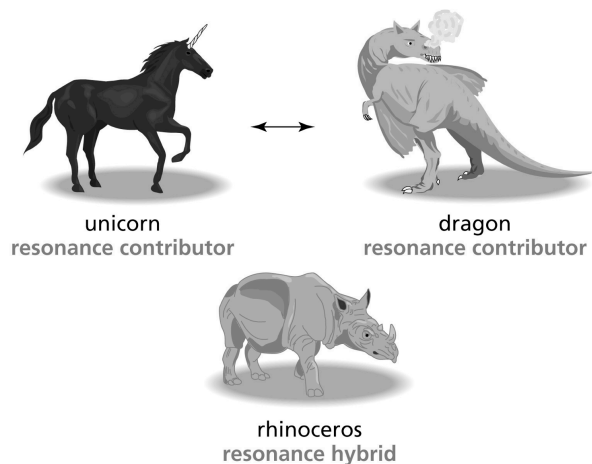


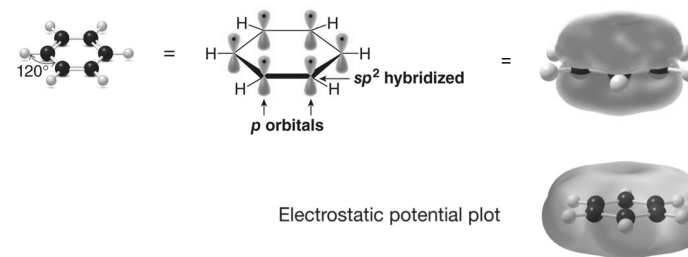
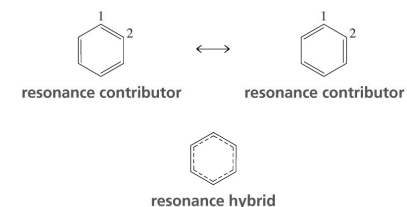
# Conjugated Unsaturated Systems

## Chapter 16



## Benzene, C<sub>6</sub>H<sub>6</sub>

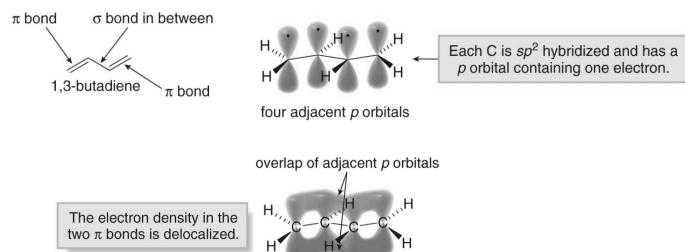
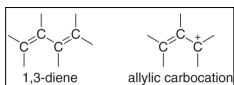
- Resonance contributors are imaginary, but the resonance hybrid is real.
- Benzene is a planar molecule.
- All six of the C-C bond lengths are identical.
- Each p electron is shared by all six carbons in a π-bonding system.
- The π electrons are **delocalized**.



L - 2

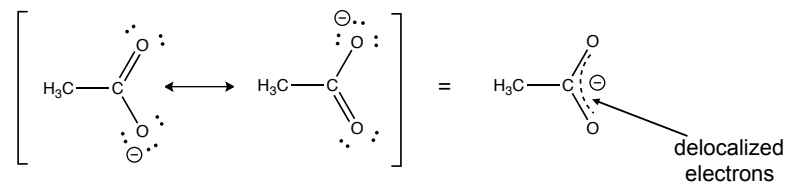
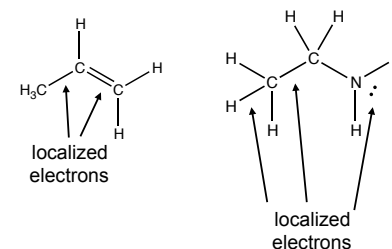
## Conjugation & Delocalization

- Conjugation** occurs whenever p orbitals can overlap on three or more adjacent atoms.
- The four p orbitals on adjacent atoms make a 1,3-diene a conjugated system.
- The p orbital at the allylic position is in conjugation with the double bond.
- Having three or more p orbitals on adjacent atoms allows p orbitals to overlap and electrons to **delocalize**.



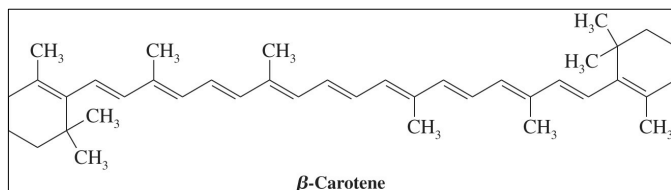
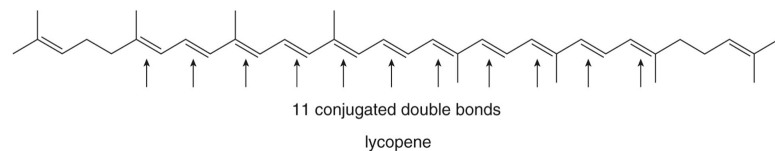
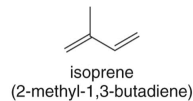
- When p orbitals overlap, the electron density in each of the π bonds is spread out over a larger volume, thus lowering the energy of the molecule and making it more stable.

## Localized vs. Delocalized Electrons



E - 4

## Conjugated, unsaturated, $\pi$ -delocalized systems

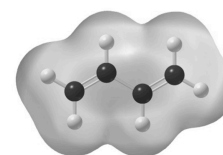
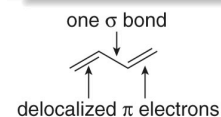


E - 5

## Dienes

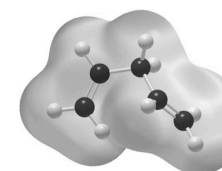
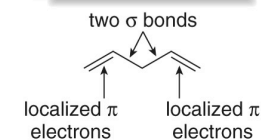
- 1,4-Pentadiene is an isolated diene.
- The  $\pi$  bonds in 1,4-pentadiene are too far apart to be conjugated and are isolated from each other by a  $sp^3$  carbon.

### 1,3-Butadiene— A conjugated diene



The red electron-rich region is spread over four adjacent atoms.

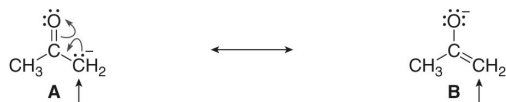
### 1,4-Pentadiene— An isolated diene



The red electron-rich regions are localized in the  $\pi$  bonds on the two ends of the molecule.

## Resonance, Hybridization, and Conjugation

There are two Lewis structures (A and B) for the resonance-stabilized acetone enolate anion ( $\text{CH}_3\text{COCH}_2^-$ )

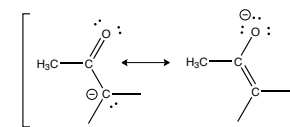


The C is surrounded by four groups—three atoms and one nonbonded electron pair.  
Is it  $sp^3$  hybridized?

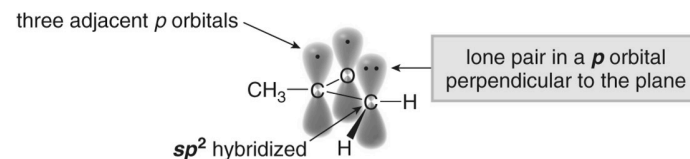
Here the C is surrounded by **three** groups—three atoms and no nonbonded electron pairs.  
Is it  $sp^2$  hybridized?

- Based on structure A, the indicated carbon is  $sp^3$  hybridized, with the lone pair of electrons in an  $sp^3$  hybrid orbital.
- Based on structure B, however, it is  $sp^2$  hybridized with the unhybridized  $p$  orbital forming the  $\pi$  portion of the double bond.

