

# CHEM 321 Organic Chemistry I - Professor Kathleen Kilway

## "Organic Chemistry" by Maitland Jones, 3rd edition

Chapter 10 - 1, 3, 5, 8, 9, 10, 11, 17, 21, 22, 23, 27, 29, 30, 31, 32, 33, 34, 35, 36, 37, 39, 41, 42, 45, 46, 55.

### CHAPTER 10: Addition to Alkenes 2: Additions to Alkynes

#### Section 10.1

##### I. Preview

#### Section 10.2

##### II. Addition of X<sub>2</sub> Reagents

##### A- Hydrogenation

- 1- It is the addition of hydrogen across a  $\pi$  bond, catalyst is required.
  - a- **Heterogeneous catalysis** is a process where the catalyst is insoluble.
    - i- Examples of heterogeneous catalysts are Pd/C, Pt/C, PtO<sub>2</sub>, and Ru/C.
  - b- **Homogeneous catalysis** is a catalytic process in which the catalyst is soluble.
    - i- Example of homogeneous catalysts is RhCl(Ph<sub>3</sub>P)<sub>3</sub>, Wilkinson's catalyst.
- 2- See Figure 10.1 on page 439 for an example of hydrogenation.
- 3- The hydrogen adds syn to the  $\pi$  bond.
- 4- Overall, hydrogenation of an alkene is exothermic by 30 kcal/mol.
- 5- Mechanism remains vague.

##### B- Additions of Halogens (MECHANISM)

- 1- Addition of molecular bromine (bromination) or chlorine (chlorination) in an anti fashion across a double bond produces a vicinal dihalide.
  - a- **Vicinal dihalide** is a species with a halide on adjacent carbons.
- 2- The mechanism is in Figure 10.13 on page 444. The intermediate is a bromonium ion.
- 3- General reaction is depicted below (bromination of cyclohexene).

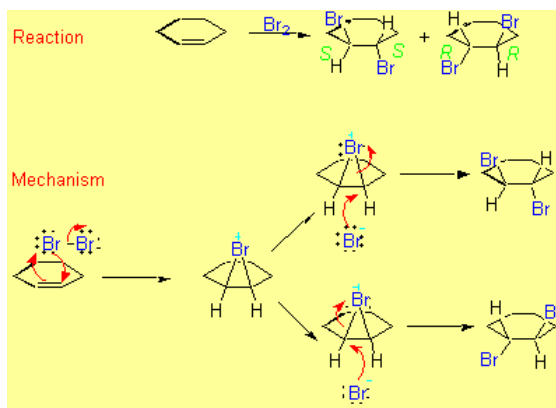


Figure 1

- 4- The chlorination reaction follows the same general mechanism with a chloronium ion as the intermediate.
- 5- The bromonium or chloronium is only symmetrical when formed from a symmetrical alkene.

- a- The more substituted carbon of the C-X bond is longer and weaker.  
 b- Therefore, there is a build-up of positive charge on that carbon. It is the one that is attacked by the nucleophile (See Figure 10.20 on page 448).

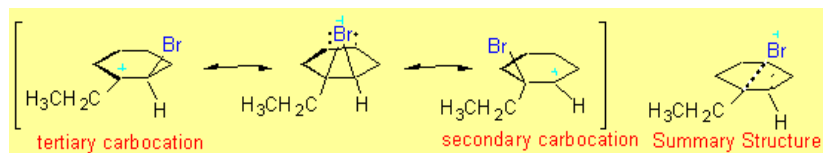


Figure 2

- 6- In the presence of other nucleophiles, other products are formed (Figure 3).

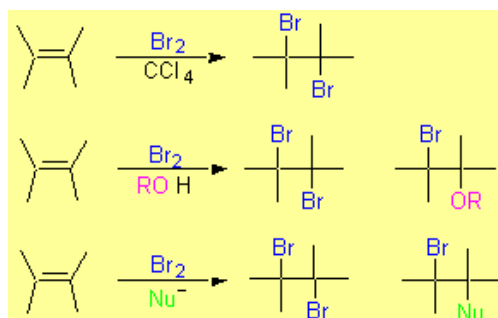


Figure 3

### Section 10.3

#### III. Hydration Through Mercury Compounds: Oxymercuration

##### A- Two-Step Process

- 1- The first step includes the formation of a cyclic, mercurinium ion; addition of water to the mercurinium intermediate; then deprotonation to form a mercury-containing alcohol (See Figure 10.24 on page 451).
- 2- The second step is the reduction of the mercury-containing alcohol with sodium borohydride ( $\text{NaBH}_4$ ) (See Figure 10.25 on page 451).

