

# Conjugated Dienes

Chapter 14  
Organic Chemistry, *8<sup>th</sup> Edition*  
John E. McMurry

# Dienes

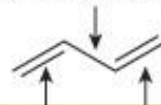
- Propadiene (allene) is a **cumulated diene**
- 1,3-Butadiene is a **conjugated diene**.
- 1,4-Pentadiene is an **isolated diene**.

**Allene –  
A cumulated diene**



**1,3-Butadiene—  
A conjugated diene**

one  $\sigma$  bond



delocalized  $\pi$  electrons

**1,4-Pentadiene—  
An isolated diene**

two  $\sigma$  bonds

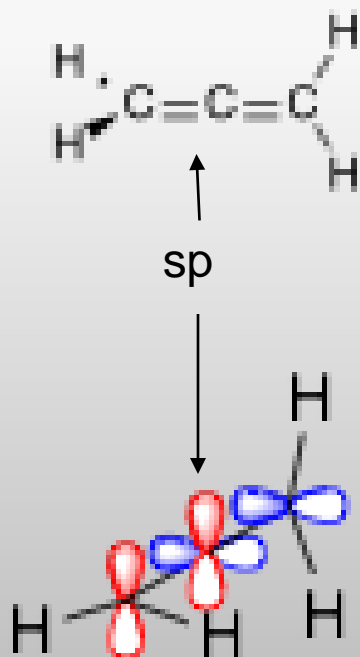


localized  $\pi$   
electrons

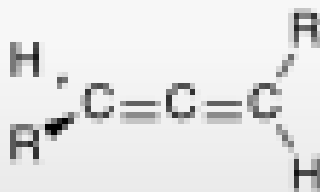
localized  $\pi$   
electrons

# Allenes

## Bonding



## Stereochemistry



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

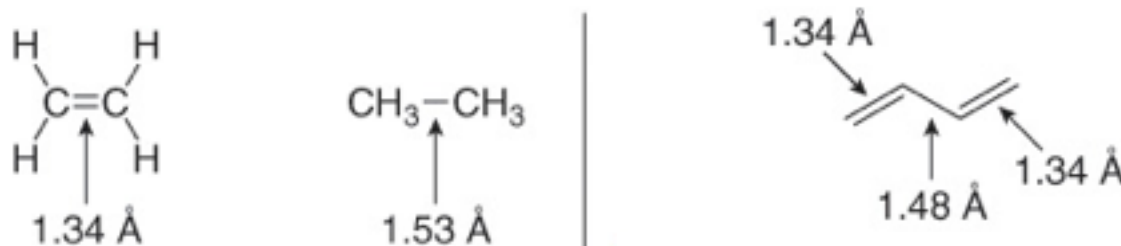
## Energetics

$\Delta H_f^\circ$   
(Kcal/mol)

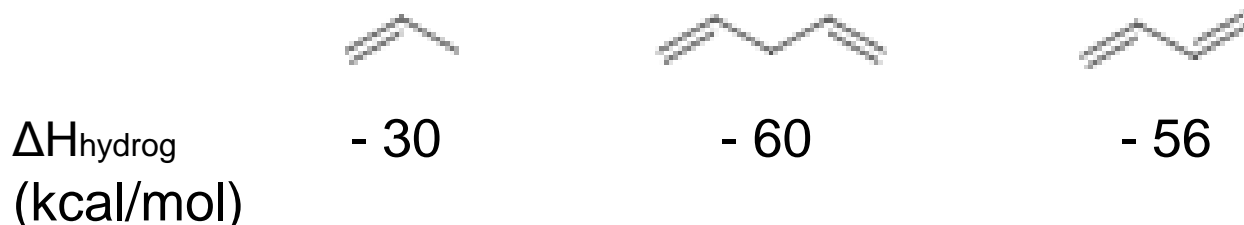


# Conjugated Dienes

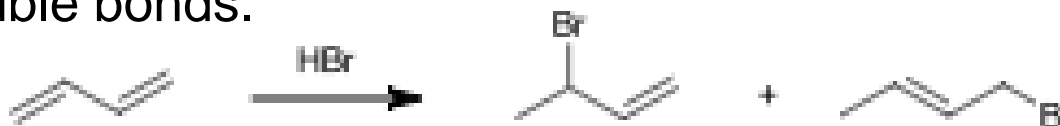
- The C—C single bond joining the two double bonds is unusually short.



- Conjugated dienes are more stable than similar isolated dienes.



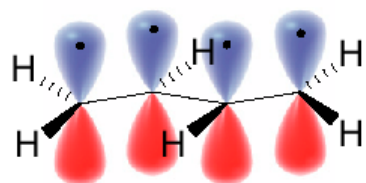
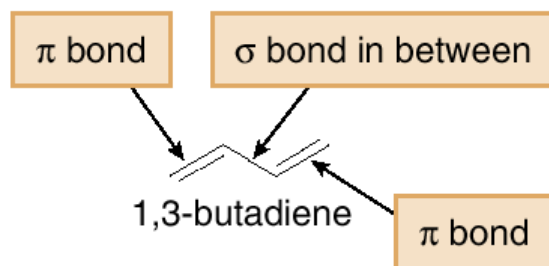
- Some reactions of conjugated dienes are different than reactions of isolated double bonds.



- Conjugated dienes absorb light at longer wavelengths than alkenes.

# Delocalisation, Resonance, and Dienes

- Delocalisation** occurs whenever  $p$  orbitals can overlap on three or more adjacent atoms.

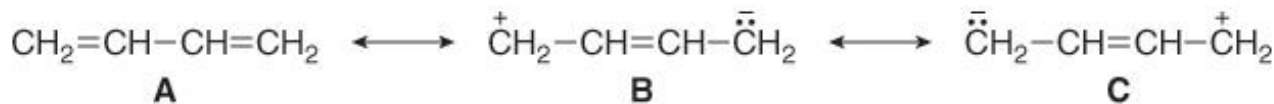
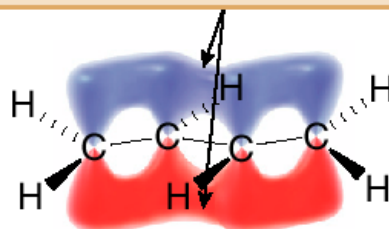


Each C is  $sp^2$  hybridized and has a  $p$  orbital containing one electron.

four adjacent  $p$  orbitals

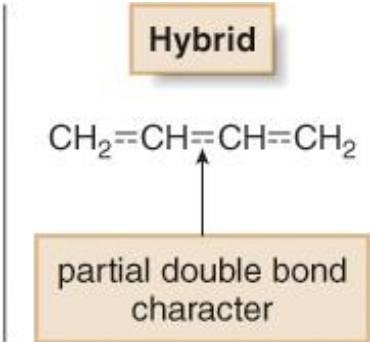
overlap of adjacent  $p$  orbitals

The electron density in the two  $\pi$  bonds is delocalized.

