

Chemistry 116 Sec. A (2:00-5:00)
Final Exam
“Organic Chemistry - Fall 2000”
December 19, 2000

Instructions: You have until 5:00 p.m. to complete the exam. At that time, I will request that all remaining test takers cease writing, turn their exams over, and pass them to their rightmost isle. If you finish before 4:55 p.m. you may turn in the exam at the front of the room prior to leaving. If you finish within the final 5 min. of class, please turn your exam over and remain seated until I call for the remaining exams to be turned in. *In fairness to all, anyone still working on the exam after “time” is called will receive a grade of zero!*

Be sure to read the instructions for each question. It may be helpful to skim the entire exam and solve the easier questions first.

Restroom Policy: Only one person at a time will be allowed to go to the restroom. If you need to go, bring your exam down to the front of the room and pick it up when you return.

Exam Agreement: I, _____, have read and agree to

(Please print)

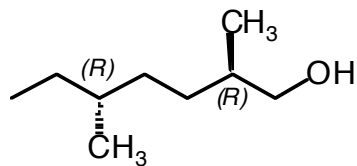
abide by the instructions above. On my honor, I have neither given nor accepted any help during this exam.

Signature: _____

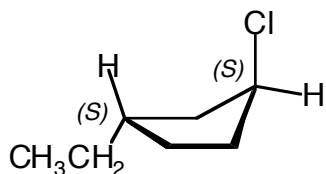
College: _____

**DO NOT OPEN THIS EXAM UNTIL
INSTRUCTED TO DO SO**

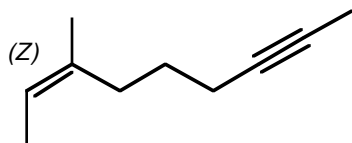
1. Provide an unambiguous (IUPAC or common) name for each of the following compounds. Be sure to indicate stereochemistry where appropriate. (18 points)



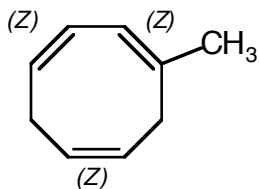
(2R,5R)-2,5-Dimethyl-1-heptanol



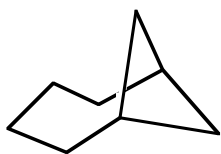
(1S,3S)-1-Chloro-3-ethylcyclopentane



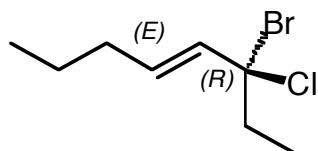
(Z)-3-methyl-2-Nonen-7-yne



1-Methyl-1,3,6-cyclooctatriene

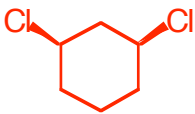
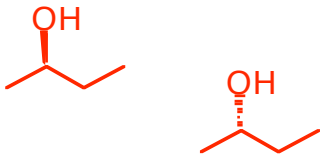
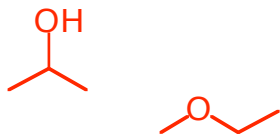
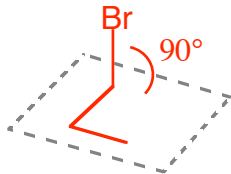
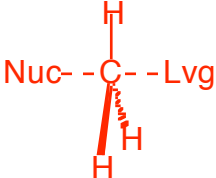


