

Chem 220 - Organic Chemistry

Problem Set 7

Solution Set

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.

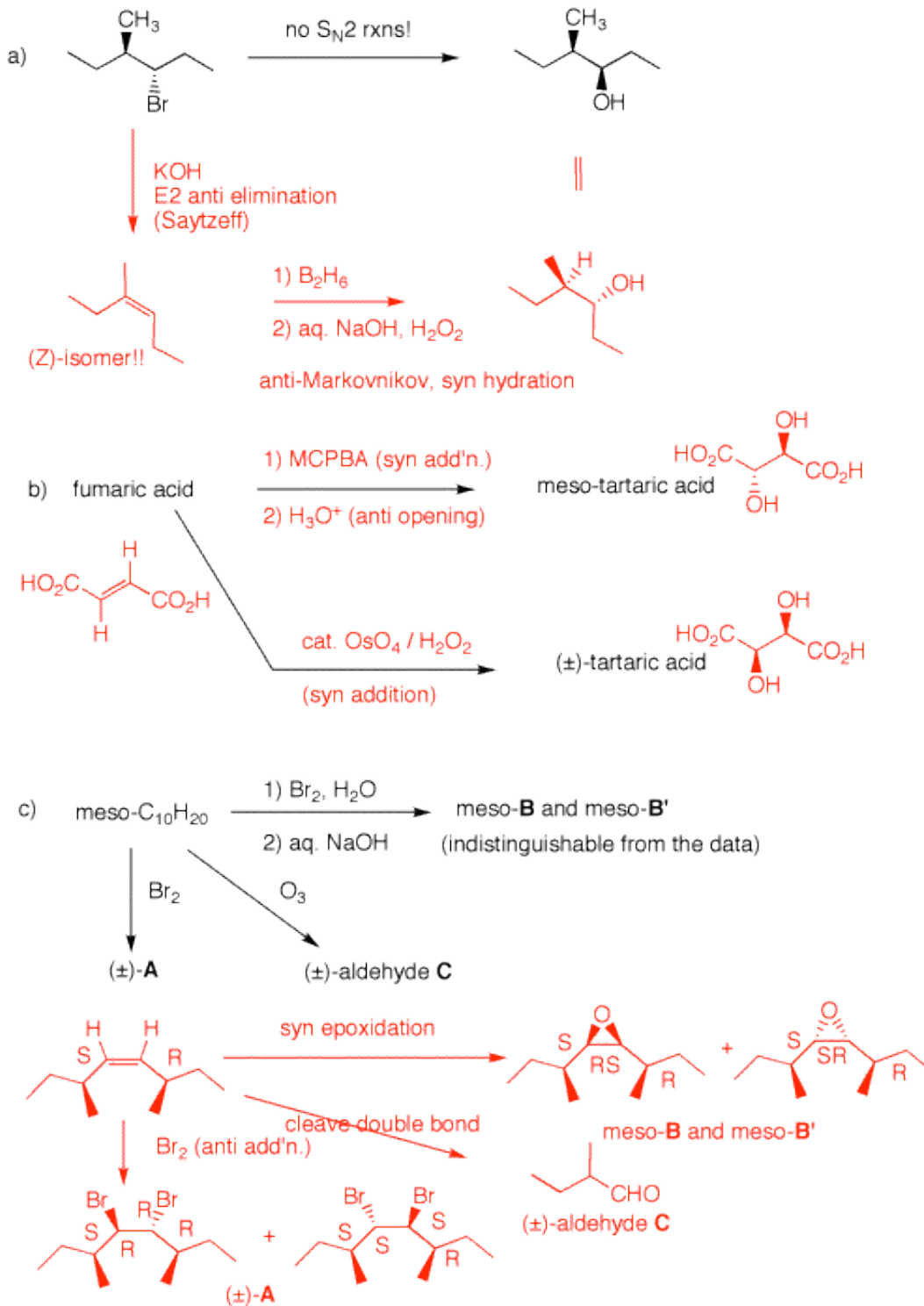
How do I approach solving problems like #2---5? [Here](#) is a step-by-step analysis of a typical problem.



