

Problem Set 2 – Chapter 8 Sections 11-17

1. Read Chapter 8 Section 11: You are responsible for knowing what a carbene is, how carbenes are formed chemically (i.e., Simmons-Smith reaction and alpha elimination of haloforms under basic conditions), why and how carbenes react with alkenes, and that the resulting products are cyclopropanes. What is the mechanism of addition of carbenes to alkenes? What is the Simmons-Smith reaction, what reagents are required for that reaction, and what products are formed by that reaction? Learn the Simmons-Smith reagent (ICH_2ZnI or CH_2I_2 , $\text{Zn}(\text{Cu})$). What type of carbene is formed by alpha elimination of bromoform and what products are formed by reaction of the resulting carbene with alkenes?

Work the following problems found in Section 11 of Chapter 8: Problems **26-28**.

Work the following problems found at the back of Chapter 8: Problems **47m, 51g, & 56d**.

2. Read Chapter 8 Section 12: You should be familiar with what an epoxide (oxirane) is and how epoxides are formed by reaction of alkenes with peroxyacids. What is a peroxyacid and what are the peroxyacids most commonly used for epoxidation (e.g., what is MCPBA)? Why is dichloromethane (CH_2Cl_2) commonly used as the solvent for carrying out epoxidation with MCPBA? What is the mechanism by which epoxidation occurs? Study mechanism 8-9 Epoxidation of Alkenes.

Work the following problem found in Section 12 of Chapter 8: Problem **29**.

Work the following problems found at the back of Chapter 8: Problems **46g, 47b & 51i**.

3. Read Chapter 8 Section 13: You are responsible for understanding acid-catalyzed ring opening of epoxides and that the products of those reactions are 1,2-diols, or glycols. Study mechanism 8-10 Acid-Catalyzed Opening of Epoxides. You should be familiar with the mechanism for acid-catalyzed ring opening of epoxides. What role does the acid catalyst play? Why does attack of water occur from the back side of a protonated epoxide ring fused to a cycloalkane? How does addition of water from the back side affect the stereochemistry of the resulting cyclic diol (glycol) product if stereocenters are formed? Why are those products *trans*-diols (glycols)?

Work the following problems found in Section 13 in Chapter 8: Problems **30, 32 & 33**.

Work the following problems found at the back of Chapter 8: Problems **46j, 47f, 49a, 50e, 51f, 56f,g & 64**.

4. Read Chapter 8 Section 14: You are responsible for knowing that oxidative cleavage of just the pi bond of alkenes can be carried out to form 1,2-diols (glycols). You should be familiar with the two methods that can be used to carry out *syn* dihydroxylation of alkenes to form 1,2-diols. Why does oxidative cleavage of the pi bond of an alkene by osmium tetroxide and peroxide (OsO_4 , H_2O_2) or cold, dilute, aqueous potassium permanganate (KMnO_4 , H_2O) result in *syn* addition of oxygen across the $\text{C}=\text{C}$ bond? How is the *syn* stereochemistry of that reaction related to the fact that delivery of the oxidizing reagents OsO_4 and MnO_4^- takes place in a concerted reaction? Why does *syn* dihydroxylation of cycloalkenes lead to *cis*-diols as the products? Compare these methods to carry out *syn* hydroxylation to that of epoxidation (section 8-12) followed by acid-catalyzed opening of epoxides (section 8-13) as a method to carry out *anti* hydroxylation.

Work the following problems found in Section 14 in Chapter 8: Problems **34 & 35**.

Work the following problems found at the end of Chapter 8: Problems **46h,i, 47d, 49b, 50d & 51f**.

- Read Chapter 8 Section 15: You are responsible for knowing that oxidative cleavage of both the sigma and pi bonds of alkenes can be carried out to form carbonyl compounds—namely, ketones, aldehydes and carboxylic acids depending on the substituents present on the carbon atoms in the C=C bond. Hot/warm concentrated permanganate (KMnO_4) is a powerful oxidizing reagent that not only cleaves the C=C bond, but any C-H bonds present on the carbon atoms in the C=C bond. What type of carbonyl compounds are produced by oxidative cleavage with hot, concentrated potassium permanganate? Ozone (O_3) is a slightly milder oxidizing reagent that also cleaves the sigma and pi bonds of alkenes when subsequently treated with a reducing reagent such as dimethylsulfide (CH_3SCH_3), but not C-H bonds present on the carbon atoms in the C=C bond. What type of carbonyl compounds are produced by oxidative cleavage with ozone? Be aware that the selectivity of potassium permanganate can be controlled to cleave just the pi bond (i.e., cold dilute KMnO_4/OH) to produce syn diols (Section 14) or both the pi and sigma bonds (hot/warm conc. KMnO_4) to produce carbonyl compounds (Section 15). What are the mechanisms by which oxidative cleavage occurs with both sets of reagents (hot/warm, conc. KMnO_4 , and 1) O_3 , 2) CH_3SCH_3)?

Work the following solved problem found in Section 15 in Chapter 8: Solved Problem 7.

Work the following problems found in Section 15 in Chapter 8: Problems **36 & 37**.

Work the following problems found at the end of Chapter 8: Problems **4d,k,l, 47c,e, 48, 50i, 51d, 62, 63 & 75**.

- Read Chapter 8 Sections 16: You should be familiar with what polymers are, the structure of polymers, how polymers are produced from alkenes, and the three different mechanisms by which polymers can be formed—namely, cationic, radical and anionic polymerization. How do you know when cationic, radical or anionic polymerization will take place? What are the requirements for those three mechanisms in terms of reagents, and also in terms of the alkene monomer? You should be able to draw polymers in compact form—that is, draw the repeat unit of a polymer in brackets. You also should be able to identify the alkene monomer used as the starting material to form a polymer. You should be familiar with the three different mechanisms.

Work the following problems found in Section 16 of Chapter 8: Problems **38-42**.

Work the following problems found at the end of Chapter 8: Problems **72 & 74**.

- Read Chapter 8 Section 17: You are responsible for understanding olefin metathesis, what an alkylidene group ($=\text{CHR}$) is, the catalysts used for olefin metathesis, and the mechanism by which alkylidene groups are exchanged. Study Mechanism 8-11 Olefin Metathesis. You should be familiar with the three major types of olefin metathesis reactions—namely, cross metathesis, ring-closing metathesis, and ring-opening metathesis polymerization. What types of alkenes are required for each of those reactions? What is the advantage in using a terminal alkene ($\text{RHC}=\text{CH}_2$) in olefin metathesis? What happens to terminal methylene (CH_2) groups in olefin metathesis reactions—what compound do they form? You should be familiar with how to represent Schrock and Grubbs catalysts in compact form, $[\text{M}]=\text{CHR}$, given that those catalysts generally are shown in reaction schemes using the compact form.

Work the following problems found in Section 17 of Chapter 8: Problems **43 & 44**.

Work the following problems found at the end of Chapter 8: Problems **46o, 52 & 52**.

8. Work the following problems found at the back of Chapter 8: **55, 60, 61, 65 & 68.**