

CHEM 321 Organic Chemistry I - Professor Kathleen Kilway

"Organic Chemistry" by Maitland Jones, 3rd edition

Chapter 9 - 3, 4, 5, 6, 8, 9, 14, 21, 22, 23, 25, 26, 28, 31, 32, 34, 36, 41, 42, 44, 47.

CHAPTER 9: Addition to Alkenes 1

Section 9.1

I. Preview

Section 9.2

II. Mechanism of the Addition of Hydrogen Halides to Alkenes

A- Two-Step Mechanism

- 1- The alkene acts as a base, is protonated by H-X to yield a carbocation.
- 2- X⁻ acts as a nucleophile and adds to the strongly Lewis acidic cation.

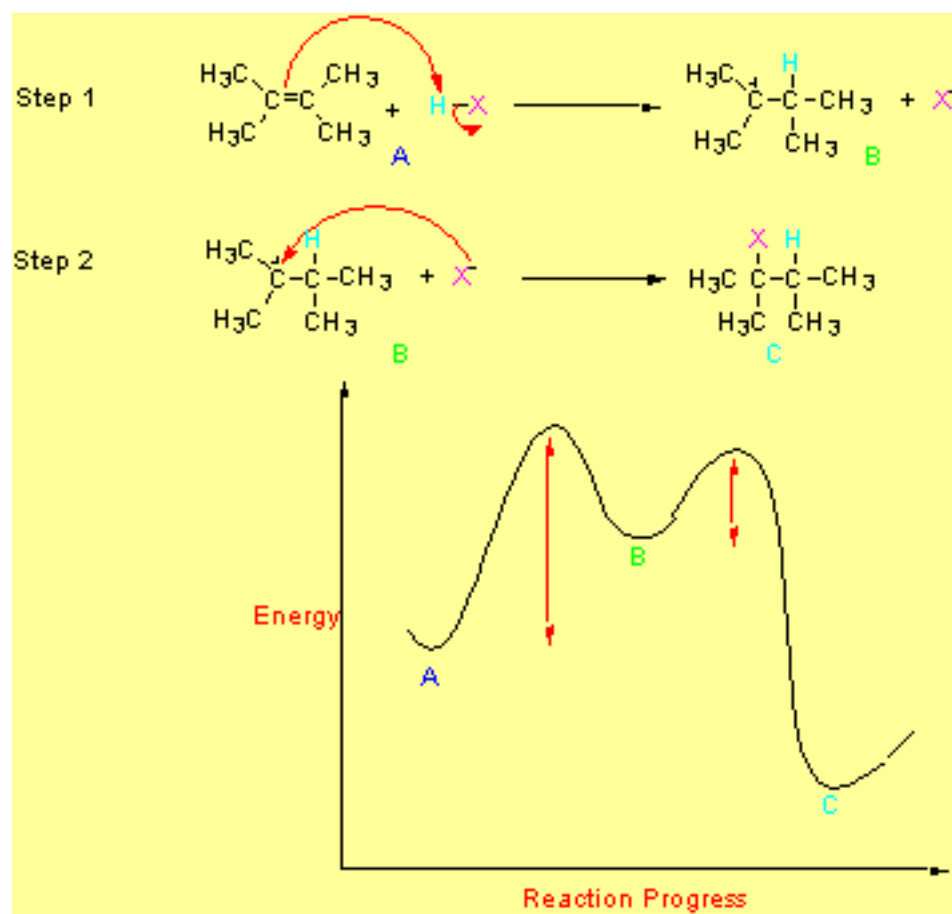


Figure 1

Section 9.3

III. Regiochemistry

A- Regiochemistry is the Difference upon Addition to an Unsymmetrical Alkene

- 1- Regioselectivity is the preferential formation of one isomer where a choice is possible.
- 2- Regiospecificity is the overwhelming predomination of one product in a reaction.

Section 9.4

IV. Resonance Effects

A- Addition of H-X to Vinyl Chloride (Chloroethylene)

- 1- Product is 1,1-dichloroethane not 1,2-dichloroethane.
- 2- The more stable cation is the one adjacent to the chlorine atom.
 - a- The chlorine stabilizes the cation in a filled-empty orbital fashion.
 - b- The chlorine can also stabilize the carbocation through resonance.
 - c- See Figure 9.8 on page 388.

B- Addition of H-X to 1,3-Butadiene

- 1- H-X adds in both a 1,2- and 1,4-fashion.
 - a- 1,2-addition yields 3-halo-1-butene.
 - b- 1,4-Addition yields 1-halo-2-butene.
- 2- Protonation at the end carbon of 1,3-butadiene yields a delocalized allyl cation, whereas protonation at the internal carbon yields a primary cation.
 - a- Allyl cation is stable due to delocalization.
 - b- See Figure 9.13 on page 390.

