

Exam #1

Chemistry 333

Principles of Organic Chemistry I

Tuesday March 14, 2006

Name: KEY.

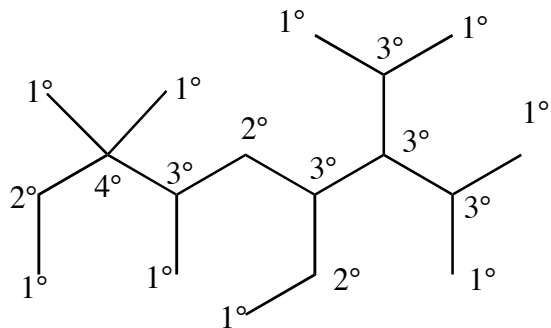
The exam is worth a total of 100 points; there are five questions. Please show all work to receive full credit for an answer.

By putting your name on this exam, you agree to abide by California State University, Northridge policies of academic honesty and integrity

Molecular models are allowed for this exam. Calculators are not needed.

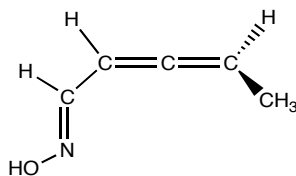
Good Luck!

1. Use the IUPAC rules to write the systematic name for the following hydrocarbon. **Identify on your structure primary (1°), secondary (2°), tertiary (3°), and quaternary (4°) carbon atoms.** (5 minutes, 10 pts)

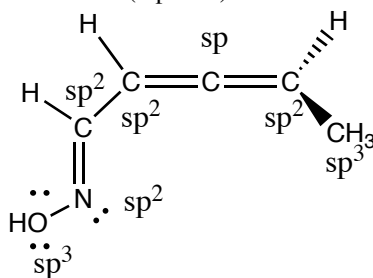


4-ethyl-3-isopropyl-2,6,7,7-tetramethylnonane

2. (20 pts, 15 minutes) For the following molecule:

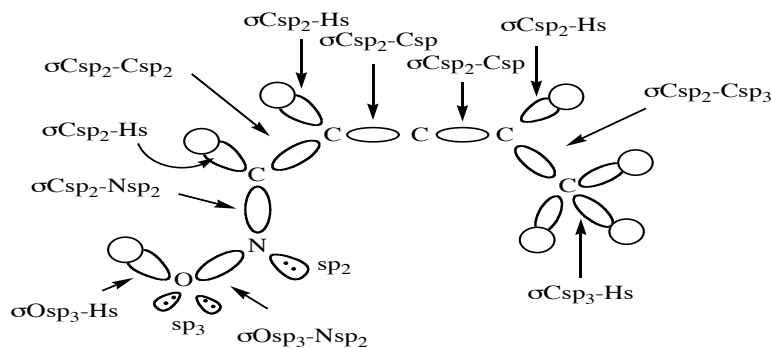


- a. Draw in all lone pairs and indicate the hybridization on all carbon, oxygen and nitrogen atoms present in the structure above. (5 points)

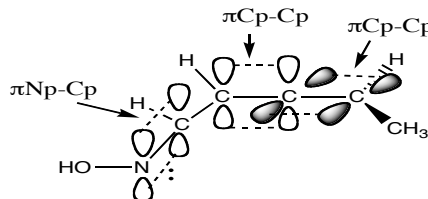


- b. Draw a three-dimensional orbital diagram of this molecule, specifying all the orbitals on each atom that overlap to form bonds. Remember to include lone pairs and indicate which orbitals they occupy. Label the bonds as follows: $\sigma_{H_{1s}-C_{sp^3}}$ etc. Draw the sigma framework first, then the pi framework separately. (15 points)

Sigma network:

