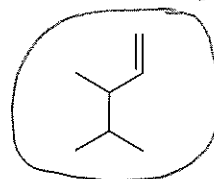
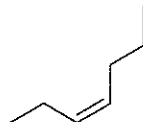
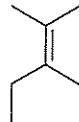
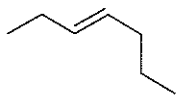
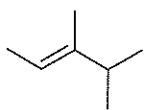


Key - Exam 3 Summer '08 Minger

1. Circle the correct response for each of the following questions (15 pts).

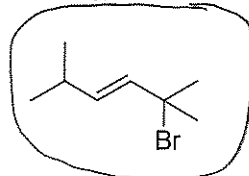
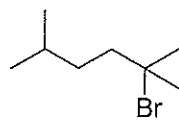
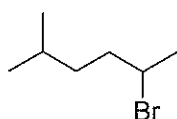
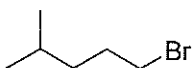
1a. Which of the following alkenes has the *largest* heat of hydrogenation?



monosubstituted

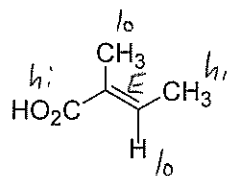
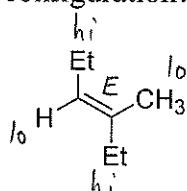
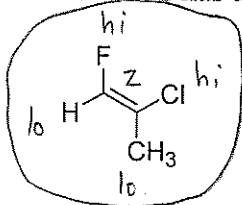
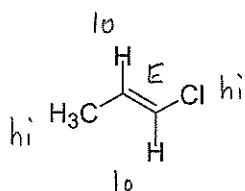
least stable

1b. Which of the following molecules would react the *fastest* under S_N1 conditions?

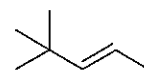
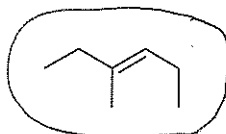
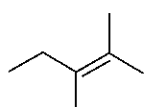
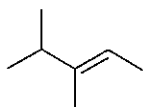


forms 3° allylic cation stabilized by resonance

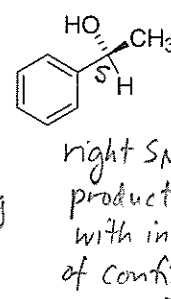
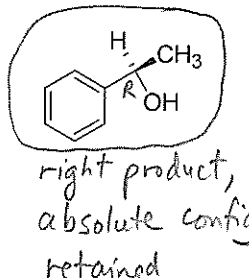
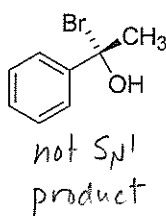
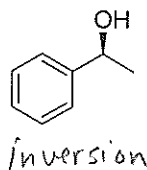
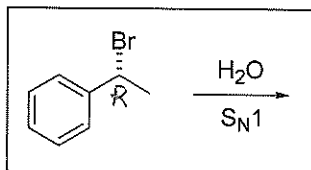
1c. Which of these alkenes has a Z configuration?



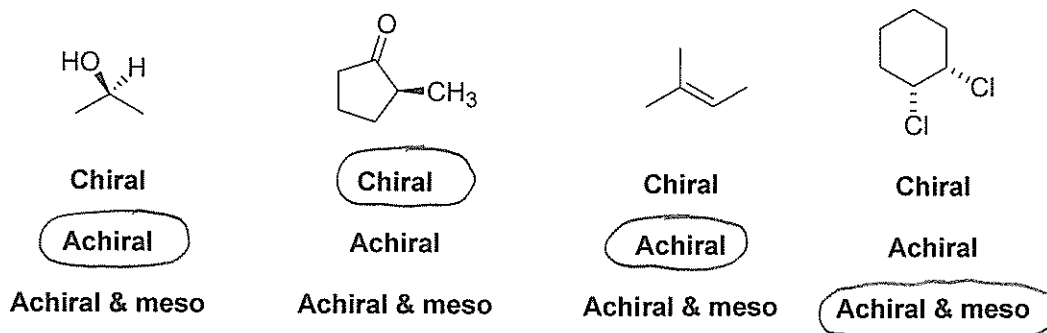
1d. Which of the following alkene isomers is properly named as a *hexene*?



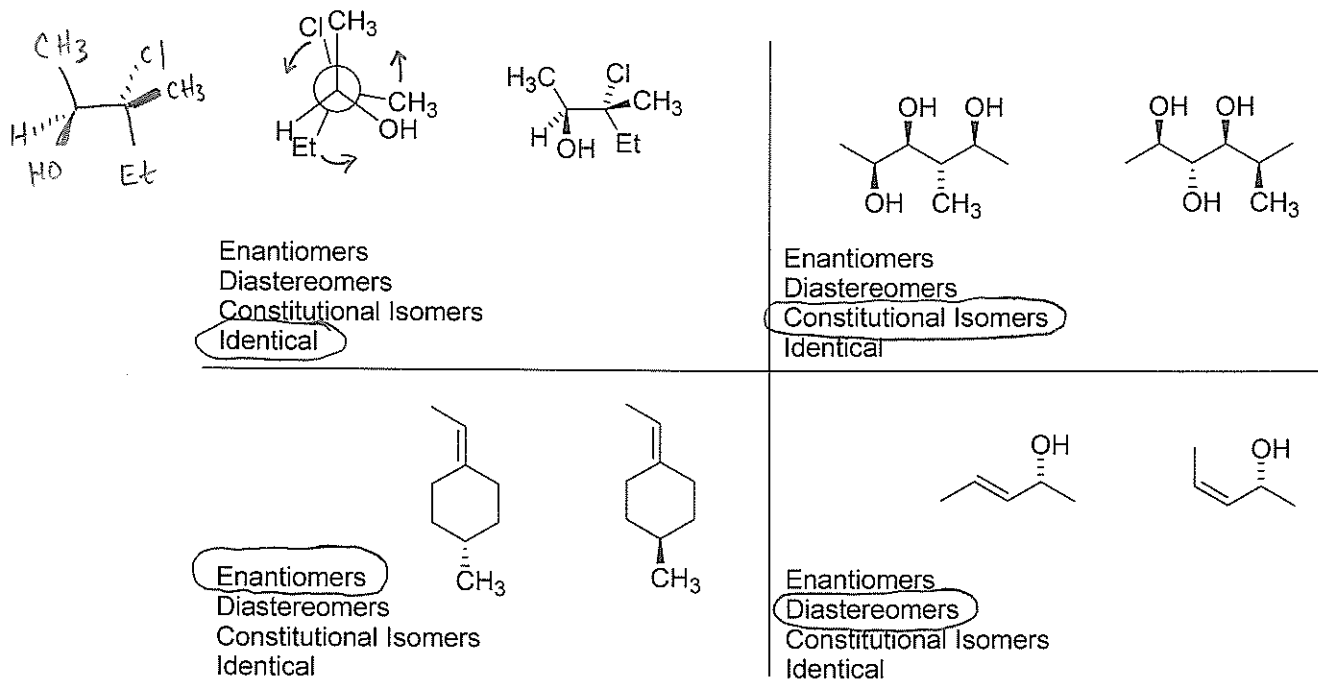
1e. Which of the following compounds is the product of the reaction shown that shows *retention of configuration* compared to the starting material?



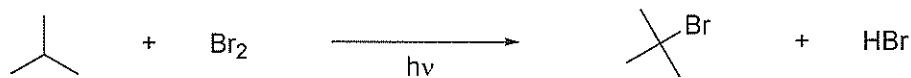
2a. Indicate whether each of the following molecules is chiral, achiral, or achiral and meso by circling the correct response (12 pts).



2b. Indicate the relationship between each of the following pairs of molecules as being enantiomers, diastereomers, constitutional isomers, or identical by circling the correct response (12 pts).



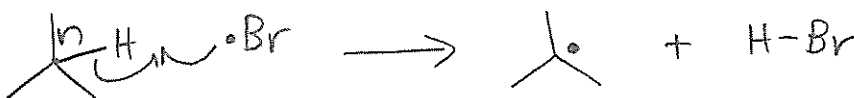
3. Consider the following free radical bromination reaction:



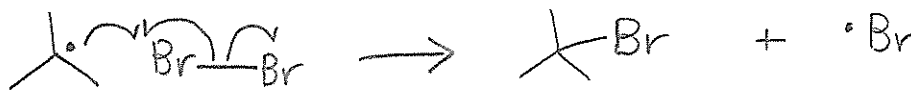
3a. Is this reaction regioselective (2 pts)? **Yes** No (circle one)

3a. Draw mechanisms for the two propagation steps for this reaction. Show all lone pairs, single electrons, curved arrows and non-zero formal charges for full credit. Show the reactants and products of each step. Draw your answers in the boxes provided (10 pts).