Vladimir Vasilovich
Markovnikov
(1838-1904)

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

a) The compounds are assumed to be racemic since there is no statement to the contrary. As drawn, the hydrogen on the carbon bearing the methyl group and the bromine are both behind the plane of the carbon chain, i. e., 60° dihedral angle. Treatment with KOH will lead to anti elimination (180° dihedral angle) and (Z)-3-methyl-3-hexene and NOT the (E)-isomer that would arise by unfavored E2 elimination from the 60° conformation or eclipsed 0° conformation. With a small base the Saytzeff product will prevail. Now, hydroborate the



alkene via anti-Markovnikov, syn addition of the elements of water.

In summary, remove HBr anti; add water syn equals S_N2 .

b) Since fumaric acid is trans, one needs to add two OH groups anti to get the meso compound.

Unknown, single reagent procedure.

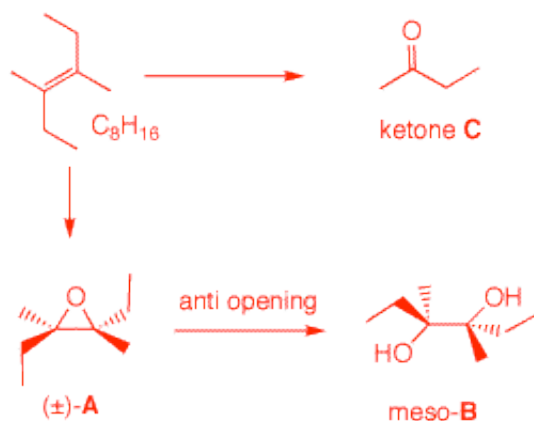
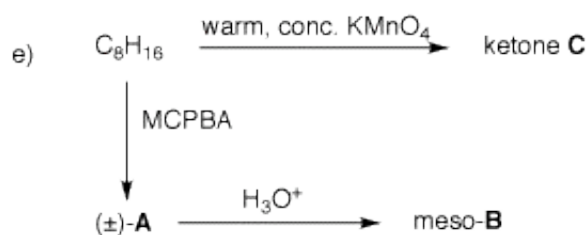
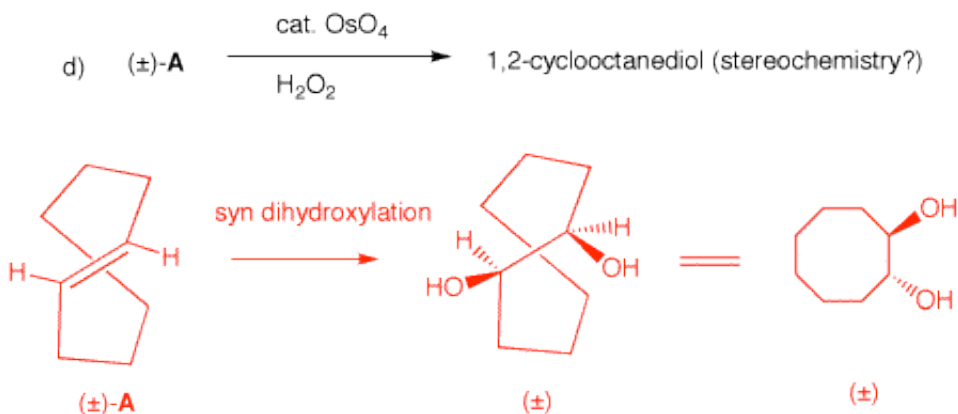
Epoxidize in a syn fashion and open the epoxide in an anti fashion with aqueous acid. For the racemic tartaric acid, dihydroxylate directly.

c) $C_{10}H_{20}$ is meso and the one degree of unsaturation says a double bond because of the reactions conducted.

The left side of the double bond reflects the right side. The alkene must be 1,2-disubstituted based on the formation of the aldehyde C. [In fact, one didn't need to know that C was an aldehyde.

There is only one way to arrange five carbons so that you get an asymmetric center. A ketone for C is impossible.]

