

CHEMISTRY 241  
EXAMINATION II  
Wednesday, March 1, 2006  
Professor William P. Dailey

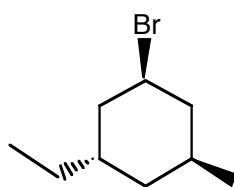
NAME: \_\_\_\_\_ **KEY** \_\_\_\_\_

Student ID number : \_\_\_\_\_

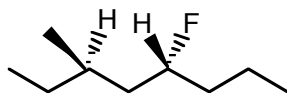
QUESTIONS	POINTS	SCORE
1.	14	_____
2.	5	_____
3.	16	_____
4.	10	_____
5.	12	_____
6.	18	_____
7.	10	_____
8.	15	_____
	TOTAL	_____

READ ALL QUESTIONS CAREFULLY BEFORE ANSWERING THEM.  
**Make sure to indicate stereochemistry if appropriate.**

1. (14 points) a. Provide correct IUPAC names for the following compounds.



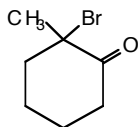
**(1S,3S,5S)-1-Bromo-3-ethyl-5-methylcyclohexane**



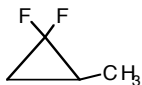
**(3R,5R)-5-Fluoro-3-methyloctane**

- b. Draw three-dimensional representations of the following.

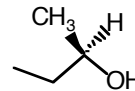
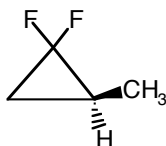
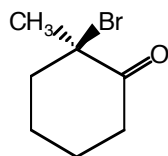
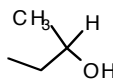
the R enantiomer of



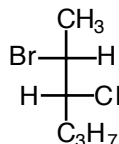
the S enantiomer of



the R enantiomer of



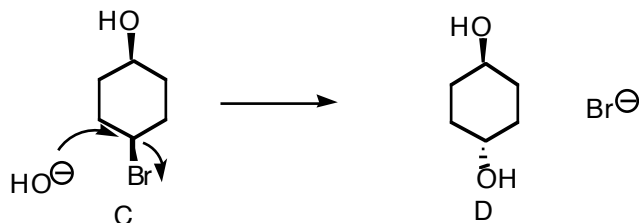
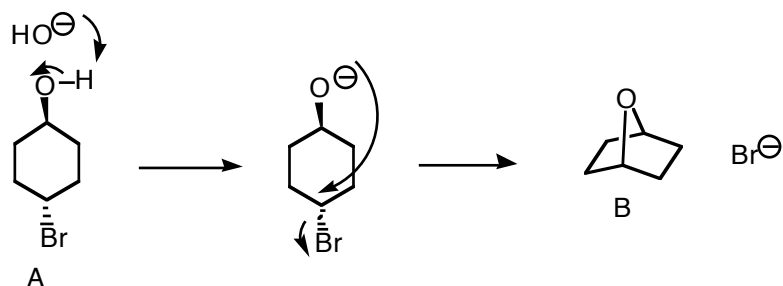
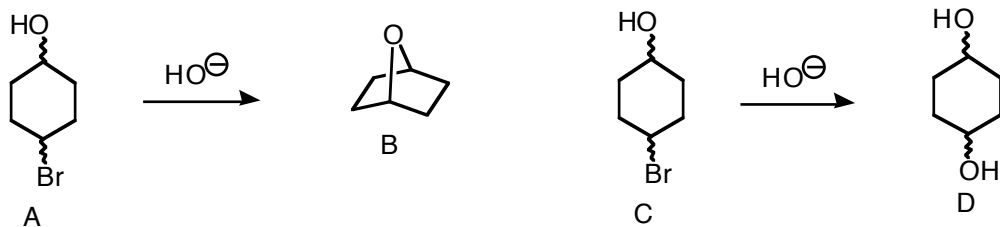
- c. Draw a Fischer projection for (2R,3R)-2-bromo-3-chlorohexane.



2. (5 points) Predict the best nucleophile in each of the following sets of compounds if the reactions are carried out in protic solvents.

- $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{S}$
- $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$
- $\text{PH}_2^-$ ,  $\text{NH}_2^-$ ,  $\text{NH}_3$
- $\text{SCN}^-$ ,  $\text{HSCN}$ ,  $\text{OCN}^-$
- $\text{CH}_3\text{OCH}_3$ ,  $\text{CH}_3\text{SCH}_3$ ,  $(\text{CH}_3)_3\text{N}$

3. (16 points) Treatment of one of the stereoisomers (cis or trans) of 4-bromocyclohexanol (**A**) with base produces compound **B** in good yield, while analogous reaction of the other stereoisomer (**C**) only produces diol **D** as a substitution product. Using the curved-arrow formalism, provide a mechanism that is consistent with this information, and provide the correct stereochemistry of compounds **A**, **C** and **D**.



B must have trans stereochemistry for the intramolecular  $\text{S}_{\text{N}}2$  reaction to proceed. C has cis stereochemistry and can't undergo intramolecular substitution. Intermolecular reaction with hydroxide ion yields only the trans isomer of D.

