Exam #1

Chemistry 333

Principles of Organic Chemistry I

Tuesday March 3, 2009

Name: KEY .

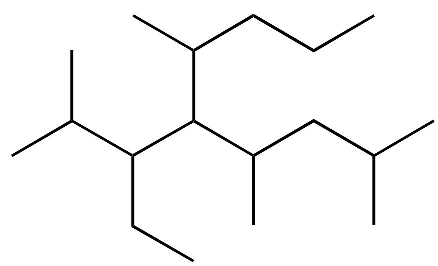
The exam is worth a total of 100 points; there are five questions. Please show all work to receive full credit for an answer.

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!

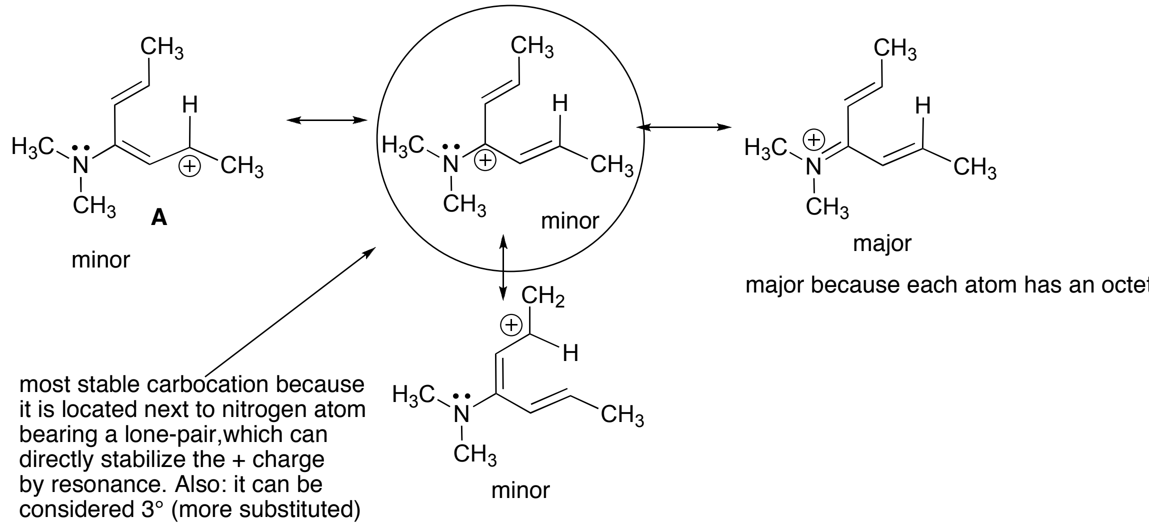
1. Use the IUPAC rules to write the systematic name for the following hydrocarbon. Identify on your structure primary (1°), secondary, (2°), tertiary (3°), and quaternary (4°) carbon atoms. (10 pts)



5-(1-ethyl-2-methylpropyl)-2,4,6-trimethylnonane

2,4,6-trimethyl-5-(2-methylpentan-3-yl)nonane

2. (20 pts) For the following molecule:

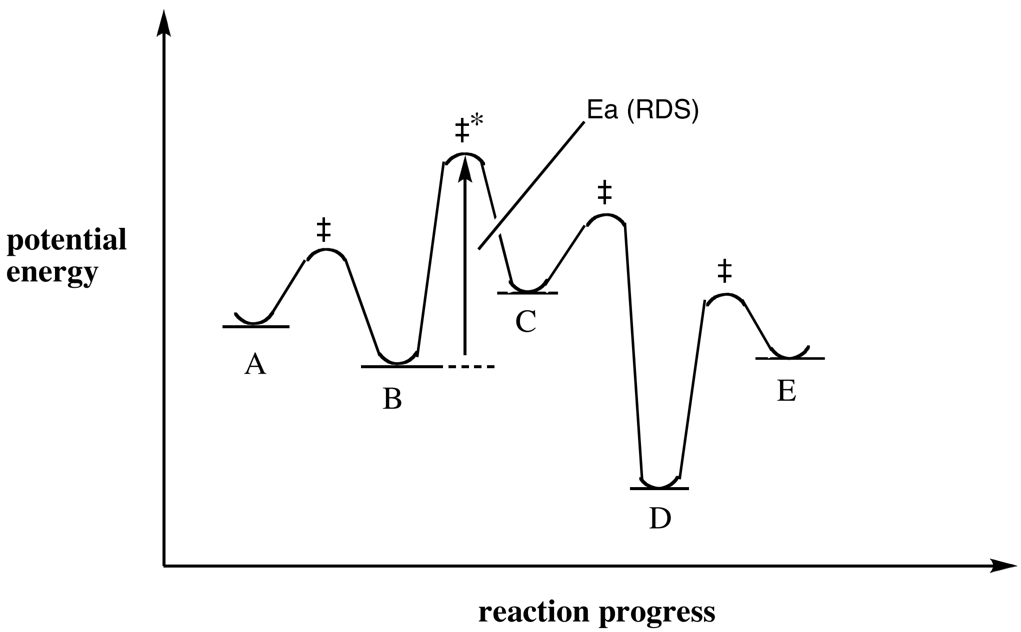


a. Draw all possible resonance forms, denoting all formal charges on non-neutral atoms. Be sure to include lone pairs on heteroatoms! 10 points (see above)
b. Label the major and minor resonance forms, briefly (1 sentence) indicating a rationale for your assignment (5 points).
c. Circle the resonance form with the most stable **carbo**cation (carbon-centered cation), and indicate why that carbocation is most stable among your resonance forms. (5 points)

