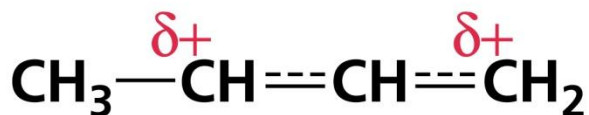
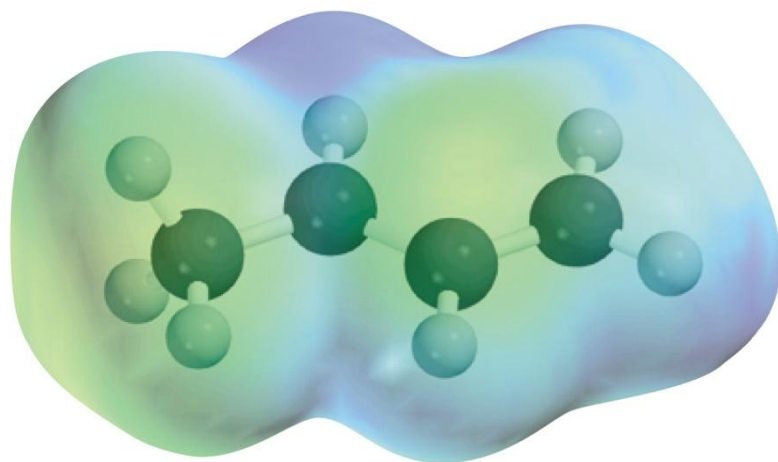


# Organic Chemistry

4<sup>th</sup> Edition

Paula Yurkanis Bruice



## Chapter 8

### Reactions of Dienes Ultraviolet and Visible Spectroscopy

Disampaikan oleh: Dr. Sri Handayani  
2013

Irene Lee  
Case Western Reserve University  
Cleveland, OH  
©2004, Prentice Hall

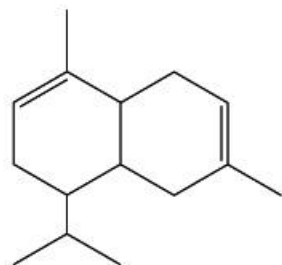
# Hydrocarbon containing

two double bonds: diene

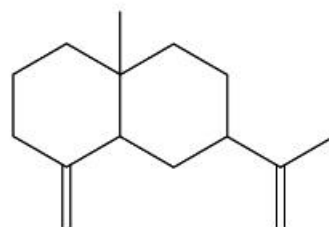
three double bonds: triene

four double bonds: tetraene

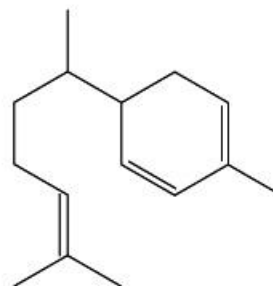
many double bonds: polyene



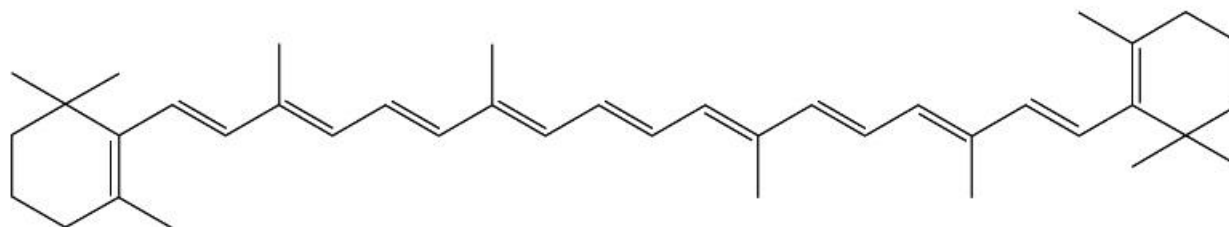
***α*-cadinene**  
oil of citronella  
a diene



***β*-selinene**  
oil of celery  
a diene

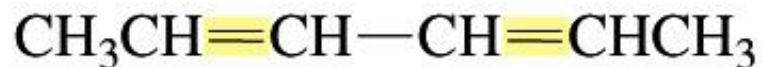


**zingiberene**  
oil of ginger  
a triene



***β*-carotene**  
a polyene

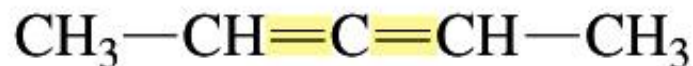
# Different Kinds of Dienes



**a conjugated diene**



**an isolated diene**

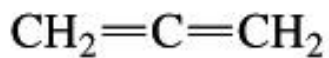


**a cumulated diene**

**an allene**

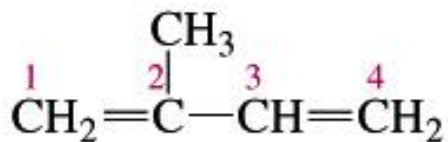
# Nomenclature of Alkenes with More than One Functional Group

1. Identify the longest continuous chain containing both double bonds
2. Give the double bonds the lowest possible number
3. The numbers indicating the double bonds are cited either before the name of the parent compound or before the suffix
4. Substituents are cited in alphabetical order

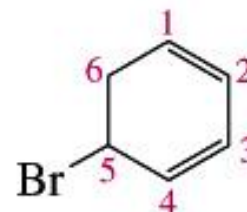


systematic:  
common:

propadiene  
allene



2-methyl-1,3-butadiene  
isoprene



5-bromo-1,3-cyclohexadiene

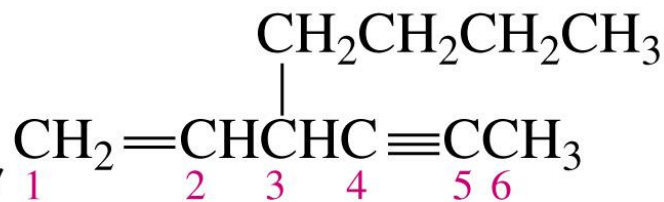
# When the double bonds are a double bond and a triple bond



**5-hepten-1-yne**  
*not* 2-hepten-6-yne  
because  $1 < 2$



**1-hepten-5-yne**  
*not* 6-hepten-2-yne  
because  $1 < 2$



**3-butyl-1-hexen-4-yne**

the longest continuous chain has eight carbons, but the 8-carbon chain does not contain both functional groups; therefore, the compound is named as a hexenyne because the longest continuous chain containing both functional groups has six carbons

If there is a tie, the double bond gets the lowest number



**2-hexen-4-yne**

*not* 4-hexen-2-yne



**1-hexen-5-yne**

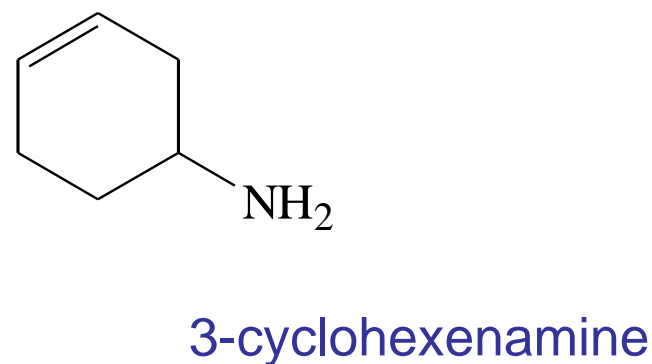
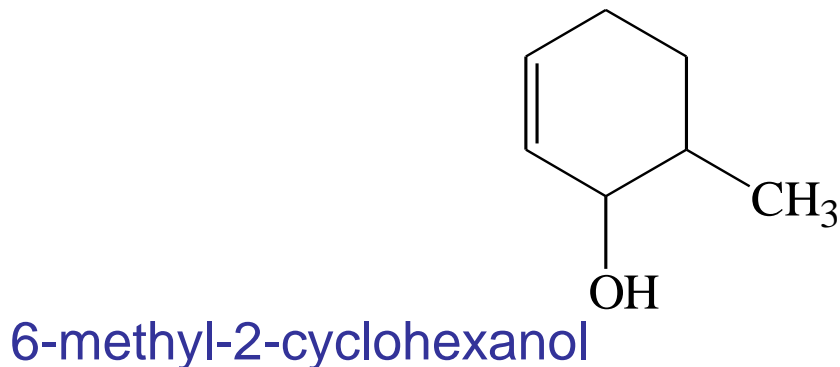
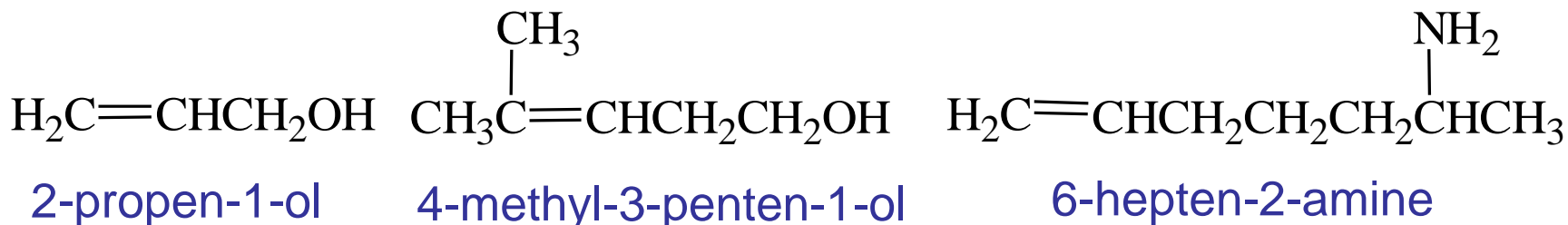
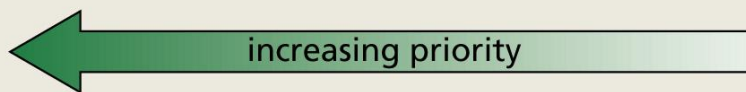
*not* 5-hexen-1-yne

A chain is numbered to give the lowest number to the functional group with the highest priority