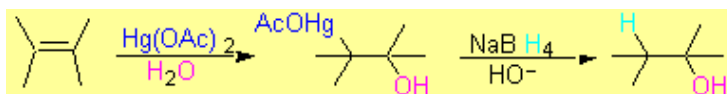


Figure 4

##### B- Three Methods of Hydration

- 1- Direct hydration - (p. 409) - proceeds through a carbocation; Markovnikov products; rearrangements occur.
- 2- Hydroboration - (p. 416) - proceeds through alkylborane; yields anti-Markovnikov products, no rearrangements occur.
- 3- Oxymercuration - (p. 449) - proceeds cyclic mercury-containing ion; yields Markovnikov products; no rearrangements occur.

### Section 10.4

#### IV. Other Addition Reactions Involving Three-Membered Rings: Oxiranes and Cyclopropanes

**A- Oxiranes (MECHANISM)**

- 1- Oxiranes (epoxides) are three-membered rings with two carbons and one oxygen.
- 2- They can be formed using an alkene and a peracid (e.g., trifluoroperacetic acid, *meta*-chloroperbenzoic acid).
  - a- These reactions are concerted, syn additions.
  - b- Regiochemistry of alkene is retained in the epoxide.
- 3- See Figure 10.27 on page 453 for an example of the epoxidation reaction.

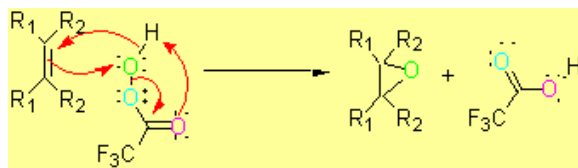


Figure 5

**B- Asymmetric (Sharpless) Epoxidation**

- 1- Reaction uses titanium isopropoxide, *tert*-butyl peroxide and one enantiomer of tartaric ester with an allylic alcohol.

**C- Further Reactions of Oxiranes (MECHANISM)**

- 1- 1,2-Glycol is a 1,2-diol, alcohols are on adjacent carbons.
- 2- Two different types of ring openings: basic and acidic.
  - a- In basic conditions, mechanism is  $S_N2$  followed by protonation.
    - i- Nucleophilic attack by hydroxide or any other nucleophile on the less sterically congested carbon.

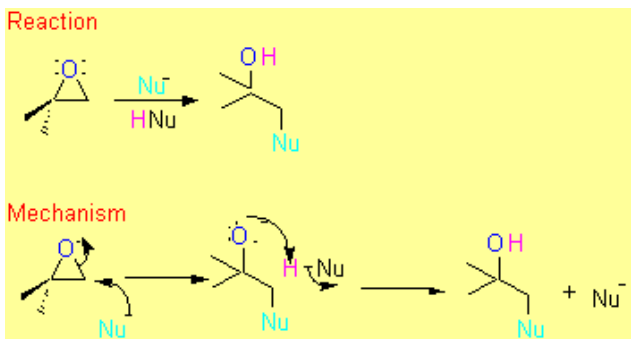


Figure 6

- b- In acidic conditions, first there is protonation,  $S_N2$  attack of the nucleophile, followed by deprotonation if water is the nucleophile.
  - i- More substituted carbon of the protonated oxirane (epoxide) will undergo nucleophilic attack.

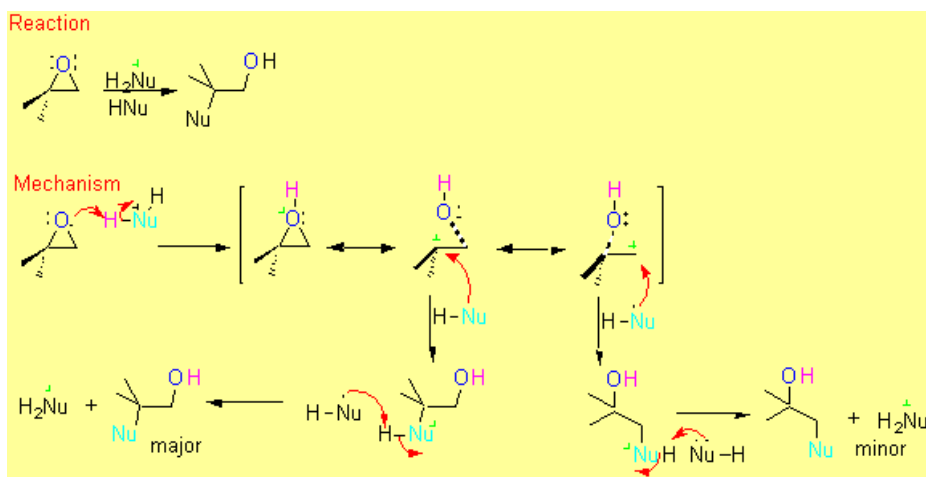


Figure 7

3- See Figure 10.32 on page 455 for an example of basic and acidic ring opening.