3. For the following four-step process:

A➔ B ➔ C ➔ D ➔ E

On the diagram below, draw a reaction profile for this process in which the **second step** (B➔C) is rate-determining. (20 points)



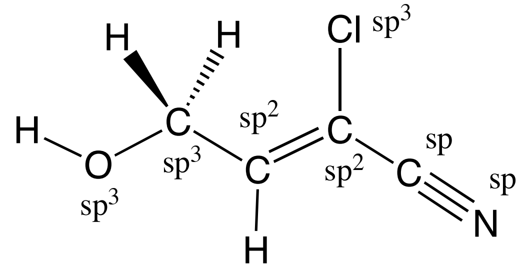
a. Is this process overall endothermic or exothermic (ΔH= <0, 0, >0)? (5 points)
   exothermic

b. On your diagram, label the activation energy (Ea) for the rate-determining step (5 points)
   see diagram

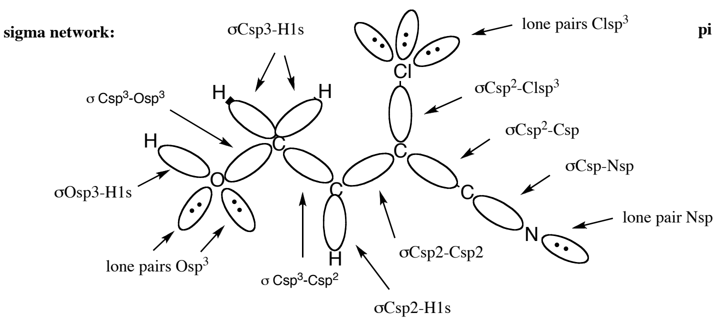
c. On your diagram, label all *transition states* with double daggers (‡), and label the rate-limiting transition state with a star (‡*). (5 points)
   see diagram

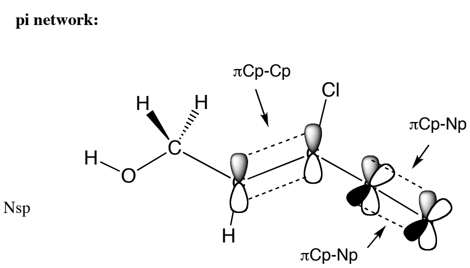
d. Is the rate-limiting transition state an early or a late transition state? Which species on the diagram (A, B, C, D, or E) does it resemble structurally? Explain, using the Hammond Postulate. (5 points)
   Late TS resembling C; endothermic. Hammond Postulate: species which are close in energy resemble each other structurally

4. (a) Indicate the hybridization on all carbon, oxygen, nitrogen and chlorine atoms present in the structure shown. (7 points)

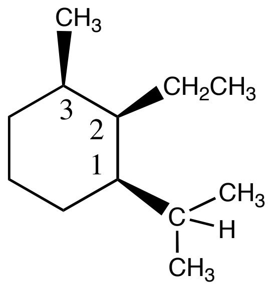


(b) Draw a three-dimensional orbital diagram of this molecule, specifying all the orbitals on each atom that overlap to form bonds. *Remember to include lone pairs and indicate which orbitals they occupy*. Label the bonds as follows: σ H_{1s}-C_{sp3} etc. It may be useful to draw two diagrams, one representing the sigma network of the molecule, and one representing the pi network.(18 points)