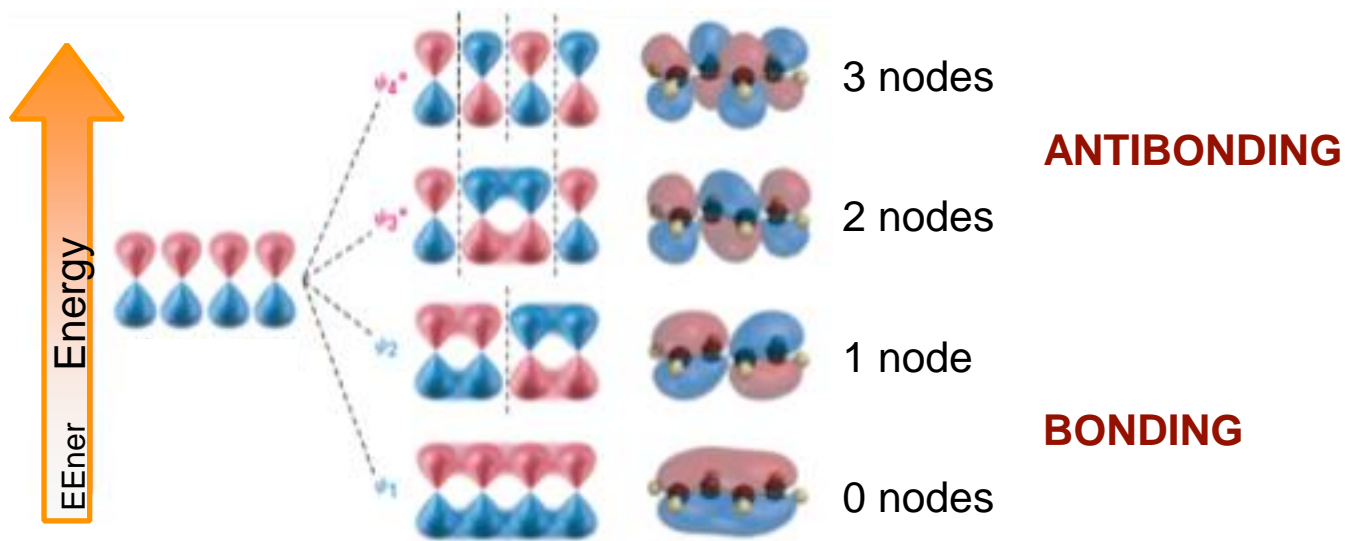


most stable resonance structure  
major contributor

less stable resonance structures  
minor contributors

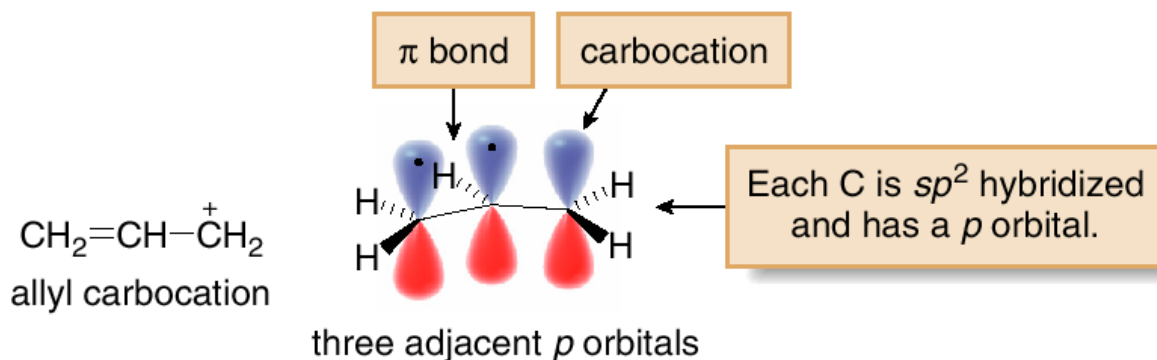


# Delocalisation, Resonance, and Dienes



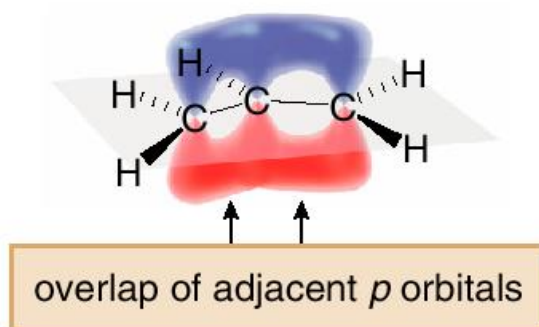
# Delocalisation, Resonance, and Dienes

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



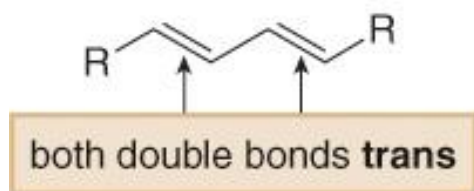
- Three  $p$  orbitals on three adjacent atoms, even if one of the  $p$  orbitals is empty, make the allyl carbocation conjugated.

- Conjugation stabilizes the allyl carbocation.

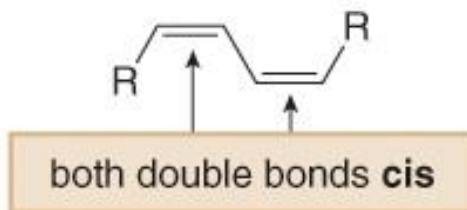


# Structure

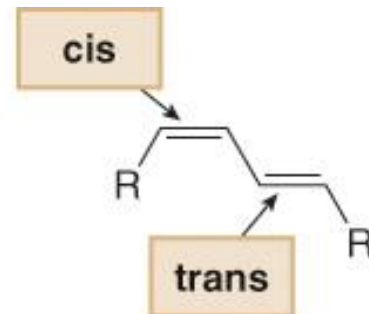
- Three stereoisomers are possible for 1,3-dienes with alkyl groups bonded to each end carbon of the diene.



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



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



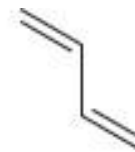
*cis, trans*-1,3-diene  
or  
*(Z,E)*-1,3-diene

