CHAPTER 14 Delocalized Pi Systems: Investigation by Ultraviolet and Visible Spectroscopy

14-1 Overlap of Three Adjacent p Orbitals: Electron Delocalization in the 2-Propenyl (Allyl) System

The C—H bond on carbon adjacent to a pi bond is unusually weak (87 versus 101 kcal/mole). This decrease on bond strength is the result of an increase in stability of the resulting allylic radical as compared to an ordinary radical. Allylic radicals are stabilized by resonance where the unpaired electron is distributed over two carbon atoms. In molecular orbital terms, the combination of three p orbitals results in the formation of three molecular orbitals: bonding; nonbonding; and antibonding. The bonding orbital has no nodes end-to-end, the nonbonding has one, and the antibonding has two. Two of the three electrons of the allylic radical are in the bonding orbital and the odd electron is in the nonbonding orbital.

14-2 Radical Allylic Halogenation

Because an allylic C—H bond is unusually weak, free radical abstraction of such a hydrogen is faster than a non-allylic hydrogen. Thus, free radical halogenation is selective for the allylic position. However, the resulting radical has two carbons that can abstract a halogen atom and only when the radical is symmetrical is a single product obtained.

14-3 Nucleophilic Substitution of Allylic Halides: SN1 and SN2

SN1 reaction of an allylic halide is facilitated because the intermediate cation is resonance stabilized. Because there are two carbons that bear positive charge in the intermediate cation, only symmetrical cations produce a single product. The SN2 transition state is also stabilized by overlap of the p orbital on the carbon undergoing substitution with the pi system of the adjacent double bond.

14-4 Allylic Organometallic Reagents: Useful Three-Carbon Nucleophiles

Allylic C—H bonds can be deprotonate by strong base, for example BuLi. The resulting anion is resonance stabilized, with negative charge on two carbons. This anion is nucleophilic and adds to, for example, ketones and aldehydes. The result products are bifunctional, having an alcohol and an alkene.

14-5 Two Neighboring Double Bonds: Conjugated Dienes

Two adjacent double bonds are said to be conjugated. The four electrons of the pi system are not localized between pairs of carbon atoms. Rather, two are spread from end to end in an orbital that results from the combination of all four of the p orbitals in phase. The remaining two electrons are also spread over the entire chain of four carbon atoms but have a node in the middle between carbons 2 and 3. This delocalization results in additional stabilization for conjugated dienes.

14-6 Electrophilic Attack on Conjugated Dienes: Kinetic and
Thermodynamic Control

Addition of a proton to a conjugated diene lead preferentially to the conjugated cation. Bromide ion addition to this cation is kintically favored at the more substituted carbon atom whereas equilibration of the allylic bromide products favors the product with the more substituted double bond. The reaction is said to be under kinetic control in the first case and thermodynamic control in the second.

14-7 Delocalization among More tha Two Pi Bonds: Extended Conjugation and Benzene

Extended conjugation with three double bonds leads to six molecular orbitals, 3 bonding and 3 antibonding. As the number of double bonds increases, the lowest bonding orbital becomes increasingly stable. In addition, as the number of double bonds increases, the energy difference or gap between the HOMO and LUMO decreases. Benzene represents a special case of conjugation where formally there are three double bonds within a six-membered ring. In reality, the electrons are distributed evenly around the ring, leading to a very significant increase in stability for benzene and other aromatic compounds.

14-8 A Special Transformation of Conjugated Dienes: Diels-Alder Cycloaddition

The Diels-Alder reaction combines a conjugated diene with an alkene (called a dienophile) in a reaction that forms a six-membered ring by a concerted pathway. The presence of an electron-withdrawing group (EWG) such as a carbonyl containing functionality on the dienophile double bond greatly increases the rate of reaction.

14-9 Electroyclic Reactions

Electroyclic reactions are similar to the Diels-Alder reaction in that they have a cyclic transition state and a concerted mechanism. Only those reactions covered in lecture will be tested.

14-10 Polymerization of Conjugated Dienes: Rubber

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14-11 Electronic Spectra: Ultraviolet and Visible Spectroscopy

covered with nmr, ir, and mass spectroscopy earlier
\[
\begin{align*}
\text{H} & \quad 101 \text{ kcal/mol Pd} \\
\text{H} & \quad 87 \\
\text{Br} & \quad \text{Br} \\
\text{Br} & \quad \text{Allyl, 2 Radical}
\end{align*}
\]
[Image of molecular orbitals and bonding]

- antibonding (anti bonding)
- nonbonding
- bonding

\( \# \pi_e = 3 \)
Cl

\[
\text{Cl} + \text{CH}_2 = \text{CH}_2 \rightarrow \text{Cl}\]

70 : 30 kinetic ratio

\[
\downarrow \Delta
\]

15 : 85 more stable
Diels - Alder

\[ \text{net change} \quad 2 \text{C=C} \rightarrow 2 \text{C-C} \]

\[ \text{C=C} \quad \pi \quad 6 \]

\[ \text{C-C} \quad \sigma \quad 8 \]

\[ \text{ cis } + \quad \text{ trans } \rightarrow \text{ cis-cis} \]