

CHEM 322 Organic Chemistry II - Professor Kathleen V. Kilway
"Organic Chemistry" by Maitland Jones, 3rd edition

Chapter 12 Homework: 1, 2, 4, 5, 6, 7, 15, 16, 17, 19, 21, 24, 26, 28, 29, 30, 38, 39, 40, 43, 45, 51, 52.

CHAPTER 12 DIENES AND THE RADICAL SYSTEM: 2p ORBITALS IN CONJUGATION

Section 12.1

I. Preview

A- Vocabulary

- 1- Dienes are compounds containing two double bonds (Chapter 3, p. 98).
- 2- Conjugated double bonds are connected in a 1,3-fashion, which react differently than double bonds separated further.

B- Essential Skills

- 1- It is important to understand the chemical and structural consequences of conjugation as in 1,3-dienes.
- 2- The difference between kinetic and thermodynamic control must be understood.
- 3- The new reaction in this chapter is the Diels-Alder reaction.

Section 12.2

II. Allenes: 1,2-Dienes

A- Allene

- 1- It contains two double bonds connected in a 1,2-fashion.
- 2- It shares a common carbon.
- 3- The central carbon is *sp* hybridized.
- 4- An allene can be chiral even though they do not contain stereogenic center.

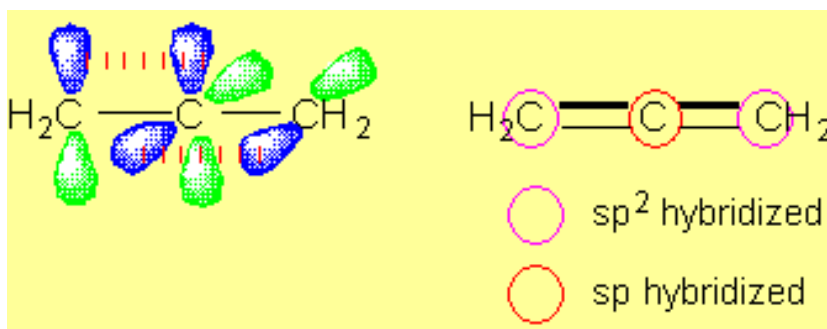


Fig 1

- 5- Allenes are high energy compounds, which have similar heats of formations as that of alkynes (e.g., propyne 44.6 versus 47.4 kcal/mol in propadiene; 1-butyne 39.5 versus 38.8 kcal/mol in 1,2-butadiene; and 2-butyne 34.7 versus 33.6 kcal/mol for 1,2-pentadiene and 31.8

kcal/mol for 2,3-pentadiene).

Section 12.3

III. Related Systems: Ketenes and Cumulenes

A- Ketenes are compounds containing a carbon which is both a carbonyl carbon and a carbon of double bond.

1- The central carbon is also *sp* hybridized.

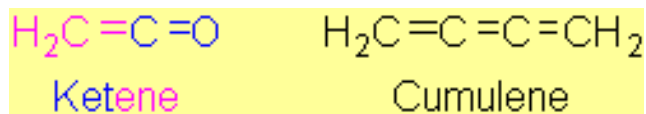


Fig 2

B- Cumulenes are compounds containing a triene connected in a 1,2,3-fashion.

1- Carbons 2 and 3 of the triene are *sp* hybridized.

Section 12.4

IV. Allenes as Intermediates in the Isomerization of Acetylenes

A- A useful reaction with alkynes is the base-catalyzed isomerization of an internal triple bond to the terminal triple bond.

1- This reaction is favored because the acetylide anion (terminal carbon) is thermodynamically more stable.

2- The pK_a s of 1-butyne and ammonia are 25 and 38, respectively.

a- **Step 1** is the deprotonation of the sp^3 -hybridized C adjacent to the *sp*-hybridized carbon of the alkyne to give a resonance-stabilized carbanion.

b- **Step 2** is reprotonation of the carbanion to form an allene.

c- **Step 3** is another deprotonation step. In this case, it is a deprotonation of the next allenyl C to generate a new, resonance-stabilized anion.

d- **Step 4** is another reprotonation step. In this case, it's a reprotonation to generate a new, terminal alkyne. These steps are repeated until a terminal alkyne is formed.

e- **Step 5** is another deprotonation step. In this case, it's a deprotonation of the hydrogen of the terminal alkyne, which is a **thermodynamic sink**.

f- **Step 6** is another reprotonation step upon the addition of water.