- 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

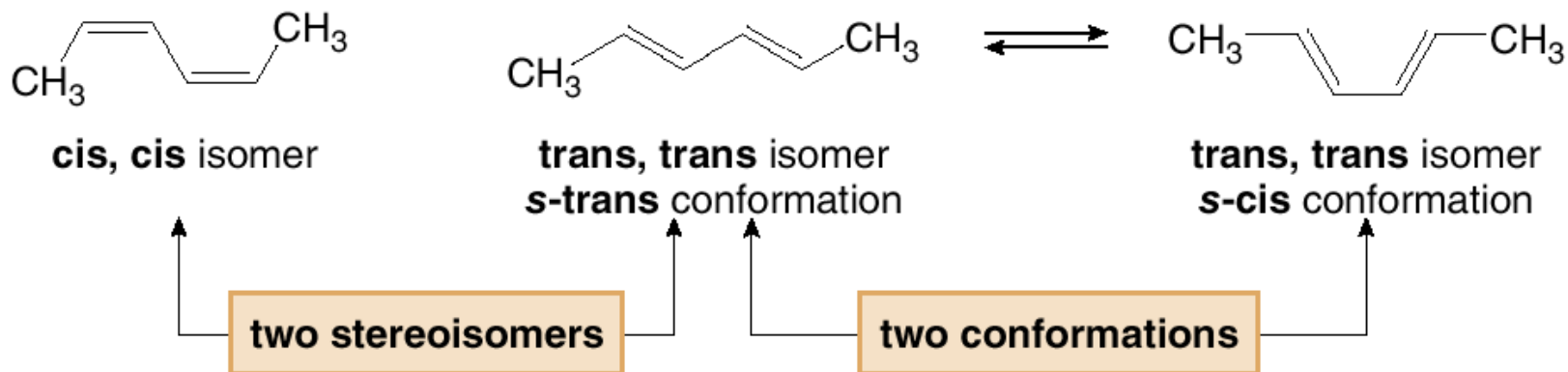


**s-trans** conformer



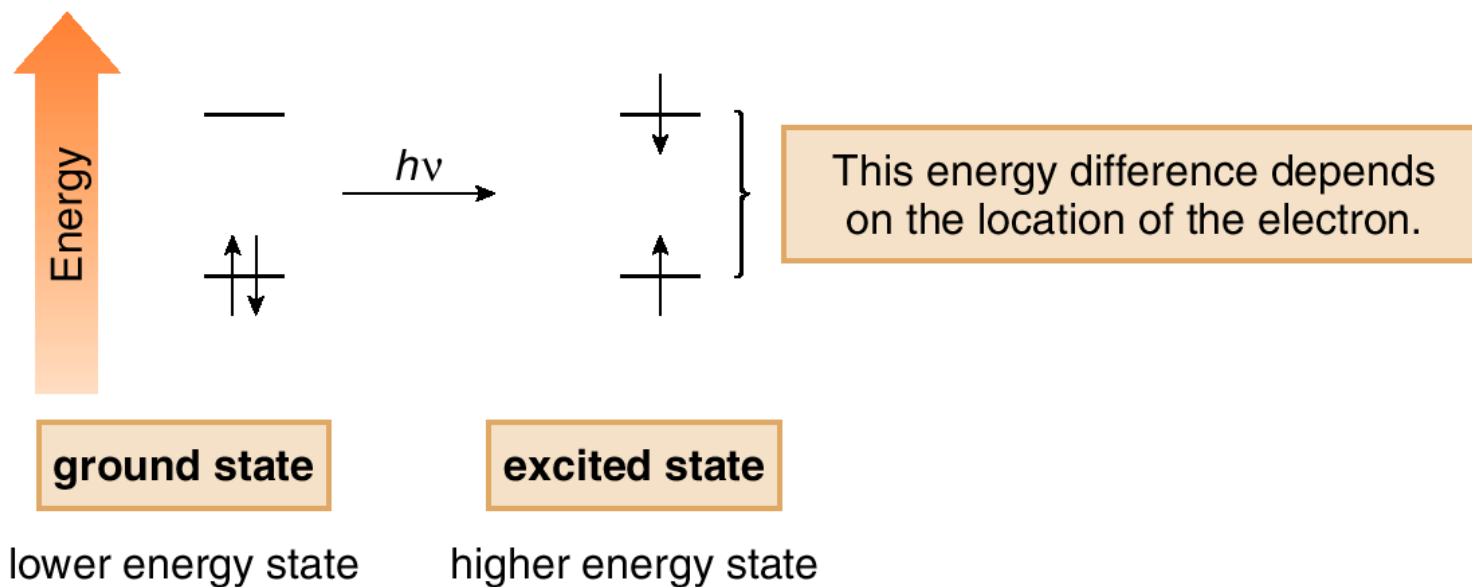
# Structure

- Stereoisomers are discrete molecules, whereas conformations interconvert.



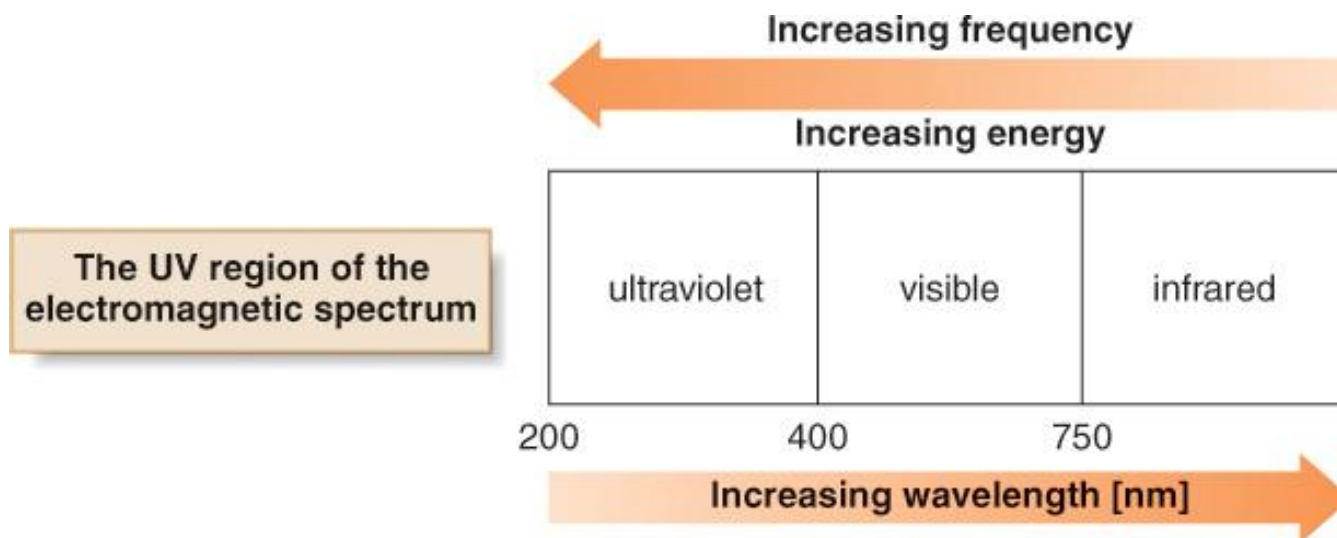
# Conjugated Dienes and Ultraviolet Light

- 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).

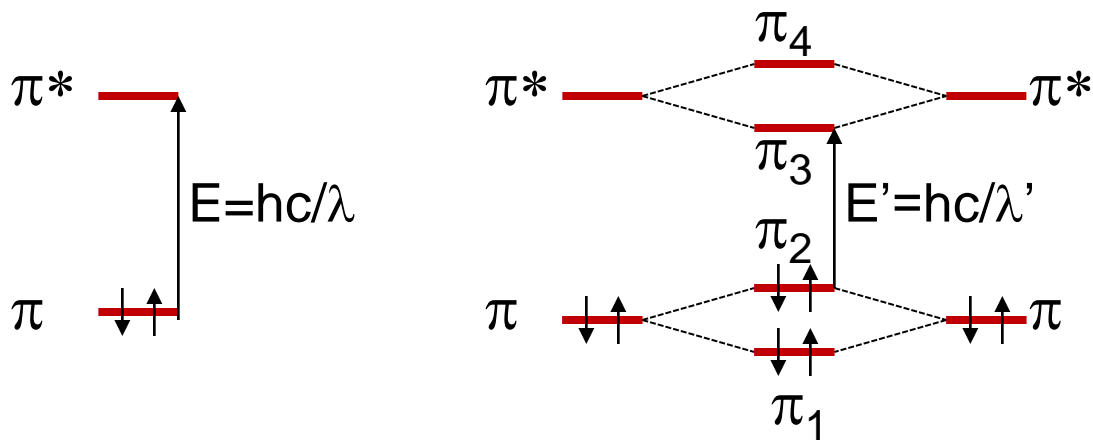


# Conjugated Dienes and Ultraviolet Light

- 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.



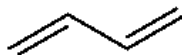
# Conjugated Dienes and Ultraviolet Light



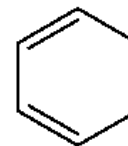
**$E' < E$  quindi  $\lambda' > \lambda$**



