

page 1 (30) _____

2 (55) _____

total (300)

3 (40) _____

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chk

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6 (40) _____

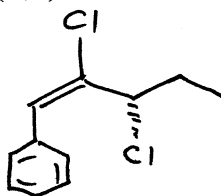
7 (30) _____

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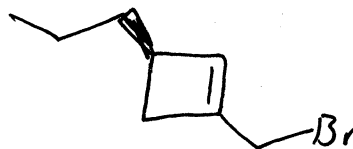
Please resist the urge to write in this space.

1. (20 points) Draw the following compounds. Show stereochemistry clearly.

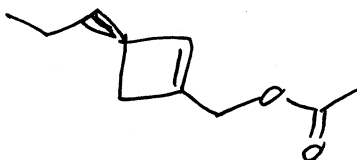
(a) (*E,S*)-2,3-dichloro-1-phenyl-1-pentene



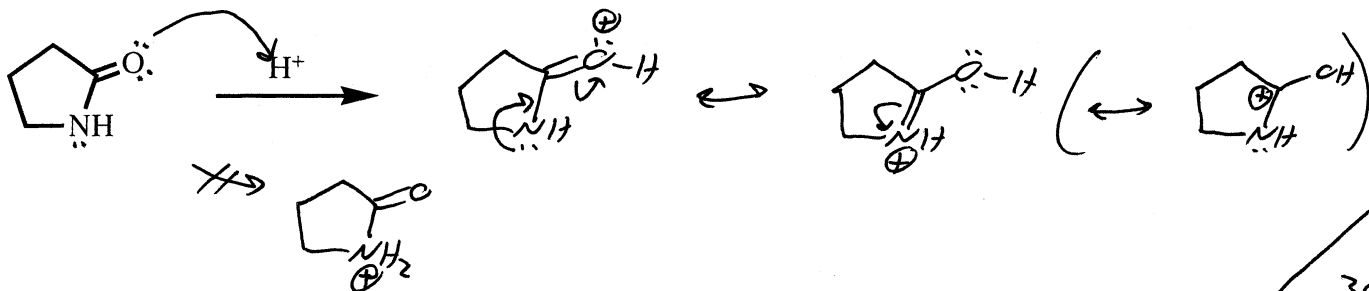
(b) (*R*)-1-(bromomethyl)-3-propylcyclobutene



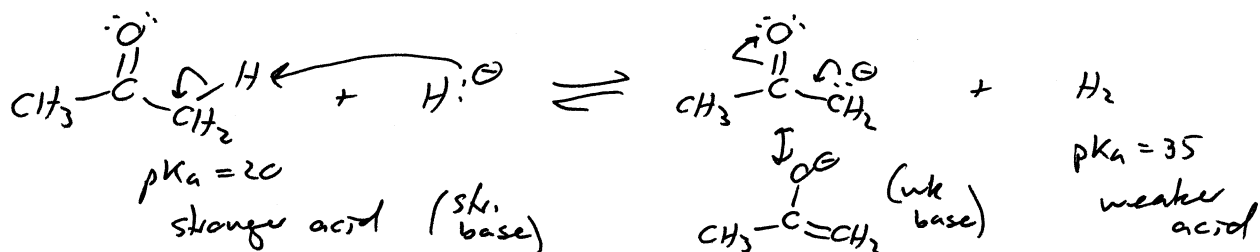
(c) Draw the product of an S_N2 reaction of the compound in part b with $\text{CH}_3\text{CO}_2\text{Na}$.



2. (10 points) The amide below can be protonated on O or N. Draw the most stable conjugate acid, including any important resonance structures.



3. (20 points) (a) Write the acid-base reaction of acetone (CH_3COCH_3 , $\text{pK}_a = 20$) and NaH . Draw all structures clearly, and illustrate the reaction with curved arrows.



(b) Label the acids with their pK_a s, and label the stronger and weaker acids.