Table 8.1 Priorities of Functional Group Suffixes



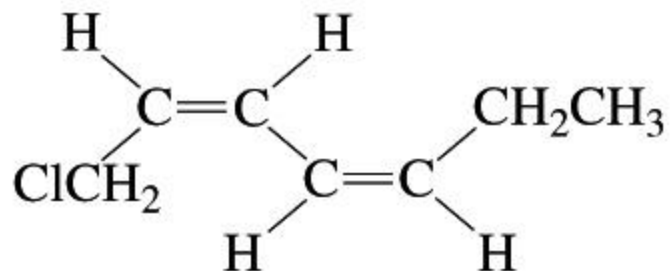
the double bond is given priority over a triple bond only when there is a tie



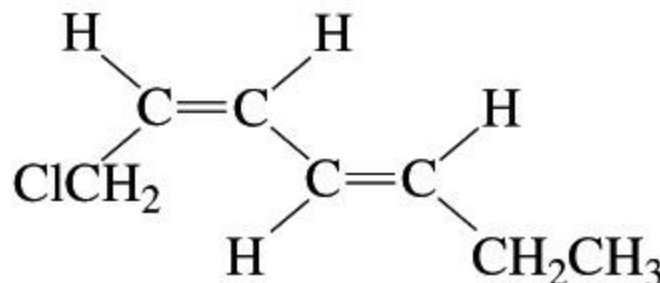


# Configurational Isomers of Dienes

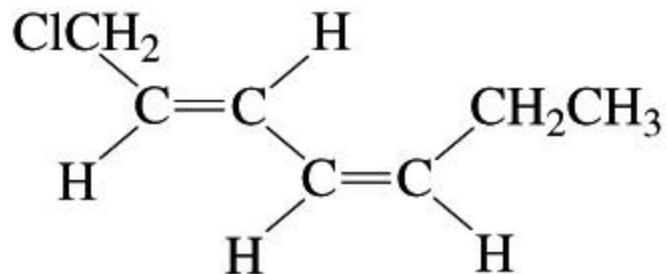
The *Z* isomer has the high-priority groups on the same side



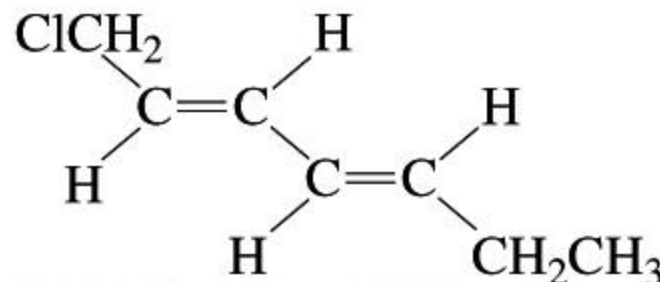
**(2*Z*,4*Z*)-1-chloro-2,4-heptadiene**



**(2*Z*,4*E*)-1-chloro-2,4-heptadiene**



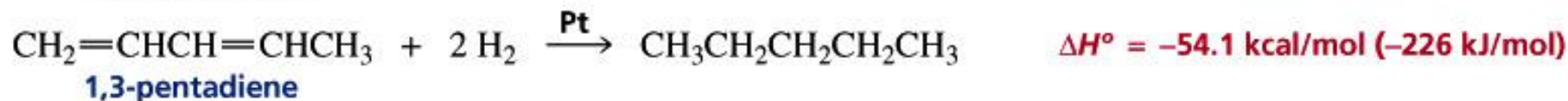
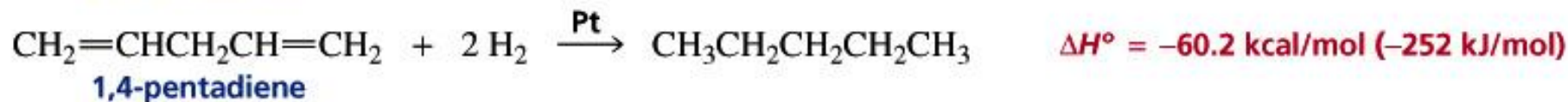
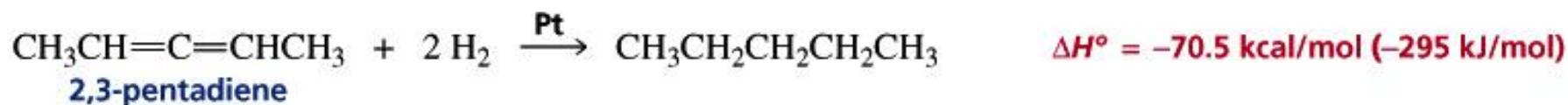
**(2*E*,4*Z*)-1-chloro-2,4-heptadiene**



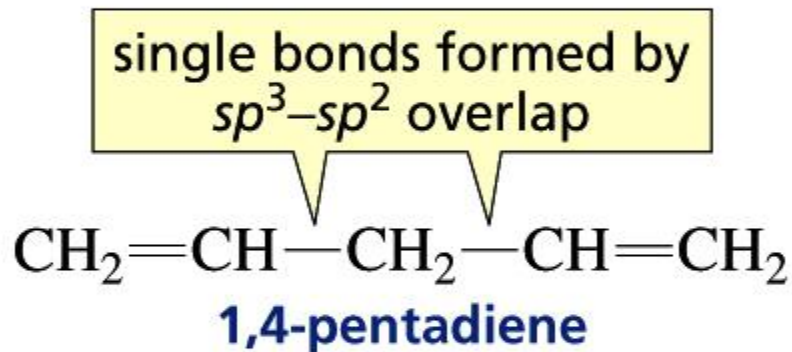
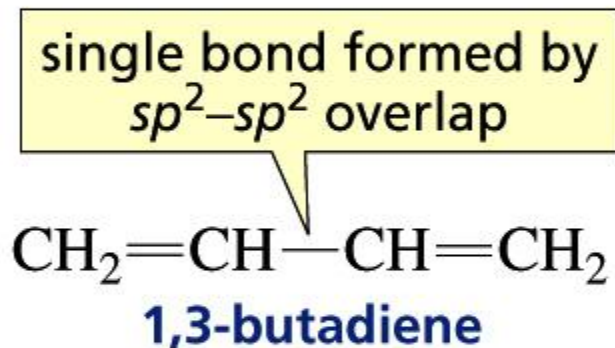
**(2*E*,4*E*)-1-chloro-2,4-heptadiene**

## relative stabilities of dienes

conjugated diene > isolated diene > cumulated diene

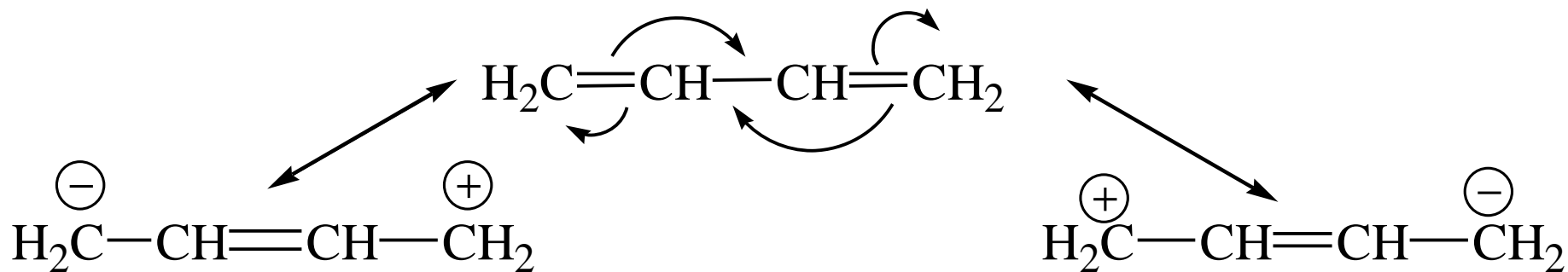


Why is conjugated diene more stable than isolated diene?

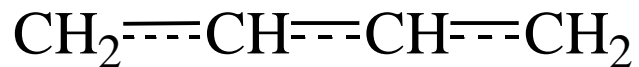


The closer the electrons are to the nucleus, the shorter and stronger is the bond

# Electron Delocalization Stabilizes a Conjugated Diene



resonance contributors



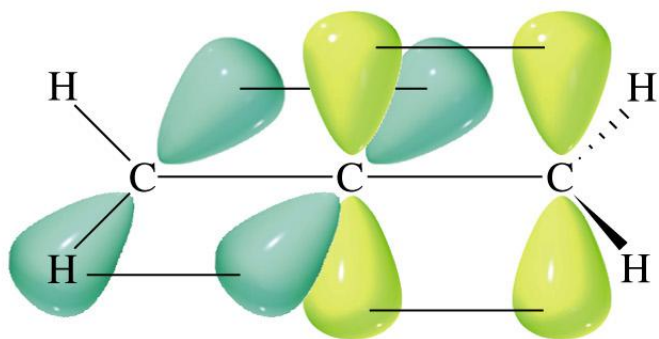
resonance hybrid

**Table 8.2 Dependence of the Length of a Carbon–Carbon Single Bond on the Hybridization of the Orbitals Used in Its Formation**

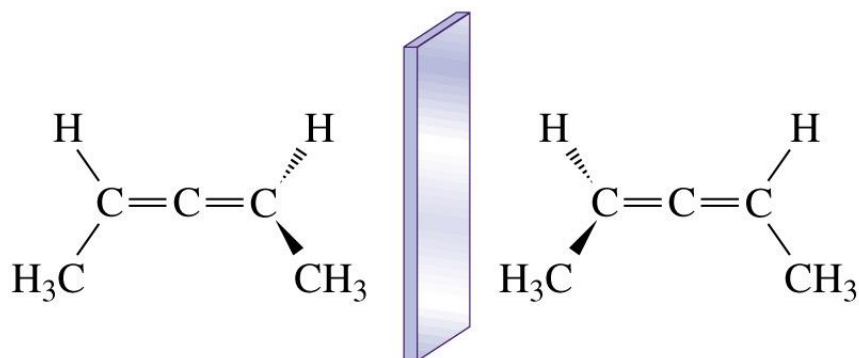
Compound	Hybridization	Bond length (Å)
$\text{H}_3\text{C}-\text{CH}_3$	$sp^3-sp^3$	1.54
$\begin{array}{c} \text{H} \\   \\ \text{H}_3\text{C}-\text{C}=\text{CH}_2 \end{array}$	$sp^3-sp^2$	1.50
$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{H}_2\text{C}=\text{C}-\text{C}=\text{CH}_2 \end{array}$	$sp^2-sp^2$	1.47
$\text{H}_3\text{C}-\text{C}\equiv\text{CH}$	$sp^3-sp$	1.46
$\begin{array}{c} \text{H} \\   \\ \text{H}_2\text{C}=\text{C}-\text{C}\equiv\text{CH} \end{array}$	$sp^2-sp$	1.43
$\text{HC}\equiv\text{C}-\text{C}\equiv\text{CH}$	$sp-sp$	1.37

A cumulated diene is less stable than an isolated diene

a.