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



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

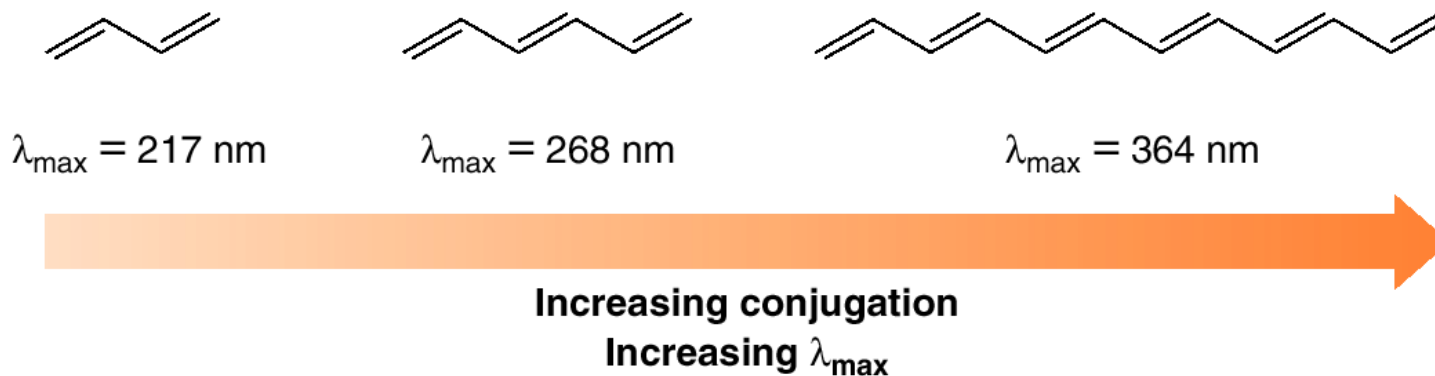


$\lambda_{\max} = 256 \text{ nm}$

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

# Conjugated Dienes and Ultraviolet Light

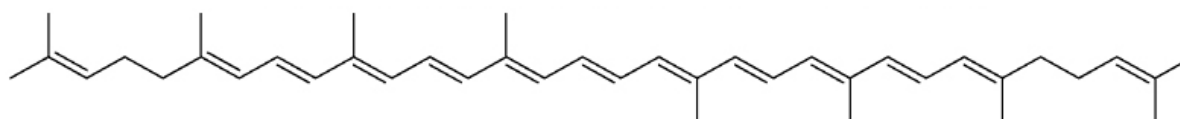
- As the number of conjugated  $\pi$  bonds increases, the energy difference between the ground and excited state decreases, shifting the absorption to longer wavelengths.



- With molecules having **eight or more** conjugated  $\pi$  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.

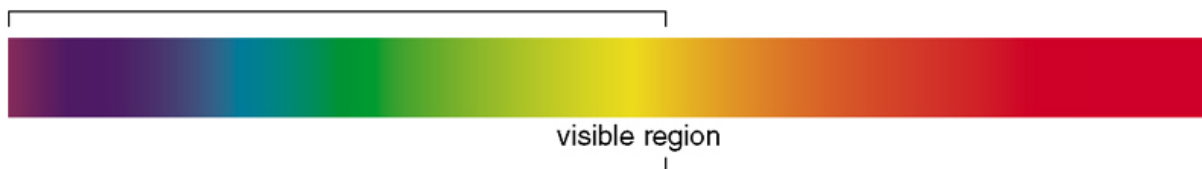
# Conjugated Dienes and Ultraviolet Light

- **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.



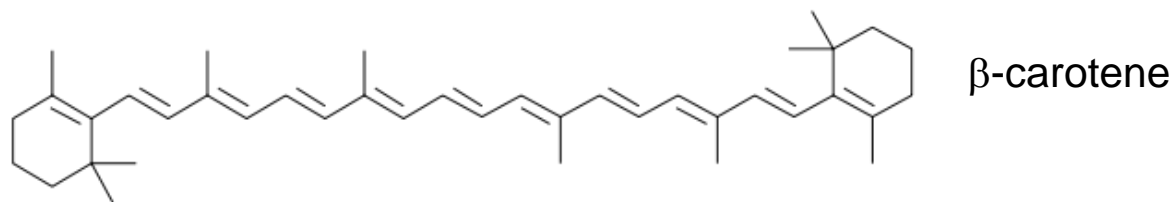
Lycopene—11 conjugated  $\pi$  bonds

Lycopene absorbs this part of the visible region.



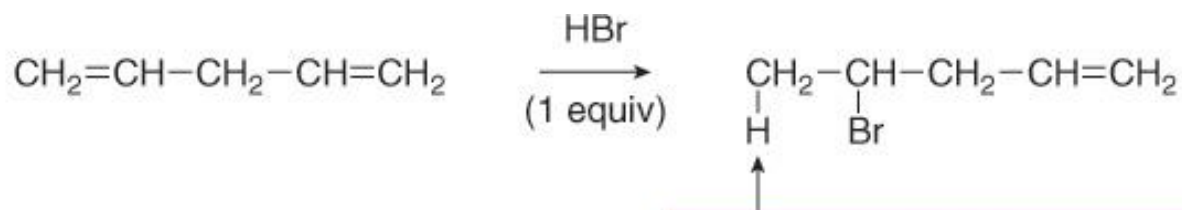
This part of the spectrum is *not* absorbed.

Lycopene appears red.



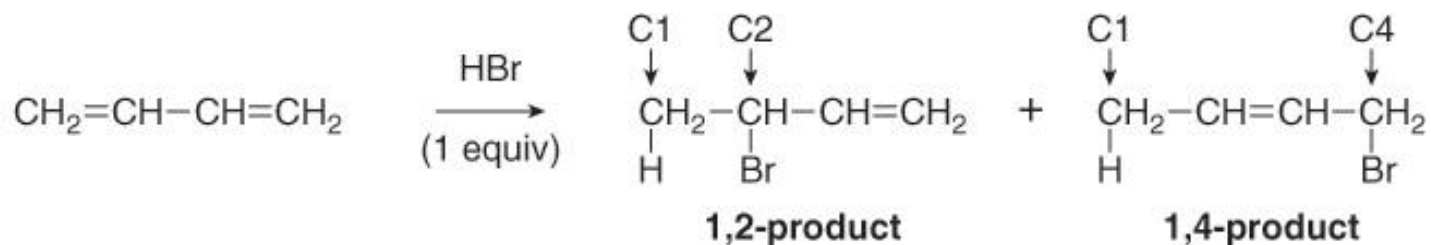
# Electrophilic Addition: 1,2- Versus 1,4-Addition

Isolated diene



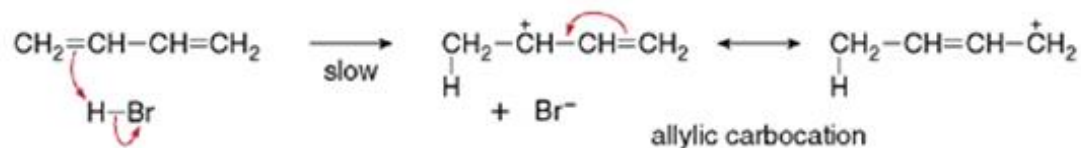
H bonds to the less substituted C.