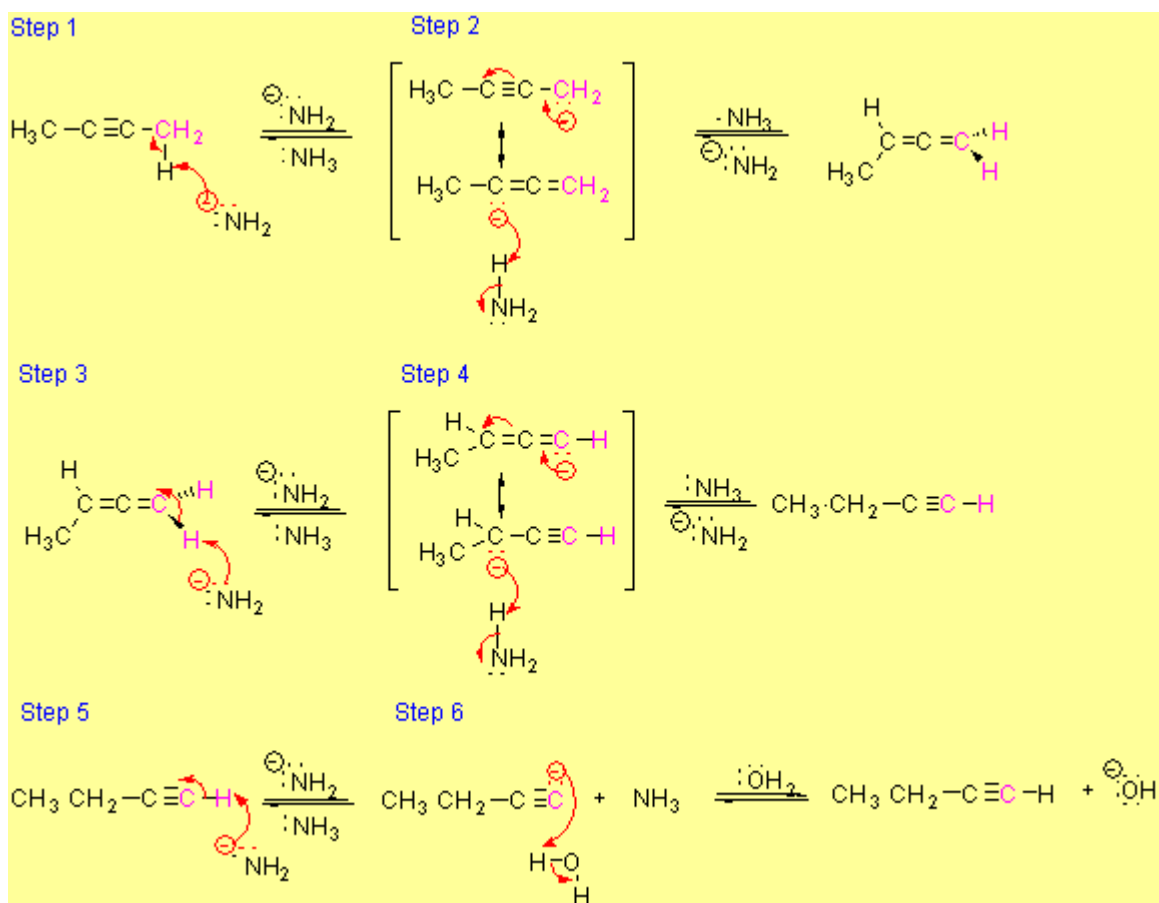


Fig 3

Section 12.5

V. 1,3-Dienes

A- 1,3-Diene is a conjugated system.

- 1- The double bonds are connected through $2p-2p$ orbital overlap.
- 2- In 1,4-pentadiene, the two double bonds are not conjugated.