Bicyclo[4.1.1]octane

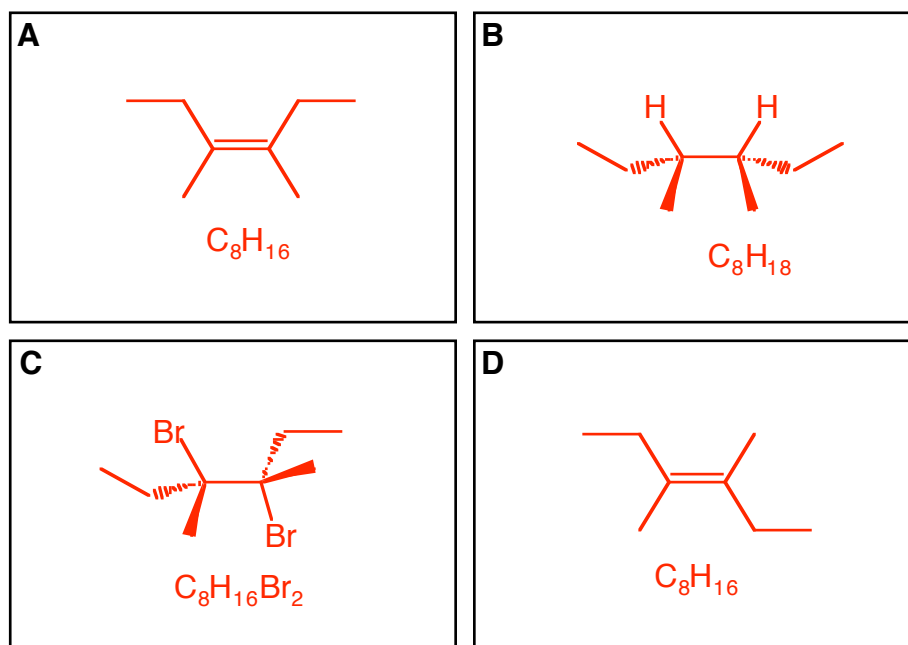


(E,R)-3-Bromo-3-chloro-4-octene

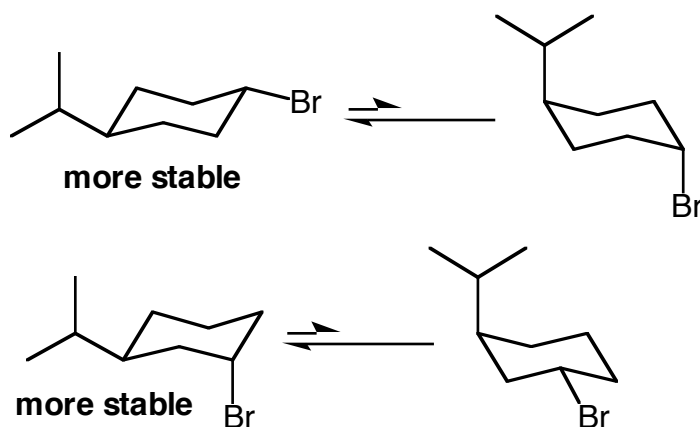
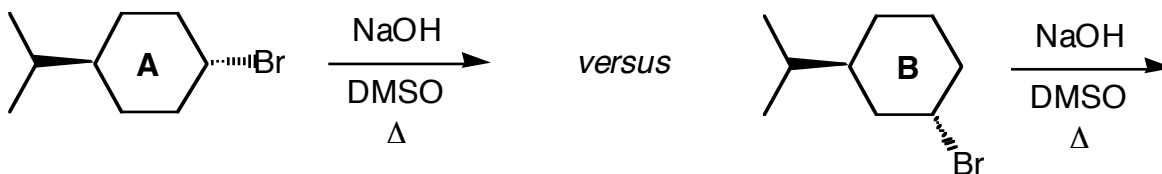
2. Fill in the boxes below. *Note: any answers outside of the boxes will not be graded.* (24 points)

	Definition	Example
A meso compound	An achiral molecule that possesses two or more stereocenters	
A racemic mixture	A 50:50 mixture of enantiomers	
A Lewis Acid (your example cannot also be a Brønsted-Lowry Acid)	An electron acceptor	BF ₃
Constitutional Isomers	Molecules with the same molecular formula but different connectivity of atoms.	
Dihedral Angle	The angle between one atom and the plane formed by the next three consecutive atoms in a molecule.	specify the value of the dihedral angle in your example 
Transition State	A fleeting structure that occurs at an energy maximum along the pathway of a reaction	

3. **A**, a molecule with the molecular formula C_8H_{16} is subjected to catalytic hydrogenation to give an achiral molecule, **B**, of molecular formula C_8H_{18} . When **A** is treated with molecular bromine in the dark, a racemic mixture of **C** ($C_8H_{16}Br_2$) is formed. Treatment of **A** with HBr, followed by refluxing with a mild base yields **D**, a stereoisomer of **A**. Provide structures for **A-D** below. (8 points)

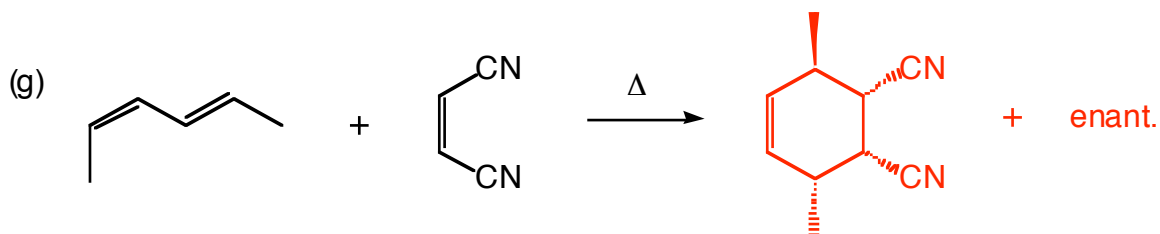
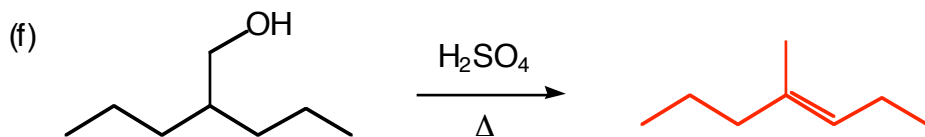
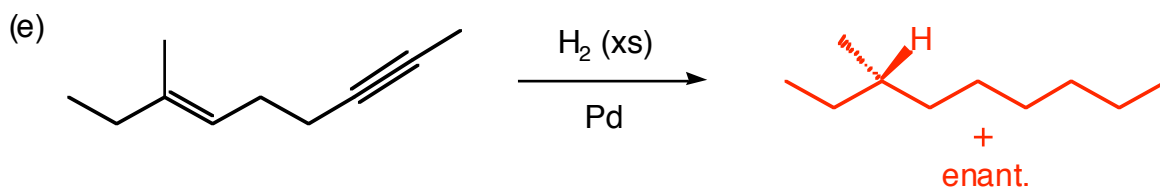
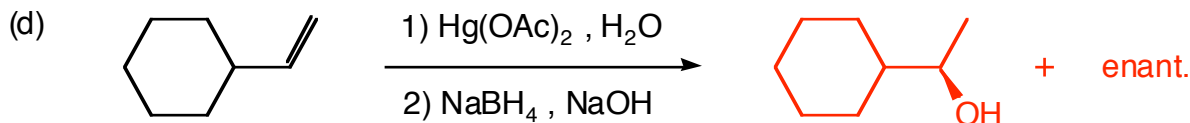
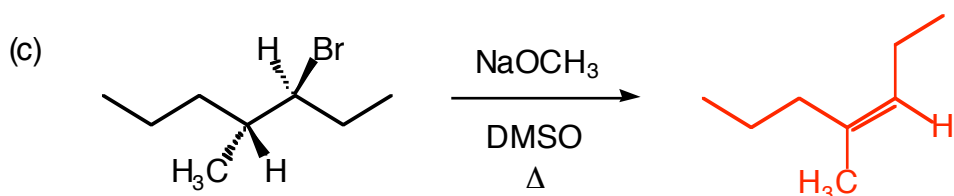
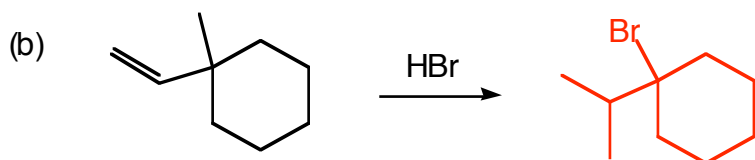
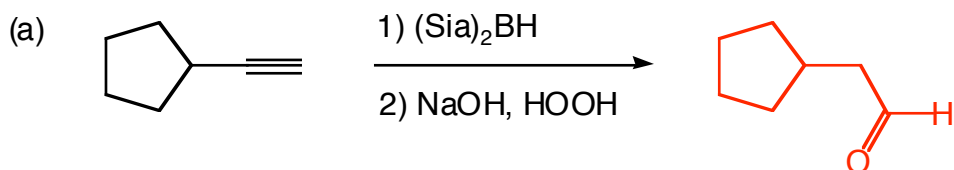