## $p$ -Orbitals Required for Conjugation



- Continue to consider the acetone enolate anion and its resonance structures.
- The electron pair on the oxygen atom adjacent to the  $\text{C}=\text{O}$  can only be delocalized if it has a  $p$  orbital that can overlap with two other  $p$  orbitals on adjacent atoms.
- The terminal carbon atom is  $sp^2$  hybridized with trigonal planar geometry.
- Three adjacent  $p$  orbitals make the anion conjugated.
- The actual hybrid has more of the charge on the oxygen and more  $\text{C}=\text{C}$  double bond character.

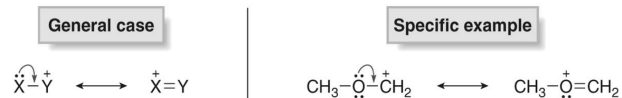




## Common Examples of Resonance

Type [3] Cations Having a Positive Charge Adjacent to a Lone Pair

- When a lone pair and a positive charge are located on adjacent atoms, two resonance structures can be drawn.

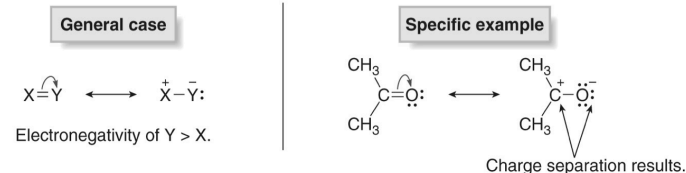


- The overall charge is the same in both resonance structures.
- Based on formal charge, a neutral X in one structure must bear a (+) charge in the other.

## Common Examples of Resonance

Type [4] Double Bonds Having One Atom More Electronegative Than the Other

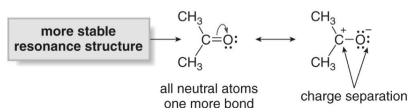
- For a double bond X=Y in which the electronegativity of Y > X, a second resonance structure can be drawn by moving the  $\pi$  electrons onto Y.



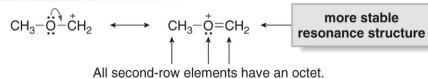
## The Resonance Hybrid is a Combination of Resonance Forms

- The actual hybrid resembles the most stable resonance structure(s).
- Three rules guide the assessment of the relative stability of resonance structures.

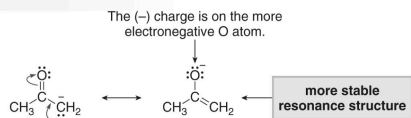
Rule [1] Resonance structures with more bonds and fewer charges are more stable.



Rule [2] Resonance structures in which every atom has an octet are more stable.

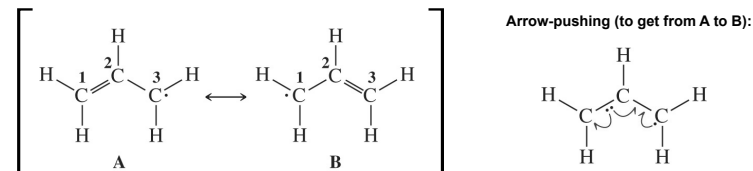


Rule [3] Resonance structures that place a negative charge on a more electronegative atom are more stable.

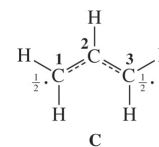


## Resonance (Valence Bond) Description of the Allyl Radical

- The allyl radical has two contributing resonance forms.
- The resonance structures are equivalent.
- Recall that equivalent resonance structures lead to much greater stability of the molecule than either structure alone would suggest.

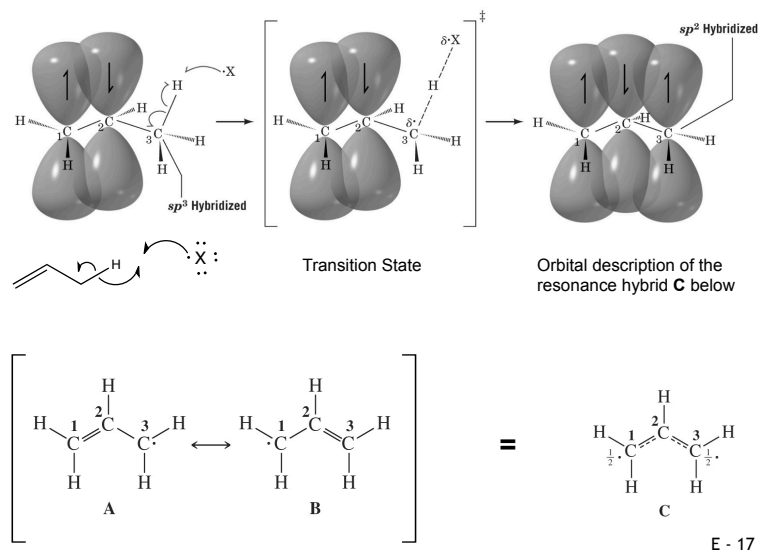


- The true structure of the allyl radical as suggested by resonance theory:





## Allyl Radical Formation & p-Orbital Overlap (Valence Bond Theory)

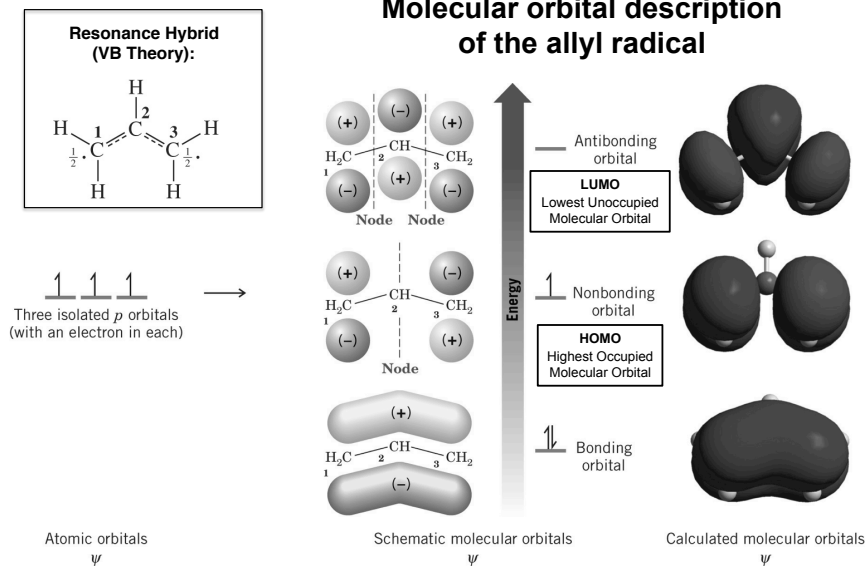


## Molecular Orbitals

- Molecular Orbitals (MO) Theory describes the molecular orbitals in molecules based on the mathematical combination of the wave functions for the overlapping atomic orbitals involved.
- Molecular orbital theory and valence bond (VB) theory (involving resonance) often describe very similar structures for compounds and predict very similar reactivities.
- However, VB theory does not properly account for some observed phenomena in reaction mechanisms and spectroscopy.
- MO theory is more consistent with observed data.
- For most of the reaction systems we study, both give a good approximation of the nature of the compounds and reactions.
- Wave functions and amplitude:
  - The lobes of the molecular orbitals are depicted with different colors, representing positive versus negative amplitudes of the wave functions.
  - In reactions, overlap of amplitudes with the same sign (or color) suggests a favorable interaction (lower energy) and overlap of opposite sign an unfavorable interaction (higher energy).

