

Conjugated Systems and UV Spectroscopy

Reading: Wade chapter 15, sections 15-1- 15-13

Study Problems: 15-25, 15-27, 15-30, 15-31, 15-33, 15-34, 15-35

Key Concepts and Skills:

- Construct the molecular orbitals of ethylene, butadiene, and the allylic system, showing the electronic configurations of ethylene, butadiene, and the allylic cation, radical, and anion
- Explain how resonance stabilization of intermediates enhances free-radical and cationic reactions.
- Predict the products of Diels-Alder reactions, including the orientation of cycloaddition with unsymmetrical reagents and the stereochemistry of the products.
- By comparing MO's of the reactants, predict which cycloadditions will be thermally allowed and which will be photochemically allowed.
- Use λ_{max} values from UV-vis spectra to estimate the length of conjugated systems.

Lecture Topics:

I. Conjugated systems

Double bonds separated by a single sigma bond are said to be **conjugated**. Conjugated dienes are more stable than isolated dienes.

Hydrogenation data indicate that conjugated dienes are more stable than both isolated and cumulated dienes:

• In general, it is found that conjugated double bonds are 3.7 kcal/mol more stable than similar compounds with isolated double bonds. This extra stability of conjugated molecules is called the resonance energy of the system.

• Conjugated systems have an interaction between the π electrons of each bond; the π electrons are not localized \rightarrow they are "delocalized"

Note that in 1,3 butadiene, the central C-C bond (between C2 and C3) is shorter than a normal single bond. There are two reasons: there is greater s character in the sp^2 orbitals bonding from each carbon, and there is partial overlap of the π -electrons from the

alkenes. Because of this, butadiene exists predominantly in a planar conformation, so that overlap of π -electrons between the two alkenes is possible. This spreading out of charge (delocalization) leads to the greater stability of conjugated systems.

Electrons in the double bonds are delocalized over the entire molecule, creating some pi overlap between C2 and C3, thus shortening this bond.

II. Molecular Orbital Descriptions of Pi Systems

Consider only the interacting contiguous p-orbitals of conjugated system in question. For ethylene, there is a π bonding orbital of lower energy than the isolated p orbitals, and a π^* antibonding orbital that is of higher energy than the isolated p orbitals. The π orbital represents a bonding combination resulting from constructive overlap of in-phase p-orbitals, the π^* antibonding orbital contains a node (region of zero electron density) resulting from destructive overlap of out-of-phase p-orbitals. The two electrons of the pi bond of ethylene are in the π bonding orbital in its stable, ground state:

The number of molecular orbitals formed is equal to the number of p atomic orbitals which overlap to form bonds. In an excited state, electrons may be transferred from the π -bonding orbital to the π^* antibonding orbital. For butadiene, four molecular orbitals (π_1 , π_2 , π_3^* , π_4^*) arise from overlap of 4 contiguous p-orbitals. The lowest energy bonding combination has no nodes; the next highest bonding combination has one node; the first antibonding orbital has two nodes, and the highest energy antibonding orbital has

three nodes. In the ground state, the four pi electrons of butadiene exist in the two bonding molecular orbitals π_1 and π_2 :

The partial double-bond character between C2 and C3 of butadiene explains why butadiene exists in a planar conformation. There are two separate planar conformations of butadiene, s-cis and s-trans. S-trans is 2.3 kcal/mol more stable than s-cis because of a lack of steric interaction of the terminal alkenyl hydrogen atoms. Owing to the partial double bond character of C2-C3, there is a 4.9 kcal/mol barrier to rotation about the C2-C3 bond (compare the barrier to rotation in a full double bond: 60 kcal/mol), low enough that interconversion between the two forms is rapid at room temperature.

III. Allylic Cations, radicals, anions

Allylic systems retain the resonance stabilization of conjugated systems. Allylic cations are formed from SN1 ionization of alkyl halides or tosylates and are as stable as secondary carbocations. Substituted allylic cations are as stable as tertiary carbocations:

Conjugated dienes undergo electrophilic additions by way of resonance-stabilized allylic cations. Addition of HBr to butadiene results in two alkyl bromide products: a 1,4 addition product and a 1,2 addition product. The ratio of these two products obtained depends on the temperature at which the reaction is run. 1,2 addition products predominate at low temperatures (-80°C) and 1,4 addition products predominate at higher temperatures (40°C):

The 1,2-addition product is the kinetic product because it is formed at a more rapid rate at low temperatures, which means it must have a lower activation energy barrier. The 1,4 addition product is known as the thermodynamic product, since it possesses the more stable disubstituted alkene. At high temperatures, equilibrium is established between the products, and the more stable product predominates. The transition state leading to the 1,2 addition product is lower in energy because it involves attack by bromide ion on a more stable secondary carbocation:

Kinetic Conditions are non-equilibrium conditions involving low temperatures; the lowest energy pathway occurs most rapidly. Under thermodynamic conditions, an

equilibrium is set up between the products, and eventually the most stable product predominates:

Allylic radicals

Stability order: $1^\circ < 2^\circ < 3^\circ < \text{allylic}$

Orbital description of the allylic system: three contiguous p orbitals overlap to spread out charge. Three molecular orbitals are formed which are bonding π_1 (no nodes), non-bonding π_2 (1 node) and antibonding π_3^* (2 nodes):

Note that the molecular orbital description indicates that for the allylic radical, the unpaired electron is in the non-bonding π_2 orbital, which has a node on the central carbon atom; thus the radical is shared equally on the terminal carbons of the allylic system. The radical will only react at C1 and C3. Similarly, for the allylic anion, the non-bonding orbital is filled, indicating that the anion exists equally at C1 and C3, but not on the central carbon; reactions with electrophiles therefore take place at C1 and C3. For the

allylic cation, the non-bonding orbital is empty, indicating that electron deficiency is equally distributed on C1 and C3, which are the observed sites of nucleophilic addition. General principle: the Highest Occupied Molecular Orbital (HOMO) or the Lowest Unoccupied MO (LUMO) determines the reactivity of the molecular fragment:

IV. SN2 reactions of Allylic Halides and Tosylates

Allylic halides and tosylates are observed to undergo SN2 reaction at much higher rates than the corresponding alkyl halides/tosylates:

The reason for the rate enhancement is the delocalization of charge in the transition state for SN2 reaction of allylic systems; the charge delocalization thus stabilizes the transition state. Such delocalization/transition state stabilization is absent for alkyl halide SN2 displacements:

V. The Diels-Alder Reaction

Probably one of the most important reactions of conjugated dienes is a [4+2] cycloaddition known as the Diels-Alder reaction. This process forms six-membered rings from the reaction of dienes with electron-deficient alkenes. The diene is the 4π electron component, and the alkene (also known as the dienophile) is the 2π electron component. In the transition state, a cyclic flow of electrons occurs, and two pi bonds are converted

into two stronger sigma bonds, providing the thermodynamic driving force for the process.

The reaction is “concerted”, that is, there is a simultaneous bond-breaking and bond-formation. The movement of electrons is cyclic. The reaction can be thought of as a combination of an electron-rich species (diene) with an electron-poor species (dienophile). In fact, good dienophiles contain one or more electron-withdrawing groups; good dienes contain one or more electron-donating groups:

Stereochemistry

The transition state of the Diels-Alder reaction involves overlap of the p-orbitals at the ends of the diene with the alkene p-orbitals of the dienophile. In order for this to occur, the diene must be in the *s-cis* conformation. Recall that for butadiene the *s-trans* conformer is more stable, and there is a 4.9 kcal/mol barrier to rotation about the C2-C3 bond. For this reason, cyclic dienes locked in *s-cis* conformation are very reactive dienes in the Diels-Alder reaction; dienes locked in *s-trans* form do not react at all, and those for which the *s-trans* form involves severe steric encumbrance react very slowly.

As can be seen from the above, the diene adds to one face of the dienophile, thus cis substituents on the dienophile remain cis (syn) in the product. Trans substituents on the dienophile remain trans (anti) in the product. The same holds true for diene substituents:

The Endo rule

p-orbitals in the electron-withdrawing group of the dienophile approach the internal carbons of the diene (C2 and C3) because of the possibility of engaging in secondary orbital overlap (allowing charge delocalization and thus stabilization of the transition state). As a result, the W group ends up in an “endo” orientation in the product.

The Ortho-Para rule (1,2;1,4 rule)

For unsymmetrical reagents, there is a preference for substituents to be either in a 1,2 or 1,4 relationship in the Diels-Alder cycloadduct. The minor resonance forms for both the diene and the dienophile are key to understanding this type of reactivity:

VI. Conservation of Orbital Symmetry

Pericyclic Reactions involve the concerted making and breaking of bonds within a closed ring of interacting orbitals. The reaction has a single transition state, and the activation energy is supplied by heat or light. According to the **Woodward-Hoffman rules**, the MO's of the reactants must flow smoothly into the MO's of the products. Only orbitals of the same phase will overlap constructively to form a bond. The highest occupied molecular orbital (HOMO) of the electron-rich species (diene) interacts with the lowest unoccupied orbital (LUMO) of the electron-deficient species (dienophile).

The Diels-Alder reaction is a thermally allowed pericyclic process because the ground-state diene HOMO and dienophile LUMO are of the correct symmetry for successful overlap of the interacting p-orbitals. This phenomenon is known as the conservation of orbital symmetry.

