EXAM 2

Comprehensive Organic Chemistry

CHEMISTRY 225b

Friday, February 24, 2006

NAME (print): _____

TA:_____ Section Day:_____ Section Time:_____

No Calculators! Take a few moments to look over the exam. Answer each question on the exam paper.

Important clues and structures are in **bold**.

Do all **preliminary** drawing or computations on the work sheets at the end of the exam. The work sheets will not be graded.

The exam is 55 minutes.

STOP writing and hand in your exam when you are asked to do so.

REMEMBER: Neatness is to your advantage.

1. (20 pts) Conformation _____

2. (30 pts) Potpourri _____

3. (20 pts) Stereochemistry _____

4. (30 pts) S_N2 Reactions _____

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Total (100 pts)

1. (20 pts) **Conformation**: Answer both questions.

A non-racemic, optically inactive compound **A** ($C_8H_{16}O$) has DG^o = 1.0 kcal/mol between its two

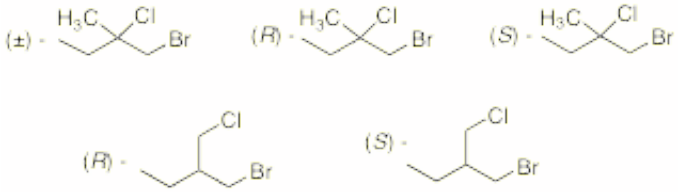
chair conformations of cyclohexane. [Energy differences for axial vs. equatorial substituents in chair cyclohexanes (kcal/mol): $-CO_2CH_3$, 1.2; $(CH_3)_2CH-$, 2.2; CH_3-, 1.7; CH_3O-, 0.7; -CN, 0.2]

a) (10 pts) What is the structure of **A**? Show the equilibrium (correct arrows) between the two chair conformations with their respective energies. Use the templates below; place the energies on the lines.

b) (10 pts) What is the structure of the stereoisomer of **A**? Show the equilibrium (correct arrows) between the two chair conformations of it with their respective energies. What is the value of DG^o (Have the sign of DG^o reflect your equilibrium) ? Use the templates below; place the energies on the lines. **Show work**.

2. (30 pts; equal weight) **Potpourri:** Answer the following questions.

a) Circle the **two** structures that best describe two of the products from the free radical chlorination of (*R*)-1-bromo-2-methylbutane.

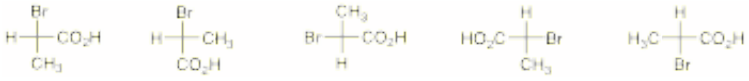


b) If a 1M aqueous solution of (*R,R*)-tartaric acid displays $[a]_D = +12^o$, what is the value of $[a]_D$ for a 0.05M solution of the same tartaric acid? **Explain briefly**.

c) Equal volumes of 0.1M solutions of (*S,S*)- and meso tartaric acid are mixed. What is the optical purity and $[a]_D$ of the new solution? **Show work**.

d) An optically-active (*R,R*)-cyclohexane (C_8H_{16}) has $[a]_D = +1.9^o$ and chair conformations that are identical (not stereoisomers). What is the structure of the cyclohexane? Explain and illustrate.

e) "One of these ~~things~~ (Fischer projections) is not like the others. One of these these ~~things~~ (Fischer projections) doesn't belong." **Circle** it.



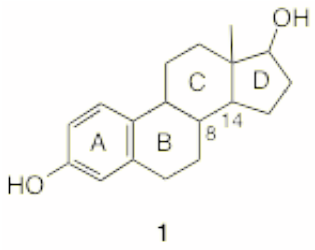
3. (20 pts) **Stereochemistry**. Answer the following questions.

Estradiol is a single stereoisomer of structure **1**.

a) (5 pts) How many possible stereoisomers of **1** are there? _____

Rings B and C are *trans*-fused. Rings C and D are also *trans*-fused. The hydrogens at C_8 and C_{14} are *anti* to one another. The methyl group and the hydroxyl group are *cis* to ring D. The configuration at C_8 is *R*.

b) (10 pts) Provide the absolute stereochemistry of **1** using the template **2**. Use bold and dotted lines to show stereochemistry along with the missing atoms and groups. Include the *R,S* assignments for the remaining chiral centers.



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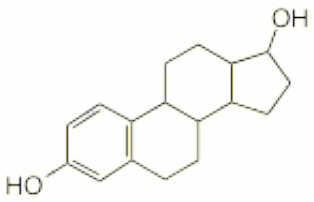

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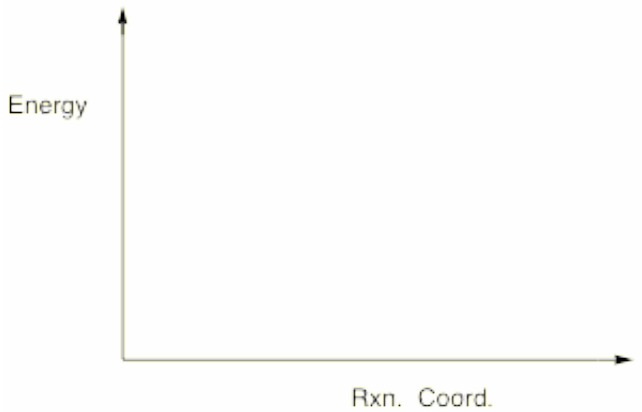
c) (5 pts) Are rings B and C capable of undergoing chair-char interconversion? Explain briefly.

4. (30 pts; equal weight) **S_N2 Reactions**: Complete each of the following questions.

a) Provide the structure of **A**.

b) Provide a reaction profile for 4a. Give consideration to the Hammond Postulate in your diagram. Label the reactants, products, any intermediates and the transition state(s).



c) **Draw** an accurate transition state for the reaction in 4a-b.

d) **Explain** the difference in relative rates in the S_N2 reaction of bromocyclobutane (cyclobutyl bromide) vs. 2-bromobutane with KCN. **Be sure** to include which one reacts faster.

e) Rank the following bromides as to their relative rate of reaction with iodide in methanol (1 → 5; fastest → slowest)

$(CH_3)_2CHBr$ $(CH_3)_3CCH_2Br$ CH_3CH_2Br $CH_3CH_2CH_2Br$ $(CH_3)_2CHCH_2Br$

_____ _____ _____ _____ _____