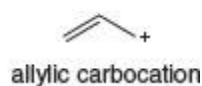
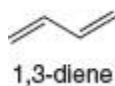


# Organic Chemistry Chapter 16: Conjugation, Resonance, and Dienes

## Conjugation

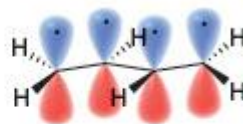
**Conjugation** occurs whenever *p* orbitals can overlap on three or more adjacent atoms. Two common conjugated systems are 1,3-dienes and allylic carbocations.



### 1,3-Dienes

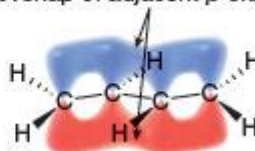


buta-1,3-diene  
one  $\sigma$  bond between the double bonds



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

overlap of adjacent *p* orbitals



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

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

A conjugated diene



buta-1,3-diene

The electrons in the  $\pi$  bonds are **delocalized**.

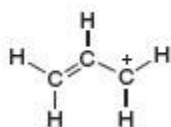
An isolated diene



penta-1,4-diene

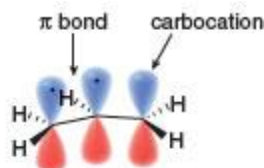
The electrons in the  $\pi$  bonds are **localized**.

### Allylic Carbocations



allyl carbocation

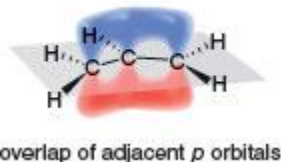
Each C is  $sp^2$  hybridized and has a *p* orbital.



three adjacent *p* orbitals

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

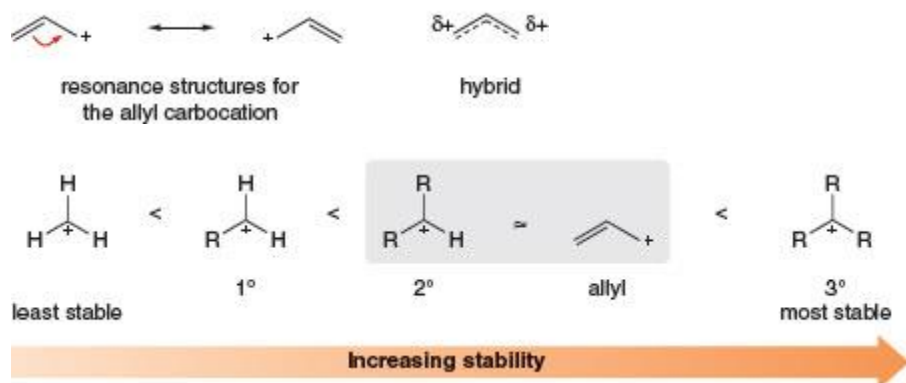
Conjugation stabilizes the allyl carbocation because overlap of three adjacent  $p$  orbitals delocalizes the electron density of the  $\pi$  bond over three atoms.



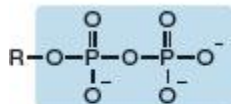
## Resonance and Allylic Carbocations

Two resonance structures differ in the placement of  $\pi$  bonds and nonbonded electrons. The placement of atoms and  $\sigma$  bonds stays the same.

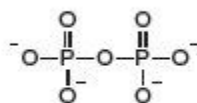
### The Stability of Allylic Carbocations



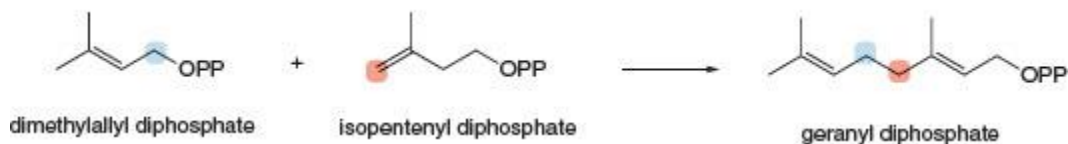
## Allylic Carbocations in Biological Reactions



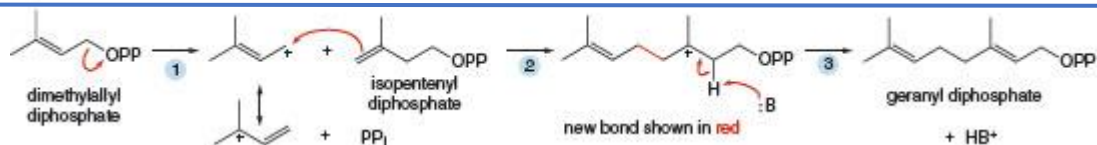
organic diphosphate



diphosphate leaving group  
PP<sub>i</sub>



### Mechanism 16.1 Biological Formation of Geranyl Diphosphate



- 1 Loss of the diphosphate leaving group forms an allylic carbocation.
- 2 Nucleophilic attack of isopentenyl diphosphate on the allylic carbocation forms the new C – C  $\sigma$  bond.
- 3 Loss of a proton (shown with the general base, B:) forms geranyl diphosphate.

### Common Examples of Resonance

Type [1] The Three Atom “Allyl” System,  $\text{X}=\text{Y}-\text{Z}^*$

- For any group of three atoms having a double bond  $\text{X}=\text{Y}$  and an atom  $\text{Z}$  that contains a  $p$  orbital with zero, one, or two electrons, two resonance structures are possible:

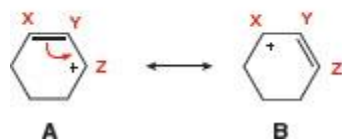


The asterisk [\*] corresponds to a charge, a radical, or a lone pair.

