Chem 220a

Problem Set 7

Chapter 8

Due: Monday, October 31, 2005

Reading Assignments

- The alkene module in ORGO.
- Ozonolysis module.

How do I approach solving problems like #1-5? These problems require factual knowledge and an ability to reason. Pretend you are a doctor and patient has certain symptoms (the facts presented) and you must call upon your knowledge to provide a diagnosis (solution). Here is a step-by-step analysis (diagnosis) of #2 PS7 from F2000. I recommend that you do question 6 first. it will give you some background.

Vladimir Vasilovich Markovnikov

(1838-1904)

1. Alkene **A** reacts with chlorine to form meso **B**. Ozonolysis of **A** forms a single compound **C**. Hydrogenation of **A** liberates 27.3 kcal/mol of heat to form a normal chain alkane **D** with an estimated ΔH_f^o of -59.8 kcal/mol. What are the structures **A-D**? Explain and illustrate.

2. Compound **A** is optically active and it absorbs two equivalents of H_2 to form optically active **B** ($C_{10}H_{20}$). Treatment of **A** with warm, concentrated $KMnO_4$ forms (*R*)-2-methylsuccinic acid (tartaric acid = 2,3-dihydroxysuccinic acid). What are the structures of **A** and **B**? Explain and illustrate.

3. Hydroboration-peroxide oxidation is said to be an anti-Markovnikov addition of water to an unsymmetrically substituted double bond. Yet, hydroboration of an unsymmetrically substituted double bond is a Markovnikov addition of borane. Explain and illustrate.

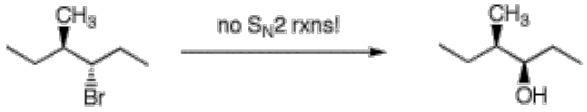
4. Hydroboration of (*Z*,*Z*)-1,4-cyclooctadiene at room temperature gives two boranes, **A** and **B**, both with the formula $C_8H_{15}B$. Alkaline peroxide oxidation of **A** gives a 1,4-cyclooctane diol (di-alcohol) while **B** gives the 1,5-isomer. When a mixture of **A** and **B**, or either one of them on their own, is heated, cooled and oxidized, **B** dominates over **A**.

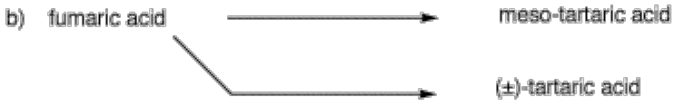
a) What is the stereochemistry of each diol?

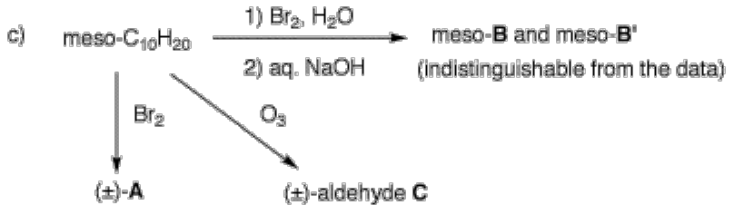
b) Explain and illustrate the conditions under which **A** and **B** are formed vs. **B** alone. A reaction co-ordinate diagram would be helpful.

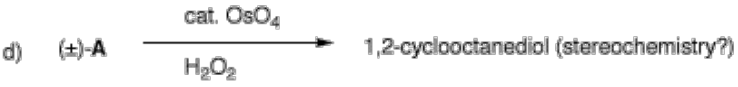
5. 2,6-Octadiene **A** (C_8H_{14}) of unknown stereochemistry reacts with catalytic OsO_4/H_2O_2 to form two racemic tetraols (four hydroxyl groups). Two geometrically isomeric 2,6-octadienes, **B** and **C,** each afford a racemic and meso tetraol. Hydrogenaton of **B** liberates 2.0 kcal/mol more heat than **C**. What are the structures of **A-C** and of the tetraols? The tetraols are best illustrated as Fischer projections.

6. Provide solutions to each of the following problems by supplying reagents, structures, and brief explanations.

a) 

b) 

c) 

d) 

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