# Organic Chemistry II / CHEM 252

## Chapter 13 – Conjugated Unsaturated Systems

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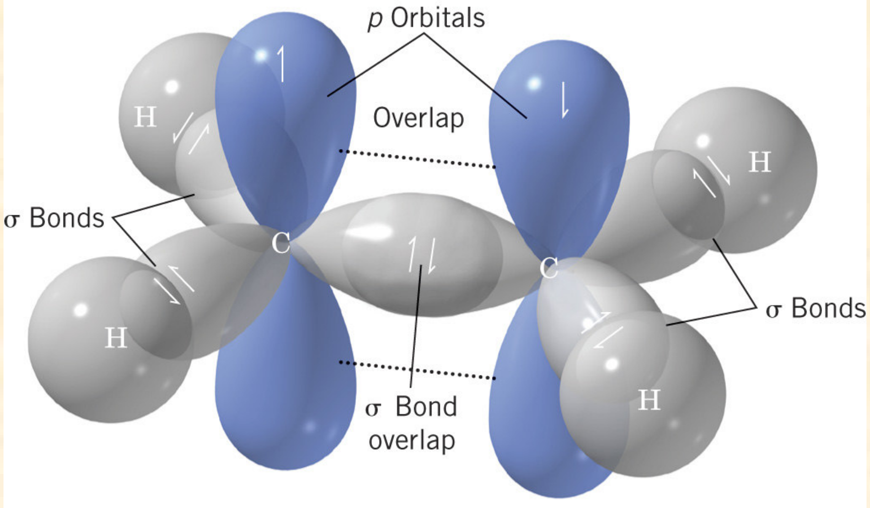
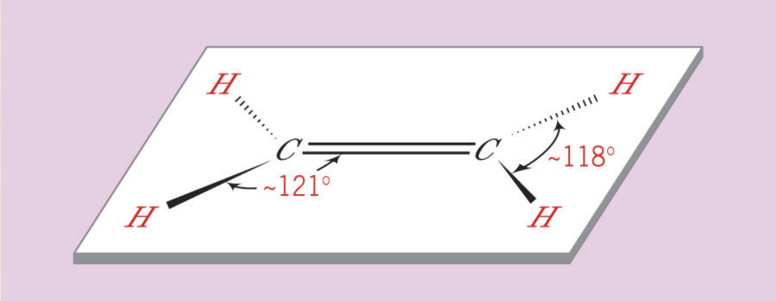
# Introduction

- 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

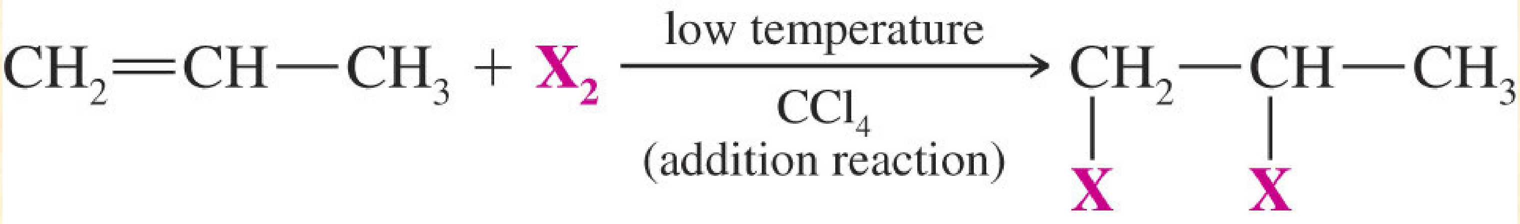




# Allylic Substitution

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



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

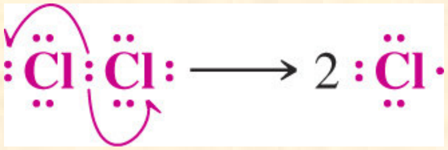
$$\underset{\textbf{Propene}}{CH_2{=}CH{-}CH_3} + X_2 \xrightarrow[\substack{\text{or low concentration of } X_2\\ \text{(substitution reaction)}}]{\text{high temperature}} CH_2{=}CH{-}CH_2X + HX$$

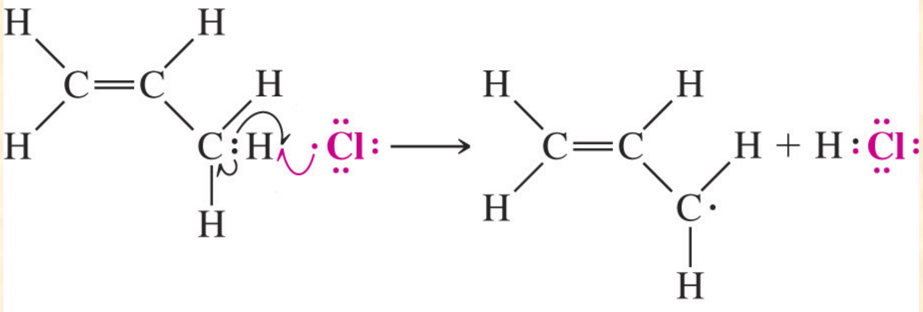
# Allylic Substitution

- Allylic Chlorination (High Temperature)
    - Allylic chlorination - 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

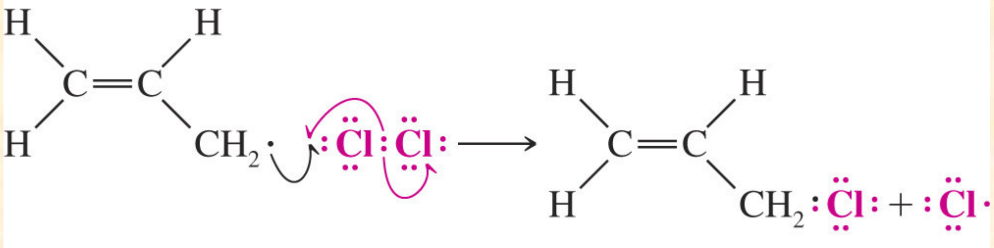
$$CH_2{=}CH{-}CH_3 + Cl_2 \xrightarrow[\text{gas phase}]{400^\circ C} CH_2{=}CH{-}CH_2Cl + HCl$$

**3-Chloropropene (allyl chloride)**





**Allyl radical**



**Allyl chloride**

# Allylic Substitution

- 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

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

**Propene** **Allyl radical**

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

**Isobutane** **3° Radical**

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

**Propane** **2° Radical**

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

**Propane** **1° Radical**

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

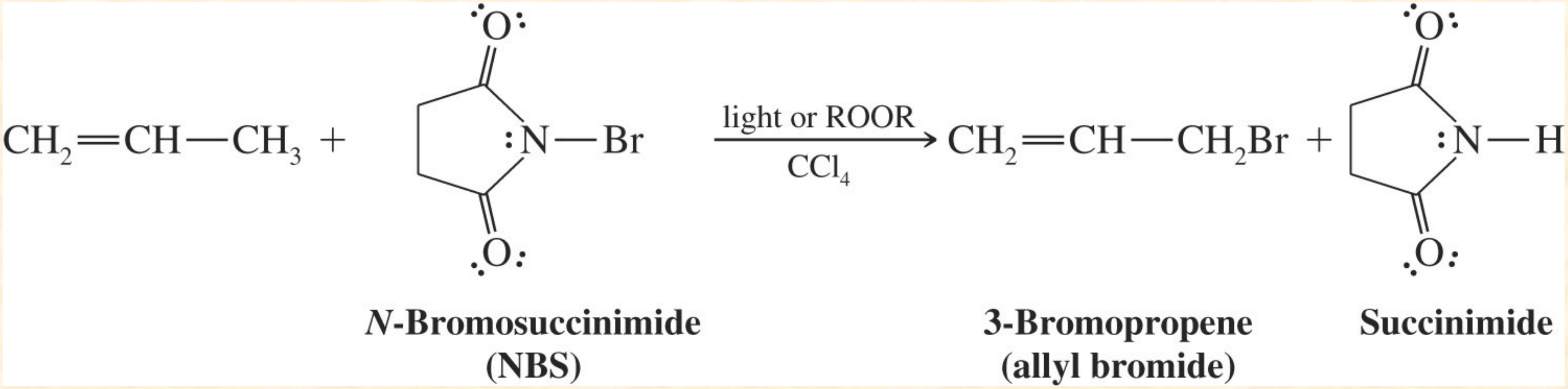
**Ethene** **Vinyl radical**

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

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

# Allylic Substitution

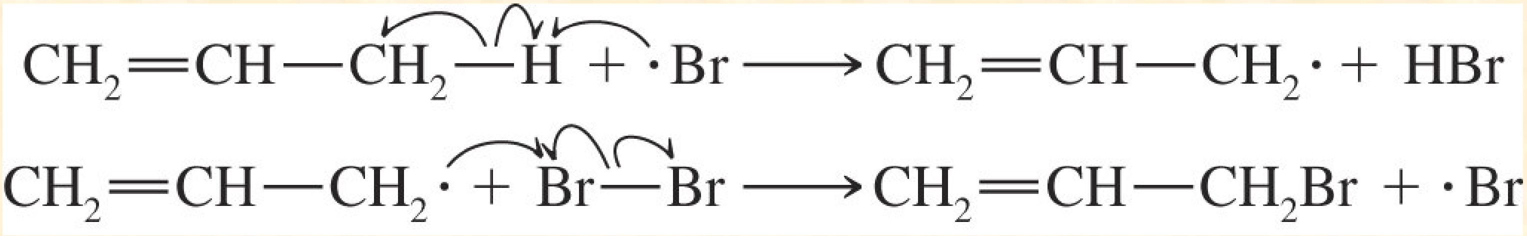
- Allylic Bromination with *N*-Bromosuccinimide
  - Propene undergoes allylic bromination with *N*-bromosuccinimide (NBS) in the presence of light or peroxides
    - NBS provides a continuous low concentration of bromine for the radical reaction
    - A low bromine concentration favors allylic substitution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



