

## Ch 14 Conjugated Dienes and UV Spectroscopy

### Conjugated Systems

- Conjugated systems have alternating single and double bonds.  
For example:  $C=C-C=C-C=C$  and  $C=C-C=O$
- This is not conjugated because the double and single bonds do not alternate:  $C=C-C-C=C$
- Triple bonds ( $C\equiv C$  and  $C\equiv N$ ) can be included in place of double bonds.  
For example:  $C\equiv C-C=C-C\equiv N$
- All of the conjugated atoms are  $sp^2$  or  $sp$ .
- Atoms with  $sp^3$  are not part of the conjugated system.

### Preparation

- Conjugated systems are typically prepared either by dehydrohalogenation of allyl halides ( $C=C-CX-C$ ) with base in alcohol, or by dehydration of 1,3-diols ( $HOC-C-COH-C$ ) with  $Al_2O_3$  and heat.

### Stability

- Conjugated dienes are more stable than non-conjugated alkenes.
- This is known because conjugated dienes release less heat than non-conjugated alkenes when hydrogenated. That is, hydrogenation of conjugated molecules is less exothermic.
- Stability results from the alternating  $\Pi$  bonds interacting with each other.

### Valence Bond Description

- The  $sp^2$  orbitals have more s character than the  $sp^3$  orbitals have.
- The  $sp^2$  orbitals are shorter and rounder than the  $sp^3$  orbitals.
- C-C  $\sigma$  bonds involving  $sp^2$  orbitals are stronger and shorter and than those that do not.
- In 1,3-butadiene,  $C=C-C=C$ , all three  $\sigma$  bonds are  $sp^2 - sp^2$ .
- In 1-butene,  $C=C-C-C$ , the first  $\sigma$  bond is  $sp^2 - sp^2$  (strongest), the second is  $sp^2 - sp^3$  (less strong), then the third is  $sp^3 - sp^3$  (weakest).

### Molecular Orbital (MO) Description

- When p orbitals bond to form  $\Pi$  bonds, each p atomic orbital becomes a  $\Pi$  molecular orbital.
- The  $\Pi$  MO's in adjacent conjugated bonds interact together as a single  $\Pi$  system.
- In 1,3-butadiene,  $C=C-C=C$ , all four C's have one  $\Pi$  MO each.  
So, there are four  $\Pi$  MO's total.
- Two are bonding orbitals (stabilizing), and the other two are anti-bonding (destabilizing).
- Each C has one  $\Pi e^-$ . So, there are four  $\Pi e^-$ 's total.  
They fill the two bonding MO's, while the antibonding MO's are left empty.
- The lowest energy MO ( $\Psi_1$ ) has no nodes and is a completely continuous system, involving all four C's with no separation.
- The next to lowest MO ( $\Psi_2$ ) has one node, between C2 and C3, and acts like two separate  $\Pi$  bonds.

- The next highest energy MO ( $\Psi_3^*$ ) is antibonding. It has two nodes, one between C1 and C2, the other between C3 and C4. So, it acts like there is only one  $\Pi$  bond. This would destabilize the molecule if occupied with  $e^{-1}$ 's.
- The highest energy MO ( $\Psi_4^*$ ) has three nodes, one between each C. This completely isolates the  $\Pi$  orbitals. It is very destabilizing (antibonding) if occupied with  $e^{-1}$ 's.

### Electrophilic Additions and Allyl Cations

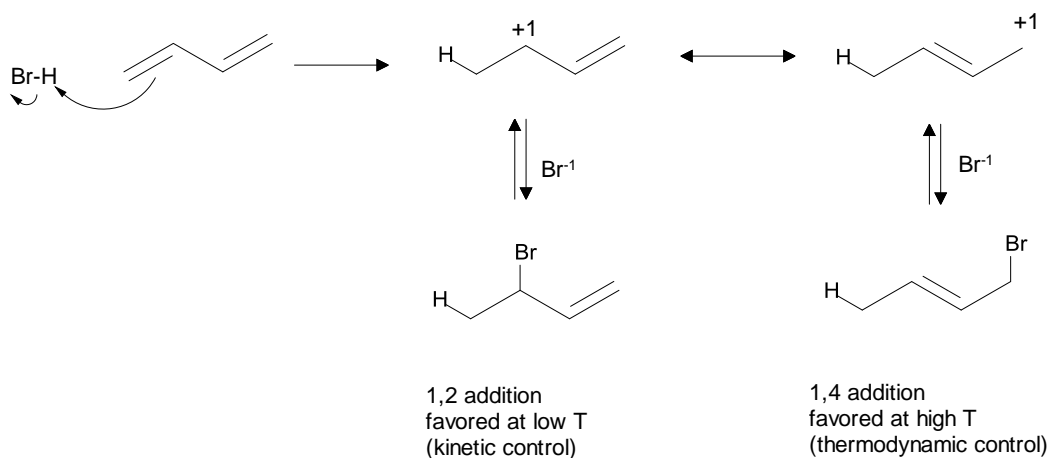
- When a conjugated diene reacts with HBr, the first step is addition of an H to the least substituted C in the  $\Pi$  system. In 1,3-butadiene,  $C=C-C=C$ , this would be an end carbon.
- The C with the positive charge will be adjacent to the one that got the H, and that C will be allylic because it is next to another double bond.
- Allylic cations, like allylic free radicals, have resonance forms, where the + charge and the adjacent  $\Pi$  bond trade places.
 
