Chem 220a

Problem Set 5

Chapter 6

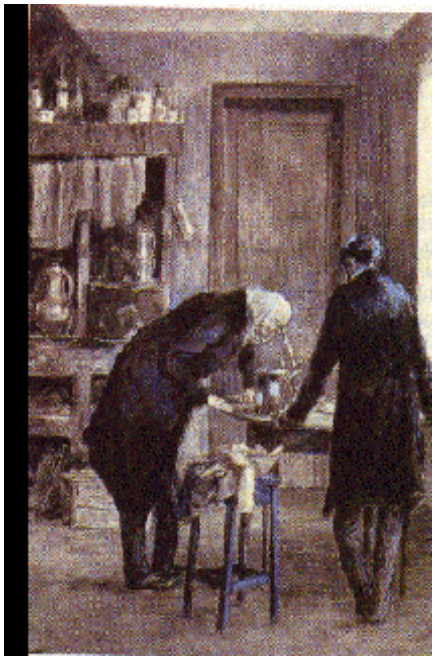
Due: Monday, October 10, 2005

1. Study #2 and #3 in the Alkyl Halide module and #1 in the Ether module in ORGO.

2. Hydrocarbon **A** forms only two monochlorinated compounds **B** and **C** in nearly equal amounts as predicted by calculation. **B** is a racemate and **C** is achiral. Compound **B** reacts with aqueous NaOH to give alcohol **D** and compound **E**. **C** reacts with water to give alcohol **F** and compound **G**. Both **E** and **G** react with hydrogen and a catalyst to give a saturated hydrocarbon with a heat of formation of -42.5 kcal/mol. What are the structures **A-G**? Explain and illustrate.

3. When 2-bromobutane is treated with alcoholic KOH at 400°K, trans- and cis-2-butene (and some 1-butene) are formed in a ratio of 6:1, respectively. In a separate experiment, the two 2-butenes are found to be stable to the reaction conditions.

a) Using the Heats of Formation and the reaction coordinate diagram on the right, predict which product is **E** and which one is **D**. Explain.



Biot examining Pasteur's tartrate crystals

b) A student recognizes that ΔG^o is not quite ΔH^o but at 400°K, $\Delta G^o = -1.84 \log_{10} K_{eq}$. The difference in the heats of formation of the two geometrical stereoisomers translates into a calculated ratio of 3.5:1. Is he using the correct analysis in spite of

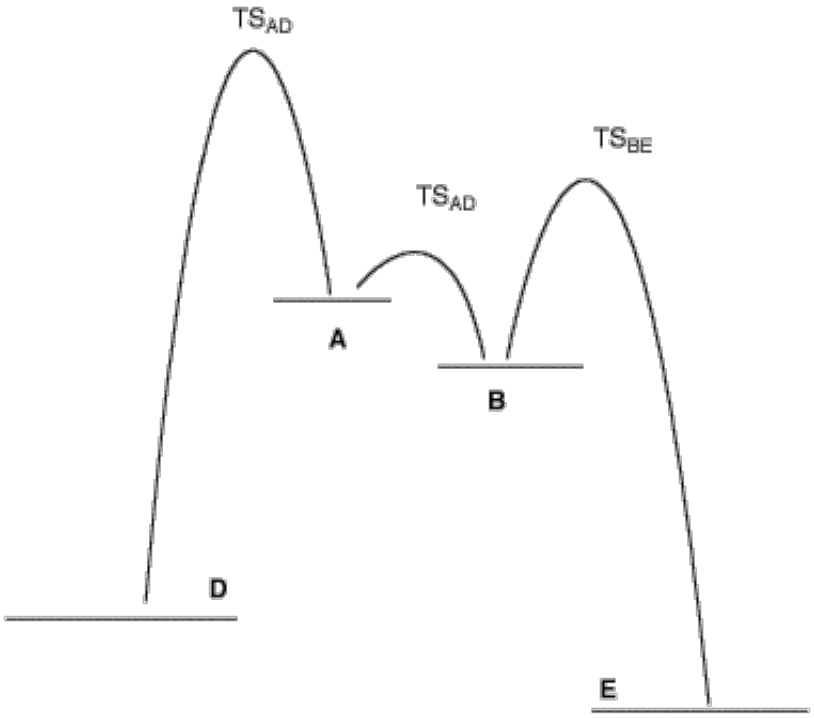
the fact that his ratio is not the observed ratio? Explain.