(c) Does the equilibrium lie to the right or the left? *right* \rightarrow

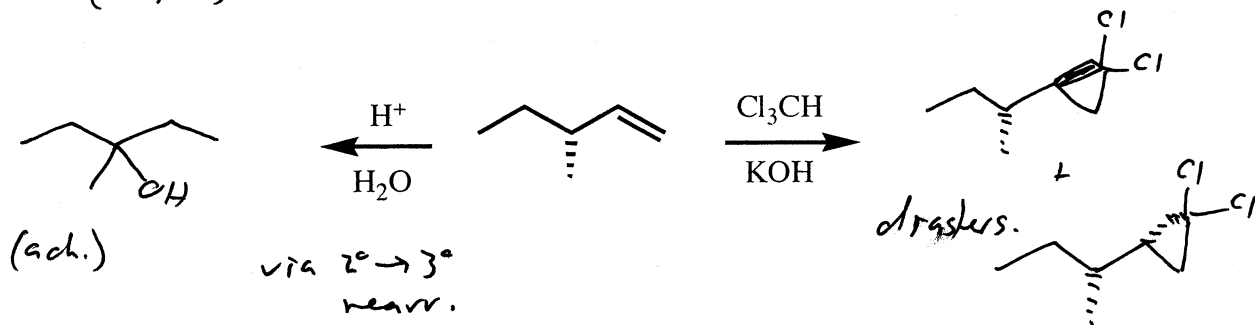
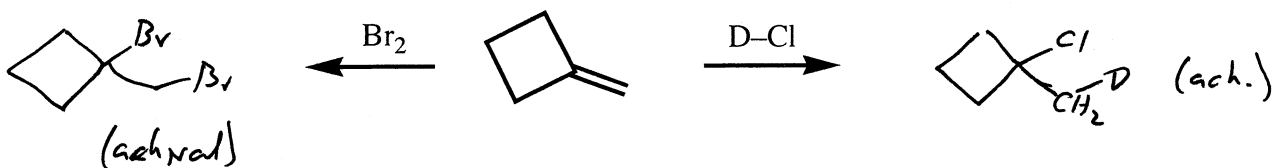
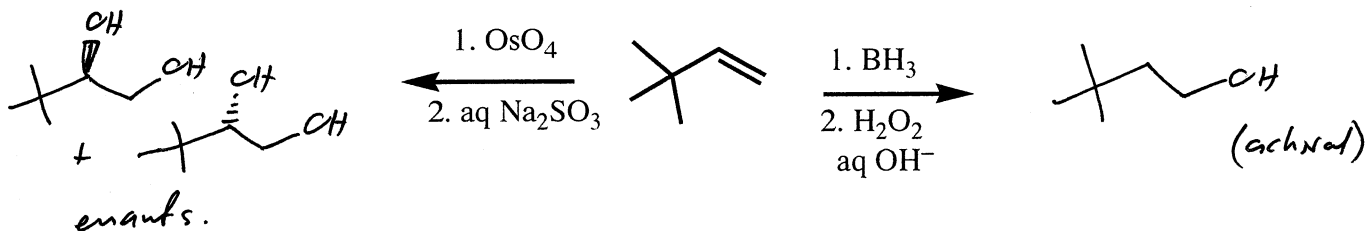
(d) Based on your pK_a s, what is the numerical value of the equilibrium constant?

$$K_{eq} = 10^{15}$$

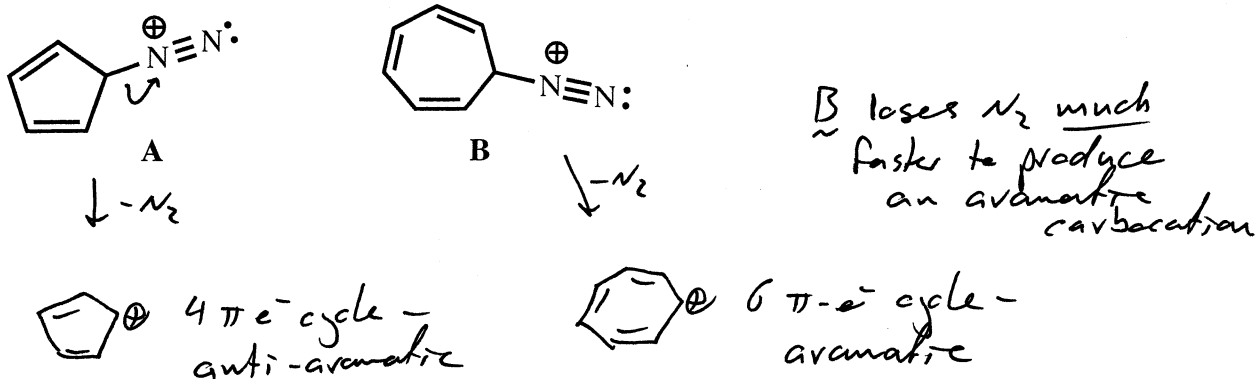
(e) Based on your answer to part d, estimate the ΔG° of the reaction.

