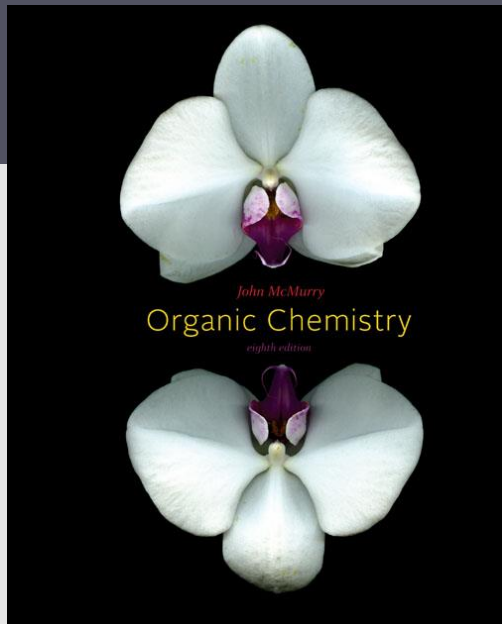


John E. McMurry

www.cengage.com/chemistry/mcmurry



Chapter 14

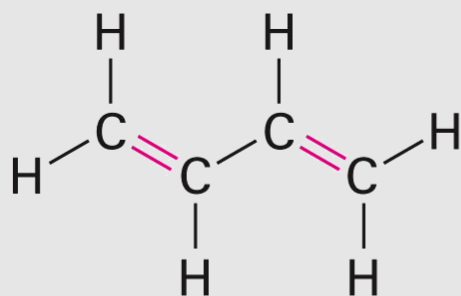
Conjugated Compounds and Ultraviolet Spectroscopy

Paul D. Adams • University of Arkansas

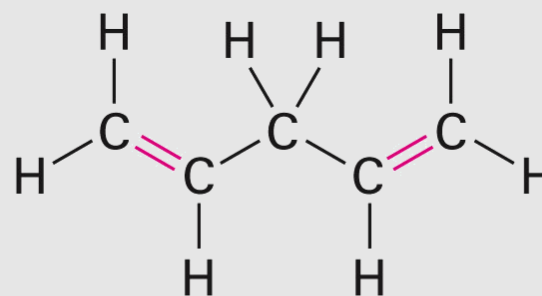
Conjugated and Nonconjugated Dienes



- Compounds can have more than one double or triple bond
- If they are separated by only one single bond they are **conjugated** and their orbitals interact
- The *conjugated diene 1,3-butadiene* has properties that are very different from those of the *nonconjugated diene, 1,4-pentadiene*.



1,3-Butadiene
(conjugated; alternating
double and single bonds)



1,4-Pentadiene
(nonconjugated; nonalternating
double and single bonds)

Why this Chapter?

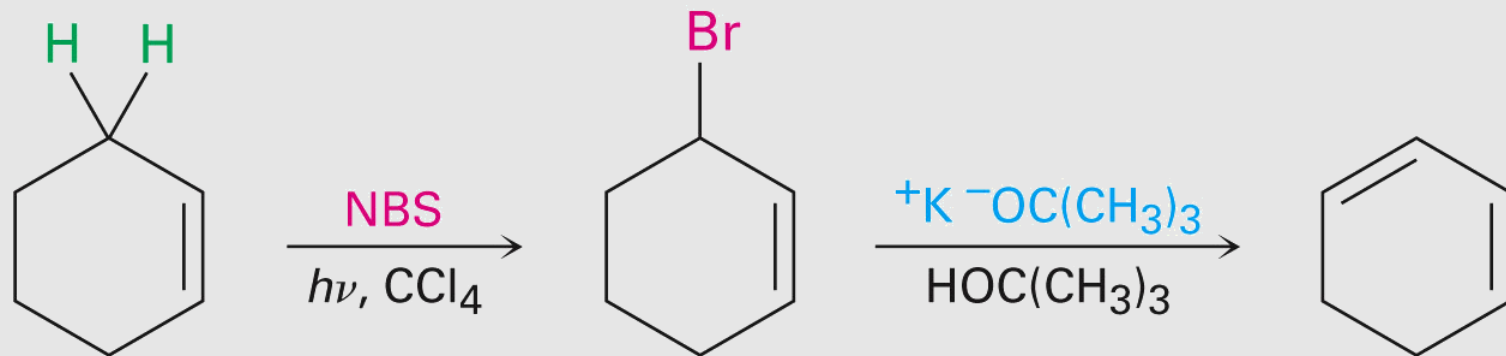


- Conjugated compounds are common in nature
- Extended conjugation leads to absorption of visible light, producing color
- Conjugated hydrocarbon with many double bonds are polyenes (lycopene is responsible for red color in tomatoes)
- Examine properties of conjugated molecules and reasons for the properties

14.1 Stability of Conjugated Dienes: Molecular Orbital Theory



- Typically by elimination in allylic halide
- Specific industrial processes for large scale production of commodities by catalytic dehydrogenation and dehydration



Cyclohexene

3-Bromocyclohexene

1,3-Cyclohexadiene (76%)

Measuring Stability



- Conjugated dienes are more stable than nonconjugated based on heats of hydrogenation
- Hydrogenating 1,3-butadiene produces 17 kJ/mol less heat than 1,4-pentadiene

	$\Delta H^\circ_{\text{hydrog}}$ (kJ/mol)	
$\text{H}_2\text{C}=\text{CHCH}_2\text{CH}=\text{CH}_2$	$-126 + (-126) = -252$	Expected
1,4-Pentadiene	<hr/> -253	Observed
	1	Difference
$\text{H}_2\text{C}=\text{CHCH}=\text{CH}_2$	$-126 + (-126) = -252$	Expected
1,3-Butadiene	<hr/> -236	Observed
	-16	Difference

