

Conjugated Dienes

Chapter 14
Organic Chemistry, *8th Edition*
John E. McMurry

Dienes

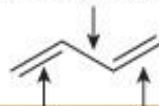
- Propadiene (allene) is a **cumulated diene**
- 1,3-Butadiene is a **conjugated diene**.
- 1,4-Pentadiene is an **isolated diene**.

**Allene –
A cumulated diene**



**1,3-Butadiene—
A conjugated diene**

one σ bond



delocalized π electrons

**1,4-Pentadiene—
An isolated diene**

two σ bonds

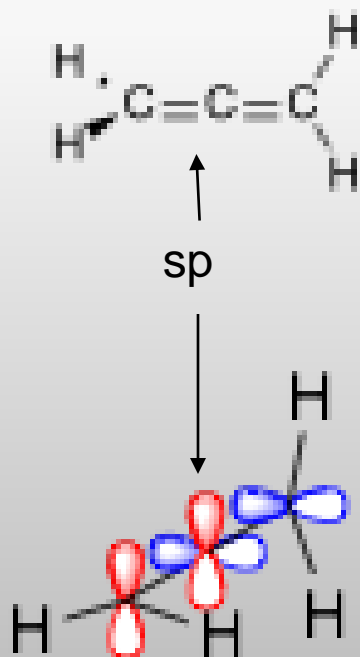


localized π
electrons

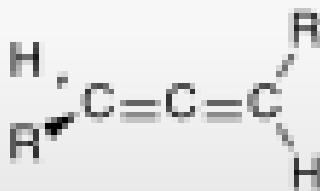
localized π
electrons

Allenes

Bonding



Stereochemistry



- Chiral
- 1,3 disubstituted allenes have no plane of symmetry
- Axial chirality

Energetics

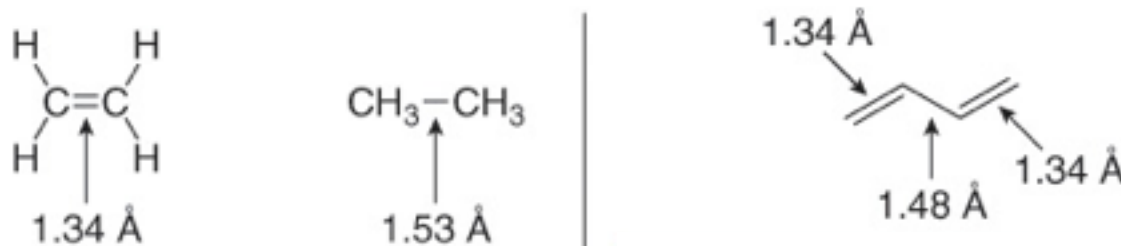
$$\Delta H_f^\circ$$

(Kcal/mol)

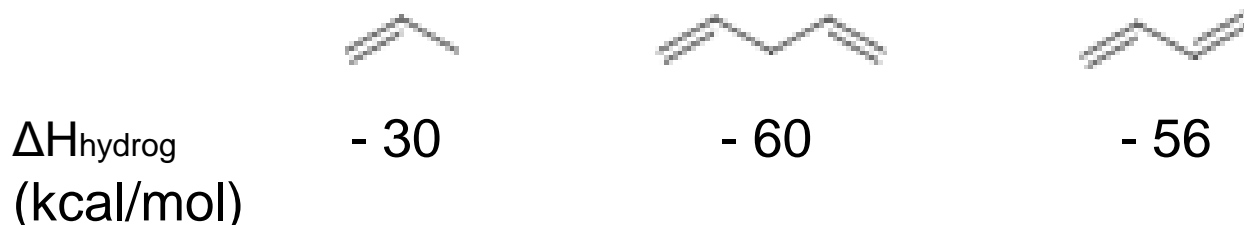


Conjugated Dienes

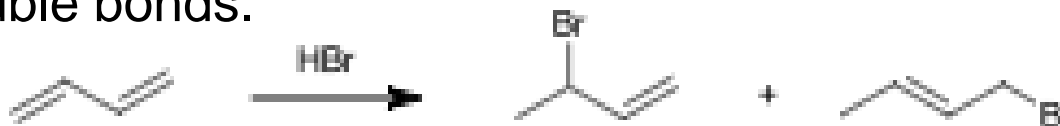
- The C—C single bond joining the two double bonds is unusually short.



- Conjugated dienes are more stable than similar isolated dienes.



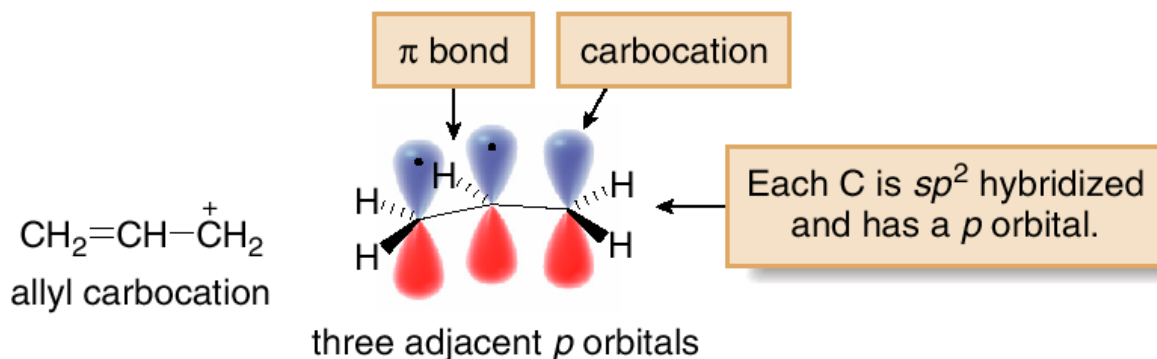
- Some reactions of conjugated dienes are different than reactions of isolated double bonds.



- Conjugated dienes absorb light at longer wavelengths than alkenes.

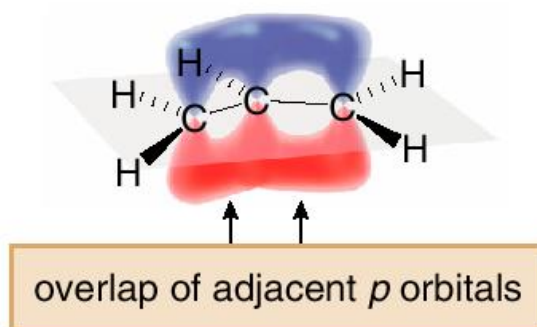
Delocalisation, Resonance, and Dienes

- The allyl carbocation is another example of a **conjugated system**.



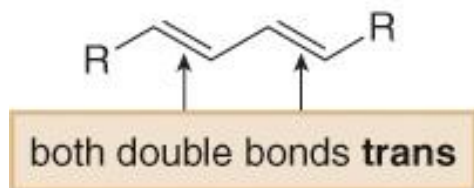
- Three p orbitals on three adjacent atoms, even if one of the p orbitals is empty, make the allyl carbocation conjugated.

- Conjugation stabilizes the allyl carbocation.

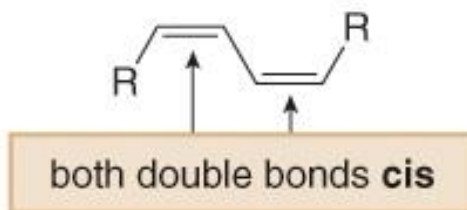


Structure

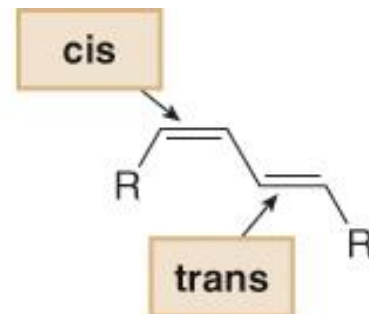
- Three stereoisomers are possible for 1,3-dienes with alkyl groups bonded to each end carbon of the diene.



trans, trans-1,3-diene
or
(E,E)-1,3-diene



cis, cis-1,3-diene
or
(Z,Z)-1,3-diene



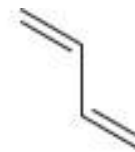
cis, trans-1,3-diene
or
(Z,E)-1,3-diene

- Two possible conformations result from rotation around the C—C bond that joins the two double bonds.