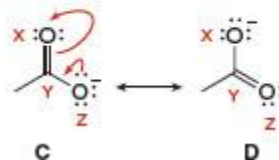
\* = +, -, ·, or ··

The two resonance structures differ in the location of the double bond, and either the charge, the radical, or the lone pair, generalized by [\*].

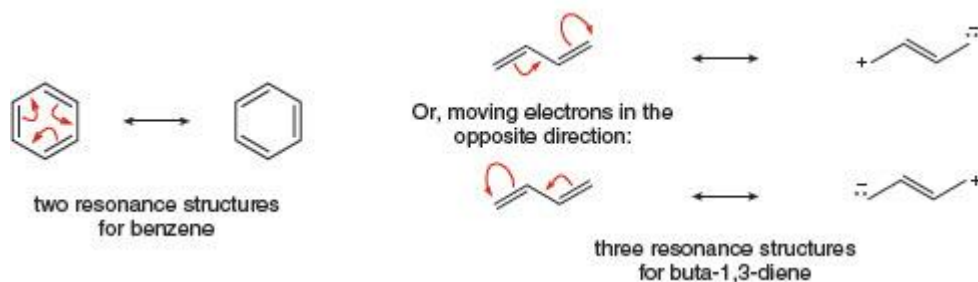
Allylic carbocation



Acetate anion

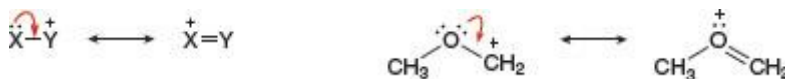


## Type [2] Conjugated Double Bonds



## 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.



## 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  $Y$ .

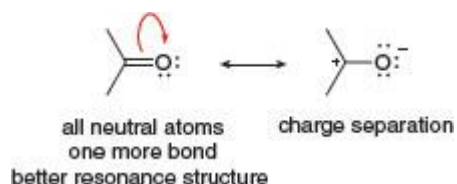


## The Resonance Hybrid

*The lower its energy, the more a resonance structure contributes to the overall structure of the hybrid.*

### Rule [1]

**Resonance structures with more bonds and fewer charges are better.**



**Rule [2] Resonance structures in which every atom has an octet are better.**



All second-row elements have an octet.  
better resonance structure

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



The (-) charge is on the more electronegative O atom.  
better resonance structure

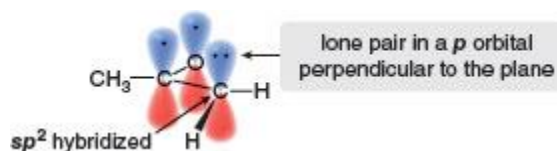
## Electron Delocalization, Hybridization, and Geometry



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

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

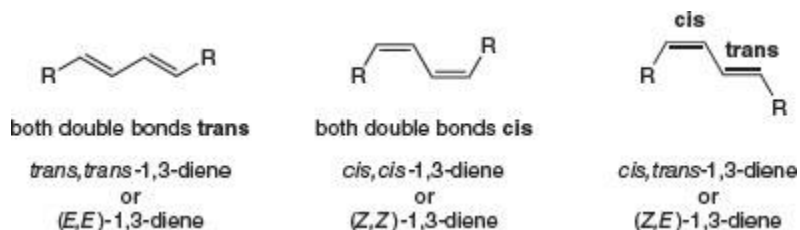
Three adjacent  $p$  orbitals make the anion conjugated.



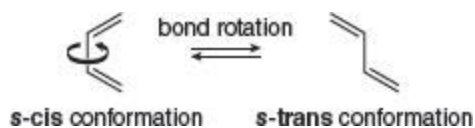
- In a system  $X = Y - Z$ , Z is generally  $sp^2$  hybridized, and the nonbonded electron pair occupies a  $p$  orbital to make the system conjugated.

## Conjugated Dienes

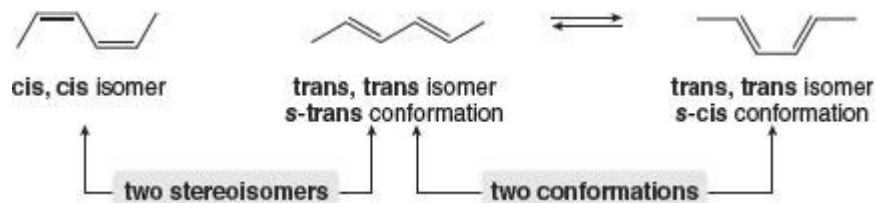
Compounds with many  $\pi$  bonds are called **polyenes**.



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



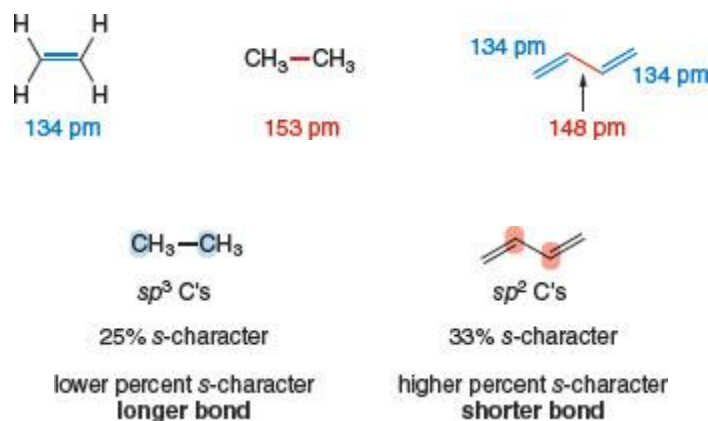
- The s-cis conformation has two double bonds on the *same* side of the single bond.
- The s-trans conformation has two double bonds on *opposite* sides of the single bond.