$$15 \times 1.36 = 20 \quad \Delta G^\circ = -20 \text{ kcal/mol}$$

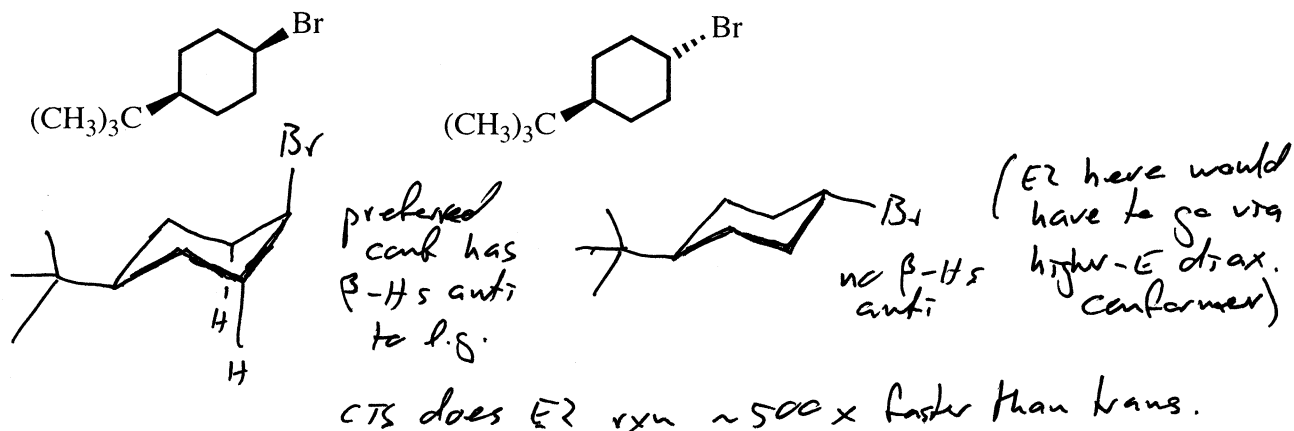
4. (35 points) Draw the organic products of the following reactions, showing stereochemistry clearly. Indicate any products that are enantiomers or diastereomers.



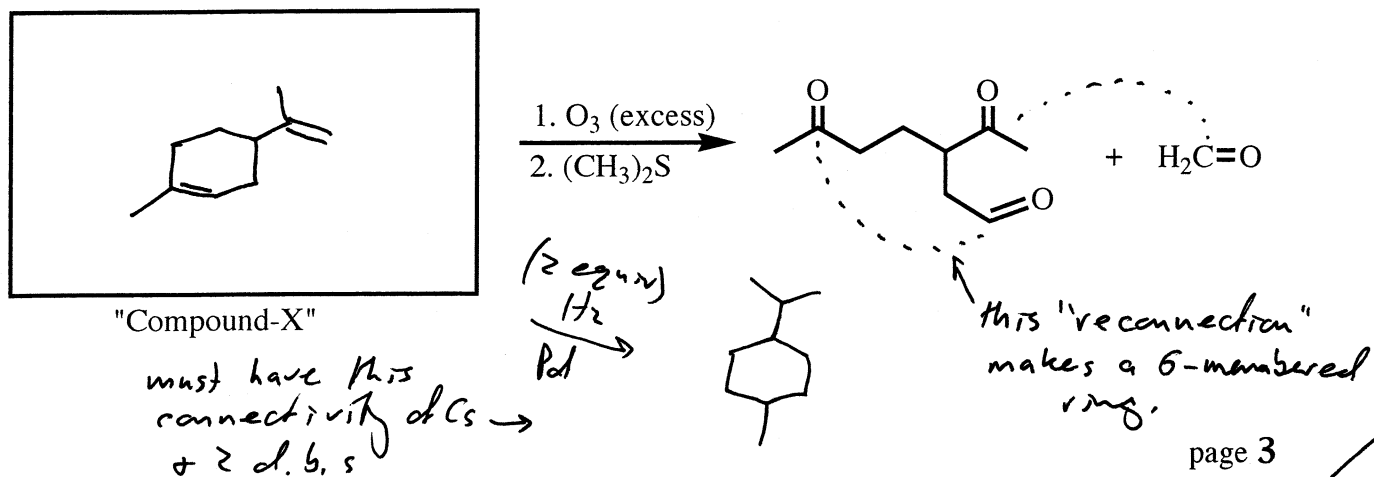
5. (13 points) Which of the diazonium ions below would lose N_2 more rapidly? Briefly explain your choice. (A clear but brief answer will likely require structures.)



