

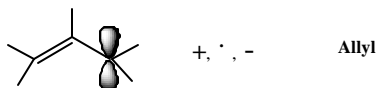
Chapter 13

Conjugated Unsaturated Systems

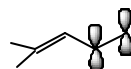
What is a conjugated system?

Conjugated unsaturated systems have a p orbital on a carbon adjacent to a double bond

- The p orbital may be empty (a carbocation)
- The p orbital may hold one electron (a radical)
- The p orbital may hold two electrons (carbanion)



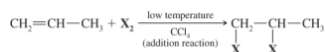
- The p orbital may be part of another multiple bond



Allylic Substitution and the Allylic Radical

Reaction of propene with bromine depends 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

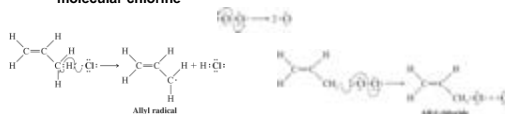


Allylic Chlorination (High Temperature)

- ◆ Allylic chlorination occurs at high temperature in the gas phase



- ◆ High temp induces a free radical chain reaction
 - Initiation step produces a low concentration of chlorine radical
 - In the first propagation step an allyl radical is formed
 - In the second propagation step the allyl radical reacts with molecular chlorine



Why selectivity for allylic position?

Allylic radicals form readily because they are more stable than ordinary primary, secondary, tertiary radicals

- This trend is reflected in C-H bond dissociation energies



The relative stability of some carbon radicals is as follows:

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

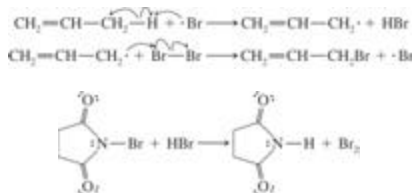
Allylic Bromination with *N*-Bromosuccinimide

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

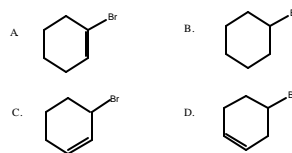
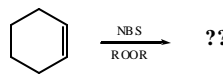


The radical reaction is initiated by a small amount of bromine radical formed by exposure of NBS to light or peroxides

- ◆ 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



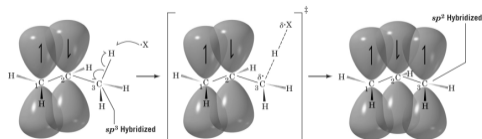
Predict the product



Molecular Orbital Description of the Allyl Radical

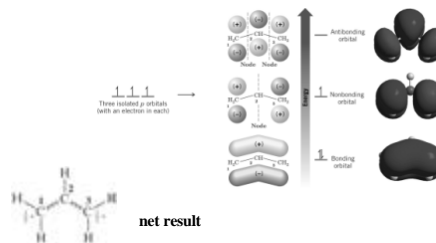
When an allylic hydrogen is abstracted, the developing *p* orbital on the allylic sp^2 carbon overlaps with the *p* orbitals of the alkene

- The new *p* orbital is conjugated with the double bond *p* orbitals
- The radical electron and the *p* 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 (MOs)

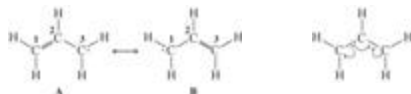
- The bonding MO contains two spin-paired electrons and this orbital increases bonding between the carbons
- The nonbonding orbital contains a lone electron which is located at carbons 1 and 3 only



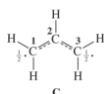
Resonance Description of the Allyl Radical

The allyl radical has two contributing resonance forms

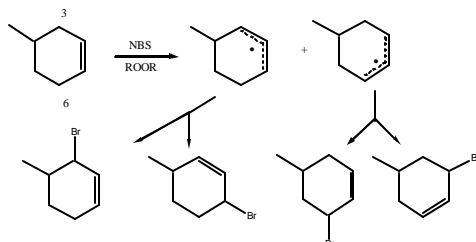
- These resonance forms can be interconverted via electron shifts
- The resonance structures are equivalent
- Overall stability of the species is greater than either structure alone