Conjugated diene

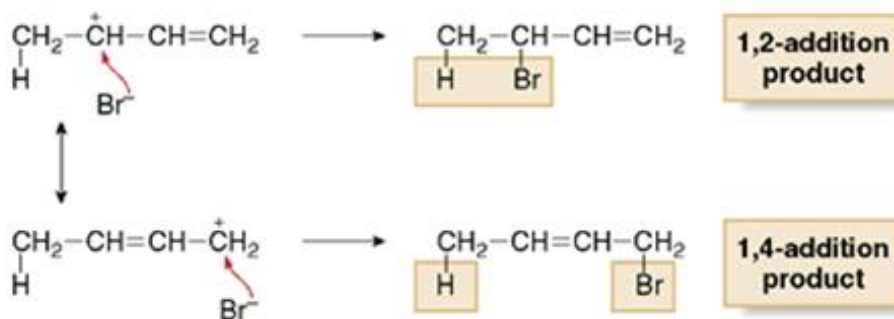


# Electrophilic Addition: 1,2- Versus 1,4-Addition

Step [1] Addition of the electrophile (H<sup>+</sup>) to the π bond



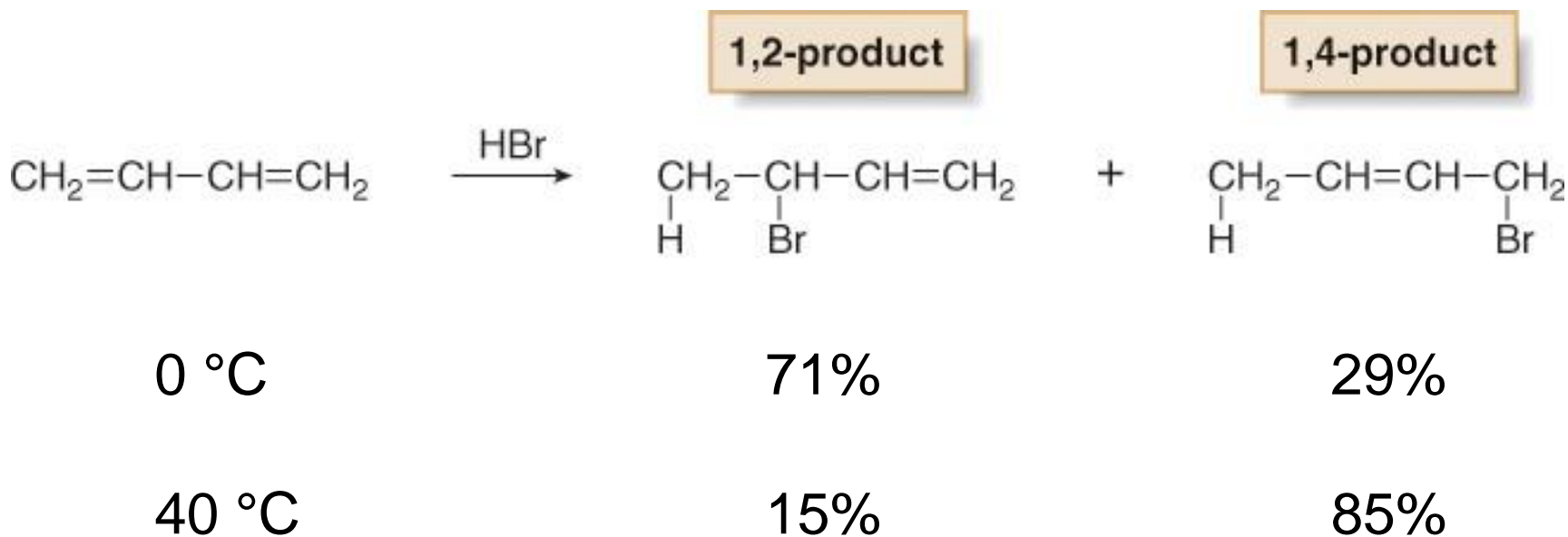
Step [2] Nucleophilic attack of Br<sup>-</sup>





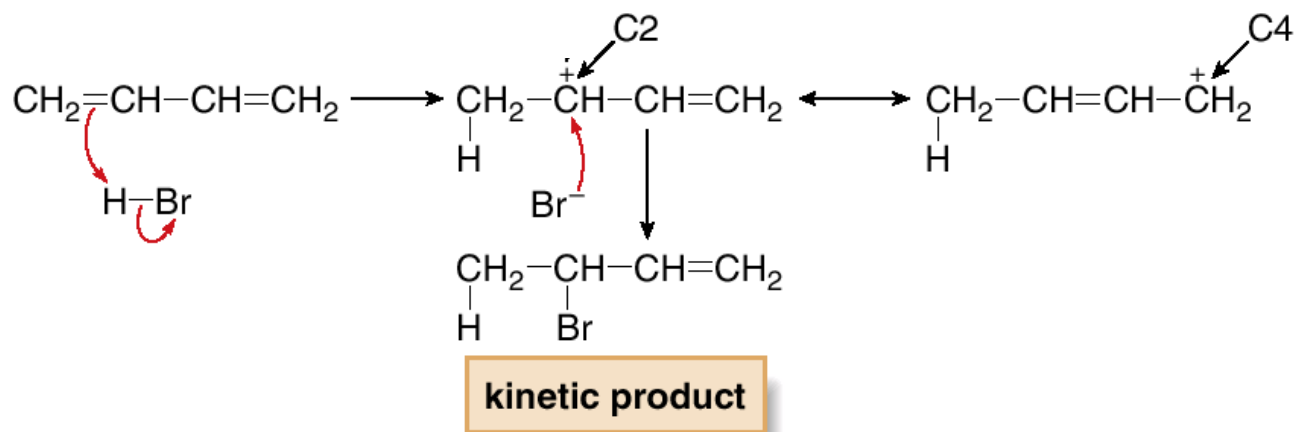
# Kinetic Versus Thermodynamic Products

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

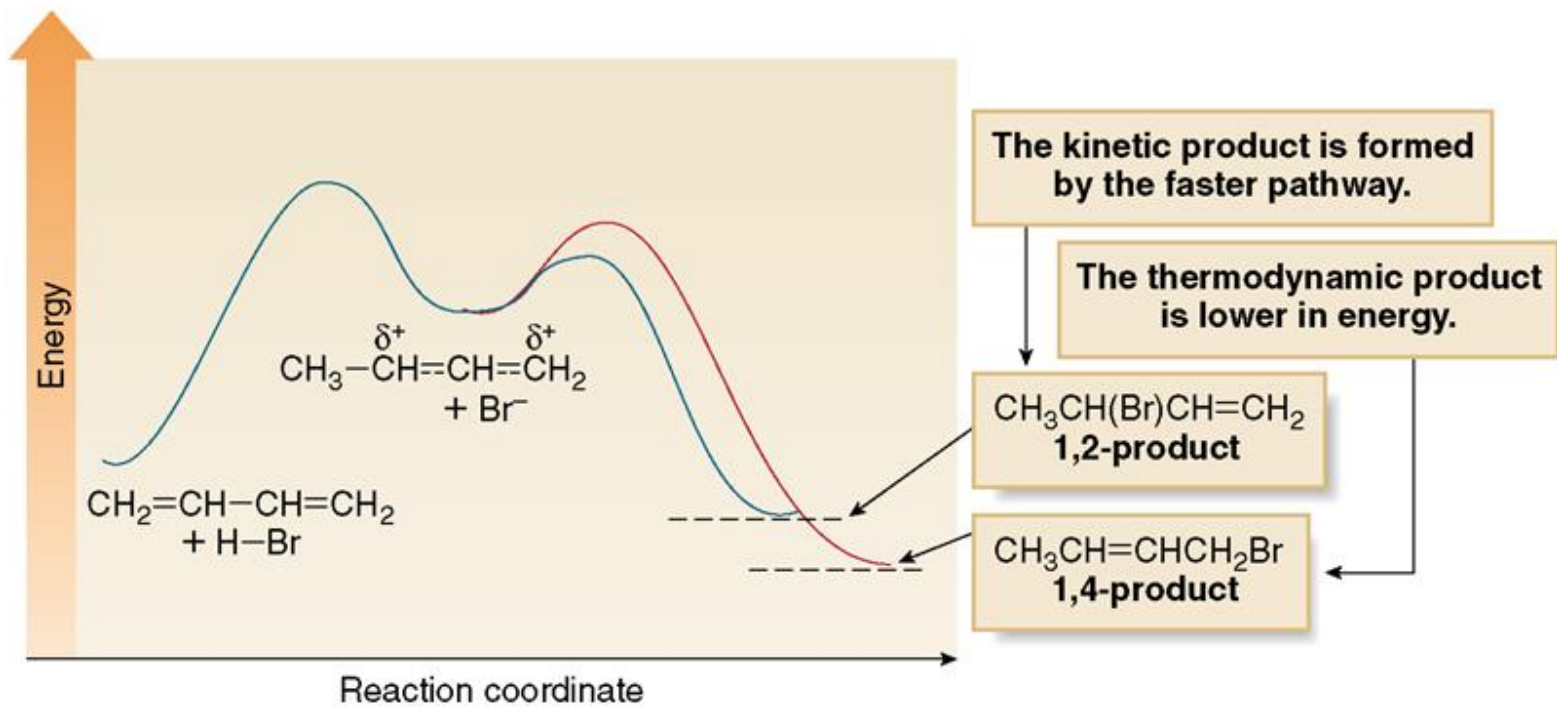


# Kinetic Versus Thermodynamic Products

- 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.

