

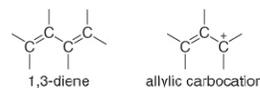
Chapter 13

Conjugated Unsaturated Systems

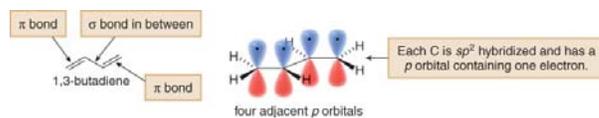
Conjugation, Resonance and Dienes

What is the conjugation?

- Conjugation occurs whenever *p* orbitals are located on three or more adjacent atoms.



- The four *p* orbitals on adjacent atoms make a 1,3-diene a conjugated system.

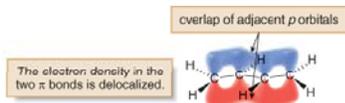


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Conjugation, Resonance and Dienes

Stability of the conjugated systems

- Having three or more *p* orbitals on adjacent atoms allows *p* orbitals to overlap and electrons to delocalize.



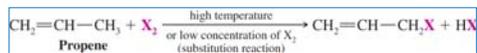
- When *p* orbitals overlap, the electron density in each of the π bonds is spread out over a larger volume, thus lowering the energy of the molecule and making it more stable.

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♦ Allylic Radical Substitution *versus* traditional Addition to double bond

Consider reaction of propene with bromine. This reaction product 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



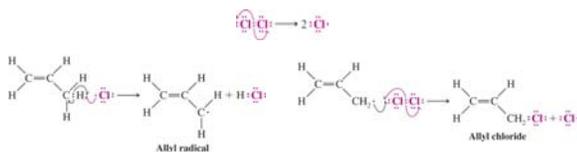
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Allylic Chlorination (High Temperature) - Mechanism

→ Allylic chlorination can be performed at high temperature in the gas phase

→ The reaction is a free radical chain reaction

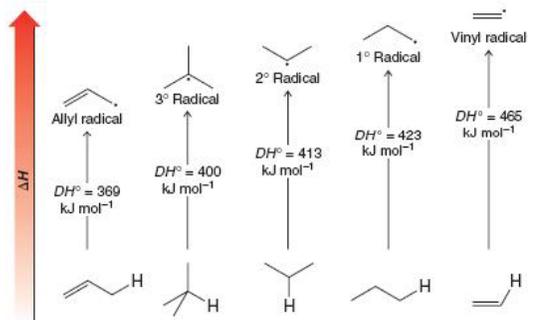
- ⚡ In the initiation step a low concentration of chlorine radical is produced
- ⚡ In the first propagation step an allyl radical is formed. BDE for the allylic carbon-hydrogen bond in propene is smaller than for other carbon-hydrogen bonds
- ⚡ In the second propagation step the allyl radical reacts with molecular chlorine



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The relative stability of the allylic radicals vs. other radicals

Bond dissociation energy "BDE" for the allylic carbon-hydrogen bond in propene is smaller than for other carbon-hydrogen bonds in alkanes and alkenes: See also Table on page 588)



Stability of the allylic radicals

Allylic radicals form readily because they are more stable than ordinary primary, secondary, tertiary, or vinyl radicals. They are stabilized by the overlap of the adjacent p orbitals

→ The relative stability of carbon radicals is as follows:

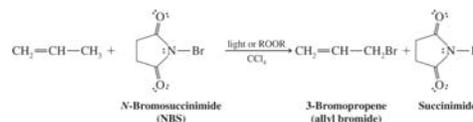


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• Allylic Bromination with N-Bromosuccinimide

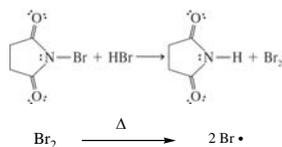
Propene undergoes allylic bromination with N-bromosuccinimide (NBS) in the presence of light or peroxides

- ⚡ NBS provides a continuous low concentration of bromine for the radical reaction
- ⚡ A low bromine concentration favors allylic substitution over alkene addition



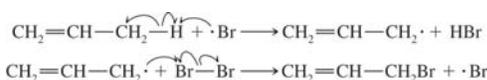
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The **initiation steps** involve the formation of bromine radical, a small amount of which is formed by exposure of NBS to light or peroxides