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



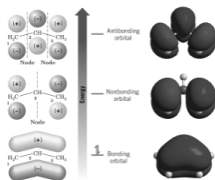
Use of Allylic Halogenation generally limited to symmetrical alkenes



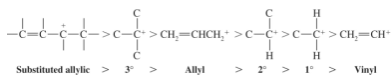
The Allyl Cation

The molecular orbital description of the allyl cation is similar to the allyl radical except it contains one fewer electron

- Stability arises from sharing of the positive charge by C1 and C3

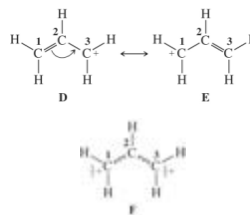


Stability is roughly that of a tertiary carbocation



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



Summary of the Rules for Resonance

- 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



What is a hybrid?



Lab



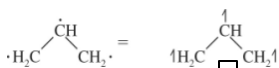
Poodle



Labradoodle

Summary of Rules for Resonance

- 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 p 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



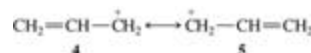
Not a valid resonance form of allyl radical

- All atoms that are part of the delocalized p-electron system must lie in a plane or be nearly planar



Not a viable geometry

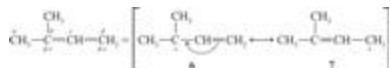
- The actual energy of the molecule is lower than the energy calculated for any one contributing resonance structure
 - Allyl cation has much lower energy than either contributing structures 4 or 5



- ◆ A system with equivalent resonance structures is particularly stable

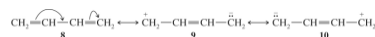
Example: the allyl cation

- ◆ The more stable a resonance structure is, the more important it is and the more it contributes to the hybrid

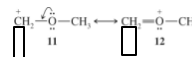


Estimating the Relative Stability of Resonance Structures

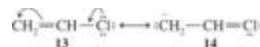
- ◆ Structures with more covalent bonds are more important



- ◆ Structures in which all atoms have complete octets are more important

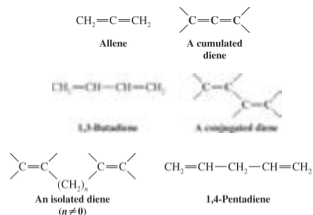


- ◆ Separation of charge decreases stability



Dienes and Polyunsaturated Hydrocarbons

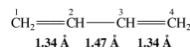
- ◆ Alkadienes (dienes) contain two double bonds
- ◆ Polyunsaturated compounds can be classified as being cumulated, conjugated or isolated
 - Conjugated dienes affect each other when they react, isolated double bonds react separately



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

1. The σ bond between C2 and C3 is made from sp^2-sp^2 overlap
2. 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*

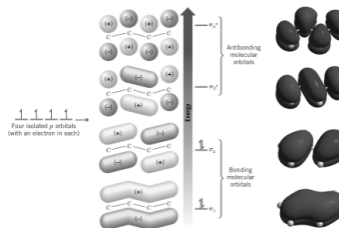
- *s* Indicates the conformations originate from rotation around a single bond
- *s-Trans* is more stable because it is less sterically hindered



Molecular Orbital Picture of 1,3-Butadiene

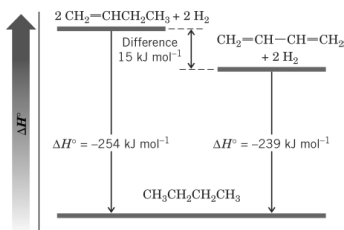
- ◆ The first p bonding molecular orbital in 1,3-butadiene shows significant overlap of the p orbitals between C2 and C3

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



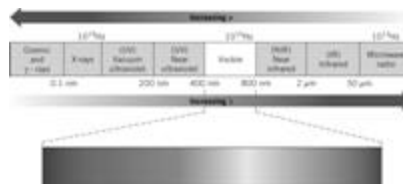
The Stability of Conjugated Dienes

- ◆ 1,3-butadiene has a lower heat of hydrogenation by 15 kJ mol⁻¹ than two molecules of 1-butene
 - Hydrogenation they lead to the same product
 - Lower heat of hydrogenation means 1,3-butadiene is more stable



