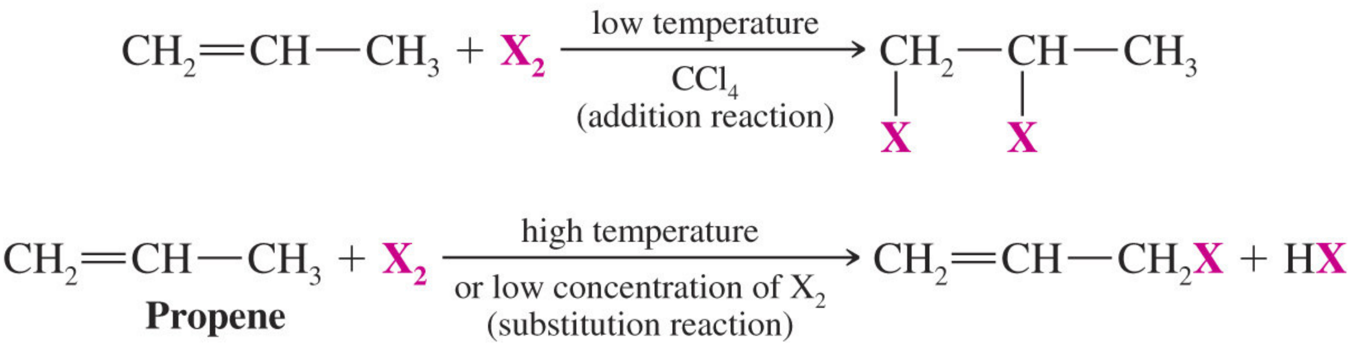
Chapter 13
Conjugated Unsaturated Systems

♦ Introduction

- Conjugated unsaturated systems have a *p* orbital on a carbon adjacent to a double bond
  - The *p* orbital can come from another double or triple bond
  - The *p* orbital may be the empty *p* orbital of a carbocation or a *p* orbital with a single electron in it (a radical)
  - Conjugation affords special stability to the molecule
  - Conjugated molecules can be detected using UV spectroscopy

♦ Allylic Substitution and the Allylic Radical

- Reaction of propene with bromine varies depending on reaction conditions
  - At low temperature the halogen adds across the double bond
  - At high temperature or at very low concentration of halogen an allylic substitution occurs



$$CH_2{=}CH{-}CH_3 + \mathbf{X_2} \xrightarrow[\substack{CCl_4 \\ \text{(addition reaction)}}]{\text{low temperature}} \underset{\mathbf{X}}{CH_2}{-}\underset{\mathbf{X}}{CH}{-}CH_3$$

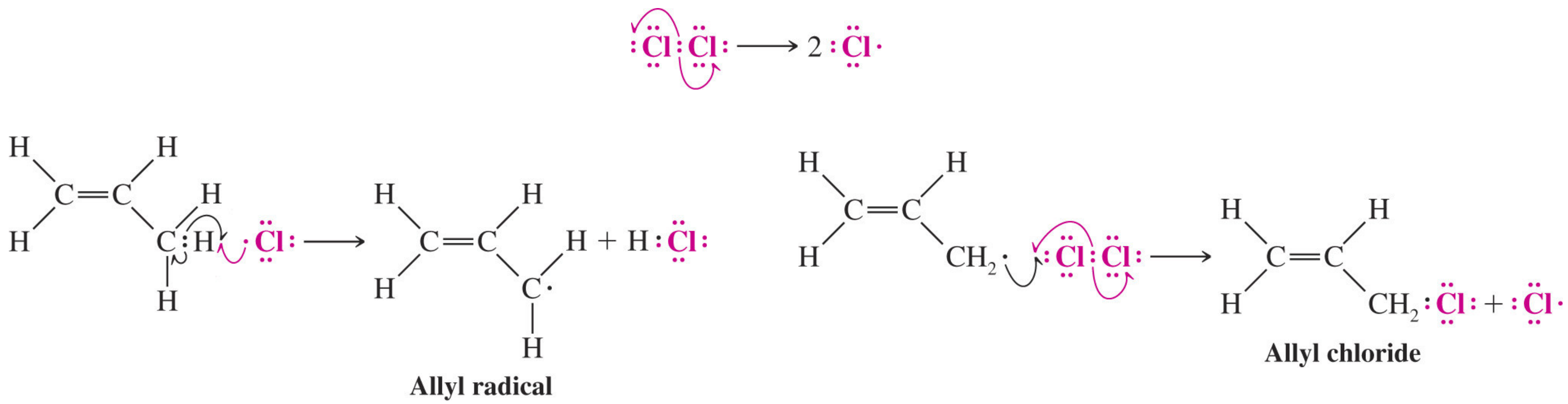
$$\underset{\textbf{Propene}}{CH_2{=}CH{-}CH_3} + \mathbf{X_2} \xrightarrow[\substack{\text{or low concentration of } X_2 \\ \text{(substitution reaction)}}]{\text{high temperature}} CH_2{=}CH{-}CH_2\mathbf{X} + H\mathbf{X}$$

Allylic Chlorination (High Temperature)

- ➔ Allylic chlorination can be performed at high temperature in the gas phase
- ➔ The reaction is a free radical chain reaction
  - In the initiation step a low concentration of chlorine radical is produced
  - In the first propagation step an allyl radical is formed
  - In the second propagation step the allyl radical reacts with molecular chlorine

$$CH_2{=}CH{-}CH_3 + Cl_2 \xrightarrow[\text{gas phase}]{400°C} CH_2{=}CH{-}CH_2Cl + HCl$$

3-Chloropropene (allyl chloride)



- ➔ **Allylic radicals form readily because they are more stable than ordinary primary, secondary, tertiary, or vinyl radicals**
  - **This trend is reflected in their respective C-H bond dissociation energies**

$$CH_2{=}CHCH_2{-}H \longrightarrow CH_2{=}CHCH_2\cdot + H\cdot \qquad DH^\circ = 369\ \mathrm{kJ\ mol^{-1}}$$

Propene **Allyl radical**

$$(CH_3)_3C{-}H \longrightarrow (CH_3)_3C\cdot + H\cdot \qquad DH^\circ = 400\ \mathrm{kJ\ mol^{-1}}$$

Isobutane **3° Radical**

$$(CH_3)_2CH{-}H \longrightarrow (CH_3)_2CH\cdot + H\cdot \qquad DH^\circ = 413\ \mathrm{kJ\ mol^{-1}}$$

Propane **2° Radical**

$$CH_3CH_2CH_2{-}H \longrightarrow CH_3CH_2CH_2\cdot + H\cdot \qquad DH^\circ = 423\ \mathrm{kJ\ mol^{-1}}$$

Propane **1° Radical**

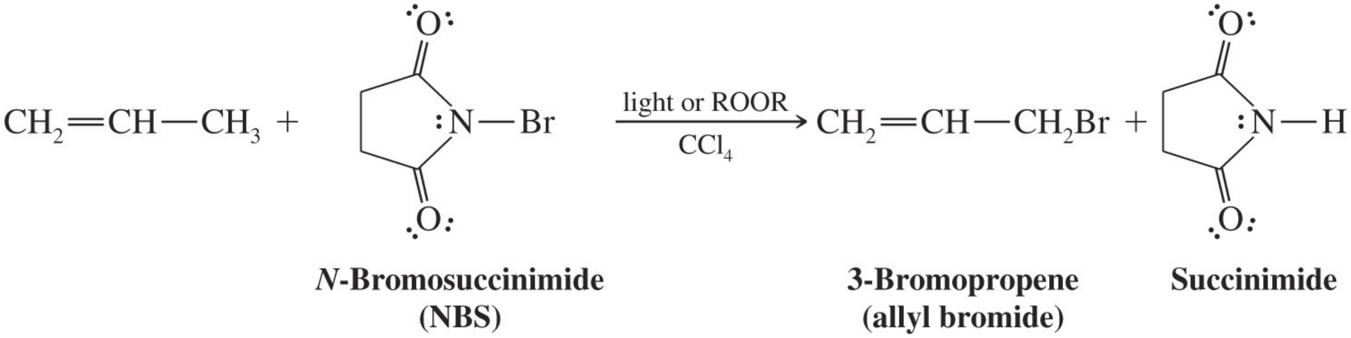
$$CH_2{=}CH{-}H \longrightarrow CH_2{=}CH\cdot + H\cdot \qquad DH^\circ = 465\ \mathrm{kJ\ mol^{-1}}$$

Ethene **Vinyl radical**

- ➔ **The relative stability of some carbon radicals is as follows:**

Relative stability: allylic or allyl $>$ 3° $>$ 2° $>$ 1° $>$ vinyl or vinylic.