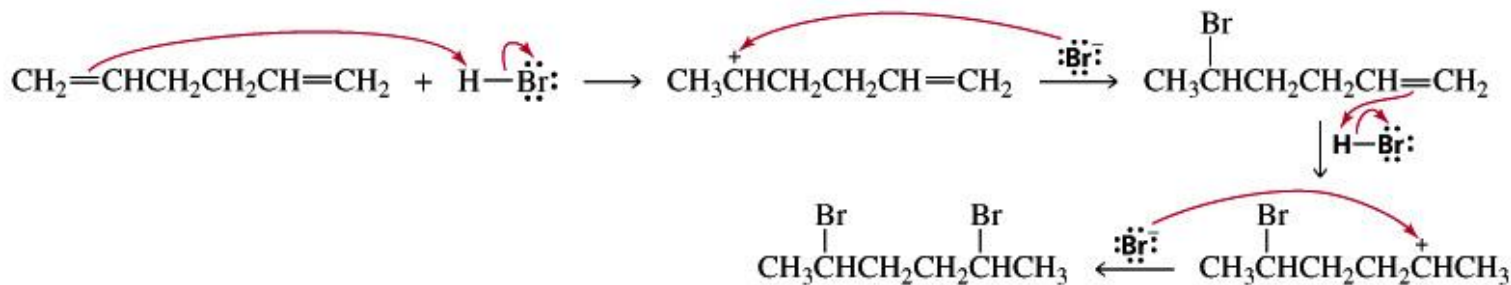
b.



# Electrophilic Addition Reactions of Isolated Dienes



mechanism for the reaction of 1,5-hexadiene with excess HBr



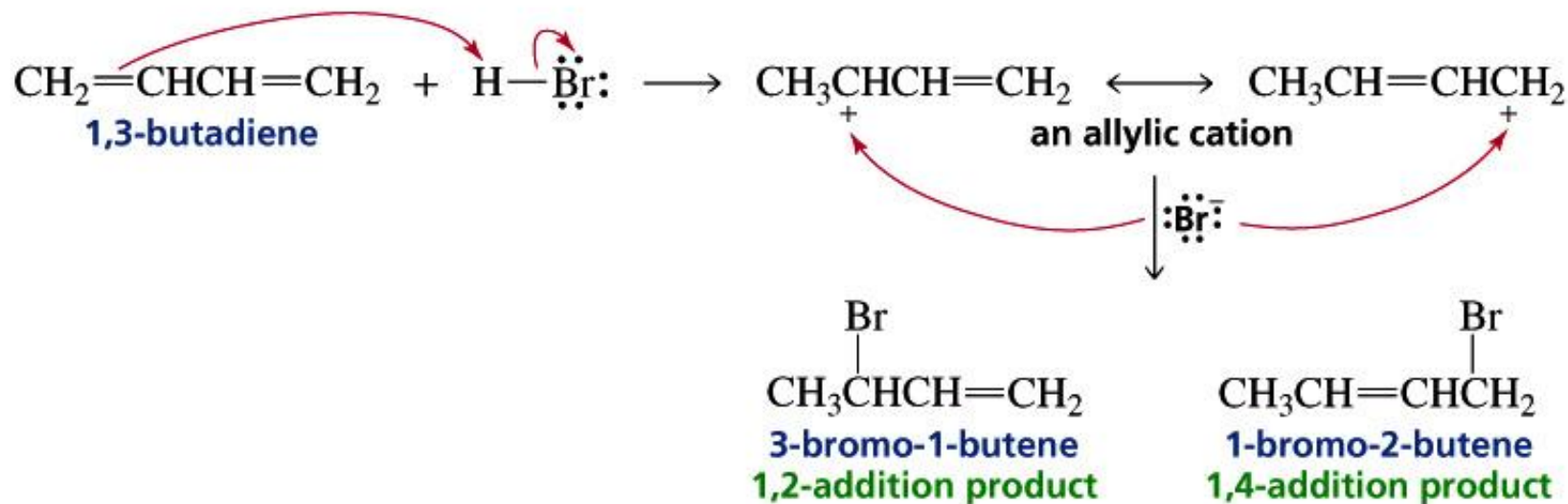
Addition can occur at only one of the double bonds when 1 mole of HBr is available

# Electrophilic Addition Reactions of Conjugated Dienes

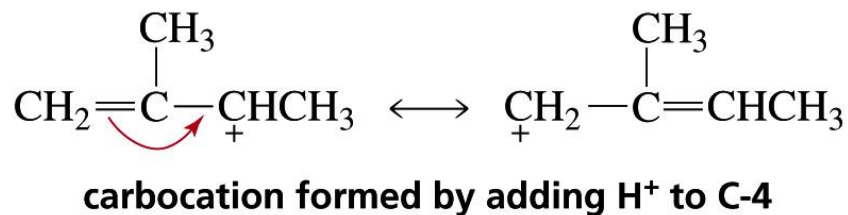
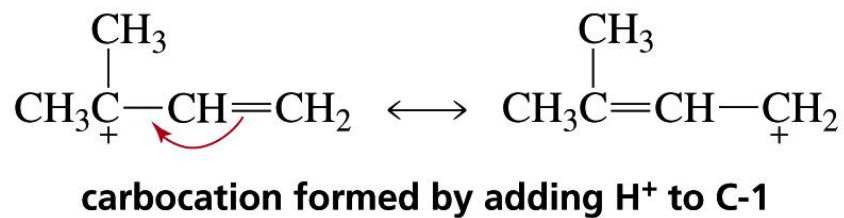
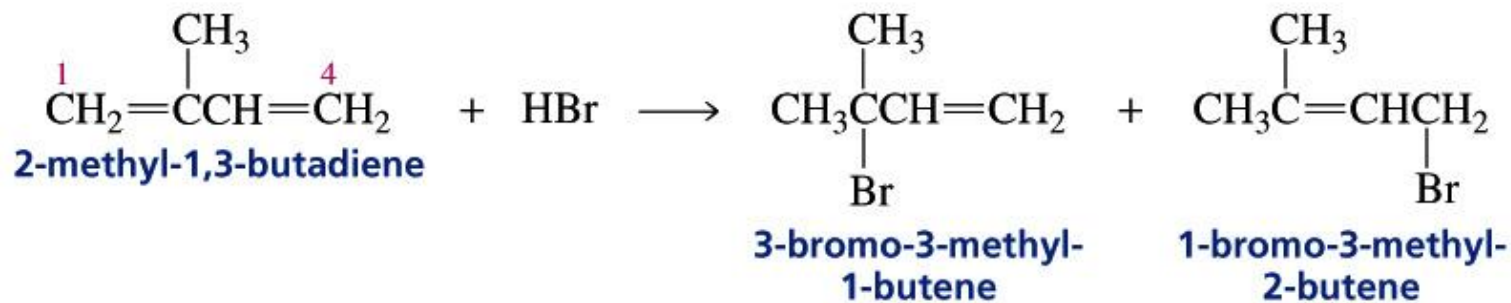




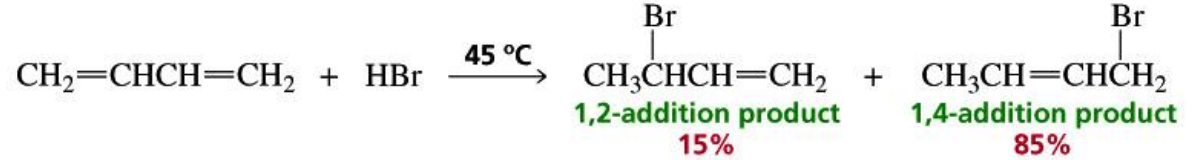
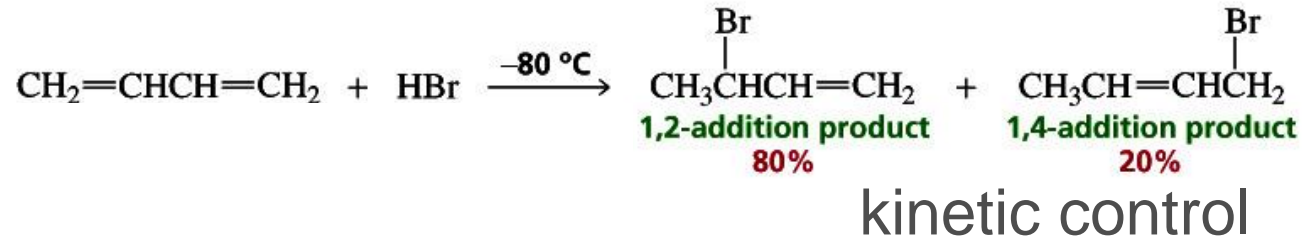
mechanism for the reaction of 1,3-butadiene with HBr