E - 18

## Molecular orbital description of the allyl radical



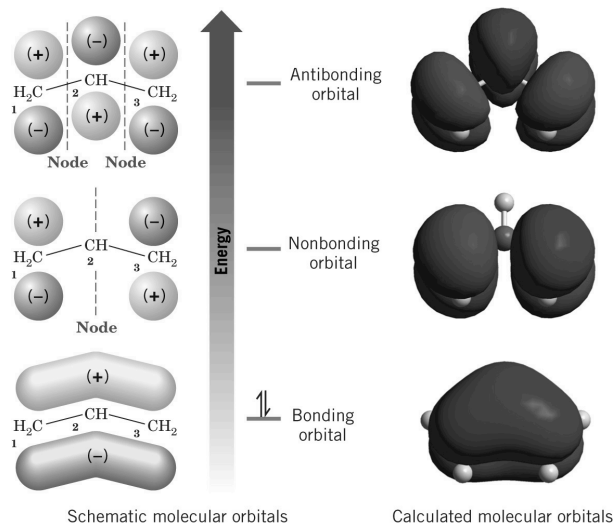
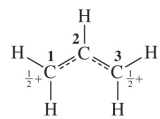
## Molecular orbitals in the allylic radical

- The three  $p$  orbitals of the allylic system combine to form three molecular orbitals.
- The bonding molecular orbital contains two spin-paired electrons and this orbital increases bonding between the carbons.
- The nonbonding orbital contains a lone electron which is located at carbons 1 and 3 only.
- The shape of the lowest energy molecular orbital is similar to the fully-conjugated system described by VB theory.
- The shape of the HOMO, or the *Highest Occupied Molecular Orbital* is consistent with the partial radical character on the two outer carbons in the resonance hybrid.
- The shape of the highest energy molecular orbital (which in this case also happens to be the LUMO or *Lowest Unoccupied Molecular Orbital*) is most similar to the shapes of the original  $p$ -orbitals, with the amplitudes inverted.
- In general, reactions of compounds involve either the HOMO, LUMO, or both.

E - 20

## The Allyl Cation – Molecular Orbital Theory

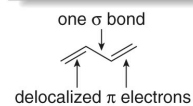
### Valence Bond Theory Resonance Hybrid:



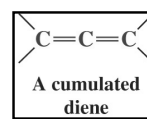
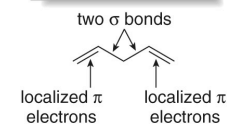
## Polyunsaturated Hydrocarbons

- Polyunsaturated compounds can be classified as being cumulated, conjugated or isolated.
- Conjugated dienes affect each other when they react, isolated double bonds react separately and do not affect each other.

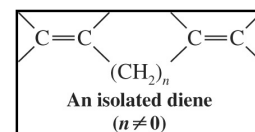
### 1,3-Butadiene— A conjugated diene



### 1,4-Pentadiene— An isolated diene

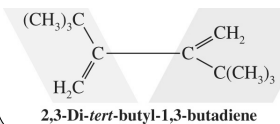


NOT conjugated

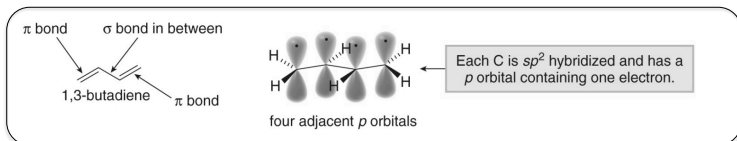


NOT conjugated

The molecule below does **not** behave like a conjugated diene because the large tert-butyl groups twist the structure and prevent the diene from being planar.



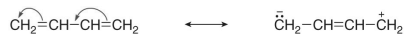
## Valence Bond Theory & 1,3-butadiene



### Three resonance structures for 1,3-butadiene

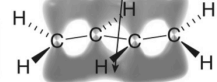


Or, moving electrons in the opposite direction:

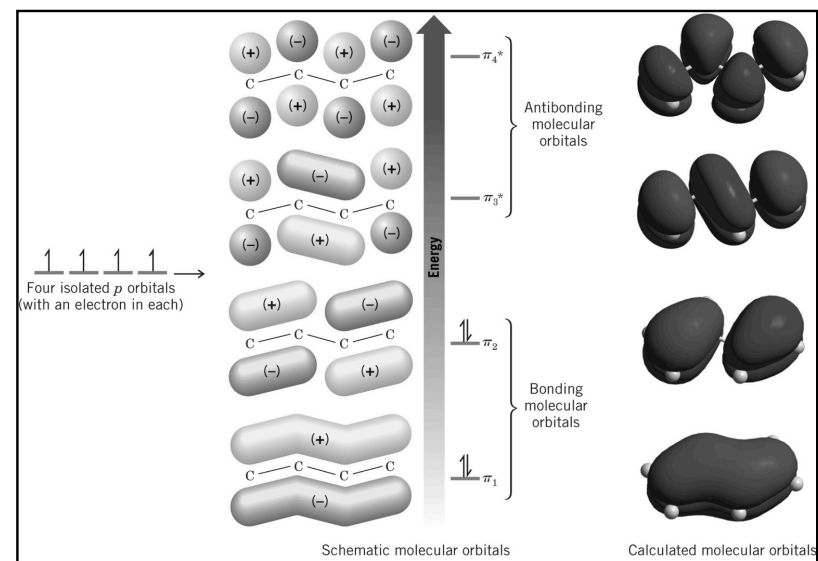


### overlap of adjacent $p$ orbitals

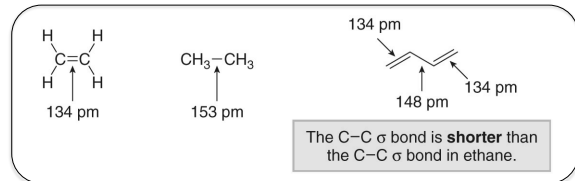
The electron density in the two  $\pi$  bonds is delocalized.



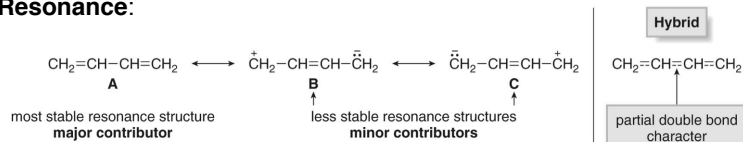
## Molecular Orbitals of 1,3-Butadiene



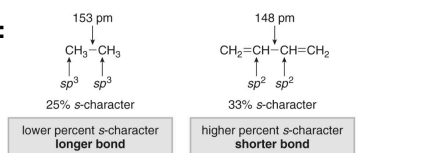
## Conjugated Diene Bond Lengths:



## Resonance:

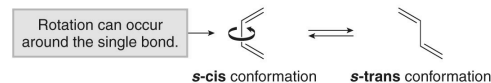


## Percent *s*-orbital Character:

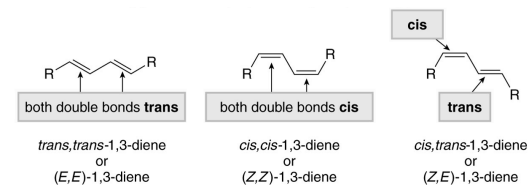


• Based on hybridization, a  $C_{sp^2}-C_{sp^2}$  bond should be shorter than a  $C_{sp^3}-C_{sp^3}$  bond because it is formed from orbitals having a higher percent *s*-character.