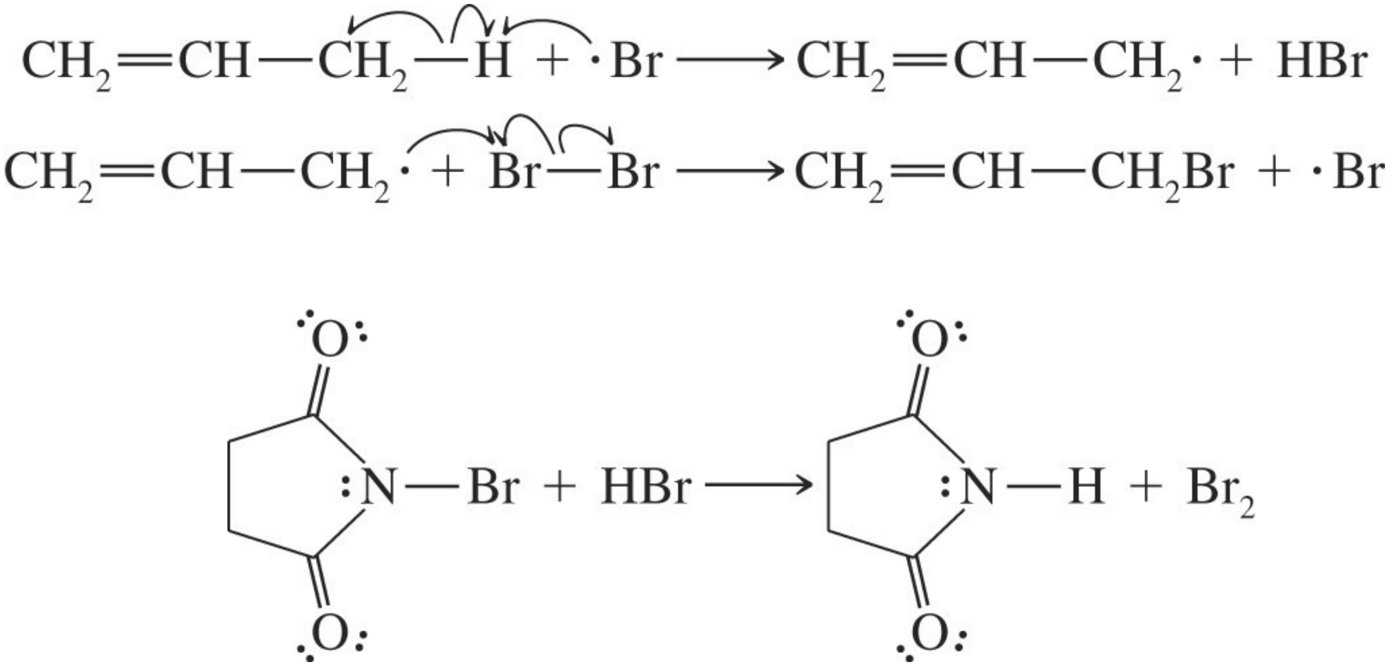
- **Allylic Bromination with *N*-Bromosuccinimide**
  - ➔ **Propene undergoes allylic bromination with *N*-bromosuccinimide (NBS) in the presence of light or peroxides**
    - **NBS provides a continuous low concentration of bromine for the radical reaction**
    - **A low bromine concentration favors allylic substitution over alkene addition**



  - ➔ **The radical reaction is initiated by a small amount of bromine radical formed by exposure of NBS to light or peroxides**

➔The propagation steps for allylic bromination with NBS are:

- **A bromine radical reacts with propene to produce an allylic radical and HBr**
- **HBr reacts with NBS to produce a bromine molecule**
- **A molecule of bromine reacts with a propene radical to regenerate a bromine radical**



$$CH_2{=}CH{-}CH_2{-}H + \cdot Br \longrightarrow CH_2{=}CH{-}CH_2\cdot + HBr$$

$$CH_2{=}CH{-}CH_2\cdot + Br{-}Br \longrightarrow CH_2{=}CH{-}CH_2Br + \cdot Br$$

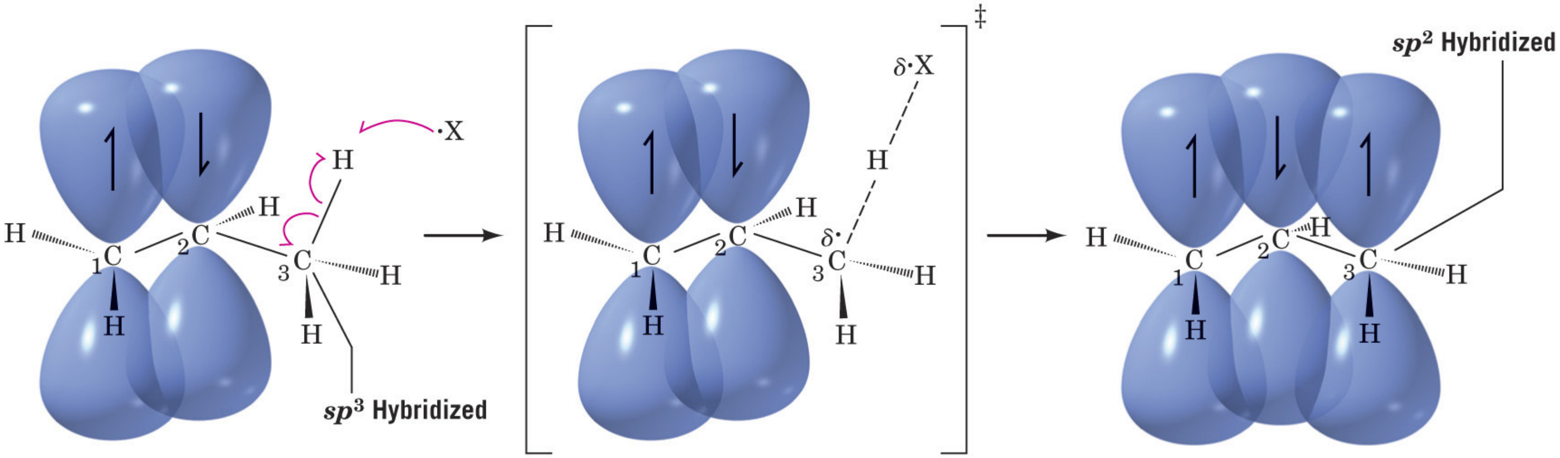
♦ The Stability of the Allyl Radical

➔ Both molecular orbital theory and resonance theory can explain the stability of allyl radicals

● Molecular Orbital Description of the Allyl Radical

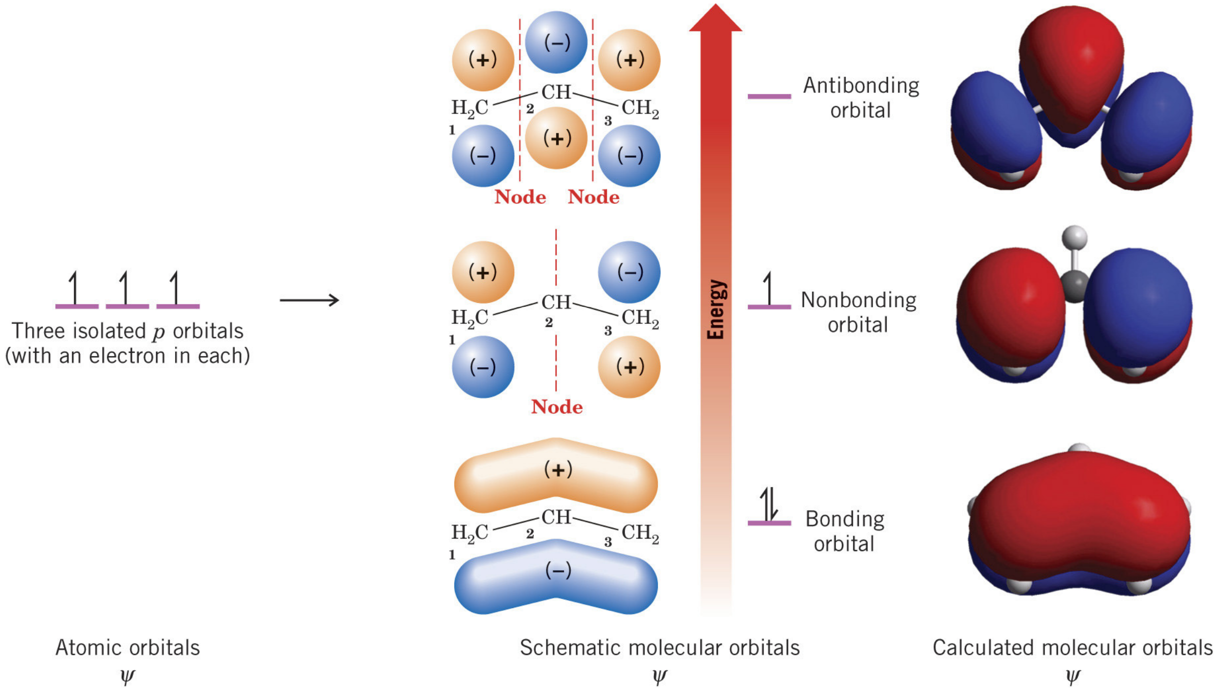
➔ When an allylic hydrogen is abstracted to form an allyl radical, the developing *p* orbital on the sp^2 carbon overlaps with the *p* orbitals of the alkene

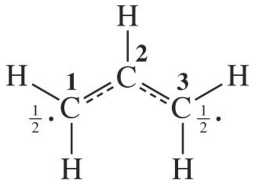
- The new *p* orbital is conjugated with the double bond p orbitals
- The radical electron and the π electrons of the alkene are delocalized over the entire conjugated system
- Delocalization of charge and electron density leads to increased stability



➔ The three *p* orbitals of the allylic system combine to form three molecular orbitals

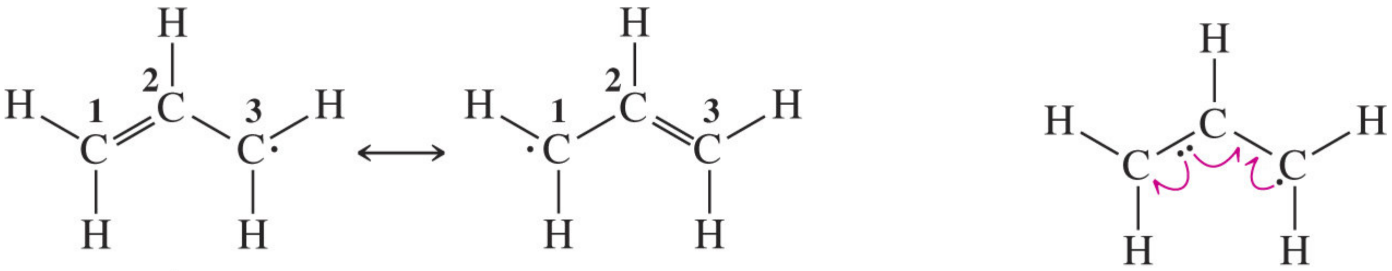
- **The bonding molecular orbital contains two spin-paired electrons and this orbital increases bonding between the carbons**
- **The nonbonding orbital contains a lone electron which is located at carbons 1 and 3 only**





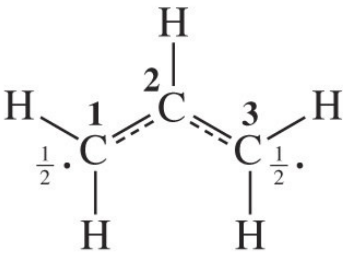
♦ Resonance Description of the Allyl Radical