Rotation can occur around the single bond.



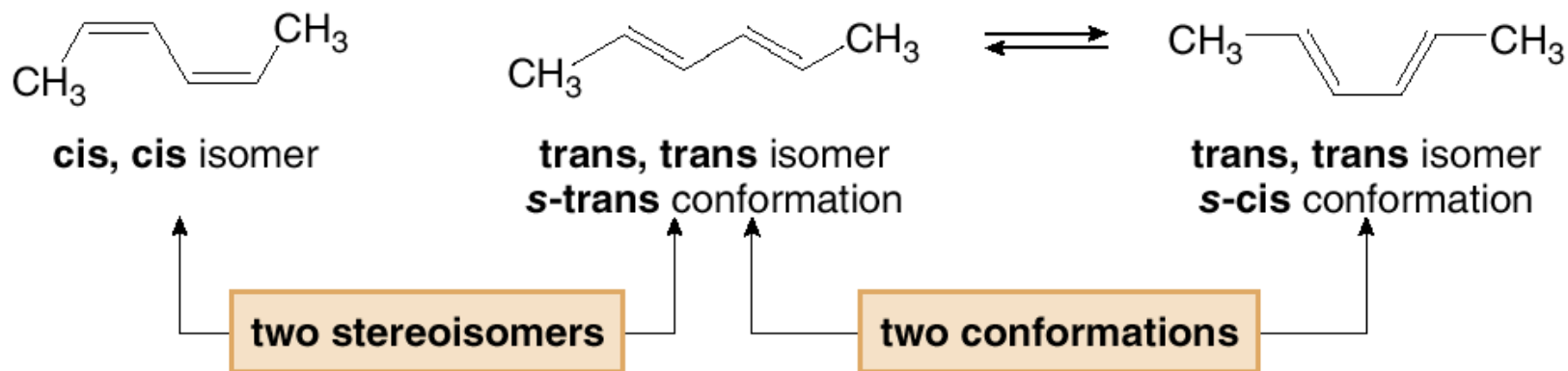
s-cis conformer



s-trans conformer

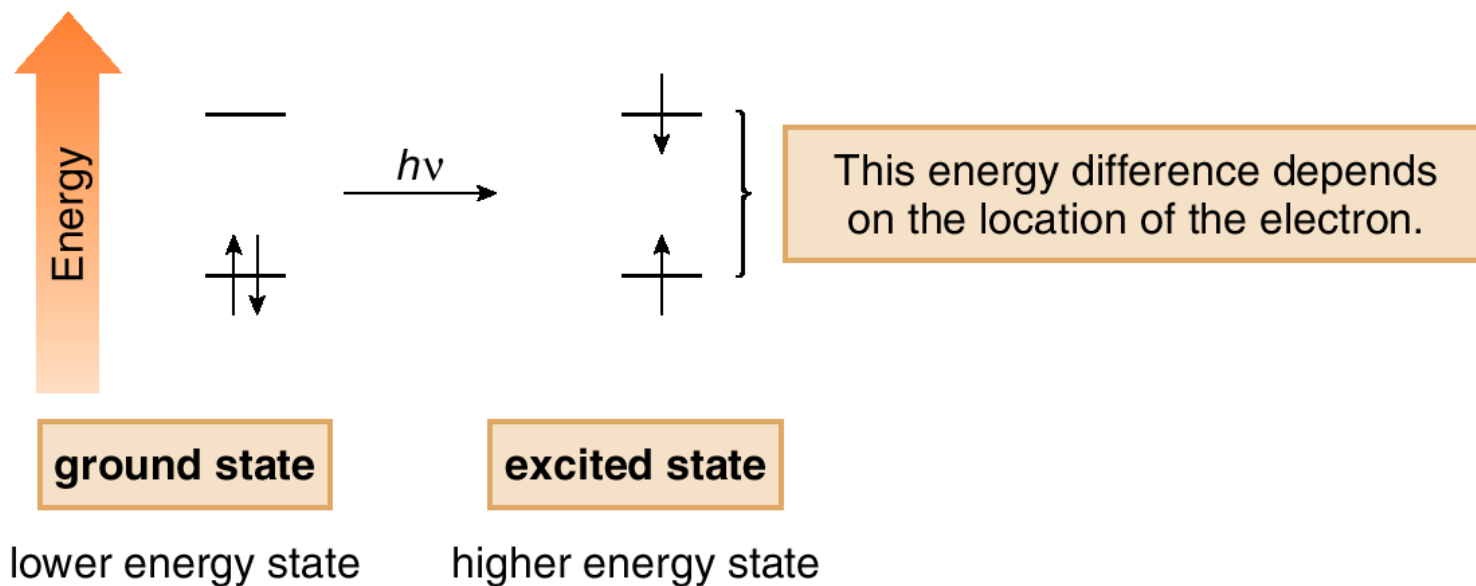
Structure

- Stereoisomers are discrete molecules, whereas conformations interconvert.



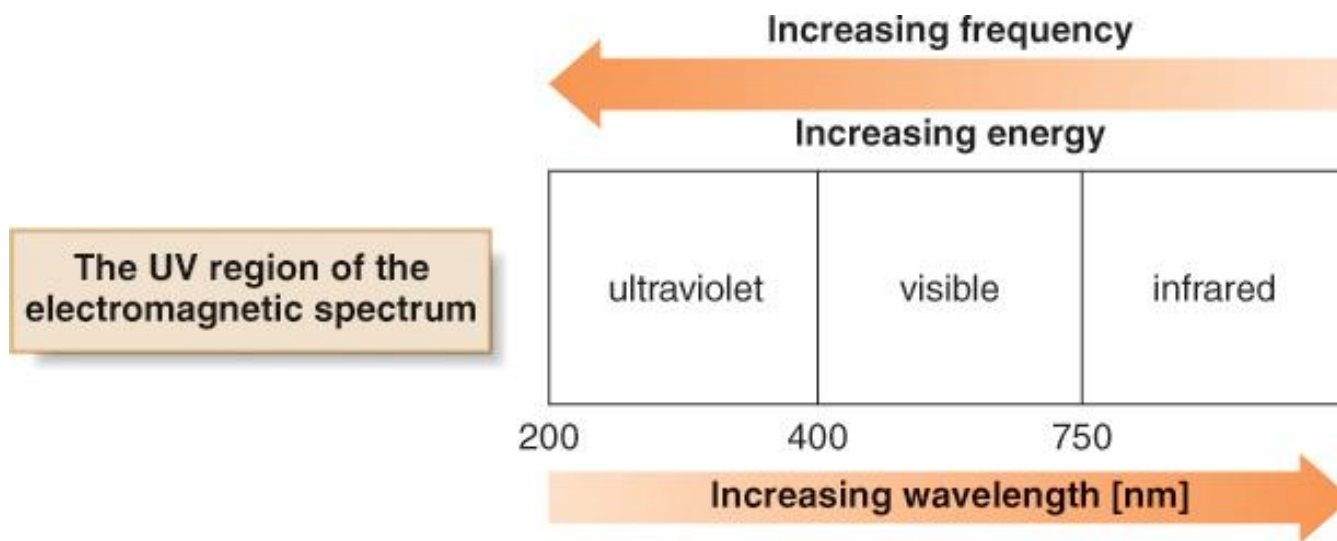
Conjugated Dienes and Ultraviolet Light

- When electrons in a lower energy state (the ground state) absorb light having the appropriate energy, an electron is promoted to a higher electronic state (excited state).