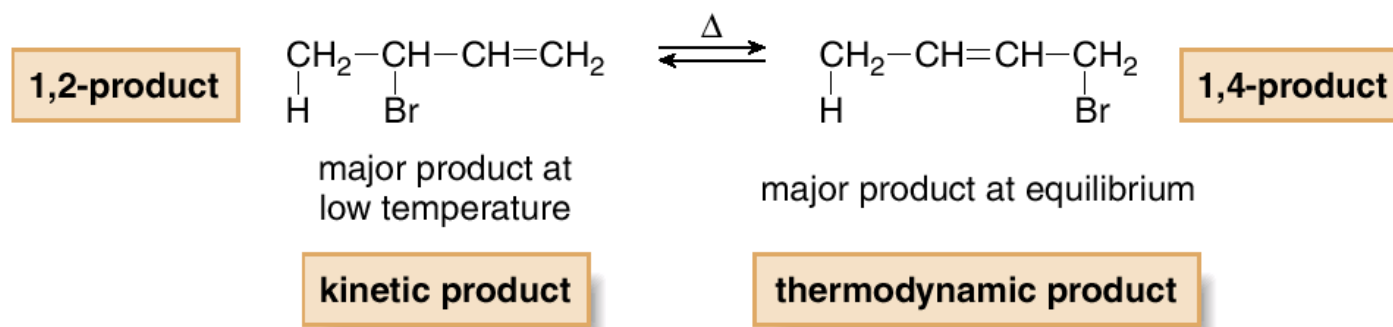


# Kinetic Versus Thermodynamic Products



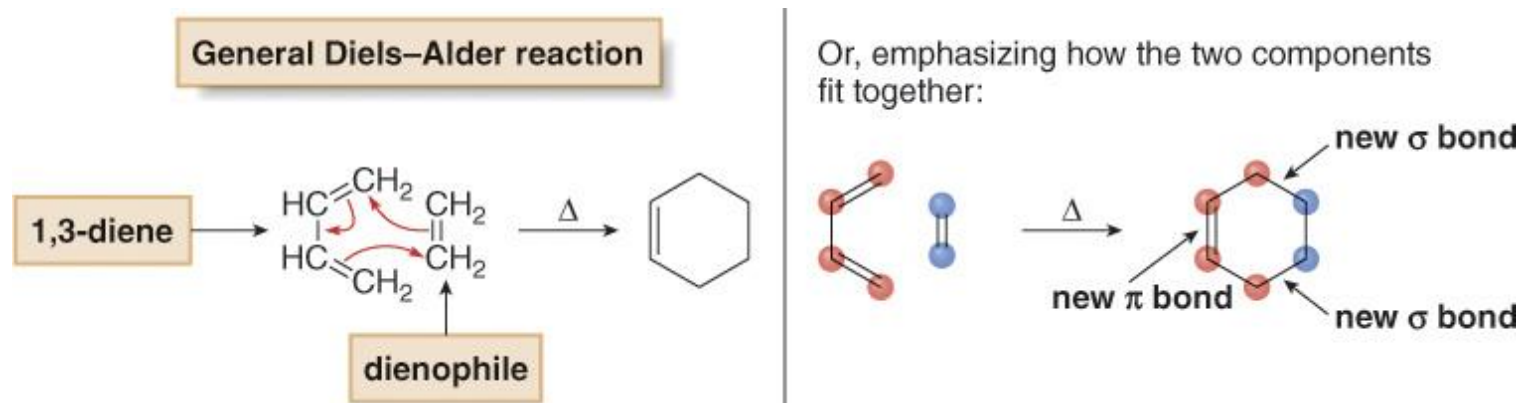
# Kinetic Versus Thermodynamic Products

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

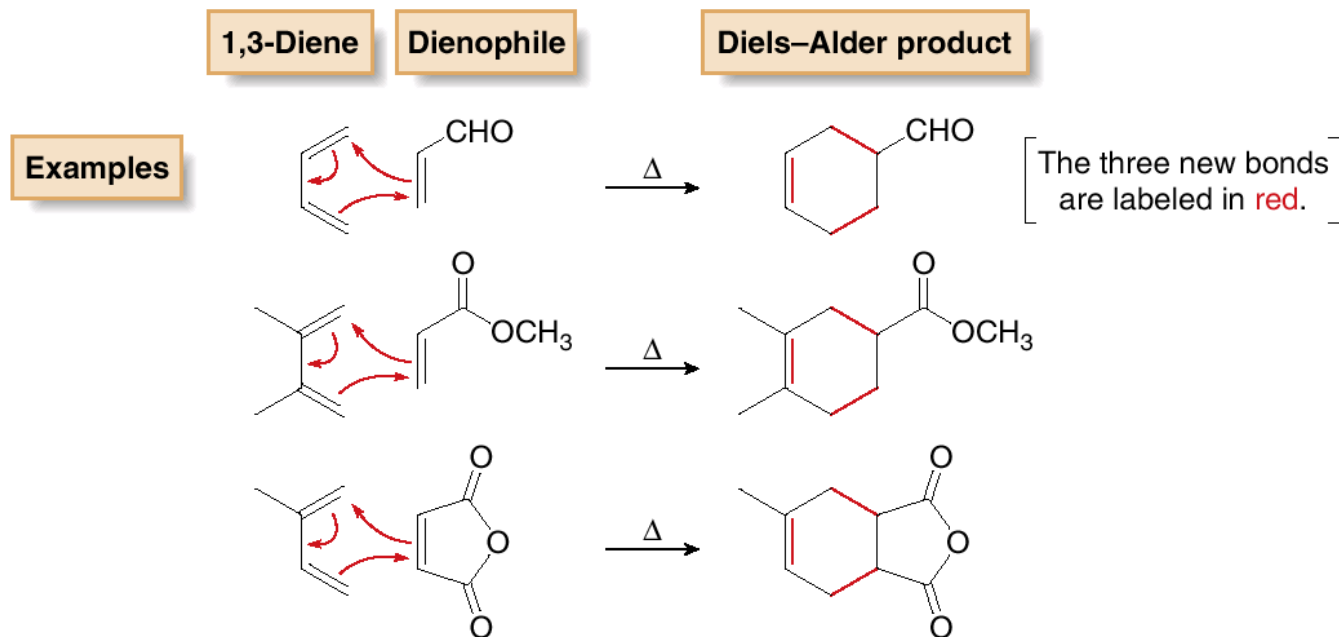


- The 1,2-product is formed faster because it predominates at low temperature. The product that is formed faster is called the *kinetic product*.
- The 1,4-product must be more stable because it predominates at equilibrium. The product that predominates at equilibrium is called the *thermodynamic product*.

# The Diels-Alder Reaction



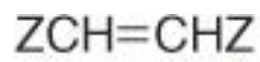
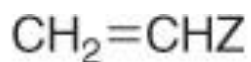
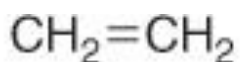
- Because each new  $\sigma$  bond is  $\sim 20$  kcal/mol stronger than a  $\pi$  bond that is broken, a typical Diels-Alder reaction releases  $\sim 40$  kcal/mol of energy.