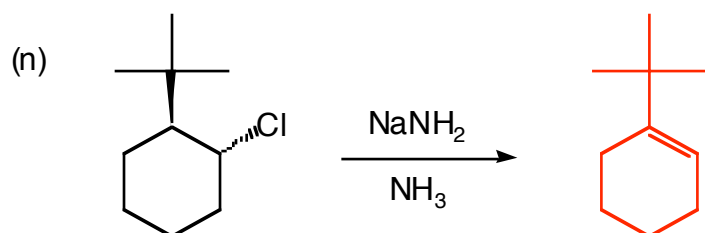
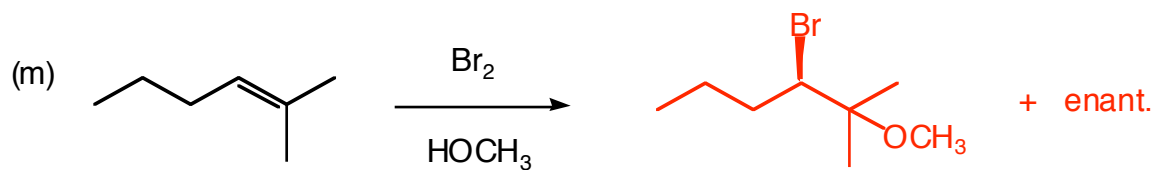
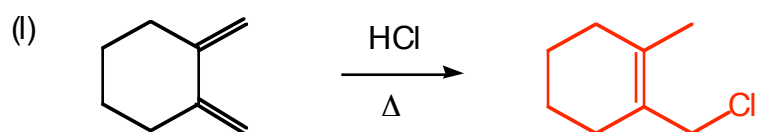
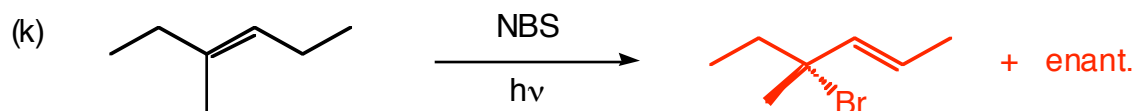
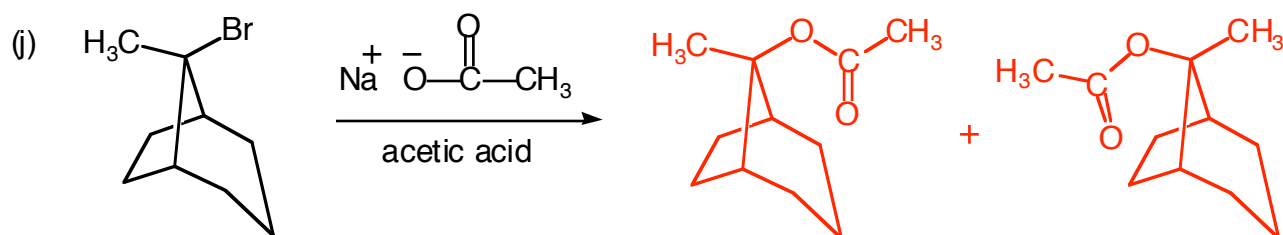
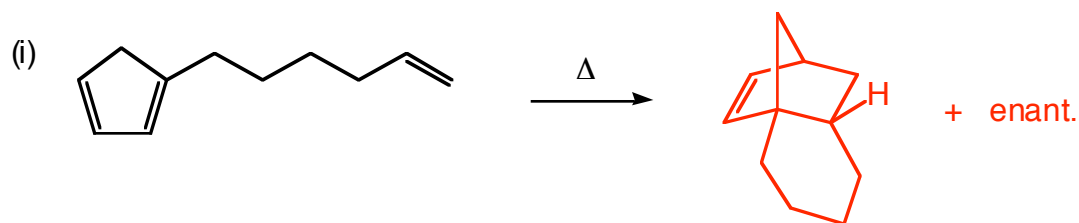
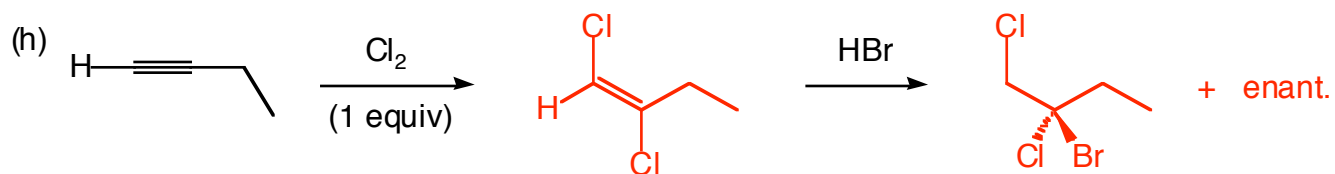
4. Determine whether **A** or **B** undergoes elimination more rapidly under the conditions shown below. Provide a rationale for your choice using both pictures *and* words. (5 points)