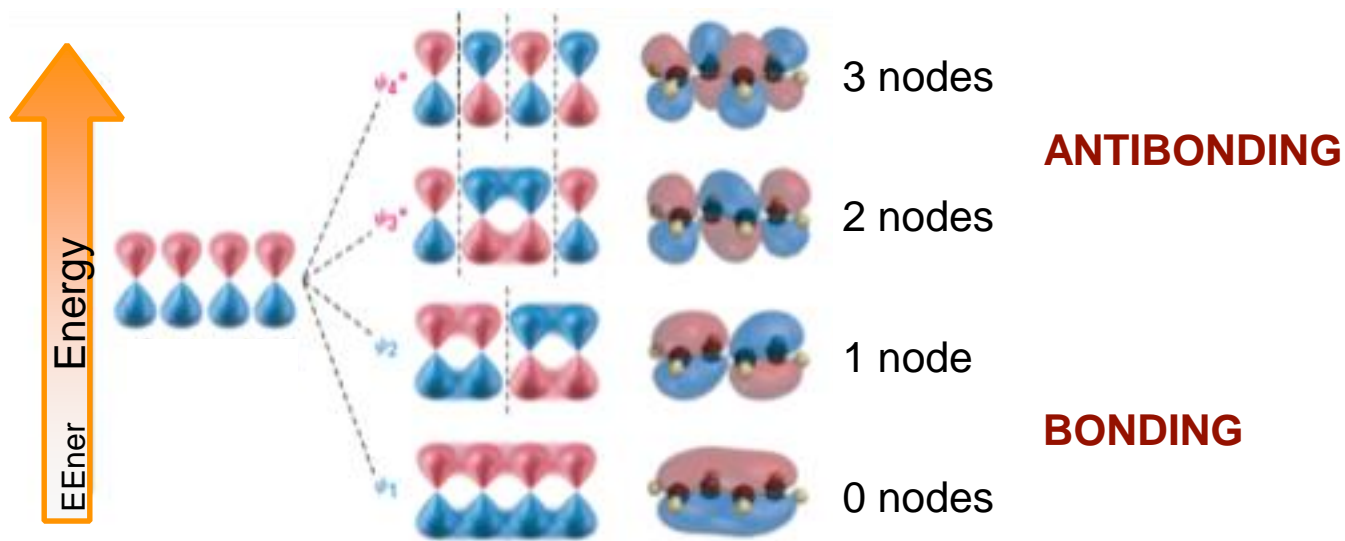


Conjugated Dienes and Ultraviolet Light

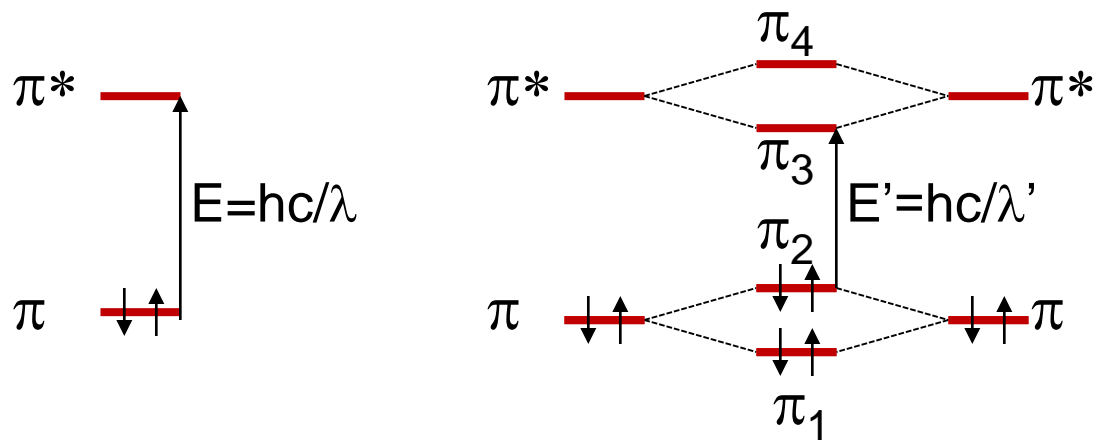
- The absorption of ultraviolet (UV) light by a molecule can promote an electron from a lower electronic state to a higher one.
- Ultraviolet light has a shorter wavelength (and thus higher frequency) than visible light.
- The most useful region of UV light for this purpose is 200-400 nm.



Delocalisation, Resonance, and Dienes



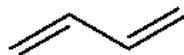
Conjugated Dienes and Ultraviolet Light



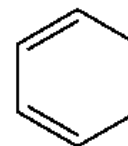
$E' < E$ quindi $\lambda' > \lambda$



$\lambda_{\max} < 200 \text{ nm}$



$\lambda_{\max} = 217 \text{ nm}$

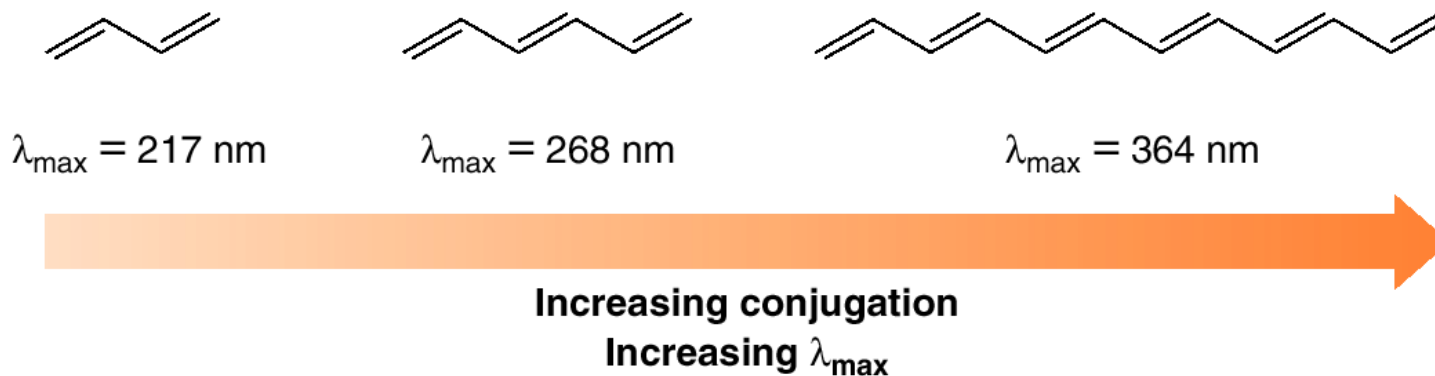


$\lambda_{\max} = 256 \text{ nm}$

- Conjugated dienes and polyenes absorb light in the UV region of the electromagnetic spectrum (200–400 nm).

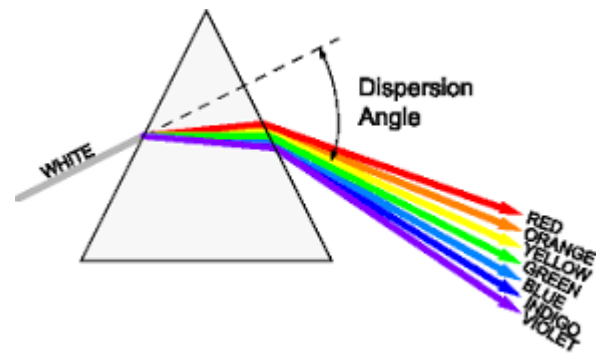
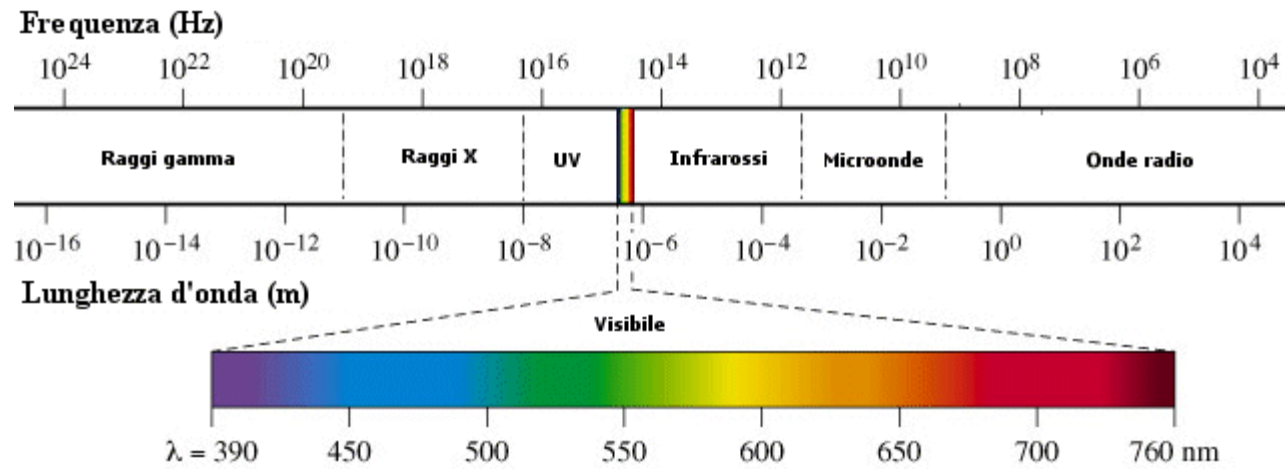
Conjugated Dienes and Ultraviolet Light

- As the number of conjugated π bonds increases, the energy difference between the ground and excited state decreases, shifting the absorption to longer wavelengths.