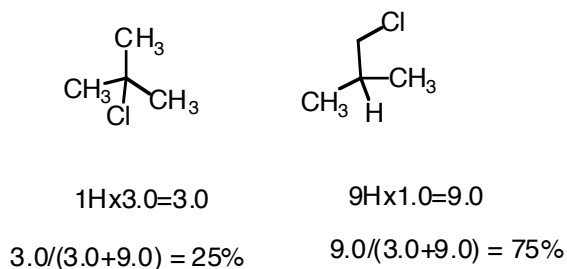
4. (10 points) a. Draw the most stable chair conformations for *trans*-1,4-dimethylcyclohexane and *cis*-1,4-dimethylcyclohexane. Label which is which.



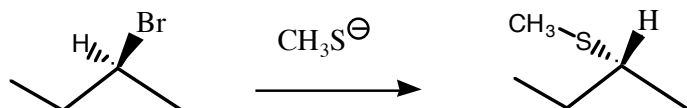
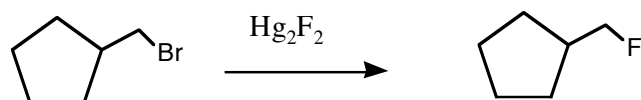
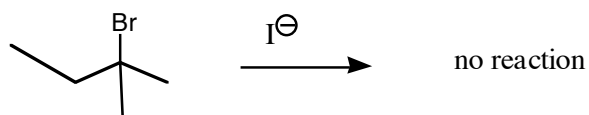
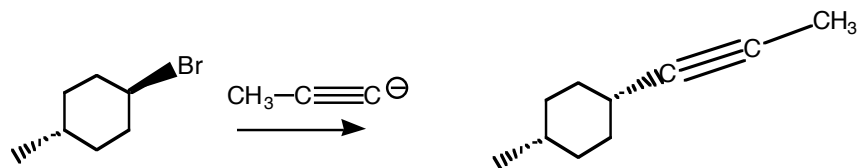
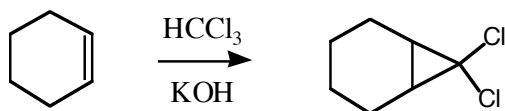
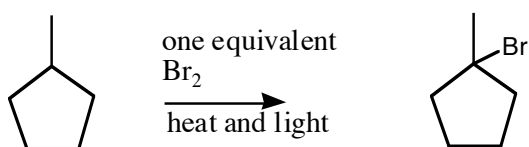
b). A single butane gauche interaction raises the energy of a molecule by about 0.9 kcal/mol. What is the energy difference between the two stereoisomers? Clearly describe your reasoning.

There are no gauche interactions in the *trans* stereoisomer because both methyl groups can occupy equatorial positions, but there are two gauche interactions from the axial methyl group in the *cis* isomer. So the *cis* isomer is  $0.9 \times 2 = 1.8$  kcal/mol LESS stable than the *trans*.

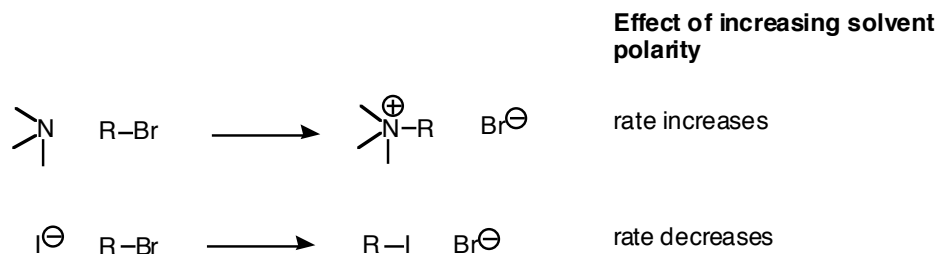
5. (12 Points) Draw all the **monochloro products** you would expect to obtain from the radical chlorination of 2-methylpropane. Given that the relative reactivity of chlorination of tertiary:secondary:primary C-H bonds is 3.0:2.0:1.0, calculate the percentage of each product that would be formed.



6. (18 points total) Complete the following reactions. If no reaction is expected, then say so.



7. (10 Points) Consider the two following substitution reactions, both of which are known to proceed via the  $\text{S}_{\text{N}}2$  mechanism. Based on what you know about the  $\text{S}_{\text{N}}2$  mechanism, explain why the two reactions respond so differently to changes in solvent polarity.



An increase in solvent polarity will help to stabilize ions (charges) by solvation. In the first reaction, the transition state and products have charges and will be stabilized more than the starting materials. This will decrease the energy of the transition state relative to starting materials and make the rate increase.

The second reaction has charge in starting material, transition state, and products. However in the starting material and products the charge is localized on one atom. In the transition state, the charge is spread over multiple atoms. So a polar solvent will stabilize the reactants and products MORE than the transition state. This leads to an increase in the difference of energy between starting materials and the transition state, and leads to a slower reaction (decrease in rate).

8. (15 points) Provide reagent(s) and conditions that would successfully convert propene to 3-methoxypropene. You may use any organic or inorganic reagents. More than one synthetic reaction step may be required. No mechanisms are required.