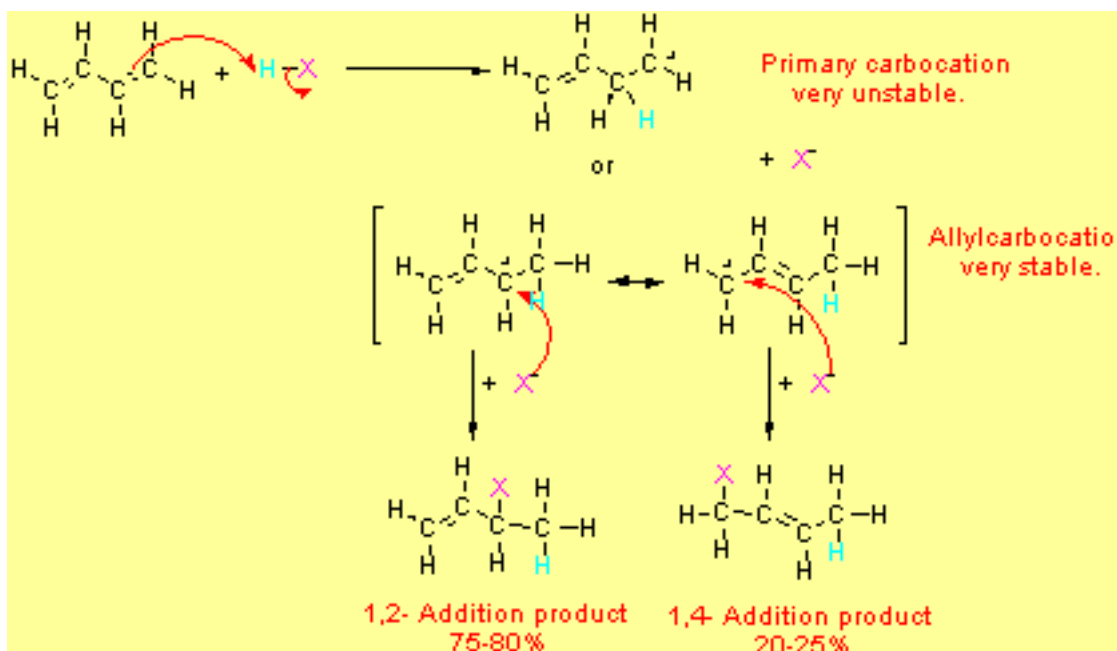


Figure 2

Section 9.5

V. Review of Resonance: How to Write Resonance Forms

A- Resonance Structures only Differ in the Distribution of Electrons and Never in the Positions of the Atoms

B- Guidelines for Resonance

- 1- Identical structures contribute equally.
- 2- The more bonds in a resonance form the more stable it is. The more resonance structures a molecule has, the more stable it is.
- 3- The number of paired and unpaired electrons must stay the same.
- 4- Charge separation is energetically unfavored.
- 5- Delocalization is important. Charges can be delocalized using adjacent double bonds or empty $2p$ orbitals.
- 6- Electronegativity is also important. It is more than likely that oxygen would have a negative charge but not a positive one.
- 7- Geometry is important. Bridgehead anions and cations cannot be used for delocalization.

Section 9.6

VI. Resonance and the Stability of Carbocations

A- The Product of the Addition of H-X to an Unsymmetrical Alkene Proceeds Through the More Stable Carbocation Intermediate

- 1- Primary carbocation intermediates will not lead to products if a more stable carbocation is possible (See Figure 9.26 on page 400).
- 2- If there are two carbocations intermediates of similar stability formed, then both will lead to products (See Figure 9.27 on page 400).

B- Markovnikov's Rule

- 1- This rule is based on the observation that the more substituted halide is formed upon addition to an alkene.
- 2- This is based on stability of carbocation intermediate.
methyl < primary < secondary < tertiary

C- Hyperconjugation

- 1- This is the stabilization of a carbocation through the overlap of a filled σ orbital with the empty $2p$ orbital on carbon.
- 2- The more interactions of such type, the more stable the cation.
 - a- It is similar to the stability of alkenes, the more sp^2 - sp^3 bonds of the carbocation, the more stable it is.
- 3- See Figure 9.33 on page 403.

D- Delocalization

- 1- Carbocations are stabilized via overlap of filled and unfilled orbitals.
- 2- Examples:
 - a- Nonbonding or lone pair electrons on adjacent atoms.
 - b- Overlap of filled s orbitals of C-H bonds.