Molecular Orbital Description of 1,3-Butadiene

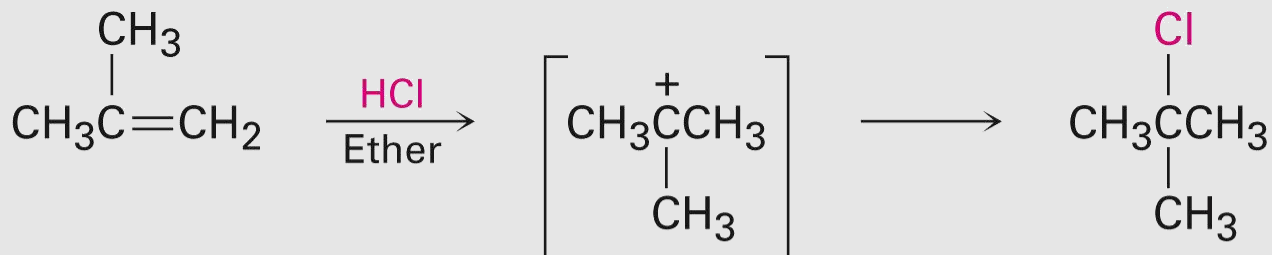


- The single bond between the conjugated double bonds is shorter and stronger than normal
- The bonding π -orbitals are made from 4 p orbitals that provide greater delocalization and lower energy than in isolated C=C
- The 4 molecular orbitals include fewer total nodes than in the isolated case (See Figures 14-1 and 14-2)
- In addition, the single bond between the two double bonds is strengthened by overlap of p orbitals
- In summary, we say electrons in 1,3-butadiene are delocalized over the π bond system
 - Delocalization leads to stabilization

14.2 Electrophilic Additions to Conjugated Dienes



- Review: addition of electrophile to C=C
 - Markovnikov regiochemistry via more stable carbocation



2-Methylpropene

**Tertiary
carbocation**

2-Chloro-2-methylpropane



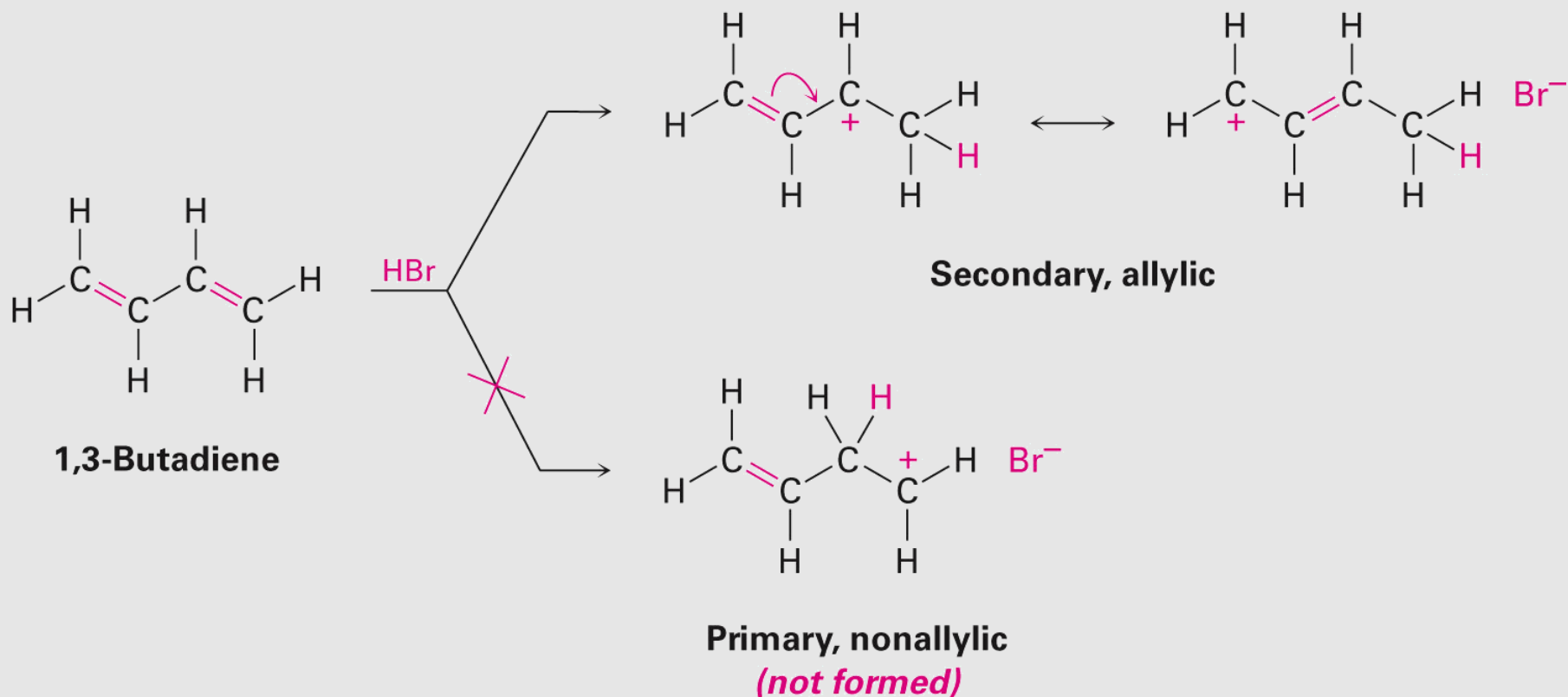
**1,4-Pentadiene
(nonconjugated)**

2,4-Dichloropentane

Carbocations from Conjugated Dienes



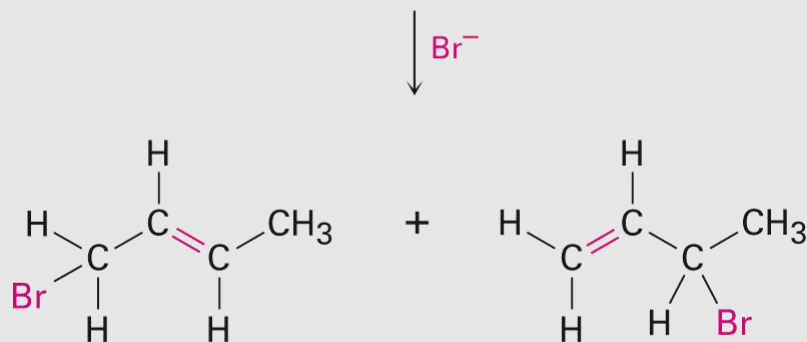
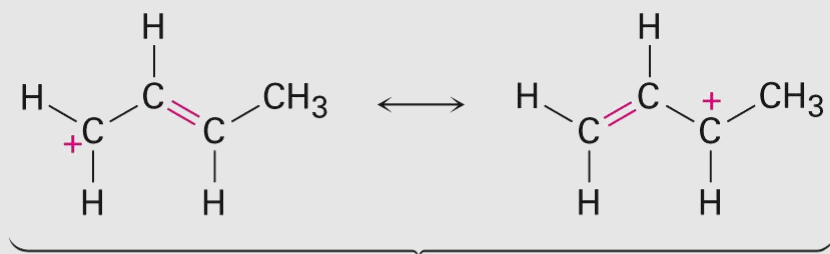
- Addition of H^+ leads to delocalized secondary allylic carbocation