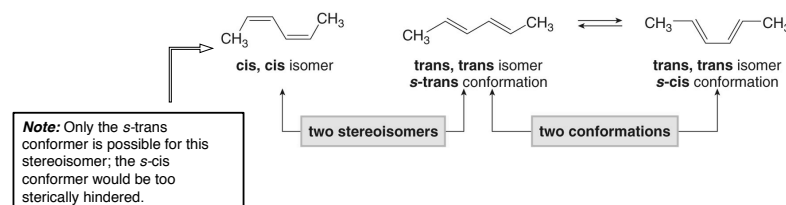
## Conjugated Diene Conformations:



## Conjugated Diene Stereoisomers:

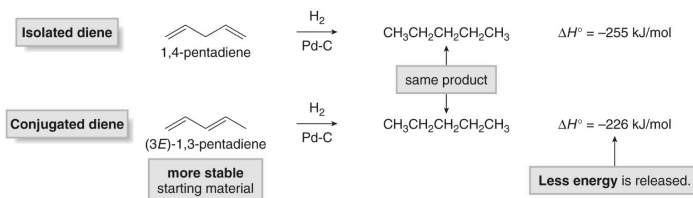


Be sure not to confuse conformational differences & stereoisomers:

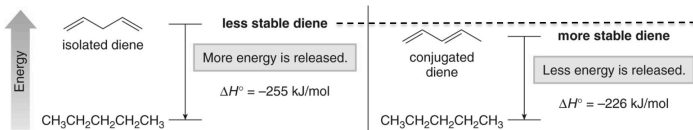


## Stability of Conjugated Dienes vs. Isolated Dienes

- When hydrogenation gives the same alkane from two dienes, the more stable diene has the smaller heat of hydrogenation.
- The conjugated diene is more stable by  $\sim 30$  kJ/mol.

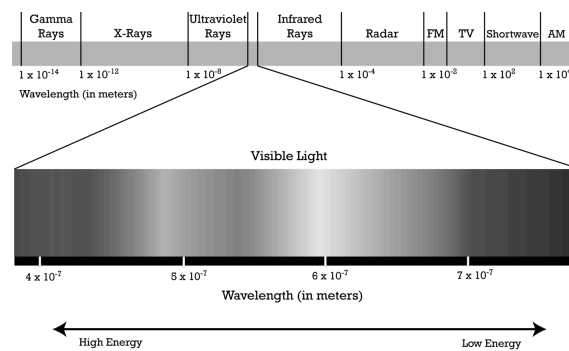


## Energy Diagram:



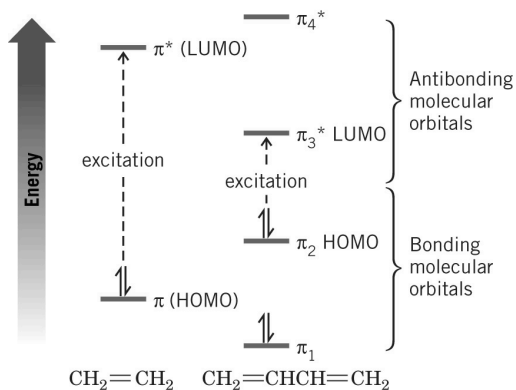
## Ultraviolet-Visible Spectroscopy

- Conjugated compounds absorb energy in the ultraviolet (UV) and visible (Vis) regions on the electromagnetic spectrum.
- The wavelength of radiation absorbed and the intensity of the absorption depend on the structure of the molecule.
- A UV-Vis spectrum is typically measured from 200-800 nm, spanning the near UV and visible regions.



## Absorbance in UV-Vis Spectroscopy

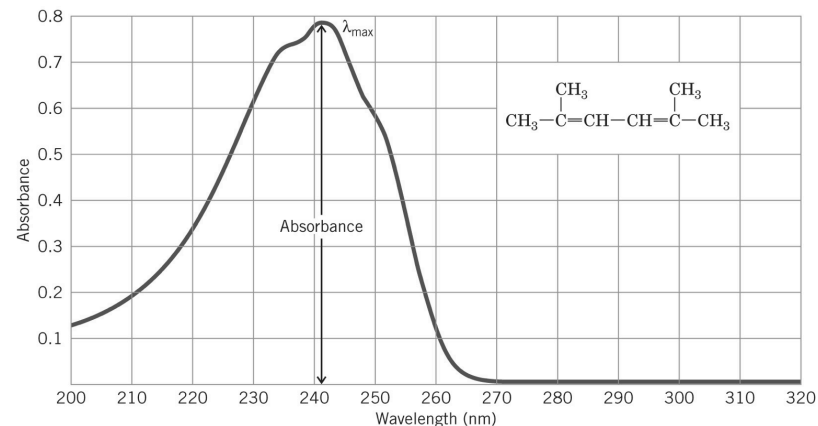
- In UV-Vis spectroscopy the electrons are excited from lower energy levels to higher ones.
- The electron is generally excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO).
- Alkenes and nonconjugated dienes have absorptions below 200 nm because the energy difference between the HOMO and LUMO is large.



- In conjugated dienes these energy levels are much closer together and the wavelengths of absorption are longer than 200 nm
- Ethene has  $\lambda_{\text{max}}$  at 171 nm and 1,3-butadiene has  $\lambda_{\text{max}}$  at 217 nm.

## UV absorption spectrum of 2,5-dimethyl-2,4-hexadiene

(in methanol at a concentration of  $5.95 \times 10^{-5}$  M in a 1.0 cm cell)



2,5-Dimethyl-2,4-hexadiene,  $\lambda_{\text{max}}^{\text{methanol}}$  242.5 nm

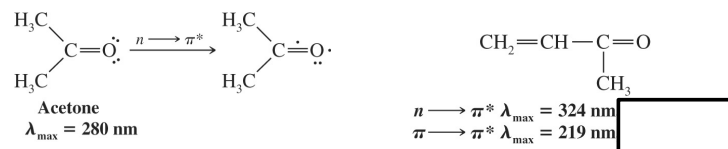
## Conjugated Dienes and Ultraviolet Light



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

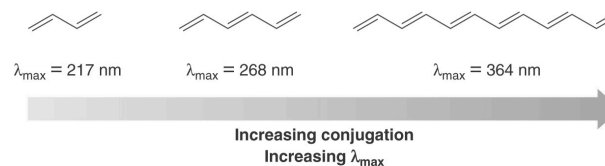
## Carbonyl Compounds

- Carbonyl compounds also absorb light in the UV region.
- An unshared electron on oxygen is promoted to a  $p^*$  orbital.

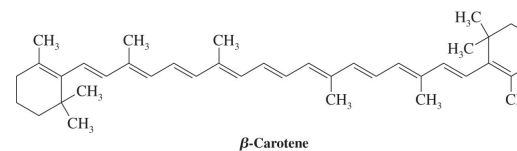


## Increasing Conjugation and Ultraviolet Light

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

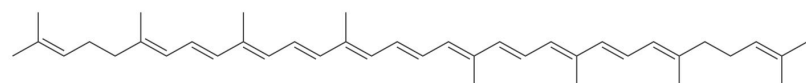


- $\beta$ -Carotene has 11 conjugated double bonds and an absorbance maximum at 497 nm which is in the blue-green region of the visible spectrum.
- $\beta$ -Carotene is perceived as red-orange, the complementary color of blue-green.



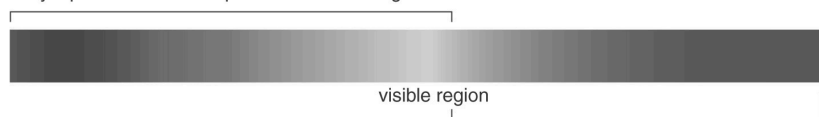
## Conjugated Dienes and Visible Light

- The longer the conjugated system, the smaller the energy difference between the HOMO and the LUMO.
- 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.