The issue is what is the configuration of the double bond,



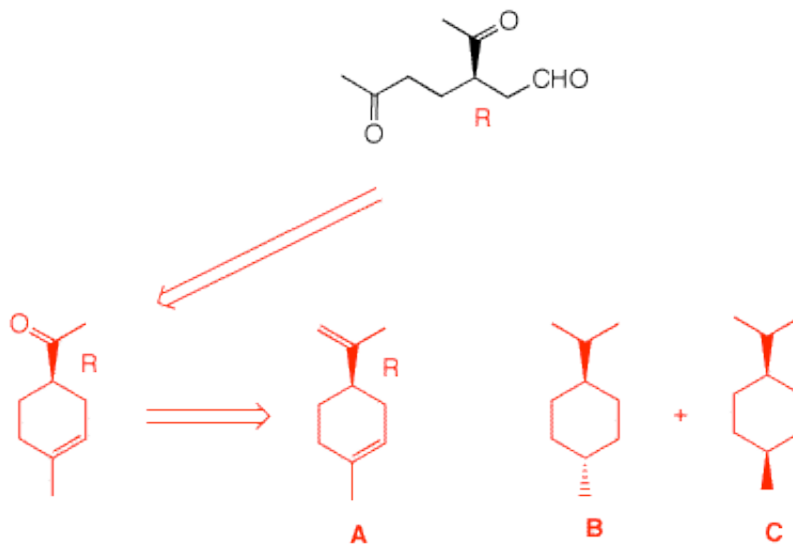
(E) or (Z)? Lets assume (Z). Bromination (anti) of the (Z)-alkene affords a dibromide SRRR (reading left to right) and its mirror image, SSSR for (±)-A. Not so fast! Check the (E)-isomer. The only difference will be one of the configurations at a bromine bearing carbon. The compounds would be SSRR and SRSR. They are diastereomers and optically inactive meso compounds. [Written another way, SSmirrorRR and SRmirrorSR.] The double bond is (Z)! Note that the epoxidation (syn) gives the same configurations as would have been obtained by bromination (anti) of the (E)-isomer. That is to say, (E)anti = (Z)syn.

d) At issue is what is the geometry of cyclooctene A, cis or trans. The cis compound would lead to a meso, cis diol. In addition, cis-cyclooctene cannot be racemic. The less stable (E)-cyclooctene is racemic, and syn dihydroxylation leads to racemic

trans diol.

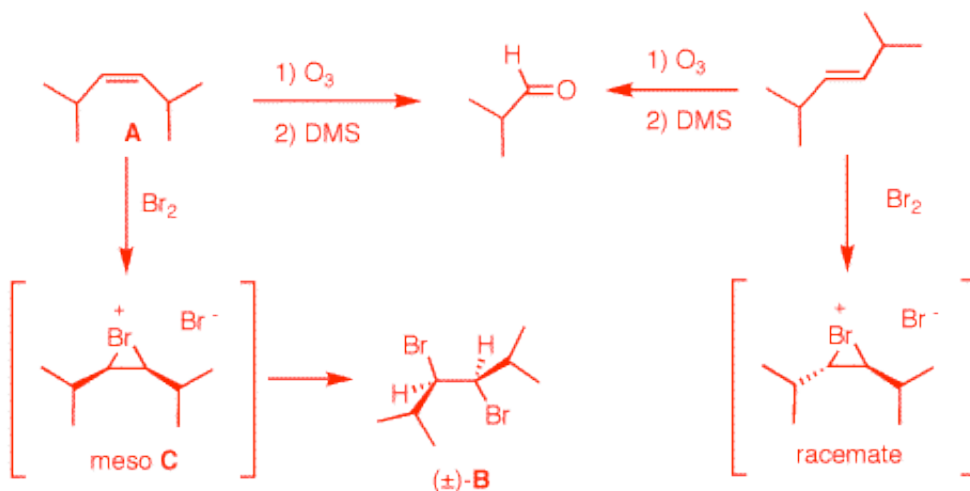
e) C₈H₁₆ has one D.U. Based on the reactions, it is an alkene. Because only a single ketone C is formed and necessarily C₄, ketone C must be 2-butanone. Since epoxidation (syn addition) gives a racemate, the double bond must be (E). Aqueous acid-catalyzed ring opening (anti) affords the meso-diol B.