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

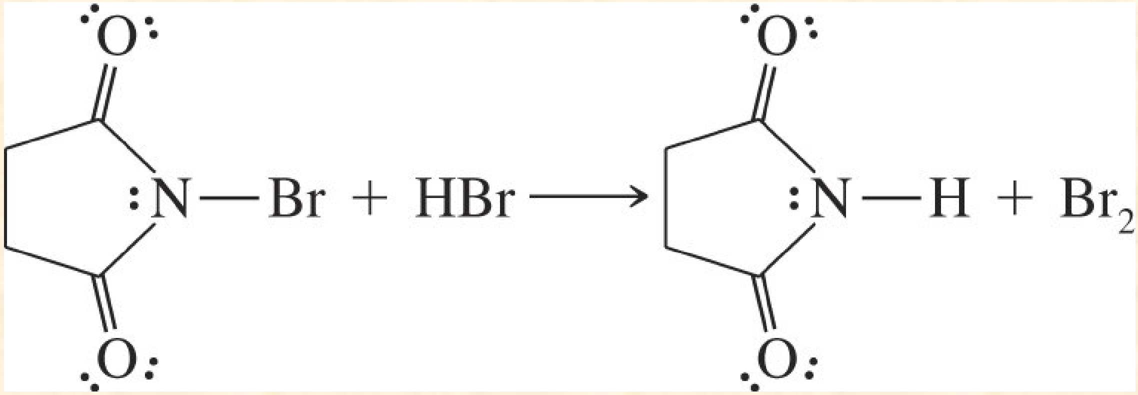
# Allylic Substitution

- 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



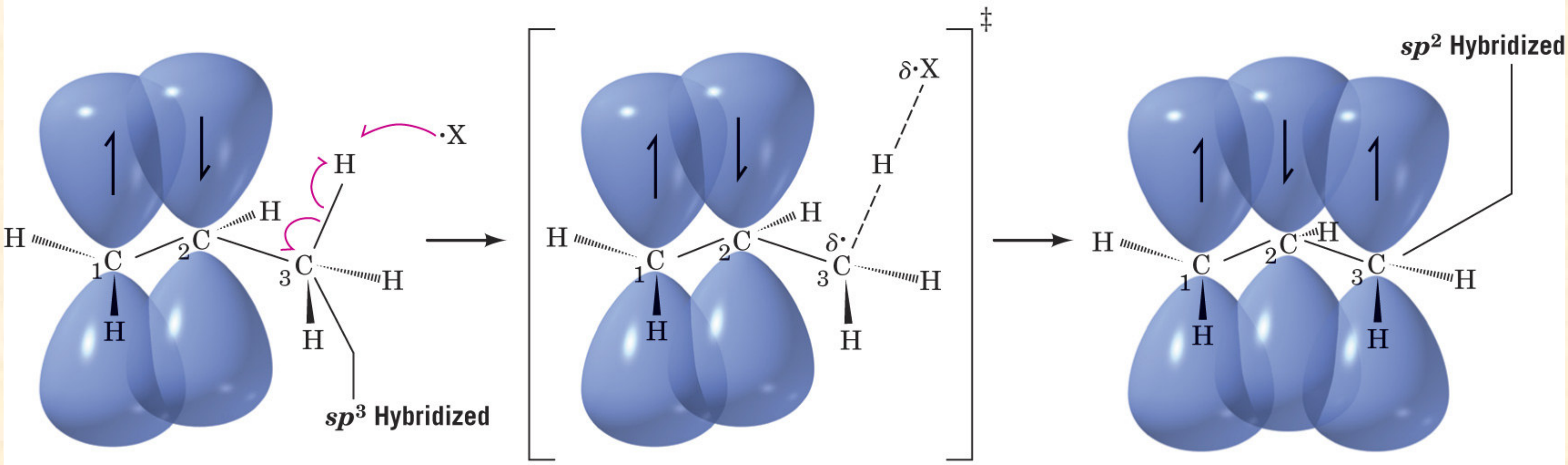
$$CH_2{=}CH{-}CH_2{-}H + \cdot Br \longrightarrow CH_2{=}CH{-}CH_2\cdot + HBr$$

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



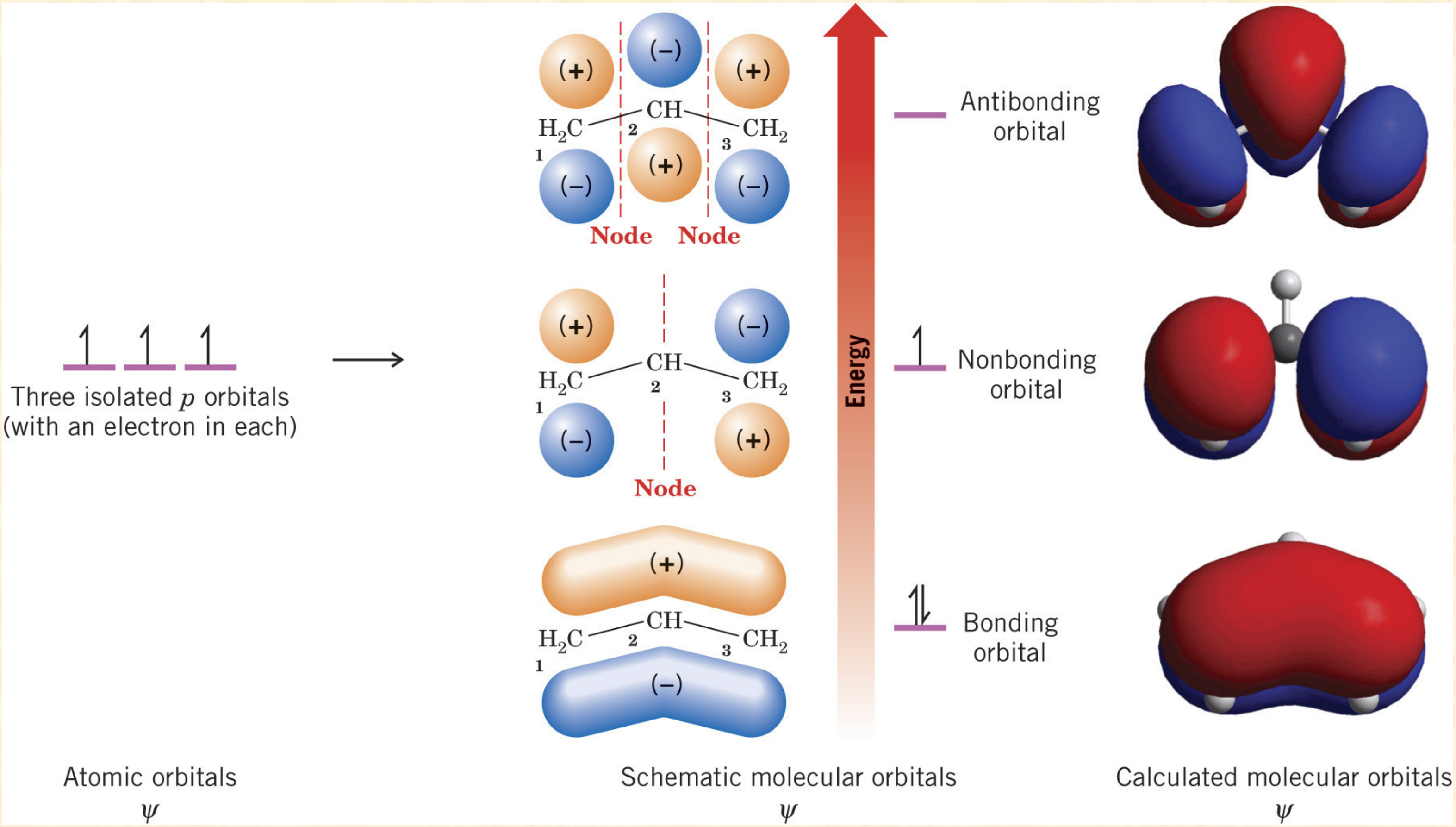
# The Allyl Radical

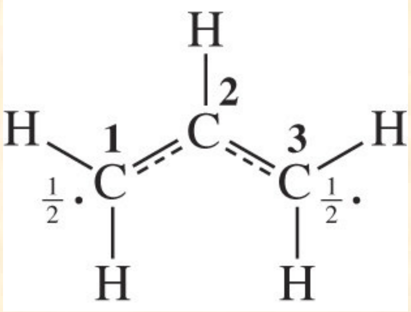
- The Stability of the Allyl Radical
    - Both molecular orbital theory and resonance theory can explain the stability of allyl radicals
  - Molecular Orbital Description of the Allyl Radical
    - When an allylic hydrogen is abstracted, the developing *p* orbital on the $sp^2$ carbon overlaps with 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 are delocalized over the entire conjugated system
      - Delocalization of charge and electron density leads to increased stability



# The Allyl Radical

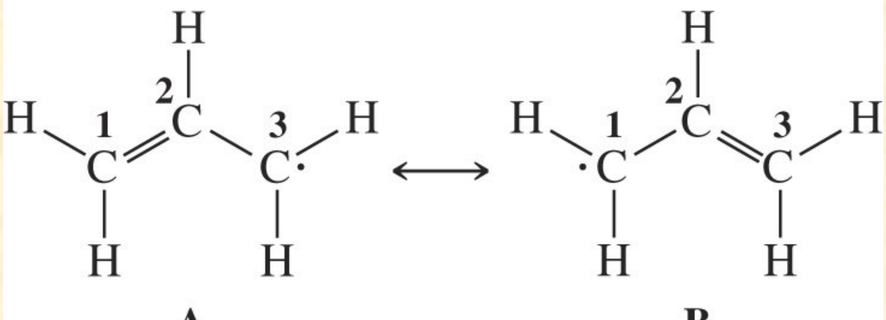
- The three *p* orbitals combine to form three molecular orbitals
  - The bonding molecular orbital contains two spin-paired electrons and this orbital increases bonding between the carbons
  - The nonbonding orbital contains a lone electron which is

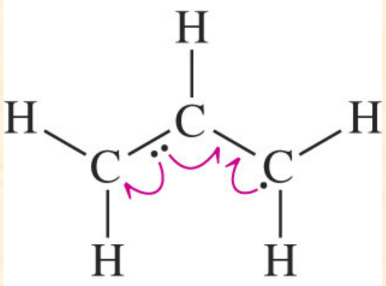




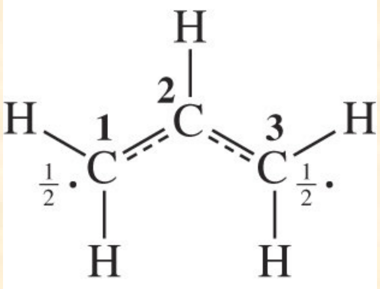
# The Allyl Radical

- Resonance Description of the Allyl Radical
  - The allyl radical has two contributing resonance forms
    - These resonance forms can be interconverted
    - The resonance structures are equivalent
    - Recall that equivalent resonance structures lead to much greater stability of the molecule than either structure alone would suggest





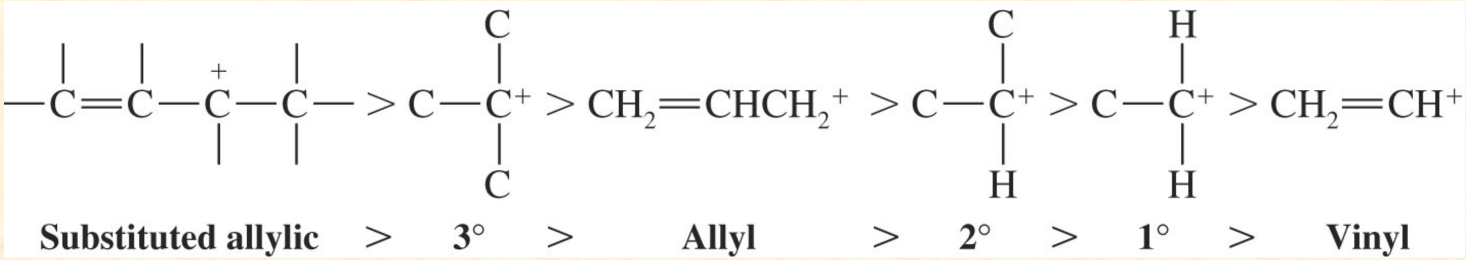
  - The true structure of the allyl radical as suggested by resonance theory is as follows