Products of Addition to Delocalized Carbocation

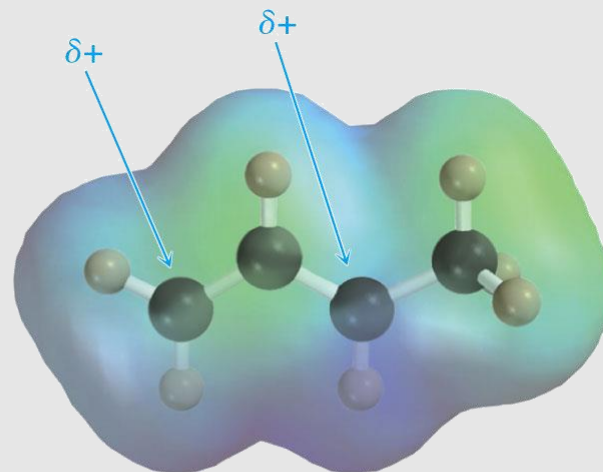


- Nucleophile can add to either cationic site
- The transition states for the two possible products are not equal in energy



1,4-Addition
(29%)

1,2-Addition
(71%)



14.3 Kinetic vs. Thermodynamic Control of Reactions

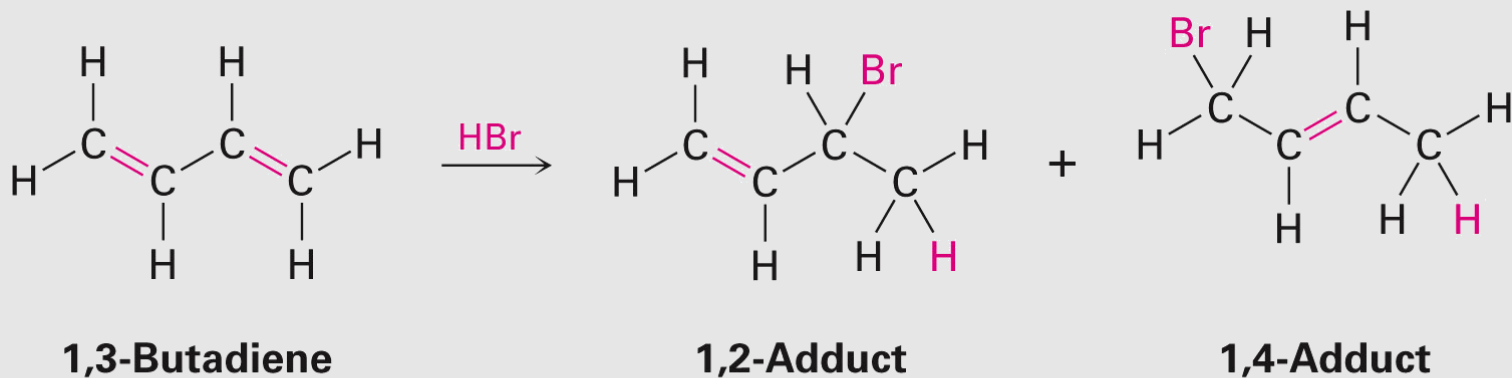


- At completion, all reactions are at equilibrium and the relative concentrations are controlled by the differences in free energies of reactants and products (**Thermodynamic Control**)
- If a reaction is irreversible or if a reaction is far from equilibrium, then the relative concentrations of products depends on how fast each forms, which is controlled by the relative free energies of the transition states leading to each (**Kinetic Control**)

Kinetic and Thermodynamic Control Example



- Addition to a conjugated diene at or below room temperature normally leads to a mixture of products in which the 1,2 adduct predominates over the 1,4 adduct
- At higher temperature, the product ratio changes and the 1,4 adduct predominates