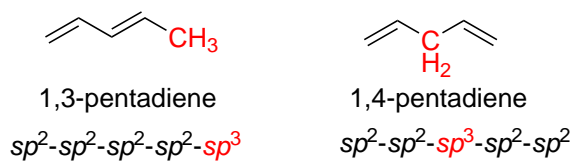


Fig 4

B-The Molecular Orbitals of 1,3-Butadiene

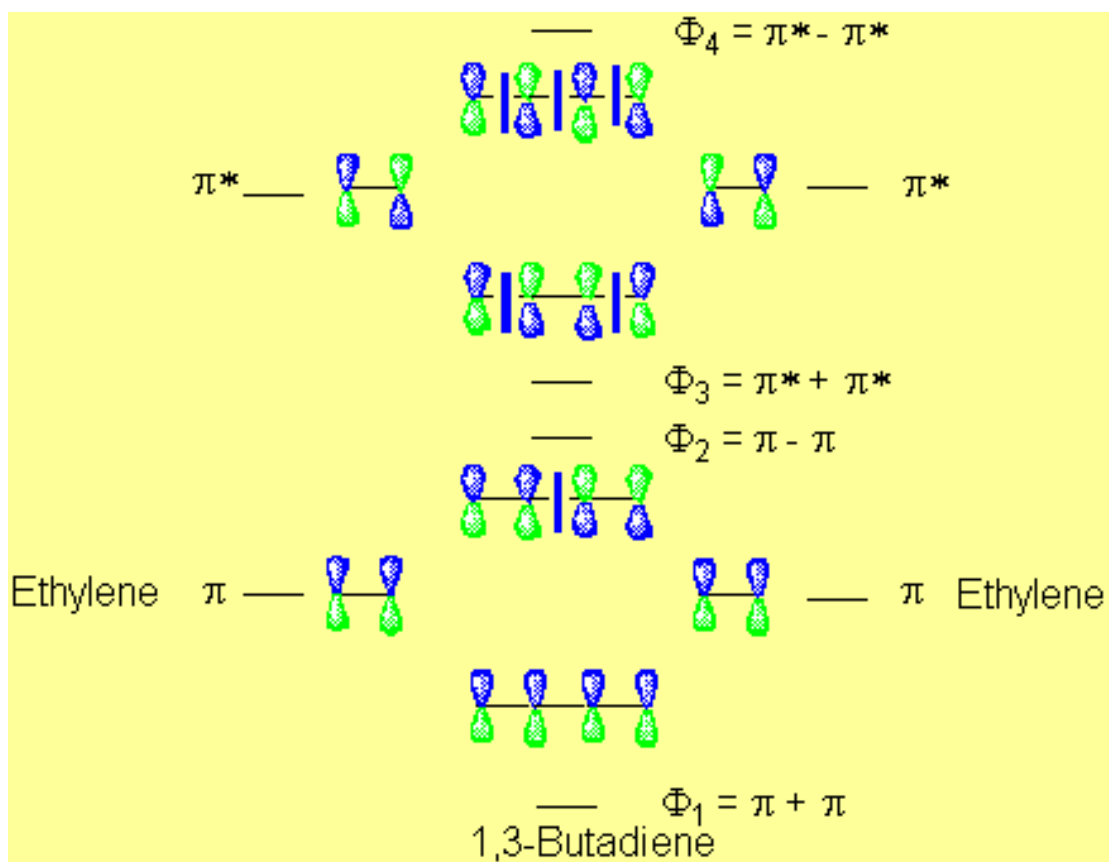


Fig 5

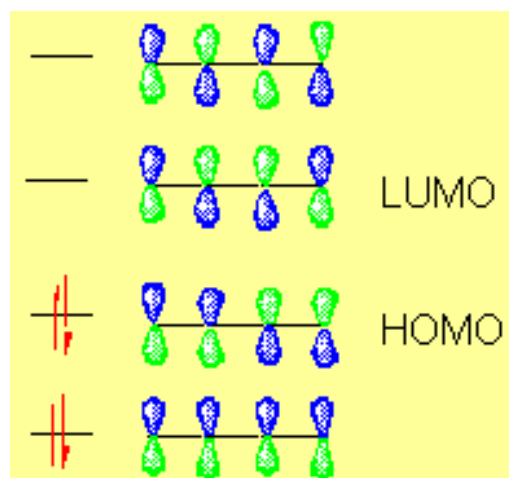


Fig 6

Section 12.6

VI. The Physical Consequences of Conjugation

A- The carbon-carbon bond length between carbons C(2) and C(3) is shorter than a single bond but longer than a double bond.

1- Comparison of C(2) - C(3) bond lengths:

butane (1.53 Å) > 1,3-butadiene (1.47 Å) > 2-butene (1.32 Å)

B- There are two isomers for the 1,3-dienes.

1- *s-cis* (single, *cisoid*).

2- *s-trans* (single, *transoid*).

3- 66 kcal/mol is required for a double bond to isomerize.

4- For the dienes, both the *s-cis* and *s-trans* are stabilized.

a- The barrier to rotation is 4-5 kcal/mol.

b- The *s-trans* is approximately 2-3 kcal/mol more stable than the *s-cis* isomer.