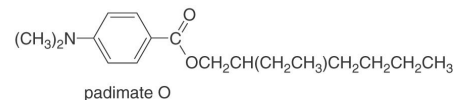
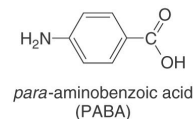


This part of the spectrum is *not* absorbed.

Lycopene appears red.

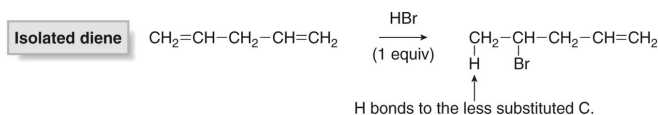
## Sunscreens

- UV radiation from the sun is high enough in energy to cleave bonds, forming radicals that can prematurely age skin and cause cancer.
- However, since much of this radiation is filtered out by the ozone layer, only UV light having wavelengths  $>290 \text{ nm}$  reaches the earth's surface.
- Much of this UV light is absorbed by melanin, the highly conjugated colored pigment in the skin that serves as the body's natural protection against the harmful effects of UV radiation. Prolonged exposure to the sun can allow more UV radiation to reach your skin than melanin can absorb.
- Sunscreens can offer some protection, because they contain conjugated compounds that absorb UV light, thus shielding the skin (for a time) from the harmful effects of UV radiation. Sunscreens are given an SPF rating (sun protection factor), according to the amount of sunscreen present.
- Two sunscreens that have been used for this purpose are para-aminobenzoic acid (PABA) and padimate O.

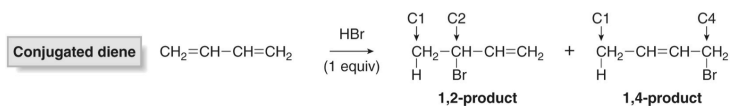


## Products of Electrophilic Addition

- Electrophilic addition of one equivalent of HBr to an isolated diene yields *one* product and Markovnikov's rule is followed.

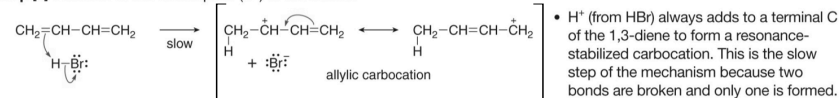


- Electrophilic addition in conjugated dienes gives a mixture of *two* products, called the 1,2- and 1,4-addition products.

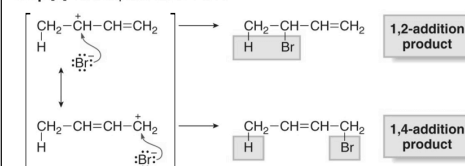


### Mechanism 16.1 Electrophilic Addition of HBr to a 1,3-Diene—1,2- and 1,4-Addition

**Step [1]** Addition of the electrophile ( $\text{H}^+$ ) to the  $\pi$  bond



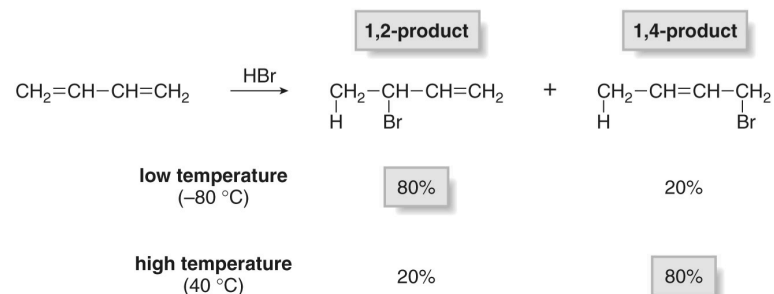
**Step [2]** Nucleophilic attack of  $\text{Br}^-$



- Nucleophilic attack of  $\text{Br}^-$  can occur at either site of the resonance-stabilized carbocation that bears a (+) charge, forming either the 1,2-addition product or the 1,4-addition product.

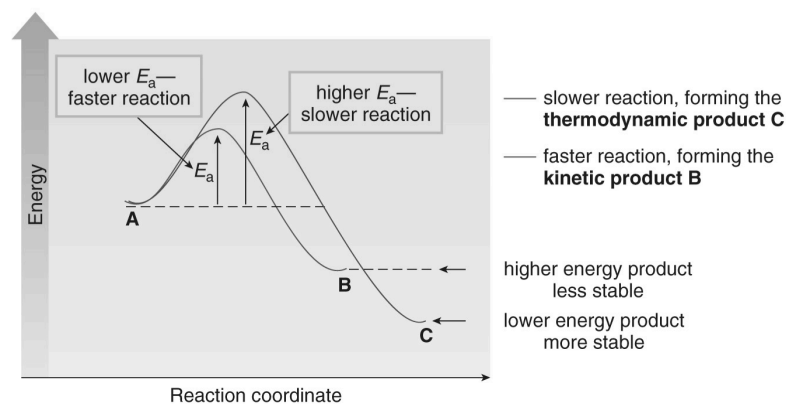
## Addition to 1,3-dienes: Reaction Conditions and Products

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

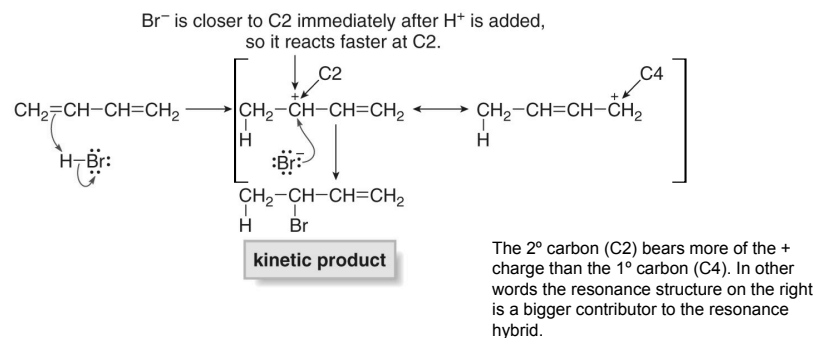


## How Kinetic vs. Thermodynamic Products Form (General)

- The rate of a reaction is determined by its energy of activation ( $E_a$ ), whereas the amount of product present at equilibrium is determined by its stability.

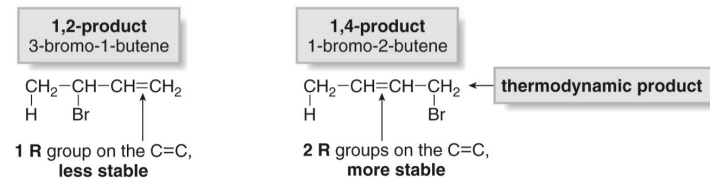


## Kinetic Effects for 1,2-Products



## Greater Stability of 1,4-Products

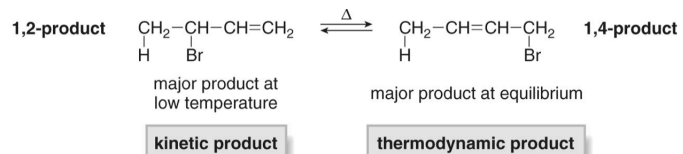
- The 1,4-product is more stable because it has two alkyl groups bonded to the carbon-carbon double bond, whereas the 1,2-product has only one.



- The more substituted alkene—1-bromo-2-butene in this case—is the thermodynamic product.