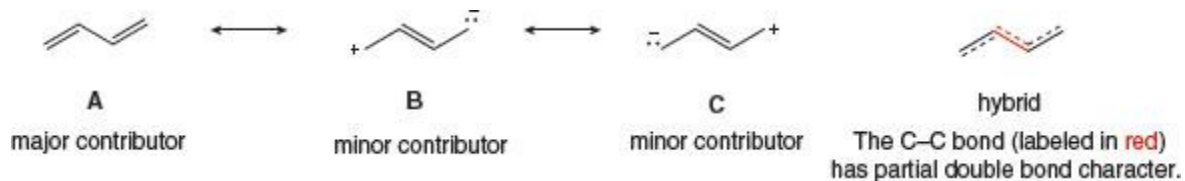
## The Carbon–Carbon $\sigma$ Bond Length in Buta-1,3-diene

*Four features distinguish conjugated dienes from isolated dienes.*

- [1] The C – C single bond joining the two double bonds is unusually short.
- [2] Conjugated dienes are more stable than similar isolated dienes.
- [3] Some reactions of conjugated dienes are different than reactions of isolated double bonds.
- [4] Conjugated dienes absorb longer wavelengths of ultraviolet light.

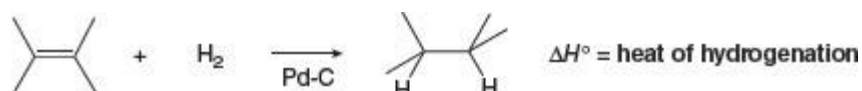


Based on hybridization, a  $\text{C}_{sp^2}-\text{C}_{sp^2}$  bond should be shorter than a  $\text{C}_{sp^3}-\text{C}_{sp^3}$  bond because it is formed from orbitals having a higher percent s-character.

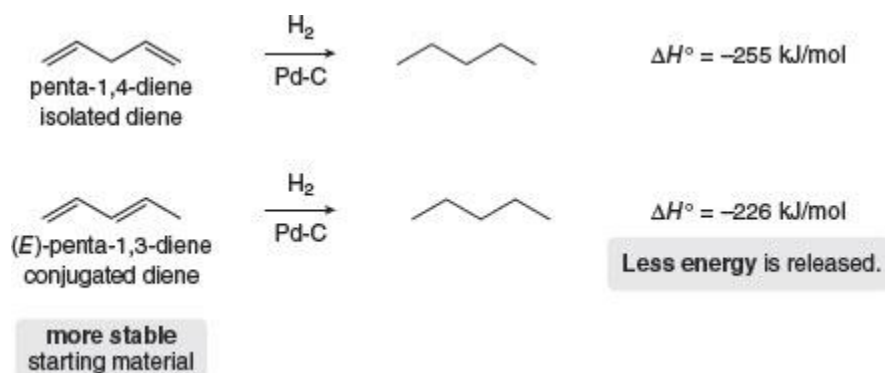


Based on resonance, the central C – C bond in buta-1,3-diene is shorter because it has partial double bond character.

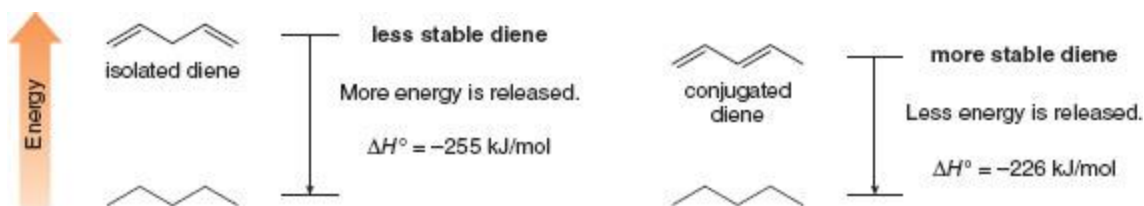
### Stability of Conjugated Dienes



When hydrogenation gives the same alkane from two dienes, the more stable diene has the smaller heat of hydrogenation.



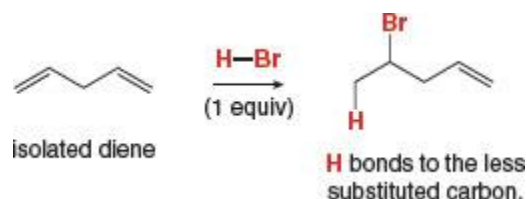
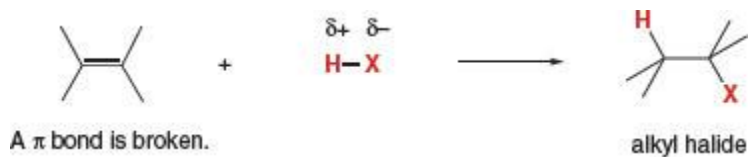
### Relative energies of an isolated and conjugated diene



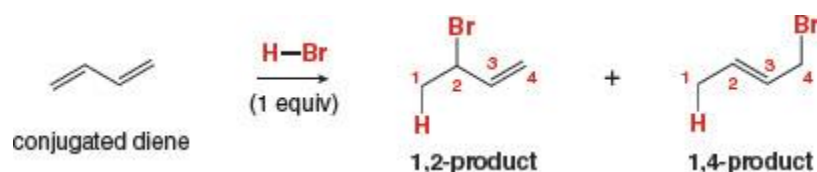
- A conjugated diene has a smaller heat of hydrogenation and is more stable than a similar isolated diene.