#### D- Carbenes

- 1- **Carbenes** are neutral compounds containing two electrons and two substituents.
- 2- They are used to form cyclopropanes from alkenes.
- 3- Carbenes are formed from diazo compounds using heat or irradiation. They can also be formed by treatment of bromoform or chloroform by a strong base (*tert*-butoxide).
- 4- It is a one-step (syn) addition so the regiochemistry of the alkene is retained in the cyclopropane.

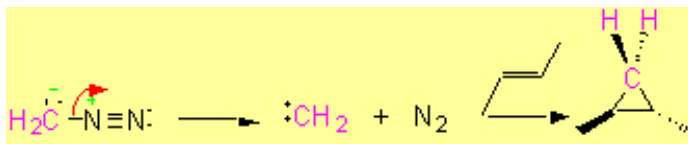


Figure 8

#### E- Triplet Carbenes

- 1- **Triplet Carbenes** are similar to Singlet Carbenes, except that the non-bonding electrons have the same spin quantum number and cannot occupy the same orbital. Both the hybrid and  $2p$  orbitals are half-occupied (See Figure 10.45 on page 462).
- 2- Triplets form diradicals, with two nonbonding electrons on different carbons.
- 3- Reactions with triplet carbenes give mixtures of cis and trans cyclopropanes.

### Section 10.5

#### V. Dipolar Addition Reactions: Ozonolysis and the Synthesis of Carbonyl ( $\text{R}_2\text{C}=\text{O}$ ) Compounds

##### A- The Mechanism of Ozonolysis

- 1- **1,3-dipoles** (1,3-dipolar reagents) are compounds where the resonance forms have positive and negative charges. They form five-membered rings.
- 2- **Ozonolysis** is the reaction of ozone with the  $\pi$  system of an alkene forming various oxidized species.

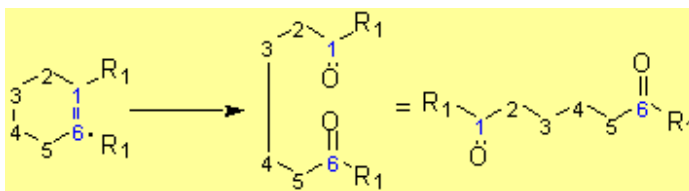


Figure 9

## 3- Steps of the ozonolysis reaction:

- a- Reaction of ozone ( $O_3$ ) with  $\pi$  system of alkene forming a primary ozonide or molozonide.
  - i- A molozonide is a five-membered ring with three consecutively bonded oxygens.
- b- The second step is a rearrangement to an ozonide.
  - i- An ozonide is a more stable intermediate, which is also a five-membered ring.
  - ii- The rearrangement occurs through a reverse 1,3-dipolar addition to form a carbonyl compound and a carbonyl oxide, which then undergo a forward 1,3-dipolar addition.
  - iii- This rearrangement is over 40 kcal/mol exothermic due to the formation of two new C-O bonds even though one O-O and C-C bond is broken.

## B- The Synthetic Potential of Ozonolysis: Carbonyl Compounds

## 1- Some definitions.

- a- **Carboxylic acids** are compounds containing a COOH (a carbon bonded to an oxygen and double-bonded to another oxygen) functional group.
- b- A **carbonyl group** is a carbon double-bonded to an oxygen.
- c- A **ketone** is a molecule belonging to a class with RCOR structure. The CO is a carbonyl group and the R groups are neither hydrogens nor another O.
- d- An **aldehyde** has the structure RCOH where CO is a carbonyl compound.
- e- **Zwitterions** are charge-separated molecules.

## 2- Reduction of Ozonide

- a- Reduction of the ozonide yields ketones and aldehydes as the final products.
  - i- Examples of reducing agents are  $H_2/Pd$ , Zn, and  $(CH_3)_2S$  (dimethyl sulfide).
  - ii- See Figure 10.62 on page 470 for an example of reductive workup.