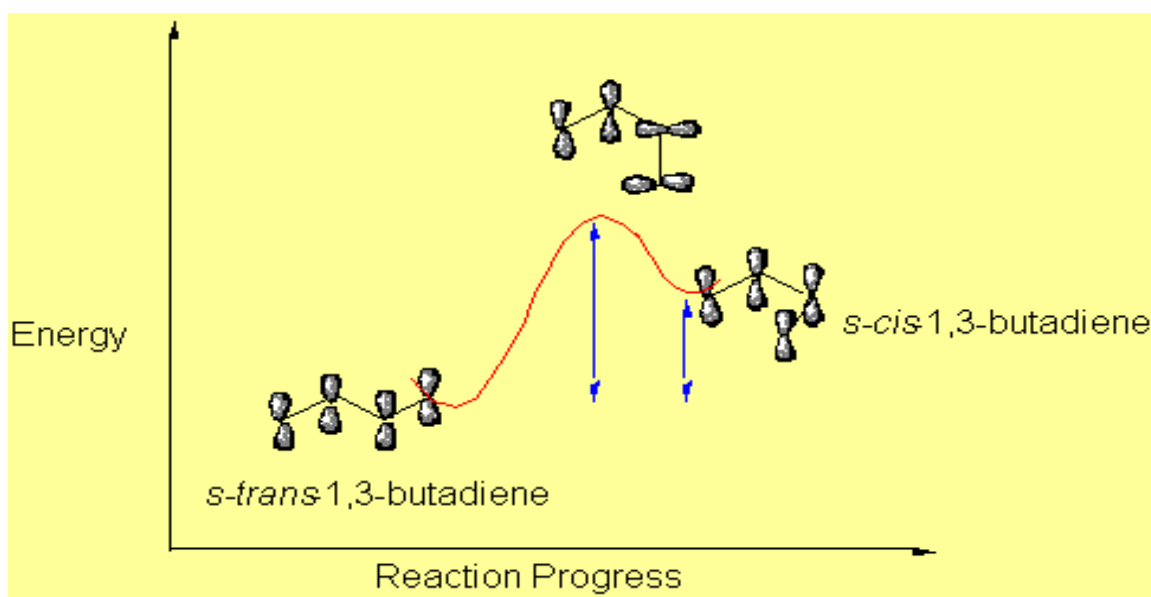


Fig 7

A- Heats of Hydrogenation

1- Difference in Heats of Hydrogenation for various double bonds.

a- The Heat of Hydrogenation for 1-butene is -30.3 kcal/mol.

b- The Heat of Hydrogenation for 1,4-pentadiene is -60.8 kcal/mol

c- The Heat of Hydrogenation for 1,5-hexadiene is -60.5 kcal/mol

d- The difference between the average Heat of Hydrogenation of unconjugated dienes is -60.7 kcal/mol and the measured Heat of Hydrogenation for 1,3-butadiene is -57.1 kcal/mol is 3.6 kcal/mol.

B- Overall Conjugation shortens bond lengths and decreases Heats of Hydrogenation.

Section 12.7

VII. Molecular Orbitals and Ultraviolet Spectroscopy

A- Spectroscopy is the study of the interactions between electromagnetic radiation and atoms and molecules.

1- Types of spectroscopy: ultraviolet/ visible (UV/vis), infrared (IR) and nuclear magnetic resonance (NMR).

B- Ultraviolet/visible Spectroscopy

1- It is called electronic spectroscopy because it deals with the absorption of energy by electrons in molecules.

$$2- \Delta E = h\nu = hc/\lambda$$

where ΔE is proportional to the frequency of light (λ),
 h is Planck's constant, and c is the speed of light.

3- Ultraviolet spectrum is between 200-400 nm. The visible spectrum is the region from 400-800 nm.

4- Extinction coefficient is the proportionality constant (ϵ) in Beer's law.

$$A = \log I_0/I = \epsilon lc$$

where I_0 is the intensity of the light entering the sample, I is the intensity of light exiting the sample, and l is the path length of the cell.

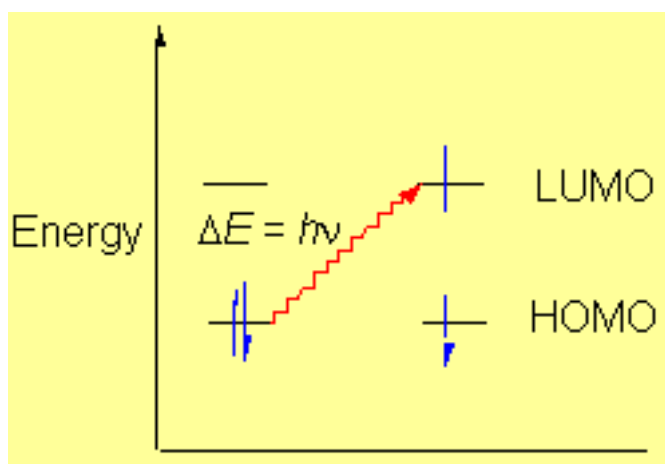


Fig 8

C- Possible UV transitions

1- s and p electrons can be promoted to σ^* or π^* .