C

# The Allyl Cation

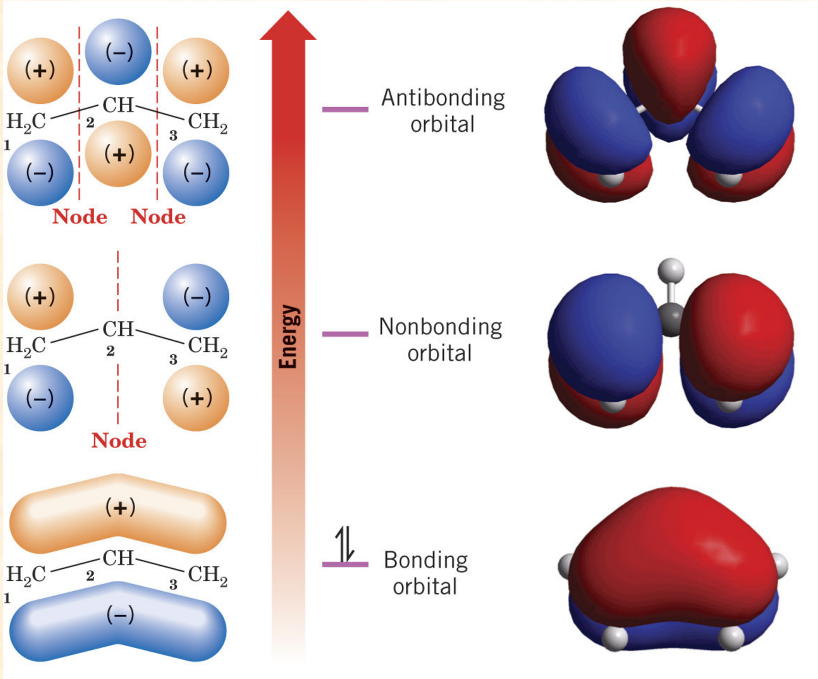
- The allyl cation is intermediate in stability between a tertiary and secondary carbocation



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

**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

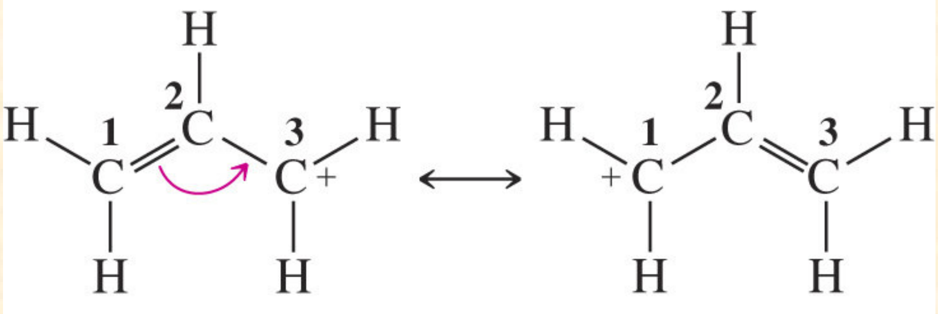


Schematic molecular orbitals

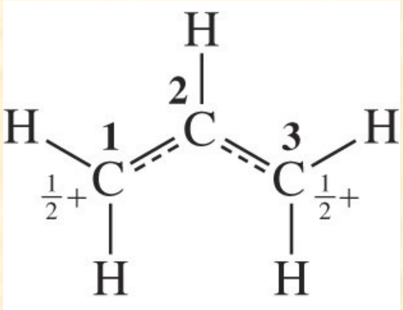
Calculated molecular orbitals

# The Allyl Cation

- 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**

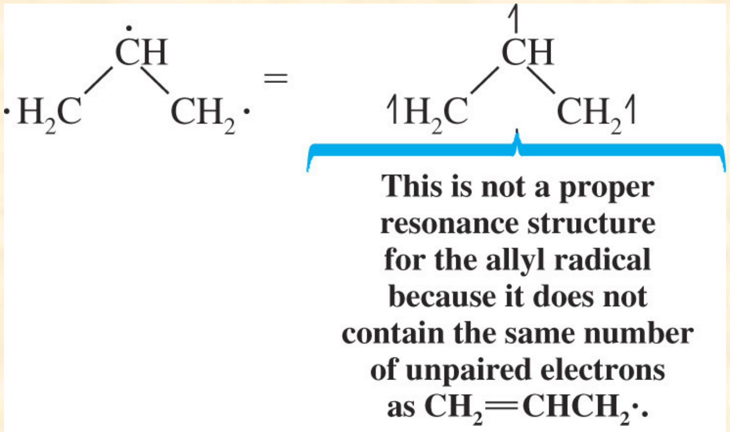
# Rules of Resonance

- Summary of Rules for Resonance

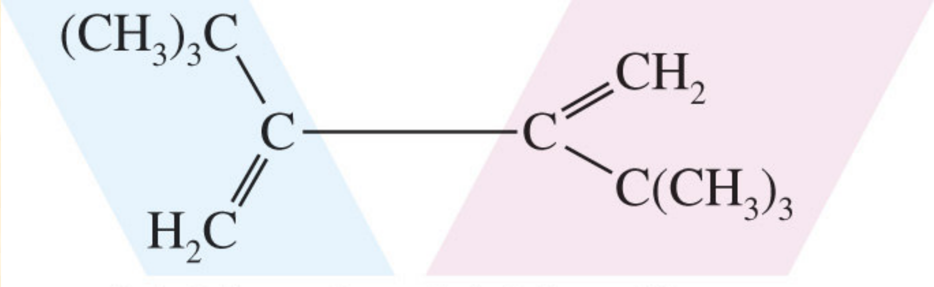
  Rules for Writing Resonance Structures

  - Individual resonance structures are not real structures - 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 have the same number of paired and unpaired electrons and must be proper Lewis structures



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



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

  - All atoms in a delocalized π-electron system must be in a plane
    - The molecule above does not behave like a conjugated diene because the large tert-butyl groups twist the structure and prevent the diene from being planar

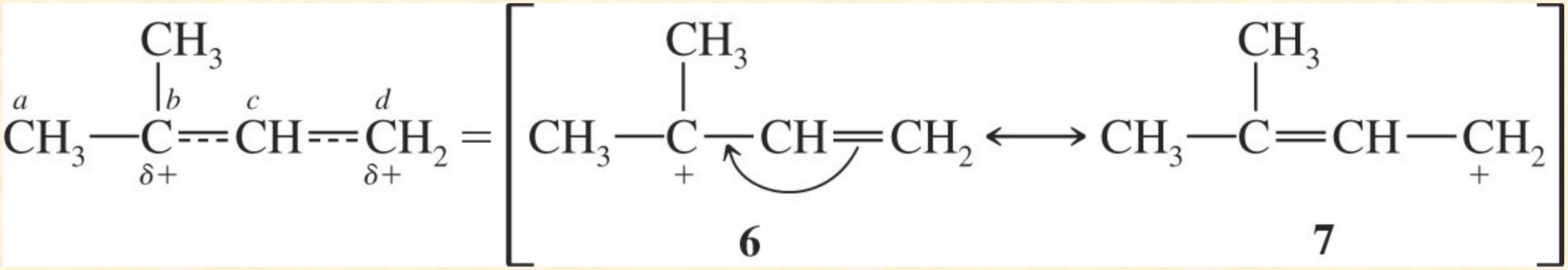
# Rules of Resonance

- 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 **4** or **5**

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

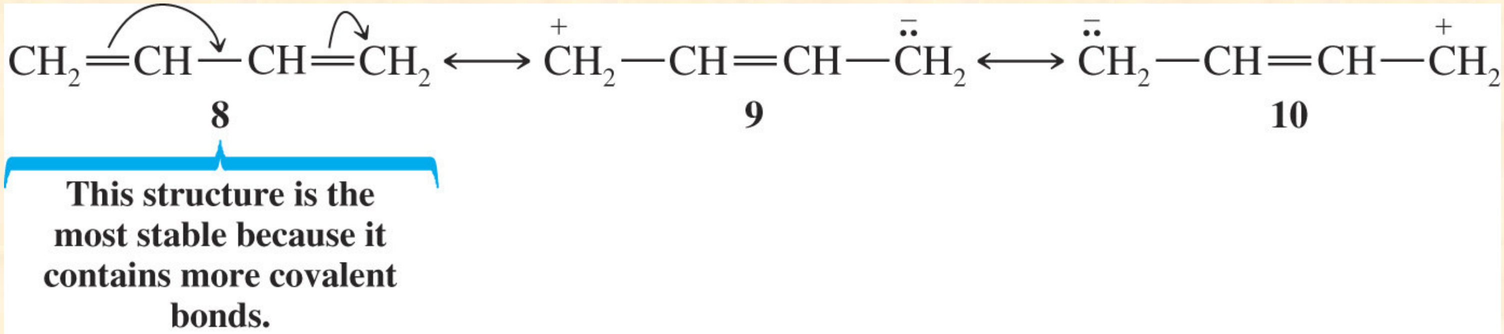
**4** **5**

- 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**



# Stability of Resonance Structures

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

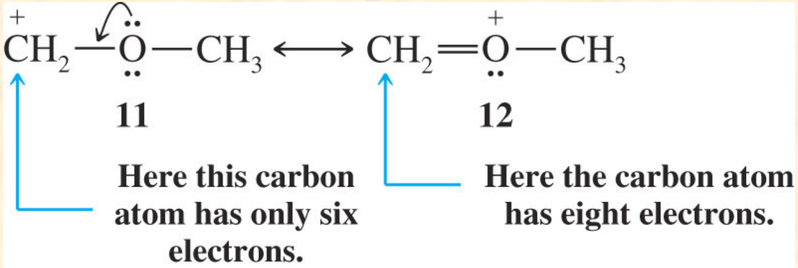


$CH_2{=}CH{-}CH{=}CH_2 \longleftrightarrow \overset{+}{C}H_2{-}CH{=}CH{-}\ddot{C}H_2 \longleftrightarrow \ddot{C}H_2{-}CH{=}CH{-}\overset{+}{C}H_2$

**8** **9** **10**

**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**



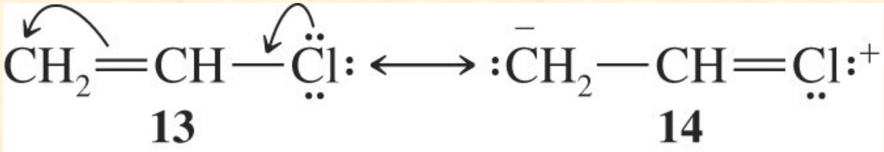
$\overset{+}{C}H_2{-}\underset{..}{\ddot{O}}{-}CH_3 \longleftrightarrow CH_2{=}\underset{..}{\overset{+}{O}}{-}CH_3$

**11** **12**

**Here this carbon atom has only six electrons.**

**Here the carbon atom has eight electrons.**

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



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

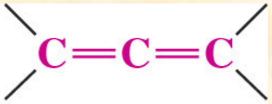
**13** **14**

# 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 bonds affect each other when they react, isolated double bonds react separately and do not affect each other

$CH_2{=}C{=}CH_2$

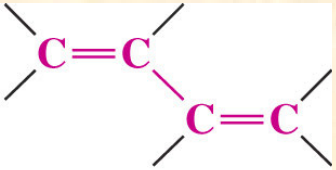
**Allene**



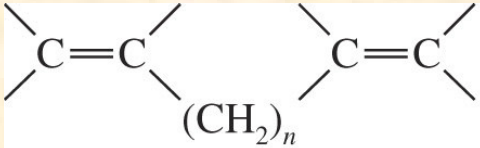
**A cumulated diene**

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

**1,3-Butadiene**



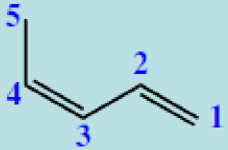
**A conjugated diene**



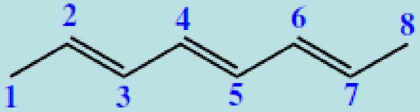
**An isolated diene**
**($n \neq 0$)**

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

**1,4-Pentadiene**



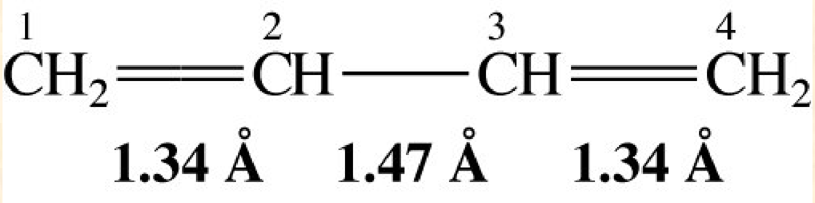
**(3*Z*)-1,3-Pentadiene**
**(*cis*-1,3-Pentadiene)**
**CONJUGATED**



