

## 8.S: ALKENES - REACTIONS AND SYNTHESIS (SUMMARY)

### CONCEPTS & VOCABULARY

#### 8.1 Preparing Alkenes: A Preview of Elimination Reactions

- Alkenes can be prepared by either E1 or E2 elimination reactions of alkyl halides.

#### 8.2 Halogenation of Alkenes: Addition of X<sub>2</sub>

- Halogen molecules can react as **electrophiles** due to polarization of the halogen-halogen bond.
- During **electrophilic addition** of halogens to pi bonds, an intermediate halonium ion is formed.
- During electrophilic halogenation, ring opening of the halonium intermediate causes **anti** stereochemistry of the halogen atoms in the dihalide product.

#### 8.3 Halohydrins from Alkenes: Addition of HOX

- Halohydrins** have a halogen and a hydroxide on adjacent carbon atoms. Bromohydrin and chlorohydrin are the specific types of halohydrins where the halogen is bromine or chlorine respectively.
- In **halohydrin** formation a carbocation intermediate is formed on the more substituted carbon (when available). This causes the hydroxide to be added to the more substituted carbon of the original alkene and the halogen to add to the less substituted carbon.

#### 8.4 Hydration of Alkenes: Addition of H<sub>2</sub>O by Oxymercuration

- Electrophilic hydration is the addition of water to an alkene with one carbon adding a hydrogen and the other carbon a hydroxide.
- The mechanism begins with addition of a proton, yielding the more substituted **carbocation**.
- Carbocations can undergo **hydride shifts** and **alkyl shifts** to form a more stable **carbocation** when possible.
- Markovnikov** addition through acid and water or oxymercuration-demercuration yields the more substituted alcohol product (when the two sides of the alkene are not equally substituted).
- Oxymercuration-demercuration avoids carbocation rearrangements through mercurinium ion bridge.

#### 8.5 Hydration of Alkenes: Addition of H<sub>2</sub>O by Hydroboration

- Hydroboration-oxidation proceeds through anti-**Markovnikov** addition of water to an alkene, yielding the less substituted alcohol.

#### 8.6 Reduction of Alkenes: Hydrogenation

- Hydrogenation reactions increase the number of carbon-hydrogen bonds, therefore are reduction reactions.
- Addition of hydrogen to carbon-carbon pi bonds is called hydrogenation.
- Hydrogenation requires a catalyst to lower the activation energy allowing the reaction to proceed (commonly nickel, palladium or platinum).
- Hydrogenation reactions occur primarily with syn addition of the two hydrogen atoms, though potential for isomerization makes this uncertain.

#### 8.7 Oxidation of Alkenes: Epoxidation and Hydroxylation

- Epoxidation** can be carried out by reacting an alkene with a peroxy acid such as MCPBA.
- Anti **dihydroxylation** is achieved by ring opening an epoxide with water under acidic or basic conditions.
- Vicinal diols have hydroxy groups on adjacent carbon atoms.
- Syn dihydroxylation occurs through reaction with osmium tetroxide, followed by reduction of the intermediate with sulfur compounds.

#### 8.8 Oxidation of Alkenes: Cleavage to Carbonyl Compounds

- Ozonolysis is the cleavage of an alkene resulting in carbonyls at each carbon of the alkene.
- Alkenes can be cleaved by potassium permanganate, which also results in carbonyls at each alkene carbon, though potassium permanganate will oxidize every carbon-hydrogen bonds on the alkene to a carbon-oxygen bond.

#### 8.9 Addition of Carbenes to Alkenes: Cyclopropane Synthesis

- Organic molecules that have a carbon with only two bonds and a lone pair of electrons are called carbenes.
- Most carbenes are highly reactive and short-lived and are often created *in situ*.
- Carbenes can be formed from diazo compounds by reacting with a copper catalyst.
- Carbenes will react with alkenes to form cyclopropane rings.

#### 8.10 Radical Addition to Alkenes: Chain-Growth Polymers

- Monomers are units that repeat to form a polymer.
- In radical polymerization, the polymer chain reaction is initiated by a radical.

- Polymer chain reactions occur through a series of steps beginning with **initiation**, continuing through **propagation**, and ending in **termination**.

### 8.11 Biological Additions of Radicals to Alkenes

### 8.12 Reaction Stereochemistry: Addition of H<sub>2</sub>O to an Achiral Alkene

- Since addition of water to an alkene proceeds through a planar carbocation intermediate, achiral alkenes lead to a racemic mixture of alcohol products.

### 8.13 Reaction Stereochemistry: Addition of H<sub>2</sub>O to a Chiral Alkene

- Addition of water to alkenes which also contain a stereocenter does not lead to a 50:50 mixture of R and S products as the chiral center can reduce reactivity from one side of the carbocation. The products of this type of reaction will be diastereomers, since the original stereocenter will not change and the product will have an additional stereocenter.