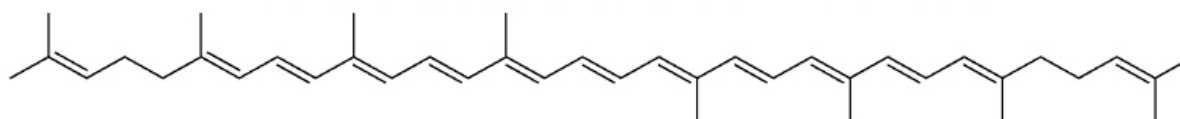
- With molecules having **eight or more** conjugated π bonds, the absorption shifts from the UV to the visible region, and the compound takes on the color of the light it does not absorb.

Electromagnetic Radiation



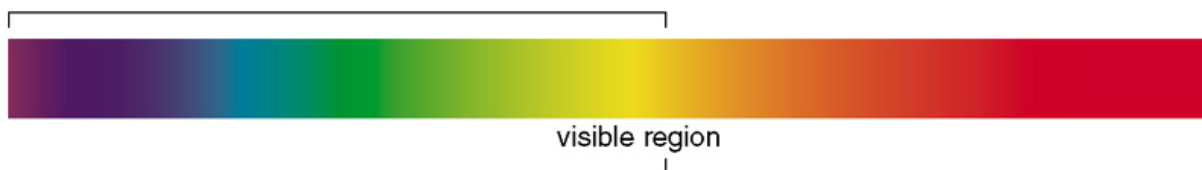
Conjugated Dienes and Ultraviolet Light

- **Lycopene** absorbs visible light at $\lambda_{\text{max}} = 470 \text{ nm}$, in the blue-green region of the visible spectrum. Because it does not absorb light in the red region, lycopene appears bright red.



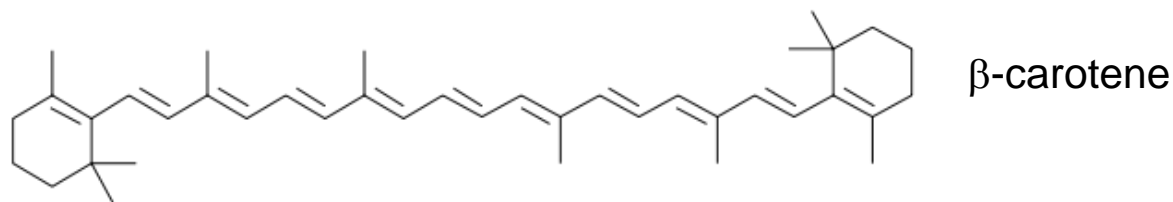
Lycopene—11 conjugated π bonds

Lycopene absorbs this part of the visible region.

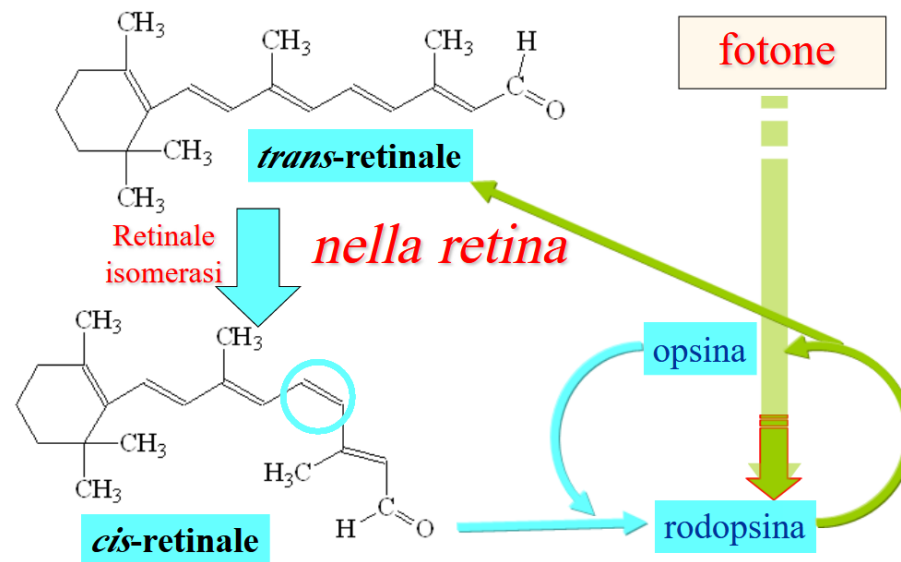
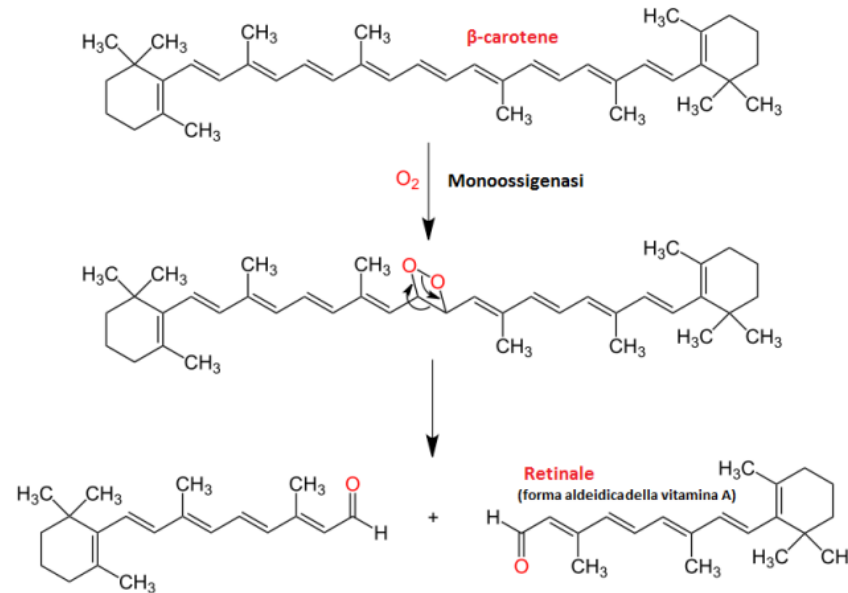


This part of the spectrum is *not* absorbed.

Lycopene appears red.