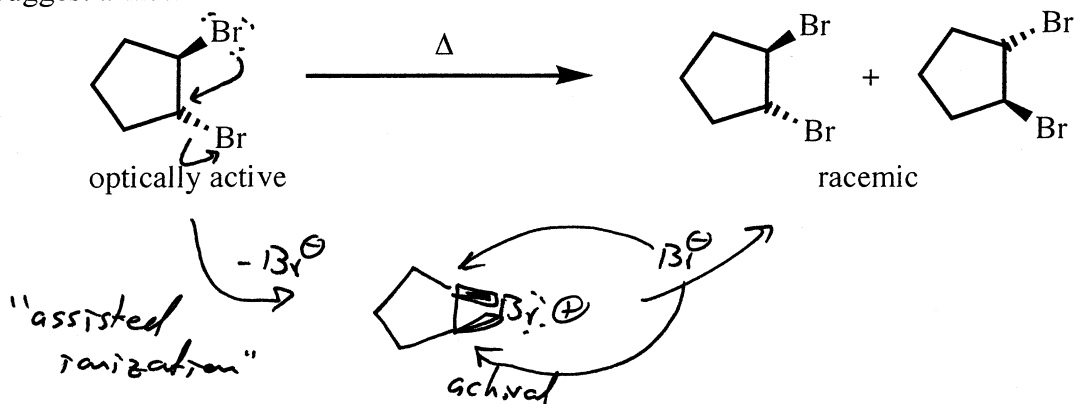
6. (12 points) When treated with potassium *tert*-butoxide, the two stereoisomers below undergo E2 elimination at very different rates. Which stereoisomer reacts more rapidly — the *cis* or the *trans* — and why? (A clear but brief answer will likely require structures.)



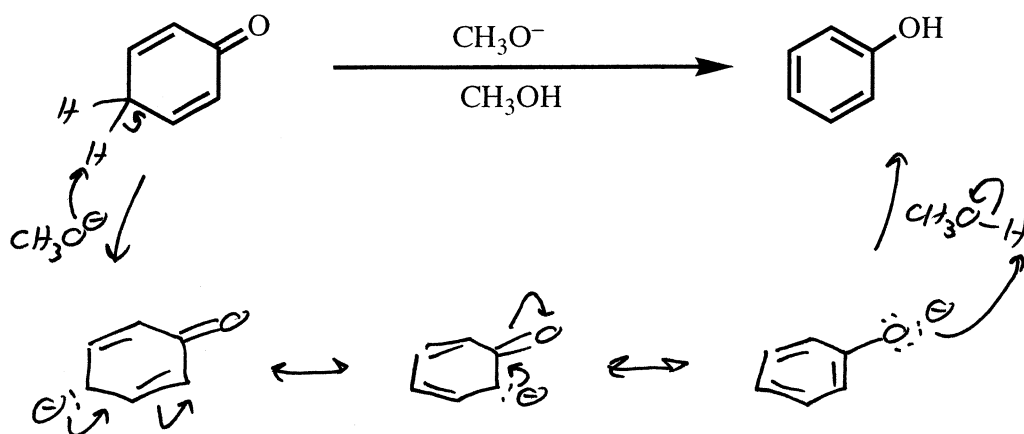
7. (15 points) A fledgling chemical company has hired you as a consultant to determine the structure of an unknown hydrocarbon ("Compound-X"), having the formula $C_{10}H_{16}$. Compound-X reacts with 2 equivalents of H_2 gas in the presence of a Pd catalyst to produce 1-isopropyl-4-methylcyclohexane. Ozonolysis of Compound-X gives the products shown below. The company will pay you \$1,500 (and 15 points) if you can draw the structure of the mystery hydrocarbon in the box.



8. (13 points) When optically active (*R,R*) *trans*-1,2-dibromocyclopentane is heated in a solvent, the optical activity is lost as the compound racemizes, but none of the *cis* stereoisomer is formed. Suggest a mechanism that accounts for these observations.