At 0 °C: 71%

29%

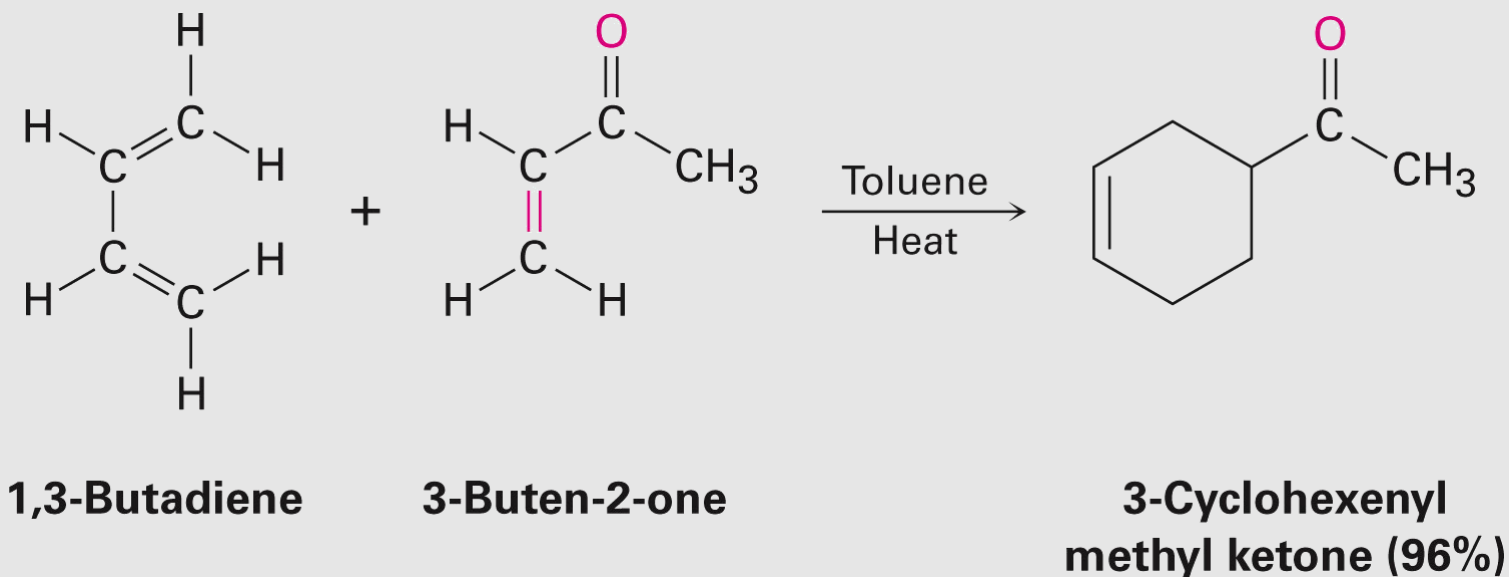
At 40 °C: 15%

85%

14.4 The Diels-Alder Cycloaddition Reaction



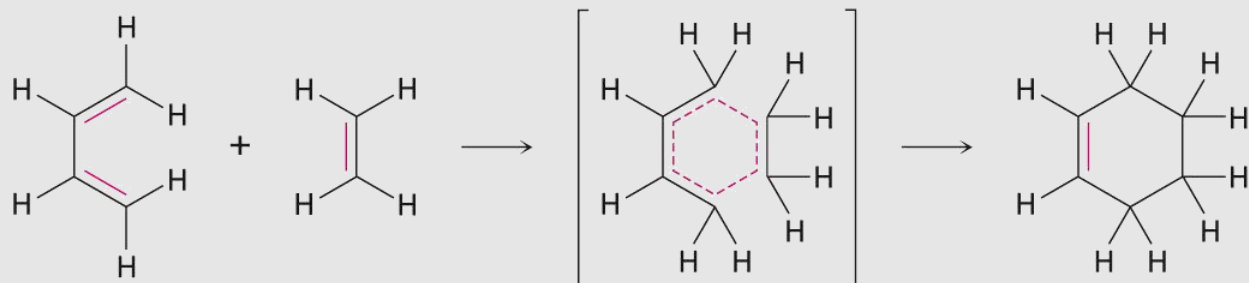
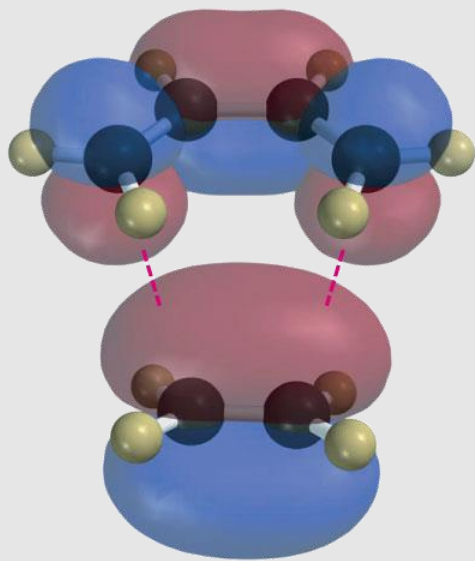
- Conjugate dienes can combine with alkenes to form six-membered cyclic compounds
- The formation of the ring involves no intermediate (concerted formation of two bonds)
- Discovered by Otto Paul Hermann Diels and Kurt Alder in Germany in the 1930's



View of the Diels-Alder Reaction



- Woodward and Hoffmann showed this reaction to be an example of the general class of *pericyclic reactions*
- Involves orbital overlap, change of hybridization and electron delocalization in transition state
- The reaction is called a *cycloaddition*

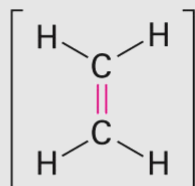


14.5 Characteristics of the Diels-Alder Reaction

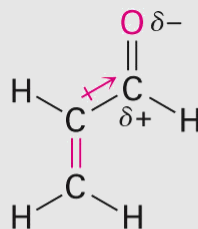


- The alkene component is called a **dienophile**
 - C=C is conjugated to an electron withdrawing group, such as C=O or C≡N
 - Alkynes can also be dienophiles

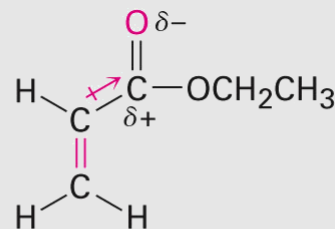
Some
Diels-Alder
dienophiles



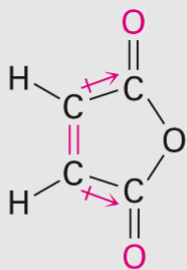
Ethylene:
unreactive



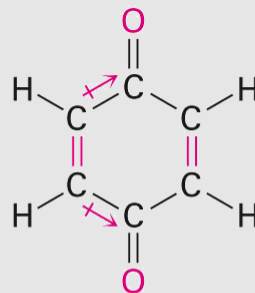
Propenal
(acrolein)



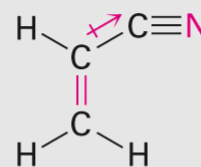
Ethyl propenoate
(ethyl acrylate)



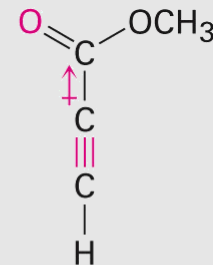
Maleic anhydride



Benzoquinone



Propenenitrile
(acrylonitrile)