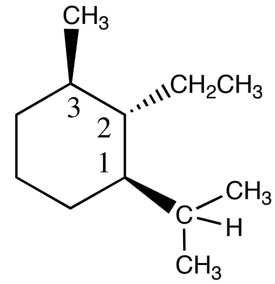


5. Consider the following molecules (25 points)



1,2,3,-*cis*

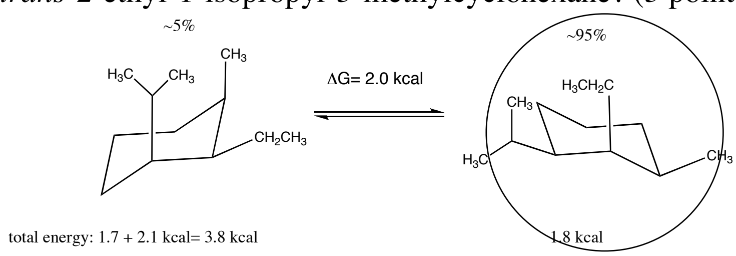
2-ethyl-1-isopropyl-3-methylcyclohexane

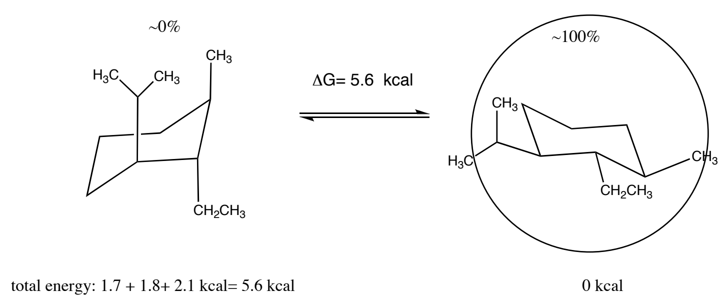


1,2-*trans*, 2,3-*trans*

2-ethyl-1-isopropyl-3-methylcyclohexane

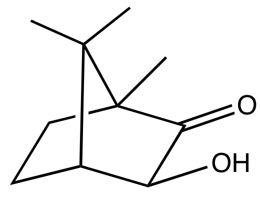
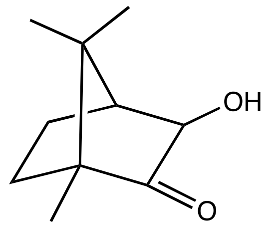
a. Assign R, S configurations for carbons 1, 2, and 3 in **both** the *cis* and *trans* compounds (6 points). Cis: R,R,R; Trans: R,S,R
b. Draw two chair forms for each compound (10 points)
c. Using the table on the back page, estimate the energy difference between the conformers, show the relative percentages of each conformer present at equilibrium (at 25°C), and circle the more stable conformer of each pair. (6 points)
d. Which is more stable, 1,2,3-*cis*-2-ethyl-1-isopropyl-3-methylcyclohexane, or 1,2-*trans*, 2,3-*trans*-2-ethyl-1-isopropyl-3-methylcyclohexane? (3 points)

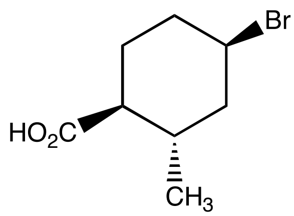
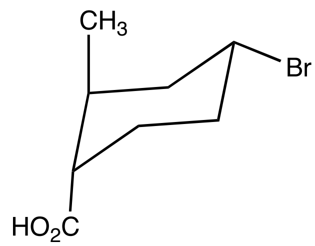


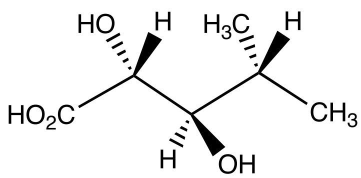
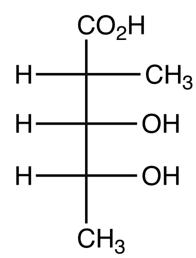


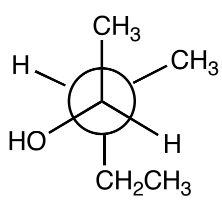
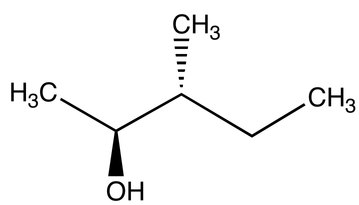
trans is clearly more stable

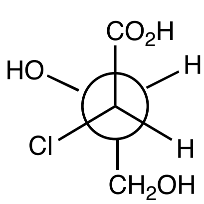
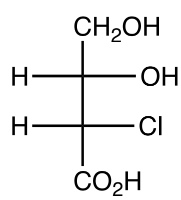
6. Bonus. Identify the relationship in the following pairs. Possibilites include: same molecules, constitutional isomers (structural isomers), diastereomers, enantiomers. (10 points)

a.  and  enantiomers

b.  and  same

c.  and  constitutional isomer

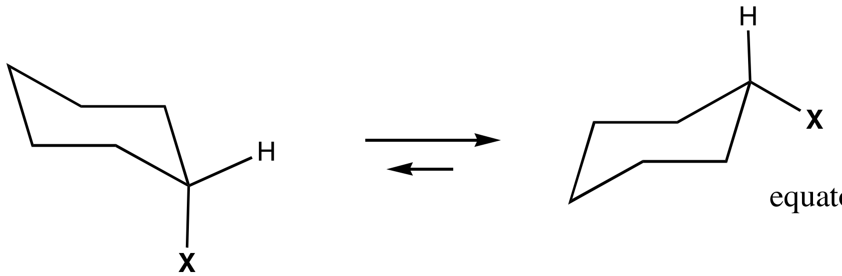
d.   enantiomer

e.  and  diastereomers

Congratulations!
Score:

1. ______________/10
2.______________/20
3.______________/20
4.______________/25
5.______________/25
Bonus___________/10
Total: ___________/100

Energy differences Between Axial and Equatorial Conformations in Monosubtsituted 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)**
$-CH_2CH_3$	**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

More stable isomer(%)	Less stable isomer (%)	Energy difference at 25°C
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	2.722 kcal/mol (11.38 kJ/mol
99.9	0.1	4.092 kcal/mol (17.11 kJ/mol