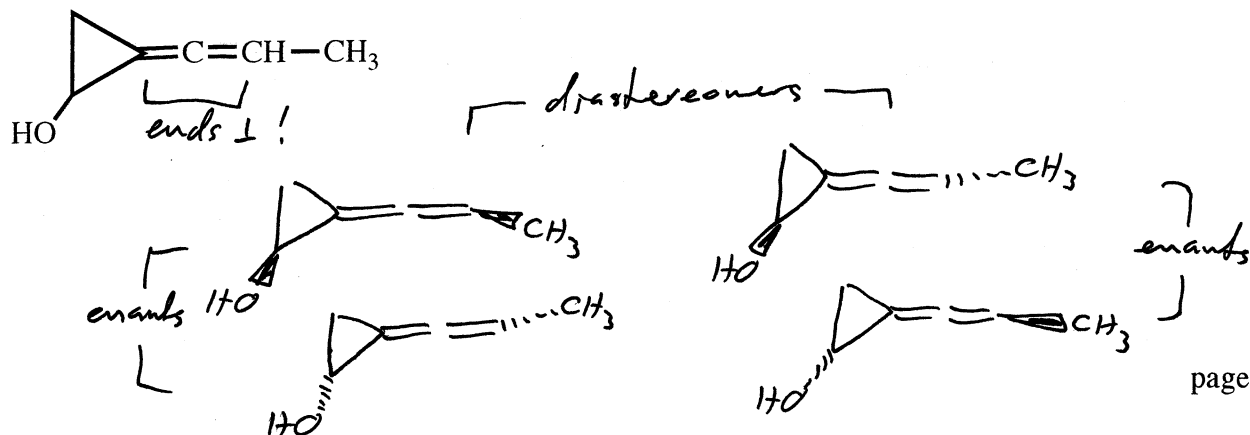
9. (17 points) (a) Write a mechanism for the tautomerization below. Illustrate each step clearly with curved arrows.



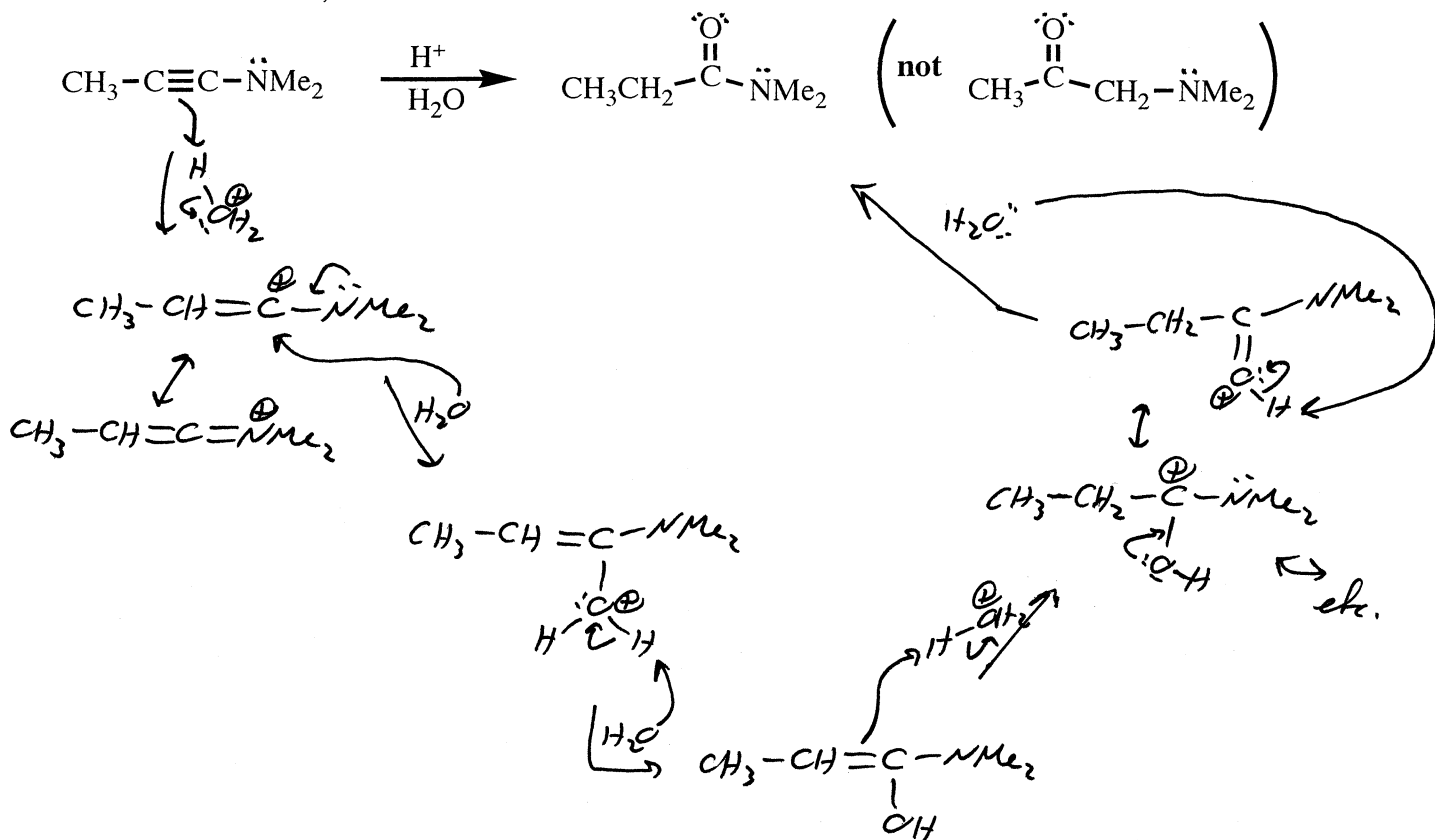
(b) In contrast to the tautomerizations that we saw in class, this one proceeds from a ketone to an enol. Why is the enol favored in this case?