- ➔ **The allyl radical has two contributing resonance forms**
  - **These resonance forms can be interconverted using single-barbed arrows**
  - **The resonance structures are equivalent**
  - **Recall that equivalent resonance structures lead to much greater stability of the molecule than either structure alone would suggest**



A **B**

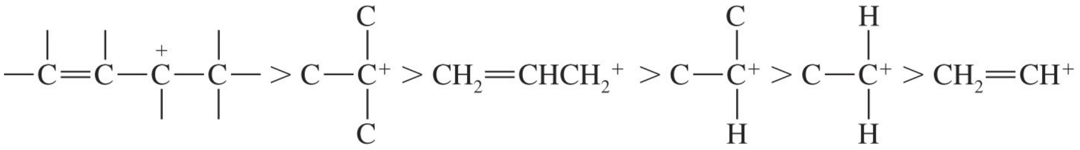
- ➔ **The true structure of the allyl radical as suggested by resonance theory is as follows**



C

♦ The Allyl Cation

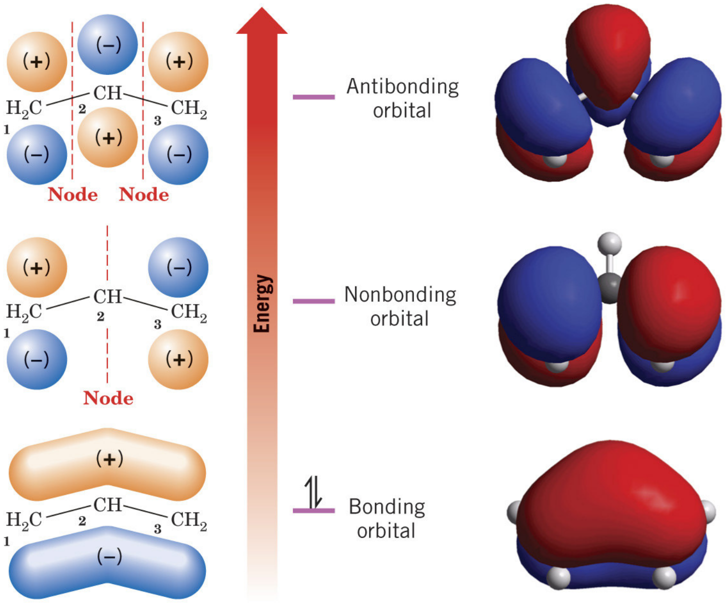
- ➔ **The allyl cation is intermediate in stability between a tertiary and secondary carbocation**



$$-\overset{|}{C}=\overset{|}{C}-\underset{|}{\overset{+}{C}}-\underset{|}{\overset{|}{C}}- > C-\underset{C}{\overset{C}{C^{+}}} > CH_2=CHCH_2^{+} > C-\underset{H}{\overset{C}{C^{+}}} > C-\underset{H}{\overset{H}{C^{+}}} > CH_2=CH^{+}$$

Substituted allylic > 3° > Allyl > 2° > 1° > Vinyl

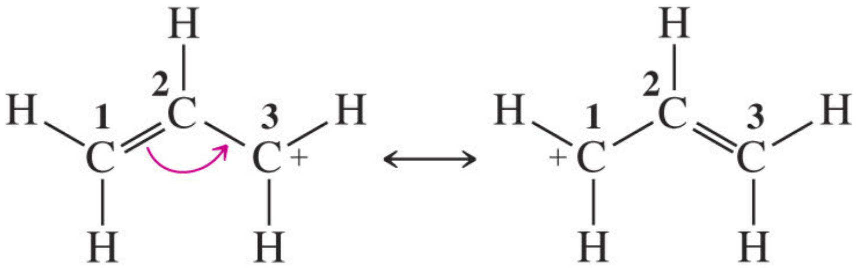
- ➔ **The molecular orbital description of the allyl cation is very similar to the allyl radical except it contains one fewer electrons**
  - **Stability arises from the delocalization of the positive charge over C1 and C3**



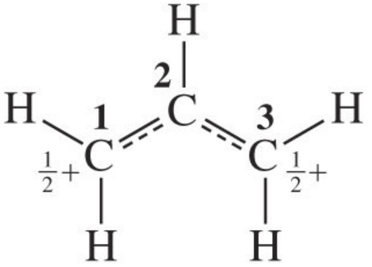
Schematic molecular orbitals

Calculated molecular orbitals

- ➔ **Resonance theory predicts that the allyl cation is a hybrid of equivalent structures D and E**
  - **Both molecular orbital theory and resonance theory suggest that structure F (below) is the best representation for the allyl cation**



D **E**

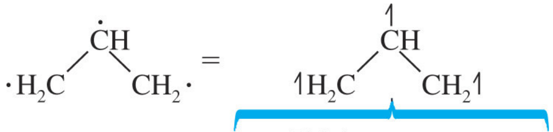


F

♦ Summary of Rules for Resonance

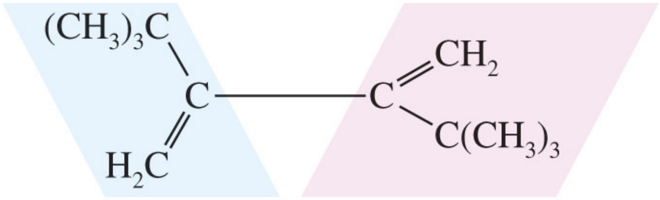
● Rules for Writing Resonance Structures

- ➔ Individual resonance structures are not a true representation of the real structure of a molecule
  - A hybrid of all major resonance structures gives an indication of the true structure
- ➔ Only electrons may be moved in resonance structures, not atoms
  - Only π and nonbonding electrons are moved
- ➔ All resonance structures must be proper Lewis structures
- ➔ All resonance structures must have the same number of paired and unpaired electrons



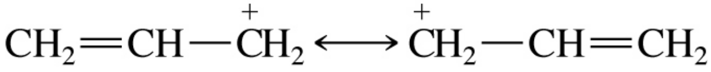
This is not a proper resonance structure for the allyl radical because it does not contain the same number of unpaired electrons as $CH_2{=}CHCH_2\cdot$.

- ➔ All atoms that are part of the delocalized π-electron system must lie in a plane or be nearly planar
  - The molecule on the next slide does not behave like a conjugated diene because the large tert-butyl groups twist the structure and prevent the diene from being planar



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

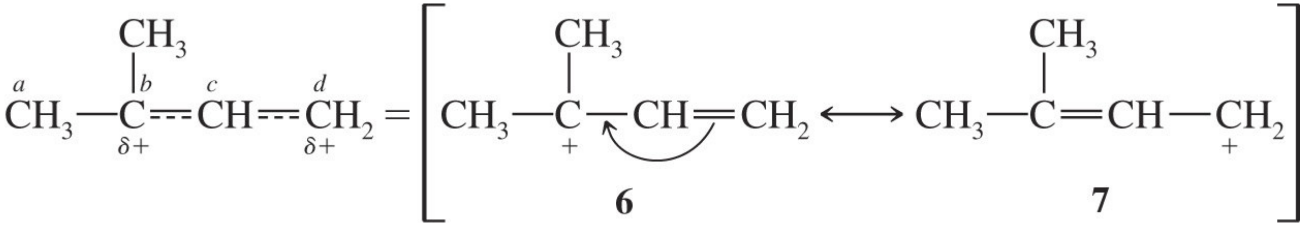
- ➔ **The energy of the actual molecule is lower than the energy calculated for any one contributing resonance structure**
  - **Allyl cation has much lower energy than either contributing structures 4 or 5**



$$\mathrm{CH_2{=}CH{-}\overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2{-}CH{=}CH_2}$$

4 **5**

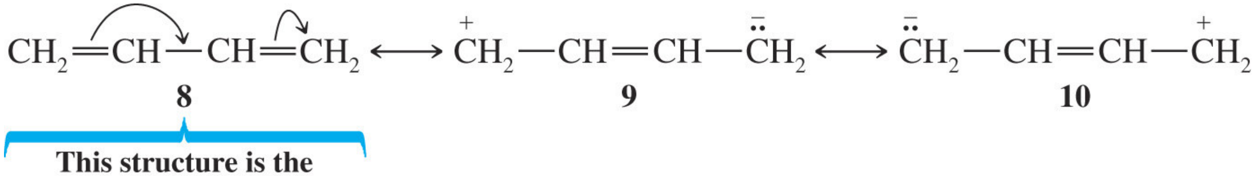
- ➔ **A system with equivalent resonance structures is particularly stable**
  - **The allyl cation has two equivalent resonance structures and is therefore particularly stable**
- ➔ **The more stable a resonance structure is, the more important it is and the more it contributes to the hybrid**
  - **Structure 6 is a more stable tertiary carbocation and contributes more than structure 7**



$$\overset{a}{\mathrm{C}}\mathrm{H_3}-\overset{\overset{\mathrm{CH_3}}{|\,b}}{\underset{\delta+}{\mathrm{C}}}\overset{c}{\cdots}\mathrm{CH}\cdots\overset{d}{\underset{\delta+}{\mathrm{C}}}\mathrm{H_2} = \left[\mathrm{CH_3}-\overset{\overset{\mathrm{CH_3}}{|}}{\underset{+}{\mathrm{C}}}-\mathrm{CH}{=}\mathrm{CH_2} \longleftrightarrow \mathrm{CH_3}-\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{C}}{=}\mathrm{CH}-\underset{+}{\mathrm{C}}\mathrm{H_2}\right]$$

6 **7**

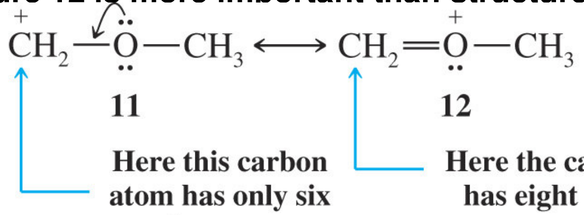
- Estimating the Relative Stability of Resonance Structures
  - ➔ Structures with more covalent bonds are more important
    - Structure 8 is more important than 9 or 10



$$CH_2{=}CH{-}CH{=}CH_2 \longleftrightarrow \overset{+}{C}H_2{-}CH{=}CH{-}\overset{-}{\ddot{C}}H_2 \longleftrightarrow \overset{-}{\ddot{C}}H_2{-}CH{=}CH{-}\overset{+}{C}H_2$$

This structure is the most stable because it contains more covalent bonds.