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

- Electrophilic addition in conjugated dienes gives a mixture of products.
- Conjugated dienes undergo a unique addition reaction not seen in alkenes or isolated dienes.



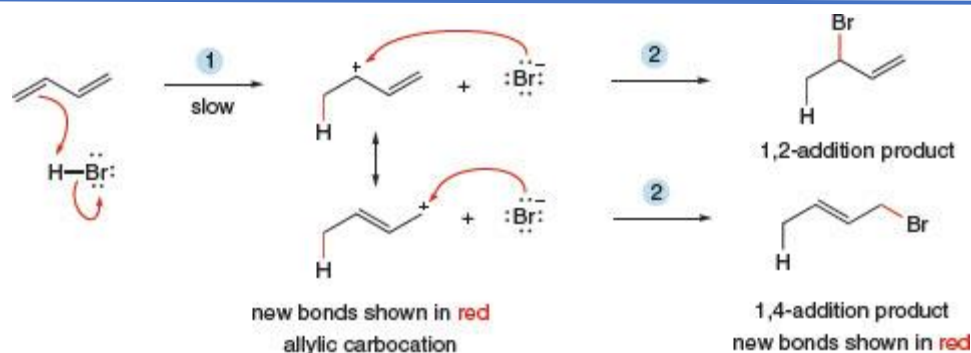
With a conjugated diene, electrophilic addition of one equivalent of HBr affords *two* products.



The ends of the 1,3-diene are called C1 and C4 arbitrarily, without regard to IUPAC numbering.

- The **1,2-addition product** results from Markovnikov addition of HBr across two adjacent carbon atoms (C1 and C2) of the diene.
- The **1,4-addition product** results from addition of HBr to the two end carbons (C1 and C4) of the diene. 1,4-Addition is also called **conjugate addition**.

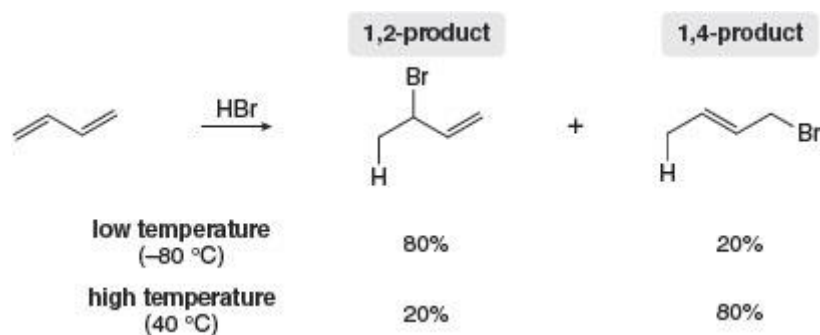
### Mechanism 16.2 Electrophilic Addition of HBr to a 1,3-Diene—1,2- and 1,4-Addition



- **1**  $\text{H}^+$  of HBr adds to a terminal carbon of the 1,3-diene to form a resonance-stabilized allylic carbocation.
- **2** Nucleophilic attack of  $\text{Br}^-$  occurs at either site of the resonance-stabilized carbocation that bears a (+) charge, forming the 1,2- and 1,4-addition products.
- **Addition of HX to a conjugated diene forms 1,2- and 1,4-products because of the resonance-stabilized allylic carbocation intermediate.**