The enol (phenol) is aromatic!

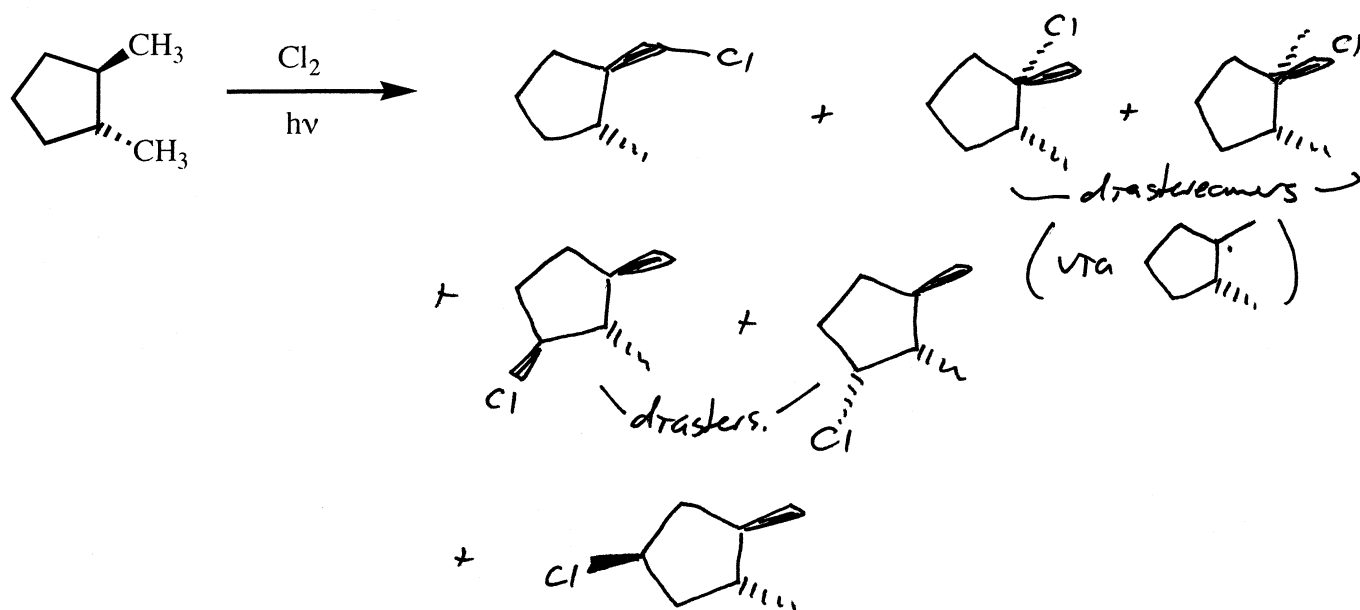
10. (15 points) Draw all the stereoisomers of the following compound. Indicate which are enantiomers and which are diastereomers.