The **propagation steps** for allylic bromination with NBS are:

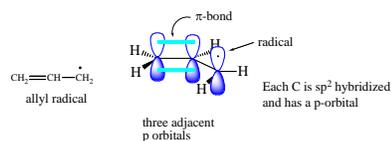
- ⚡ A bromine radical reacts with propene to produce an allylic radical and HBr
- ⚡ HBr reacts with NBS to produce a bromine molecule
- ⚡ A molecule of bromine reacts with a propene radical to regenerate a bromine radical



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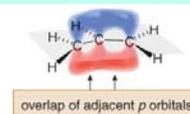
The stability of the Allyl Radical

- The allyl radical is another example of a conjugated system.



Three p orbitals on three adjacent atoms make the allyl radical conjugated

- Conjugation stabilizes the allyl radical. Three electrons overlap over three adjacent carbons (over three p orbitals)

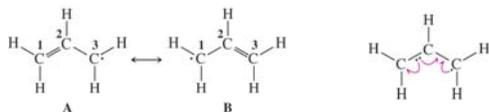


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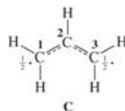
♦ Resonance Description of the Allyl Radical

→ The allyl radical has two contributing resonance forms

- ⚡ These resonance forms can be interconverted using half-headed arrows
- ⚡ The two resonance structures are equivalent
- ⚡ Recall that equivalent resonance structures lead to much greater stability of the molecule than either structure alone would suggest



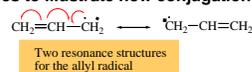
→ The true structure of the allyl radical as suggested by resonance theory is:



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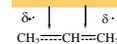
Allyl radicals – resonance structure

- Drawing resonance structures for the allyl radical is a way to see how to use Lewis structures to illustrate how conjugation delocalizes electrons.



- The true allyl radical is a hybrid of the two resonance forms.

The π bond is delocalized



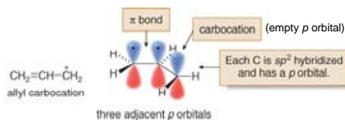
The odd electron is delocalized

- In the hybrid, the odd electron is **delocalized** over the two terminal carbons.
- Delocalizing electron density lowers the energy of the hybrid, thus stabilizing the allyl radical and making it more stable than a normal 1° radical.

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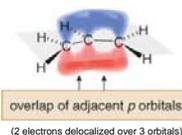
The allyl carbocation

- The allyl carbocation is another example of a conjugated system.



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

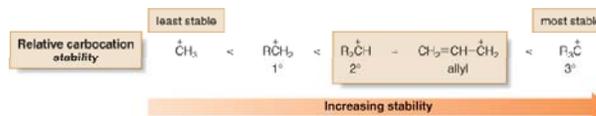
- Conjugation stabilizes the allyl carbocation.



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Do you remember the stability order of the carbocations? Similar trend as radicals

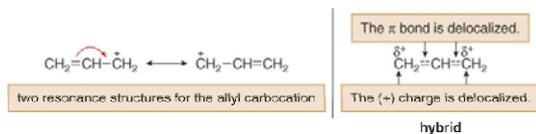
- Experimental data show that the stability of the allyl cation is comparable to a more highly substituted 2° carbocation.



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Resonance structure -revisited

- Drawing resonance structures for the allyl carbocation is a way to see how to use Lewis structures to illustrate how conjugation delocalizes electrons.



- The true allyl cation is a hybrid of the two resonance forms.
- In the hybrid, the positive charge is delocalized over the two terminal carbons.
- Delocalizing electron density lowers the energy of the hybrid, thus stabilizing the allyl carbocation and making it more stable than a normal 1° carbocation.