$$C-C^+-C=C \leftrightarrow C-C=C-C^+$$
- The H added to C1, now the Br can add to either C2 (1,2 addition) or C4 (1,4 addition). So, the two products are  $H_3C-CHBr-CH=CH_2$  and  $H_3C-CH=CH-CH_2Br$ .

### Kinetic Control (Low T)

- At low T, less energy is available for  $E_a$ , and the reactions are less reversible.
- The 1,2 addition has a lower  $E_a$ , and forms primarily.
- The 1,2 addition does not need to switch to the 2<sup>nd</sup> carbocation resonance form. Therefore, it forms faster and predominates.

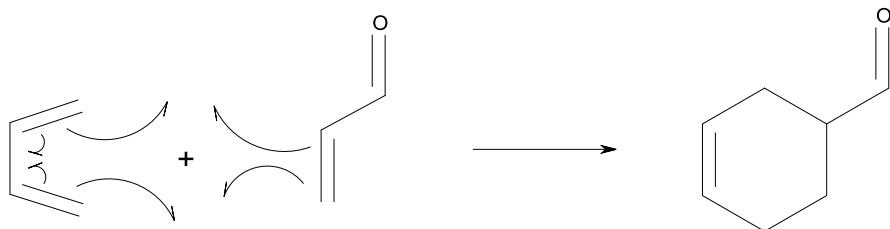
### Thermodynamic Control (High T)

- At high T, more energy is available to be used as activation energy for reactions. The system is fully reversible at high T, and it can therefore achieve equilibrium.
- The more stable 1,4 product (more substituted alkene) forms primarily.
- Since more  $E_a$  is available, the 1,2 product can revert back to the carbocation, and also the 2<sup>nd</sup> resonance form has enough  $E_a$  to form the 1,4 product.



### Diels Alder Cycloaddition

- Cycloaddition is one of the few general methods to create cyclic organic compounds.
- A conjugated diene (4 C's) reacts with a dienophile (2 C's) to form a cyclohexene ring (6 C's).
- The mechanism is neither polar, nor radical. It is pericyclic.
- The six  $\pi$   $e^{-1}$ 's act in concert (simultaneously) to form a cyclic transition state.
- The diene's two inside  $\pi$   $e^{-1}$ 's form a new  $\pi$  bond, and the other four  $\pi$   $e^{-1}$ 's form two new  $\sigma$  bonds, which create the new ring.



Diene  
must be in s-cis  
configuration

Dienophile  
 $\pi$  Bond must be connected to  
an electron withdrawing group  
(EWG)

Product has two new  
single bonds and  
contains a six-membered  
cyclohexene ring

### Dienophile

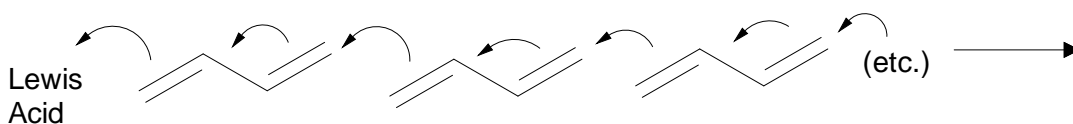
- Needs to have an  $e^{-1}$  withdrawing group (EWG) that is attached to at least one of the  $\pi$  bonded C's.
- The most typical EWG's are carbonyls ( $C=O$ ) and nitriles ( $C\equiv N$ ).
- Alkyl groups are not EWG's.
- An EWG will pull  $e^{-1}$ 's toward itself, so that the  $\pi$  bond C's become  $\delta+$ , and can react with the  $e^{-1}$  rich diene.