**(2*E*,4*E*,6*E*)-2,4,6-Octatriene**
**(*trans*, *trans*, *trans*-2,4,6-Octatriene)**
**CONJUGATED**

# Alkadienes and Polyunsaturated Hydrocarbons

- 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

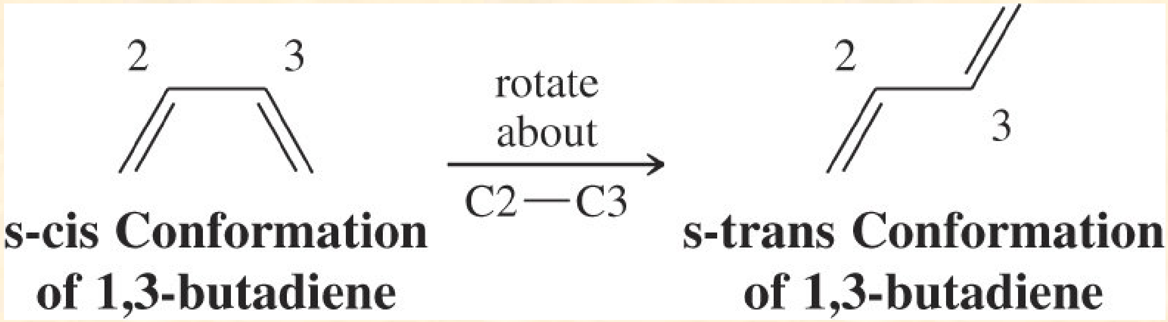


$$\overset{1}{C}H_2 \underset{1.34\ \text{Å}}{=\!=} \overset{2}{C}H \underset{1.47\ \text{Å}}{-\!-} \overset{3}{C}H \underset{1.34\ \text{Å}}{=\!=} \overset{4}{C}H_2$$

    - 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

# Alkadienes and Polyunsaturated Hydrocarbons

- 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

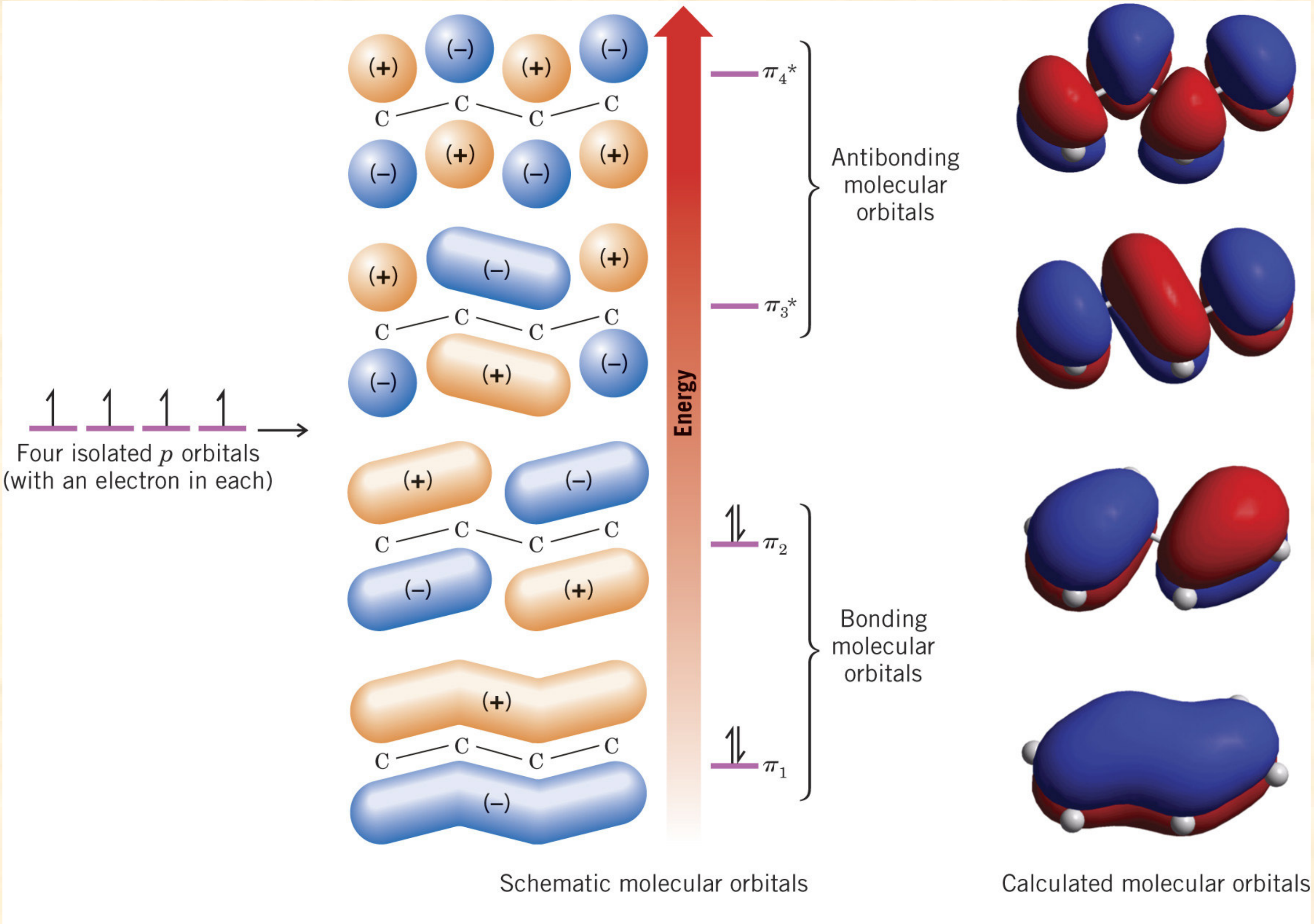


**s-cis Conformation of 1,3-butadiene**

**s-trans Conformation of 1,3-butadiene**

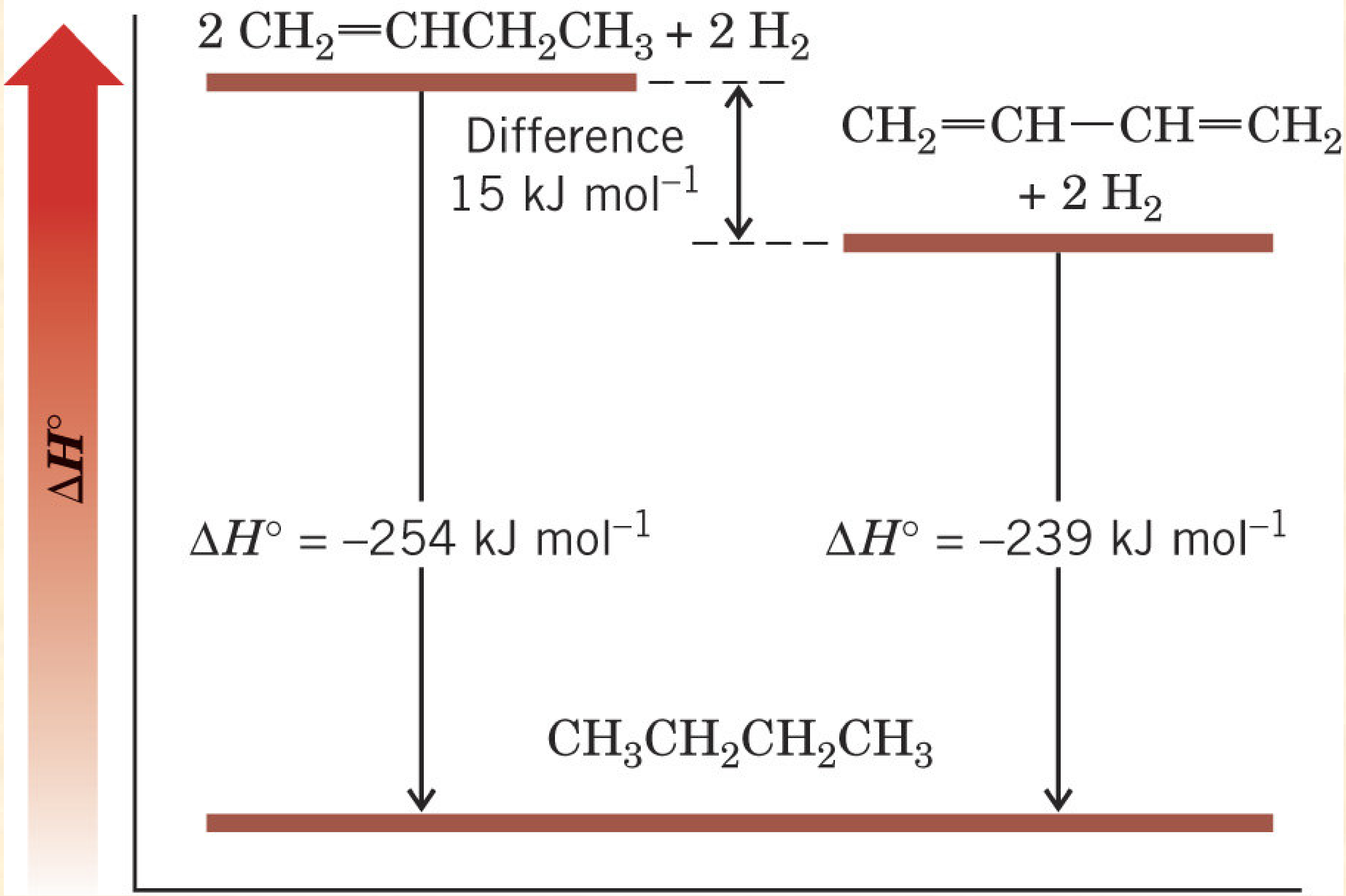
# Alkadienes and Polyunsaturated Hydrocarbons

- 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 orbital in 1,3-butadiene is the highest occupied molecular orbital (HOMO) and shows no overlap between C2 and C3

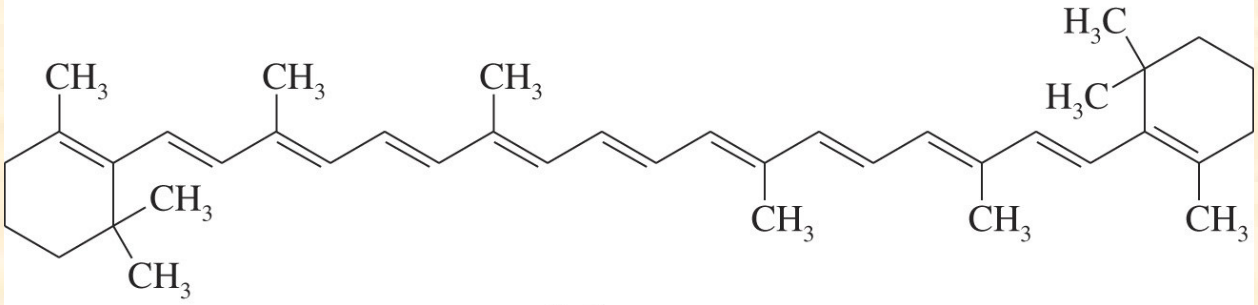


# Alkadienes and Polyunsaturated Hydrocarbons

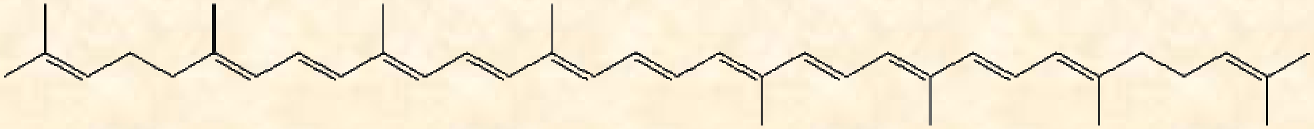
- The Stability of Conjugated Dienes
  - 1,3-butadiene has a lower heat of hydrogenation by 15 kJ mol$^{-1}$ than two molecules of 1-butene
    - – A lower heat of hydrogenation means 1,3-butadiene is more stable
    - – These molecules can be compared directly because upon hydrogenation they lead to the same product