# A conjugated diene undergoes both 1,2- and 1,4-addition



# Compare the two addition product distribution at different reaction temperatures

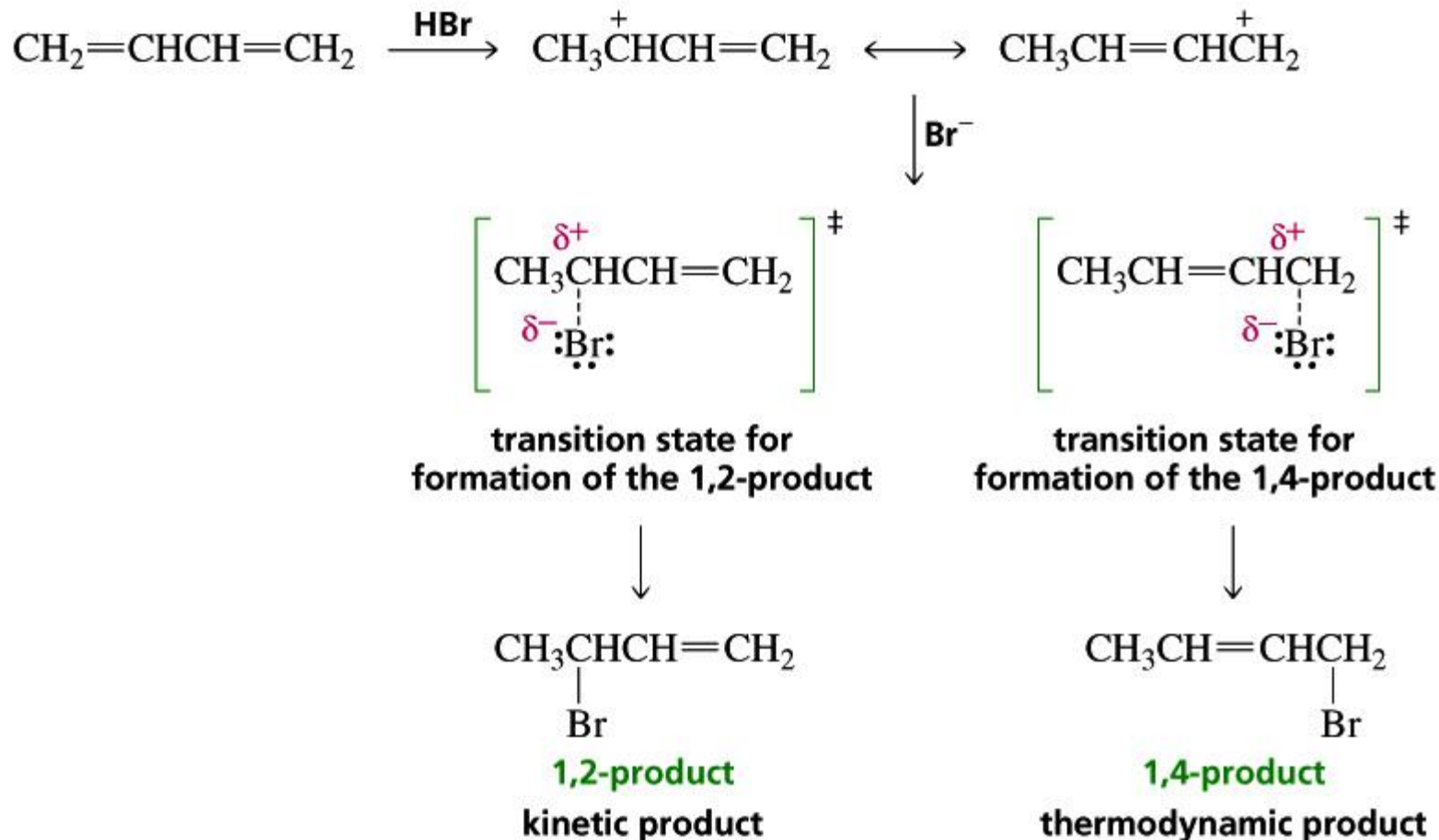


thermodynamic or equilibrium control

# Thermodynamic Versus Kinetic Control

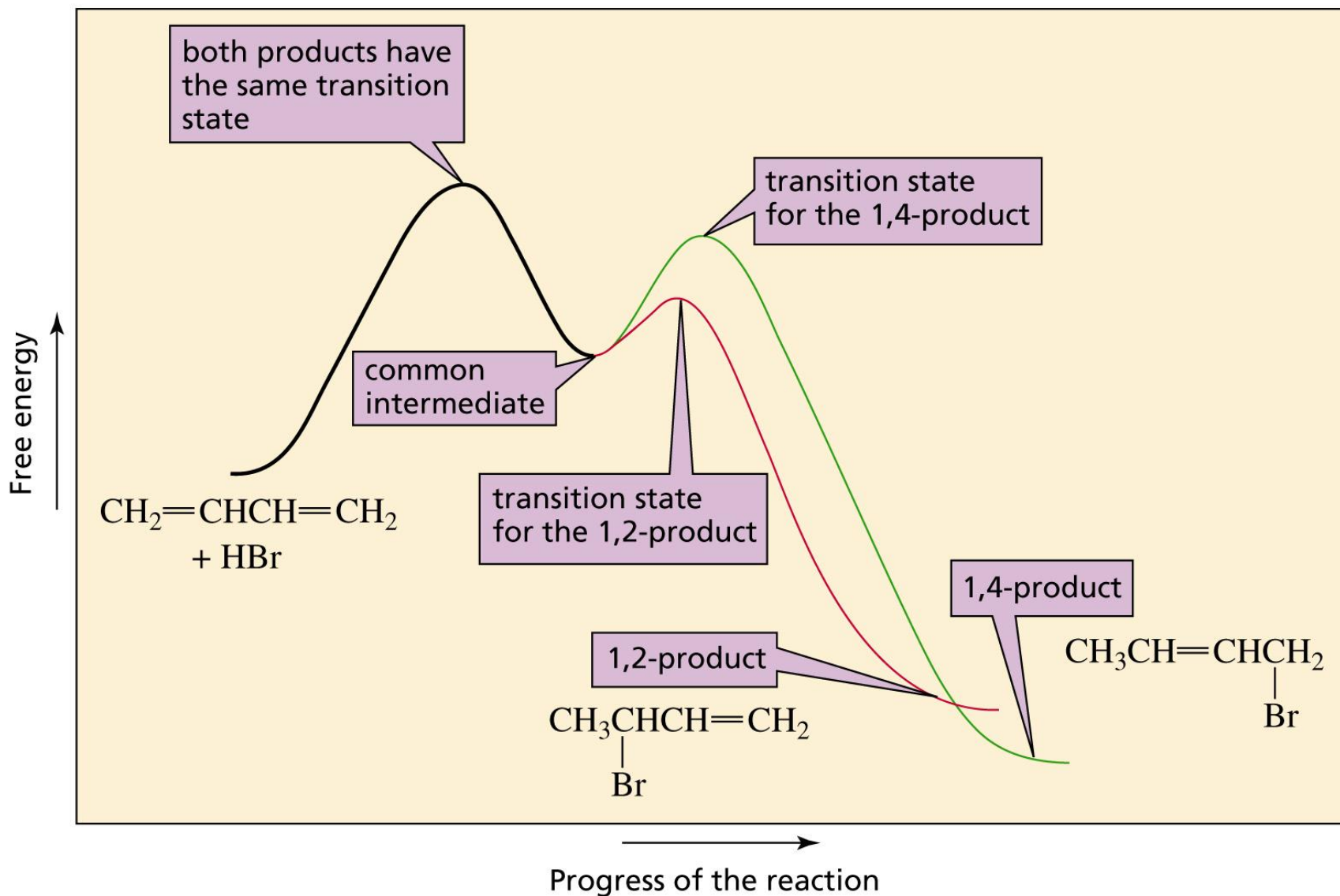
- The thermodynamic product is the most stable product
- The thermodynamic product predominates when the reaction is reversible (thermodynamic control)
- The kinetic product is the product that is formed most rapidly
- The kinetic product predominates when the reaction is irreversible (kinetic control)

The 1,4-addition product has the greater number of alkyl groups bonded to the  $sp^2$  carbon (more stable)

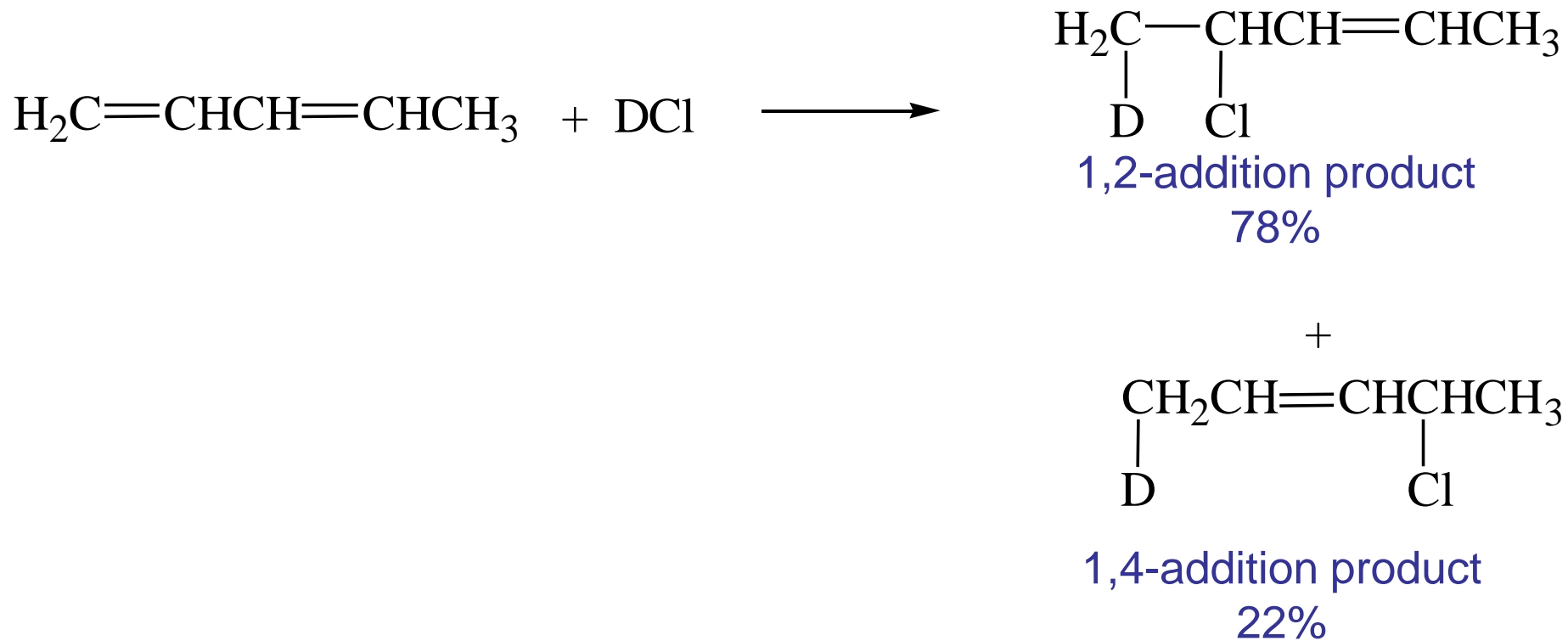


Why is the 1,2-addition product the kinetic product?