[2+2] cycloadditions are thermally forbidden because the LUMO of one ethylene molecule does not have the correct symmetry for in-phase overlap with the HOMO of another ethylene molecule. However, if one ethylene molecule is photochemically excited (in which an electron is promoted from the π bonding to the π^* antibonding orbital, the HOMO and LUMO now have the correct symmetry for in-phase overlap. Thus, an excited state ethylene molecule can react with a ground-state ethylene molecule to produce cyclobutane. This reaction is therefore thermally forbidden but photochemically allowed.

Note that Diels-Alder cycloadditions are thermally allowed but photochemically forbidden.

VII. Ultraviolet Spectroscopy

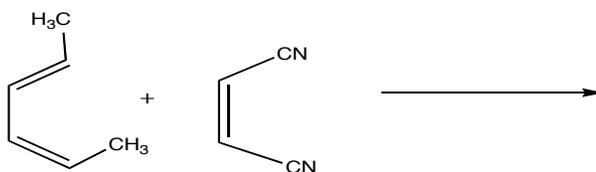
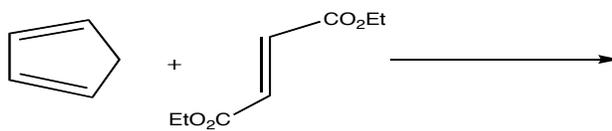
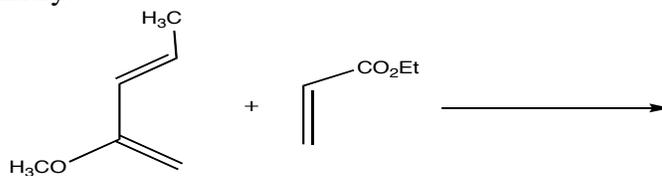
UV spectroscopy detects the electronic transitions of conjugated systems and provides information about the length and structure of conjugated parts of molecules. The wavelength range for UV spectroscopy is 200-400 nm, with energies of 70-140 kcal/mol. In contrast, IR wavelength ranges are 2.5-25 μm (1.1-11 kcal/mol), far less energetic radiation. The wavelengths of UV light absorbed by a molecule are determined by the electronic energy differences between orbitals in the molecule. σ bonds are strong and stable, and thus there is a large energy gap between σ and σ^* molecular orbitals; more energetic radiation than UV light is required for excitation of electrons in σ bonds.

However, conjugated systems have low-lying vacant π^* orbitals, and electronic transitions into these orbitals from π molecular orbitals are the transitions characteristic of UV absorptions. The π - π^* gap in ethylene is 164 kcal/mol (171 nm); in butadiene, the π_2 - π_3^* gap is 129 kcal/mol (217 nm). In general, the energy difference between HOMO and LUMO for a given molecule decreases as the length of conjugation increases, and thus less energetic radiation is required for excitation.

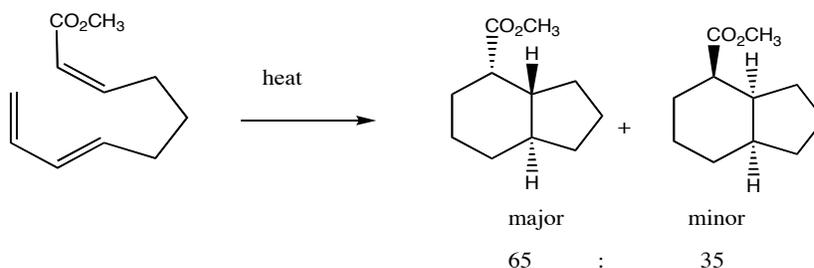
Compounds containing longer chains of conjugated double bonds absorb light at longer wavelengths. Non-conjugated double bonds display no such shift to longer wavelengths. An Additional conjugated double bond increases λ_{max} by 30-40 nm; An additional alkyl group increases λ_{max} by 5 nm.

Additional Problems for practice:

1. Treatment of 3-buten-2-ol with cold hydrogen bromide gives 1-bromo-2-butene and 3-bromo-1-butene in a 15:85 ratio. On heating, this ratio changes to give mainly 1-bromo-2-butene. Explain.
2. Addition of 1 equivalent of bromine to 1,3,5-hexatriene gives 3 dibromide products. Draw the structure of the products and indicate which product(s) are formed in excess at low temperatures and which product(s) are formed in excess at high temperatures.
3. Predict the product(s) of the following reactions. Be sure to indicate stereochemistry:



4. Explain why the major product of the Diels-Alder reaction shown below is formed in excess:.



5. Show how you could prepare the following compounds using a Diels-Alder reaction:

