

I. REACTIONS OF ALKENES: ELECTROPHILIC ADDITION (Sections 4.2-4.4; 4.6)

Electrophilic addition reactions are the most important reactions that alkenes undergo. There are four examples of electrophilic addition reactions that we will study. *All electrophilic addition reactions of alkenes involve a carbocation intermediate*

- General reaction mechanism
- Stability of carbocation intermediates and carbocation rearrangements
- Reaction energy diagrams
- Regiochemistry of the reaction

II. ADDITION OF HX (Section 4.1)

- Reaction of hydrohalic acids with *alkenes* results in formation of Markovnikov *alkyl halides*

III. ADDITION OF X₂ (Section 4.7)

- Addition of X₂ to an *alkene* results in formation of a *dihaloalkane*
- Addition of Br₂ to an alkene occurs with ANTI stereochemistry, i.e., the two halogens will have a trans relationship in the product. Important with cycloalkenes

IV. ACID-CATALYZED ADDITION OF H₂O and Alcohols (Section 4.5; 4.8)

- Addition of water to an *alkene* results in formation of a Markovnikov *alcohol*.
 - A catalyst is necessary for water to react with the alkene. Two common catalysts:
 - H⁺ (acid such as sulfuric, phosphoric, acetic etc...)
 - HgX₂ followed by treatment with sodium borohydride (NaBH₄)
- Addition of an alcohol to an *alkene* results in formation of a Markovnikov *ether*.

V. ADDITION OF X₂, H₂O (Section 4.7)

- Addition of X₂ in the presence of water to an *alkene* results in formation of a *halohydrin*
- Halogen bonded to the least substituted C; OH bonded to the most substituted C.
- Reaction occurs with ANTI stereochemistry, i.e., the X and OH have a trans relationship in the product

VI. REACTIONS OF ALKENES: SINGLE STEP ADDITION REACTIONS

Single step addition reactions to alkenes involve simultaneous bond formation between the two carbon atoms of the alkene and another molecule. *Single step addition reactions do not involve a carbocation intermediate but instead a cyclic transition state.* There are four examples of single step addition reactions that we will study.

A. ADDITION OF H₂ (Section 4.11)

- Addition of H₂ to an *alkene* results in formation of an *alkane*.
- Addition of H₂ to an alkene is a reduction, i.e., the # of H atoms increases from starting material to product.
- Addition of H₂ to an alkene occurs via SYN addition, i.e., H atoms are added on the same side of the double bond. In cycloalkenes, this results in the two H atoms having a CIS relationship.

B. ADDITION OF BH₃ followed by reaction with H₂O₂, NaOH (Section 4.10)

- Addition of BH₃ to an *alkene* results in formation of an *alkyl borane*.
- Addition of BH₃ to an alkene occurs in ANTI-MARKOVNIKOV fashion, i.e., B bonds to least substituted carbon
- Addition of BH₃ to an alkene occurs via SYN addition, i.e., B and H atoms are added on the same side of the double bond. In cycloalkenes, this results in the B atom and the H atom having a CIS relationship.
- Reaction of alkylboranes with H₂O₂, NaOH gives an alcohol. This is an ANTI-MARKOVNIKOV alcohol.

C. ADDITION OF OXYGEN: EPOXIDATION OF ALKENES

- Reaction of alkenes with peroxyacids result in formation of epoxides.
- Reaction of peroxyacids with alkenes occurs with SYN stereochemistry

VII. MULTISTEP REACTION: RADICAL ADDITIONS (Section 11.6)

- A. ADDITION OF HBr, HOOH
 - 1. Reaction of HBr with alkenes in the presence of H_2O_2 results in formation of ANTI-MARKOVNIKOV alkyl bromides
- B. ALLYLIC BROMINATION (Section 11.8)
Allylic bromides can be generated by treatment of alkenes with NBS, $h\nu$ through a radical substitution reaction.

VIII. REACTIONS OF ALKYNES: ELECTROPHILIC ADDITION

Electrophilic additions of alkynes always involve a VINYLIC CARBOCATION INTERMEDIATE.

- A. ADDITION OF HX (Section 6.6)
Addition of HX to alkynes results in formation of *vinyl halides*
- B. ADDITION OF X_2 (Section 6.6)
Addition of X_2 to alkynes results in formation of *dihaloalkenes*
- C. ADDITION OF H_2O with acid or 1) HgX_2 2) NaBH_4 (Section 6.7)
 - 1. Addition of water and acid to alkynes results in formation of *enols* which undergo rearrangement to *carbonyl* compounds.
 - 2. Addition of water and acid to alkynes occurs with Markovnikov regiochemistry.

IX. REACTIONS OF ALKYNES: SINGLE STEP ADDITIONS

- A. ADDITION OF H_2 (Section 6.9)
Addition of H_2 to alkynes can be accomplished in two ways.
 - 1. Addition of H_2 to alkynes with Pt, Pd or Rh catalyst results in formation of alkanes.
 - 2. Addition of H_2 to alkynes with Lindlar's catalyst results in formation of *cis*-alkenes.
- B. ADDITION OF BH_3 followed by treatment with H_2O_2 , HO^- (Section 6.8)
 - 1. Addition of BH_3 to alkynes followed by reaction with H_2O_2 , HO^- results in formations of *enols* which rearrange to *carbonyl* compounds.
 - 2. Addition of BH_3 to alkynes followed by reaction with H_2O_2 , HO^- occurs with *anti* Markovnikov regiochemistry.

X. OTHER REACTIONS OF ALKYNES: MULTISTEP REACTIONS

- A. ACETYLIDE IONS
 - 1. Preparation of internal alkynes: deprotonation / alkylation of terminal alkynes

XI. PREPARATION OF ALKENES

- A. E_1 ELIMINATION (Section 9.3)
 - 1. Alkenes can be prepared from 2° , 3° alkyl halides via a dehydrohalogenation reaction, i.e., loss of hydrohalic acid. The reaction is generally carried out under acidic conditions.
 - 2. Alkenes can be prepared from 2° , 3° alkyl halides via a dehydration reaction, i.e., loss of water. The reaction is carried out under acidic conditions or with POCl_3 .
- B. E_2 ELIMINATION (Section 9.1-9.2)
 - 1. Alkenes can be prepared from 1° , 2° , and 3° alkyl halides via a dehydrohalogenation reaction
The reaction is done under basic conditions.

XII. PREPARATION OF ALKYNES: There are two general preparations of alkynes

- A. E_2 Elimination of Organodihalides
- B. Preparation of Internal Alkynes: Deprotonation / Alkylation Of Terminal Alkynes