2- For unconjugated alkenes such as ethylene, the π to π^* transition costs 173 kcal/mol.

3- When there is conjugation present, the energy required for a π to π^* transition becomes smaller. It absorbs at a much longer wavelength.

4- Therefore, conjugation decreases the energy gap between HOMO and LUMO shifting the lowest energy absorption to longer wavelength.

5- It also increases the number of transitions.

D- Woodward's Rules of Acyclic Dienes and Fiesers' Rules for Steroid Dienes

1- Do not memorize but understand the concepts.

2- Each additional conjugated double bond shifts the wavelength towards into the visible range.

Section 12.8

IIX. Polyenes and Vision

A- Vision.

- 1- In vision (Vitamin A), the terminal alcohol in *trans*-retinol is oxidized to an aldehyde by the enzyme retinol dehydrogenase.
- 2- Then, a *trans* double bond in the resulting *trans*-retinal is isomerized to a *cis* double bond by the enzyme retinal isomerase.
- 3- The resulting *cis*-retinal binds to the pocket of opsin to form rhodopsin which isomerizes the *cis* to the *trans* double bond.

Section 12.9

IX. The Chemical Consequences of Conjugation: Addition Reactions of Dienes

A- Addition of HBr and HCl at $-78\text{ }^{\circ}\text{C}$ (i.e., low temperatures).

- 1- Addition of HCl to 1,3-butadiene yields two major products, 3-chloro-1-butene (75.5%) and *trans*-1-chloro-2-butene (24%).

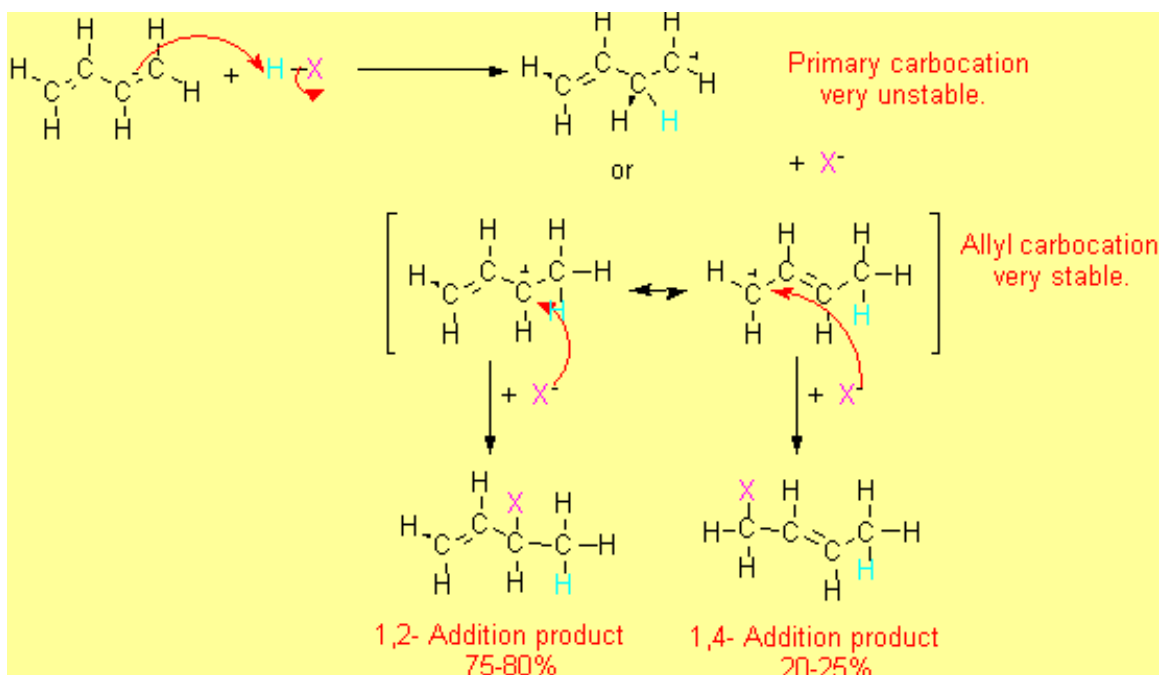


Fig 9

2- See Chapter 9, pg. 389.