Ultraviolet-Visible Spectroscopy

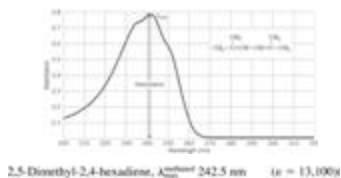
- ◆ Conjugated compounds absorb energy in the ultraviolet (UV) and visible (Vis) regions on the electromagnetic spectrum
 - The wavelength of radiation absorbed and the intensity of the absorption depend on the structure of the molecule
- ◆ UV-Vis Spectrophotometers
 - A UV-Vis spectrum is typically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



- ◆ Wavelength of maximum absorption (λ_{max}) reported in nanometers (nm)
- ◆ Molar absorptivity (ϵ) is also reported as 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

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

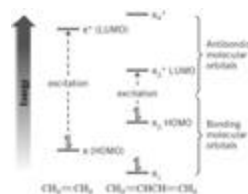
- ◆ Example: UV absorption spectrum of 2,5-dimethyl-2,4-hexadiene in methanol at a concentration of 5.95×10^{-5} M in a 1.0 cm cell



Origins of UV absorption

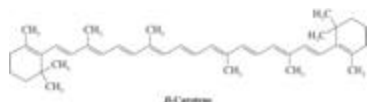
- ◆ In UV-Vis spectroscopy the electrons are excited from lower energy levels to higher ones
 - An electron is excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO)
 - Alkenes have absorptions below 200 nm because the energy difference between the HOMO and LUMO is large
 - In conjugated dienes these energy levels are closer together and the wavelengths of absorption are longer than 200 nm

Ethene: $\lambda_{max} = 171$ nm
 1,3-butadiene: $\lambda_{max} = 217$ nm



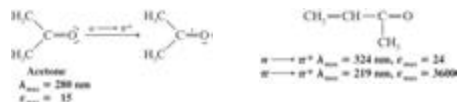
Extended conjugated systems

- ◆ The longer the conjugated system, the smaller the energy difference between the HOMO and the LUMO
 - Smaller energy gap = longer λ_{max} in the UV-vis spectrum
 - b-Carotene has 11 conjugated double bonds and an absorbance maximum at 497 nm which is in the blue-green region of the visible spectrum
 - b-Carotene is perceived as red-orange, the complementary color of blue-green



Carbonyl compounds absorb light in the UV region

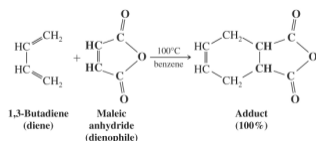
- ◆ An unshared (n) electron on oxygen is promoted to a p^* orbital
- ◆ Absorption is weak because orbitals are of different types and geometries



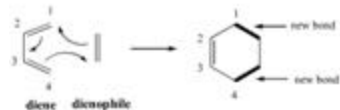
The Diels-Alder Reaction

A 1,4-Cycloaddition Reaction of Dienes

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



General form of the Diels-Alder Reaction



1. Always produces a 6-membered ring with a double bond
2. Two new σ bonds are formed at the expense of two π bonds
3. The conjugated diene is a 4 π -electron system
4. The dienophile ("diene lover") is a 2 π -electron system
5. The reaction is also called a 4+2 cycloaddition

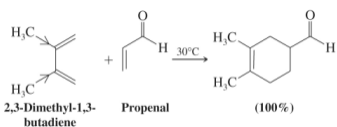
Factors Favoring the Diels-Alder Reaction

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



A dienophile with electron-withdrawing groups gives better yields

- It also helps if the diene has electron-releasing groups

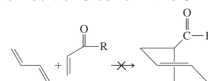


Conformation Requirement for the Diels-Alder Reaction

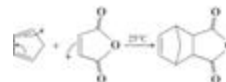
The diene must be in *s-cis* conformation



s-trans conformation doesn't align well with dienophile would lead to a strained trans bond in the 6-membered ring