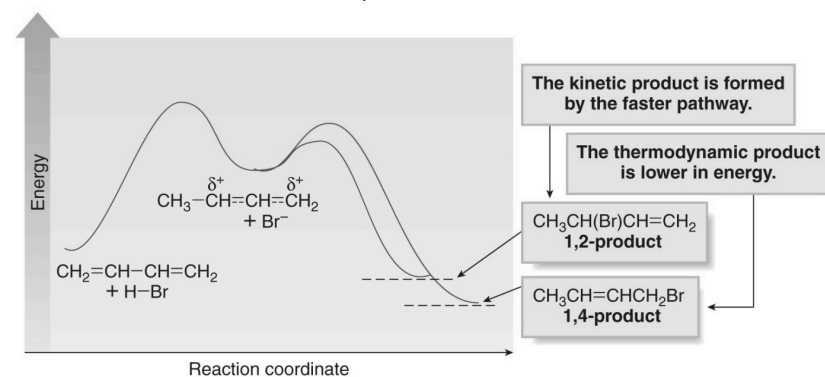
## Kinetic vs. Thermodynamic Products

- When a reaction 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*.

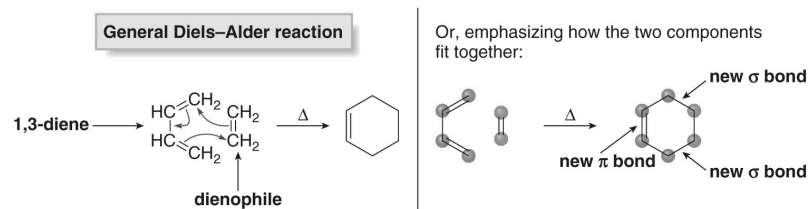
## Energy Diagram for the Two-Step Mechanism for the addition of HBr to 1,3-butadiene



- At low temperature, the lower energy of activation pathway is followed, since most molecules do not have enough energy to overcome the higher barrier.
- At higher temperature, most molecules have enough kinetic energy to reach either transition state and equilibrium favors the more stable product.

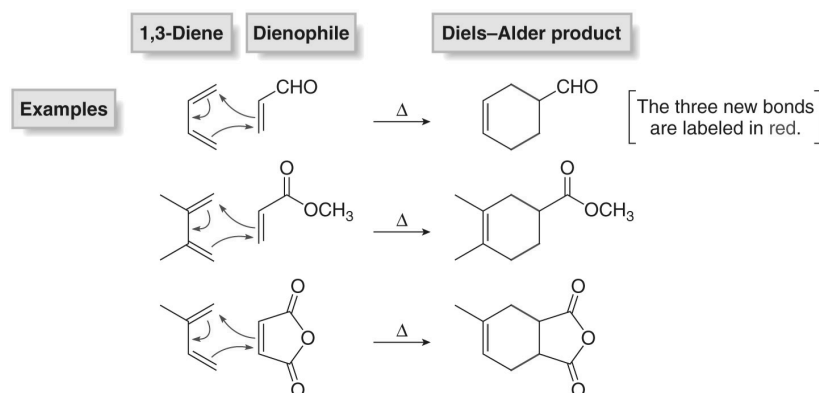
## The Diels–Alder Reaction

- The **Diels–Alder reaction** is an addition reaction between a **1,3-diene** and an alkene (called a **dienophile**), to form a new six-membered ring.

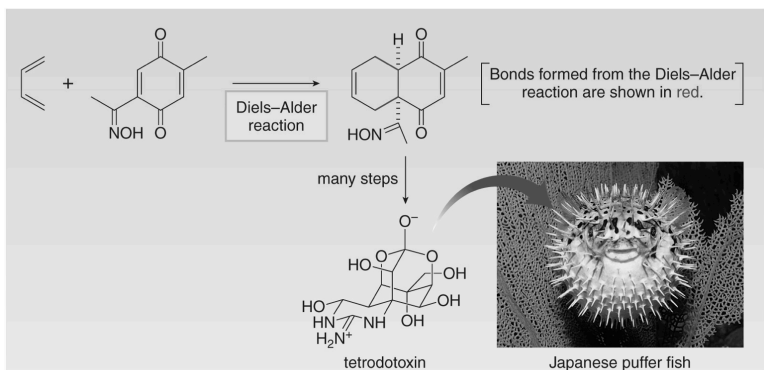


- Because each new  $\sigma$  bond is  $\sim 80$  kJ/mol stronger than a  $\pi$  bond that is broken, a typical Diels–Alder reaction releases  $\sim 160$  kJ/mol of energy.
- Heating is sometimes necessary to overcome the activation energy barrier, even though the reaction is exothermic.

## Examples of the Diels–Alder Reaction



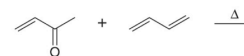
## Synthesis Using the Diels–Alder Reaction



- Tetrodotoxin, a complex natural product containing several six-membered rings joined together, is a poison isolated from the ovaries and liver of the puffer fish, so named because the fish inflates itself into a ball when alarmed. Eating fish tainted with trace amounts of this potent toxin results in weakness, paralysis, and eventually death. One step in the synthesis of tetrodotoxin involves forming a six-membered ring by a Diels–Alder reaction.

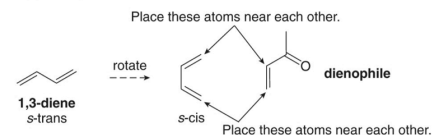
### How To Draw the Product of a Diels–Alder Reaction

**Example** Draw the product of the following Diels–Alder reaction:

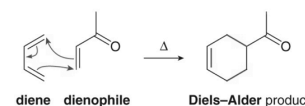


**Step [1]** Arrange the 1,3-diene and the dienophile next to each other, with the diene drawn in the *s-cis* conformation.

- This step is key: **Rotate the diene** so that it is drawn in the *s-cis* conformation, and place the end C's of the diene close to the double bond of the dienophile.



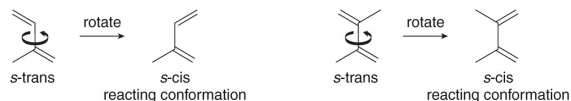
**Step [2]** Cleave the three  $\pi$  bonds and use arrows to show where the new bonds will be formed.



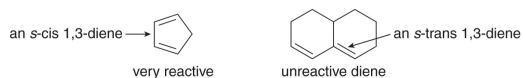
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## Rules of the Diels–Alder Reaction

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



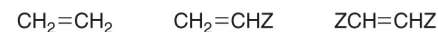
- This rotation is prevented in cyclic alkenes.
- When the two double bonds are constrained to an *s-cis* conformation, the diene is unusually reactive.
- When the two double bonds are constrained in the *s-trans* conformation, the diene is unreactive.



