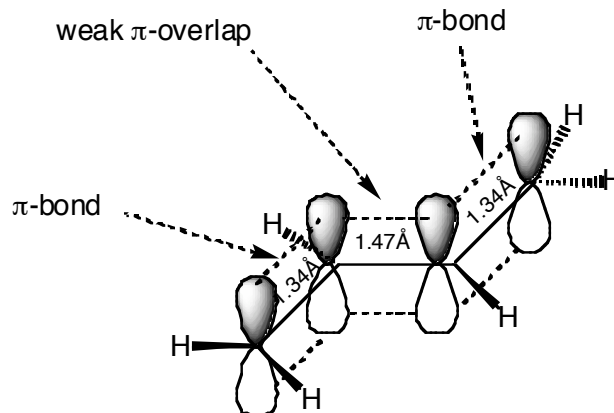


Chemistry 0320 - Organic Chemistry 2

Delocalized π -Systems

Conjugation occurs when one or more electrons can be delocalized over an adjacent π -system. Three center - three electron systems that are stabilized in this fashion are the allylic radicals, allylic anions, and the allylic cations.

Similarly, conjugation in 1,3-butadiene resulting from an overlap of the π -bond stabilizes the diene by 3.5 kcal/mol. The central bond is shorter than that in an alkane. 1,3-Butadiene can exist in two planar conformations, the **s-cis** and the **s-trans** conformation. The prefix *s* refers to the fact that the bridge between C2 and C3 constitutes a single bond. The *s-cis* form is almost 3 kcal/mol less stable than the *s-trans* configuration because of the steric interference between the two hydrogens on the inside of the diene unit. When more than two double bonds are in conjugation, the molecule is called an **extended π -system**.



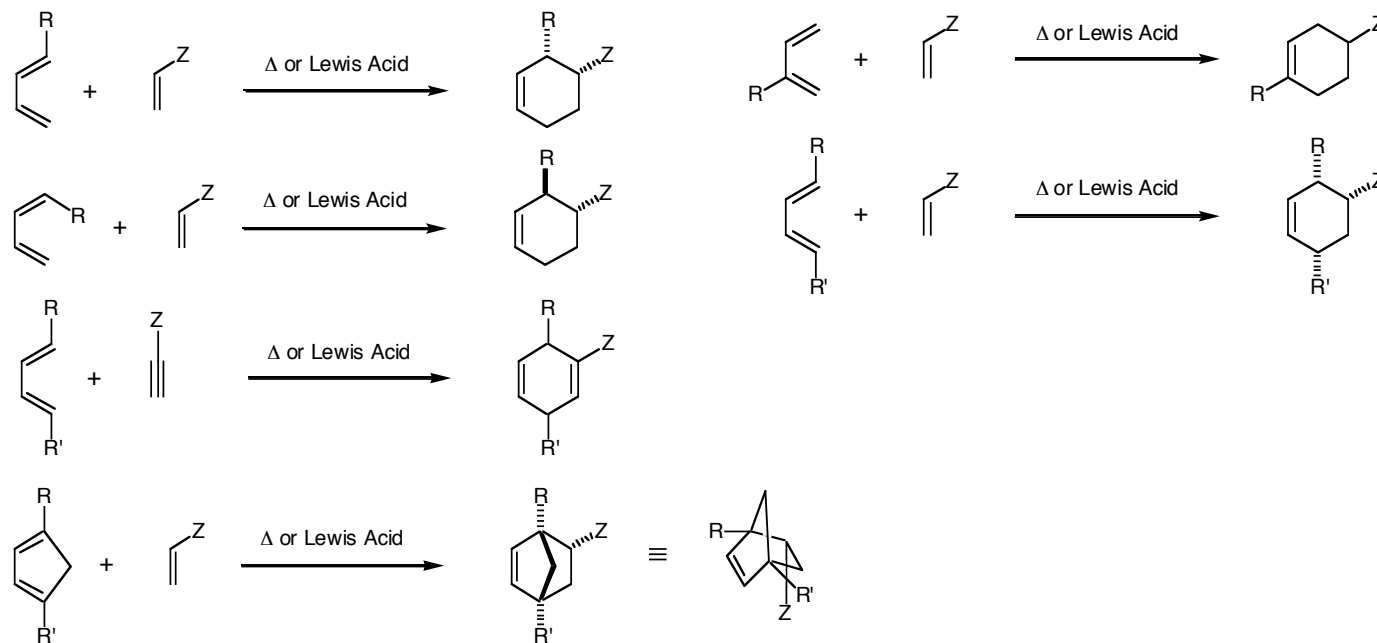
Extended π -systems are thermodynamically stable but kinetically reactive. The increased reactivity of extended π -systems in spite of their higher thermodynamic stability is due to the low activation barriers for electrophilic additions, which proceed through highly delocalized carbocations (transition states for these reactions have lower energy due to delocalization of charges through the π -system).

- **Allylic halogenations with NBS**: N-Bromosuccinimide serves as a radical chain initiator and quenches HBr to give Br_2 .

