Chem 220 - Organic Chemistry

Problem Set 7

Chapter 8, Reactions of Alkenes

Due: Monday, November 1, 2010

Ozone

In 1840, Christian Friedrich Schönbein (1799-1868) discovered ozone (Gr.; odorant), the sharp odor produced by electrical discharges. Seven years later (1847) he observed that ozone oxidizes organic compounds but not to their ultimate products of oxidation, carbon dioxide and water. [Two years prior, he had spilled nitric and sulfuric acid on his Frau's apron in her kitchen. The apron, made of cotton, combusted and thus was discovered gun cotton, nitrocellulose. Schönbein also observed that hydrogen peroxide (Threnard; 1818) is oxidized to oxygen gas in the presence of hemoglobin.] In the period 1903-1916, Carl Dietrich Harries (1866-1923), an assistant to both Hofmann (of the eponymous elimination and rearrangement) and Fischer (of projection and carbohydrate fame) at Berlin, published some 80 papers on the reactions of ozone with organic compounds. His interest was stimulated by the reaction of ozone with rubber, a process that causes rubber to become hard and brittle. These studies led to the analytical and synthetic uses of ozone. From 1904-1916 he was a professor at Kiel. Disenchanted with academic life, he became Director of Research for Siemens and Halske, the German company co-founded by the electrical pioneer, Werner von Siemens, his father-in-law. Not surprisingly, Siemens went into the business of producing ozone generators. The studies of Rudolf Criegee (1902-1975; Karlsruhe) produced a unified mechanism for the process of ozonolysis.

M. Rubin, *Bull. Hist. Chem.*, **2001**, *26*, 40.

M. Rubin, *Helv. Chem. Acta*, **2003**, *86*, 930.

Reading assignments:

a)The alkene module in ORGO.

b) Ozonolysis module.

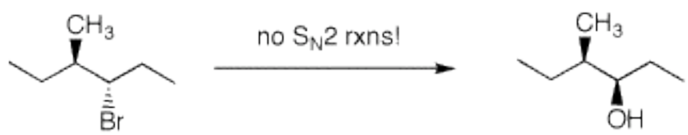
How do I approach solving problems like #2---5? Here is a step-by-step analysis of a typical problem.

Vladimir Vasilovich
Markovnikov

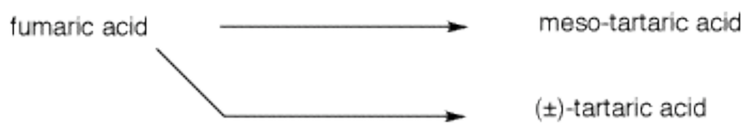
(1838-1904)

1. Provide the missing information in each of the following problems: reagents or unknown structures. Explain your reasoning.

a)



b)



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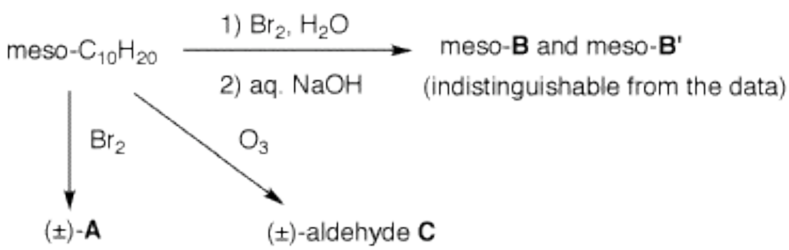

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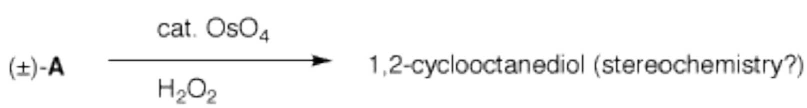
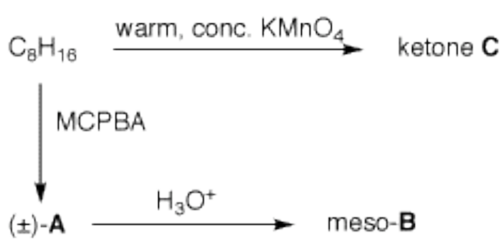
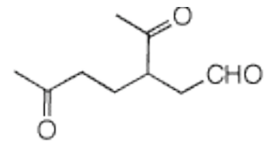


e)



2. Optically active monoterpene **A** reacts with 2 molar equivalents of hydrogen to produce diastereomeric, disubstituted cyclohexanes **B** and

C, both of which are optically inactive. Compound **B** has a smaller heat of combustion than **C**. Ozonolysis and dimethyl sulfide reduction of **A** affords the compound on the right as a reaction product as its (*R*)-enantiomer [**Hint:** Count carbons]. What are the structures **A-C**? Explain and illustrate.



3. Compound **A** reacts with Br_2 in CCl_4 to give **B**. The intermediate in this reaction (**C**) is a meso species. Ozonolysis of **A** affords only 2-methylpropanal (isobutyraldehyde). What are the structures **A-C**? Explain and illustrate. Pay attention to stereochemistry.

4. Compound **A** ($C_{10}H_{20}$) undergoes ozonolysis to produce a **single, optically active** compound (*S*)-**B**. The reaction of compound **A** with Br_2 in CCl_4 provides a **single, optically active** compound **C**. What are the structures of **A-C**? Show their stereochemistry. Show your reasoning.

5. Compound **A**, C_7H_{12}, [Degree of Unsaturation?] affords a *single* ketoaldehyde **B** upon ozonolysis and dimethyl sulfide reduction. Hydrogenation of **A** gives methylcyclohexane. Treatment of **A** with HBr in the presence of *peroxide* gives two stereoisomeric bromides, **C** and **D**. Compound **C** reacts with C_2H_5ONa/C_2H_5OH to give **E** while under the same conditions, compound **D** gives mainly **A** and some of compound **E**. Ozonolysis of **E** gives a single dialdehyde **F**. What are the structures of **A-F**? Explain and illustrate. Pay attention to stereochemistry.