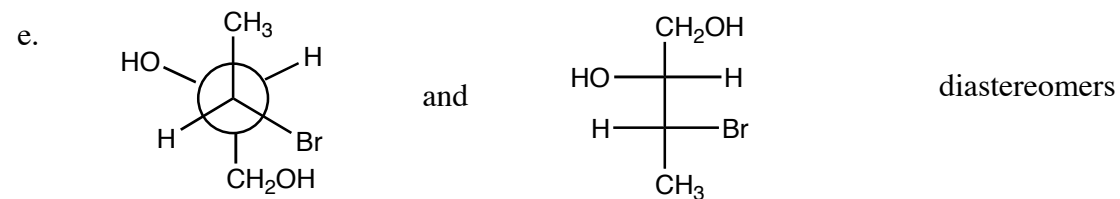
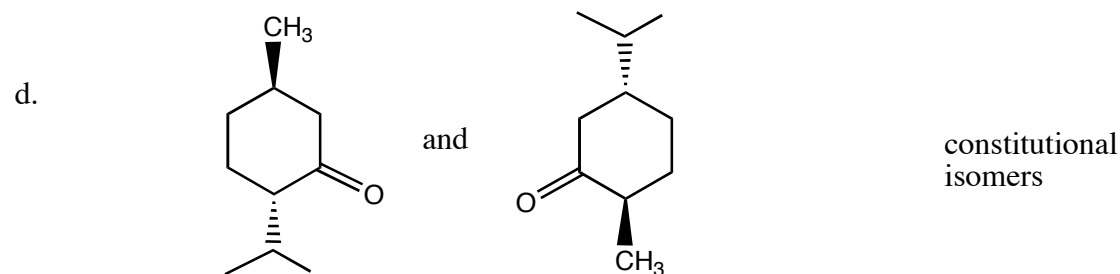
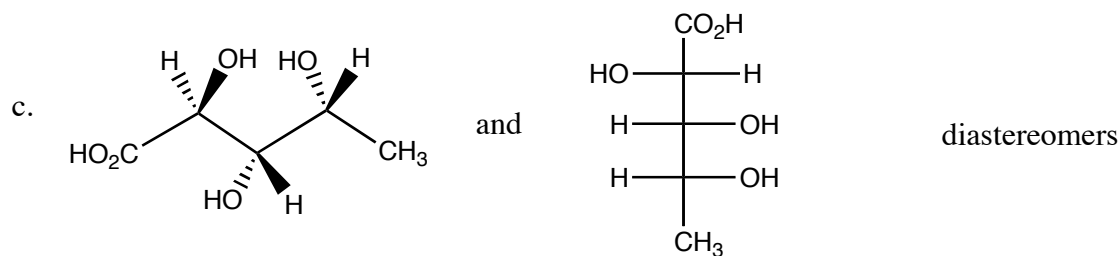
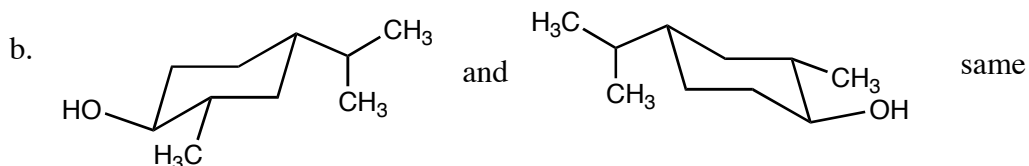
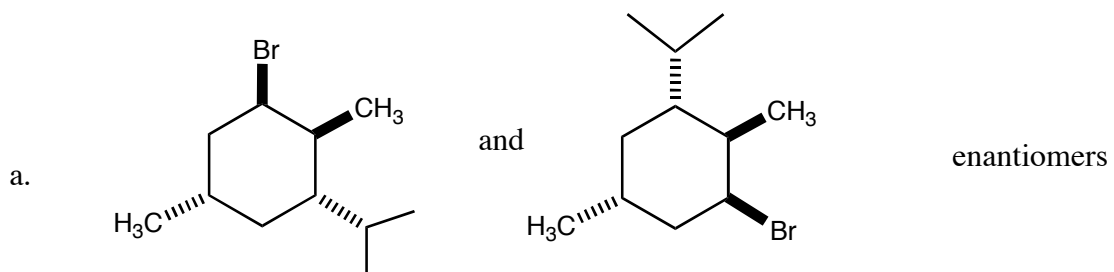


Pi-framework:

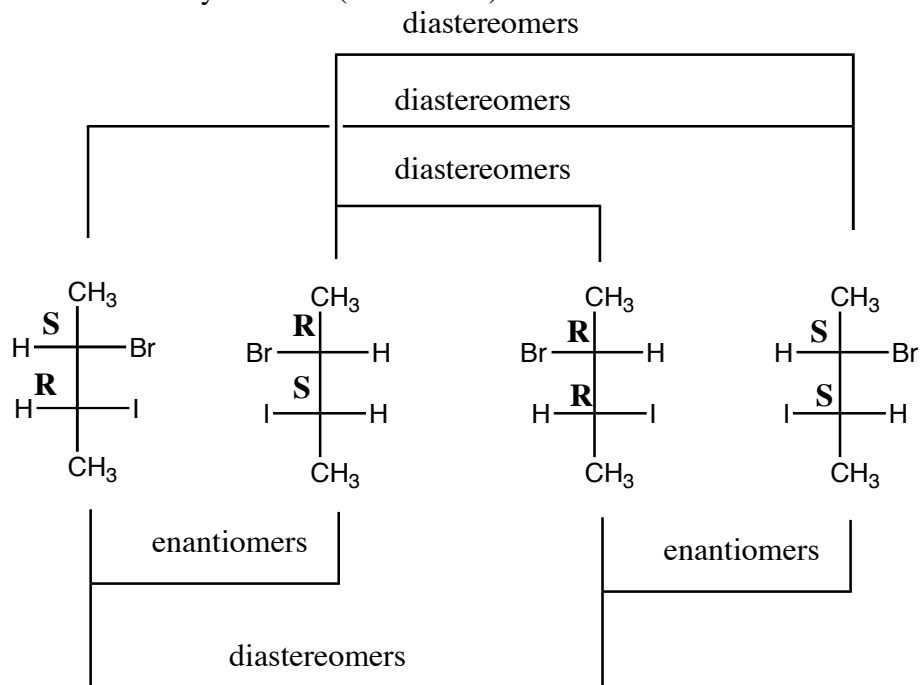


3. Identify the relationship in the following pairs. Possibilities include: same molecules, constitutional isomers (structural isomers), diastereomers, enantiomers. (20 points) (10 minutes)

Relationship



4. Use Fischer projections to draw all possible stereoisomers of 2-bromo-3-iodobutane. (20 points)
- Label pairs of compounds that are enantiomers or diastereomers
 - assign configurations (*R* or *S*) for all asymmetric carbon atoms in each structure you draw. (10 minutes)

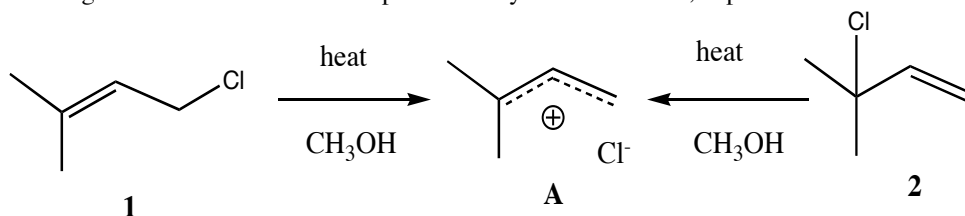


c. If (2*R*, 3*S*)-2-bromo-3-iodobutane has $[\alpha]_D = -22^\circ$, what will be the observed rotation for a solution containing 1 gram of (2*R*, 3*S*)-2-bromo-3-iodobutane and 3 grams of (2*S*, 3*R*)-2-bromo-3-iodobutane? (5 points)

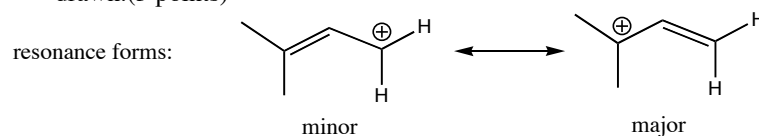
$$\text{e.e.} = \frac{3-1}{3+1} = 0.5 * 100 = 50\%$$

$$\text{observed rotation} = (0.5)(+22^\circ) = +11^\circ$$

5. Heating halides **1** or **2** in methanol produces allylic cation salt **A**, depicted as a resonance hybrid:



- a. Draw the individual resonance forms that contribute to resonance hybrid **A**, and indicate which is the major and which is (are) the minor resonance forms. Give a rationale for your assignment, discussing the relative **stabilities** of the resonance forms you have drawn. (5 points)

