

Chem 220 - Organic Chemistry

Problem Set 7

Chapter 8, Reactions of Alkenes

Due: Monday, November 2, 2009

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:

- The alkene module in [ORGO](#).
- [Ozonolysis](#) module.

How do I approach solving problems like #1---5? [Here](#) is a step-by-step analysis of a typical problem.

1. An optically active compound **A** (C_8H_{14}) reacts with catalytic



OsO_4 and stoichiometric H_2O_2 to form (*R,R*)-diol **B**. Ozonolysis and dimethyl sulfide reduction of **A** forms $\text{OHC}(\text{CH}_2)_6\text{CHO}$. What are the structures of **A** and **B**? Explain.

Vladimir Vasilovich
Markovnikov

(1838-1904)

2. 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 $\text{C}_2\text{H}_5\text{ONa}/\text{C}_2\text{H}_5\text{OH}$ 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.

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

4. Optically active terpene **A** reacts with 2 molar equivalents of hydrogen to produce diastereomers **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 pyruvaldehyde **D** ($\text{C}_3\text{H}_4\text{O}_2$, [Google](#) it) and (*S*)-isopropylsuccindialdehyde **E** ($\text{OHCCH}(i\text{-Pr})\text{CH}_2\text{CHO}$; tartaric acid = 2,3-dihydroxysuccinic acid). What are the structures **A-E**? What are the sign and value of the optical rotation of **A** (Review [PS4](#))? Explain.

5. Compound **A** ($\text{C}_{10}\text{H}_{20}$) undergoes ozonolysis to produce a *single, optically active* compound (*R*)-**B**. The reaction of compound **A** with ethereal OsO_4 or aqueous KMnO_4 provides a *single, optically active* compound **C**. What are the structures of **A-C**? Show their stereochemistry. Show your reasoning.

6. Provide the products, reagents, and/or reagents as required in each of the following problems. Explanations are required for all.