First propagation step:



Second propagation step:



3b. The overall enthalpy of this reaction (ΔH_{rxn}) is -14 kcal/mol. Use this information and the following table of bond dissociation energies to calculate the energy of the carbon-bromine bond that forms *in this reaction*. You can use your cell phone calculator if you want. Show all work so we can give partial credit if you happen to set the problem up correctly but make an arithmetic error (3 pts).

Bond dissociation energies
(kcal/mol)

H-Br	88
Br-Br	46
CH ₃ -H	104
1° C-H	98
2° C-H	95
3° C-H	91
CH ₃ -Br	70
2° C-Br	68
3° C-Br	?

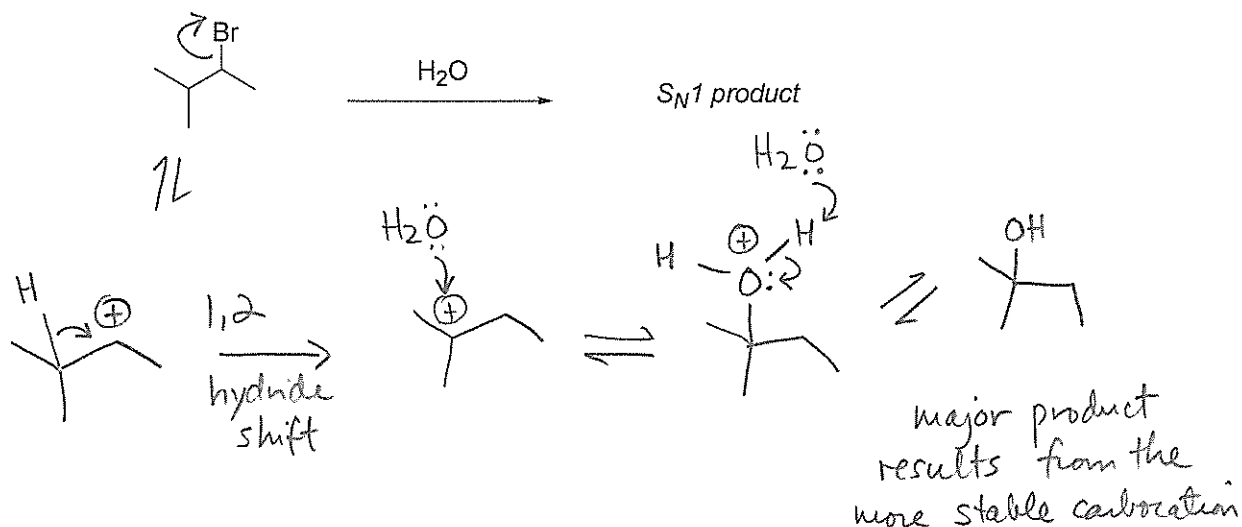
Bonds formed (-)	Bonds broken (+)
H-Br -88	Br-Br + 46
3° C-Br ?	3° C-H + 91
-X	<u>137</u>

$$\Delta H = -14 \text{ kcal/mol} = +137 - 88 - X$$

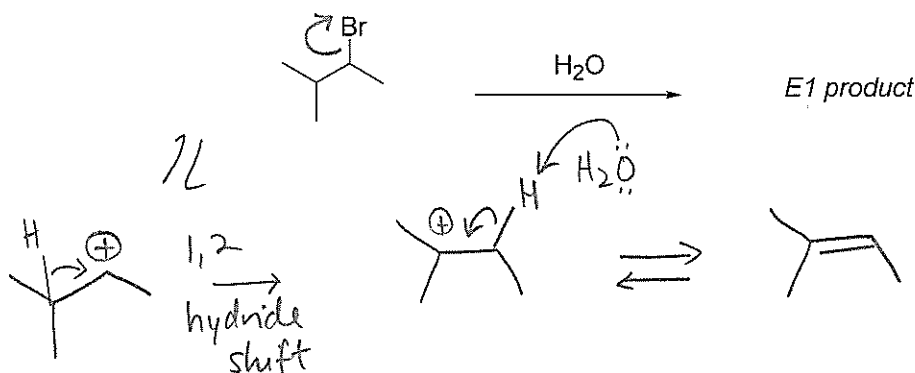
$$3^\circ \text{C-Br} = -63 \text{ kcal/mol}$$