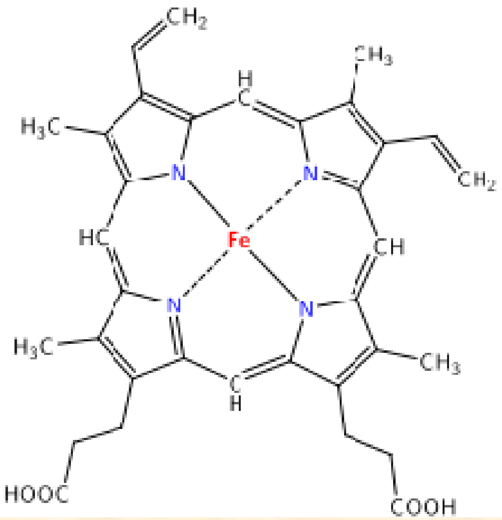
# Alkadienes and Polyunsaturated Hydrocarbons



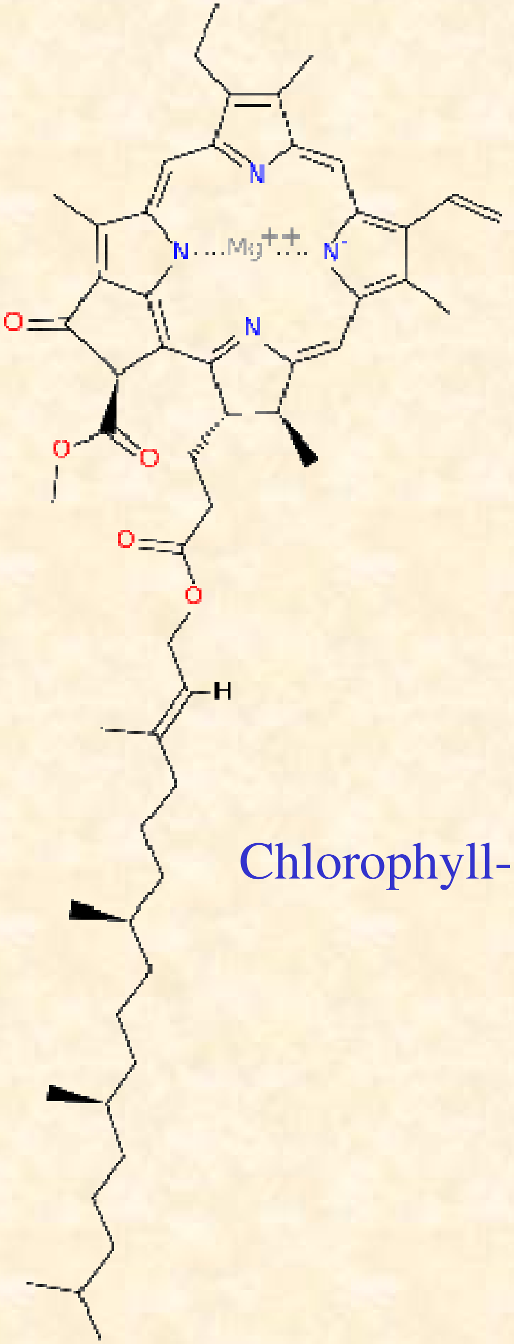
**β-Carotene**



lycopene

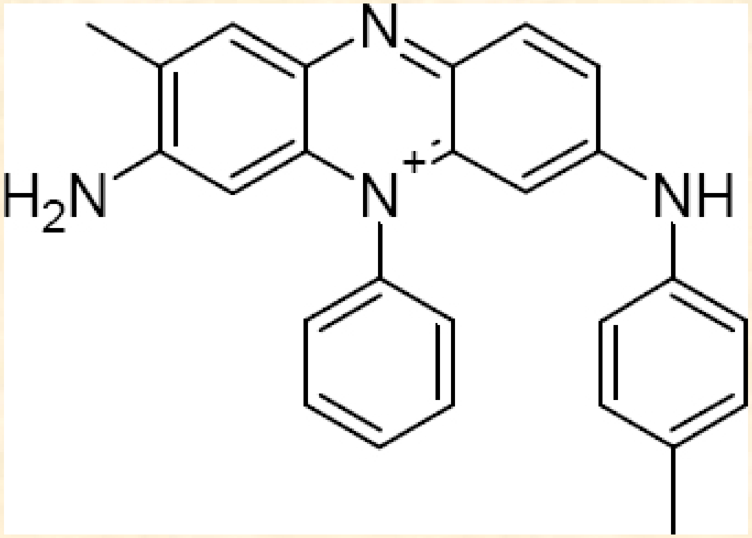


heme

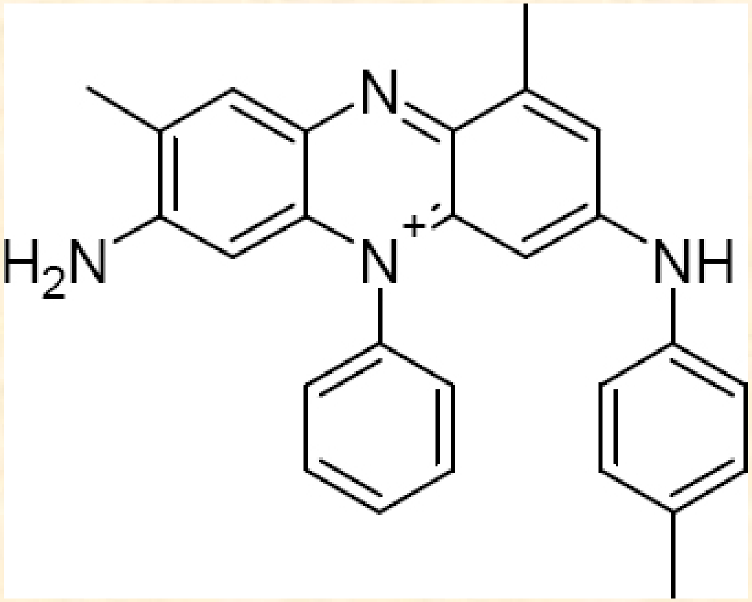


Chlorophyll-a

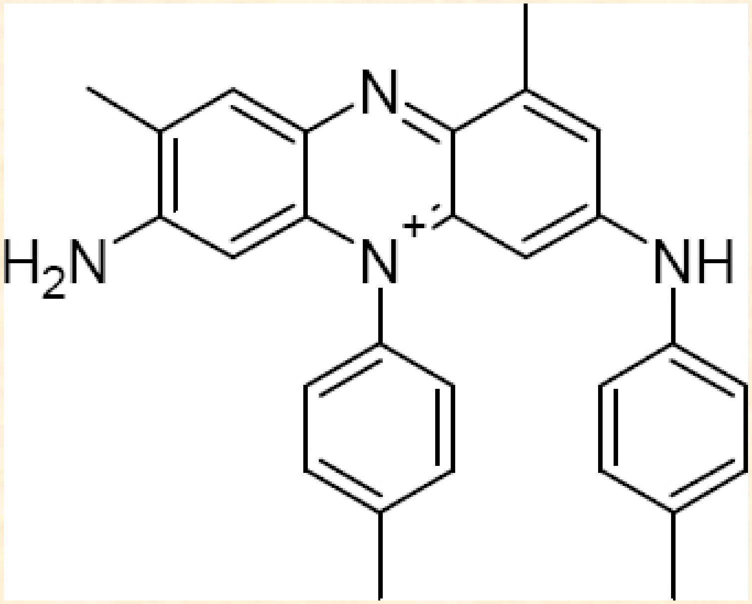
# Alkadienes and Polyunsaturated Hydrocarbons