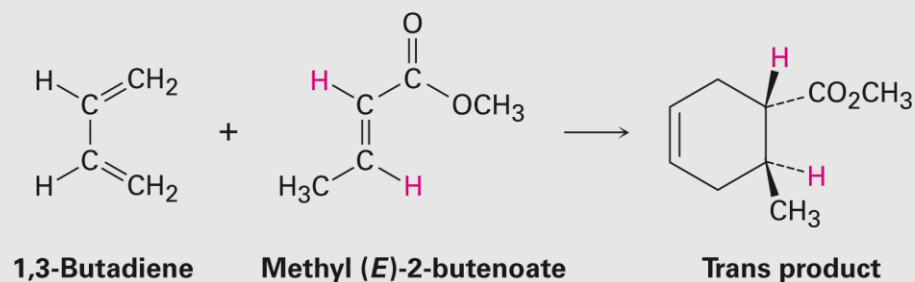
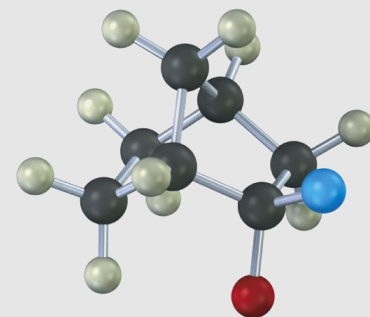
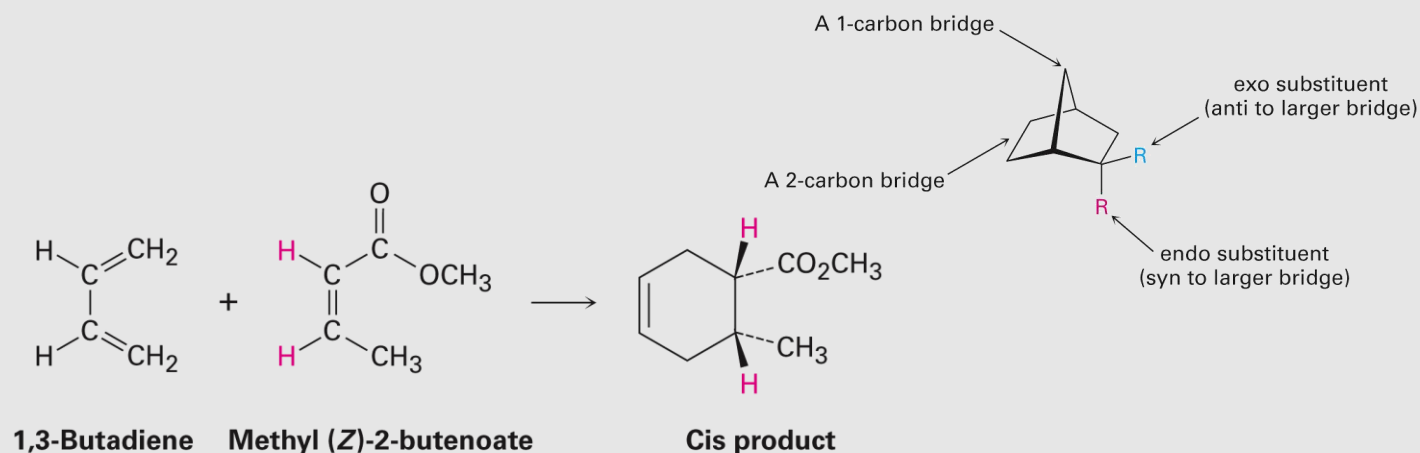


Methyl
propynoate

Stereospecificity of the Diels-Alder Reaction



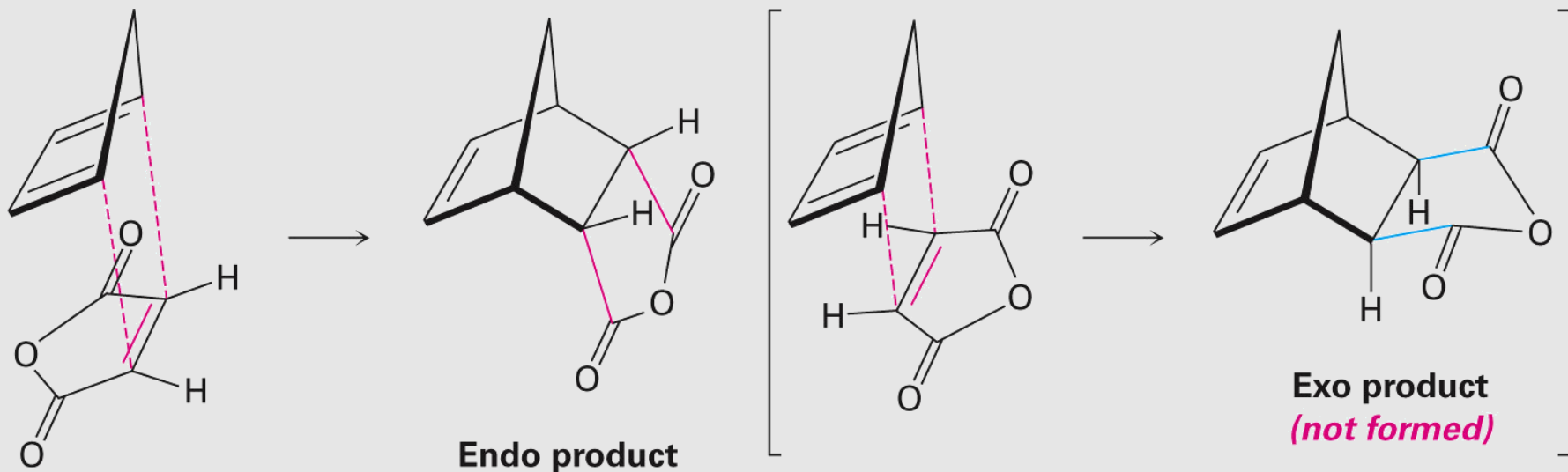
- The reaction is **stereospecific**, maintaining relative relationships from reactant to product
 - There is a one-to-one relationship between stereoisomeric reactants and products



Regiochemistry of the Diels-Alder Reaction



- Reactants align to produce *endo* (rather than *exo*) product
 - *endo* and *exo* indicate relative stereochemistry in bicyclic structures
 - Substituent on one bridge is *exo* if it is *anti* (*trans*) to the larger of the other two bridges and *endo* if it is *syn* (*cis*) to the larger of the other two bridges