# Consider the reaction coordinate diagram ...



## Consider 1,3-pentadiene + DCl



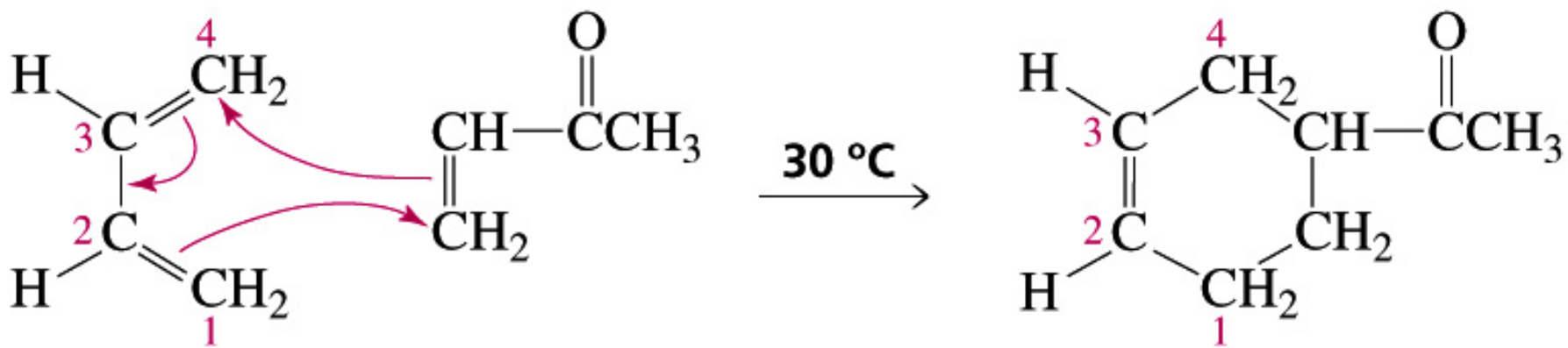
The 1,2-addition is the major product because the chloride ion can stabilize the positive charge better at C-2 than at C-4 simply because it is closer to C-2 (the proximity effect)

Do not assume that the 1,4-addition product is always the thermodynamic product ...



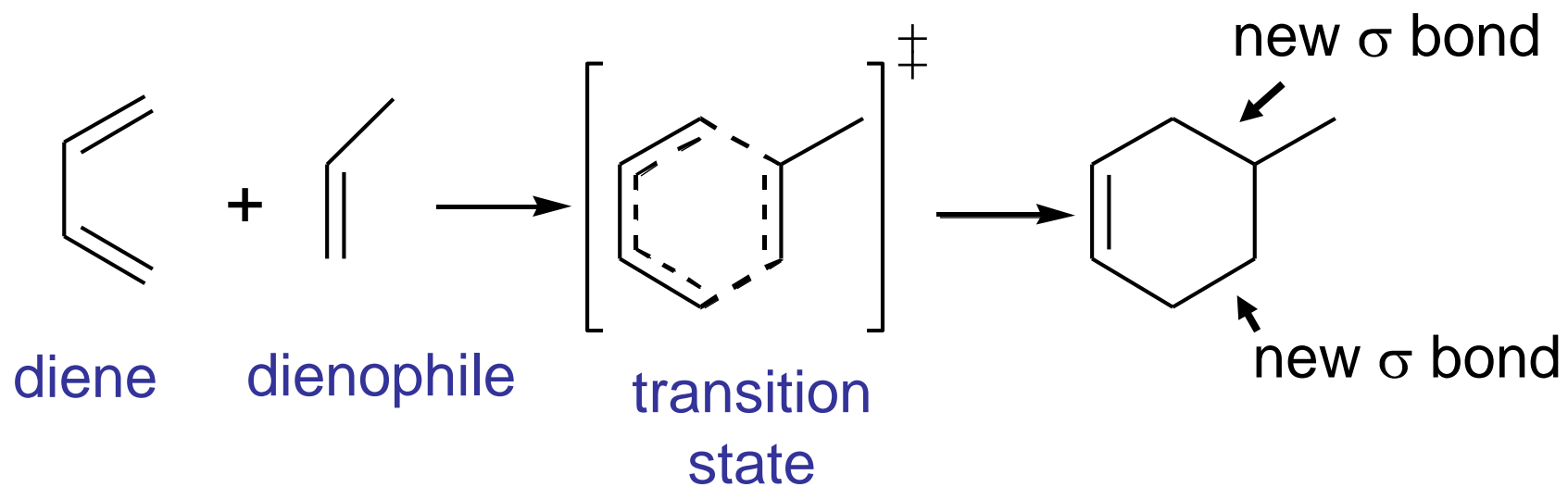


# The Diels–Alder Reaction: A 1,4-Addition Reaction

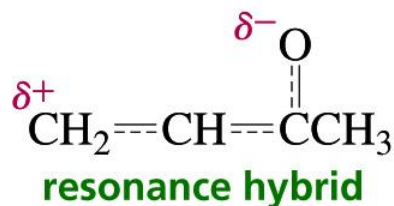
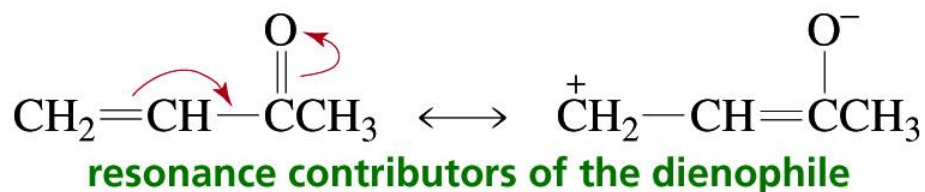
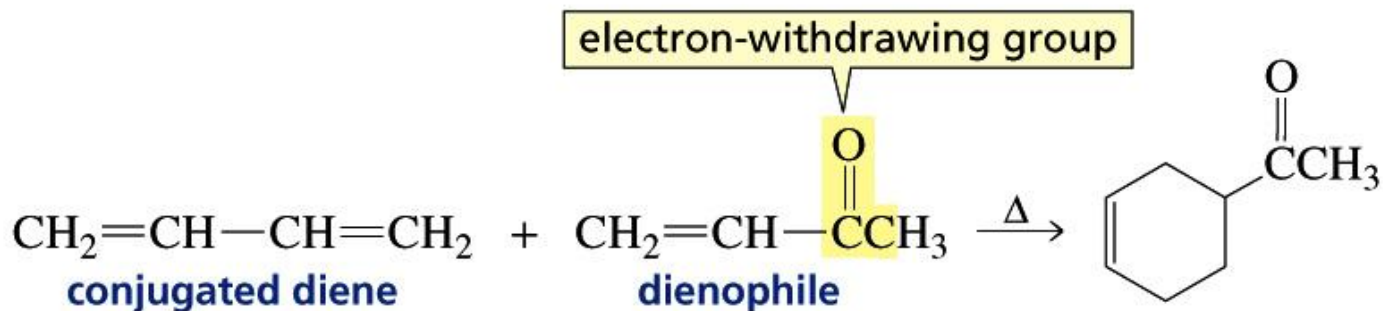


a 1,4-addition reaction to 1,3-butadiene

The Diels–Alder reaction is a pericyclic reaction; a [4+2] cycloaddition reaction

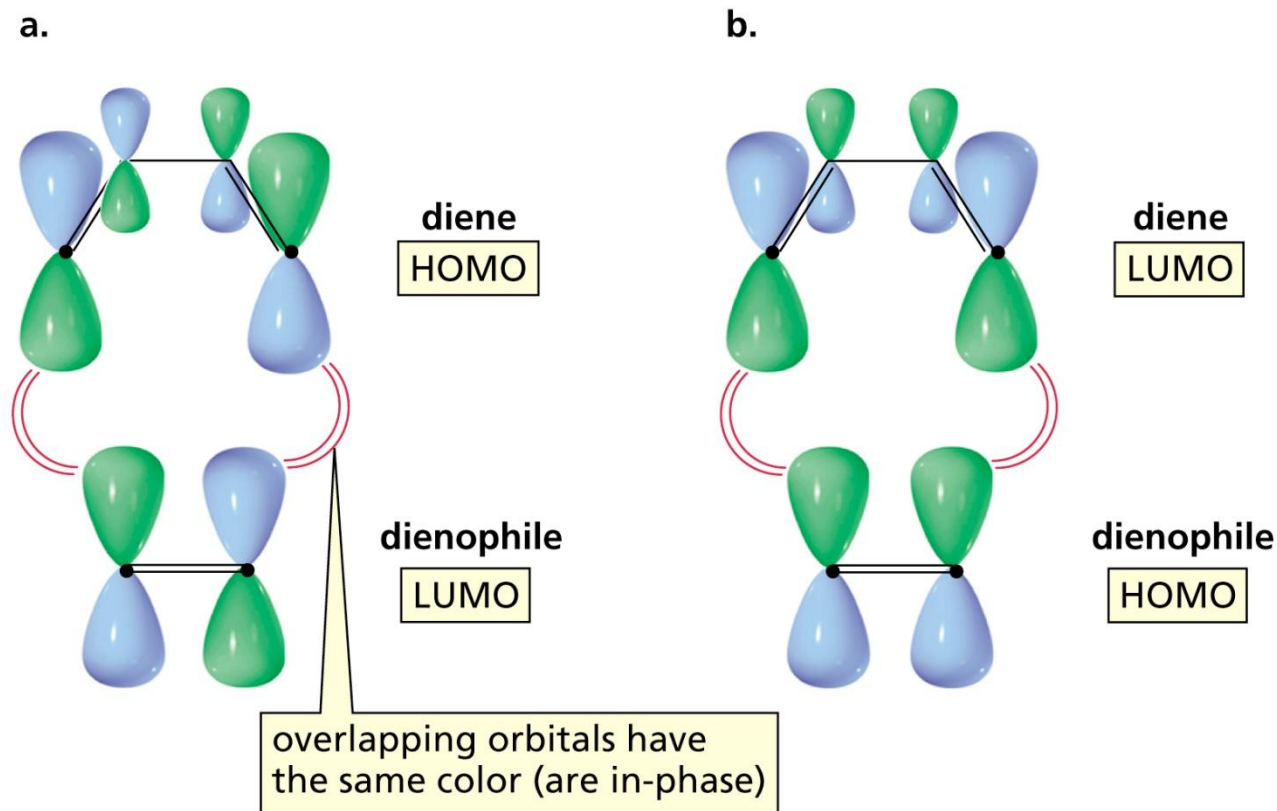


The reactivity of the dienophile is increased if one or more electron-withdrawing groups are attached to its  $sp^2$  carbons