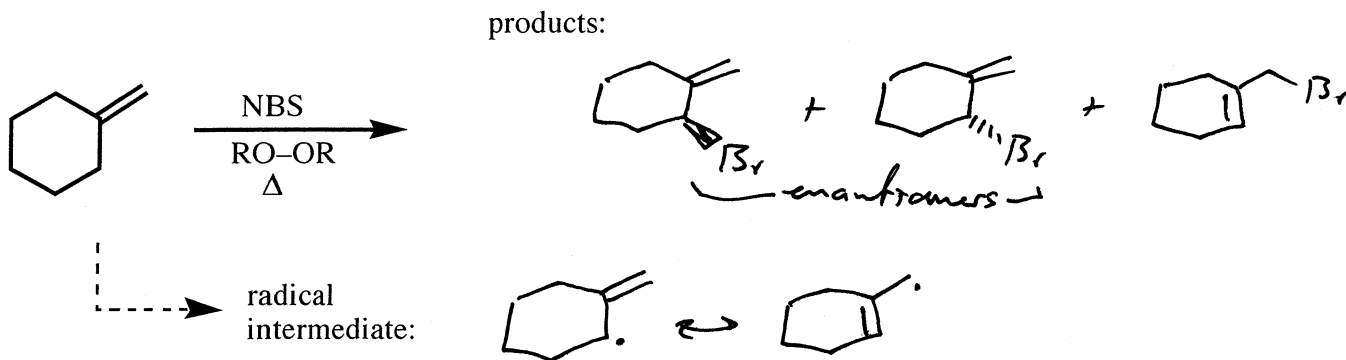
11. (25 points) Hydration of acetylenic amines works *without* the usual Hg^{2+} catalyst. Write a complete mechanism for the acid-catalyzed hydration below. Illustrate each step clearly with curved arrows, and show *Cs* and *Hs* explicitly – don't draw skeletal structures. Your mechanism should also explain the observed regiochemistry – i.e. formation of the amide and not the isomeric keto-amine, as shown.



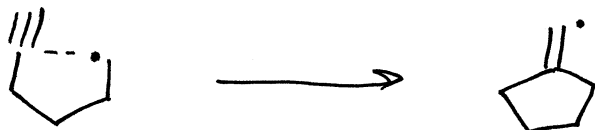
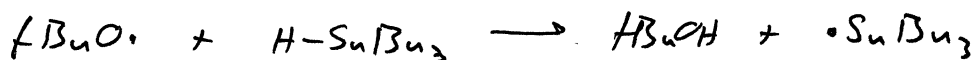
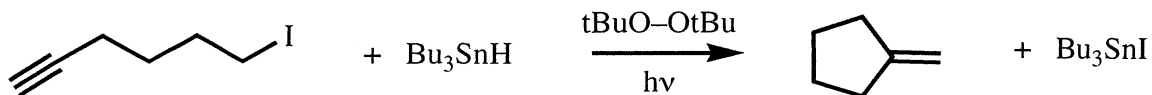
12. (15 points) Free radical chlorination of the optically active alkane below produces a mixture of several mono-chlorides. Draw them, showing stereochemistry clearly. Be sure you don't draw the same product twice.



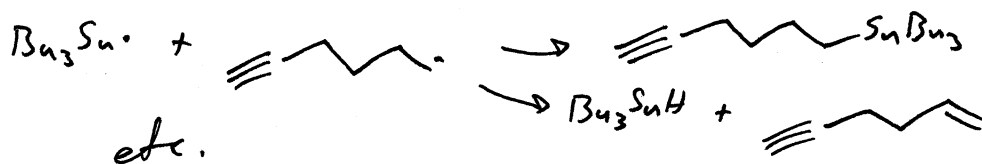
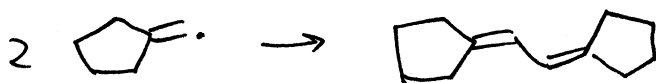
13. (15 points) (a) For the following NBS bromination, draw the organic *radical* intermediate(s), then draw the product(s), showing stereochemistry.



14. (25 points) The reaction below proceeds by a free radical chain mechanism. Photolysis of di-*tert*-butylperoxide initiates the reaction. The resulting *tert*-butoxy radicals abstract H to produce the chain-carrying $\text{Bu}_3\text{Sn}\cdot$ radical. (a) Write the initiation and propagation steps of the mechanism.