## SKILLS TO MASTER

- Skill 8.1 Draw accurate Electrophilic Addition Mechanisms incorporating halonium intermediates.
- Skill 8.2 Draw accurate Electrophilic Addition Mechanisms incorporating carbocation intermediates.
- Skill 8.3 Draw Markovnikov products of alkene additions based on the most substituted carbocation intermediate.
- Skill 8.4 Draw hydrogenation products of alkenes.
- Skill 8.5 Draw appropriate epoxidation products including stereochemistry.
- Skill 8.6 Describe how to prepare syn and anti diols from alkenes.
- Skill 8.7 Draw products of oxidative cleavage reactions.
- Skill 8.8 Describe radical chain reactions to form polymers.

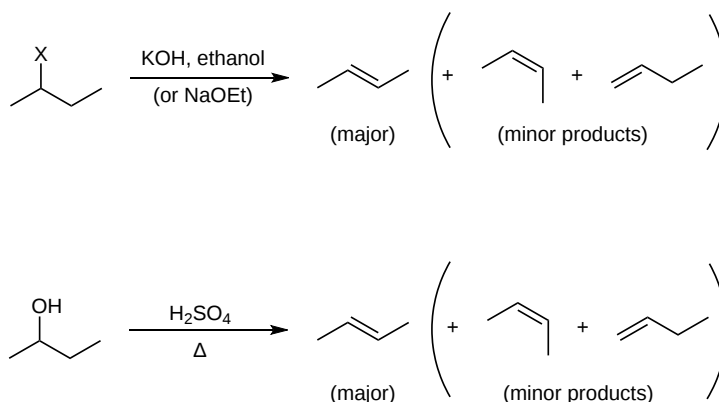
## MEMORIZATION TASKS

MT 8.1 Memorize reagents for alkene reactions.

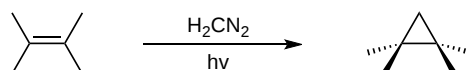
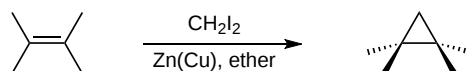
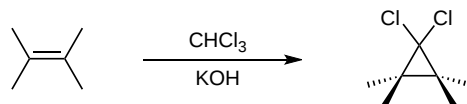
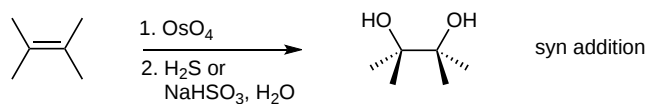
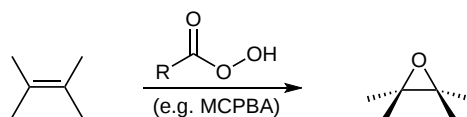
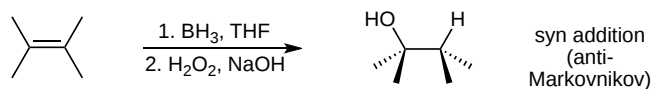
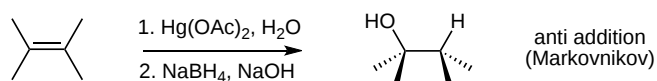
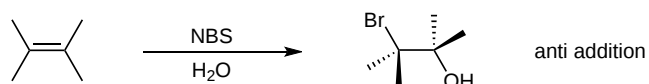
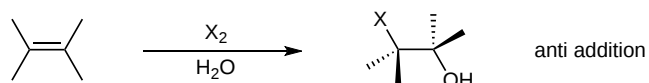
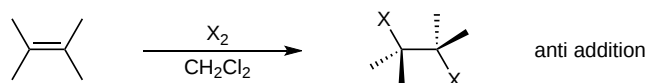
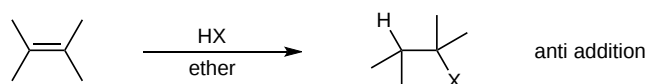
MT 8.2 Memorize stability order of carbocations.

## SUMMARY OF REACTIONS

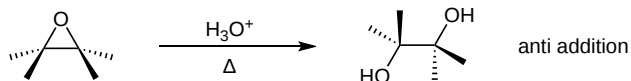
### Preparation of Alkenes



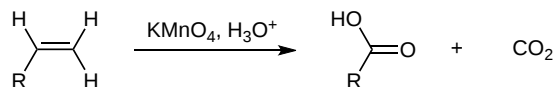
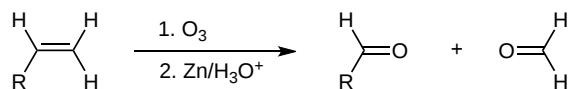
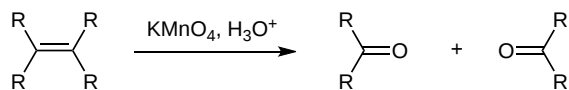
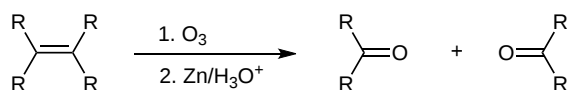
### Addition Reactions



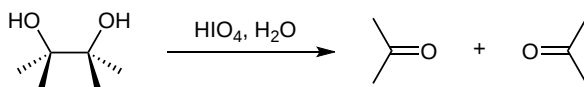
### Anti-hydroxylation



### Oxidative Cleavage



### Diol Cleavage



### CONTRIBUTORS

- Layne Morsch (University of Illinois Springfield)
- Dr. Krista Cunningham

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