$$\text{so } 63 \text{ kcal/mol}$$

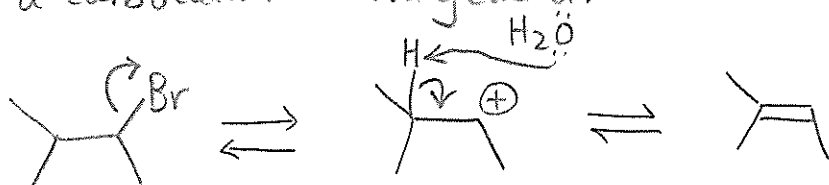
4a. Draw an arrow-pushing mechanism to show the formation of the **major S_N1 product** that would form under the conditions shown. Show all bonds, lone pairs, single electrons, curved arrows and non-zero formal charges for full credit (8 pts).



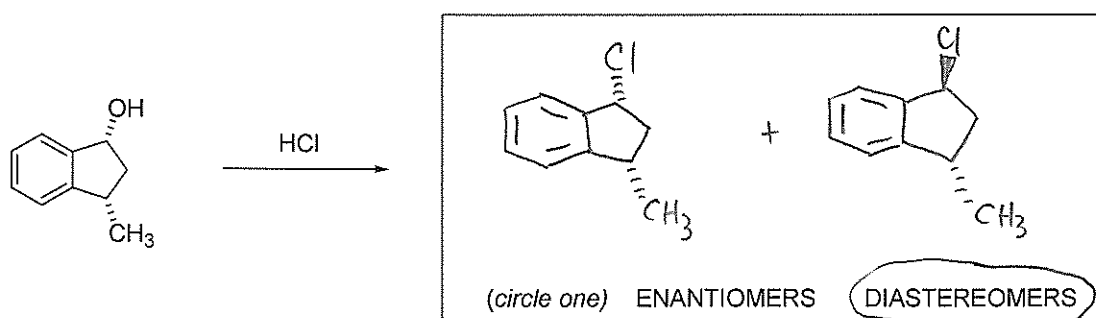
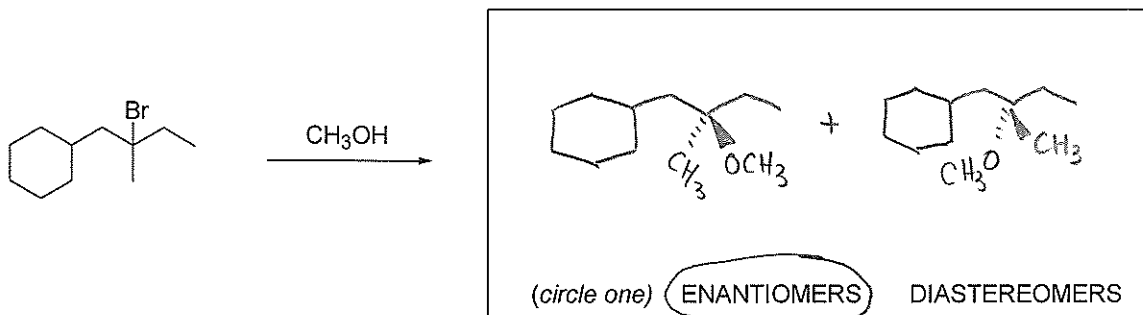
4b. Now, recalling that S_N1 and $E1$ reaction mechanisms nearly always compete with each other, draw an arrow-pushing mechanism to show the formation of the **major E1 product** that would form under the conditions shown. Show all bonds, lone pairs, single electrons, curved arrows and non-zero formal charges for full credit (8 pts).