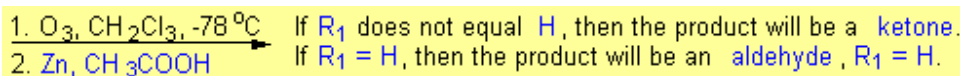


Figure 10

- b- Oxidation of the ozonide yields ketones and carboxylic acids.
  - i- An example of an oxidative workup is  $H_2O_2/HCOOH$ .
  - ii- See Figure 10.63 on page 471 for an example of oxidative workup.

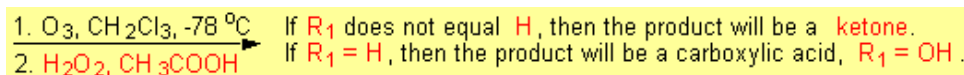


Figure 11

**B- Oxidation with Permanganate or Osmium Tetroxide**

- Both add to alkenes to form five-membered rings, which decompose to form vicinal diols.
- Both yield syn diols.

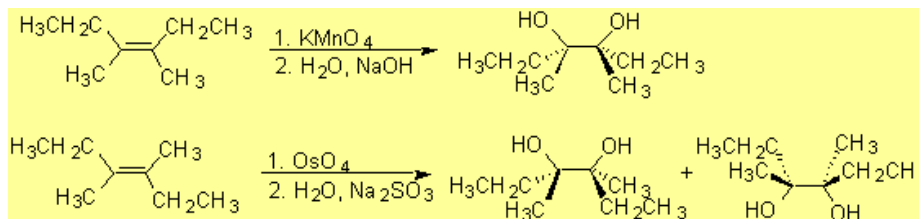


Figure 12

**Section 10.6****VI. Addition Reactions of Alkynes: H-X Addition (MECHANISM)****A- Addition of H-X to Alkynes (where X = Cl, Br, and I)**

- First addition of H-X to an alkyne yields a vinyl halide (alkene).
- The reaction proceeds through a vinyl cation.
  - Addition of nucleophile will be at more substituted position.
- Second addition of HX to the vinyl halide yields a geminal dihalide (1,1-disubstitution).
- There is a mixture of two products, vinyl halide and geminal dihalide.
- See Figure 10.73 of page 478.

**B- Mechanism**

- First step is protonation forming a cyclic protonium ion.
  - Secondary vinyl cations are more stable than primary vinyl cations but equally stable with primary carbocations.
- Next step is a backside attack by the halide ( $\text{X}^-$ ) favoring the Markovnikov product.
- Another addition of H-X to the resulting alkene competes with addition to the alkyne.
- The second addition produces a geminal (1,1-disubstituted) dihalide.
  - Resonance effects direct the products.

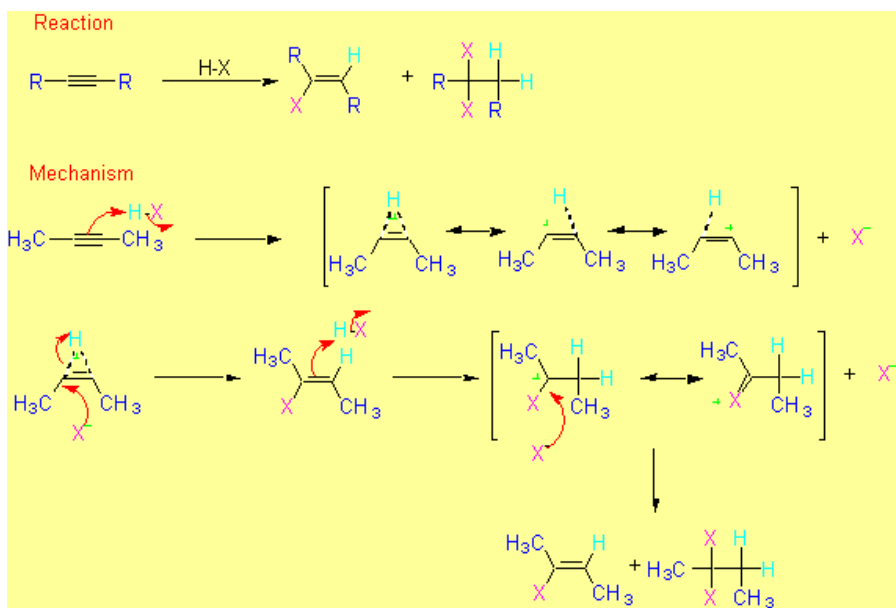


Figure 13

## Section 10.7

VII. Addition of  $\text{X}_2$  Reagents to Alkynes

A- Mechanism is not well known

B-  $\text{X}_2$  adds to Alkynes to Give Vicinal 1,2-Dihalides

C- A second Addition to the Resulting Vicinal Dihalide Gives Tetrahalides

1- Tetrahalides are the major products.