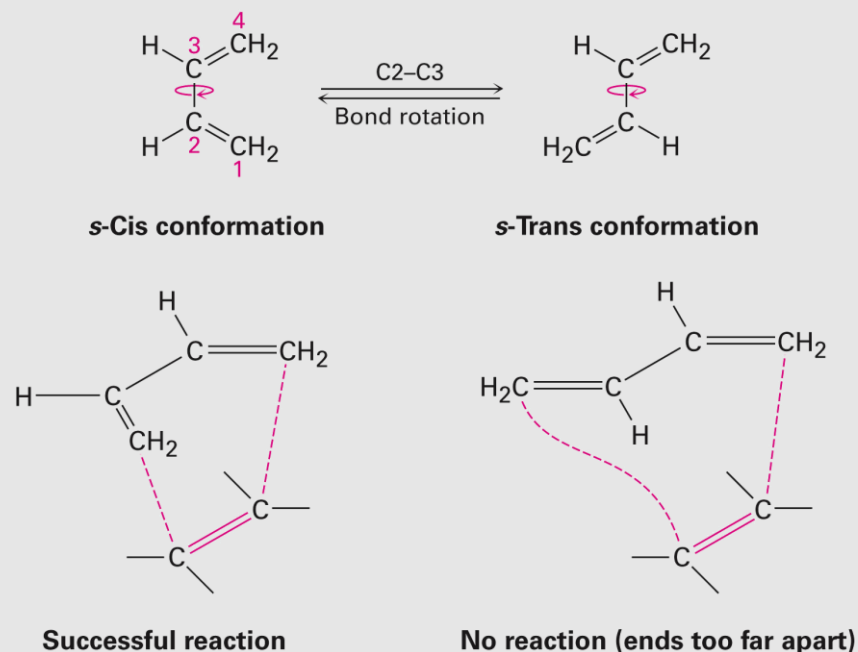
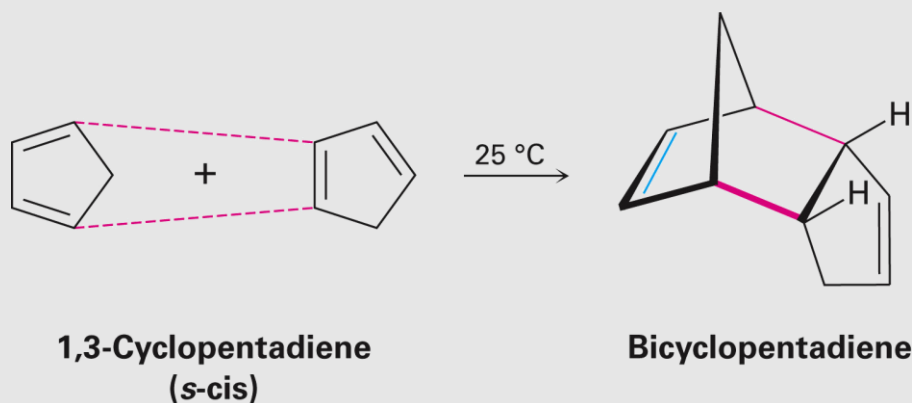


Maleic anhydride

Conformations of Dienes in the Diels-Alder Reaction



- The relative positions of the two double bonds in the diene are “*cis*” or “*trans*” to each other about the single bond (being in a plane maximizes overlap)
- These conformations are called *s-cis* and *s-trans* (“*s*” stands for “single bond”)
- Dienes react in the *s-cis conformation* in the Diels-Alder reaction



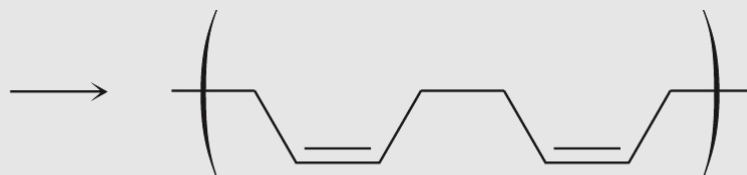
14.6 Diene Polymers: Natural and Synthetic Rubbers



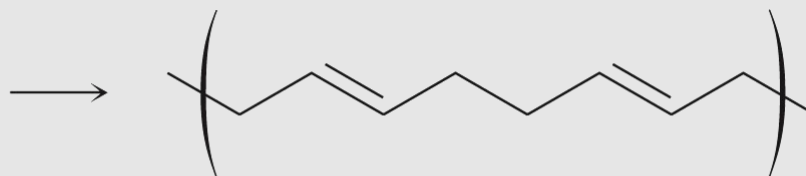
- Conjugated dienes can be polymerized
- The initiator for the reaction can be a radical, or an acid
- Polymerization: 1,4 addition of growing chain to conjugated diene monomer



1,3-Butadiene



cis-Polybutadiene

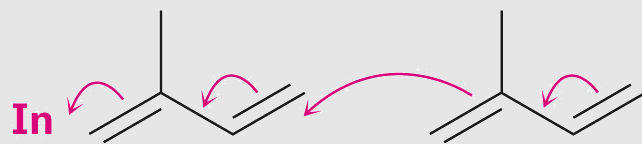


trans-Polybutadiene

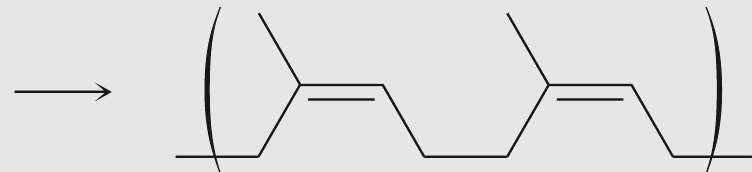
Natural Rubber



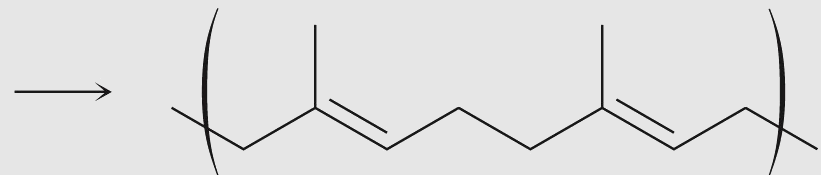
- A material from latex, in plant sap
- In rubber repeating unit has 5 carbons and **Z** stereochemistry of all C=C
 - Gutta-Percha is natural material with **E** in all C=C
- Looks as if it is the head-to-tail polymer of isoprene (2-methyl-1,3-butadiene)



