EXAM 2

CHEMISTRY 220a

Friday, October 14, 2005

NAME (print): _____ Your ID#: _____

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**.

BDE Table, pg. 13; Heats of Formation Table, pg. 14.

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. (25 pts) Thermochemistry _____

2. (25 pts) Unknown Compounds _____

3. (25 pts) Potpourri _____

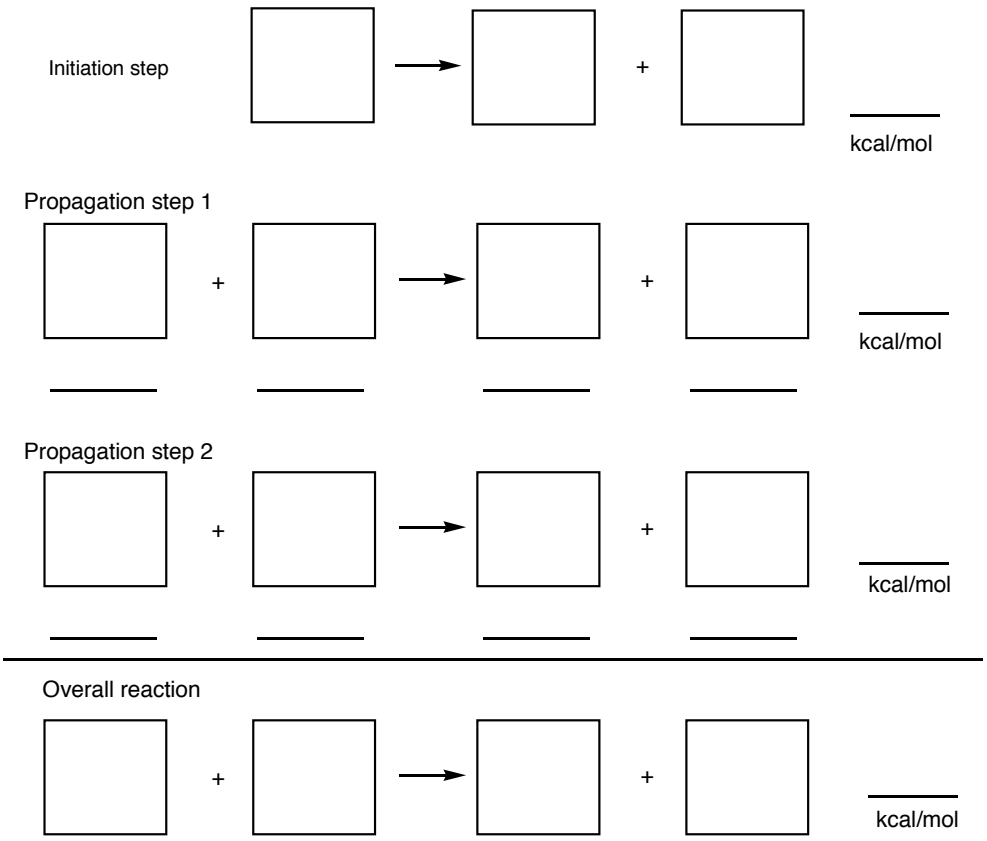
4. (25 pts) Reactions _____

_____

Total (100 pts)

1. (25 pts) **Thermochemistry:** A chemist wishes to assess the viability of preparing ethyl iodide from ethane in the presence of **gaseous** I_2 at 298 °C.

a) (10 pts) Illustrate the initiation and propagation steps for this reaction. Using BDEs (see attached sheet), determine ΔH^o for the four steps below. Place reactants and products in the squares and numerical values on the lines.



b) (5 pts) Determine the heat of sublimation of **solid** I_2 at 298 °K using the heats of formation tables provided (see attached tables) and the answer to a). **Show work**.

c) (5 pts) Provide an Energy vs. Reaction Coordinate diagram for this reaction. Label the appropriate energies from part a). Be sure your diagram illustrates early and late transition states Hammond Postulate).

d) (5 pts) Is this process a good preparative reaction? Explain.