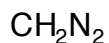
In each case, the more stable conformer is the one with the bulky isopropyl group in an equatorial position. This forces the Br to be equatorial in the 1,4-case, but axial in the 1,3-case. Since the solvent (DMSO) is polar aprotic, the reaction will proceed via an E2, which requires an anti-periplanar relationship between the β -proton and the leaving group. In cyclohexane rings, only axial leaving groups have protons that are anti-periplanar to them. Since the 1,4-isomer must undergo a ring flip to the less stable axial conformer, it will spend less time in that conformation and take longer to react.

5. Draw the **major product** of each of the following reactions. *Be sure to include stereochemistry in your answers where appropriate.* (4 points each)

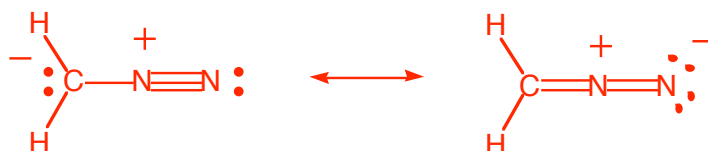




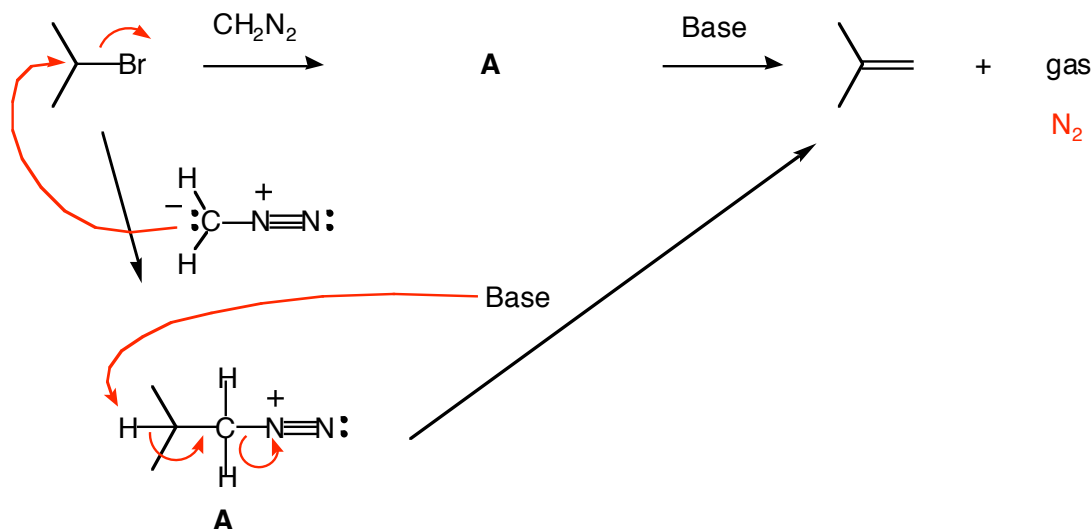
6. The molecule shown below is known as diazomethane:



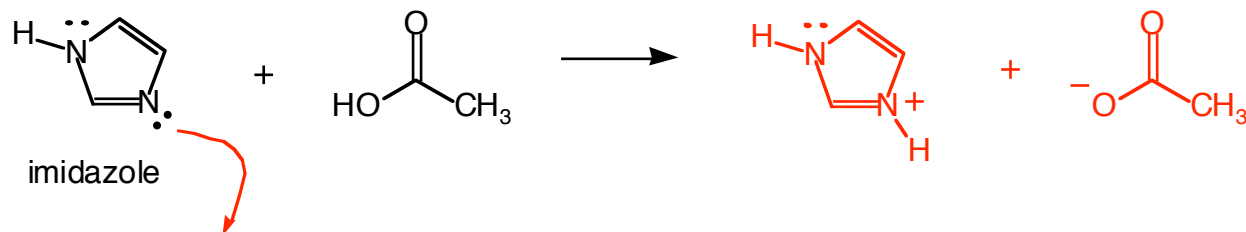
- a) Draw the two most stable resonance contributors for diazomethane and rank them according to their stability (1=most stable, 2=least stable). For full credit, you must show all lone pairs of electrons and formal charges. (8 points)