Isoprene
(2-methyl-1,3-butadiene)



Natural rubber (**Z**)

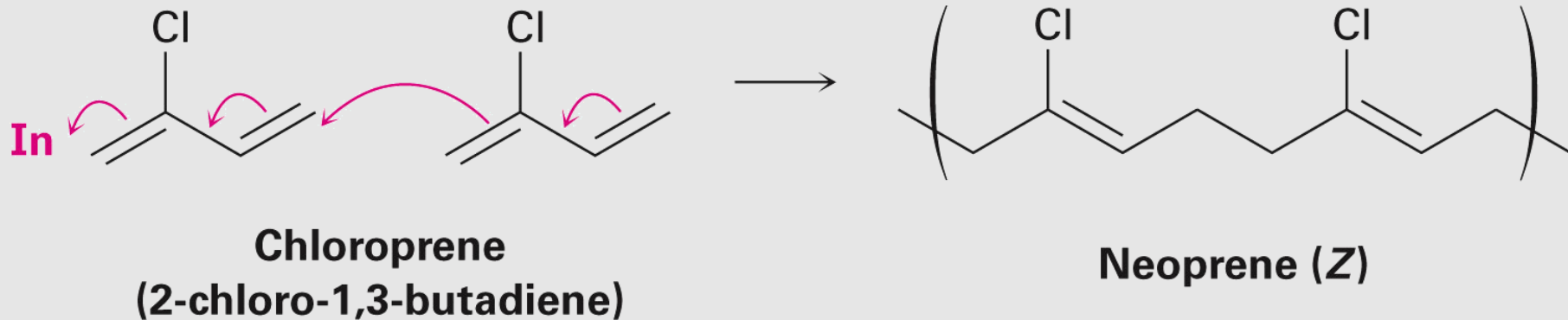


Gutta-percha (**E**)

Synthetic Rubber



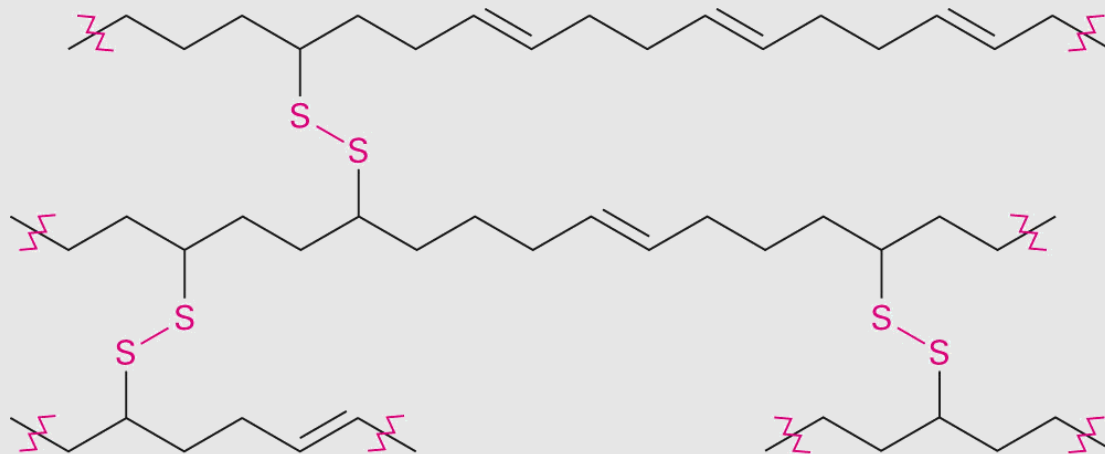
- Chemical polymerization of isoprene does not produce rubber (stereochemistry is not controlled)
- Synthetic alternatives include neoprene, polymer of 2-chloro-1,3-butadiene
- This resists weathering better than rubber



Vulcanization



- Natural and synthetic rubbers are too soft to be used in products
- Charles Goodyear discovered heating with small amount of sulfur produces strong material
- Sulfur forms bridges between hydrocarbon chains (cross-links)