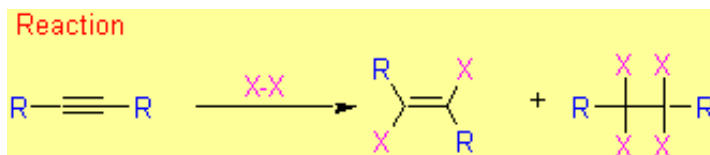


Figure 14

## Section 10.8

## VIII. Hydration of Alkynes

A- Oxymercuration Yields an Enol which Yields a Ketone

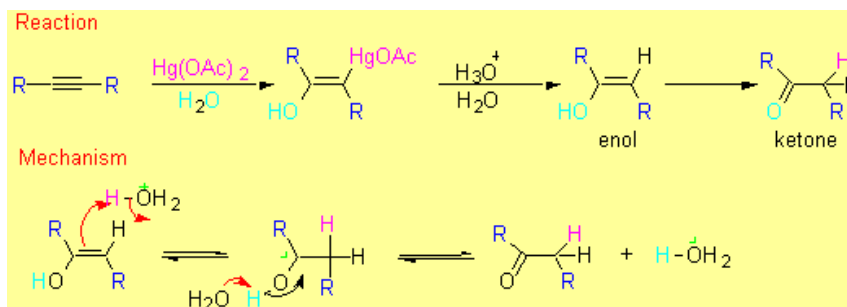
1- An **enol** is a molecule that is part alkene and part alcohol.2- A **ketone** is a molecule, which has a carbon-oxygen double bond attached to two other carbons.

Figure 15

## Section 10.9

## IX. Hydroboration of Alkynes (MECHANISM)

## A- Reaction is Similar to Addition to Hydroboration of Alkenes

- 1- Addition of  $\text{BH}_3$  is cis.
- 2- Boron becomes attached to the less substituted end of alkyne.

## B- The Alkenyl Boranes are Converted to Alcohols, Enols

## C- These Enols are in Equilibrium with Ketones and Aldehydes

## D- Products are Anti-Markovnikov Products

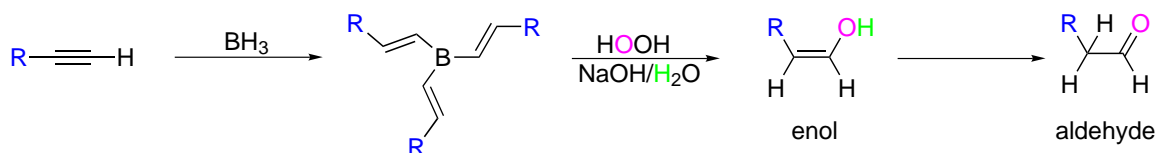


Figure 16

## Section 10.10

## X. Hydrogenation of Alkynes: An Alkene Synthesis Through Syn Hydrogenation

## A- Normally Alkynes are Reduced to Alkanes

## B- The Exception is Using a "Poison" Catalyst

- 1- Examples of a "poison" are Lindlar catalyst -  $\text{Pd}/\text{CaCO}_3/\text{Pb}$ .
- 2- With a poison, the product is the cis alkene.
- 3- See Figure 10.82 on page 483 for an example.

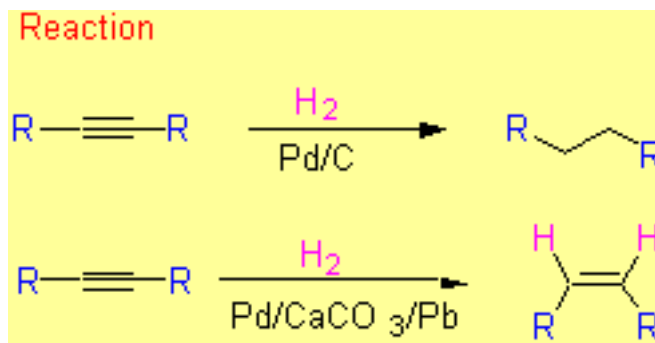


Figure 17

## Section 10.11

## XI. Reduction by Sodium in Ammonia: An Alkene Synthesis Through Anti Hydrogenation (MECHANISM)

## A- Reduction of Alkynes Using Sodium in Liquid Ammonia

- 1- It proceeds via a radical mechanism using solvated electrons.
- 2- Radical anion is an intermediate.
- 3- The final product is a trans alkene.
- 4- See Figure 18 for the mechanism of anti hydrogenation.