- b) Diazomethane acts as a nucleophile and reacts with 2-bromopropane to produce **A**. When **A** is treated with base, the alkene shown below is formed. This step of the reaction is also accompanied by vigorous bubbling due to the release of an unknown gas. Identify product **A** and the gas. Also, provide a mechanism for the entire reaction sequence. (8 points)

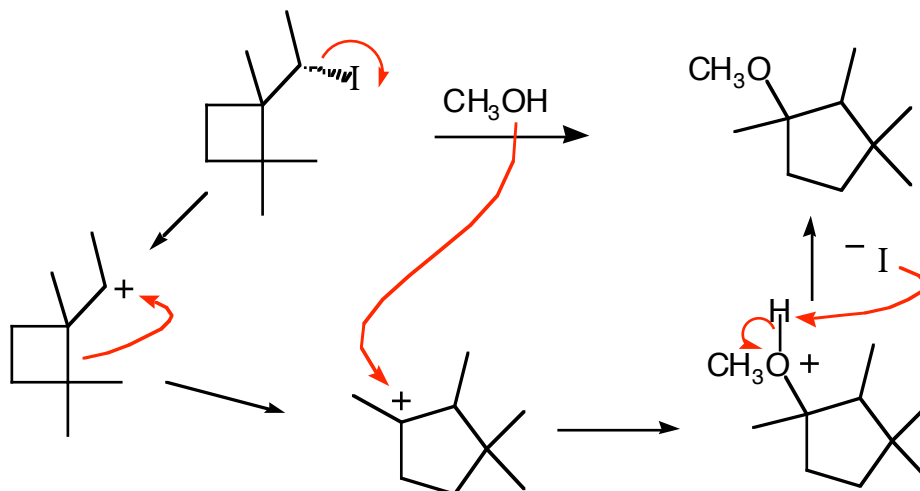


7. Imidazole will undergo an acid-base reaction with a mild acid such as acetic acid. Draw the product of this reaction and explain why you chose the atom that you chose to act as the Lewis base. (8 points)

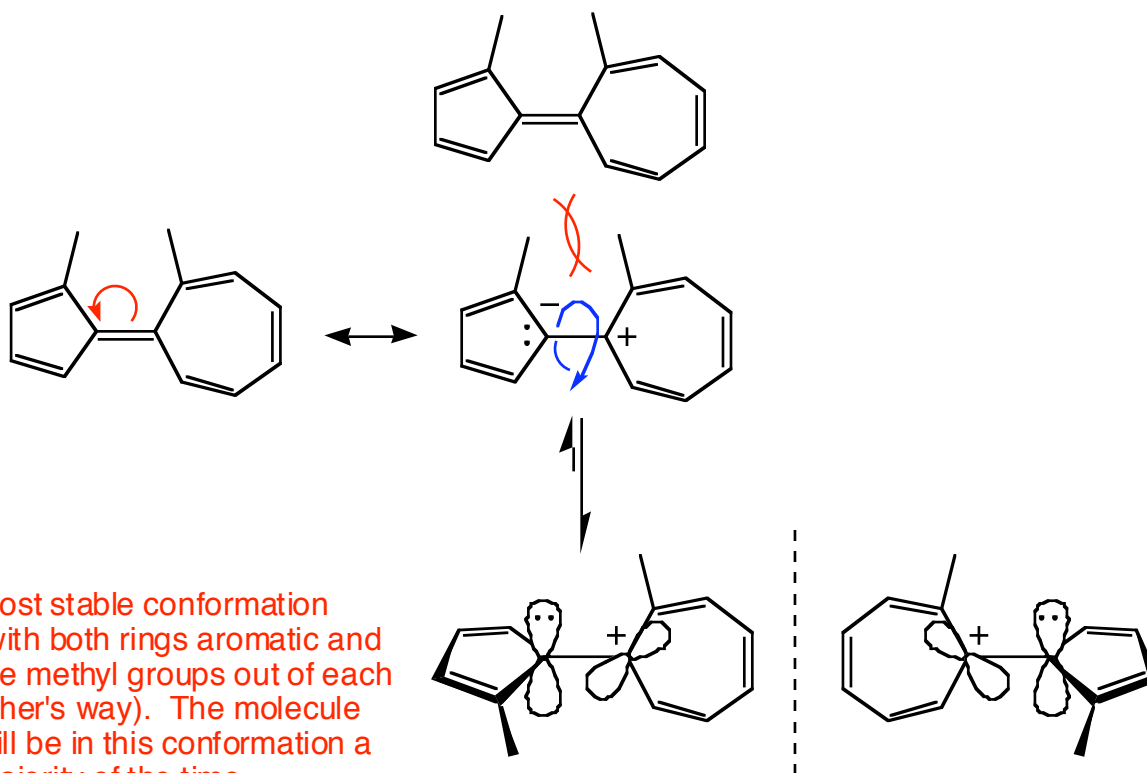


This is the only pair of electrons that is not part of the conjugated and aromatic π system. This electron pair resides in an sp^2 orbital, while the remaining electrons or lone pairs reside in p orbitals. Thus, only this electron pair is readily available to react. Reaction of any of the other electrons breaks the aromaticity of the ring.