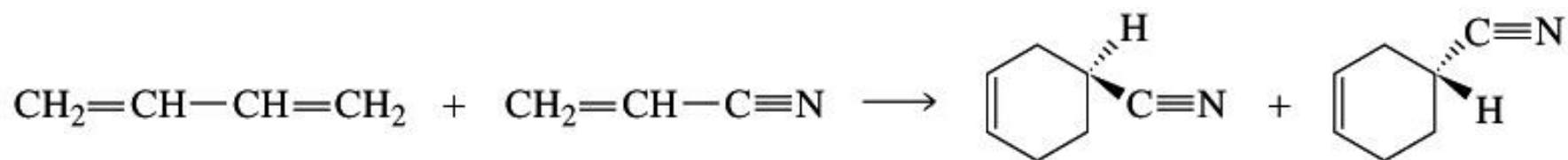


# A Molecular Orbital Description of the Diels–Alder Reaction

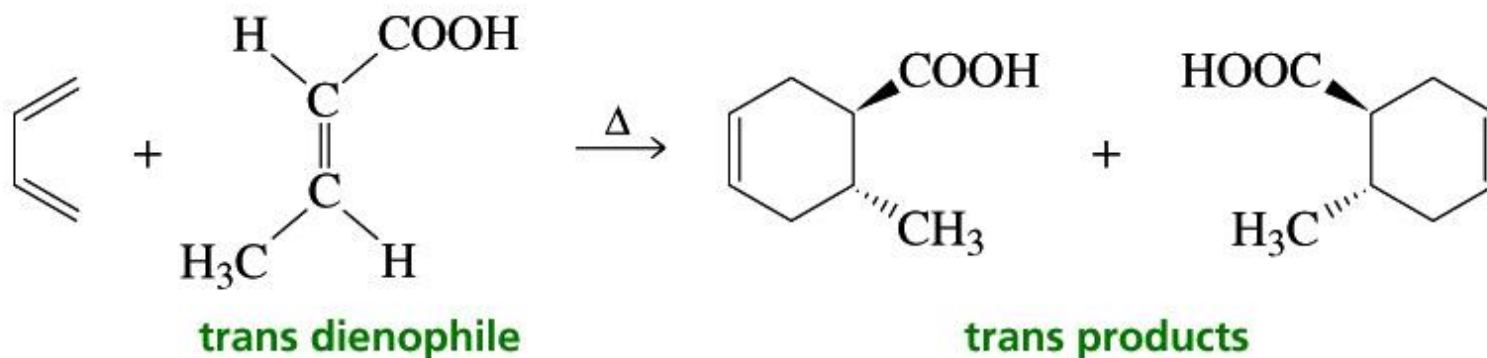
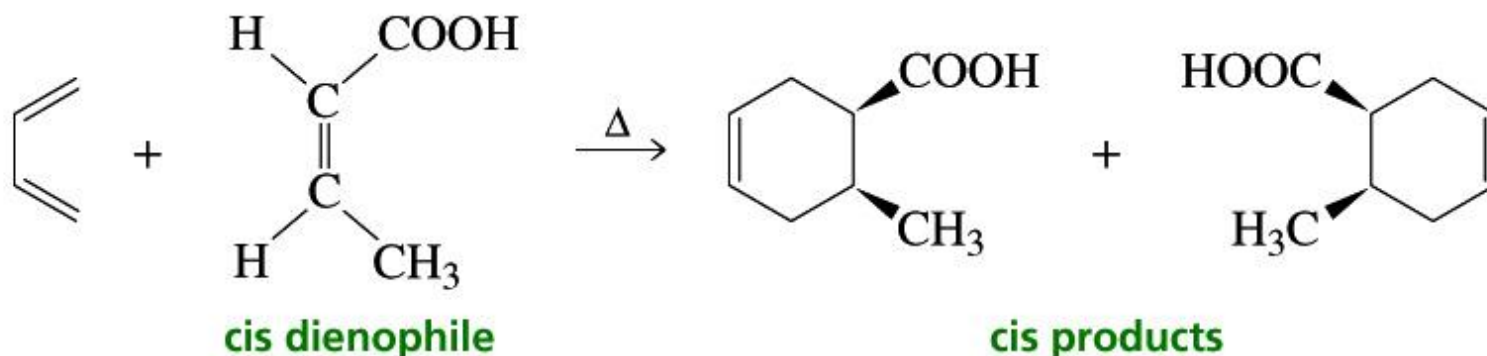
Let's focus on the HOMO and the LUMO of the reactants



# Stereochemistry of the Diels–Alder Reaction



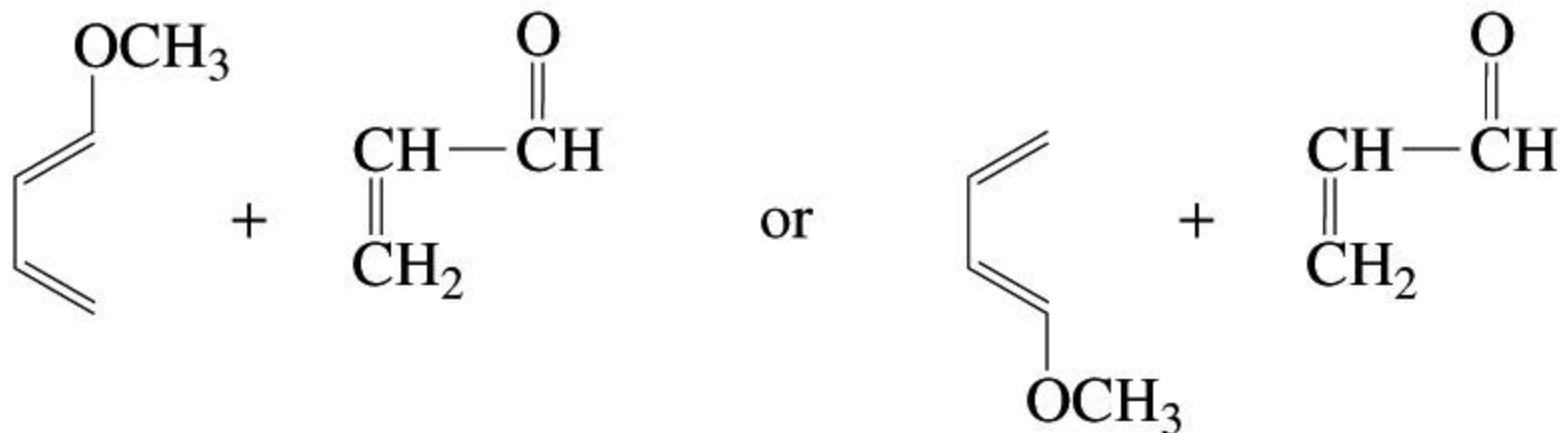
## The reaction is a syn addition



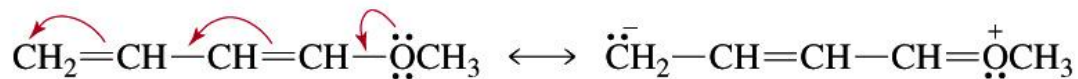
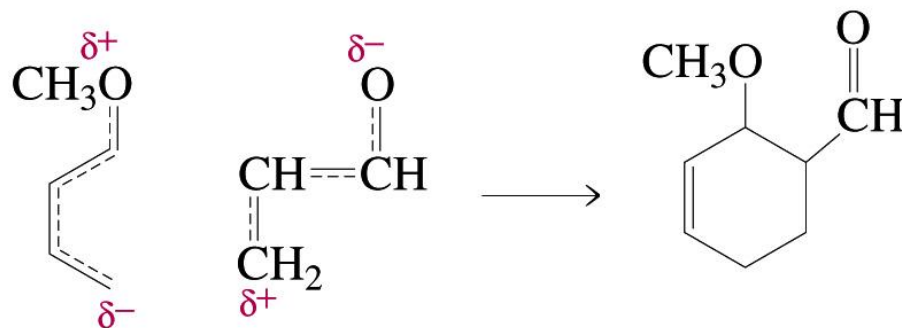
- The Diels–Alder reaction is stereospecific
- The configuration of the reactants is maintained
- The reaction is concerted

# Predicting the reaction products

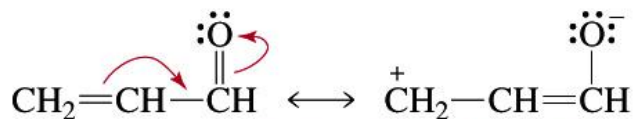
1. Consider the alignment of the reactants



