EXAM 1

Comprehensive Organic Chemistry

CHEMISTRY 225

Friday, February 15, 2008

NAME (print clearly): _____

TA:_____ Sect. Day:_____ Sect. Time:_____

Take a few moments to look over the exam. Answer each question on the exam paper.

No calculators, texts, notes, or laptops. 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. (20pts) Conformation I _____

2. (20 pts) Potpourri II _____

3. (20 pts) Resonance (Do 1 of 3) _____

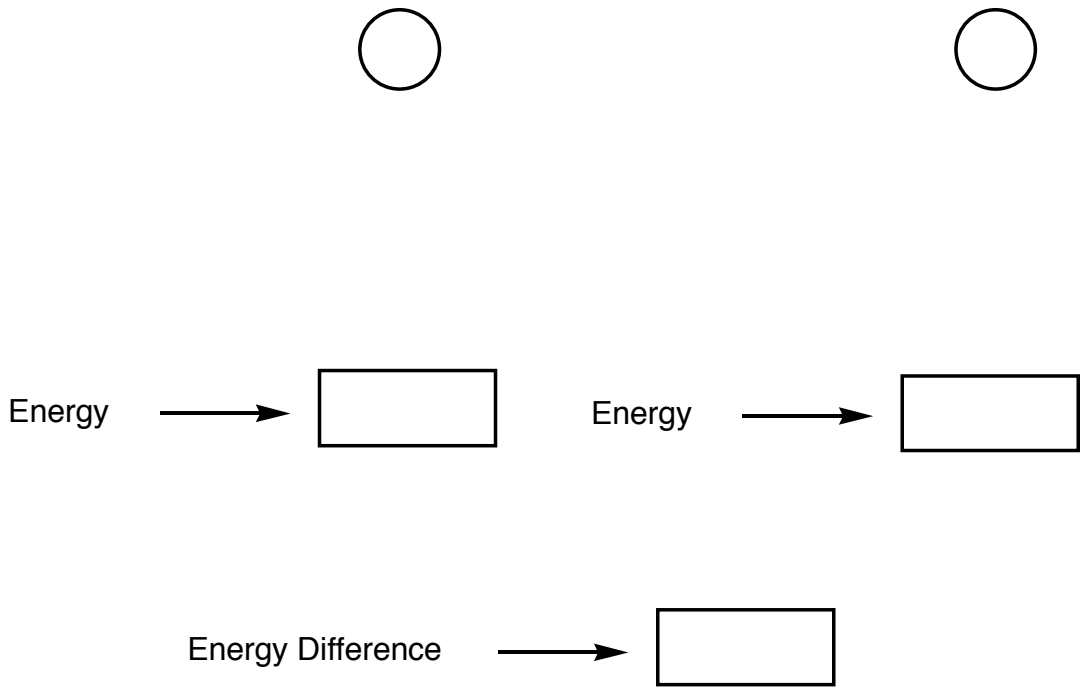
4. (20 pts) Conformation II _____

5. (20 pts) Thermochemistry _____

_____

Total (100 pts)

1. **Conformation I:** (20 pts) Draw the most stable **Newman projection** conformations of 2,3-dimethylbutane viewed along the C_2-C_3 sigma bond. Place the appropriate energies in the Newman projections below. [Use the **circles** as templates for the Newman projections.] Calculate the energy (kcal/mol) of both conformations. Place your answers in the appropriate **boxes**. **Show work**. [H/H, eclipsed, 1.0 kcal/mol; CH_3/H eclipsed, 1.3 kcal/mol; C_2H_5/H, eclipsed, 1.4 kcal/mol; CH_3/CH_3, eclipsed, 3.0 kcal/mol; CH_3/CH_3, gauche, 0.9 kcal/mol; CH_3/C_2H_5, gauche, 1.0 kcal/mol.] **Show your work!**



2. **Potpourri**: (30 pts.; equal weight) **Circle** the best answer(s) in each of the following:

a) 2-Methylpentane and 2,3-dimethylbutane have a difference of 0.8 kcal/mol in their heats of formation. What is the difference in their heats of combustion in kcal/mol?

0 0.8 -5 5 157 -157

b) The heat of formation of 2-methylpentane is -41.7 kcal/mol (previous question). What is the expected heat of formation of 2-methylhexane? Show work.

c) **Circle** the acids that are readily deprotonated by $NaOCH_3$.

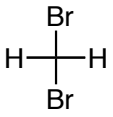
NH_3 cyclopropane HCCH NH_4^+ $CH_3CH_2CO_2H$

d) **Circle** the species with sp^2 hybridization

NH_4^+ ethylene BF_4^- ethane $(CH_3)_2CO$

e) **Circle** the compounds with net dipole moments.

cis-BrCH=CHBr $BrCH_2CH_2Br$ BrHC=C=CHBr $CHBr_3$



3. **Resonance:** (20 pts.) The concept of resonance plays an important role in organic chemistry. Explain and illustrate the role of resonance in **one** of the following cases. Use orbitals in your explanations.

a) The higher pKa value of peracid RCO_3H vs. carboxylic acid RCO_2H

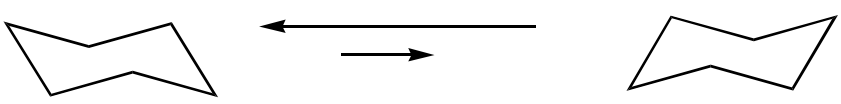
b) The lower bond dissociation energy of the sp^3 C-H bond in propene compared with the same bond in propane.

c) Relative stabilization of the carbocation $RCHOCH_3$ vs. RCHCl

4. **Conformation II:** (20 pts.) Vinyl compound **A**, $C_{10}H_{18}$, absorbs a maximum of one mole of hydrogen to form a 1,4-disubstituted cyclohexane **B** that has K_{eq}=0 kcal/mol for the equilibrium between its chair conformations.

a) (12 pts.) What are the structures of **A** and **B**? Explain briefly.

b) (8 pts.) Place the substituents for **A** in their appropriate locations in the chair equilibrium shown below.



5. **Thermochemistry:** (20 pts) Alkane **A**, C_6H_{12} gives a **single** free radical monochlorination product **B**. No other monochlorinated products are possible. The overall heat of the reaction is ΔH^o_{rxn} = -30 kcal/mol. BDEs: Cl_2 = 58 kcal/mol; HCl = 103 kcal/mol; R-H: (primary) = 98 kcal/mol, (secondary) = 95 kcal/mol, (tertiary) = 91 kcal/mol.

a) What are the structures and names of alkanes **A** and **B**?

b) Show the propagation steps for this reaction.

c) Calculate the heat of each propagation step and the BDE of R-Cl. **Illustrate and show work.**

Work Sheets

Name:____________________________________

Work Sheets

Name:____________________________________

Work Sheets