8. Propose a mechanism for the following reaction. For full credit, show the products of each step and any formal charges. (8 points)



9. Explain why the molecule shown below rotates plane polarized light at room temperature. You must use words **and** pictures in your explanation. (10 points)

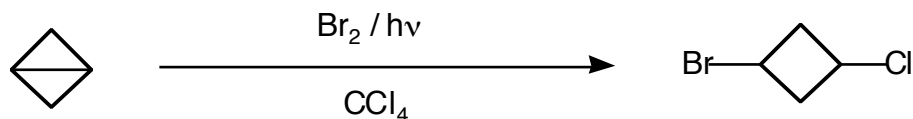


Most stable conformation (with both rings aromatic and the methyl groups out of each other's way). The molecule will be in this conformation a majority of the time.

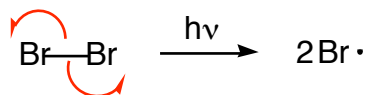
This conformation is chiral and will rotate plane polarized light.

10. Read these instructions carefully before proceeding. Provide a mechanism for the following reaction, paying close attention to the following details: (10 points)

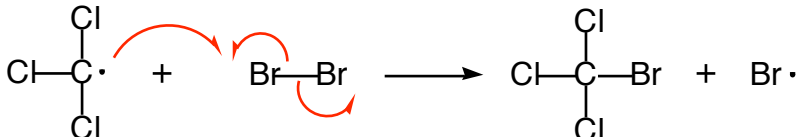
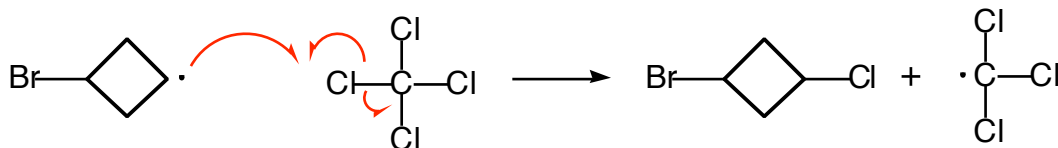
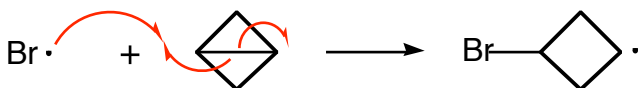
- label the three major steps of the reaction (initiation, propagation, and termination),
- include any intermediates in your mechanism, and
- provide at least 4 plausible termination steps



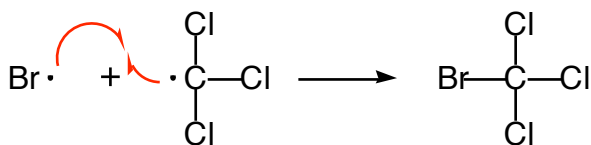
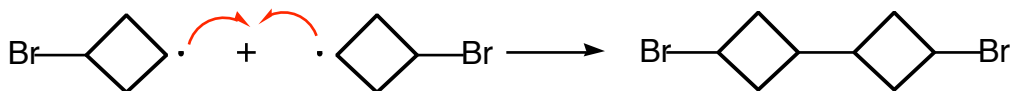
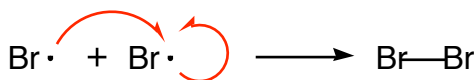
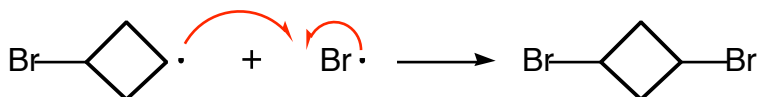
Initiation