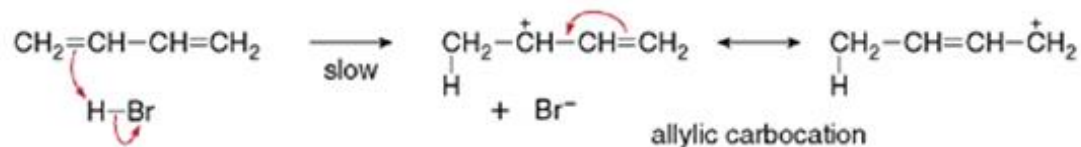


Vitamina A: retinale

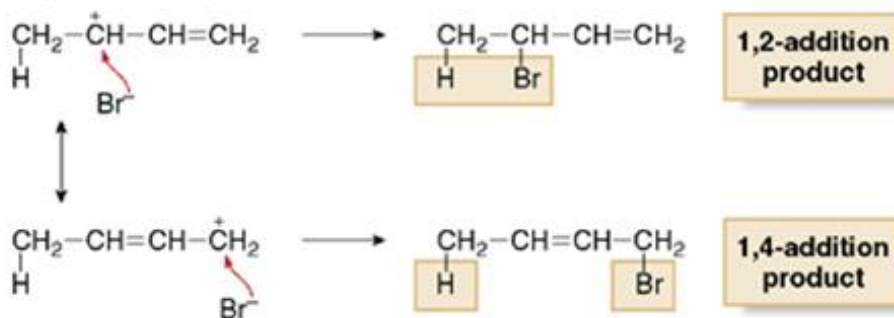


Electrophilic Addition: 1,2- Versus 1,4-Addition

Step [1] Addition of the electrophile (H⁺) to the π bond

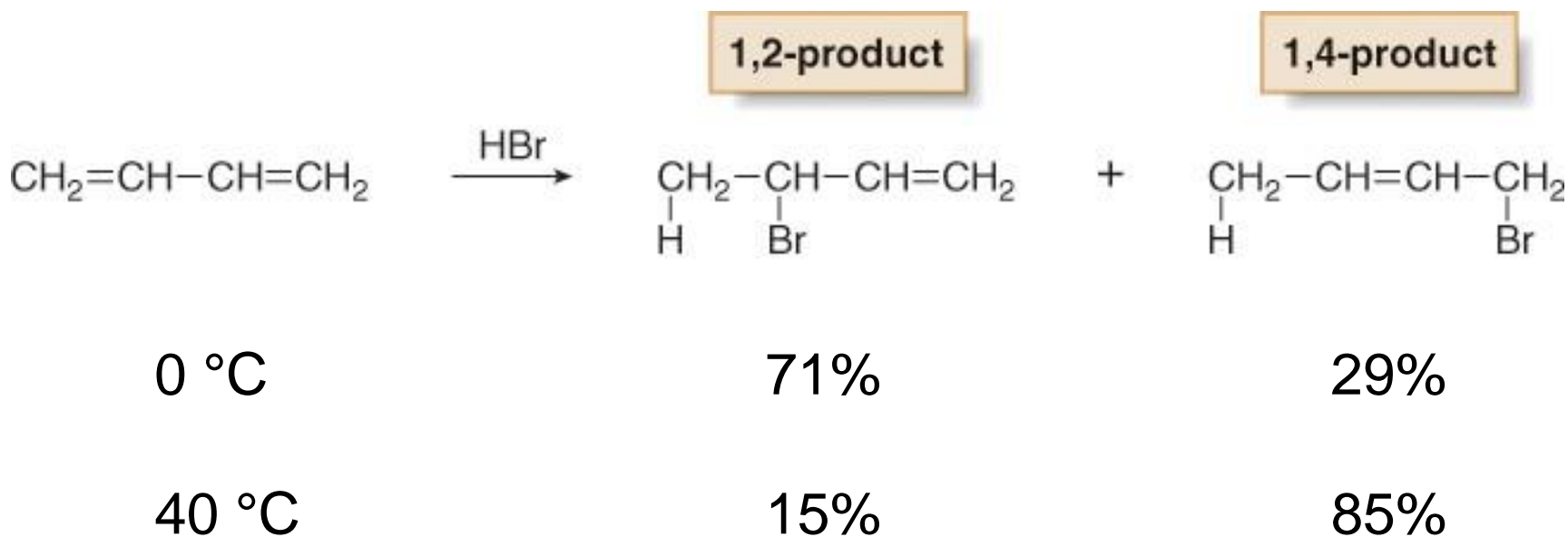


Step [2] Nucleophilic attack of Br⁻



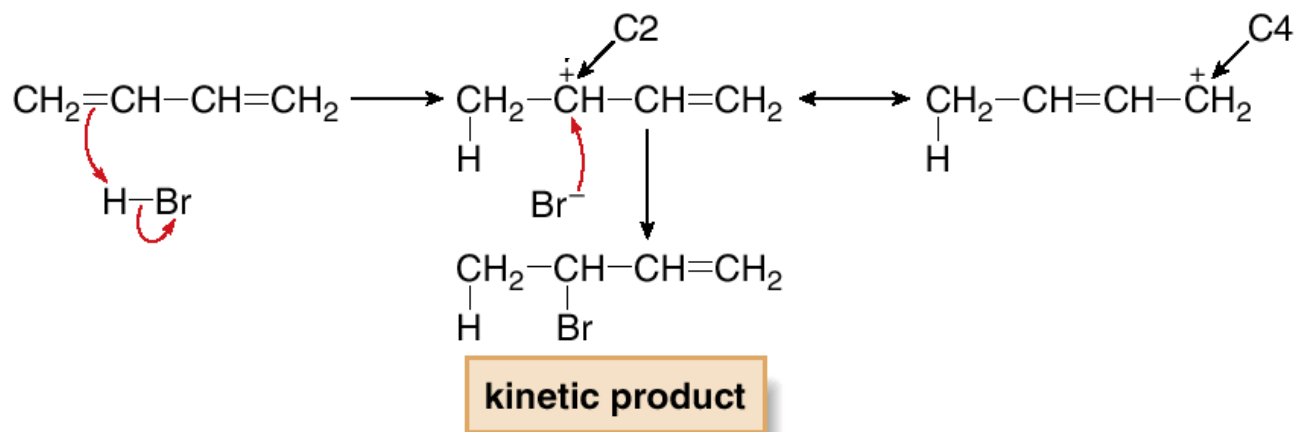
Kinetic Versus Thermodynamic Products

- The amount of 1,2- and 1,4-addition products formed in electrophilic addition reactions of conjugated dienes depends greatly on the reaction conditions.

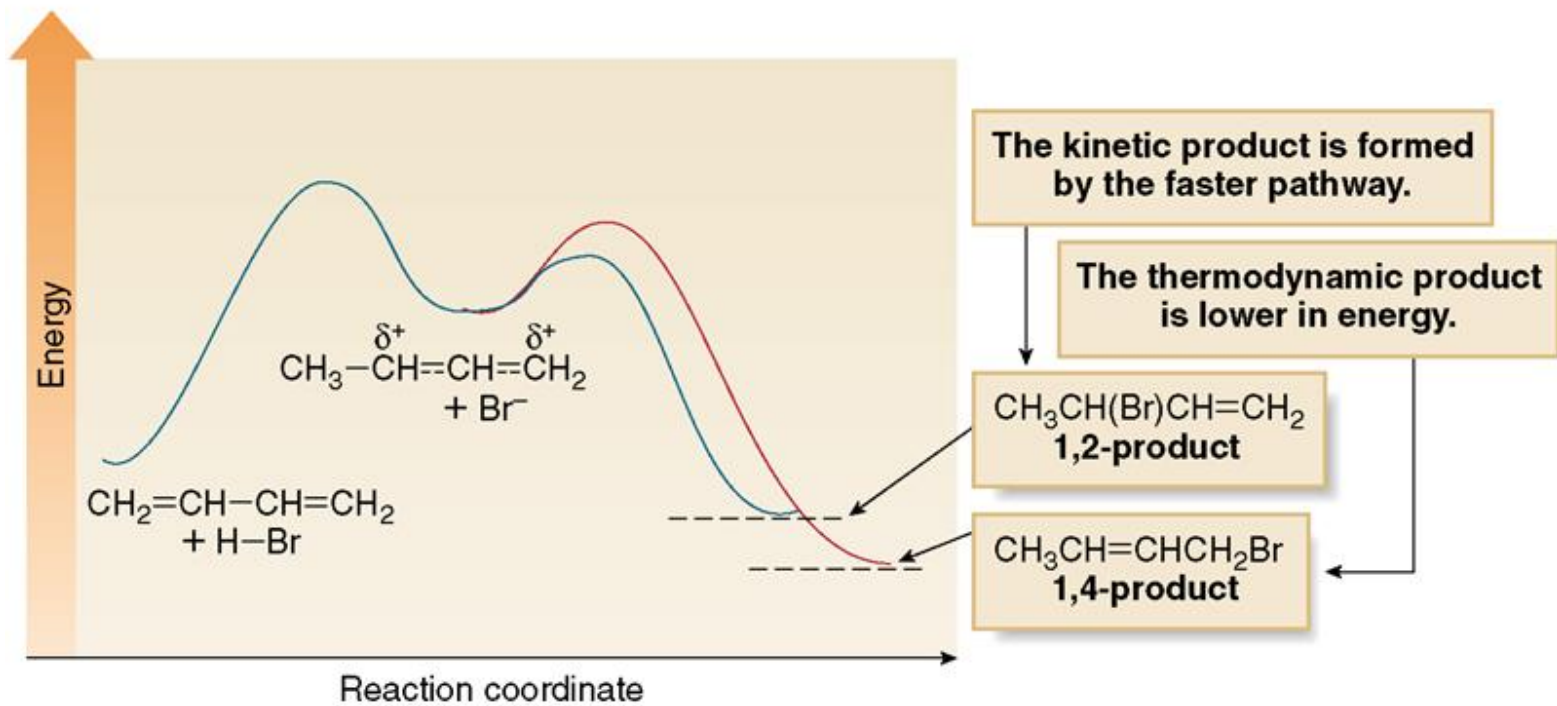


Kinetic Versus Thermodynamic Products

- The 1,2-product is the kinetic product because:
 - a) the charge on C2 is higher (because C4 is a primary carbon)
 - b) a proximity effect.