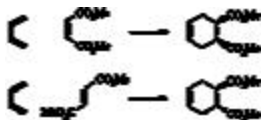
Cyclic dienes react well as they must be in the *s-cis* conformation



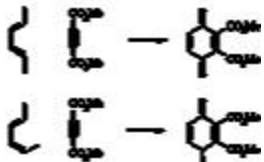
The Diels-Alder Reaction is stereospecific

Syn addition with retention of configuration in both the

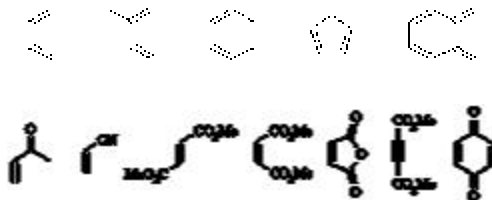
dienophile



and the diene

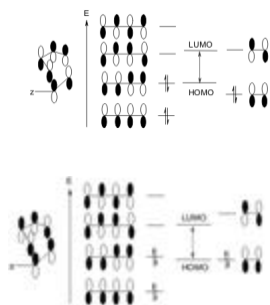


Some typical dienes and dienophiles

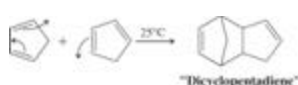


Molecular orbital basis for Diels-Alder Reaction

Synchronous formation of new bonds is facilitated by favorable overlap of HOMO of each partner with the LUMO of the other

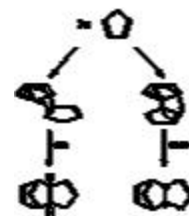


Cyclopentadiene is so reactive it spontaneously undergoes Diels-Alder reaction with itself at room temperature

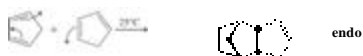


This dimer can be "cracked" (a retro-Diels-Alder reaction) by heating

Introduces another point of selectivity

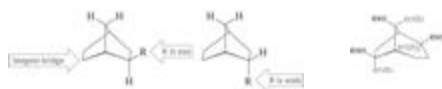


2 possible structures for the dimer



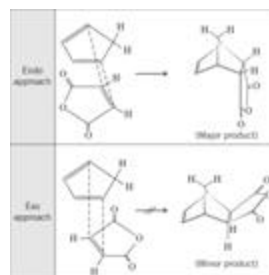
◆ The Diels-Alder reaction occurs primarily in an endo rather than an exo fashion when the reaction is kinetically controlled

- A group that is exo in a bicyclic ring system is anti to the longest bridge (exo= out, opposite)
- A group that is endo is on the same side as the longest bridge

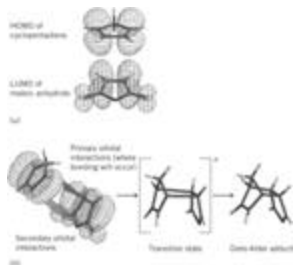


Endo products are favored in Diels-Alder reactions

Maleic anhydride and cyclopentadiene

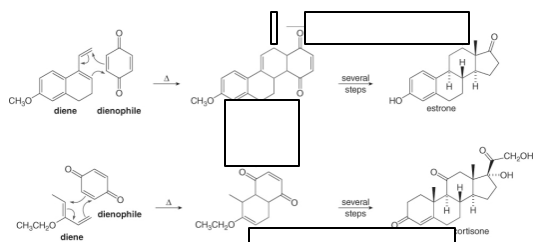


Secondary orbital interactions between the LUMO of the carbonyl groups and the HOMO of the cyclopentadiene carbons at the C2 and C3 positions of the diene favor the endo configuration



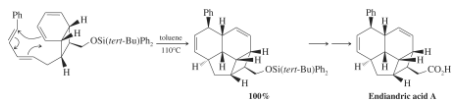
Use of Diels-Alder to make Steroids

The need to synthesize 6-membered rings is very common and an ideal application for Diels-Alder reactions



● **Intramolecular Diels-Alder Reactions**

◆ Intramolecular reactions are those in which the reacting groups are part of the same molecule



◆ What diene and dienophile would be needed to make the compound below