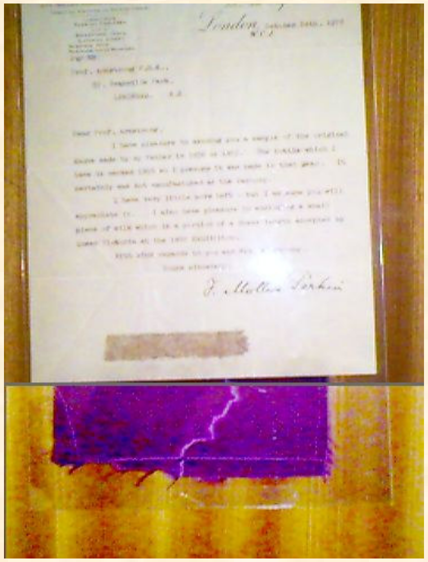
Mauveine-A



Mauveine-B

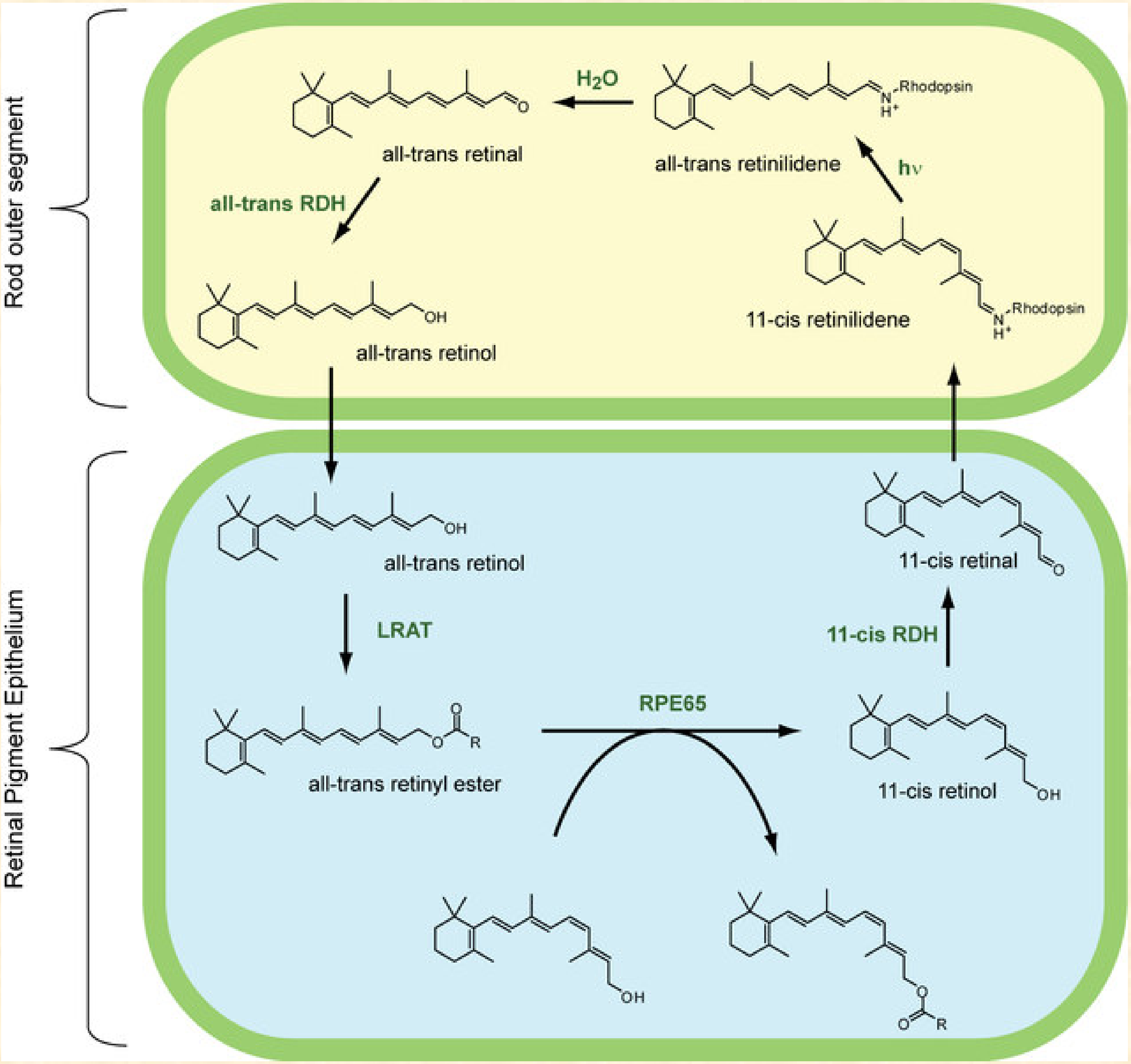


Mauveine-C



William Perkin

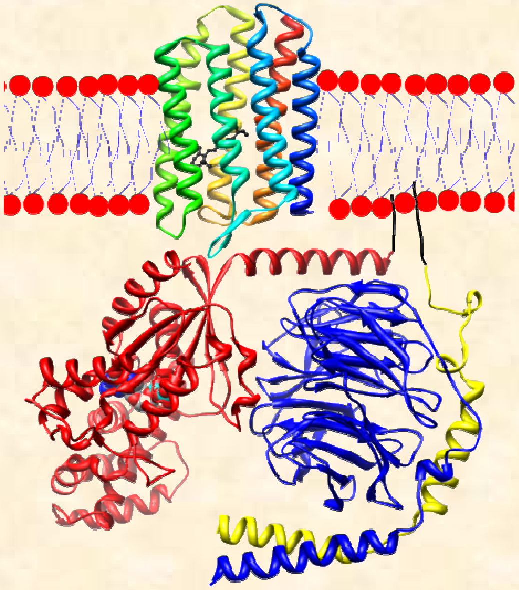
# Alkadienes and Polyunsaturated Hydrocarbons



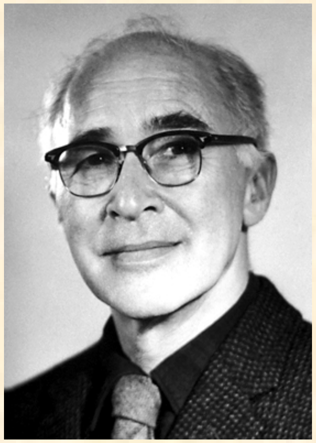
# Alkadienes and Polyunsaturated Hydrocarbons

**Nobel Prize in Medicine**

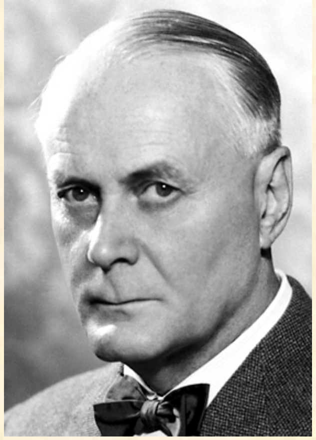
**1967**



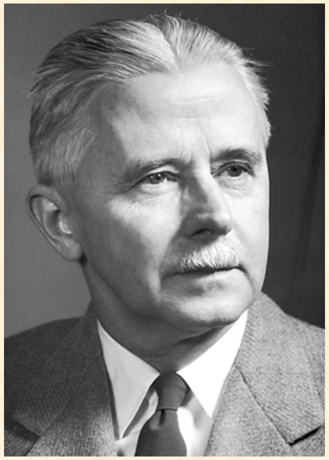
Type 2 rhodopsin



George Wald



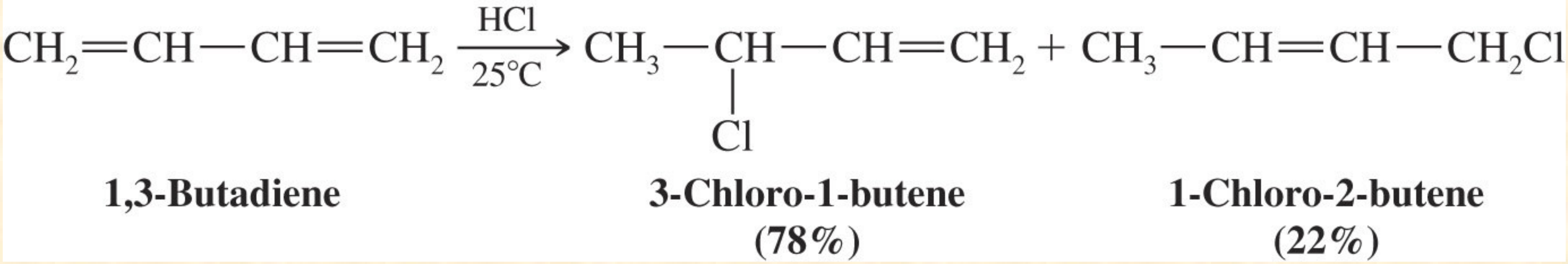
Ragnar Granite



Haldan K. Hartline

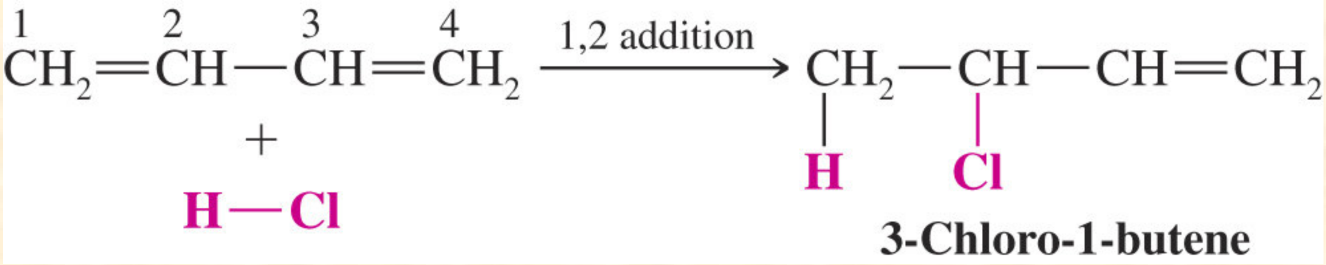
# Electrophilic Reactions

- **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



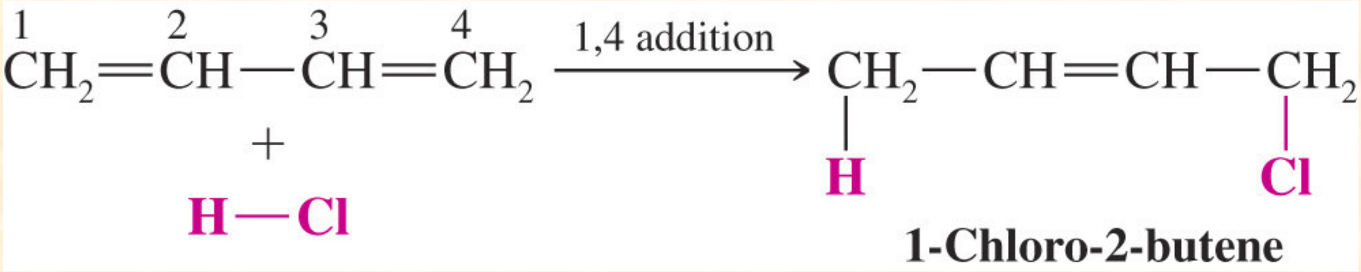
$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow[25^\circ C]{HCl} CH_3{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-}CH{=}CH_2 + CH_3{-}CH{=}CH{-}CH_2Cl$$

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



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

**3-Chloro-1-butene**

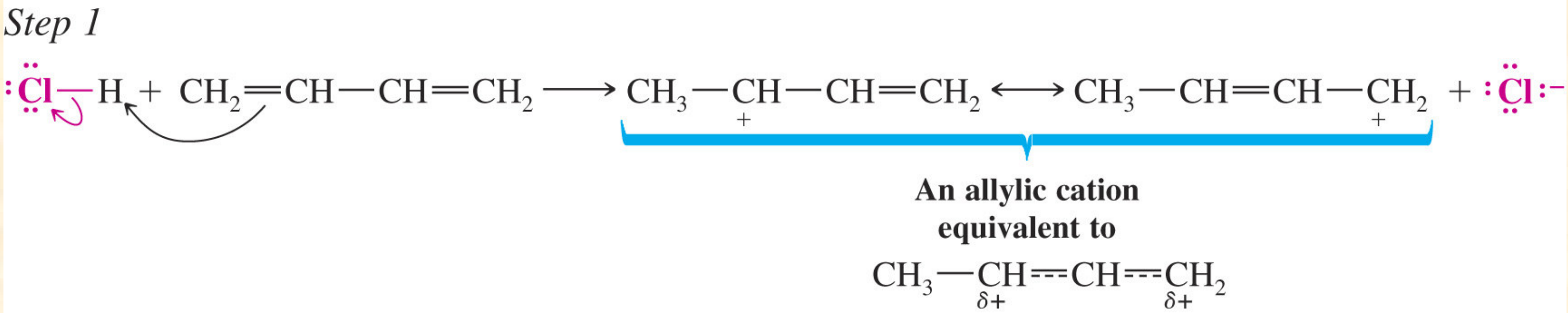


$$\overset{1}{CH_2}{=}\overset{2}{CH}{-}\overset{3}{CH}{=}\overset{4}{CH_2} + H{-}Cl \xrightarrow{\text{1,4 addition}} \underset{\displaystyle H}{\underset{|}{CH_2}}{-}CH{=}CH{-}\underset{\displaystyle Cl}{\underset{|}{CH_2}}$$

**1-Chloro-2-butene**

# Electrophilic Reactions

- In step 1 hydrogen chloride reacts to add hydrogen to a terminal carbon which gives a stable allyl cation intermediate
    - Addition of hydrogen to C2 leads to an unstable 1° carbocation



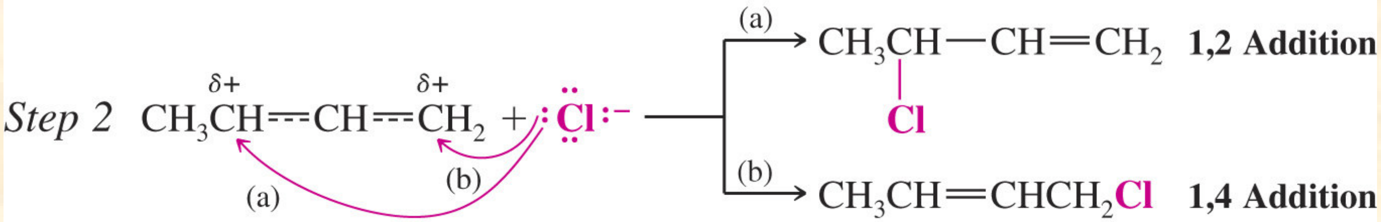
*Step 1*

$$:\ddot{\underset{..}{Cl}}-H + CH_2=CH-CH=CH_2 \longrightarrow \underbrace{CH_3-\underset{+}{CH}-CH=CH_2 \longleftrightarrow CH_3-CH=CH-\underset{+}{CH_2}} + :\ddot{\underset{..}{Cl}}:^-$$