B- Addition of Br₂ and Cl₂.

- 1- Addition of dihalides yields two products.
- 2- Both the 1,2- and 1,4-addition products are formed as in the addition of hydrogen halides.

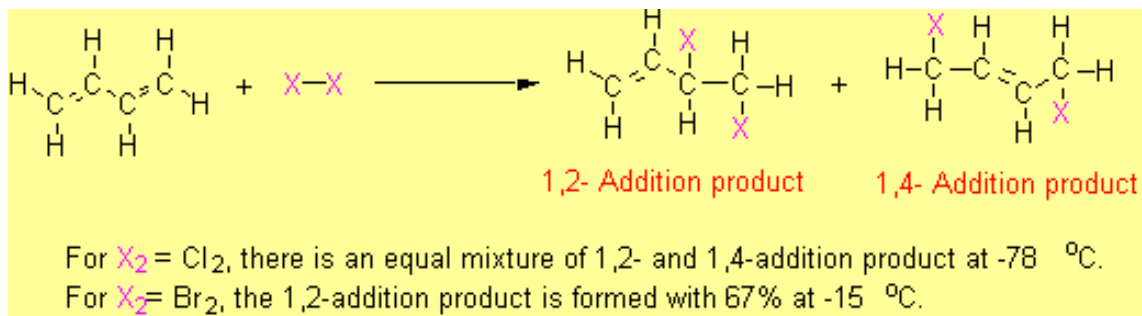


Fig 10

Section 12.10**X. Thermodynamic and Kinetic Control of Addition Reactions****A- Thermodynamic vs. Kinetic Control.**

- 1- Thermodynamic Control is when the product distribution depends on the energy differences between the products (long reaction times and/or severe conditions).
- 2- Kinetic Control is when the product distribution depends on the relative energies of the transition states leading to products (short reaction times and/or mild conditions).
- 3- The temperature and time affects the product distribution and control.
 - a- An increased temperature favors or increases the percentage of 1,4-addition product.
 - b- An increased time for reaction will also increase the percentage of 1,4-addition product.
- 4- The 1,4-addition product is more stable thermodynamically even though the 1,2-addition product is formed first.
 - a- 1,4-addition product contains an internal double bond.
 - b- 1,2-addition product contains a terminal double bond.
- 5- Overall, there is a proximity effect.

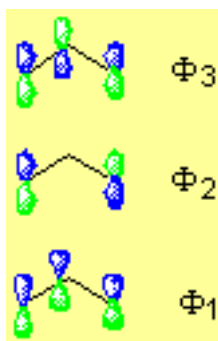
Section 12.11**XI. The Allyl System: Three Overlapping 2p Orbitals****Molecular Orbital Description.**

Fig 10

A- Resonance Stabilization increases reactivity for allylic halides towards S_N1 Solvolysis of Allylic Halides.

- 1- Allyl version of alkane will react faster due to increased stability of carbocation through resonance.
- 2- All of the data is set for the solvolysis of R-Cl in 50% ethanol at 45 °C, relative to chloropropane = 1.
 - a- 2-chloropropane = 1.7
 - b- 3-chloropropene = 14.3
 - c- 3-chloro-2-methyl-1-propene = 21.4
 - d- 1-chloro-2-butene = 1300
 - e- 2-chloro-2-methylpropane = 3×10^4
 - f- 1-chloro-3-methyl-2-butene = 1.9×10^6
 - g- 3-chloro-3-methyl-1-butene = 7.9×10^6

B- S_N2 Reactions of Allylic Halides.

- 1- The transition state is of lower energy in the case of the allyl halide.
- 2- There is a delocalization of charge which increases the rate of reaction.
- 3- All of the data is set for the solvolysis of R-Cl in 50% ethanol at 45 °C, relative to chloropropane = 1.
 - a- 3-chloropropene = 37.0
 - b- 3-chloro-2-methyl-1-propene = 33.0
 - c- 1-chloro-2-butene = 97
 - d- 3-chloro-1-butene = 1.85
 - e- 1-chloro-3-methyl-2-butene = 556

C- The Allyl Radical.

- 1- It is much easier to form a resonance-stabilized allylic radical rather than an undelocalized one.
- 2- See Chapter 11 (pg. 553).

D- The Allyl Anion.

- 1- pK_a of propane is ~60 whereas the pK_a of propene is 43.

Section 12.12

XII. The Diels-Alder Reaction of Dienes

A- The Diels-Alder Reaction is a one-step, concerted, thermal ring formation using a diene and a dienophile.