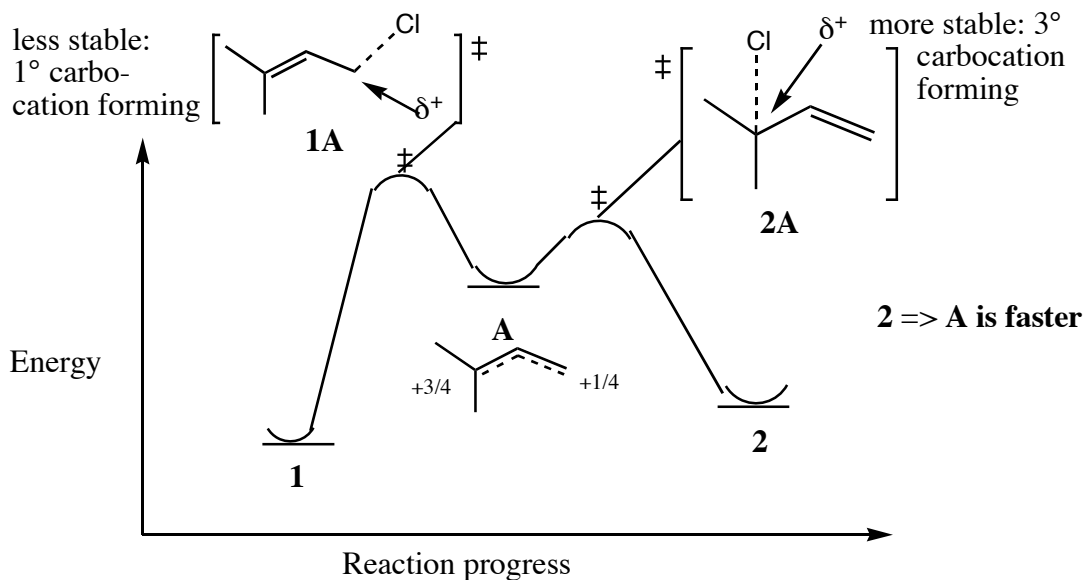


more substituted cations are more stable $3^\circ > 2^\circ > 1^\circ$; additional alkyl substitution contributes electron density to the electron-deficient center both inductively and hyperconjugatively.

The major resonance form is more representative of the actual structure of the molecule. The resonance hybrid might thus be represented:

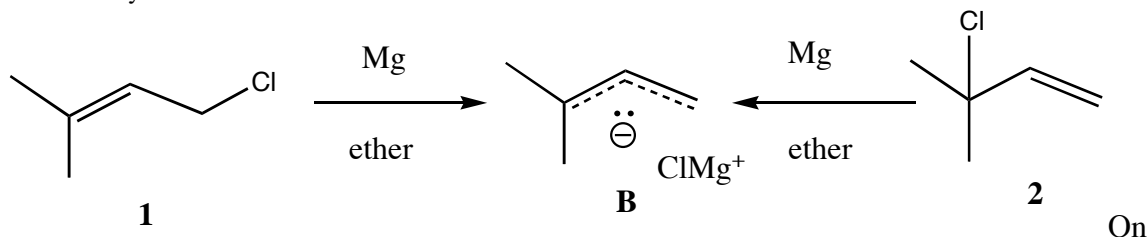


- b. Based on your answer to (a), indicate which process occurs faster (i.e., has a more stable, lower energy transition state): **1** \rightarrow **A** or **2** \rightarrow **A**. Show this on the graph below, drawing transition state structures depicting the process of C-Cl bond cleavage. (10 pts)

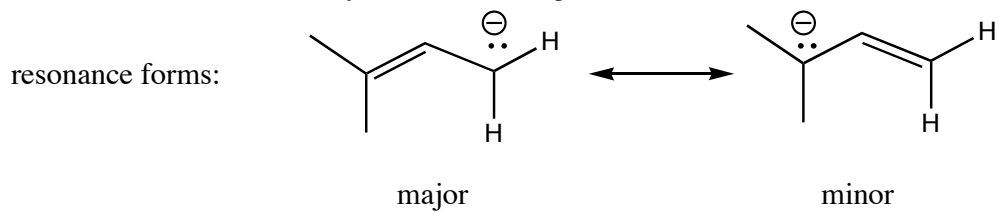


Transition state **2A** is more stable than transition state **1A**, since positive charge buildup is occurring on a 3° carbon atom, more resembling intermediate **A**. For **1A**, initial positive charge buildup occurs on a 1° carbon atom, less resembling **A**.

5c. Treatment of halides **1** or **2** with magnesium metal in ether produces allylic anion salt **B**, depicted as a resonance hybrid:



Draw the individual resonance forms that contribute to resonance hybrid **B**, and indicate which is the major and which is (are) the minor resonance forms. Give a rationale for your assignment, discussing the relative stabilities of the resonance forms you have drawn. (5 pts)