## Rules of the Diels–Alder Reaction

**2. Electron-withdrawing substituents in the dienophile increase the reaction rate.**

- In a Diels–Alder reaction, the conjugated diene acts as a nucleophile and the dienophile acts as an electrophile.
- Electron-withdrawing groups make the dienophile more electrophilic (and thus more reactive) by withdrawing electron density from the carbon–carbon double bond.
- If Z is an electron-withdrawing group, then the reactivity of the dienophile increases as follows:

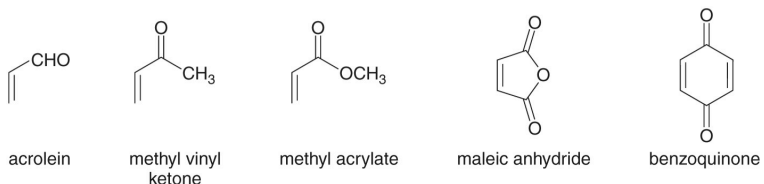


Increasing reactivity  $\rightarrow$



## Dienophiles in the Diels–Alder Reaction

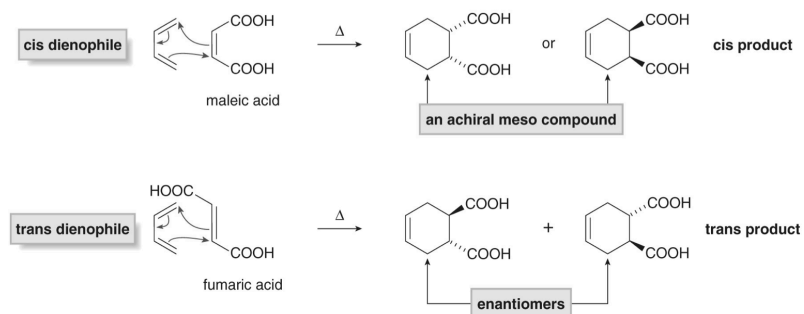
- A carbonyl group adjacent to the double bond is an effective electron-withdrawing group because it bears a partial positive charge ( $\delta^+$ ), which withdraws electron density from the carbon–carbon double bond of the dienophile.
- Some common dienophiles are shown below:



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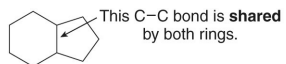
## Rules of the Diels–Alder Reaction

### 3. The stereochemistry of the dienophile is retained.



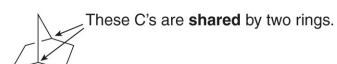
## Fused and Bridged Bicyclic Ring Systems

### A fused bicyclic system



- One bond is shared by two rings.
- The shared C's are adjacent.

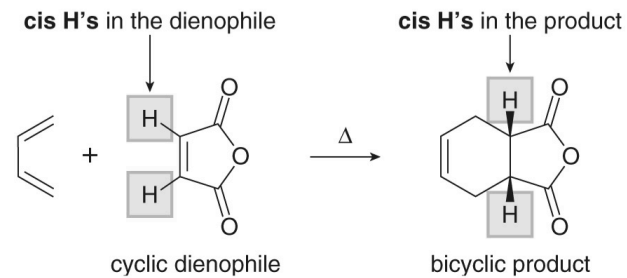
### A bridged bicyclic system



- Two non-adjacent atoms are shared by both rings.

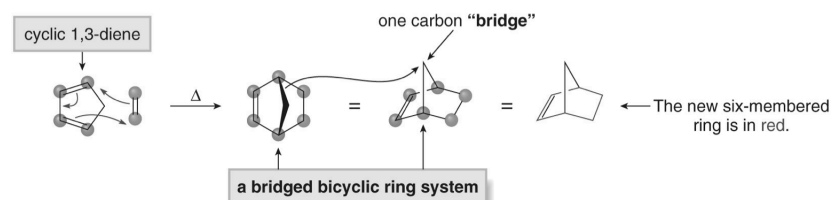
## Formation of Fused Ring Systems

- A cyclic dienophile forms a bicyclic product.
- A bicyclic system in which two rings share a common C–C bond is called a fused ring system.
- The two H atoms of the ring fusion must be *cis*, because they were *cis* in the starting dienophile.
- A bicyclic system of this sort is said to be *cis* fused.



## Formation of Bridged Bicyclic Ring Systems

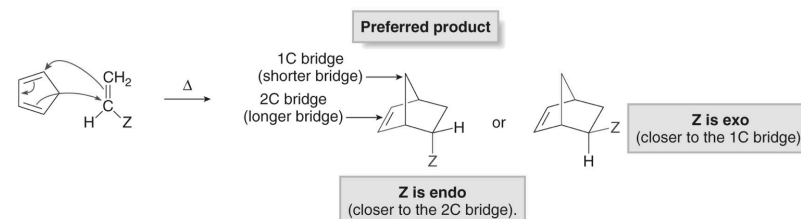
- When ethylene reacts with 1,3-cyclopentadiene, a new six-membered ring forms and above the ring there is a one atom "bridge."
- Thus, the product is bicyclic, but the carbon atoms shared by both rings are nonadjacent.
- A bicyclic ring system in which the two rings share nonadjacent carbon atoms is called a bridged ring system.



## Rules of the Diels–Alder Reaction

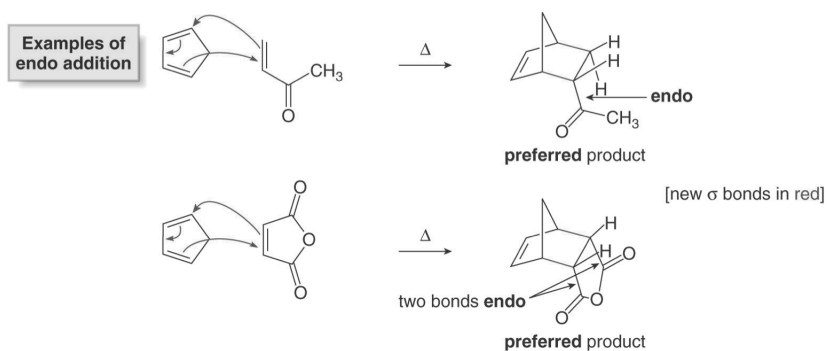
### 4. Preference for Endo Orientation

- When cyclopentadiene reacts with a substituted alkene as the dienophile ( $\text{CH}_2=\text{CHZ}$ ), the substituent Z can be oriented in one of two ways in the product, exo or endo.
- In these cases, the endo product is preferred.



## Endo Addition

- The transition state leading to the endo product allows more interaction between the electron-rich diene and the electron-withdrawing substituent Z on the dienophile.
- This is an energetically favorable arrangement.



## Mechanism for Endo and Exo Addition

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

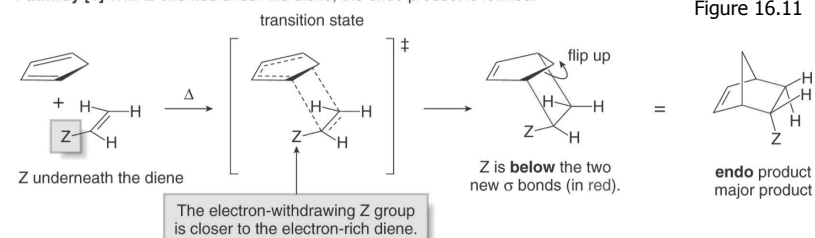
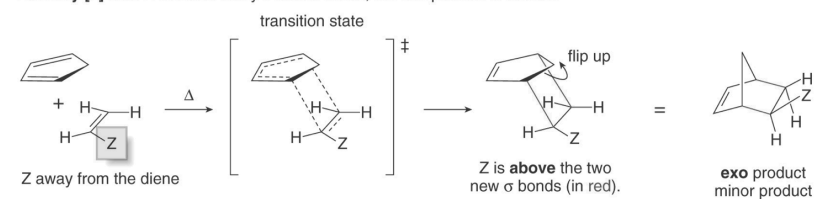
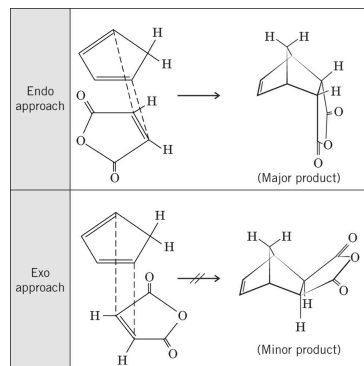