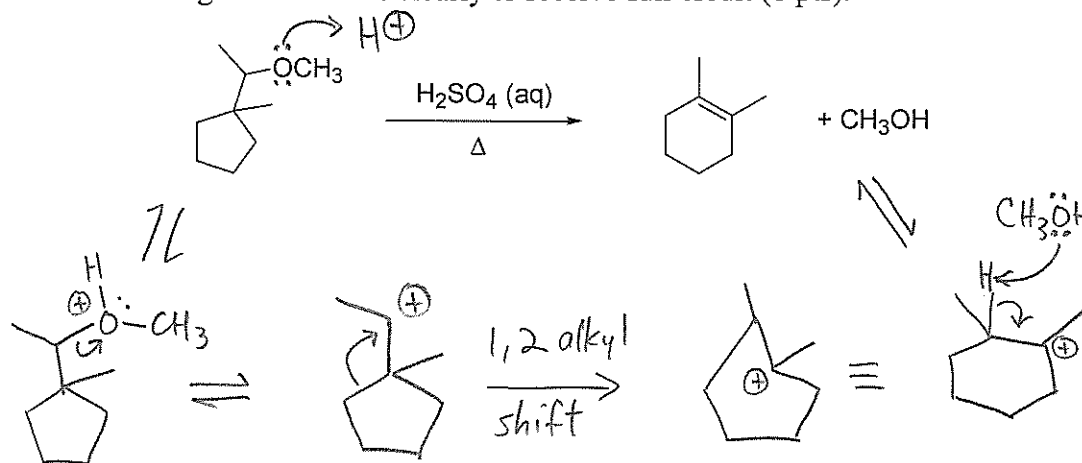
You can also draw formation of the same product without invoking a carbocation rearrangement:



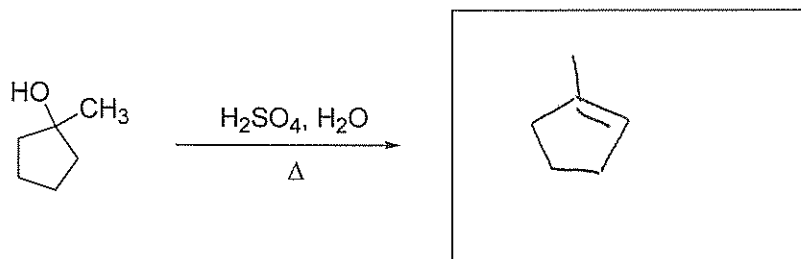
5a. Predict the products of each of the following S_N1 reactions. Show stereochemistry in your structures at all asymmetric carbons. Then identify the correct stereochemical relationship between the structures (enantiomers or diastereomers) (12 pts).



5b. Draw an arrow-pushing mechanism to rationalize the formation of the alkene product shown in the following transformation. Show all bonds, necessary electrons, non-zero formal charges and arrows clearly to receive full credit (8 pts).



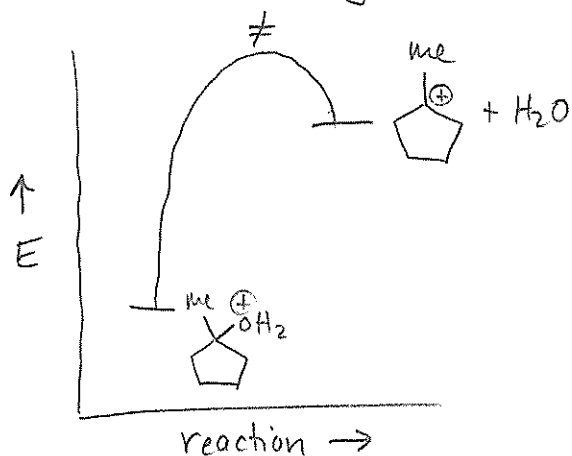
6a. Draw the product of the following reaction (1 pt).



6b. In the reaction in 6a, suppose that instead of water as the solvent, you used a non-polar solvent like hexane. What would be the effect on the rate of reaction, and why? Provide a clear, logical and thorough argument to support your answer. You must include at least one diagram and/or structure to illustrate your point (7 pts).

Using a nonpolar solvent such as hexane would slow the rate of reaction compared to using water.

The rate limiting step is endothermic carbocation formation;



Because this is an endothermic step, Hammond postulate states that the structure of the transition state most closely resembles the product (here, the carbocation intermediate).

As the C-O bond breaks in the transition state, charge develops at C that can be stabilized by ion-dipole interactions between solvent (H_2O) and transition state. Stabilization of charge lowers E of \ddagger (and thus E_{act}) compared to the absence of this intermolecular force, as would be the case if a nonpolar solvent like hexane were used.