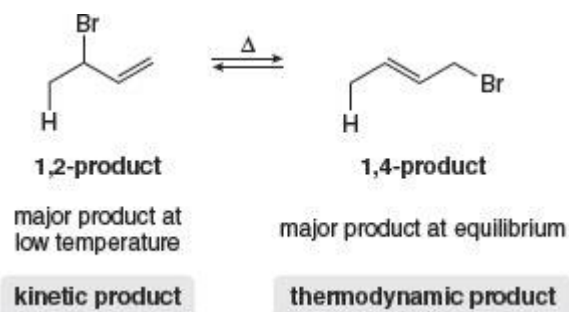


## Kinetic Versus Thermodynamic Products

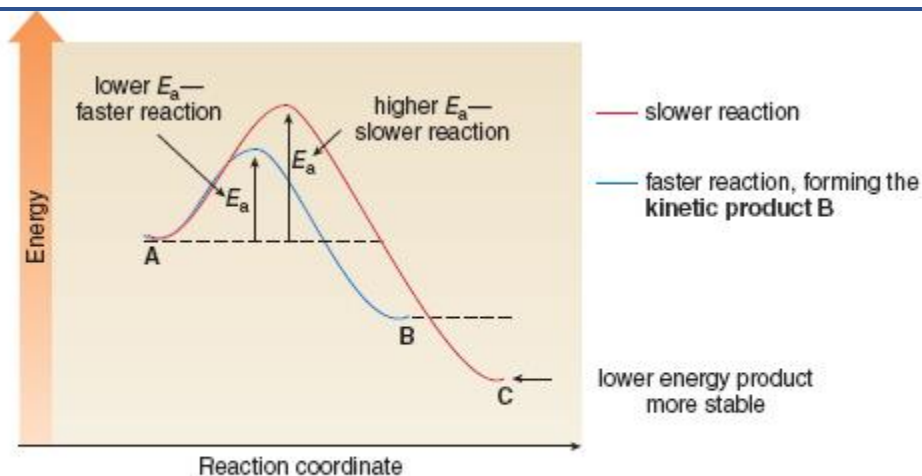


Page 619

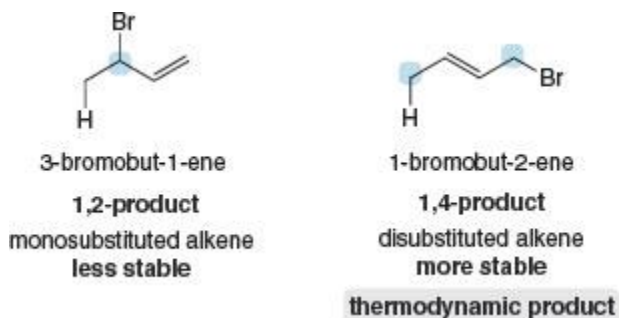
- At low temperature the major product is formed by 1,2-addition.
- At higher temperature the major product is formed by 1,4-addition.



- 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 conversion of A → B is a faster reaction because the energy of activation leading to B is lower. B is the kinetic product.
- Because C is lower in energy, C is the thermodynamic product.



Page 620

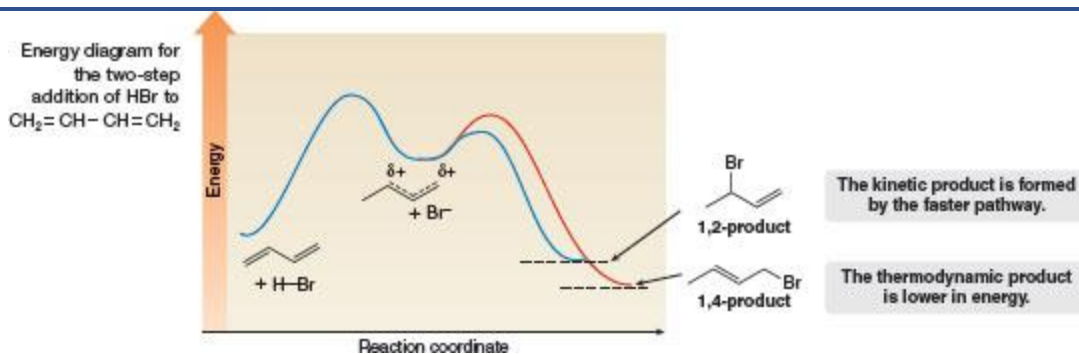
- The more substituted alkene—1-bromobut-2-ene in this case—is the thermodynamic product.



A **proximity effect** occurs because one species is close to another.

- The 1,2-product forms faster because of the proximity of Br<sup>-</sup> to C2.

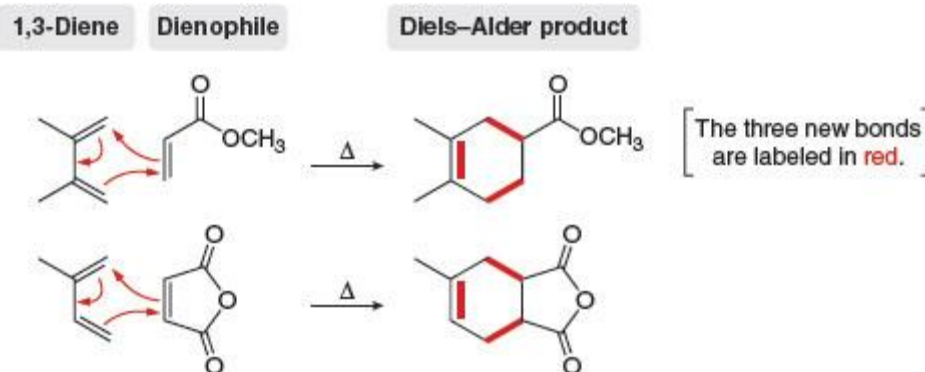
*Energy diagram for the two-step addition of HBr to CH<sub>2</sub> = CH - CH = CH<sub>2</sub>*



Why is the ratio of products temperature dependent?

- At low temperature, the energy of activation is the more important factor. Because most molecules do not have enough kinetic energy to overcome the higher energy barrier at lower temperature, they react by the faster pathway, forming the kinetic product.
- At higher temperature, most molecules have enough kinetic energy to reach either transition state. The two products are in equilibrium with each other, and the more stable compound—which is lower in energy—becomes the major product.

## The Diels–Alder Reaction

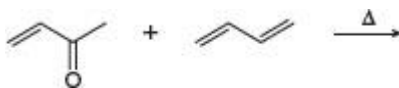


All Diels–Alder reactions have the following features in common:

- [1] They are initiated by heat; that is, the Diels–Alder reaction is a *thermal* reaction.
- [2] They form new six-membered rings.
- [3] Three  $\pi$  bonds break, and two new C – C  $\sigma$  bonds and one new C – C  $\pi$  bond form.
- [4] They are concerted; that is, all bonds are broken and formed in a single step.

