Chem 220a

Problem Set 7

Chapter 8

Due: Monday, October 29, 2001

1. The alkene module in ORGO will give you a solid review of Chapter 7 and also introduce you to concepts covered in Chapter 8. After the reading do problem #6 first before tackling 2-5. You should also read the ozonolysis module.

How do I approach solving problems like #2? Here is a step-by-step analysis of #2 PS7 from F2000.

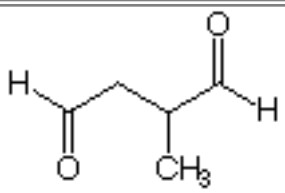
[Note: All ozonolysis reactions in 2-4 include a reductive treatment with dimethyl sulfide.]

2. An optically active compound **A**, $C_8H_{17}Br$, reacts with sodium ethoxide in ethanol to afford Saytzeff products **B** (C_8H_{16}) and (*S*)-**C** (C_8H_{16}). Compound **B** reacts with OsO_4 to give a meso compound **D** while ozonolysis of **B** gives a single four carbon ketone **E**. Ozonolysis of **C** provides a ketone **F** and aldehyde **G**. What are the structures a **A-G**? Explain your reasoning. Assign R/S configurations to all centers of chirality. [Hint: Solve for **B** before **C**. **C** has a stereoisomer (*S*)-**C'**. Why is none, or very little of (*S*)-**C'**, formed?]

Vladimir Vasilovich Markovnikov

(1838-1904)

3. Optically active compound **A**, $C_{10}H_{16}$, reacts with H_2 in the presence of Pt to form optically inactive **B**, $C_{10}H_{20}$. The heat of hydrogenation is 57.2 kcal/mol. [Hint: pg. 307] Ozonolysis of **A** produces (*R*)-dialdehyde **C**. What are the structures of **A-C**? Explain.

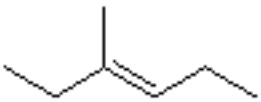


C

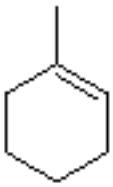
4. Compound (*S*)-**A**, C_6H_{12}, liberates ~30 kcal/mol of heat upon hydrogenation to give optically inactive **B**. Treatment of **A** with HBr forms three bromides, namely, optically inactive **C** and optically active **D** and **D'**, both having the formula $C_6H_{13}Br$. Compound **D** is of the (*S, S*)-configuration. Compound **C** reacts readily with water to form **E**, $C_6H_{14}O$. E2 elimination of **C** forms two compounds (*E*) and (*Z*)-**H** and **I** but no **A**. Compounds **H** form aldehyde **J** and ketone **K** on ozonolysis while **I** forms a C_5 ketone **L** and **M**. When **A** reacts with HBr in the presence of a peroxide, optically active bromide **F**, $C_6H_{13}Br$, is formed. Treatment of **F** with aqueous NaOH gives mainly optically active **G**, $C_6H_{14}O$, and a small amount of **A**. Hydroboration of **A** followed by oxidation with alkaline peroxide also gives **G**. What are the structures of **A** - **M**. Explain. Provide a mechanism that explains why more of (*E*)-**H** is formed than (*Z*)-**H.** [Hint: The structure of **A** is in the first sentence!]

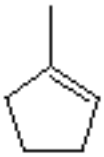
5. Compound **A**, C_6H_{12}, reacts with O_3 to give a single product **B**. The reaction of **A** with Cl_2/H_2O gives (±)-**C**, $C_6H_{13}ClO$. The reaction of **C** with aqueous KOH affords (±)-**D**, $C_6H_{12}O$. Compound does not contain a carbonyl group. [Hint: One of the problems in 6-64 on pg. 290 is of help.]

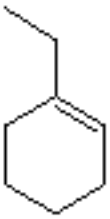
6. Predict the major product of each of the following reactions. Pay attention to stereochemistry. Provide a brief rationale for your choice.

a)  1) BH_3 → 2) aq. NaOH, H_2O_2

b)  Br_2 in ethanol →

c)  HCl, peroxide →

d)  HBr, peroxide →

e)  cat. OsO_4 → H_2O_2

f) (Z)-4-octene Cl_2, CCl_4 →