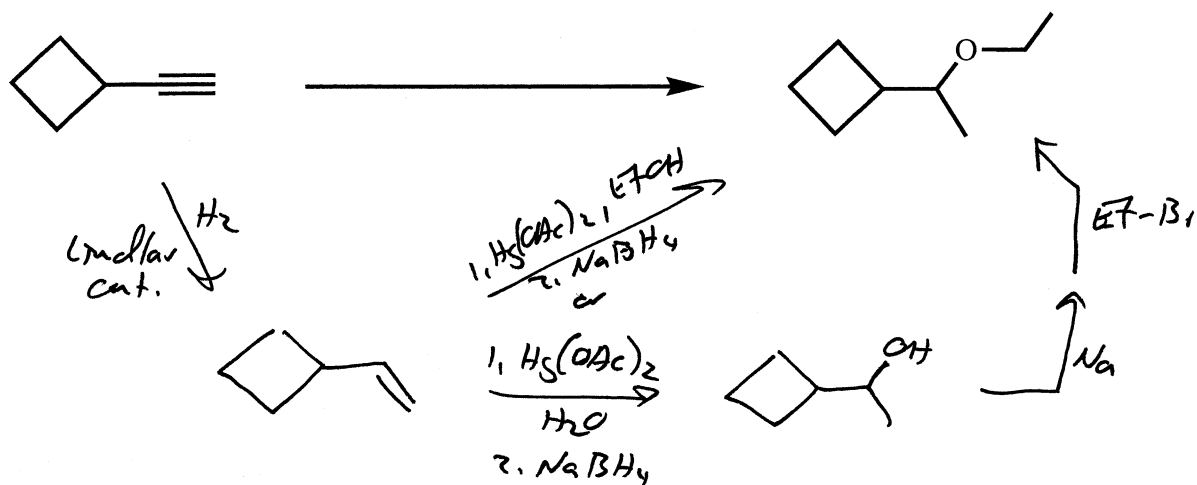


(b) Write two example of chain termination steps.

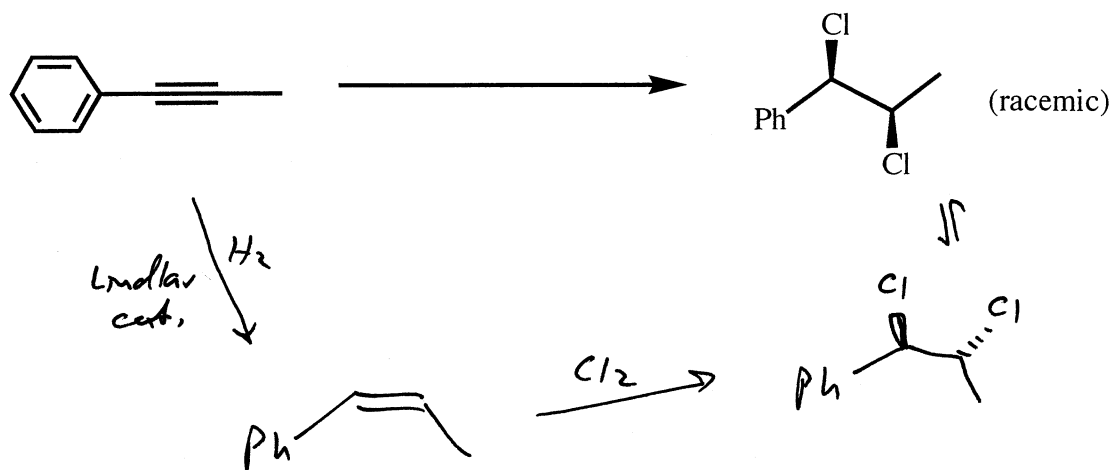


15. (60 points) Suggest a synthetic route for carrying out each of the following transformations in good yield. Pay attention to stereochemistry. As long as you start with the compound shown, you can use any other organic or inorganic compounds you need.

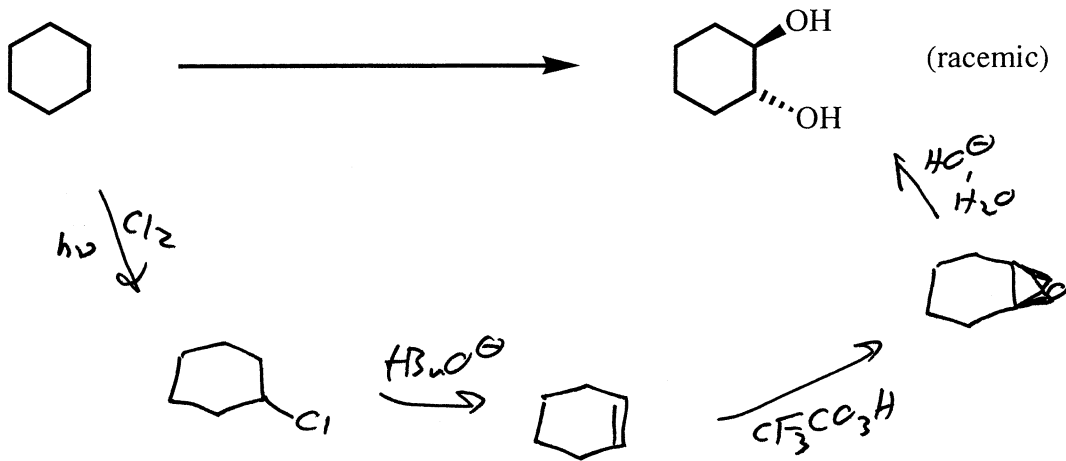
(a)



(b)



(c)



(d)