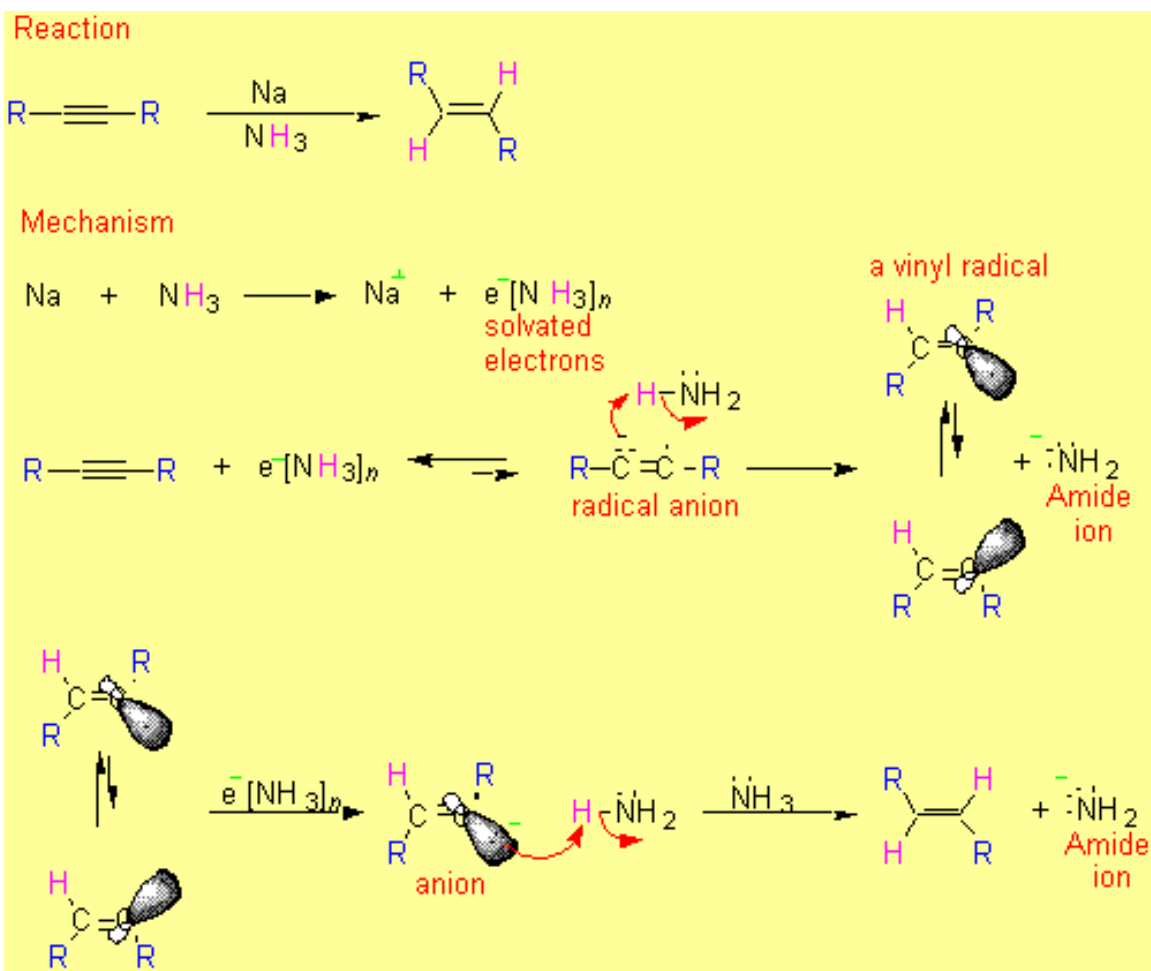


Figure 18

**Section 10.12****XII. Special Topic: Three-Membered Rings in Biochemistry**

- 1- Nature finds ways to make cyclopropanes in spite of the inherent strain, such as Pyrethroids found in the members of the chrysanthemum family.

**Section 10.13****XIII. Summary**

- 1- Addition of  $\text{X}_2$  reagents.
- 2- Oxymercuration.
- 3- Oxiranes and Cyclopropanes.
- 4- Dipolar addition reactions.
- 5- Addition reactions of alkynes.
- 6- Hydration, hydroboration and hydrogenation of alkynes.