  - ➔ Structures in which all atoms have complete octets are more important
    - Structure 12 is more important than structure 11

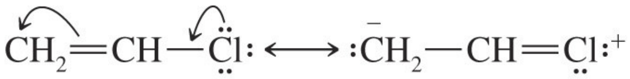


$$\overset{+}{C}H_2{-}\underset{..}{\ddot{O}}{-}CH_3 \longleftrightarrow CH_2{=}\underset{..}{\overset{+}{O}}{-}CH_3$$

Here this carbon atom has only six electrons.

Here the carbon atom has eight electrons.

  - ➔ Separation of charge decreases stability
    - Structure 13 is more important because it does not have a separation of charge



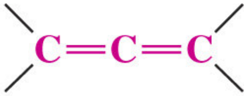
$$CH_2{=}CH{-}\underset{..}{\ddot{Cl}}: \longleftrightarrow :\overset{-}{C}H_2{-}CH{=}\underset{..}{Cl}:^{+}$$

♦ Alkadienes and Polyunsaturated Hydrocarbons

- ➔ **Alkadienes contain two double bonds**
  - These are often referred to simply as dienes
  - Alkadiynes contain 2 triple bonds and alkenynes contain a double and a triple bond
- ➔ **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

$CH_2{=}C{=}CH_2$

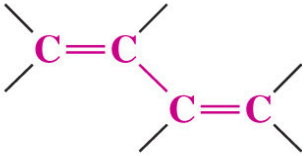
Allene



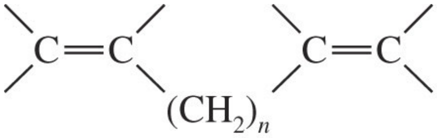
A cumulated diene

$CH_2{=}CH{-}CH{=}CH_2$

1,3-Butadiene



A conjugated diene



An isolated diene ($n \neq 0$)

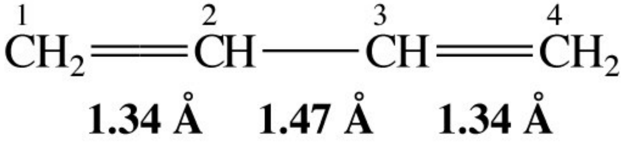
$CH_2{=}CH{-}CH_2{-}CH{=}CH_2$

1,4-Pentadiene

♦ 1,3-Butadiene: Electron Delocalization

● Bond Lengths of 1,3-Butadiene

- ➔ The double bonds of 1,3-butadiene have the expected length of regular double bonds
- ➔ The central bond is much shorter than a regular carbon-carbon single bond
  - Ethane has a carbon-carbon bond length of 1.54 Å



$$\overset{1}{C}H_2 = \overset{2}{C}H - \overset{3}{C}H = \overset{4}{C}H_2$$

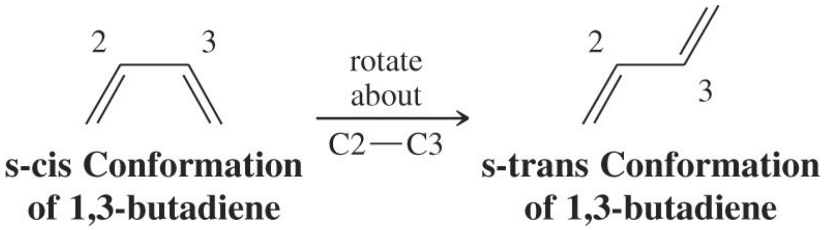
$$\underset{1.34\ \text{Å}}{} \quad \underset{1.47\ \text{Å}}{} \quad \underset{1.34\ \text{Å}}{}$$

- ➔ The central bond in 1,3-butadiene is shorter than that in ethene for two reasons
  - The σ bond between C2 and C3 is made from *sp*^{2}-*sp*^{2} overlap
  - There is significant overlap between the C2-C3 *p* orbitals

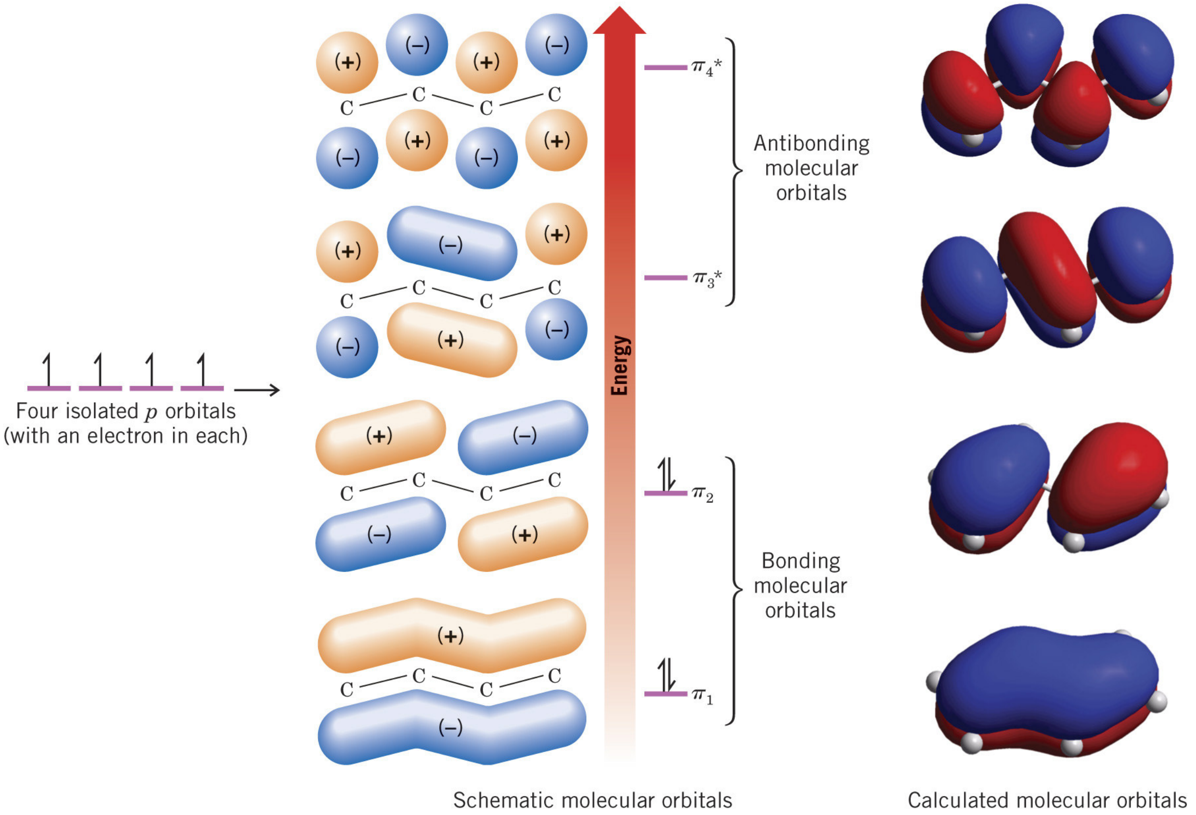
● Conformations of 1,3-Butadiene

➔ **There are two possible planar conformations of 1,3-butadiene called s-cis and s-trans**

- **s Indicates the conformations originate from rotation around a single bond**
- **s-Trans is more stable because it is less sterically hindered**



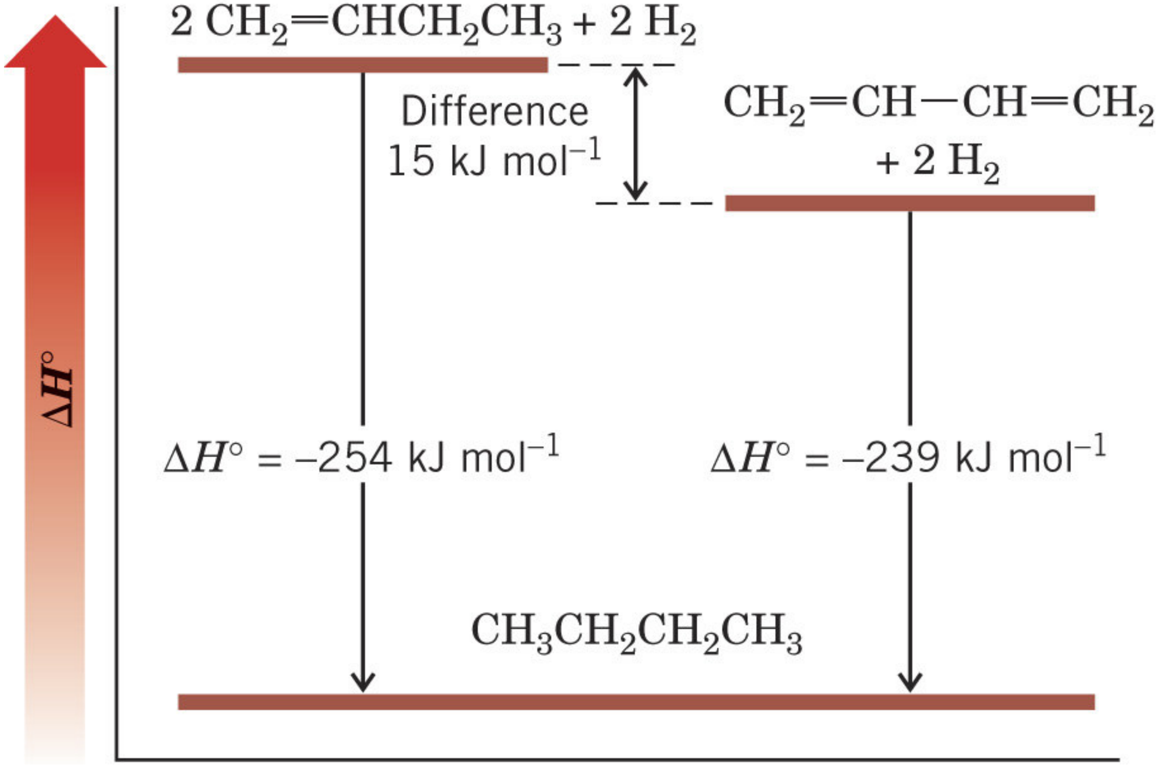
- **Molecular Orbitals of 1,3-Butadiene**
  - ➔ **The first (lowest energy) π bonding molecular orbital in 1,3-butadiene shows significant overlap of the *p* orbitals between C2 and C3**
    - **The second π bonding molecular orbital in 1,3-butadiene is the highest occupied molecular orbital (HOMO) and shows no overlap between C2 and C3**