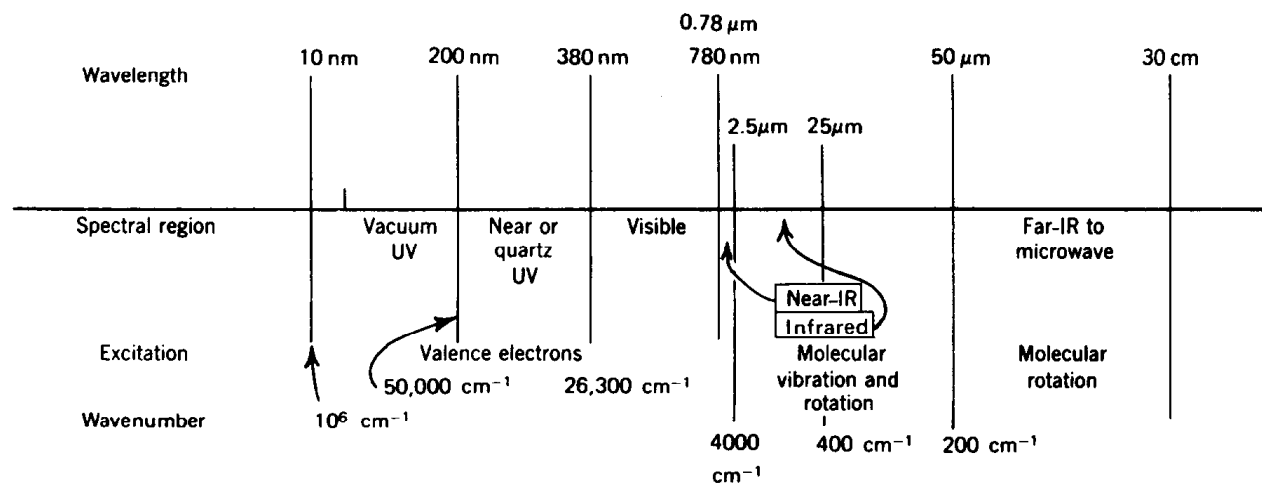
- **Nucleophilic substitutions** of allylic halides are accelerated for both $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ pathways.

- **1,4-Addition in conjugated dienes** occurs simultaneously to 1,2-addition and provides the more stable internal double bonds when under thermodynamic control.

- The **Diels-Alder** reaction is an important 1,4-addition to dienes. A diene in its *s-cis* conformation reacts with a **dienophile**, usually an alkene attached to an electron-withdrawing group (Z). The product is a substituted cyclohexene, and *ortho*- or *para*-substitution is favored. If the diene is cyclic, a bicyclic compound is formed and the electron-withdrawing substituent on the dienophile usually favors the **endo**-orientation (*cis* to the larger bridge).



The electromagnetic spectrum:



Molecular absorption in the ultraviolet (UV) and visible region of the spectrum is dependent on the electronic structure of the molecule. Absorption of energy is quantized, resulting in the elevation of electrons from orbitals in the ground state to higher energy orbitals in an excited state. An advantage of UV absorption is the selectivity of excitation: Characteristic functional groups may be recognized in molecules of widely varying complexities because large portions of the molecular skeleton are transparent between 200-800 nm. Lambert-Beers law gives the relationship between concentration, extinction coefficients, and absorbance.

Summary of electronic transitions:

Example	Electronic Transition	λ_{\max} (nm)	ϵ_{\max}	Band ^a
Ethane	$\sigma \rightarrow \sigma^*$	135		
Water	$n \rightarrow \sigma^*$	167	7,000	
Methanol	$n \rightarrow \sigma^*$	183	500	
1-Hexanethiol	$n \rightarrow \sigma^*$	224	126	
<i>n</i> -Butyl iodide	$n \rightarrow \sigma^*$	257	486	
Ethylene	$\pi \rightarrow \pi^*$	165	10,000	
Acetylene	$\pi \rightarrow \pi^*$	173	6,000	
Acetone	$\pi \rightarrow \pi^*$	~150		
	$n \rightarrow \sigma^*$	188	1,860	
	$n \rightarrow \pi^*$	279	15	<i>R</i>
1,3-Butadiene	$\pi \rightarrow \pi^*$	217	21,000	<i>K</i>
1,3,5-Hexatriene	$\pi \rightarrow \pi^*$	258	35,000	<i>K</i>
Acrolein	$\pi \rightarrow \pi^*$	210	11,500	<i>K</i>
	$n \rightarrow \pi^*$	315	14	<i>R</i>
Benzene	Aromatic $\pi \rightarrow \pi^*$	~180	60,000	<i>E</i> ₁
	Aromatic $\pi \rightarrow \pi^*$	~200	8,000	<i>E</i> ₂
	Aromatic $\pi \rightarrow \pi^*$	255	215	<i>B</i>
Styrene	Aromatic $\pi \rightarrow \pi^*$	244	12,000	<i>K</i>
	Aromatic $\pi \rightarrow \pi^*$	282	450	<i>B</i>
Toluene	Aromatic $\pi \rightarrow \pi^*$	208	2,460	<i>E</i> ₂
	Aromatic $\pi \rightarrow \pi^*$	262	174	<i>B</i>
Acetophenone	Aromatic $\pi \rightarrow \pi^*$	240	13,000	<i>K</i>
	Aromatic $\pi \rightarrow \pi^*$	278	1,110	<i>B</i>
	$n \rightarrow \pi^*$	319	50	<i>R</i>
Phenol	Aromatic $\pi \rightarrow \pi^*$	210	6,200	<i>E</i> ₂
	Aromatic $\pi \rightarrow \pi^*$	270	1,450	<i>B</i>

^aThe *R* band, German *radikalartig*; *K* band, German, *konjugierte*; *B* band, benzenoid; *E* band, ethylenic; see: A. Burawoy, *Berichte*, **63**, 3155 (1930); *J. Chem. Soc.*, 1177 (1939); also see the chapter by E. A. Braude listed in the reference section.