c) **A** and **B** represent two relevant, staggered conformations of 2-bromobutane. Assign **A** and **B** as Newman projections. Explain your choice.

d) Why is the third staggered conformation **C** not included on the diagram?

e) What are the two fastest processes in this diagram: **A**-->**B**, **B**-->**E**, **E**-->**B**, **B**-->**A**, **A**-->**D**, or **D**-->**A**? Explain.

f) Another student suggests that the observed ratio is determined by the difference in the rate of formation of **D** vs. **E**. Show how this difference is reflected in the diagram.

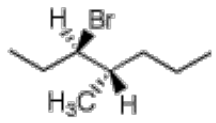


4. Provide the products in each of the following questions and mechanisms for their formation. Pay attention to stereochemistry. Be explicit about enantiomers.

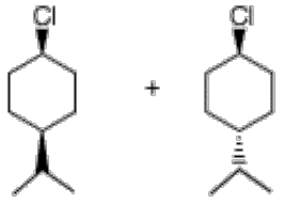
a) (*2R, 3R*)-2-bromo-3-methylpentane $\xrightarrow[KOH]{\text{aqueous}}$ **A** (major) + **B** (minor)

b) (*2R, 3S*)-2-chloro-3-methylhexane $\xrightarrow[CH_3OH]{CH_3ONa}$ **A** (major) + **B** (minor)

c) (3S)-3-chloro-3-methyloctane $\xrightarrow[\text{ethanol}]{\text{excess}}$ **A**

d)  $\xrightarrow{\text{EtONa, EtOH}}$ **A** (major) + B (minor)

e) (*R*)- $CH_3CH_2CH_2CH_2CHDBr$ $\xrightarrow[\text{aq. NaOH}]{CH_3CH_2CH_2SH}$

f)  1 equiv. + 1 equiv. $\xrightarrow[t\text{-}C_4H_9OH]{\text{1 equiv. } t\text{-}C_4H_9OK}$ **A** + **B** (not an alkene not an ether)

5. Compound **A** reacts very slowly with hot KOH to form alcohol **B**. No products of elimination are formed. When **A** is heated with aqueous $AgNO_3$, AgBr is formed in addition to **C** ($C_5H_{12}O$), **D** (major) and **E** (minor). **D** and **E** absorb 1 equiv. of H_2 in the presence of a Pd catalyst to form 2-methylbutane. What are the structures of **A-E**? Explain and illustrate.

6. Compound **A**, (*1S, 2R, 5S*)-1-chloro-2-isopropyl-5-methylcyclohexane, and compound **B**, (*1S, 2S, 5R*)-1-chloro-2-isopropyl-5-methylcyclohexane both react with C_2H_5ONa in ethanol to give products of elimination. **A** gives only **C** while **B** gives a 1:3 ratio of **D** and **E**, respectively. Compounds **C**, **D**, and **E** are reduced with H_2 to give cyclohexanes. Reduction of **C** or **D** gives **F**, while reduction of **E**

affords **F** and **G**.

a) What are the structures **A-G**? Explain and illustrate. Provide clear mechanisms for the formation of **C-E**.

b) What is the relationship between **C** and **D**?

c) Which compounds are optically active? Which ones are not?

d) Imagine that an equimolar mixture of **A** and **B** reacts with half as much sodium ethoxide. Does a **A** or **B** react faster? Why? What is formed?