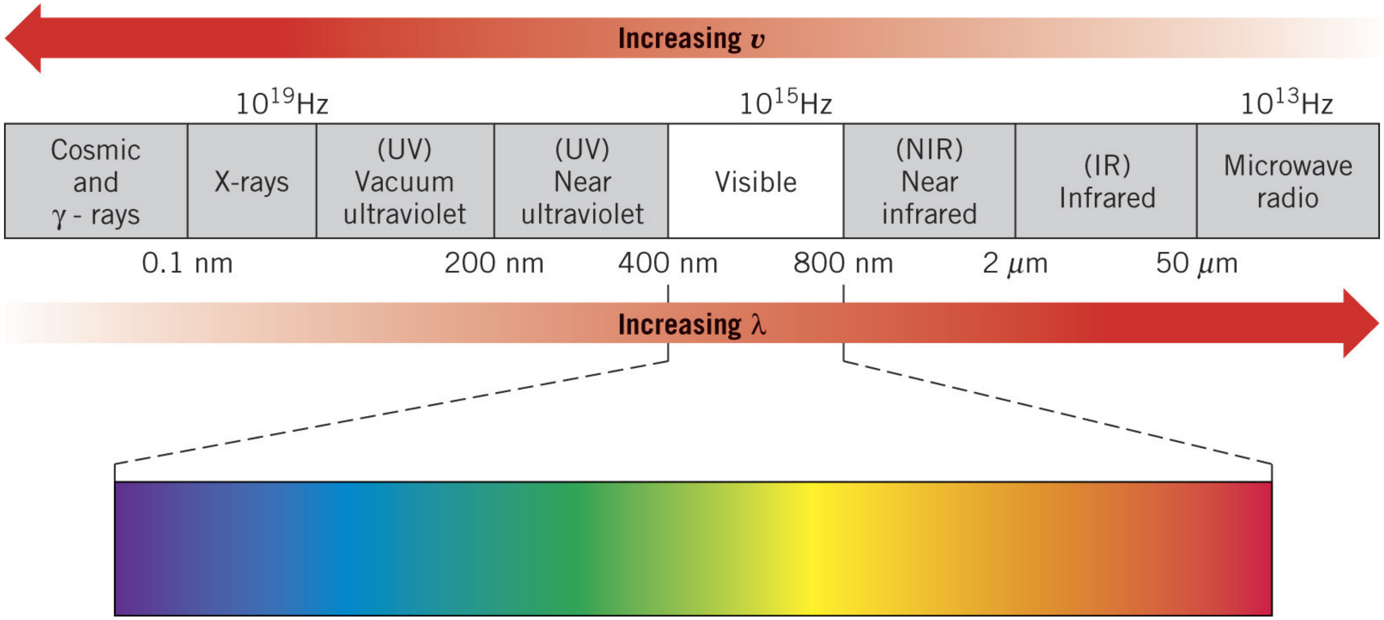
♦ The Stability of Conjugated Dienes

➔1,3-butadiene has a lower heat of hydrogenation by 15 kJ mol^{-1} than two molecules of 1-butene

- A lower heat of hydrogenation means 1,3-butadiene is more stable
- These molecules can be compared directly because upon hydrogenation they lead to the same product



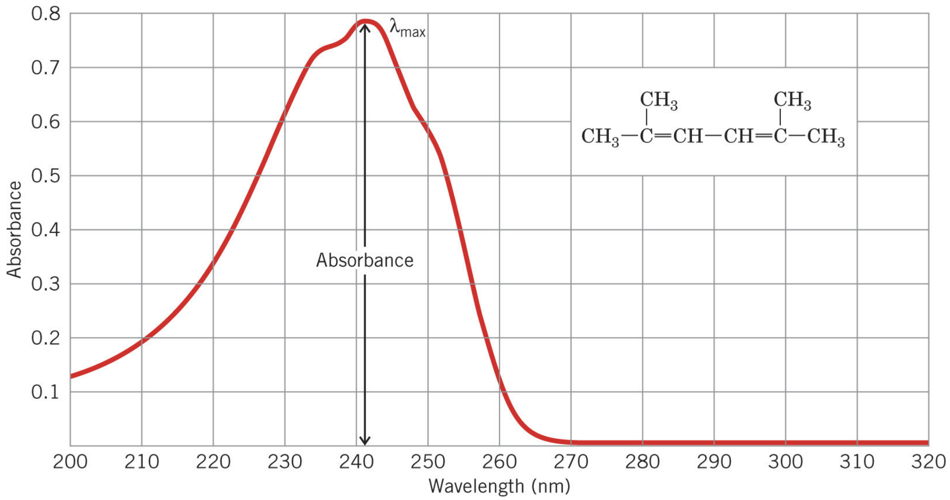
- ♦ **Ultraviolet-Visible Spectroscopy**
  - ➔ **Conjugated compounds absorb energy in the ultraviolet (UV) and visible (Vis) regions on the electromagnetic spectrum**
    - **The wavelength of radiation absorbed and the intensity of the absorption depend on the structure of the molecule**
- ● **UV-Vis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



- ➔ **The wavelength of maximum absorption (λ_{max}) is reported in units of nanometers (nm)**
- ➔ **Molar absorptivity (ε) is also reported**
  - **ε Is the intensity of the absorption**
  - **A is the observed absorbance, C is the molar concentration of the sample and l is length of the sample cell in centimeters**

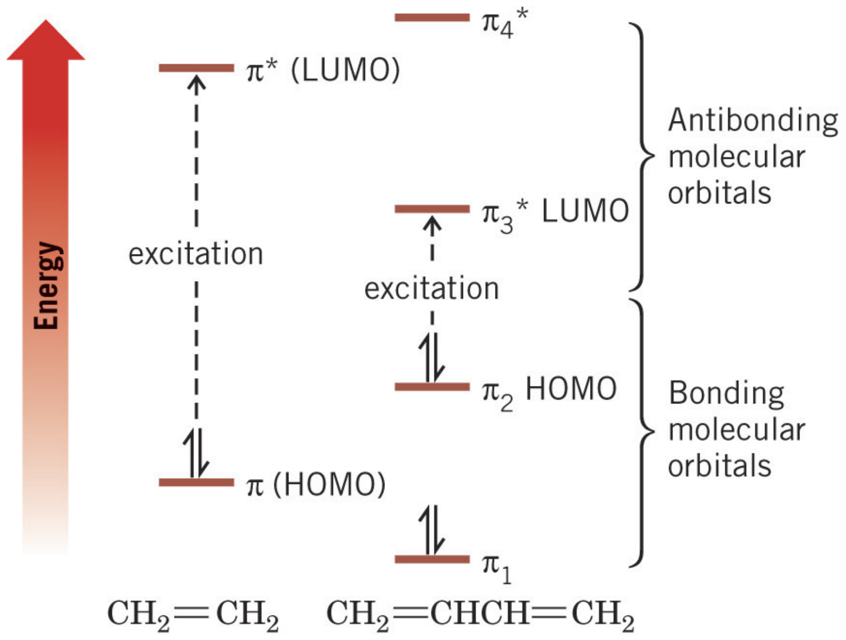
$$A = \varepsilon \times C \times l \quad \text{or} \quad \varepsilon = \frac{A}{C \times l}$$

- ➔ **Example: UV absorption spectrum of 2,5-dimethyl-2,4-hexadiene in methanol at a concentration of 5.95 x 10^{-5} M in a 1.0 cm cell**

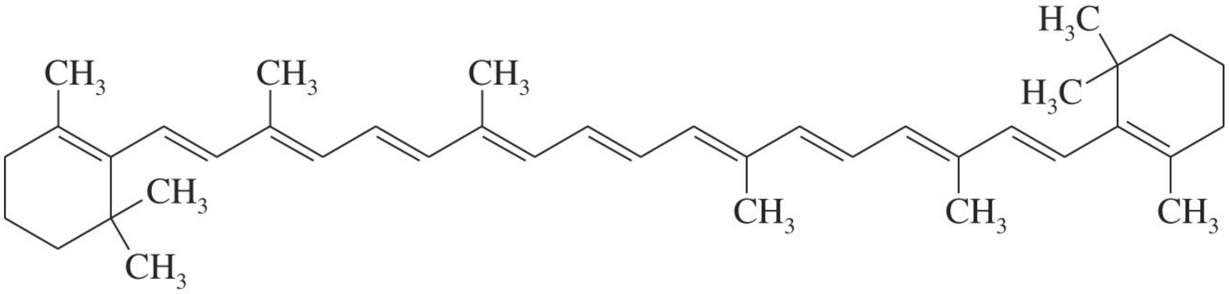


2,5-Dimethyl-2,4-hexadiene, $\lambda_{max}^{methanol}$ 242.5 nm (ε = 13,100)

- **Absorption Maxima for Nonconjugated and Conjugated Dienes**
  - ➔ **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 λ_{max} at 171 nm and 1,3-butadiene has λ_{max} at 217 nm**

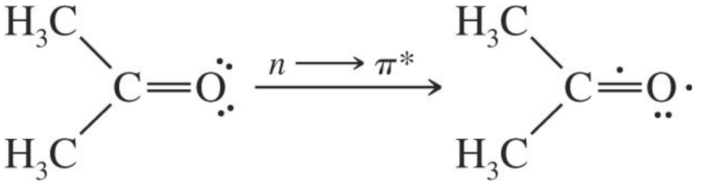


- ➔ **The longer the conjugated system, the smaller the energy difference between the HOMO and the LUMO**
  - **A smaller energy gap results in longer λ_{max} in the ultraviolet -visible spectrum**
  - **β-Carotene has 11 conjugated double bonds and an absorbance maximum at 497 nm which is in the blue-green region of the visible spectrum**
  - **β-Carotene is perceived as red-orange, the complementary color of blue-green**