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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

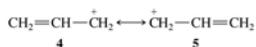
↳ Only π and nonbonding electrons are moved

→ All resonance structures must be proper Lewis structures

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→ 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

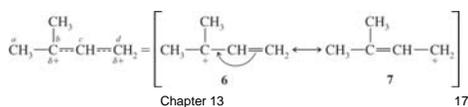


→ A system with equivalent resonance structures is particularly stable

↳ 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



Chemistry of Dienes

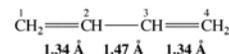
1,3-Butadiene: Electron Delocalization

• 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



→ 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 sp²-sp² overlap
 ↳ There is significant overlap between the C2-C3 p orbitals

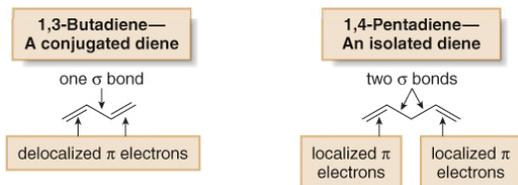
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Remember that there are two different kinds of dienes

• 1,3-butadiene is a **conjugated diene**

• 1,4-pentadiene is an **isolated diene**.

The π bonds in 1,4-pentadiene are too far apart to be conjugated.

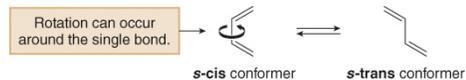


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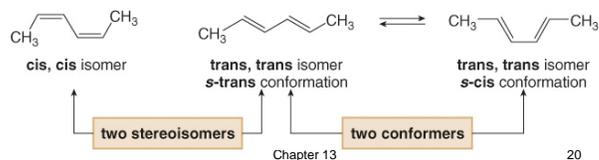
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1,3-Conjugated Dienes - Conformations

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



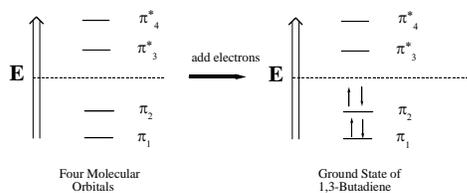
• Note that stereoisomers are distinct molecules, whereas conformers interconvert.



• Molecular Orbitals of 1,3-Butadiene

The four atomic (2p) orbitals, one from each carbon atom in 1,3-butadiene, combine to form four molecular orbitals.

Then, the four π electrons are placed in the molecular orbitals according to the same rules that are used to put electrons into atomic orbitals (Aufbau Principle, Hund's Rule, Pauli Exclusion Principle) resulting in the ground state of 1,3-butadiene.

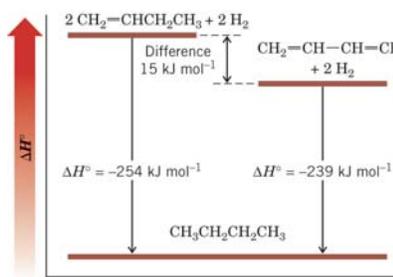


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♦ The Stability of Conjugated Dienes

→ 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



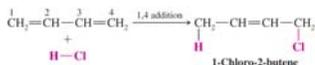
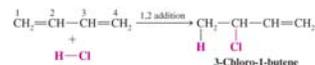
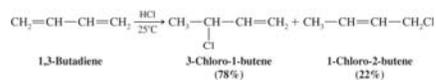
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Electrophilic Attack on Conjugated Dienes:

1,2 Addition and 1,4-Addition (Important concept)

When 1,3-butadiene reacts with one equivalent of HCl at room temperature two products are obtained

- 78% of the 1,2-addition product (Markovnikov addition !), and
- 22% of the 1,4-addition product (How?)

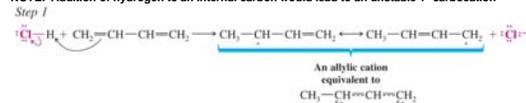


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1,2 Addition vs. 1,4-Addition - mechanism

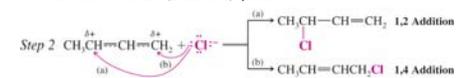
→ In step 1 hydrogen chloride reacts to add a proton to a terminal carbon (Markovnikov rule) which gives a stable allyl carbocation intermediate

NOTE: Addition of hydrogen to an internal carbon would lead to an unstable 1° carbocation