14.7 Structure Determination in Conjugated Systems: UV Spectroscopy

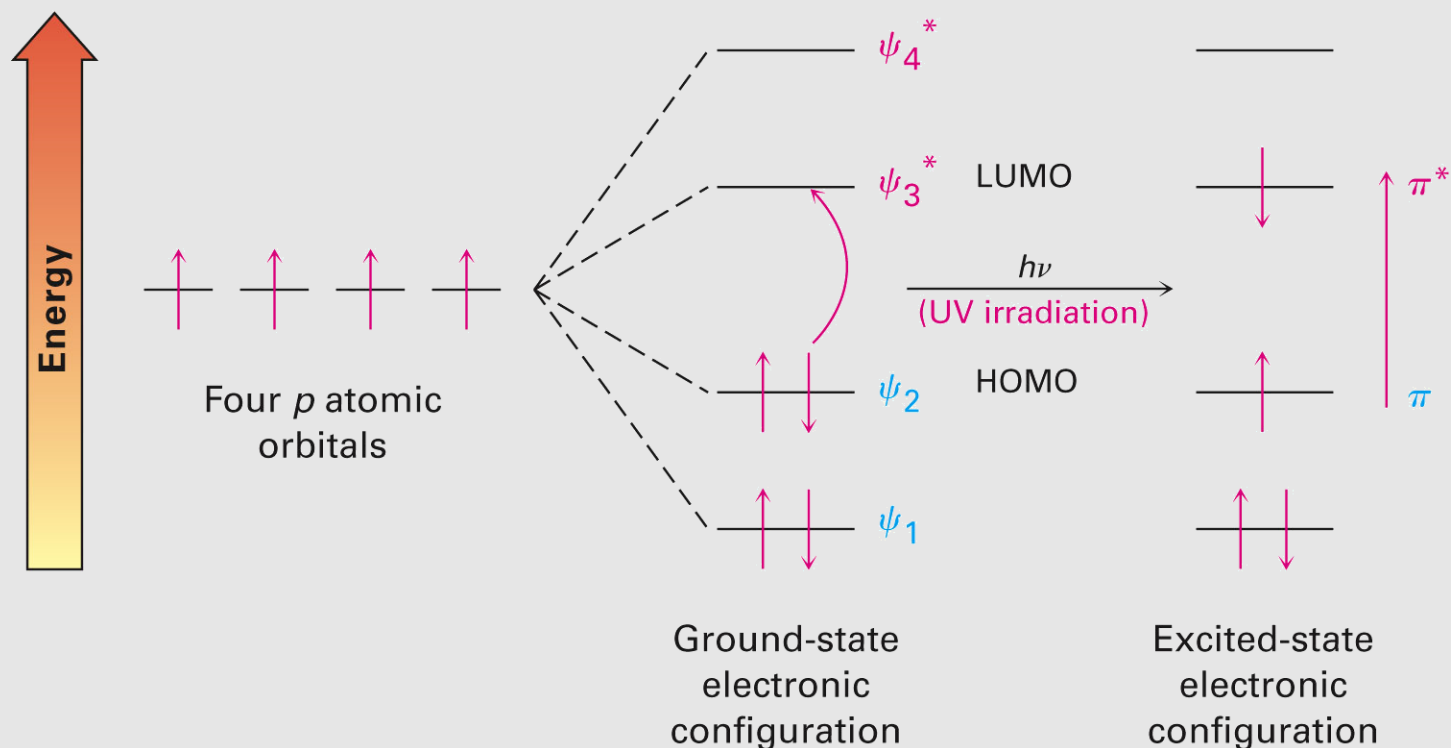


- Conjugated compounds can absorb light in the ultraviolet region of the spectrum
- The electrons in the highest occupied molecular orbital (HOMO) undergo a transition to the lowest unoccupied molecular orbital (LUMO)
- The region from $2 \times 10^{-7}\text{m}$ to $4 \times 10^{-7}\text{m}$ (200 to 400 nm) is most useful in organic chemistry
- A plot of absorbance (log of the ratio of the intensity of light in over light transmitted) against wavelength in this region is an **ultraviolet spectrum** – see Figure 14-11

Ultraviolet Spectrum of 1,3-Butadiene



- Example: 1,3-butadiene has four π molecular orbitals with the lowest two occupied
- Electronic transition is from HOMO to LUMO at 217 nm (peak is broad because of combination with stretching, bending)



Quantitative Use of UV Spectra



- Absorbance for a particular compound in a specific solvent at a specified wavelength is directly proportional to its concentration
- You can follow changes in concentration with time by recording absorbance at the wavelength
- Beers' law: $\text{absorbance} = \epsilon c l$
 - “ ϵ ” is molar absorptivity (extinction coefficient)
 - “ c ” is concentration in mol/L
 - “ l ” is path of light through sample in cm

14.8 Interpreting UV Spectra: The Effect of Conjugation

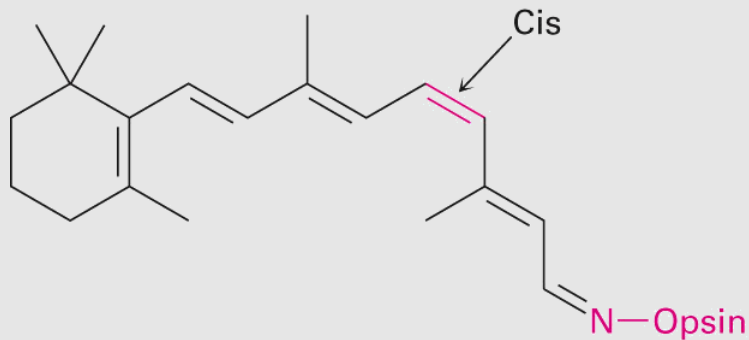


- λ_{\max} : wavelength where UV absorbance for a compound is greatest
- Energy difference between HOMO and LUMO decreases as the extent of conjugation increases
- λ_{\max} increases as conjugation increases (lower energy)
 - 1,3-butadiene: 217 nm, 1,3,5-hexatriene: 258 nm
- Substituents on π system increase λ_{\max}
- See Table 14-2

14.9 Conjugation, Color, and the Chemistry of Vision

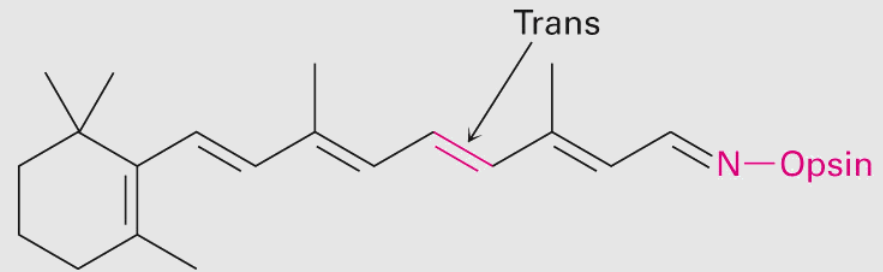


- Visible region is about 400 to 800 nm
- Extended systems of conjugation absorb in visible region
- β -Carotene, 11 double bonds in conjugation, $\lambda_{\text{max}} = 455 \text{ nm}$
- Visual pigments are responsible for absorbing light in eye and triggering nerves to send signal to brain



Rhodopsin

Light \rightarrow

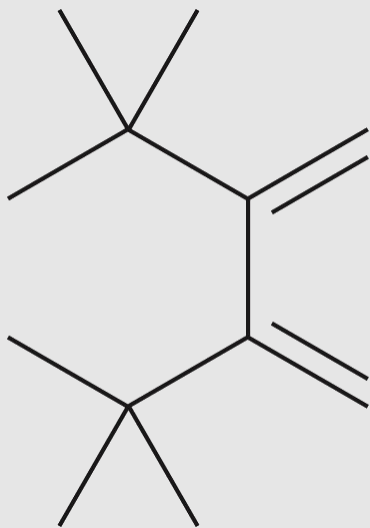


Metarhodopsin II

Let's Work a Problem



Explain why 2,3-di-*tert*-butyl-1,3-butadiene does not undergo Diels-Alder reactions.



2,3-Di-*tert*-butyl-1,3-butadiene

Answer



This compound has the tertiary butyl groups in a *cis* relationship with each other. This brings about a steric strain from the proximity of the bulky substituents. As a result, the compounds undergoes a change to a trans conformation to relieve strain, but Diels-Alder reaction cannot take place.