β-Carotene

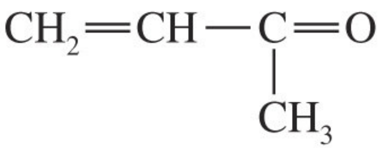
- ➔ **Carbonyl compounds also absorb light in the UV region**
  - **An unshared (n) electron on oxygen is promoted to a π* orbital**



Acetone

$\boldsymbol{\lambda_{max} = 280\ \text{nm}}$

$\boldsymbol{\varepsilon_{max} = 15}$



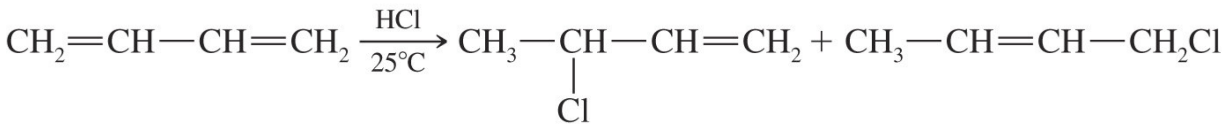
$CH_2{=}CH{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}O$

$\boldsymbol{n \longrightarrow \pi^*\ \lambda_{max} = 324\ \text{nm},\ \varepsilon_{max} = 24}$

$\boldsymbol{\pi \longrightarrow \pi^*\ \lambda_{max} = 219\ \text{nm},\ \varepsilon_{max} = 3600}$

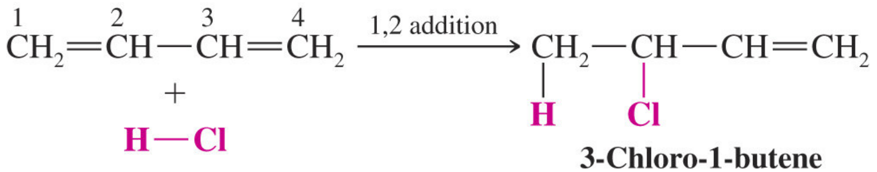
♦ Electrophilic Attack on Conjugated Dienes: 1,4 Addition

- ➔ **When 1,3-butadiene reacts with one equivalent of HCl at room temperature 78% of the 1,2 addition product and 22% of the 1,4 addition product are obtained**



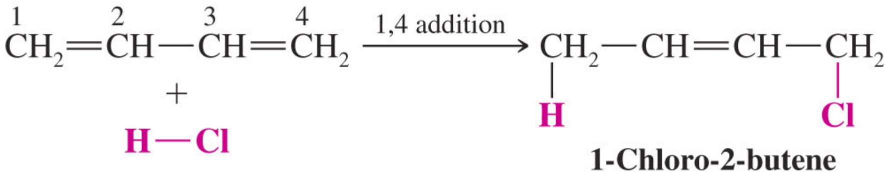
$$\mathrm{CH_2{=}CH{-}CH{=}CH_2} \xrightarrow[25^\circ\mathrm{C}]{\mathrm{HCl}} \mathrm{CH_3{-}}\underset{\mathrm{Cl}}{\underset{|}{\mathrm{CH}}}\mathrm{{-}CH{=}CH_2} + \mathrm{CH_3{-}CH{=}CH{-}CH_2Cl}$$

1,3-Butadiene **3-Chloro-1-butene (78%)** **1-Chloro-2-butene (22%)**



$$\overset{1}{\mathrm{CH_2}}{=}\overset{2}{\mathrm{CH}}{-}\overset{3}{\mathrm{CH}}{=}\overset{4}{\mathrm{CH_2}} + \mathrm{H{-}Cl} \xrightarrow{\text{1,2 addition}} \underset{\mathrm{H}}{\underset{|}{\mathrm{CH_2}}}{-}\underset{\mathrm{Cl}}{\underset{|}{\mathrm{CH}}}{-}\mathrm{CH{=}CH_2}$$

3-Chloro-1-butene

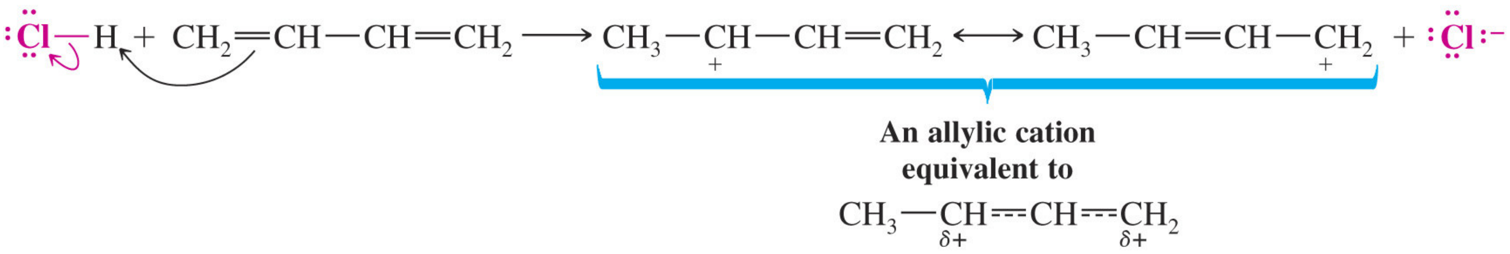


$$\overset{1}{\mathrm{CH_2}}{=}\overset{2}{\mathrm{CH}}{-}\overset{3}{\mathrm{CH}}{=}\overset{4}{\mathrm{CH_2}} + \mathrm{H{-}Cl} \xrightarrow{\text{1,4 addition}} \underset{\mathrm{H}}{\underset{|}{\mathrm{CH_2}}}{-}\mathrm{CH{=}CH}{-}\underset{\mathrm{Cl}}{\underset{|}{\mathrm{CH_2}}}$$

1-Chloro-2-butene

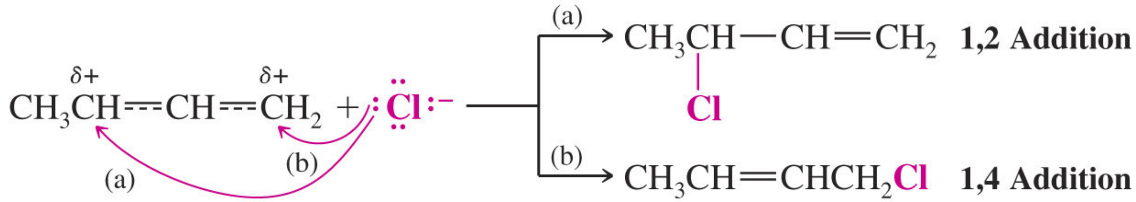
- ➔ **In step 1 hydrogen chloride reacts to add hydrogen to a terminal carbon which gives a stable allyl cation intermediate**
  - **Addition of hydrogen to in internal carbon leads to an unstable 1º carbocation**

Step 1



- ➔ **In step 2 chloride can react at either end of the allyl cation**
  - **This leads to either 1,2 or 1,4 product**

Step 2

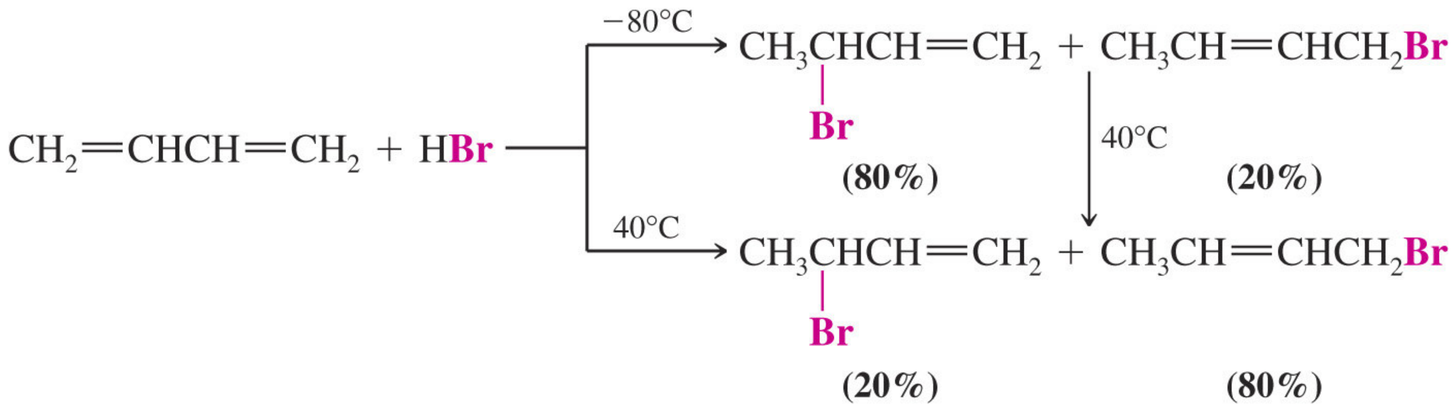


- ➔ **Other electrophilic reagents add to conjugated dienes in similar fashion**

$$CH_2{=}CHCH{=}CH_2 \xrightarrow[40^\circ C]{HBr} \underset{\textbf{(20\%)}}{CH_3CHBrCH{=}CH_2} + \underset{\textbf{(80\%)}}{CH_3CH{=}CHCH_2Br}$$

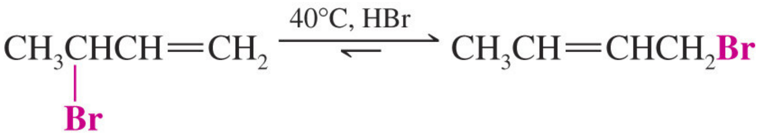
$$CH_2{=}CHCH{=}CH_2 \xrightarrow[-15^\circ C]{Br_2} \underset{\textbf{(54\%)}}{CH_2BrCHBrCH{=}CH_2} + \underset{\textbf{(46\%)}}{CH_2BrCH{=}CHCH_2Br}$$