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. *A monoterpene is a C₁₀ compound, a natural product. A absorbs two moles of hydrogen (2 D.U.) and leads to two cyclohexanes (1 D.U.). Thus, A has 3 D.U. and its formula is C₁₀H₁₆. [Double 3, subtract from 22]. There is only one way to form a six-membered ring from the ozonolysis product. Connect the aldehyde carbon with the remote ketone carbon. The product of ozonolysis has 9 carbons, one C₁ carbonyl compound is missing, formaldehyde, CH₂=O. Formaldehyde and the remaining methyl ketone group lead to the structure for A. The hydrogenation gives *trans* **B** and *cis* **A**. **B** emits less heat on combustion than **C** because it is more stable. If you had read*

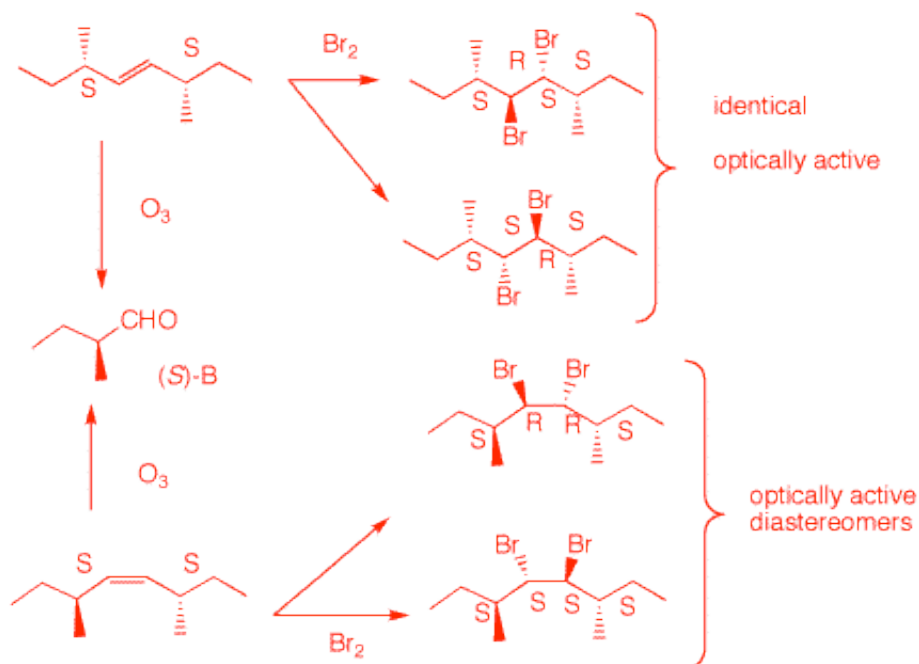


[StudyAids/Mechanism/Ozonolysis](#), you would have seen this problem at the end as well as the "Try this problem" link.

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. *Since only isobutyraldehyde is formed upon ozonolysis, **A** (C_8H_{16}) must be symmetrical about the double bond: either (E)- or (Z)-2,5-dimethyl-3-hexene. Only the (Z)-stereoisomer **A** will afford a meso intermediate bromonium ion **C**. The intermediate leads to racemic 3,4-dibromo-2,5-dimethylhexane **B**.*



4. Compound **A** ($\text{C}_{10}\text{H}_{20}$) 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. *See 1c above for guidance. There are two possibilities: (E)- or (Z)-alkene. Bromination of the (E)-isomer gives ONLY the SRSS (SRSS = SSRS) enantiomer, while the (Z)-isomer affords both the optically active SRRS and SSSS diastereomers.*