2. Consider the charge distribution in each of the reactants



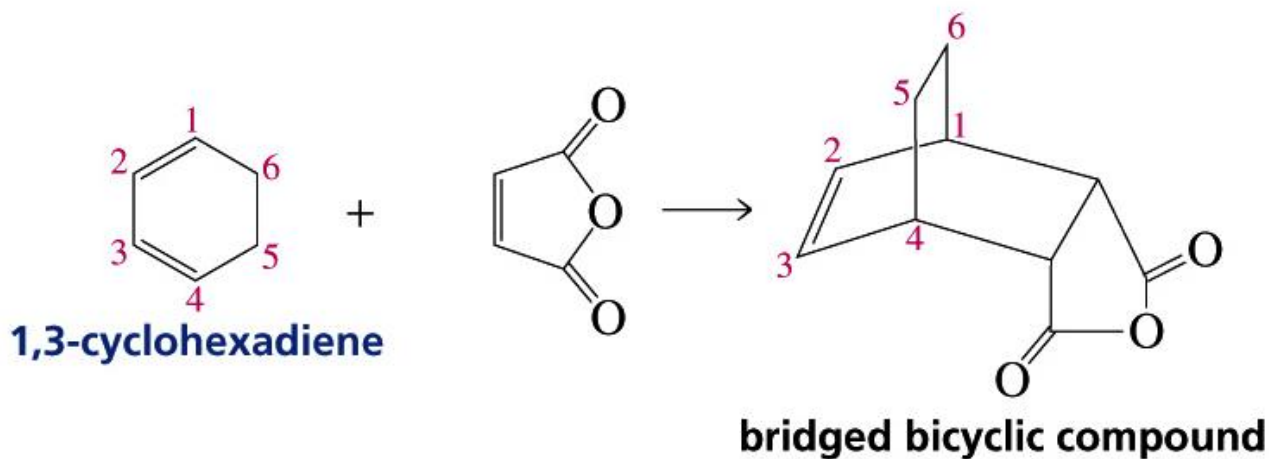
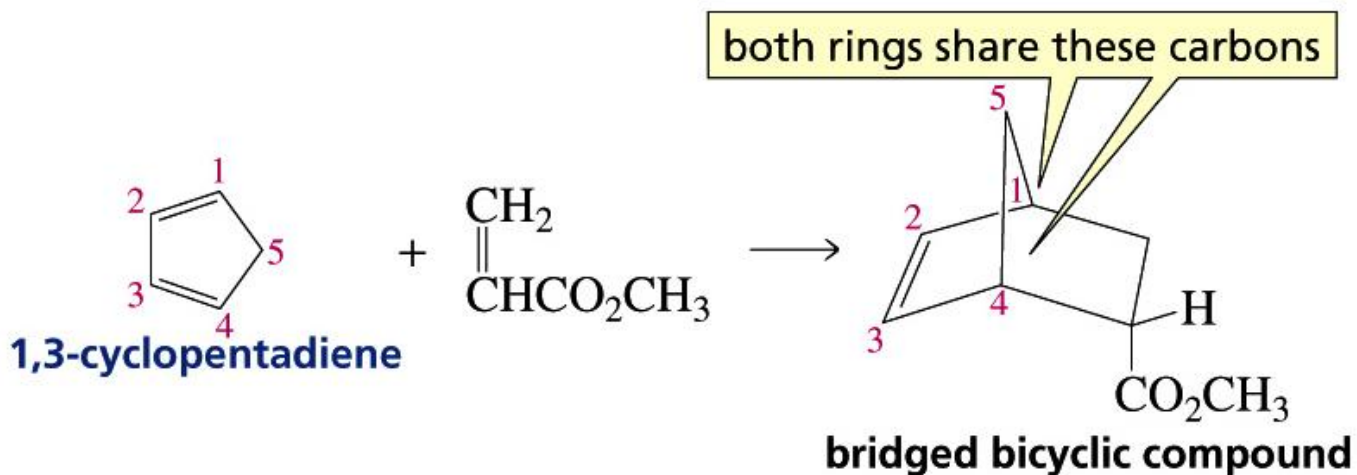
resonance contributors of the diene



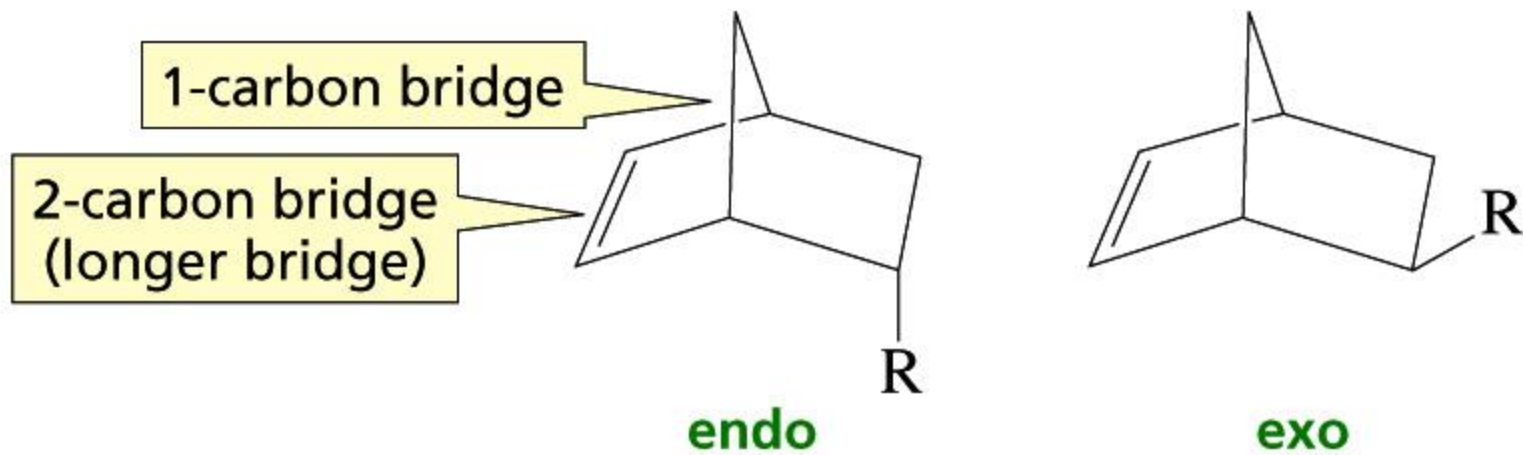
resonance contributors of the dienophile



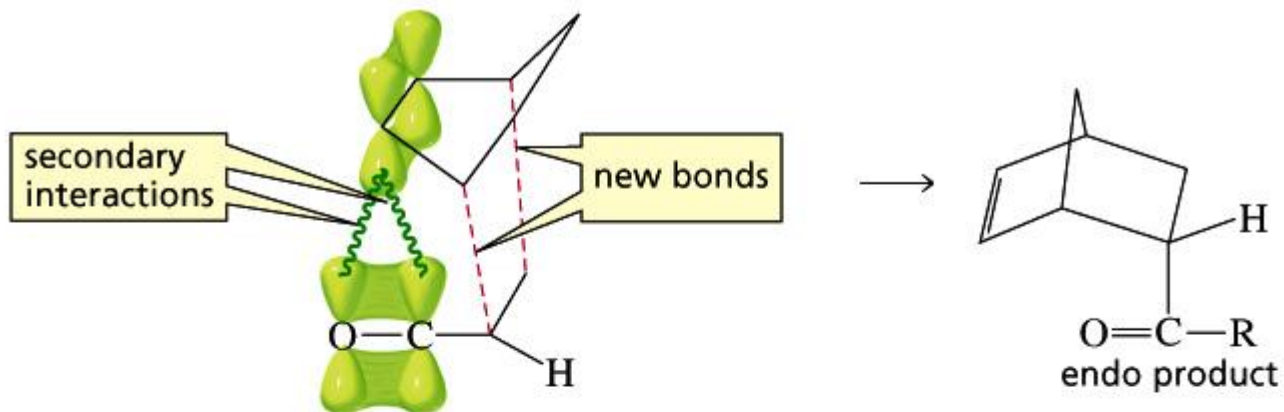
# Only the cis conformation can participate in a Diels–Alder reaction



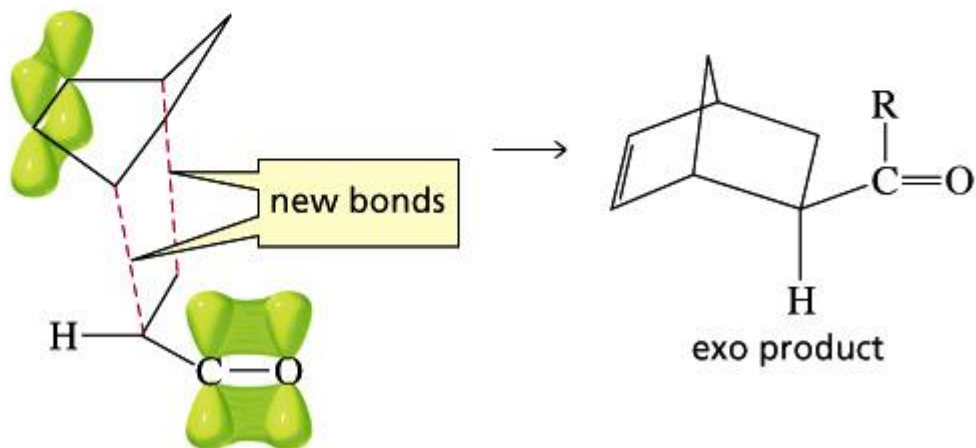
# Two Possible Configurations of Bridged Bicyclic Compounds