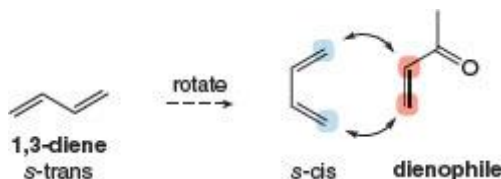
## How To Draw the Product of a Diels—Alder Reaction

Example Draw the product of the following Diels—Alder reaction:

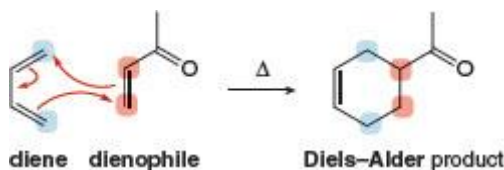


**Step [1]** Arrange the 1,3-diene and the dienophile next to each other, with the diene drawn in the *s-cis* conformation.

- 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.



## Specific Rules Governing the Diels—Alder Reaction

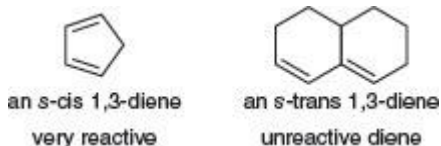
### Diene Reactivity

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



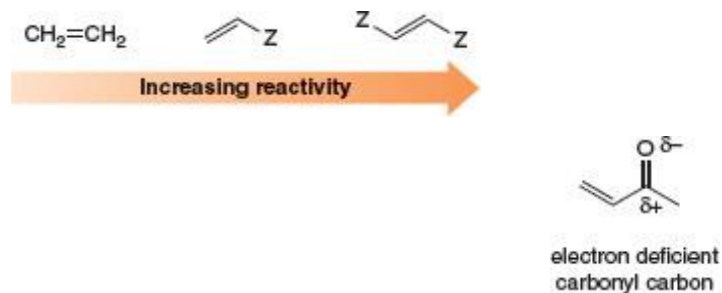
This rotation is prevented in cyclic dienes. As a result:

- When the two double bonds are constrained in the *s-cis* conformation, the diene is unusually *reactive*.
- When the two double bonds are constrained in the *s-trans* conformation, the diene is *unreactive*.

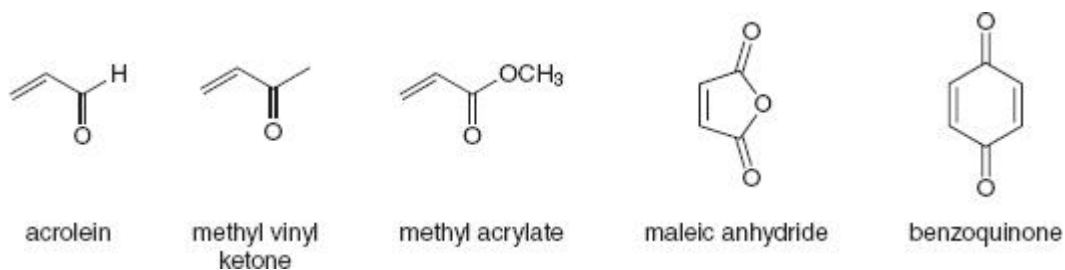


## Dienophile Reactivity

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



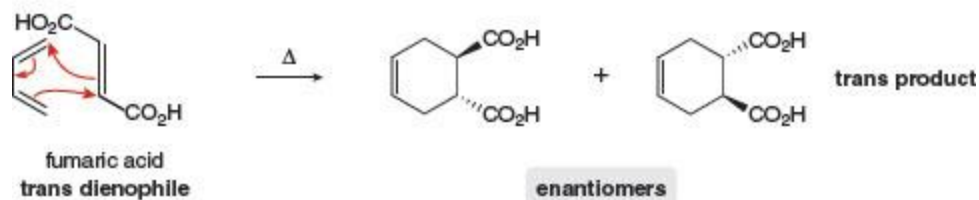
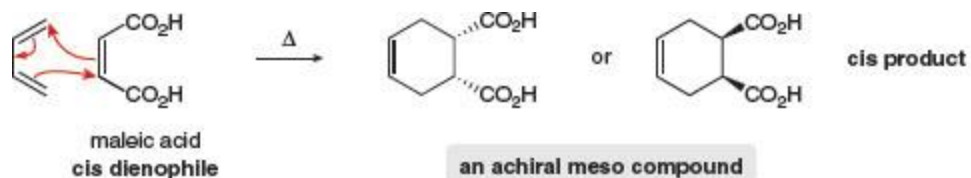
### Common dienophiles in the Diels–Alder reaction



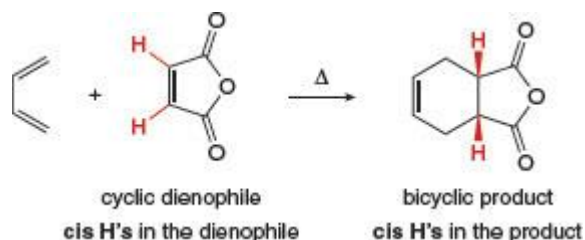
## Stereospecificity

**Rule [3]** The stereochemistry of the dienophile is retained in the product.

- A cis dienophile forms a cis-substituted cyclohexene.
- A trans dienophile forms a trans-substituted cyclohexene.



- A **cyclic dienophile** forms a **bicyclic product**. A bicyclic system in which the two rings share a common C – C bond is called a **fused ring system**. The two H atoms at 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**.



## The Rule of Endo Addition

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

[4]



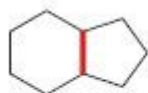
cyclic 1,3-diene

a bridged bicyclic ring system

A bicyclic ring system in which the two rings share non-adjacent carbon atoms is called a **bridged ring system**.