Section 9.7

VII. Inductive Effects on Addition Reactions

A- Inductive Effects

- 1- They are effects, which are transmitted through the s bonds.
- 2- There are two types of inductive effects.
 - a- Destabilizing - Protonation in a Markovnikov sense, which places a full positive charge adjacent to an already partially positive charged atom.
 - i- Examples are halogens.
 - b- Stabilizing - The reverse of the above.
 - i- Example is an adjacent methyl group.
- 3- These effects are balanced by resonance effects.

Section 8.8

VIII. H-X Addition Reactions: Hydration

A- Hydration Reaction

- 1- This is the addition of water across the double bond.
- 2- A catalyst (increases the rate of reaction and is neither created nor destroyed) is used in this reaction.
- 3- The steps of this reaction are as follows:
 - a- Alkene is protonated to form a carbocation (same as H-X addition to an alkene).
 - b- The carbocation intermediate is attacked by water to form an oxonium ion.
 - c- This oxonium ion is deprotonated by water to regenerate the catalyst and produce an alcohol.

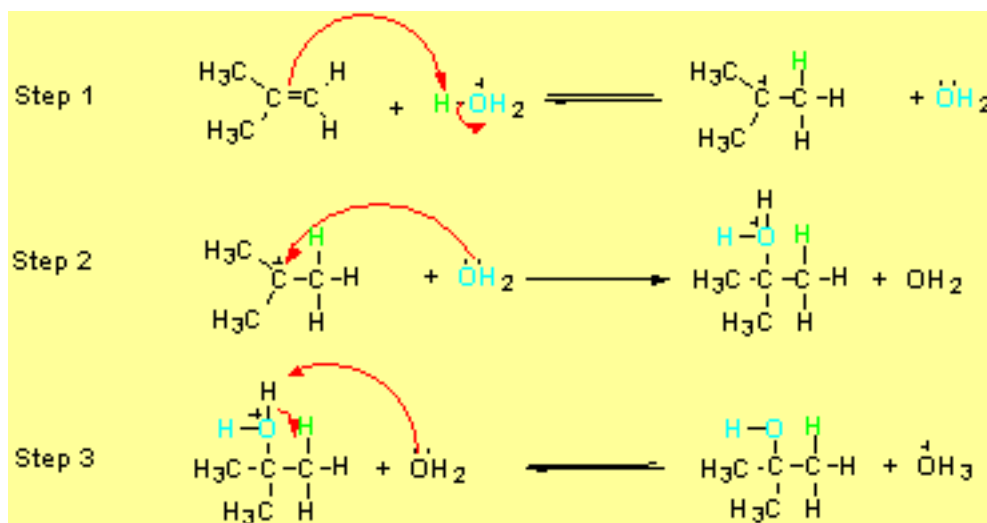


Figure 3

- 4- The hydration reaction follows Markovnikov's rule.
- 5- Concentrated sulfuric acid is needed for hydration of ethylene.

a- See Figure 9.45 on page 409 for an example.

Section 9.9

IX. Dimerization and Polymerization of Alkenes

A- Cationic Polymerization

- 1- It is the cation-induced polymerization of alkenes.
- 2- Alkene acts as the Lewis base (π bond); the catalyst (H-OH_2^+) is the Lewis acid.

Section 9.10

X. Rearrangements During H-X Addition to Alkenes

A- Rearrangement

- 1- It is the migration of an atom or groups of atoms from one place to another in a molecule.
- 2- Hydride shift is the migration of a hydride (H^-) generally to form a more stable carbocation (See Figure 9.53 on page 413).
- 3- Wagner-Meerwein rearrangement is essentially a methyl shift with its pair of electrons to form a more stable carbocation (See Figure 9.54 on page 414).

B- Occurrence

- 1- Occur when carbocations are formed (e.g. hydration).
- 2- Otherwise, do not occur (e.g. hydroboration).
- 3- See Figure 9.56 on page 415.

Section 9.11

XI. Hydroboration

A- BH_3 and BF_3 Act as Strong Lewis Acids

- 1- BH_3 dimerizes to diborane (B_2H_6).
- 2- One molecule of BH_3 will complex with one molecule of ether.