**An allylic cation equivalent to**

$$CH_3-\underset{\delta+}{CH}\text{=-=}CH\text{=-=}\underset{\delta+}{CH_2}$$

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

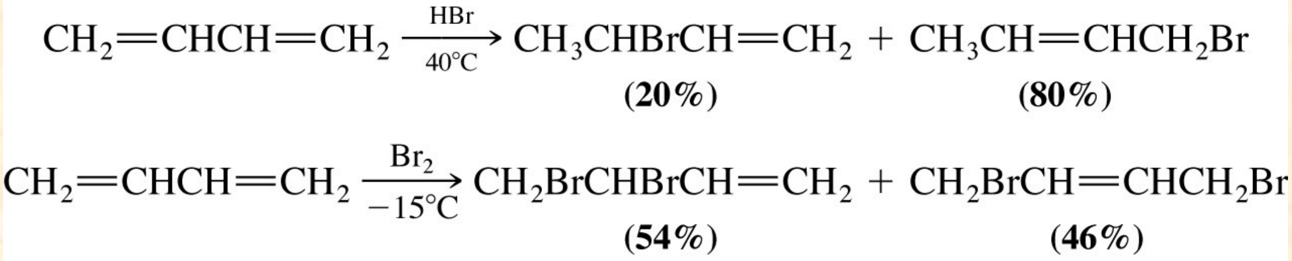


*Step 2* $CH_3\overset{\delta+}{CH}\text{=-=}CH\text{=-=}\overset{\delta+}{CH_2} + :\ddot{\underset{..}{Cl}}:^-$

(a) $CH_3CH(Cl)-CH=CH_2$ **1,2 Addition**

(b) $CH_3CH=CHCH_2Cl$ **1,4 Addition**

- Other electrophilic reagents add to conjugated dienes in similar fashion

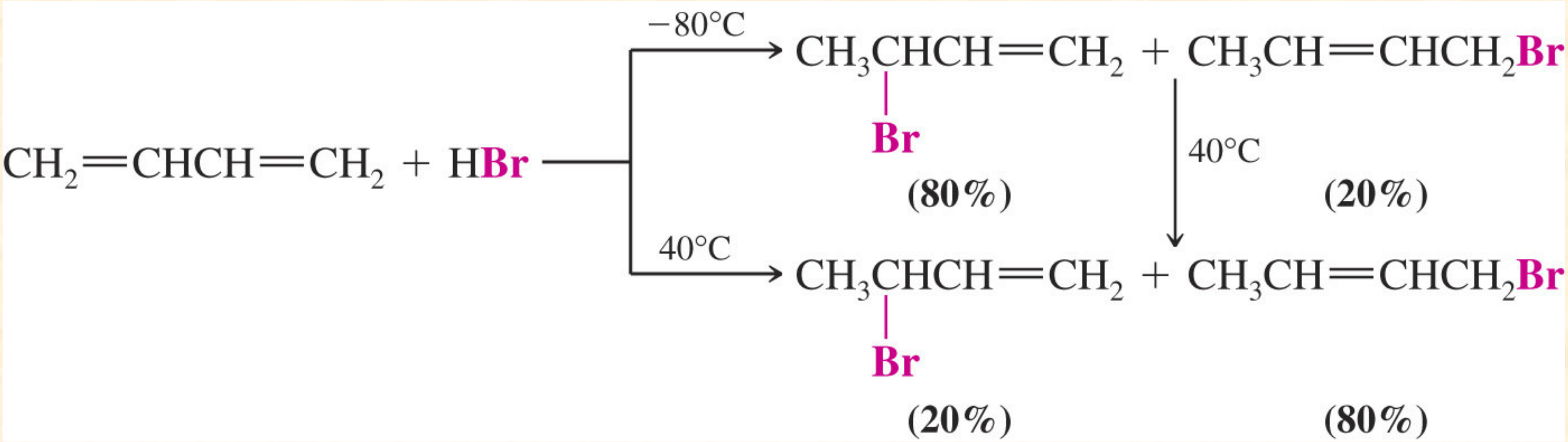


$$CH_2=CHCH=CH_2 \xrightarrow[40^\circ C]{HBr} \underset{\textbf{(20\%)}}{CH_3CHBrCH=CH_2} + \underset{\textbf{(80\%)}}{CH_3CH=CHCH_2Br}$$

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

# Electrophilic Reactions

- <u>Kinetic Control</u> versus <u>Thermodynamic Control</u> 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

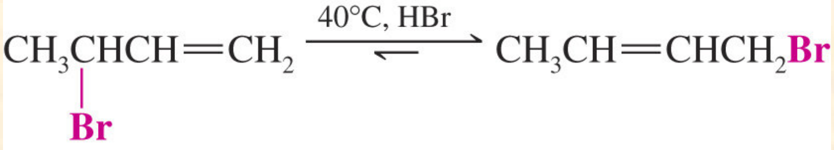


$$CH_2{=}CHCH{=}CH_2 + HBr \xrightarrow{-80^\circ C} \underset{\underset{(80\%)}{Br}}{CH_3CHCH{=}CH_2} + \underset{(20\%)}{CH_3CH{=}CHCH_2Br}$$

$$CH_2{=}CHCH{=}CH_2 + HBr \xrightarrow{40^\circ C} \underset{\underset{(20\%)}{Br}}{CH_3CHCH{=}CH_2} + \underset{(80\%)}{CH_3CH{=}CHCH_2Br}$$

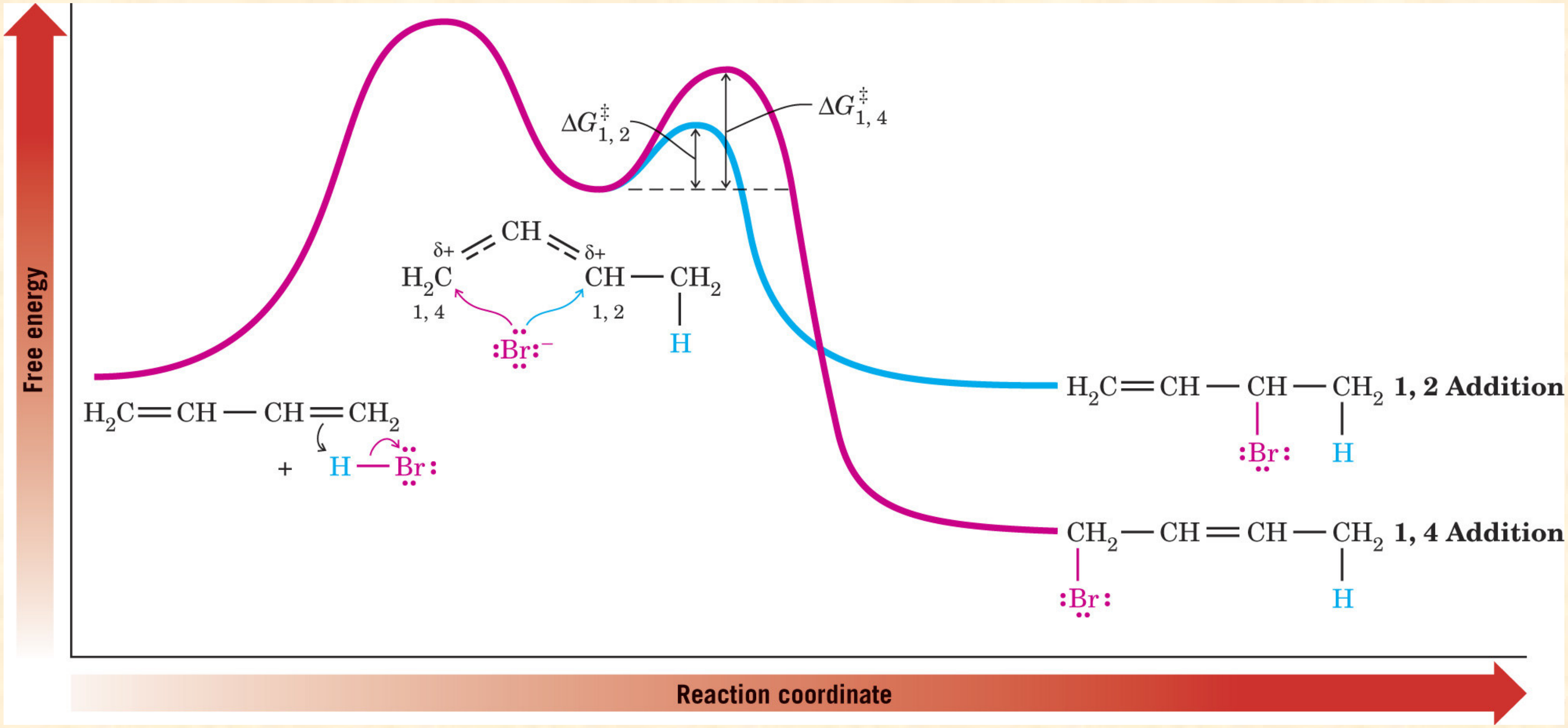
# Electrophilic Reactions

- 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



$$\underset{\textstyle \mathbf{Br}}{CH_3\overset{|}{C}HCH{=}CH_2} \underset{}{\overset{40°C,\ HBr}{\rightleftharpoons}} CH_3CH{=}CHCH_2\mathbf{Br}$$

**1,2-Addition product** **1,4-Addition product**

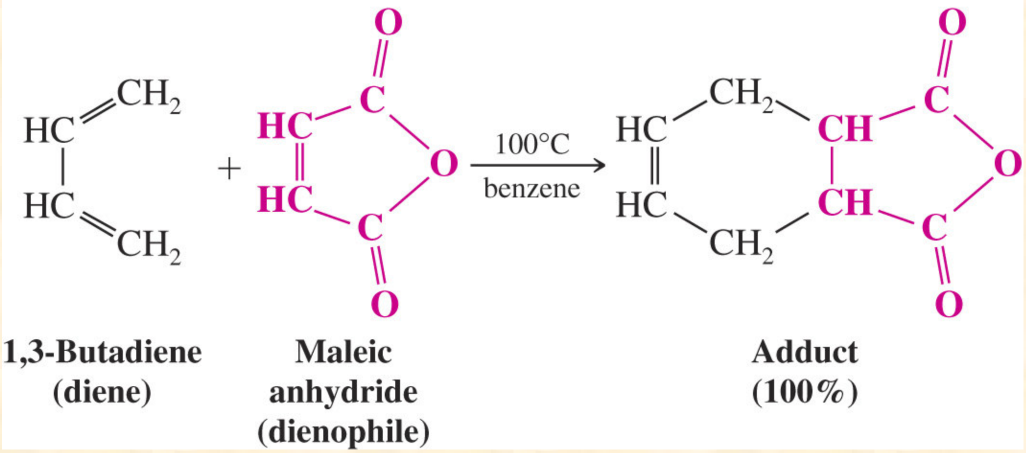


# Electrophilic Reactions

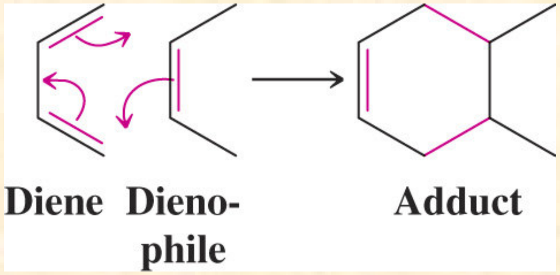
- At lower temperatures the proportion of products is determined by the relative rates of formation of product
  - 1,2-addition product forms faster and is the major product
  - The $\Delta G^{\ddagger}$ for formation of 1,2- product is lower than for 1,4- product
  - At low temperatures fewer molecules 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 both 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
  - The reaction is said to be under thermodynamic control
- The 1,4 product is most stable - disubstituted double bond
- The 1,2-addition product forms faster because the allyl cation has more $\delta+$ charge density at the $2^{o}$ rather than the $1^{o}$ carbon