### Fused and bridged bicyclic ring systems compared

a. A fused bicyclic system

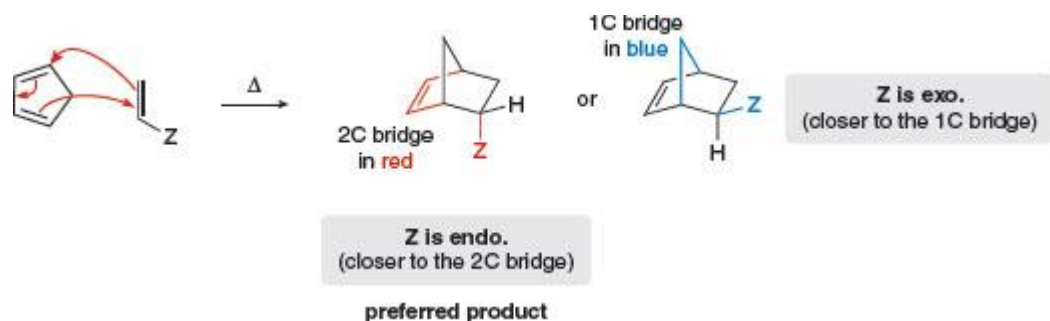


- One bond (in red) is shared by two rings.
- The shared C's are adjacent.

b. A bridged bicyclic system

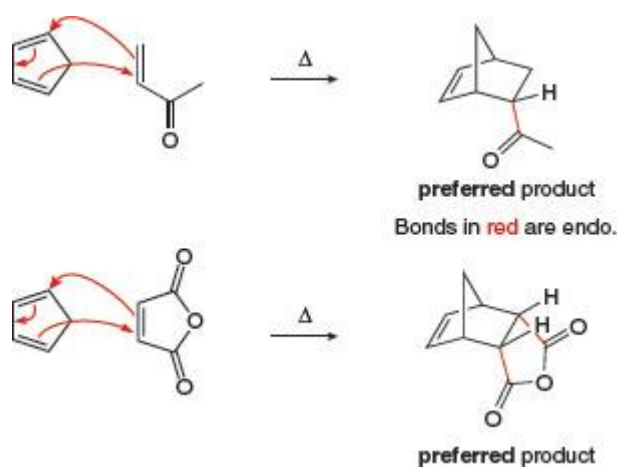


- Two non-adjacent atoms (labeled in blue) are shared by both rings.



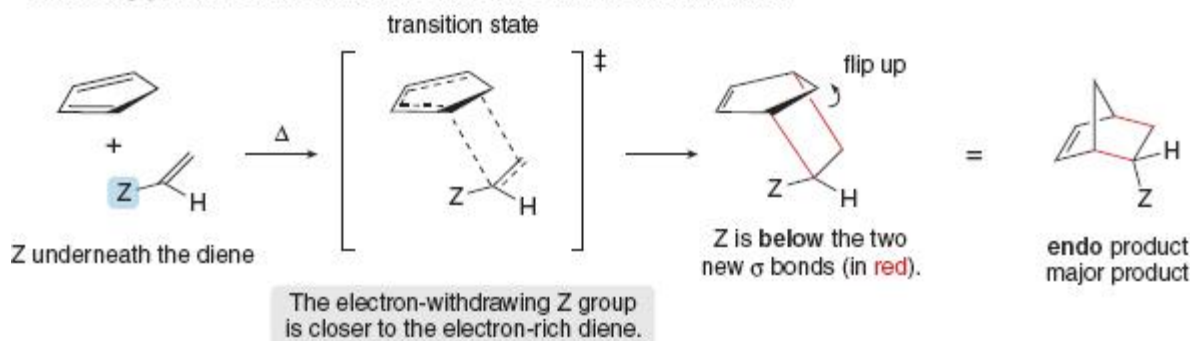
- A substituent on one bridge is *endo* if it is closer to the *longer* bridge that joins the two carbons common to both rings.
- A substituent is *exo* if it is closer to the *shorter* bridge that joins the carbons together.

In a Diels—Alder reaction, the endo product is preferred, as shown in two examples.