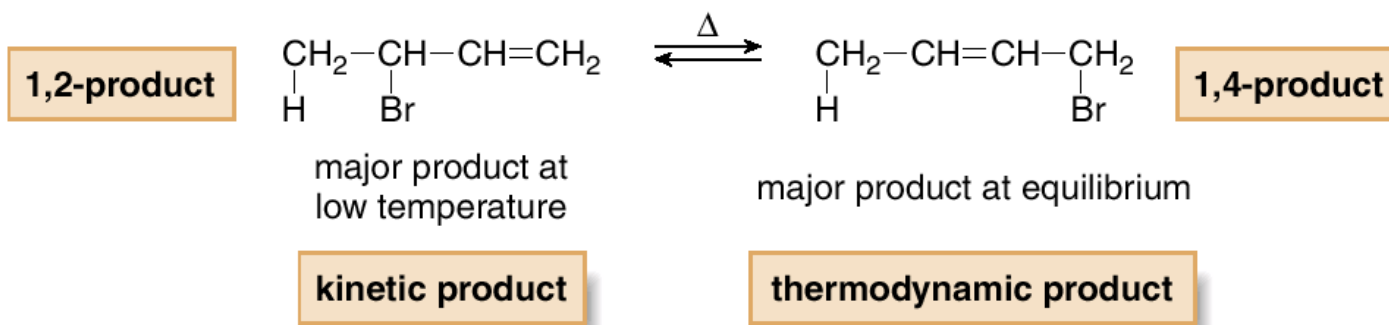


Kinetic Versus Thermodynamic Products



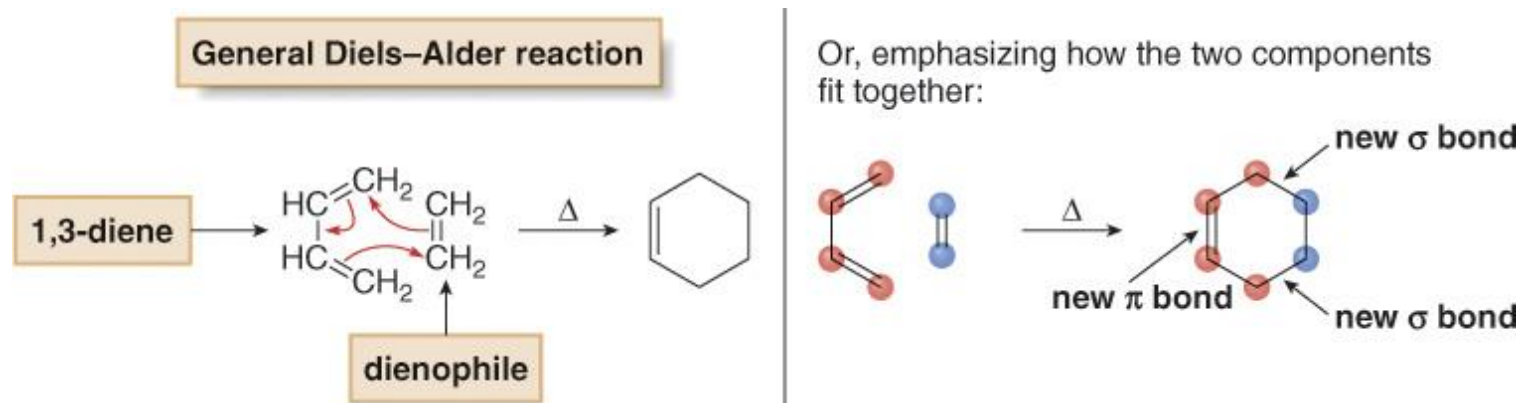
Kinetic Versus Thermodynamic Products

- When a mixture containing predominantly the 1,2-product is heated, the 1,4-addition product becomes the major product at equilibrium.

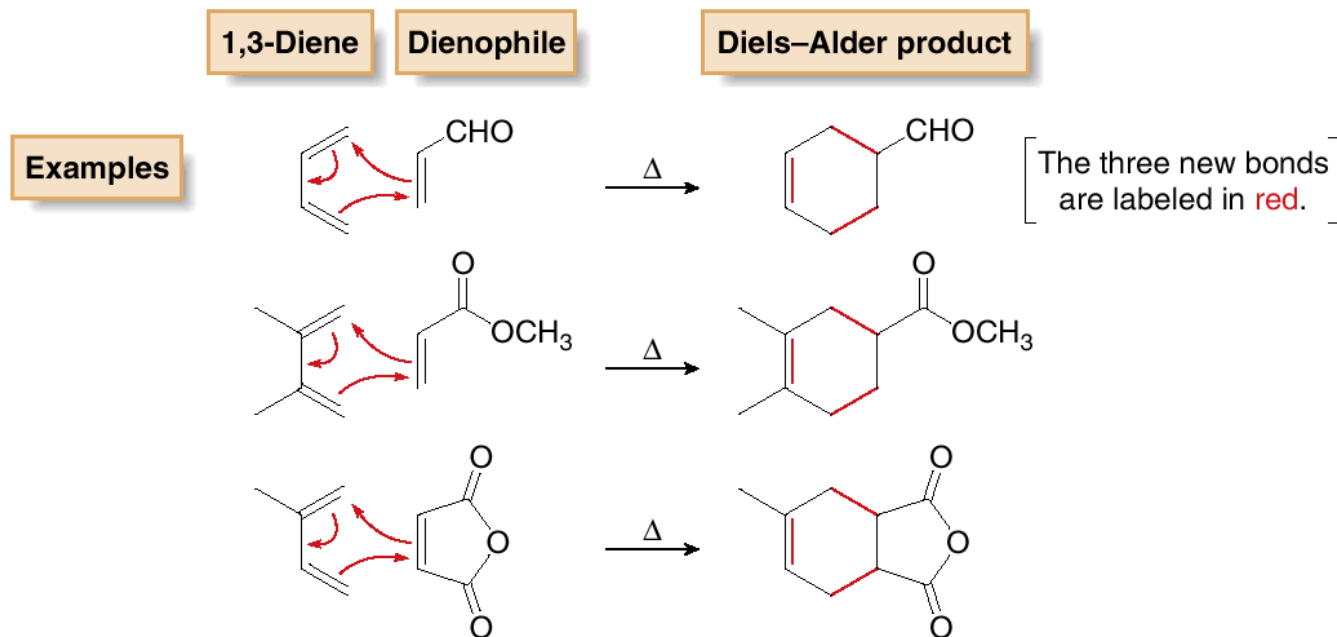


- The 1,2-product is formed faster because it predominates at low temperature. The product that is formed faster is called the *kinetic product*.
- The 1,4-product must be more stable because it predominates at equilibrium. The product that predominates at equilibrium is called the *thermodynamic product*.

The Diels-Alder Reaction



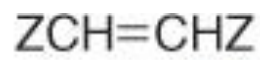
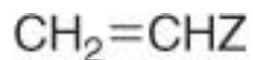
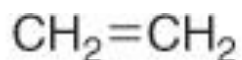
- Because each new σ bond is ~ 20 kcal/mol stronger than a π bond that is broken, a typical Diels-Alder reaction releases ~ 40 kcal/mol of energy.



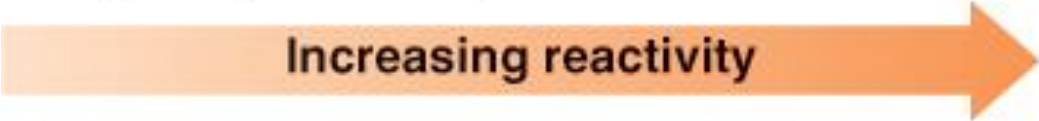
Rules for The Diels-Alder Reaction

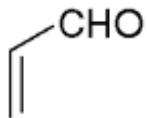
1. Electron-withdrawing substituents in the dienophile increase the reaction rate.