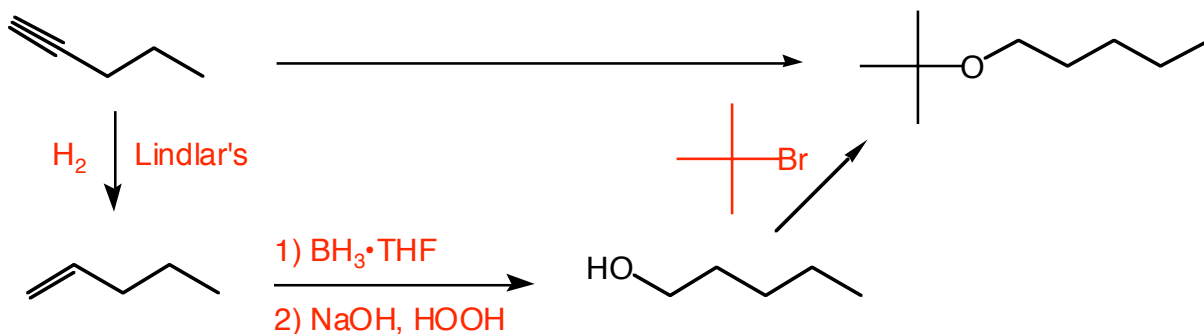
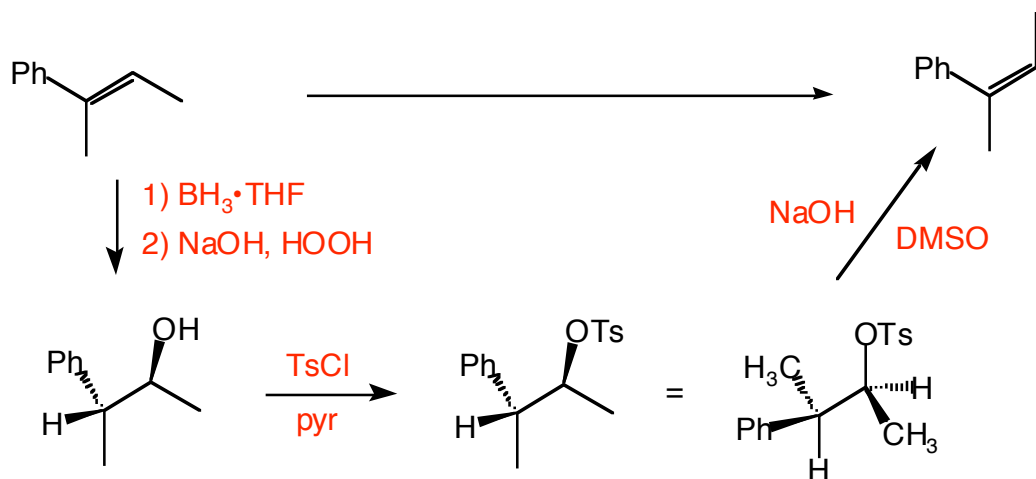
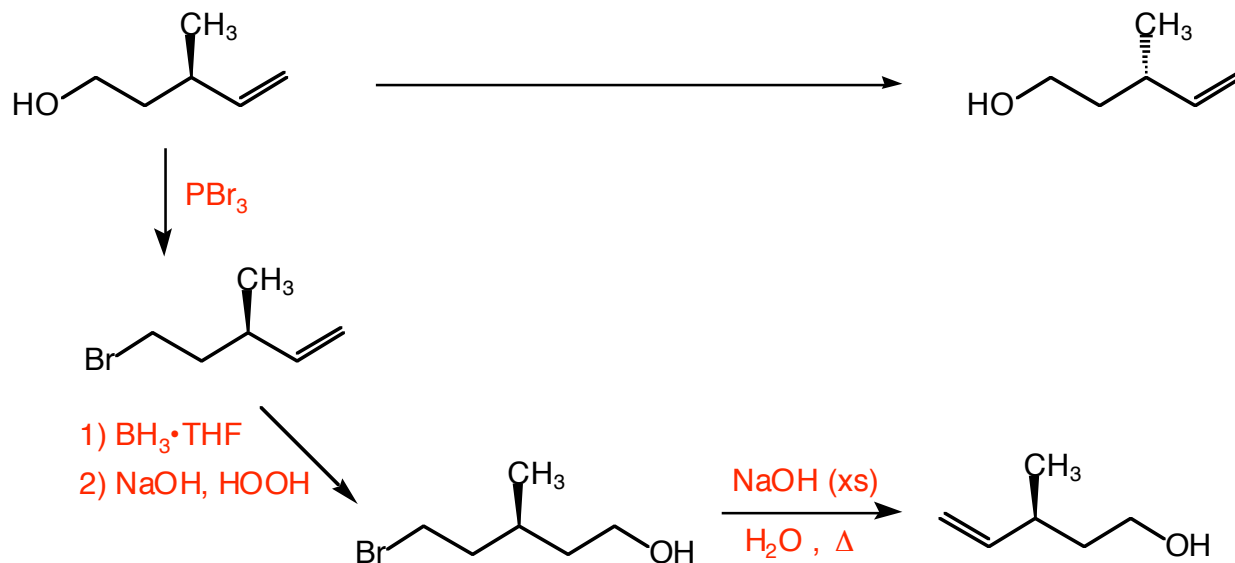
Propagation