- 1- The reaction is exothermic.
- 2- Three π bonds are converted into one π and two σ bonds.
- 3- The overall reaction is 38 kcal/mol exothermic [$66 \text{ kcal/mol} + 2(85 \text{ kcal/mol})$] - [$3 \times 66 \text{ kcal/mol}$]
- 4- The reactive form of the diene is the *s-cis* form.
- 5- A strained product (i.e., containing a bridgehead double bond) will not be formed.

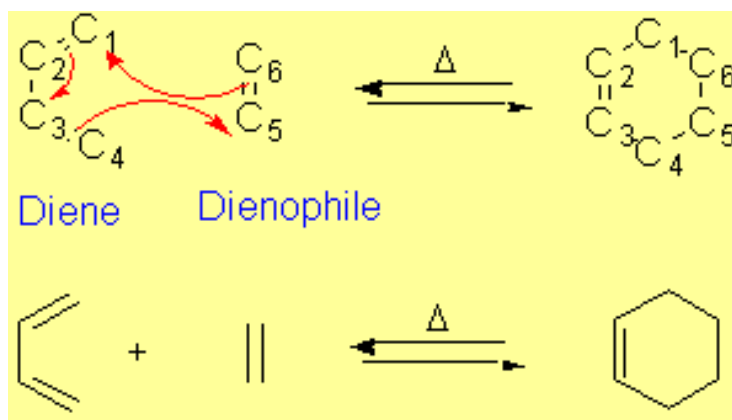


Fig 12

B- The relative stereochemistry is retained.

1- If the dienophile is a *cis*-alkene, then the two groups must stay *cis* to one another.

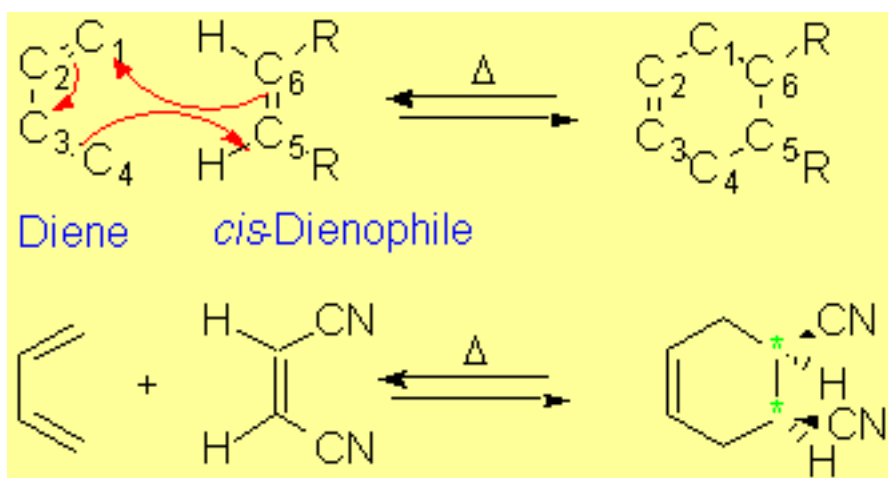


Fig 13

2- Likewise, if the dienophile is a *trans*-alkene, then the two groups must stay *trans* to one another.

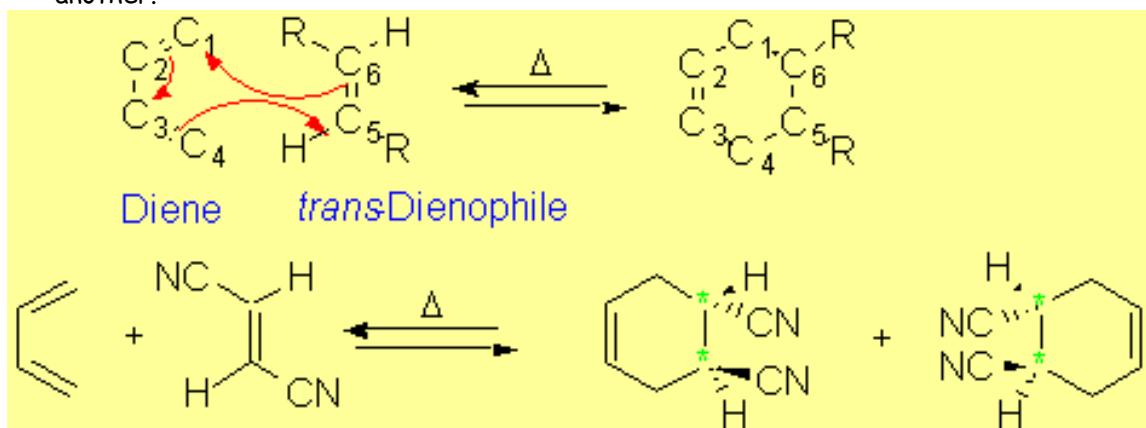


Fig 14

3- The Diels-Alder reaction proceeds with retention of stereochemistry.