- The diene acts as a nucleophile and the dienophile acts as an electrophile.
- Electron-withdrawing groups make the dienophile more electrophilic

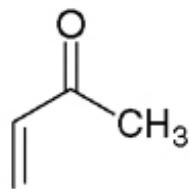


Z : electron-withdrawing group

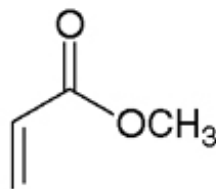
Increasing reactivity 



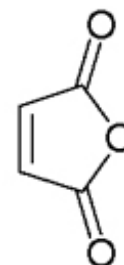
acrolein



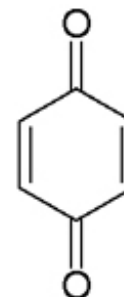
methyl vinyl ketone



methyl acrylate



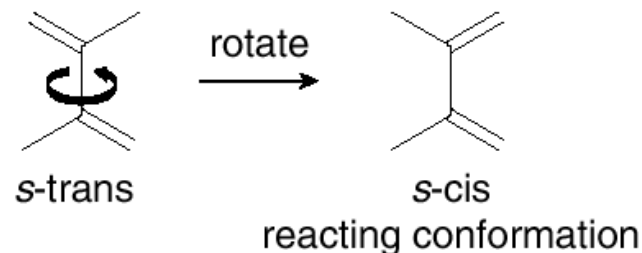
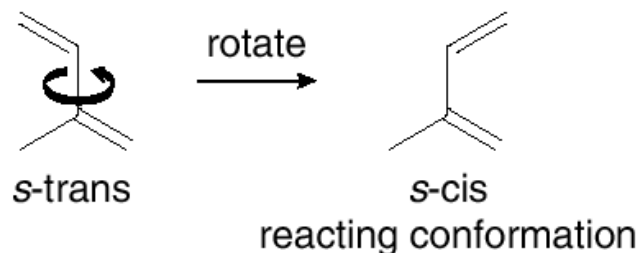
maleic anhydride



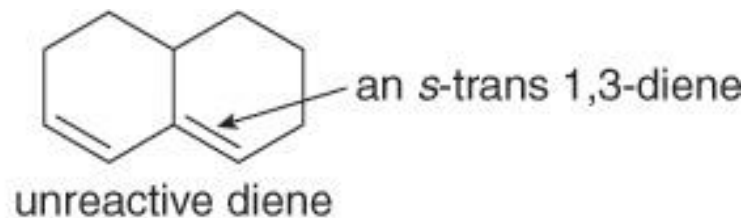
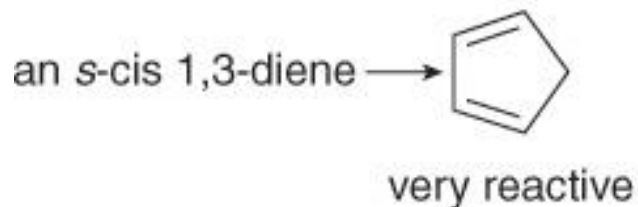
benzoquinone

Rules for The Diels-Alder Reaction

2. The diene can react only when it adopts the *s-cis* conformation.

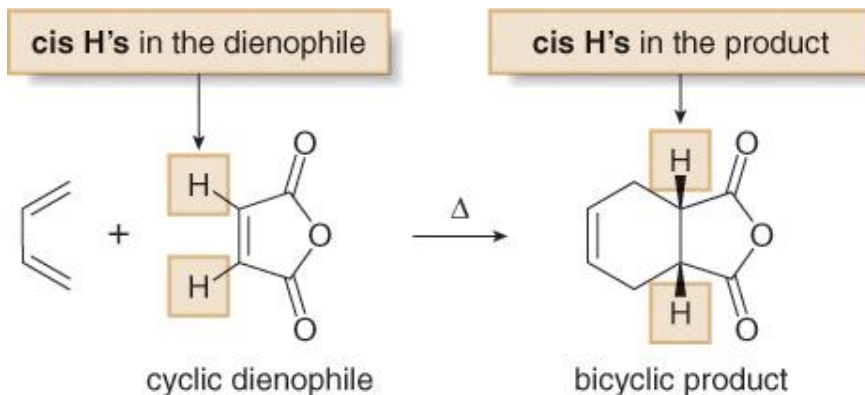
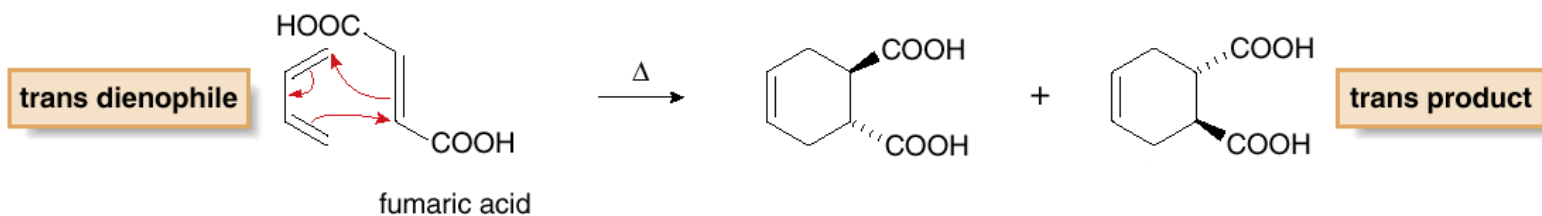
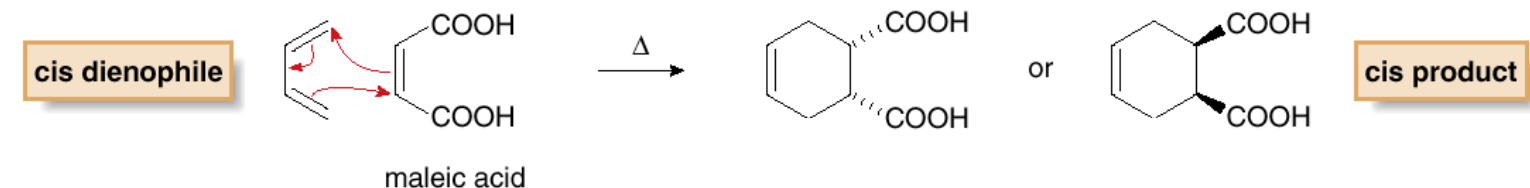


This rotation is prevented in cyclic alkenes.