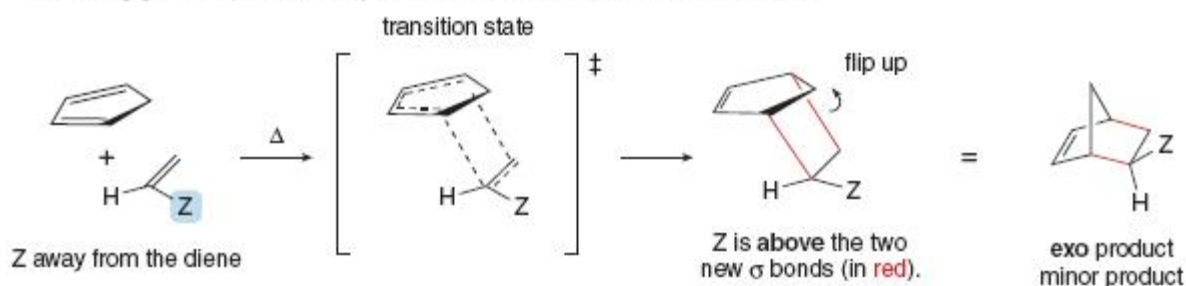


How endo and exo products are formed in the Diels—Alder reaction

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



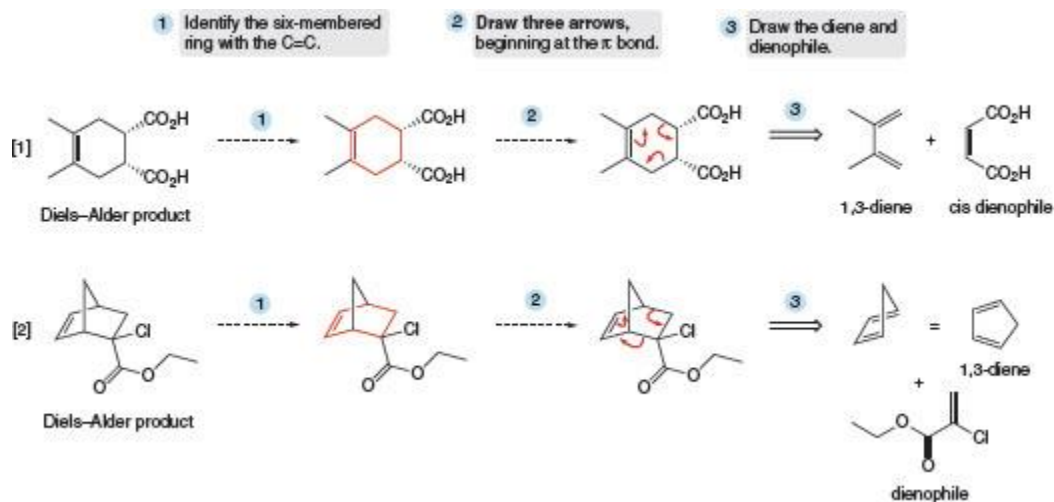
Pathway [2] With Z oriented away from the diene, the exo product is formed.



## Other Facts About the Diels—Alder Reaction

- Locate the six-membered ring that contains the  $C=C$ .
- Draw three arrows around the cyclohexene ring, beginning with the  $\pi$  bond. Each arrow moves two electrons to the adjacent bond, cleaving one  $\pi$  bond and two  $\sigma$  bonds, and forming three  $\pi$  bonds.
- Retain the stereochemistry of substituents on the  $C=C$  of the dienophile. Cis substituents on the six-membered ring give a cis dienophile.

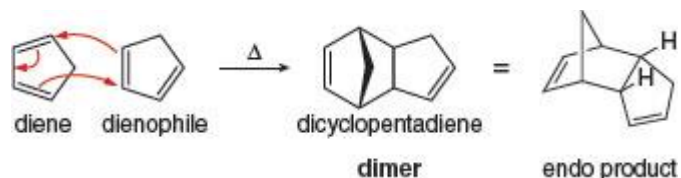
### Finding the diene and dienophile needed for a Diels—Alder reaction



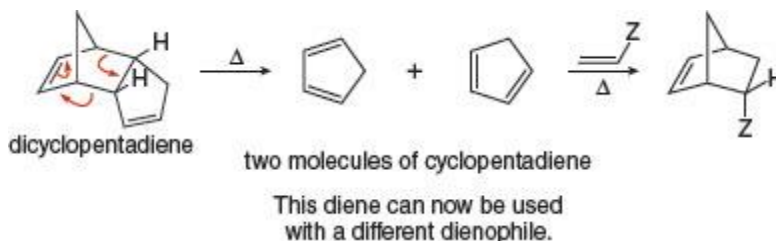


## Retro Diels—Alder Reaction

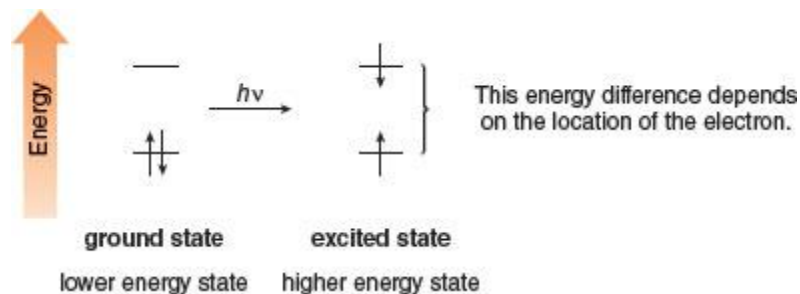
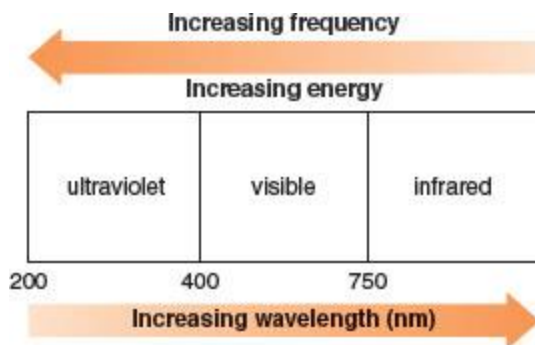
- A reactive diene like cyclopenta-1,3-diene readily undergoes a Diels—Alder reaction with *itself*; that is, **cyclopenta-1,3-diene dimerizes because one molecule acts as the diene and another acts as the dienophile.**



When heated, dicyclopentadiene undergoes a **retro Diels—Alder reaction**, and two molecules of cyclopentadiene are re-formed. If cyclopentadiene is immediately treated with a different dienophile, it reacts to form a new Diels—Alder adduct with this dienophile.



## Conjugated Dienes and Ultraviolet Light





Page 631

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