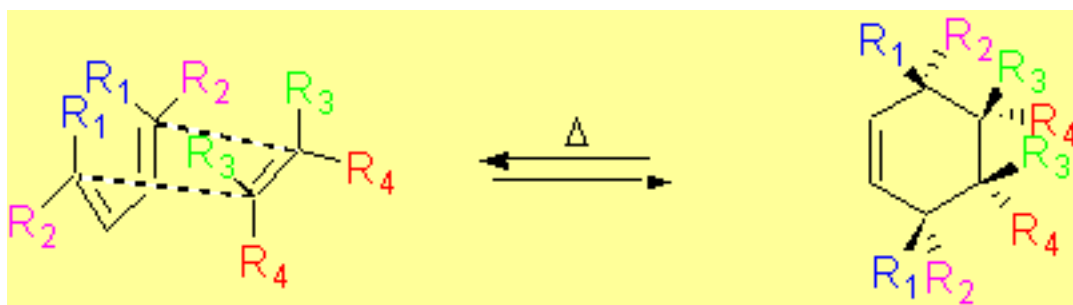


Fig 15

C- At high temperatures, the reverse Diels-Alder occurs.

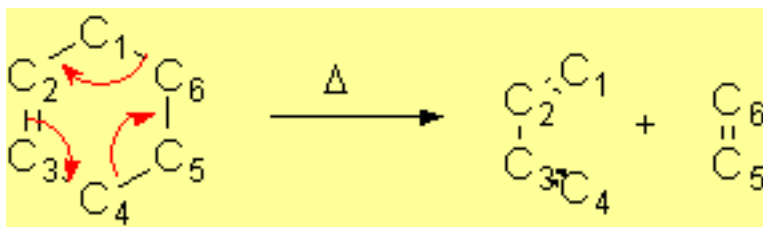


Fig 16

D- The Dienophile can be an alkyne (just as long as it has π electrons).

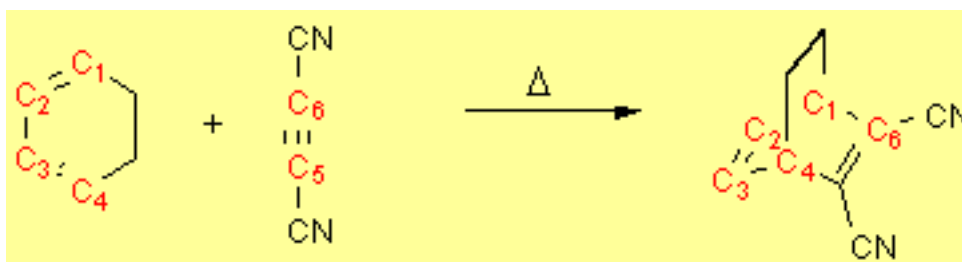


Fig 17

E- Endo vs. Exo compounds.

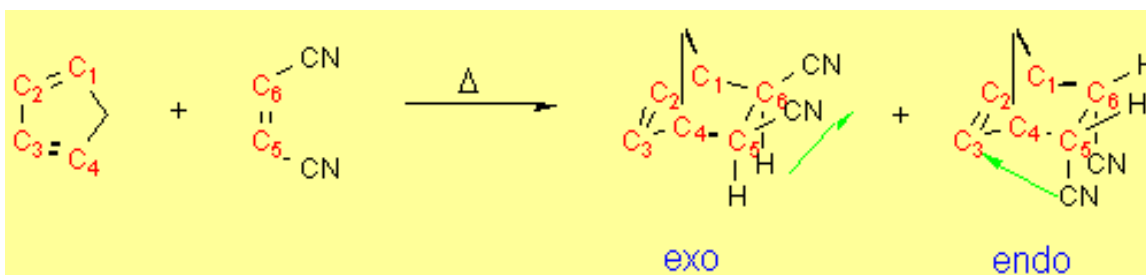


Fig 18

- 1- **Endo** compound has the substituents aimed towards the double bond.
- 2- **Exo** compound has the substituents aimed away from the double bond.
- 3- Even though the exo compounds are more stable, the endo compounds are the major products because they are favored kinetically.

Section 12.13

IIVX. Special Topic: Biosynthesis of Terpenes