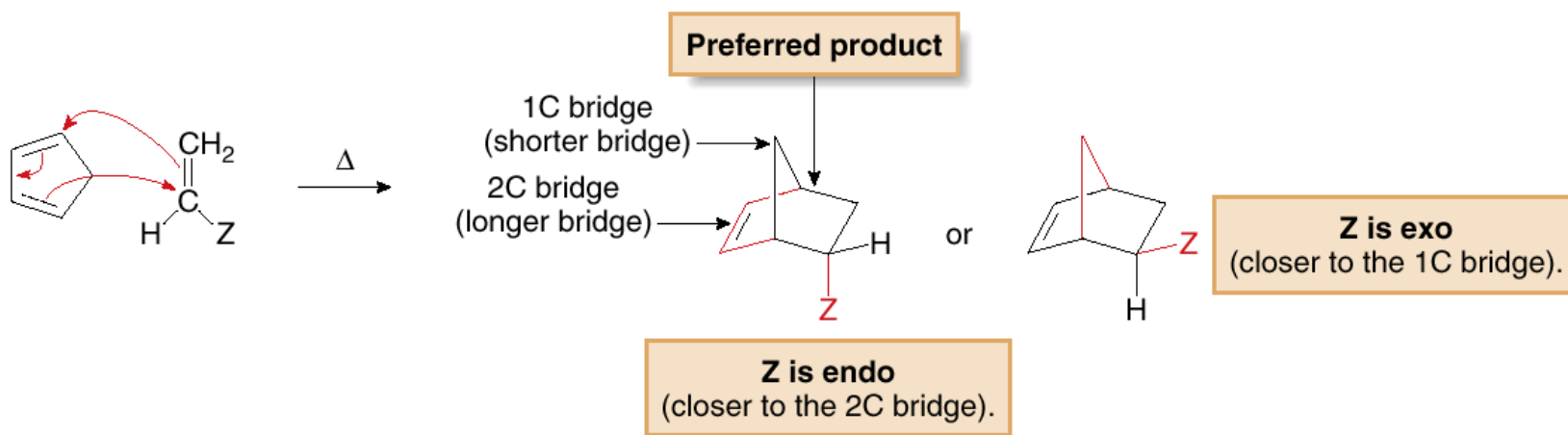
Rules for The Diels-Alder Reaction

3. The stereochemistry of the dienophile is retained.



Rules for The Diels-Alder Reaction

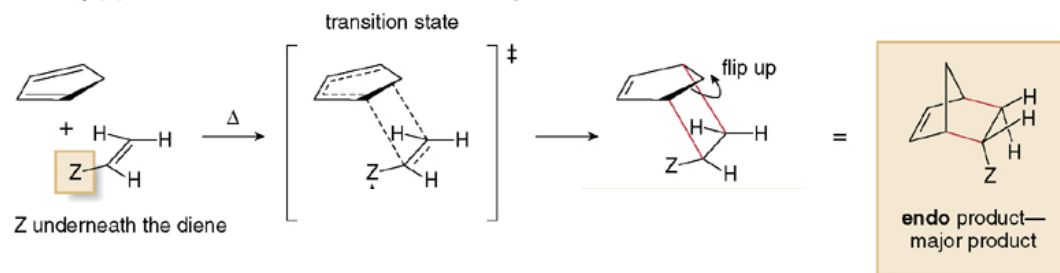
4. When endo and exo products are possible, the endo product is preferred.



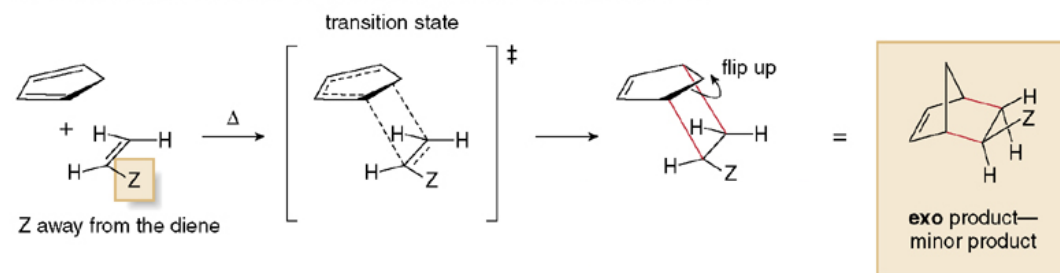
- A substituent on one bridge is *endo* if it is closer to the *longer* bridge that joins the two carbons common to both rings.
- A substituent is *exo* if it is closer to the *shorter* bridge that joins the carbons together.

Rules for The Diels-Alder Reaction

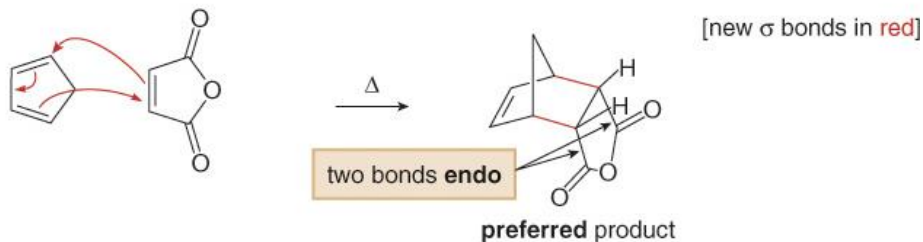
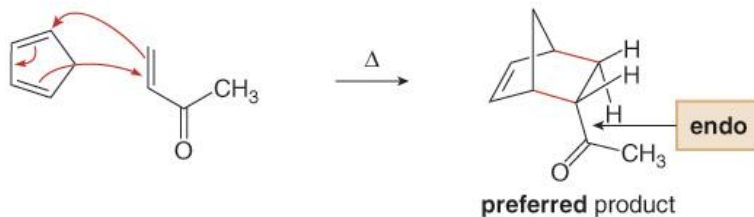
Pathway [1] With Z oriented under the diene, the endo product is formed.



Pathway [2] With Z oriented away from the diene, the exo product is formed.



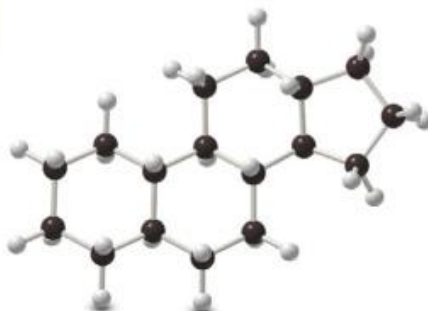
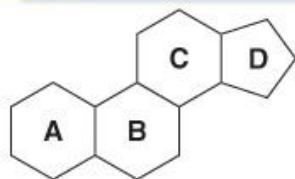
Examples of endo addition



The Diels-Alder Reaction in Organic Synthesis

- Steroids are tetracyclic lipids.

The steroid skeleton

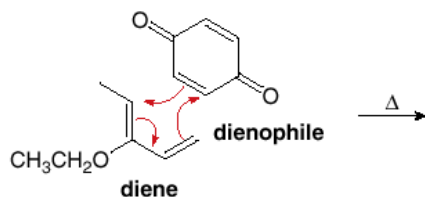
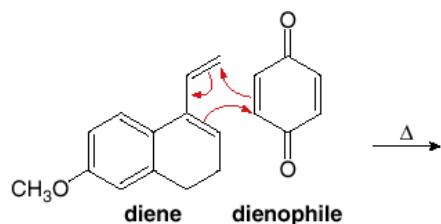


three-dimensional view
from above

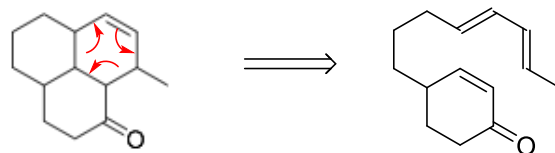
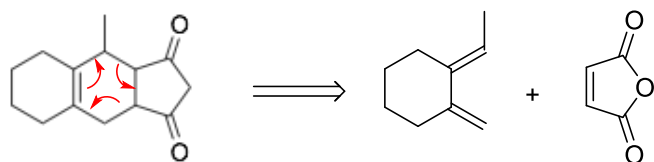
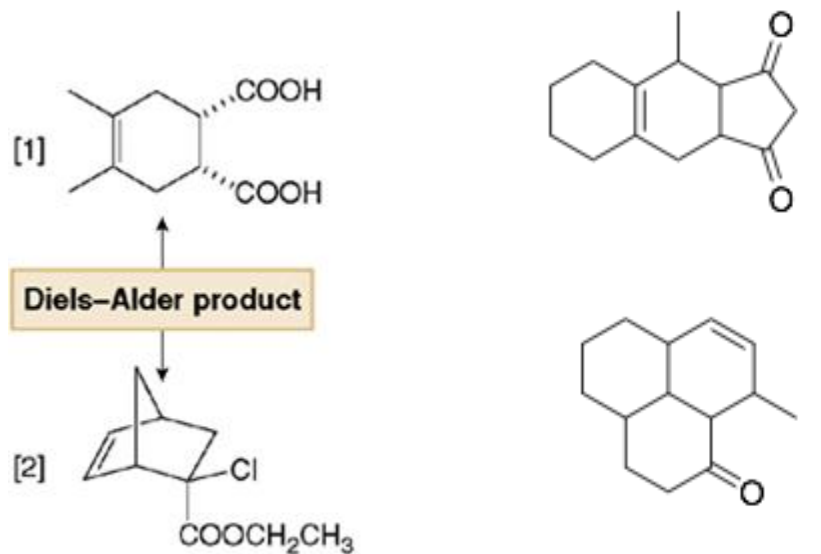


carbon skeleton
viewed from the side

[Note the chair conformations
of the three cyclohexane rings.]



The Diels-Alder Reaction in Organic Synthesis



The Diels-Alder Reaction in Organic Synthesis

