all of the π molecular orbitals for both reactants. Label the HOMO and the LUMO in this reaction and explain why the reaction is expected to be concerted under thermal conditions.

- c) Although there are no consequences in the stereochemistry of the product shown above, there is experimental evidence that the reaction proceeds through an exo transition state. Using dotted lines to represent bonds that are being made and broken, draw a Lewis structure for the exo transition state that shows me that you know the difference between “endo” and “exo” cycloaddition transition states.
- d) Recall that Diels-Alder reactions usually prefer endo transition states (due to favorable secondary orbital overlap). Using MO theory, suggest a reason that the exo transition state is favored. **HINT: Regardless of your assignment in part b, use the HOMO of the cation and the LUMO of cyclopentadiene.**

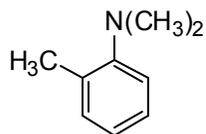
Problem 3 (a common example—I might have seen it somewhere in Evans' lecture slides, too. I try not to plagiarize problems). If you want to be able to set up your own home meth lab, you'll have to master organic synthesis. Starting from any molecules bearing five carbons or fewer, provide concise synthetic routes to the following two compounds.



Problem 4 (a common example). Even though compound **B** has an extra electron donating substituent on its ring, compound **A** reacts significantly faster in electrophilic aromatic substitution reactions. Explain this ostensibly counterintuitive observation.



A



B

Problem 5 (based on material from *Advanced Organic Chemistry* by B. Miller, p. 148). Provide an arrow pushing mechanism for the following transformation. No, this is not busy work.