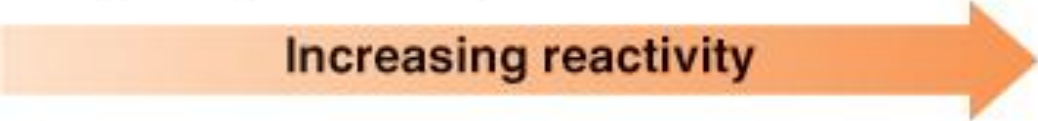
# Rules for The Diels-Alder Reaction

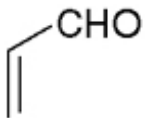
1. Electron-withdrawing substituents in the dienophile increase the reaction rate.

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

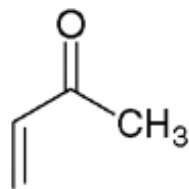


Z : electron-withdrawing group

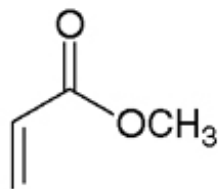
Increasing reactivity 



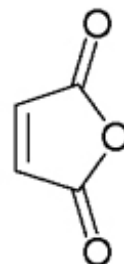
acrolein



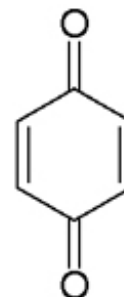
methyl vinyl ketone



methyl acrylate



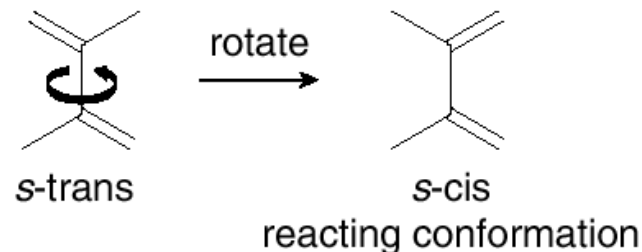
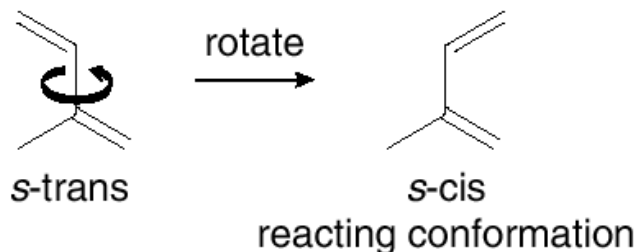
maleic anhydride



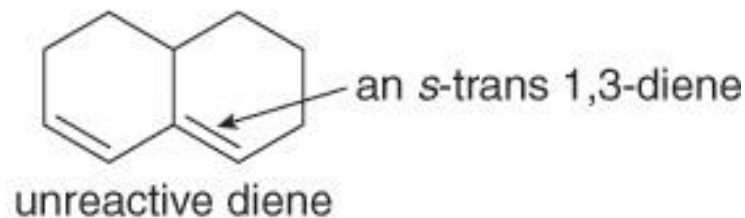
benzoquinone

# Rules for The Diels-Alder Reaction

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

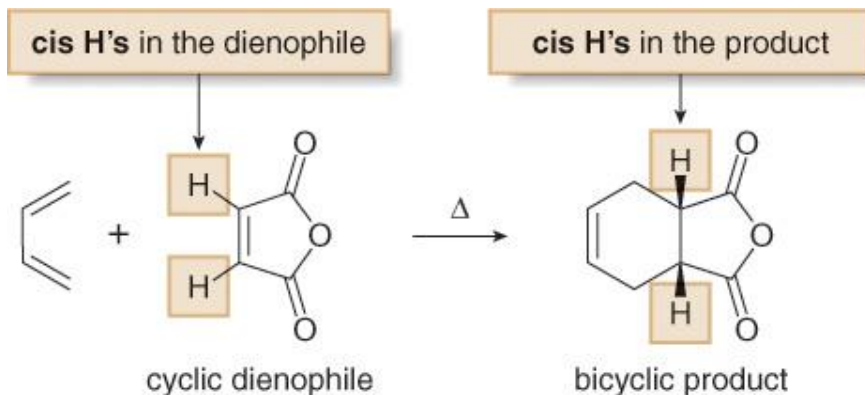
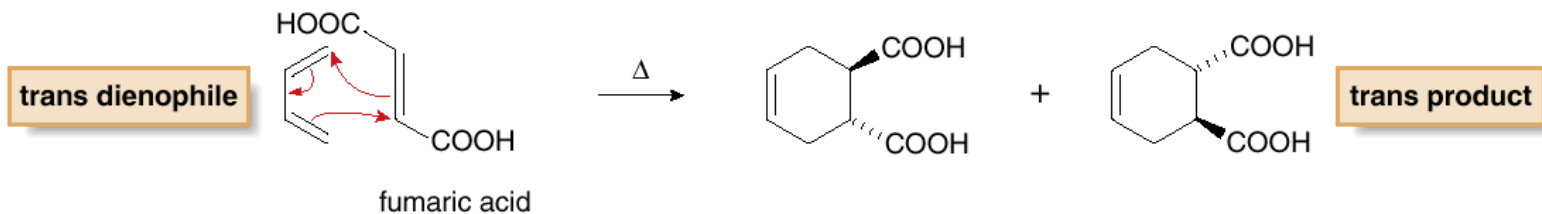
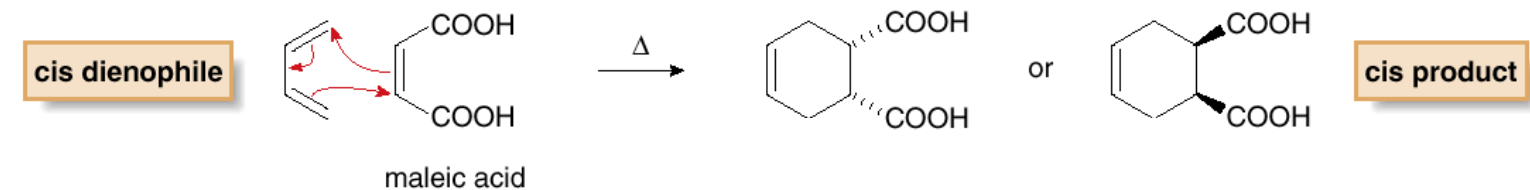


This rotation is prevented in cyclic alkenes.



# Rules for The Diels-Alder Reaction

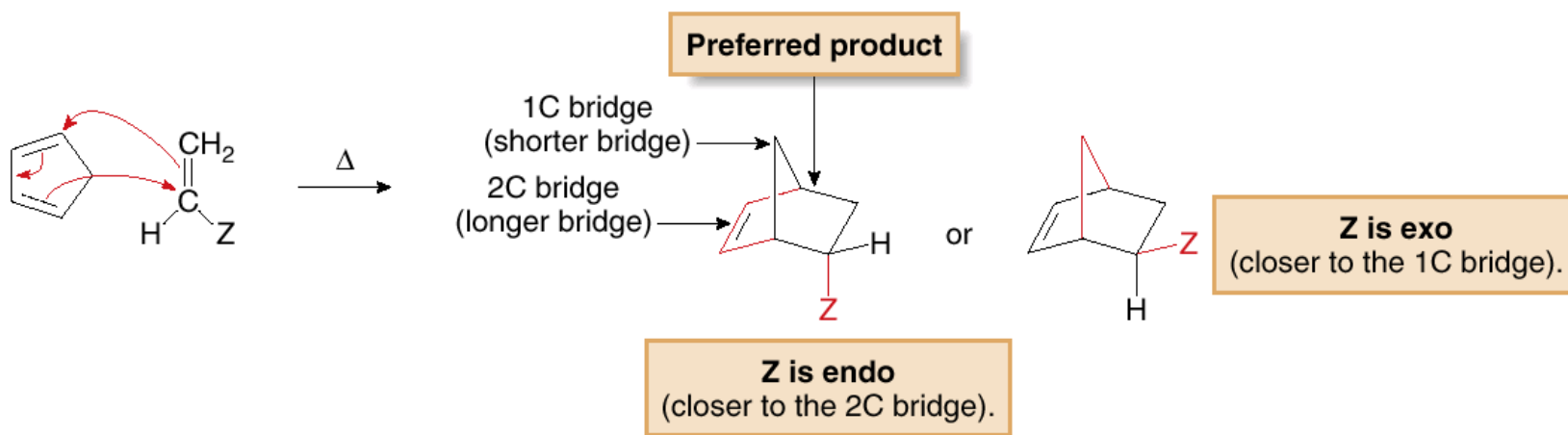
3. The stereochemistry of the dienophile is retained.