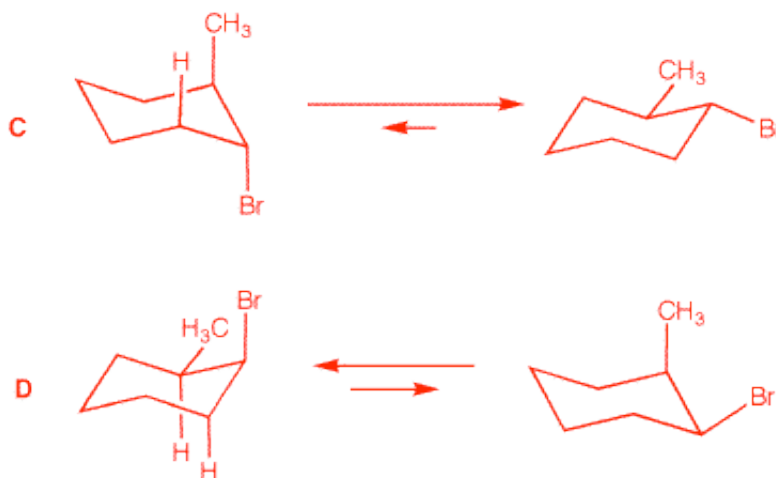
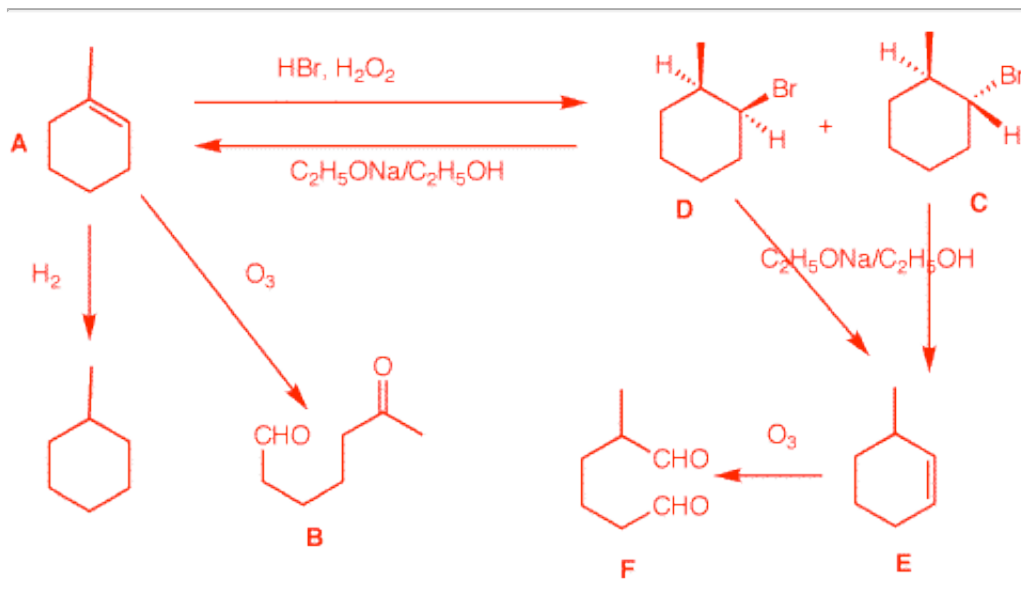


5. Compound **A**, C_7H_{12} , [[Degree of Unsaturation?](#)] affords a *single* ketoaldehyde **B** upon ozonolysis and dimethyl sulfide reduction. Hydrogenation of **A** gives methylcyclohexane. Treatment of **A** with HBr in the presence of *peroxide* gives two stereoisomeric bromides, **C** and **D**. 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.

$DU = 2$. The reaction with O_3 suggests an alkene and hydrogenation gives methylcyclohexane. The double bond must be trisubstituted because there is a *single keto aldehyde* formed. **A** must be 1-methyl-1-cyclohexene. Peroxide and HBr produces bromine radicals that add to the less substituted end of the double bond of **A**.

Stereochemistry is established in the second propagation step. **C** and **D** are *cis* and *trans* 2-methyl-1-bromocyclohexane. But which one is which? The base treatment to give **E** elimination gives the answer.

For E_2 elimination to occur, the cyclohexane ring must be in a conformation having the bromine axial. The less stable conformation of *trans* isomer **C** has the bromine and one β -hydrogen axial. This loss of HBr affords alkene **E**. On the other hand, the more



*stable conformation of the cis-isomer **D** has an axial bromine and two axial hydrogens. With small bases such as ethoxide, the Saytzeff rule applies, more of the more substituted alkene **A** and less of **E**.*