# The Diels-Alder Reaction

- 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

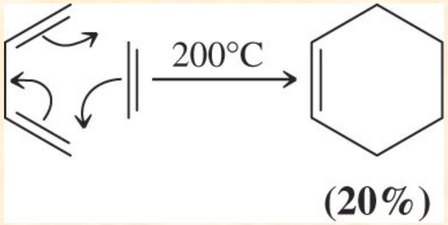


  - The simplest Diels-Alder reaction forms a cylohexene product
    - Overall, two new σ bonds are formed at the expense of two π bonds
    - The conjugated diene is a 4π-electron system
    - The dienophile ("diene lover") is a 2π-electron system
    - The product is called an adduct

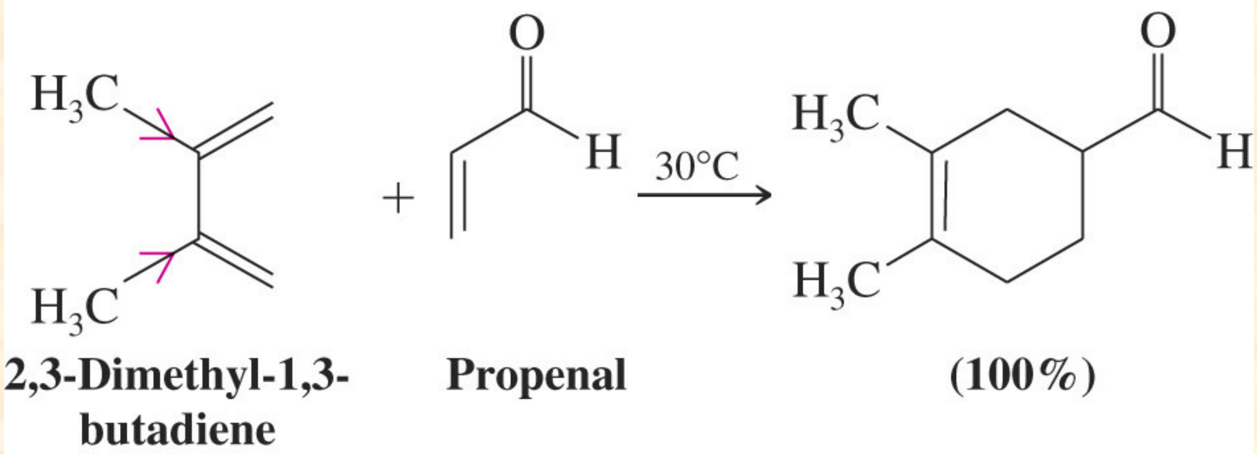


# The Diels-Alder Reaction

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

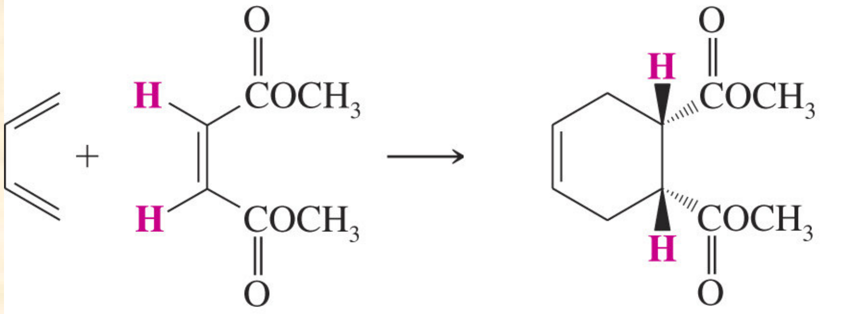


  - To proceed in good yield and at low temperature the dienophile should have electron-withdrawing groups
    - It also helps if the diene has electron-releasing groups
    - Dienes with electron-donating groups and dienophiles with electron-withdrawing group can also react well together



# The Diels-Alder Reaction

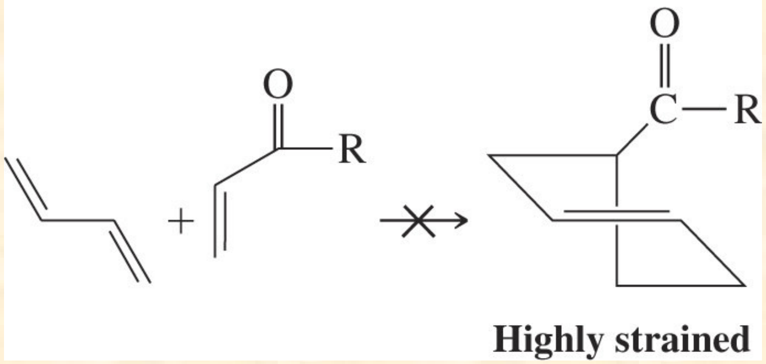
- Stereochemistry of the Diels-Alder Reaction
  - The Diels-Alder reaction is stereospecific *i.e.* the reaction is a syn addition, and the configuration of the dienophile is retained

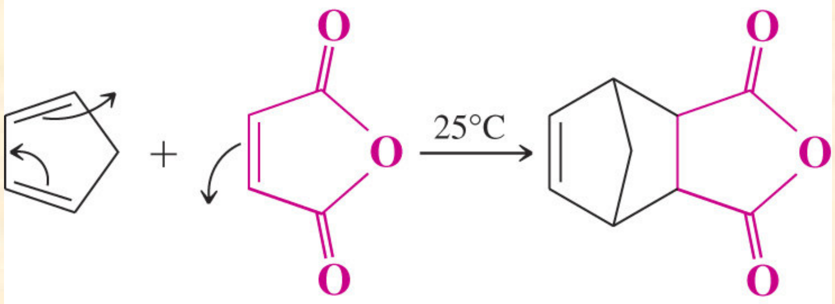


**Dimethyl maleate (a *cis*-dienophile)**

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

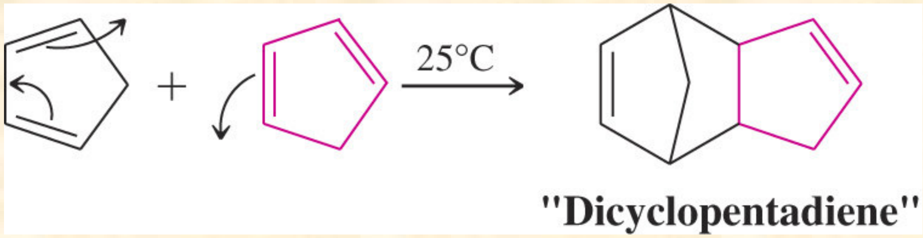
  - The diene must be in the *s*-cis conformation to react
    - *s*-Trans conformation would lead to formation of a highly unstable trans bond in a 6-membered ring
    - Cyclic dienes (rigid *s*-cis conformation!) are highly reactive



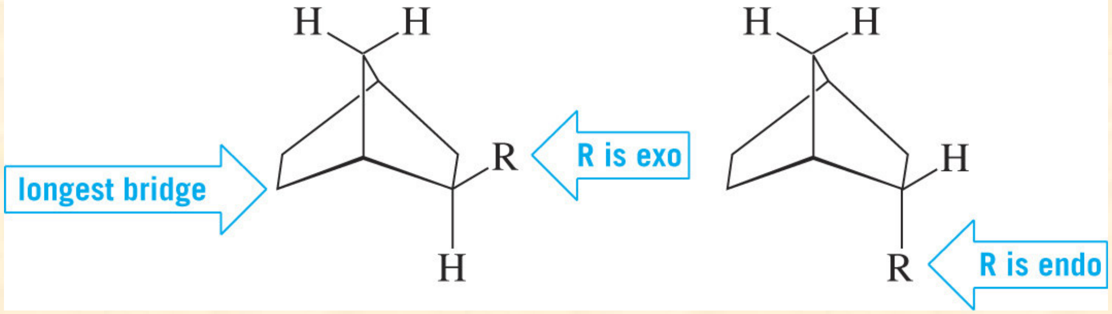


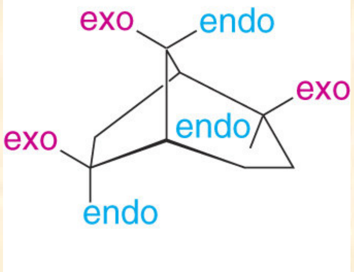
# The Diels-Alder Reaction

- 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.

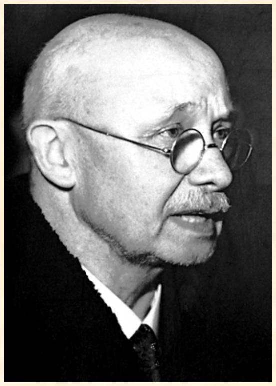


- The Diels-Alder reaction occurs primarily in an endo rather than an exo fashion when the reaction is kinetically controlled
  - A group that is exo in a bicyclic ring system is anti to the longest bridge
  - A group that is endo is on the same side as the longest bridge





# The Diels-Alder Reaction



**Nobel Prize in Chemistry**

**1950**

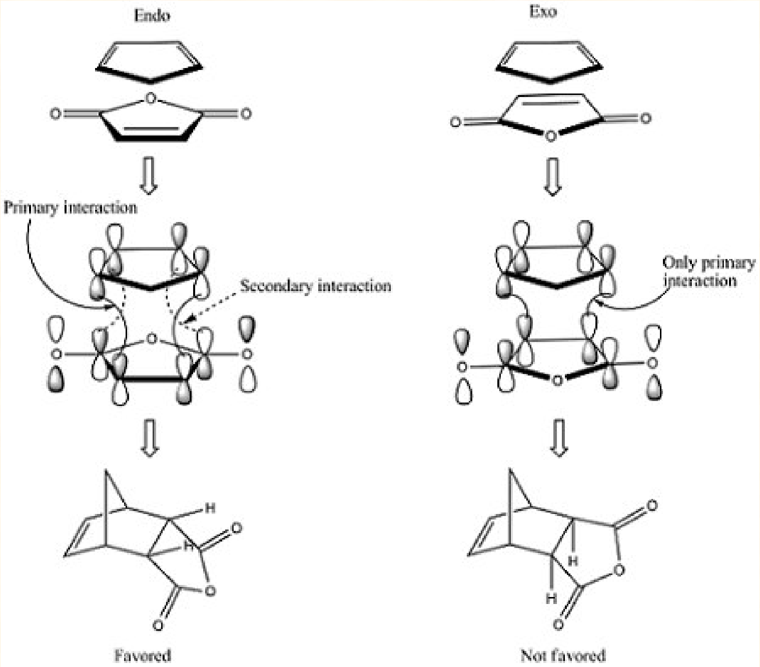
Otto P. H. Diels

Kurt Alder

Interpretation

**Nobel Prize in Chemistry**

**1981**



Robert B. Woodward

Roald Hoffmann

Kenichi Fukui