# Rules for The Diels-Alder Reaction

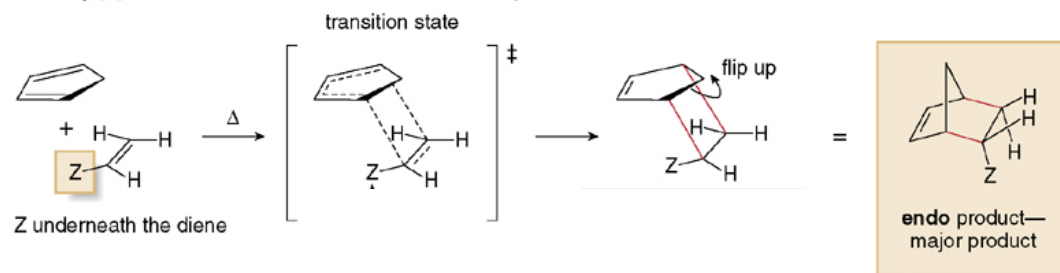
4. When endo and exo products are possible, the endo product is preferred.



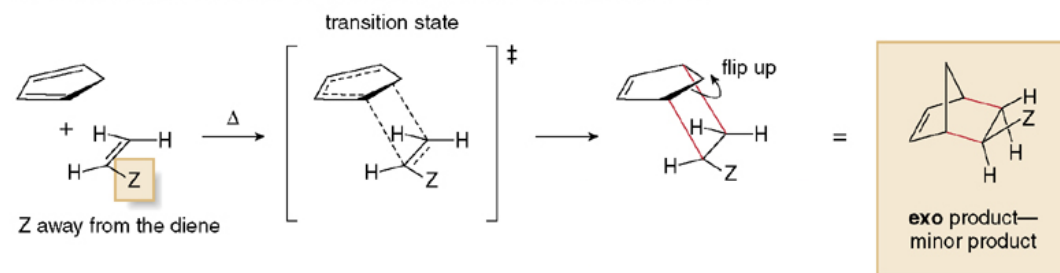
- A substituent on one bridge is *endo* if it is closer to the *longer* bridge that joins the two carbons common to both rings.
- A substituent is *exo* if it is closer to the *shorter* bridge that joins the carbons together.

# Rules for The Diels-Alder Reaction

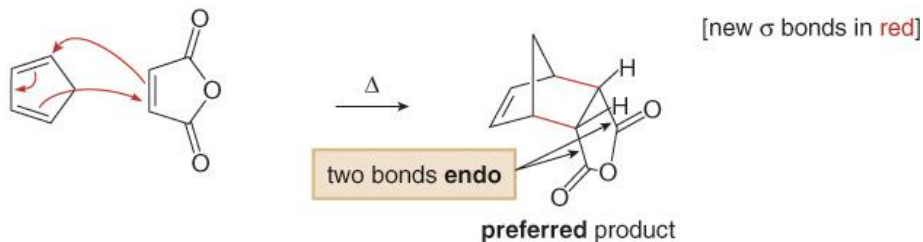
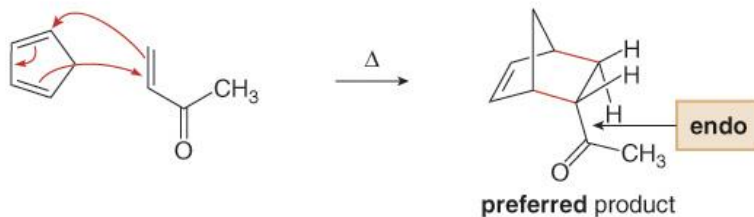
**Pathway [1]** With Z oriented under the diene, the endo product is formed.



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



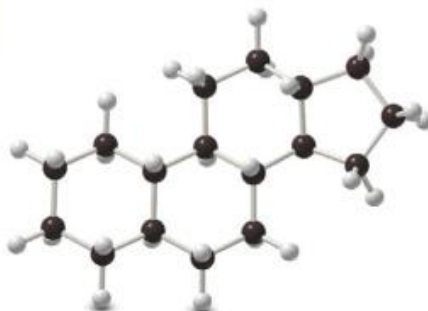
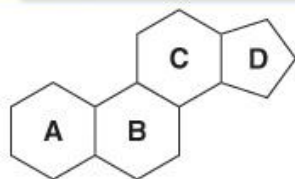
**Examples of  
endo addition**



# The Diels-Alder Reaction in Organic Synthesis

- Steroids are tetracyclic lipids.

The steroid skeleton

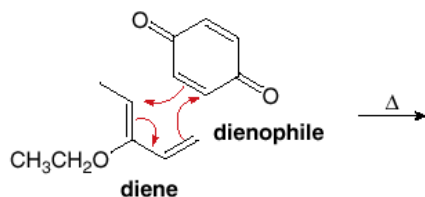
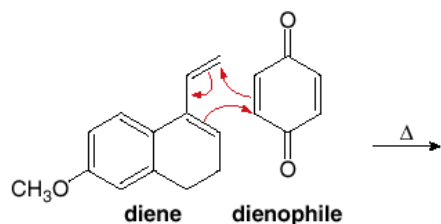


three-dimensional view  
from above

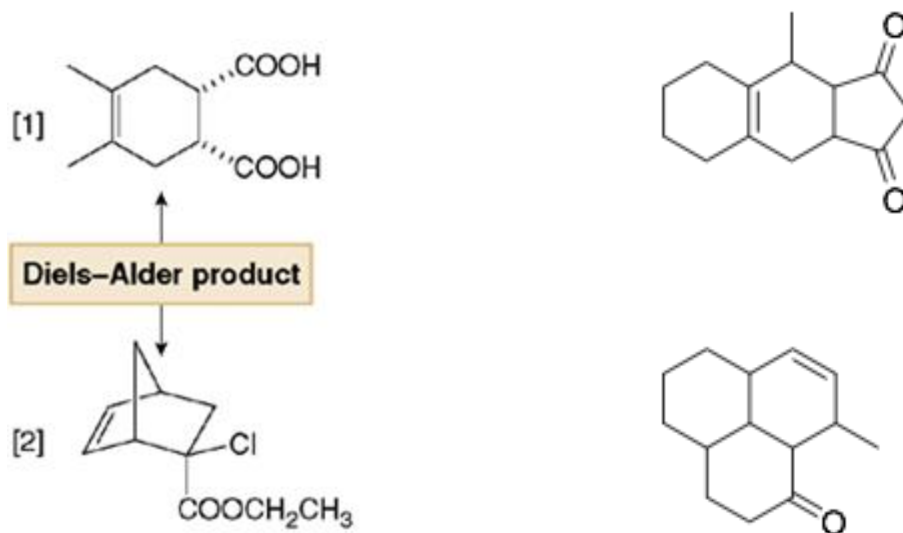


carbon skeleton  
viewed from the side

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



# The Diels-Alder Reaction in Organic Synthesis



# The Diels-Alder Reaction in Organic Synthesis