2. (25 pts) **Unknown Structures:** Compound **A** (C_6H_{14}; what are the possibilities?) undergoes free radical bromination to form principally (>90%) monobromide **B**. When the free radical chlorination of **A** is conducted, five monochloro constitutional isomers are formed. Compound **B** is immiscible in water, forming two layers. However, when the test tube is shaken, heat is liberated and the sample now appears homogeneous, forming compound **C**. If compound **B** is treated with aqueous NaOH, no **C** is formed, but **D** (major) and **E** (minor) are produced.

   a) (15 pts) What are the structures **A-E**? Explain and illustrate.

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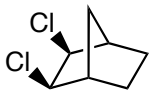
b) (10 pts) Draw the structures of the monochlorides in the first column. Place an "X" in the boxes that apply to each structure, i.e.; achiral, racemic, and/or optically active.

Monochloride	**Achiral**	**Racemic**	**Optically Active**

3. (25 pts) **Potpourri:** Answer **4 of 5** of the following questions. **If you do five questions, cross out the one that you do not want graded.**

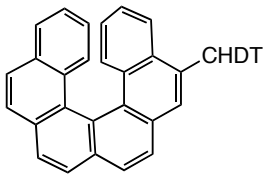
a) Bicyclo[2.2.1]heptane (**1**) is achiral and not meso while the dichloride **2** is both achiral and meso. Explain.

1

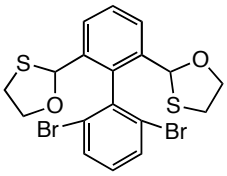


2

b) The number of possible stereoisomers of **A** and **B** is given in parentheses. Explain **only one** of the examples. **Pay attention to stereocenters and atropisomerism.**



A (4)



B (3)

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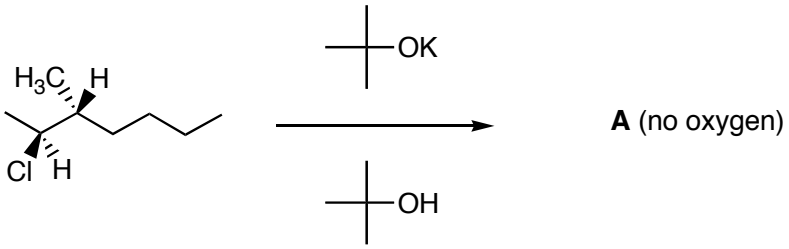
c) A mixture of enantiomers has an optical purity of 70% and an observed specific rotation $[\alpha]_D$ = -84°. What is the specific rotation of the minor enantiomer and what percentage is it of the mixture? **Show work**.

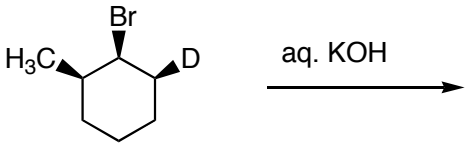
d) Upon free radical chlorination, (*R*)-2-chlorobutane forms -- among other dichlorides – dichloride **1** (optically inactive) and its stereoisomer **2** (optically active). If the ratio **1/2** = 4, what is the expected ratio when racemic 2-chlorobutane undergoes the reaction? Name the dichlorides **1** and **2**.

e) A 0.1M solution of an enantiomer has $[\alpha]_D$ +120°. What is the value of $[\alpha]_D$ when the concentration of the solution is halved? Explain.

4. (25 pts) **Reactions:** Provide the product in **4 of 5** of the following reactions. Provide a brief explanation**. If you do five questions, cross out the one that you do not want graded.**

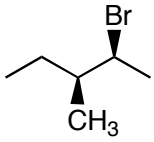
a) 

A (no oxygen)

b) 

aq. KOH

A (no oxygen)

c) 

opt. active

aqueous $AgNO_3$

A (achiral alcohol)

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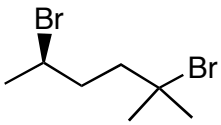
4. Continued…

d) (*S*)- $CH_3CH_2CH_2CH_2CDHBr$ $\xrightarrow[\text{aq. KOH}]{CH_3CH_2SH}$

e) 

opt. act.

$\xrightarrow[\text{room temp.}]{\text{ethanol}}$ **A** [opt. act. or (±)?]

BDEs

http://classes.yale.edu/chem220a/studyaids/thermo/BDE.html

Heats of Formation

http://classes.yale.edu/chem220a/studyaids/thermo/heats-formation.html