- **Kinetic Control versus Thermodynamic Control of a Chemical Reaction**
  - ➔ **When HBr adds to 1,3-butadiene the temperature of reaction greatly affects the distribution of 1,2 and 1,4 products**
    - **Low temperature (e.g., -80°C) favors 1,2-addition product**
    - **High temperature (e.g., 40°C) favors 1,4-addition product**
    - **When the mixture of products formed at low temperature is heated, the product ratios change to favor 1,4-addition product**



$$\begin{tikzcd} & CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH{=}CH_2 \; (80\%) + CH_3CH{=}CHCH_2Br \; (20\%) \arrow[d, "40°C"] \\ CH_2{=}CHCH{=}CH_2 + HBr \arrow[ur, "-80°C"] \arrow[r, "40°C"] & CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH{=}CH_2 \; (20\%) + CH_3CH{=}CHCH_2Br \; (80\%) \end{tikzcd}$$

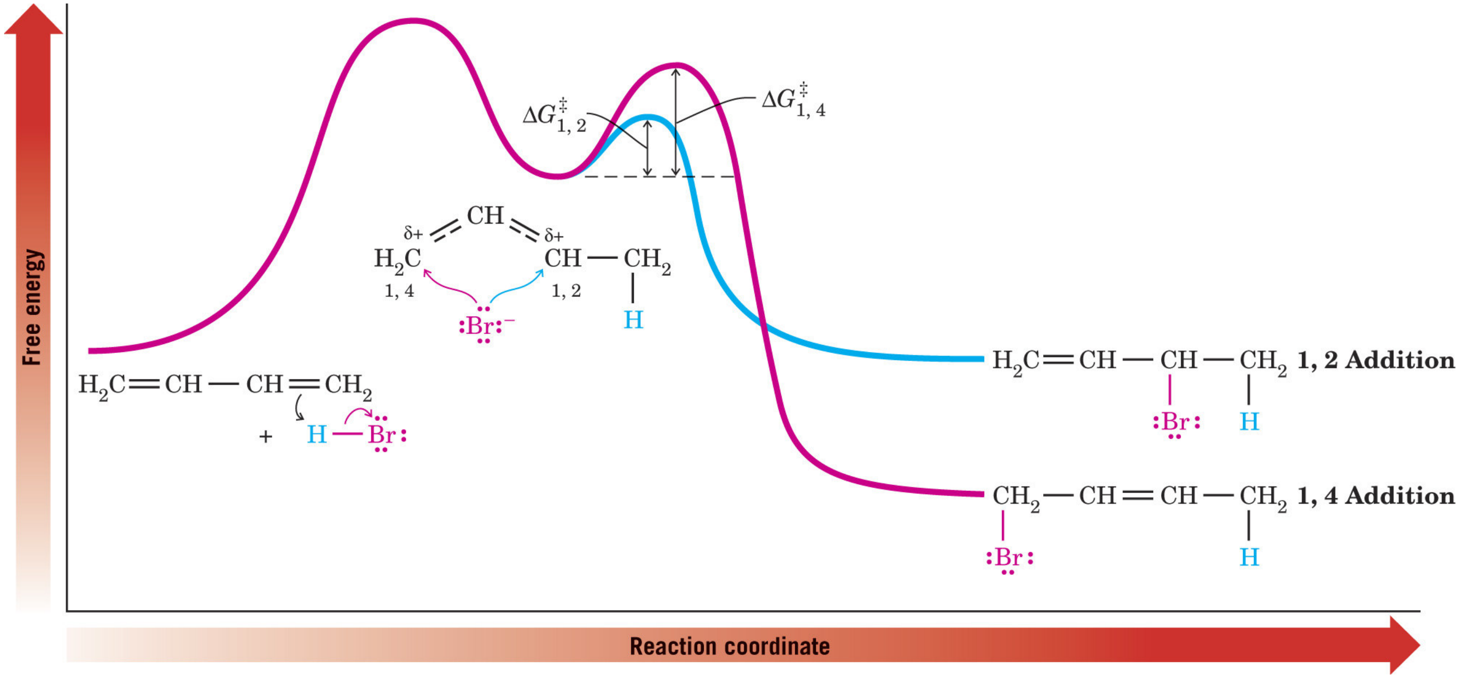
- ➔ **Heating the 1,2-addition product leads to an equilibrium which favors the 1,4-addition product**
  - **Because equilibrium conditions favor the 1,4-addition product it must be the most stable**



$$\underset{\textbf{Br}}{CH_3\overset{|}{C}HCH{=}CH_2} \xrightleftharpoons{40°C,\ HBr} CH_3CH{=}CHCH_2\textbf{Br}$$

1,2-Addition product

1,4-Addition product

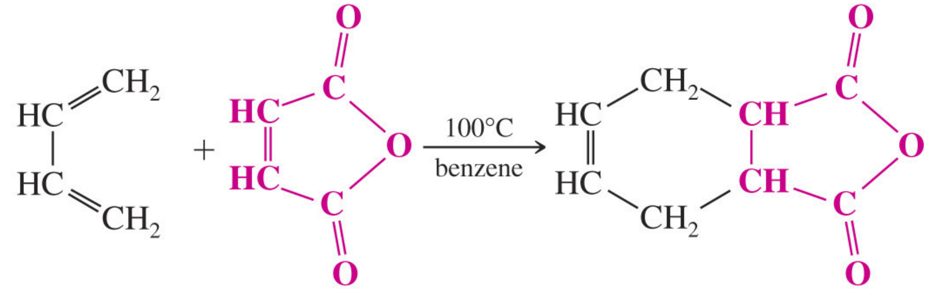


- At lower temperatures the proportion of products is determined by the relative rates of formation of product
  - 1,2-addition product is formed faster and is the major product at low temperatures
  - The $\Delta G^{\ddagger}$ for formation of 1,2-addition product is lower than for 1,4-addition product
  - At low temperatures fewer molecules have enough energy to overcome the higher $\Delta G^{\ddagger}$ for formation of the 1,4-addition product
  - The reaction is said to be under kinetic control
- At higher temperatures when an equilibrium is established, the most stable product predominates
  - Enough energy is available to overcome $\Delta G^{\ddagger}$ barriers for formation of 1,2- and 1,4-addition products and for the reverse reactions
  - An equilibrium situation exists and the most stable product is the major one
  - 1,4-addition product is more stable and is the major product at high temperatures
  - The reaction is said to be under thermodynamic control

- The 1,4 product is most stable because it leads to a disubstituted double bond
  - 1,2-addition product has a less stable monosubstituted double bond
- The 1,2-addition product is formed faster because the allyl cation has more $\delta+$ charge density at the 2° rather than the 1° carbon

♦ The Diels-Alder Reaction: A 1,4-Cycloaddition Reaction of Dienes

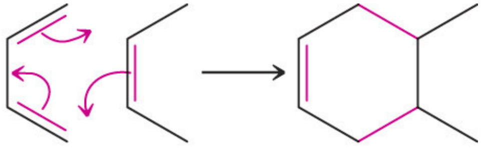
➔ Heating 1,3-butadiene and maleic anhydride gives a 6-membered ring product in 100% yield



1,3-Butadiene (diene) Maleic anhydride (dienophile) Adduct (100%)

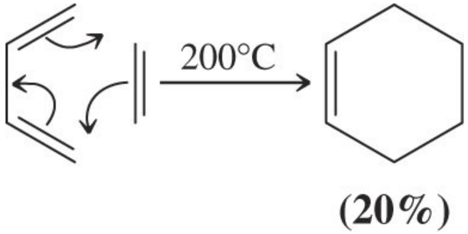
➔ The general Diels-Alder reaction forms a cylohexene product

- Overall, two new σ bonds are formed at the expense of two π bonds
- The conjugated diene is a 4π-electron system
- The dienophile (“diene lover”) is a 2π-electron system
- The product is called an adduct

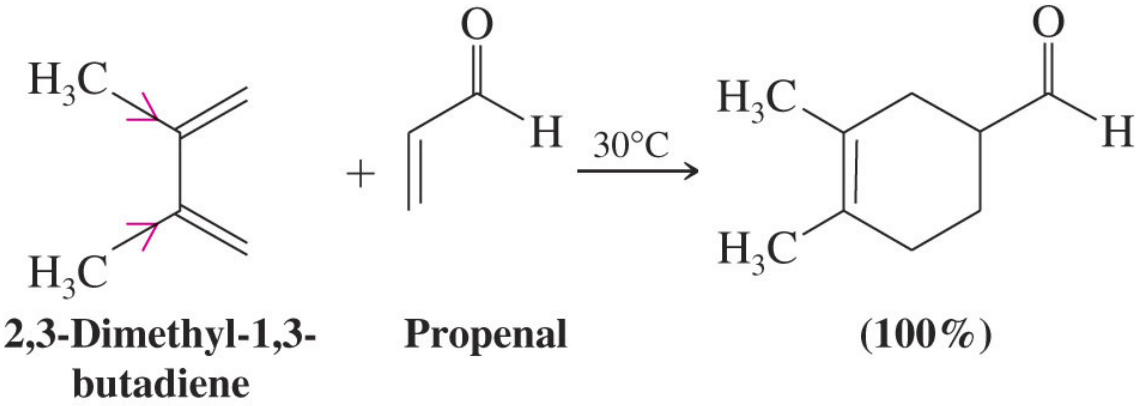


Diene Dieno-phile Adduct

- **Factors Favoring the Diels-Alder Reaction**
  - ➔The simplest possible example of a Diels-Alder reaction goes at very low yield and requires high temperatures

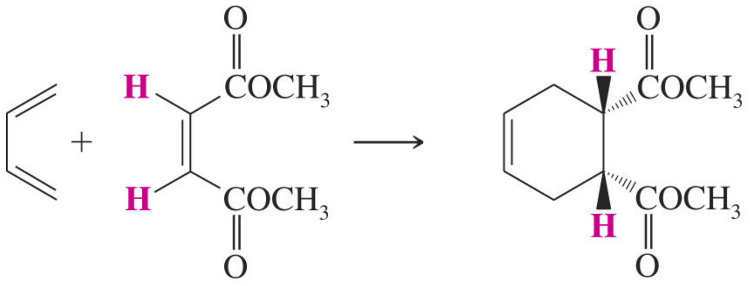


  - ➔To proceed in good yield and at low temperature the dienophile should have electron-withdrawing groups
    - It also helps if the diene has electron-releasing groups
    - Dienes with electron-donating groups and dienophiles with electron-withdrawing group can also react well together