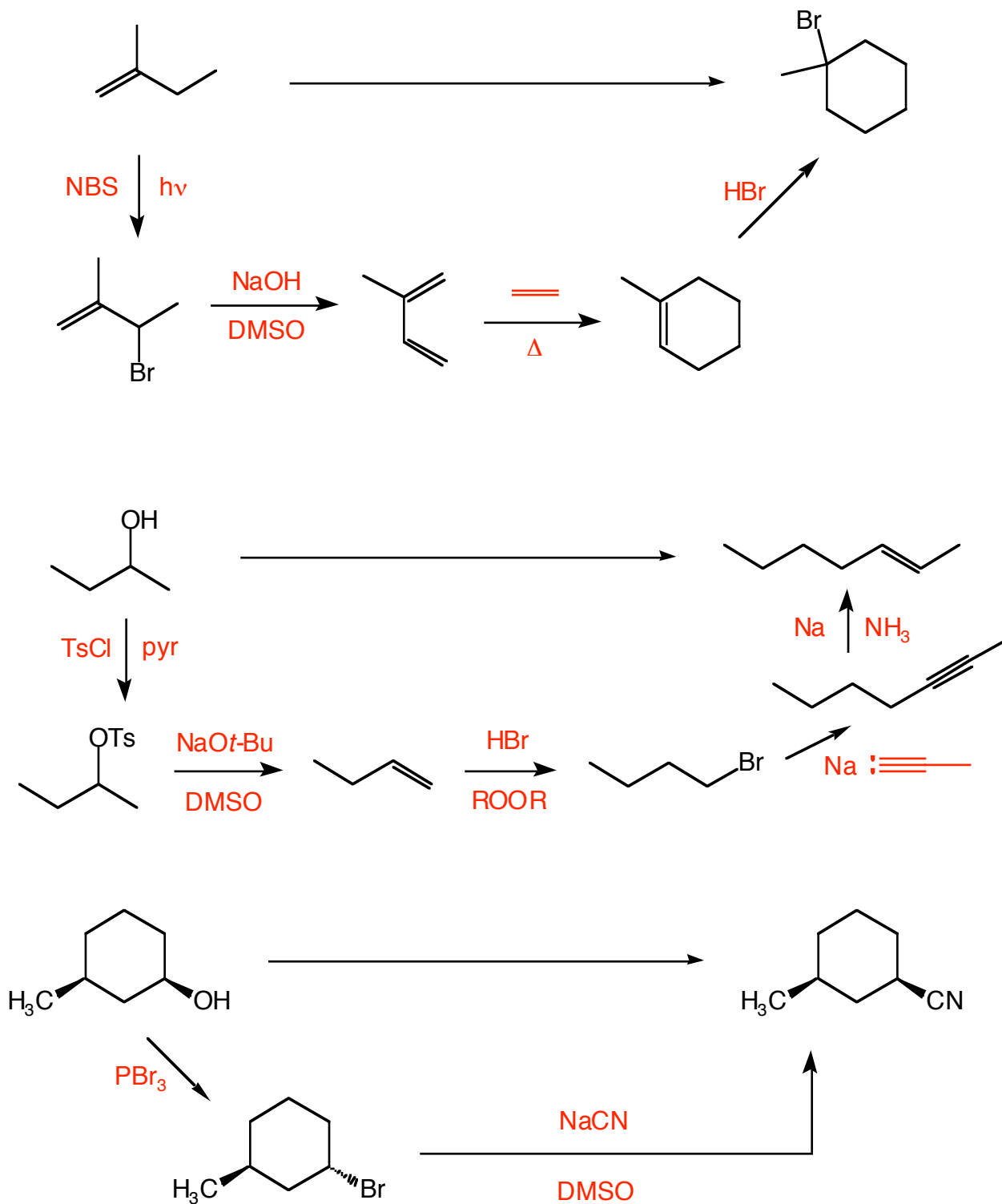
Termination



11. (Choose 4 out of 6) Propose a synthesis (sequence of reactions) that will accomplish each of the following transformations. *Be sure to include the products of each step.* Clearly indicate which four you wish for me to grade. If no indication is made, I will grade the first four. (8 points each)

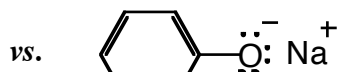
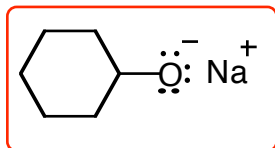


synthesis (cont'd)...



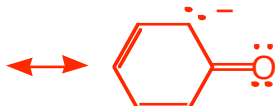
12. For each pair of molecules shown, circle the one that best fits the accompanying description and provide a concise rationale for your choice. Pictures *may* be required for full credit! (3 points each)

Most basic molecule

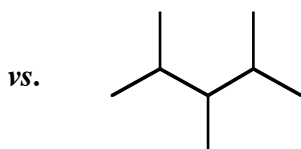
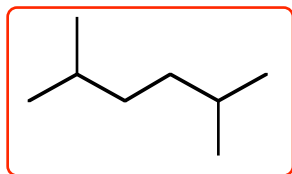


The circled molecule does not have any resonance which can delocalize the negative charge. It is therefore less stable (more reactive) than the other anion and therefore more basic.

2 other resonance structures

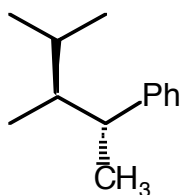


Highest boiling point

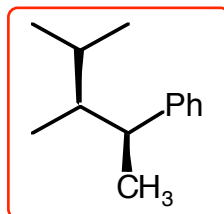


The circled molecule has less branching and thus more surface area for London forces. The more London forces, the more energy needed to break the intermolecular interactions and the higher the boiling point.

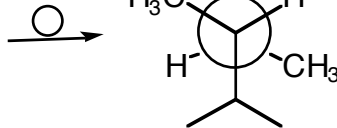
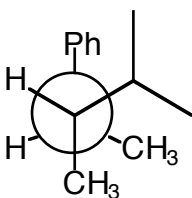
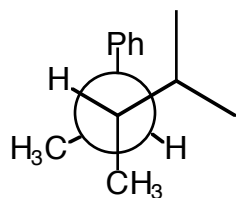
The molecule with the greatest overall stability



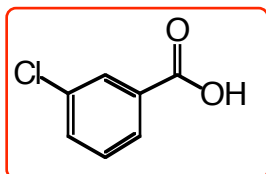
vs.



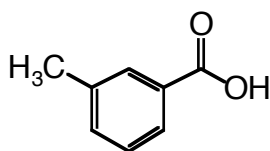
Both molecules have conformers with 2 gauche interactions. However, the circled molecule has a methyl and an isopropyl gauche to each other whereas the other molecule has a phenyl and an isopropyl gauche to each other.



Most acidic molecule



vs.



The circled molecule possesses a conjugate base in which the charge can be delocalized via induction by the electronegative chlorine atom. This helps to stabilize the conjugate base, causing the equilibrium to favor the side containing the products. This makes the original molecule more acidic.