Figure 16.11

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



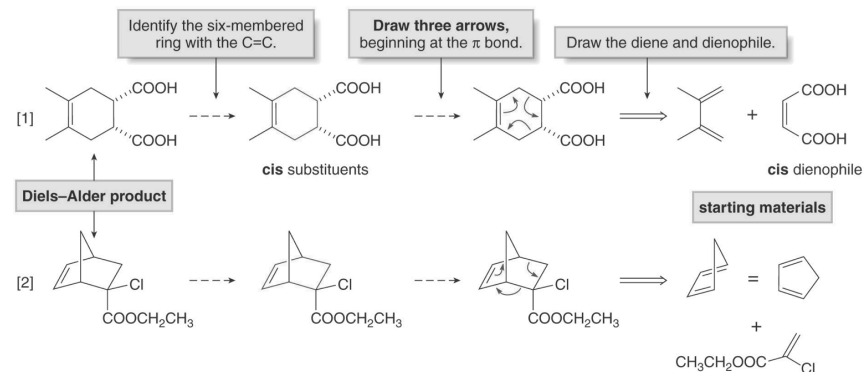
## Reaction of maleic anhydride and cyclopentadiene



[http://www.chemtube3d.com/DAendo\\_vs\\_exo.cyclopentadiene\\_and\\_maleic\\_anhydride.html](http://www.chemtube3d.com/DAendo_vs_exo.cyclopentadiene_and_maleic_anhydride.html)

## Retrosynthetic Analysis

To draw the starting materials from a given Diels-Alder adduct:

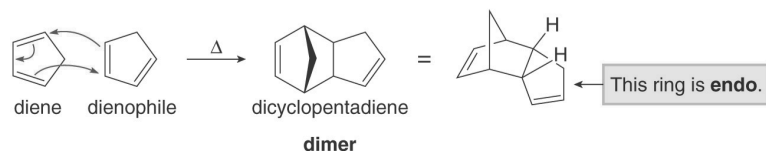


### Notes:

- Retain the stereochemistry of substituents on the C=C of the dienophile.
- Cis substituents on the six-membered ring give a cis dienophile.

## Diels-Alder Reaction Dimers

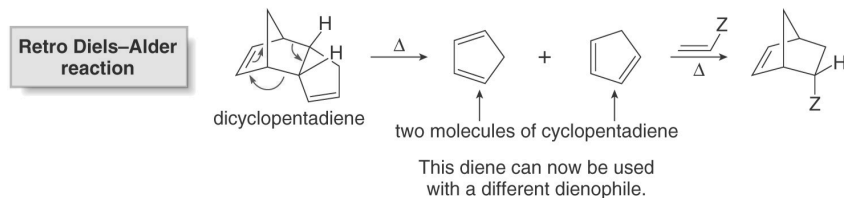
- A reactive molecule like 1,3-cyclopentadiene readily undergoes a Diels-Alder reaction with itself: that is, 1,3-cyclopentadiene dimerizes because one molecule acts as the diene and another acts as the dienophile.



- The formation of dicyclopentadiene is so rapid that it takes only a few hours at room temperature for cyclopentadiene to completely dimerize.

## The Retro Diels-Alder Reaction

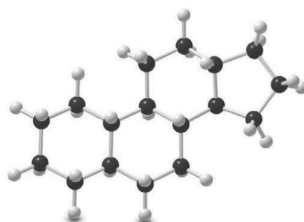
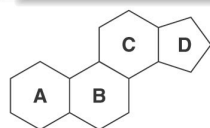
- When heated, dicyclopentadiene undergoes a retro Diels-Alder reaction, and two molecules of cyclopentadiene are re-formed.
- If the newly produced cyclopentadiene is immediately treated with a different dienophile, it reacts to form a new Diels-Alder adduct with this dienophile.
- This is how cyclopentadiene, used in Diels-Alder reactions, is produced.



## Steroid Synthesis

- Diels–Alder reactions have been widely used in the laboratory synthesis of steroids.
- Steroids are tetracyclic lipids containing three six-membered rings and one five-membered ring.
- The four rings are designated as A, B, C, and D.

### The steroid skeleton



three-dimensional view from above

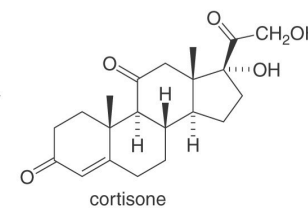
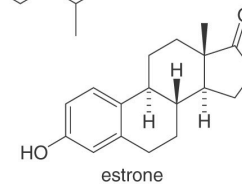
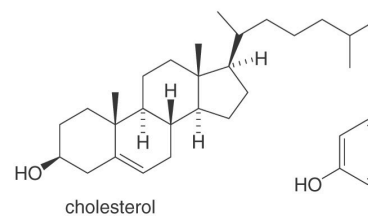


carbon skeleton viewed from the side

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

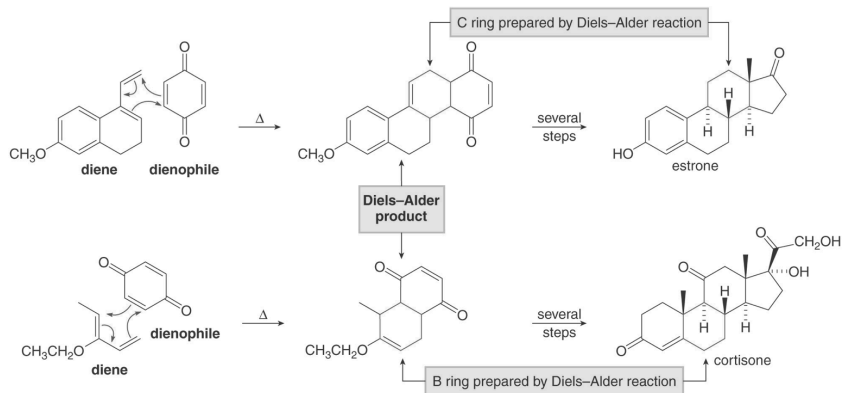
## Some Common Steroids

- Steroids exhibit a wide range of biological properties, depending on the substitution pattern of the functional groups on the rings.
- Some examples of steroids are below:

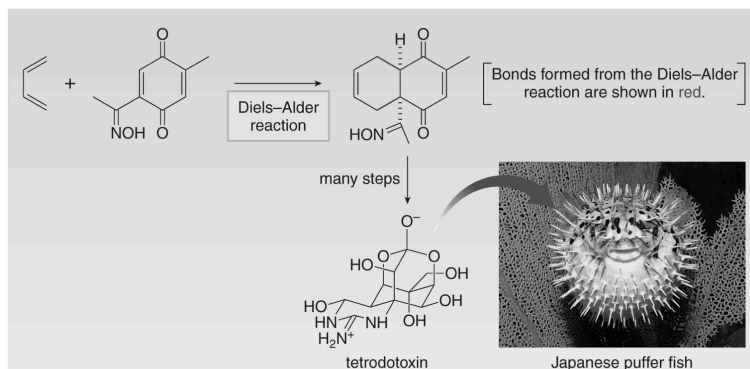


## Steroid Synthesis

- The key Diels–Alder reactions used to prepare the C ring of estrone and the B ring of cortisone are as follows:



## Synthesis Using the Diels–Alder Reaction



- Tetrodotoxin, a complex natural product containing several six-membered rings joined together, is a poison isolated from the ovaries and liver of the puffer fish, so named because the fish inflates itself into a ball when alarmed. Eating fish tainted with trace amounts of this potent toxin results in weakness, paralysis, and eventually death. One step in the synthesis of tetrodotoxin involves forming a six-membered ring by a Diels–Alder reaction.