Stereochemistry of the Diels-Alder Reaction

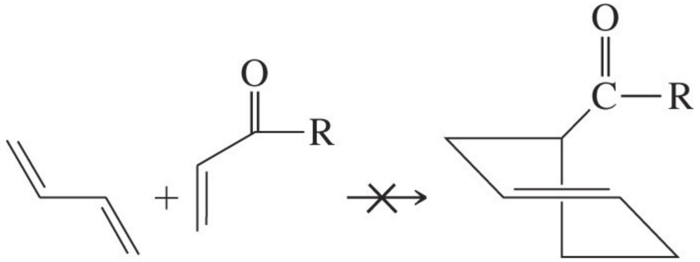
- ➔ The Diels-Alder reaction is stereospecific *i.e.* the reaction is a syn addition, and the configuration of the dienophile is retained in the product



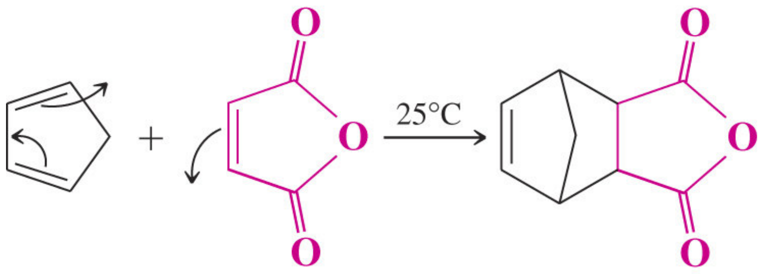
Dimethyl maleate (a *cis*-dienophile)

Dimethyl cyclohex-4-ene-*cis*-1,2-dicarboxylate

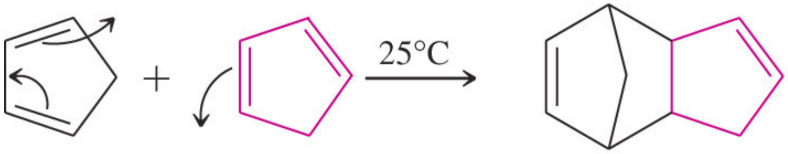
- ➔ The diene must be in the *s*-cis conformation to react
  - *s*-Trans conformation would lead to formation of a highly unstable trans bond in a 6-membered ring
  - Cyclic dienes which must be in the *s*-cis conformation are highly reactive



Highly strained

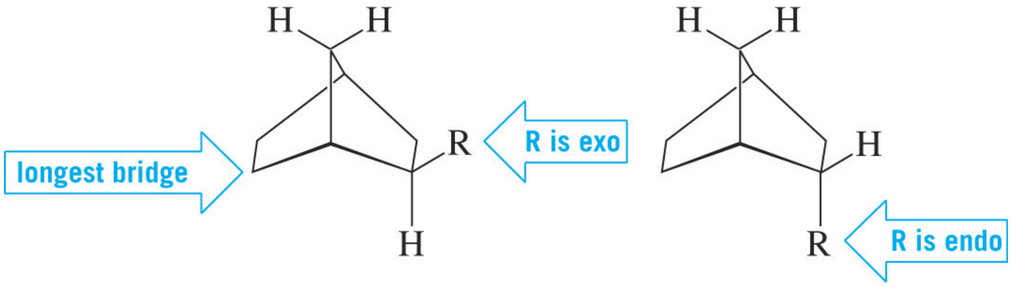


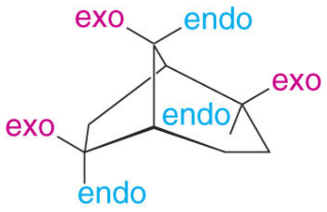
- **Cyclopentadiene is so reactive it spontaneously undergoes Diels-Alder reaction with itself at room temperature**
  - **This dimer can be “cracked” (undergo retro-Diels-Alder reaction) by heating and the cyclopentadiene product isolated by distillation.**



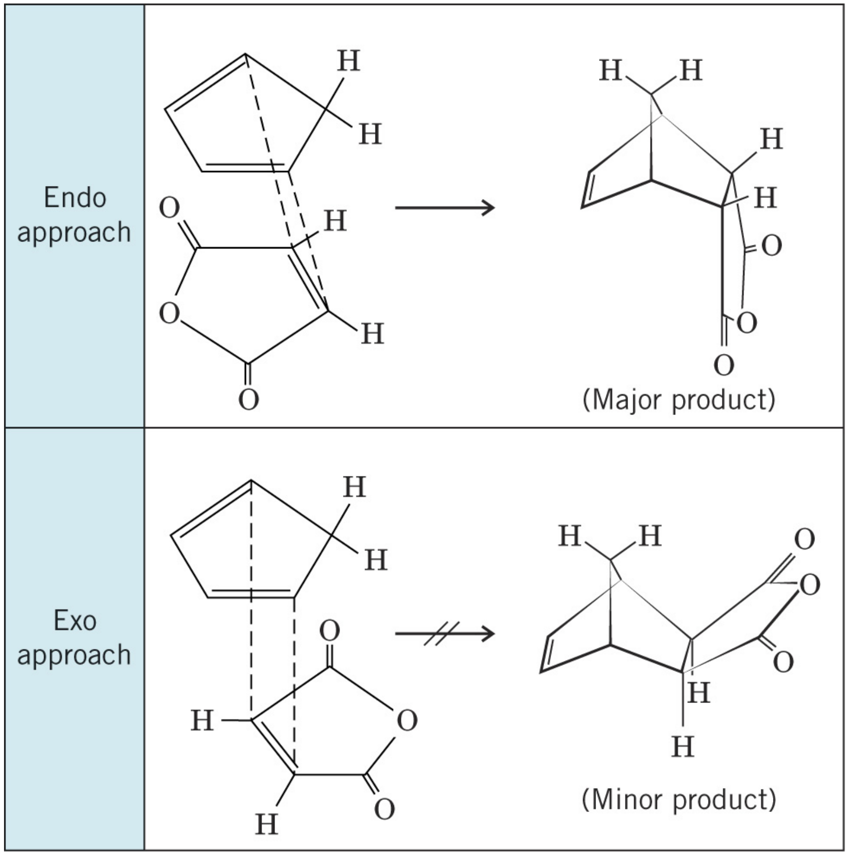
"Dicyclopentadiene"

- **The Diels-Alder reaction occurs primarily in an endo rather than an exo fashion when the reaction is kinetically controlled**
  - **A group that is exo in a bicyclic ring system is anti to the longest bridge**
  - **A group that is endo is on the same side as the longest bridge**

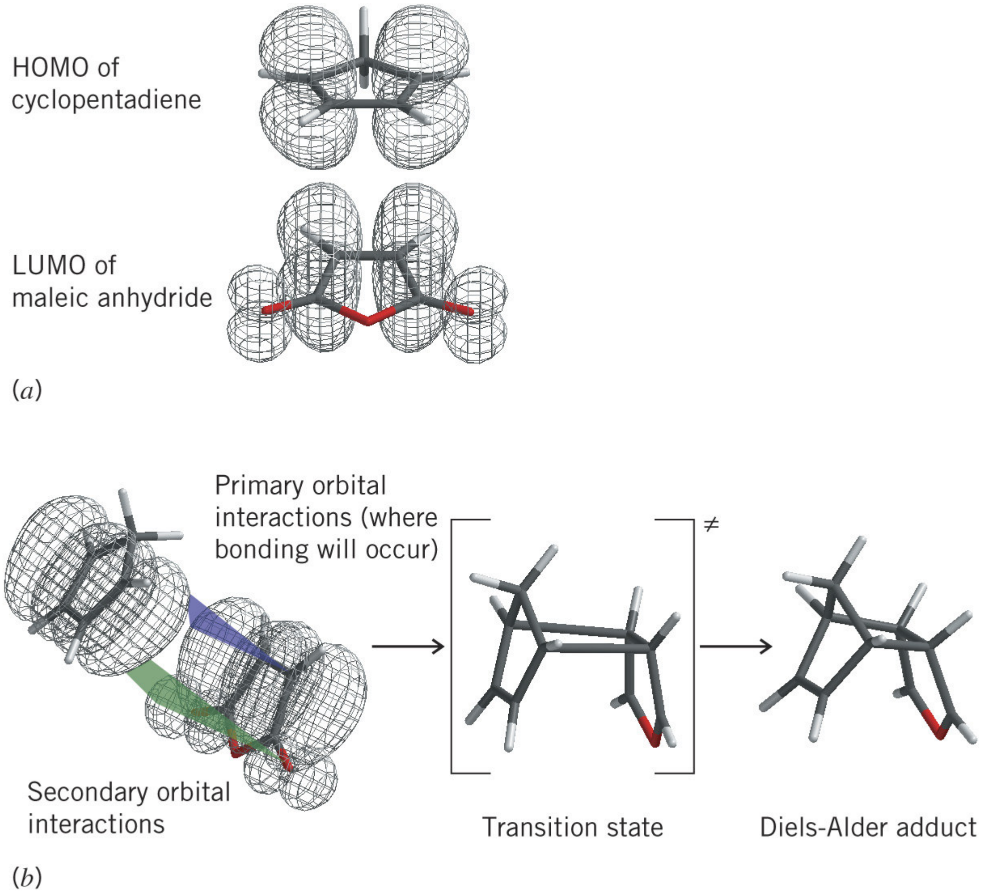




- **Molecular Orbital Considerations that Favor an Endo Transition State**
  - **When maleic anhydride and cyclopentadiene react the major product is the endo product**
    - **The major product has the anhydride linkage endo**



- **➔ When the molecules approach each other there are favorable interactions between the LUMO of maleic anhydride and the HOMO of cyclopentadiene**
  - **In the endo orientation favorable secondary oribtal interactions between the LUMO of the carbonyl groups and the HOMO of the cyclopentadiene carbons at the C2 and C3 positions of the diene can also occur**



- **Intramolecular Diels-Alder Reactions**
  - ➔Intramolecular reactions are those in which the reacting groups are part of the same molecule