# Secondary orbital overlap favors the endo product formation



secondary orbital overlap in the endo transition state

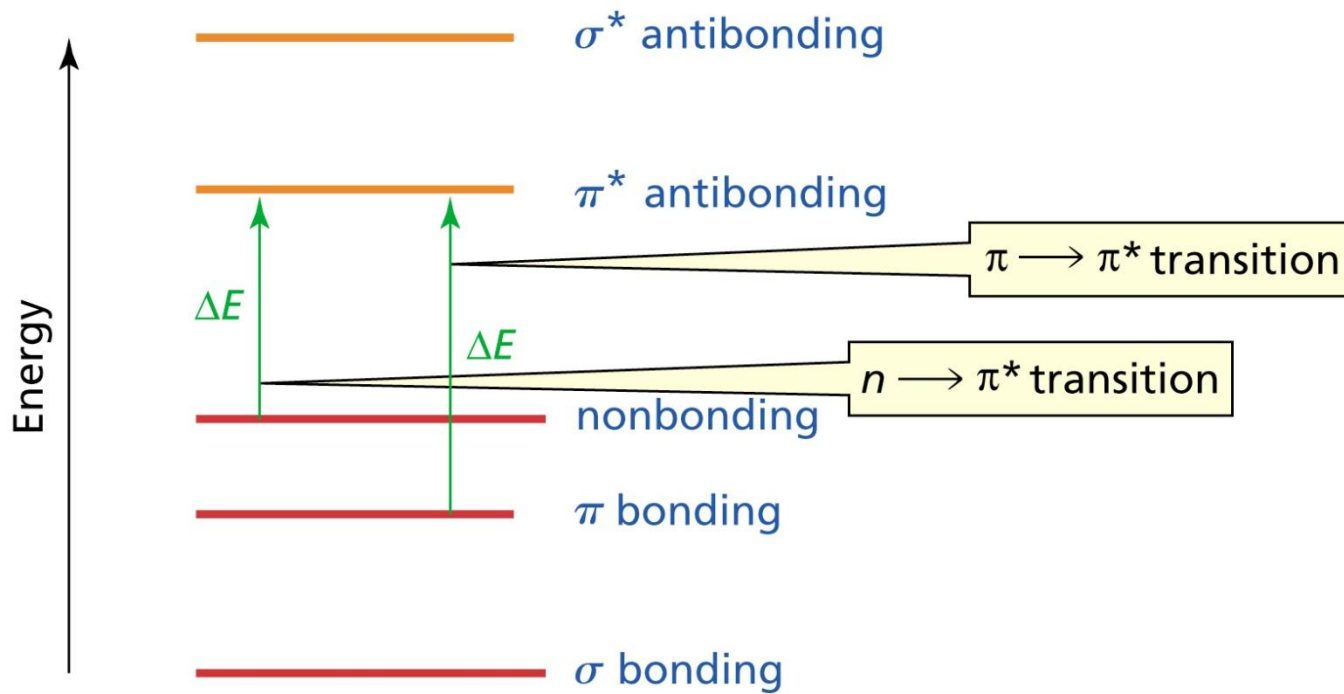


no secondary orbital overlap in the exo transition state

# Ultraviolet and Visible Spectroscopy

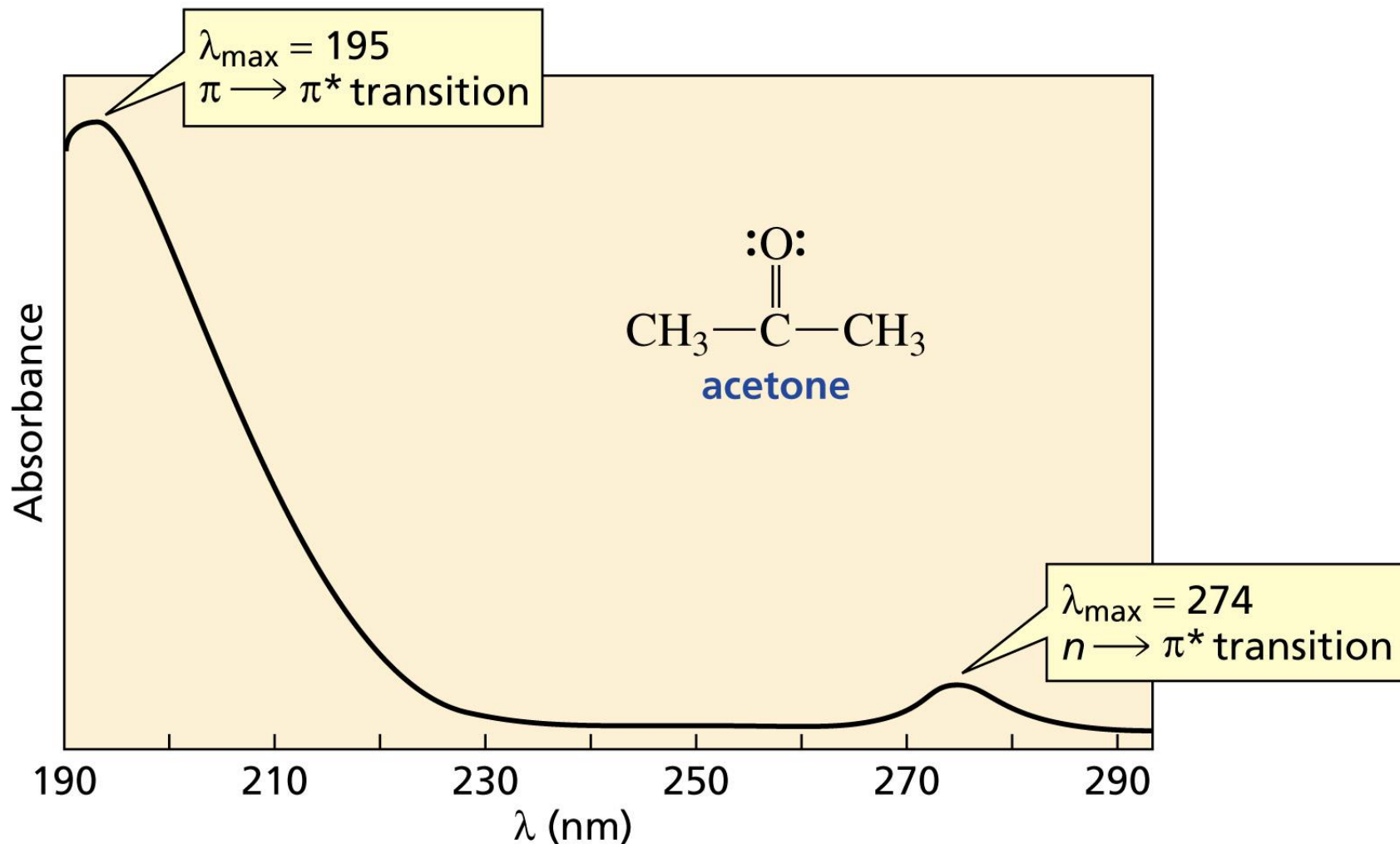
- Spectroscopy is the study of the interaction between matter and electromagnetic radiation
- UV/Vis spectroscopy provides information about compounds with conjugated double bonds

# UV and Vis light cause only two kinds of electronic transition



- Only organic compounds with  $\pi$  electrons can UV/Vis spectra
- A visible spectrum is obtained if visible light is absorbed
- A UV spectrum is obtained if UV light is absorbed

A chromophore is the part of a molecule which absorbs UV or visible light



# The Beer–Lambert Law

$$A = cl\varepsilon$$

$$A = \log(I_0/I)$$

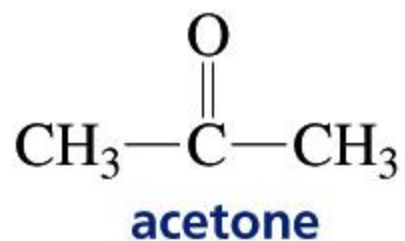
$c$  = concentration of substance  
in solution

$l$  = length of the cell in cm

$\varepsilon$  = molar absorptivity

The molar absorptivity of a compound is a constant that is characteristic of the compound at a particular wavelength

# Effect of Conjugation on $\lambda_{\max}$



$$n \longrightarrow \pi^* \quad \lambda_{\max} = 270 \text{ nm}$$

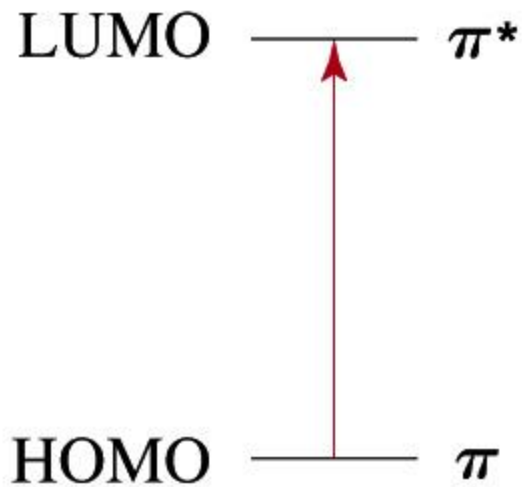
$$\pi \longrightarrow \pi^* \quad \lambda_{\max} = 187 \text{ nm}$$



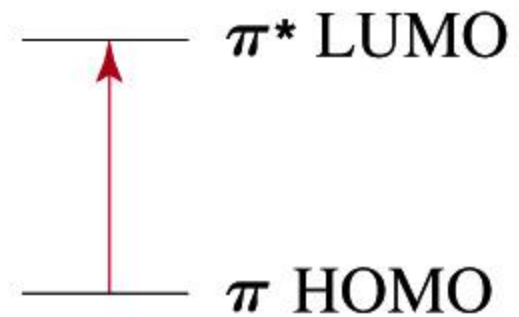
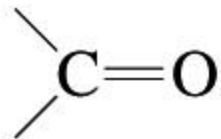
$$\lambda_{\max} = 324 \text{ nm}$$

$$\lambda_{\max} = 219 \text{ nm}$$

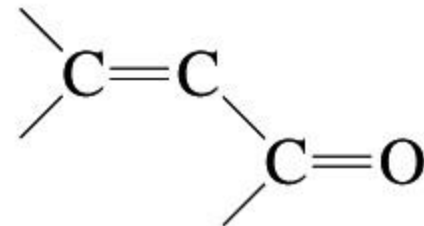









**nonconjugated  $\pi$  electrons**



**conjugated  $\pi$  electrons**



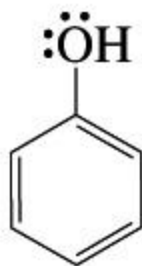
Both the  $\lambda_{\max}$  and  $\epsilon$  increase as the number of conjugated double bonds increases

Compound	$\lambda_{\max}$ (nm)	$\epsilon$
$\text{H}_2\text{C}=\text{CH}_2$	165	15,000
	217	21,000
	256	50,000
	290	85,000
	334	125,000
	364	138,000

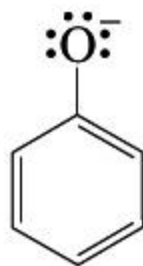
An auxochrome is a substituent in a chromophore that alters the  $\lambda_{\max}$  and the intensity of the absorption



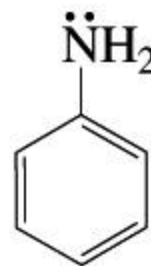
**benzene**  
**255 nm**



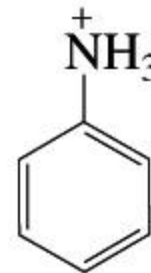
**phenol**  
**270 nm**



**phenolate ion**  
**287 nm**



**aniline**  
**280 nm**



**anilinium ion**  
**254 nm**

# The Visible Spectrum and Color

**Table 8.4 Dependence of the Color Observed on the Wavelength of Light Absorbed**

<b>Wavelengths absorbed (nm)</b>	<b>Observed color</b>
380–460	yellow
380–500	orange
440–560	red
480–610	purple
540–650	blue
380–420 and 610–700	green

# Uses of UV/Vis Spectroscopy

- Measure the rates of a reaction
- Determine the  $pK_a$  of a compound
- Estimate the nucleotide composition of DNA