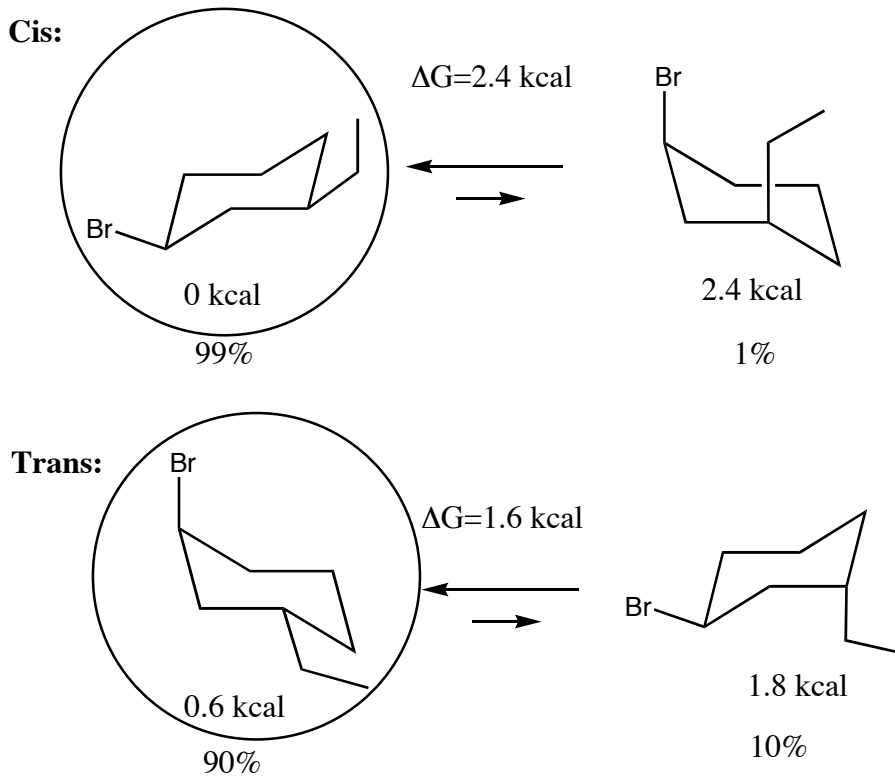


less substituted anions are more stable $1^\circ > 2^\circ > 3^\circ$; they are already electron-rich.

The major resonance form is more representative of the actual structure of the molecule. The resonance hybrid might thus be represented:



6. (Bonus) Draw the two chair forms for *cis*-1-bromo-3-ethylcyclohexane and for *trans*-1-bromo-3-ethylcyclohexane, estimate the energy difference between the conformers, show the relative percentages of each conformer present at equilibrium, circle the more stable conformer of each pair, and indicate which is more stable, the *cis* or the *trans* isomer.(10 points)



cis is more stable since 99% of the molecules are in the more stable *trans* diequatorial form

Congratulations!

Score:

1. _____ /10

2. _____ /20

3. _____ /20

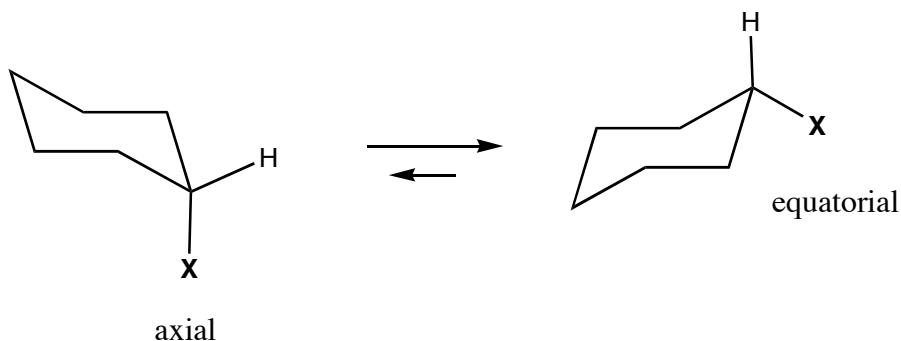
4. _____ /25

5. _____ /25

Bonus: _____ /10

Total: _____ /100

Energy differences Between Axial and Equatorial Conformations in Monosubstituted Cyclohexanes



X	E(axial)-E(equatorial)
-F	0.2 kcal/mol (0.8 kJ/mol)
-CN	0.2 kcal/mol (0.8 kJ/mol)
-Cl	0.5 kcal/mol (2.1 kJ/mol)
-Br	0.6 kcal/mol (2.5 kJ/mol)
-OH	1.0 kcal/mol (4.1 kJ/mol)
-COOH	1.4 kcal/mol (5.9 kJ/mol)
-CH ₃	1.7 kcal/mol (7.1 kJ/mol)
-CH ₂ CH ₃	1.8 kcal/mol (7.5 kJ/mol)
-CH(CH ₃) ₂	2.1 kcal/mol (8.8 kJ/mol)
-C(CH ₃) ₃	5.4 kcal/mol (23 kJ/mol)

The relationship between stability and isomer percentages at equilibrium

<u>More stable isomer (%)</u>	<u>Less stable isomer (%)</u>	<u>Energy difference at 25°C</u>
50	50	0 kcal/mol (0 kJ/mol)
75	25	0.651 kcal/mol (2.72 kJ/mol)
90	10	1.302 kcal/mol (5.45 kJ/mol)
95	5	1.744 kcal/mol (7.29 kJ/mol)
99	1	2.500 kcal/mol (11.38 kJ/mol)
99.9	0.1	4.092 kcal/mol (17.11 kJ/mol)