B- Initial Product of Hydroboration is an Alkylborane

C- BH_3 will add to an Alkene until all of the Hydrides are replaced by Carbons

D- The Addition is in a Syn Fashion

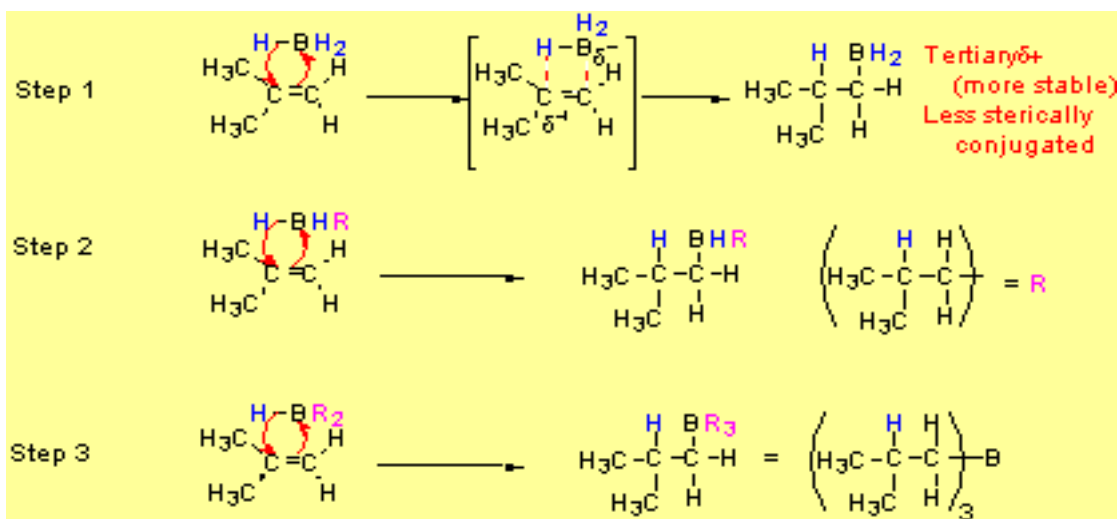


Figure 4

Section 9.12

XII. Hydroboration in Synthesis: Alcohol Formation

A- Alcohol Formation

- 1- For one molecule of trialkylborane, three molecules are formed upon addition of hydrogen peroxide (H_2O_2) and hydroxide (OH^-).

B- Steps of Alcohol Formation

- 1- Addition of peroxidate ion (H-O-O^-) to the borane.
- 2- R group adds to the oxygen and kicks off the hydroxide.
- 3- This step is repeated two more times.
- 4- Hydroxide displaces the alkoxides, followed by protonation of the alkoxide to form the alcohol and boric acid.

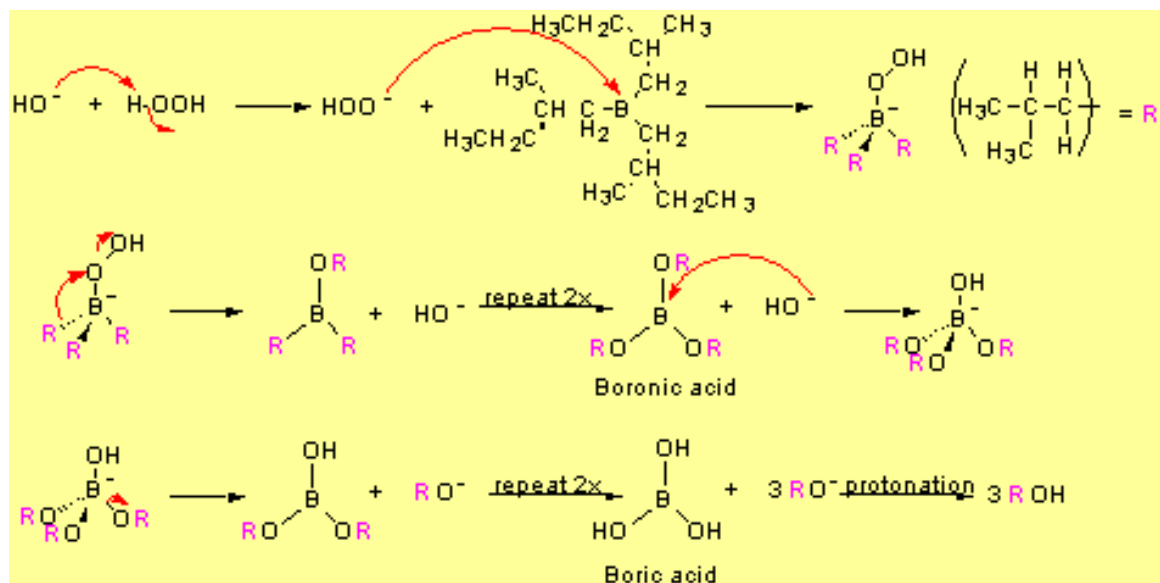


Figure 5

C- Addition is Overall Anti-Markovnikov

- 1- Less stable alkene is formed.

D- No Rearrangements can Occur

Section 9.13

XIII. Special Topic: Rearrangements in Biological Processes

- 1- Intramolecular hydride shift in biological reactions.
- 2- Secondary carbocation intermediate in *S*-Adenosylmethionine undergoes hydride shift to give a more stable tertiary carbocation to ultimately become 10-Methylstearate.

Section 8.14

XIV. Summary

- 1- H-X addition to alkenes.
- 2- Regiochemistry related to possible intermediate carbocations.
- 3- Resonance stabilization.
- 4- Inductive effects.