### Diene

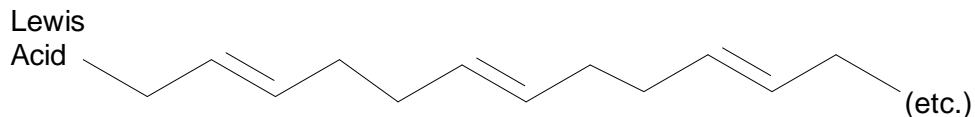
- Must have "s-cis" at the  $\sigma$  bond between the two  $\pi$  bonds.
- Not exactly cis because it involves only the  $\sigma$  bond, but the two  $\pi$  bonds face each other.
- Note that  $\sigma$  bonds can rotate, and s-trans is more stable because there is less steric strain between the  $\pi$  bonds.
- For the reaction to occur, the s-trans must typically rotate to the higher E s-cis state.

## Diene Rubbers

- Formed from repeated 1,4 addition of diene molecules to a growing chain.
- Intermediates can be cationic, like the 1,4 cation in 1,4 addition of HBr. This occurs if an acid catalyst is used.
- Intermediates can also be free radicals, with an initiation, propagation, and termination, as in section 8.10. Here a free-radical initiator is used to start the reaction.
- The original double bonds are broken to create new single bonds, which link the monomer units together.
- The polymers will have new double bonds for the C's that were single bonded between two double bonds.
- The new double bonds can be Z (cis) or E (trans). For example, there are both cis and trans polybutadienes. Neoprene is a Z polymer made from chloroprene units.
- Rubbers polymers are initially soft and tacky when formed, but can be made firmer and non-sticky by vulcanization (heating with S). Essentially, S creates cross-linked disulfide bridges (R-S-S-R)



1,3-butadiene monomers



(Z) - polybutadiene polymer (has new single bonds between monomer units)

## UV Spectroscopy

- Absorptions have  $\lambda = 200 - 400$  nm. Range is next to visible with  $\lambda$  shorter than visible,
- Absorptions correspond to  $\Pi \rightarrow \Pi^*$  transitions that are  $\Pi$  to  $\Pi^*$  (bonding to antibonding).
- For a single molecule and photon,  $E = h\nu = hc/\lambda$ . So, E of UV is higher than visible.
- For a mole, we have  $E = N_A h\nu = N_A hc/\lambda$ .
- Spectra of samples are measured by their Absorbance:  
$$A = -\log(I/I_0) = -\log(T)$$

$I_0$  is incoming light,  $I$  is transmitted thru the sample, and  $T$  is transmittance.
- Beer's Law is used to find absorptivity ( $\epsilon$ ), which is a constant for a particular molecule at a particular wavelength.  
$$A = \epsilon LC$$

$L$  is the pathlength (cm) and  $C$  is concentration (mol/L)
- Spectra are  $A$  vs  $\lambda$ , and are usually a simple curve with one  $\lambda_{\max}$ .
- $\lambda_{\max}$  is the wavelength with the highest  $A$  (and  $\epsilon$ )

## Effect of conjugation on $\lambda_{\max}$

- $\lambda_{\max}$  is a function of the E gap between the highest occupied bonding MO ( $\Psi$ ) and the lowest unoccupied antibonding MO ( $\Psi^*$ )
- As the extent of conjugation (number of conjugated  $\Pi$  bonds) increases, the E gap decreases. This causes  $\lambda_{\max}$  to increase, so that it becomes closer to the visible range.
- Different types of molecules, such as conjugated alkenes, enones ( $C=C-C=O$ ), and aromatic compounds (benzene rings) have characteristic  $\lambda_{\max}$  and  $\epsilon$  that can be used to identify them.

## Conjugation, Color, and Vision

- With extended conjugation systems, the  $\lambda_{\max}$  extends into the visible range.
- The molecule then absorbs blue-violet, and it appears as the complementary color, which is yellow-orange, like  $\beta$ -carotene (from carrots).
- $\beta$ -carotene is converted to all-trans retinol (vitamin A) by the body, which then converts it to 11-cis retinal. This molecule is attached to a protein called opsin, and becomes rhodopsin.
- Rhodopsin is also 11-cis, and is the light sensor in our rod cells. It is isomerized to all-trans metarhodopsin II by light.
- The isomerization would practically never happen without the presence of light.