→ In step 2, chloride ion can react at either end of the allyl carbocation

• This leads to both the 1,2 and the 1,4 product



→ Other electrophilic reagents add to conjugated dienes in similar fashion

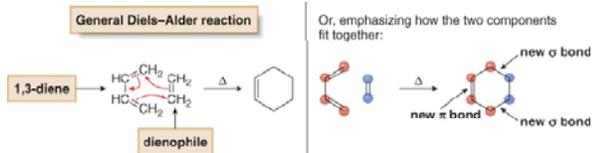


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The Diels-Alder Reaction

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: **1,4 Cycloaddition reaction**

▪ Nobel Prize in Chemistry in 1950: A novel method to synthesize cyclic compounds from two acyclic (linear) precursors (alkenes)

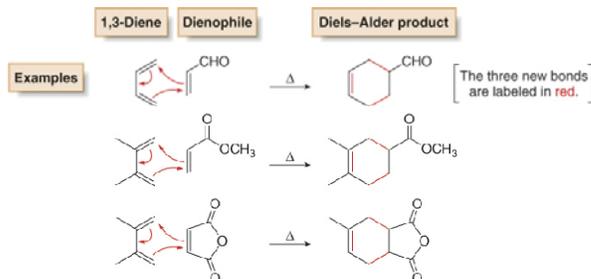


Three curved arrows are needed to show the cyclic movement of electron pairs because **three π bonds break and two σ bonds and one π bond form**.

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The Diels-Alder Reaction

Some examples of Diels-Alder reactions are shown below:

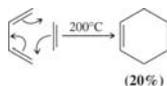


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The Diels-Alder Reaction—Reaction Rules

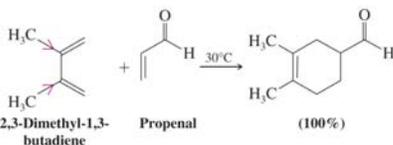
Factors Favoring the Diels-Alder Reaction

→ 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



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The Diels-Alder Reaction—Reaction Rules

Several other rules govern the course of the Diels-Alder reaction

The diene can react only when it adopts the **s-cis conformation** (along the singular bond).



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.

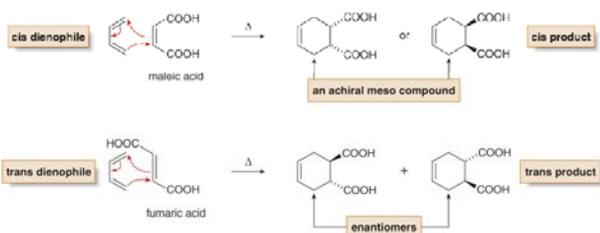


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The Diels-Alder Reaction—Reaction Rules

The stereochemistry of the dienophile is retained.

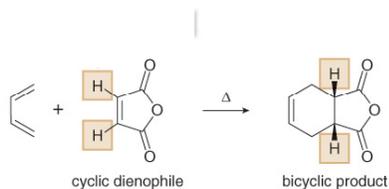
i.e., if the dienophile is *cis*, then the product is *cis*; if the dienophile is *trans*, then the product is *trans*.



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The Diels-Alder Reaction—Reaction Rules

- If the dienophile is cyclic, a bicyclic product forms since a new six-membered ring has to be always formed

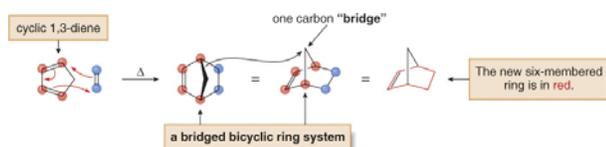


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The Diels-Alder Reaction—Reaction Rules

If the diene is cyclic, a bridged bicyclic product forms.

- Consider the reaction of 1,3-cyclopentadiene with ethylene. A new six-membered ring forms and above the ring there is a one atom "bridge."
- A bicyclic ring system in which the two rings share non-adjacent carbon atoms is called a **bridged ring system**.

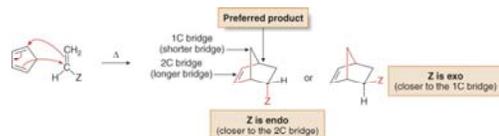


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The Diels-Alder Reaction—Reaction Rules

- 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.
- The terms *endo* and *exo* are used to indicate the position of the substituent Z.



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