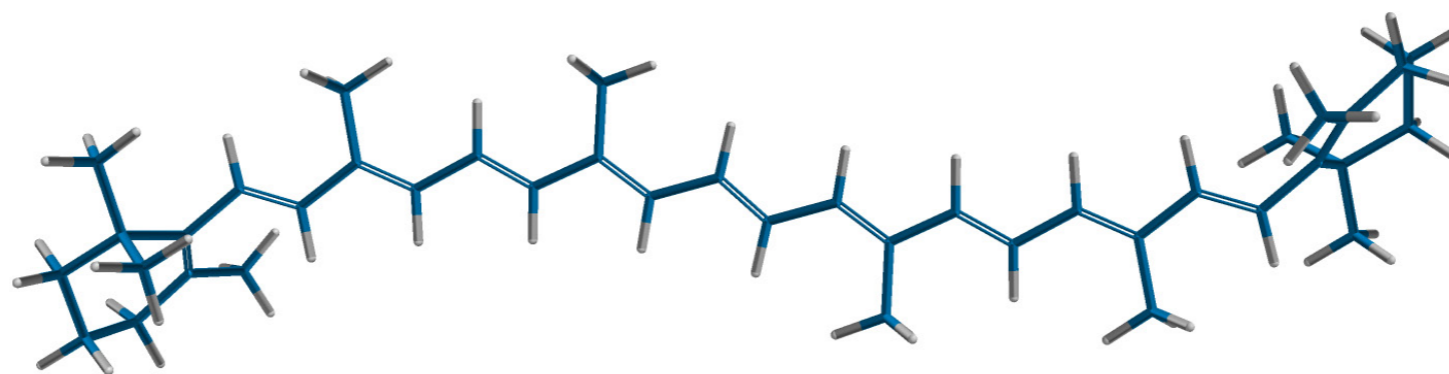
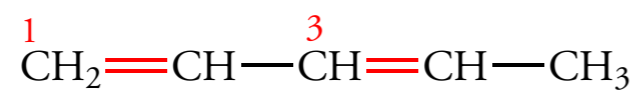


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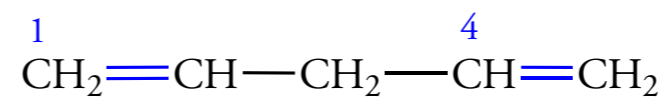
CONJUGATED ALKENES AND ALLYLIC SYSTEMS



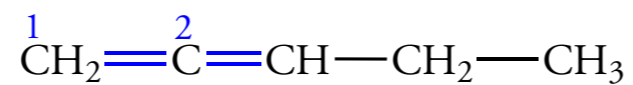
11.1 CLASSES OF DIENES



1,3-pentadiene, conjugated diene



1,4-pentadiene, nonconjugated diene



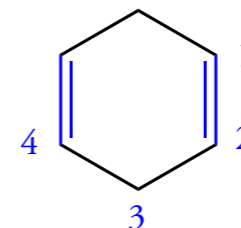
1,2-pentadiene, cumulated diene



cyclopentadiene



1,3-cyclohexadiene



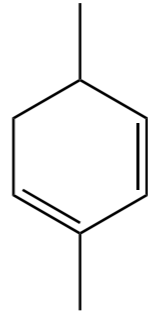
1,4-cyclohexadiene

conjugated dienes

nonconjugated diene

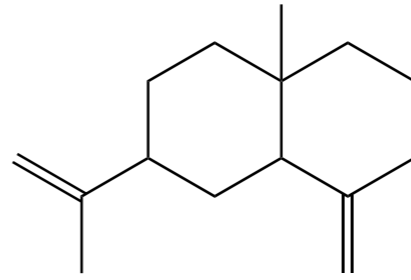
Figure 11.1 Structures of a few terpenes.

Monoterpene



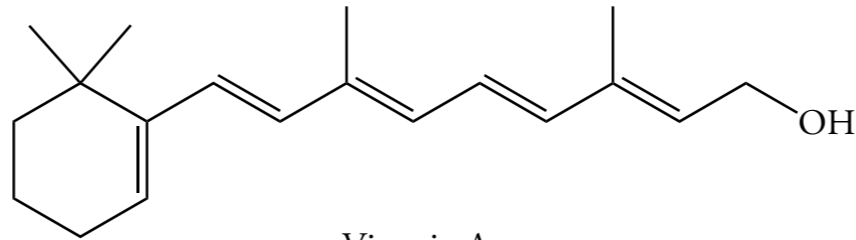
α -phellandrene
(eucalyptus)

Sesquiterpene

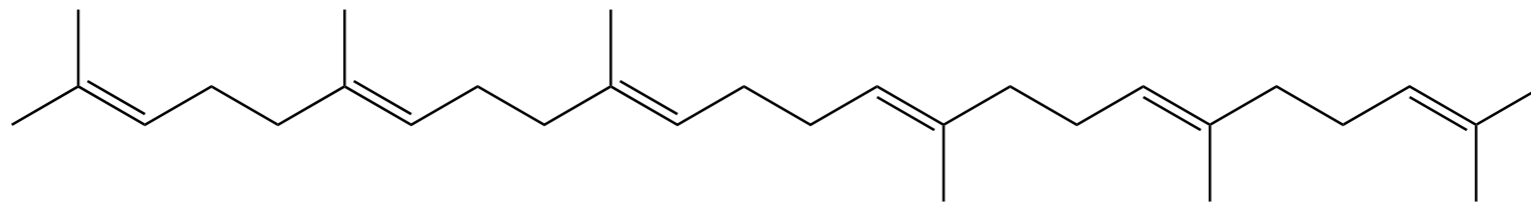


α -selinene
(celery)

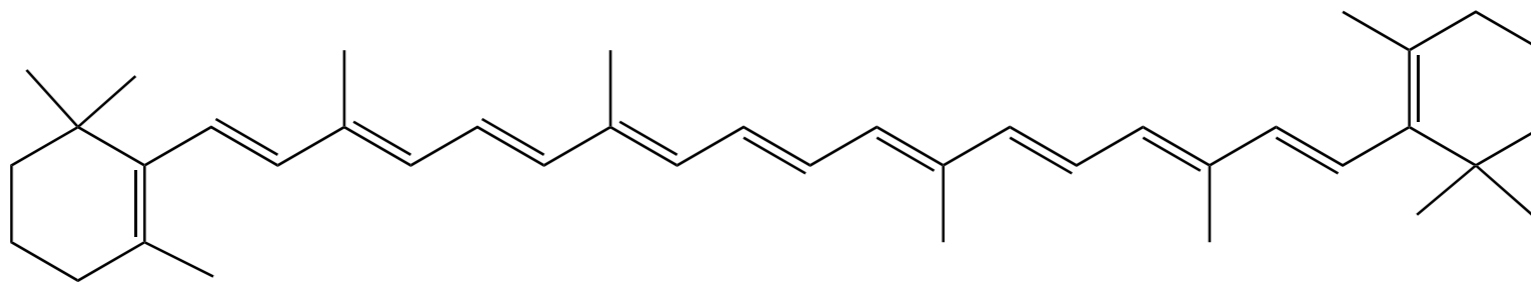
diterpene



Vitamin A
(present in mammalian tissue and fish oil)



Squalene
(triterpene)



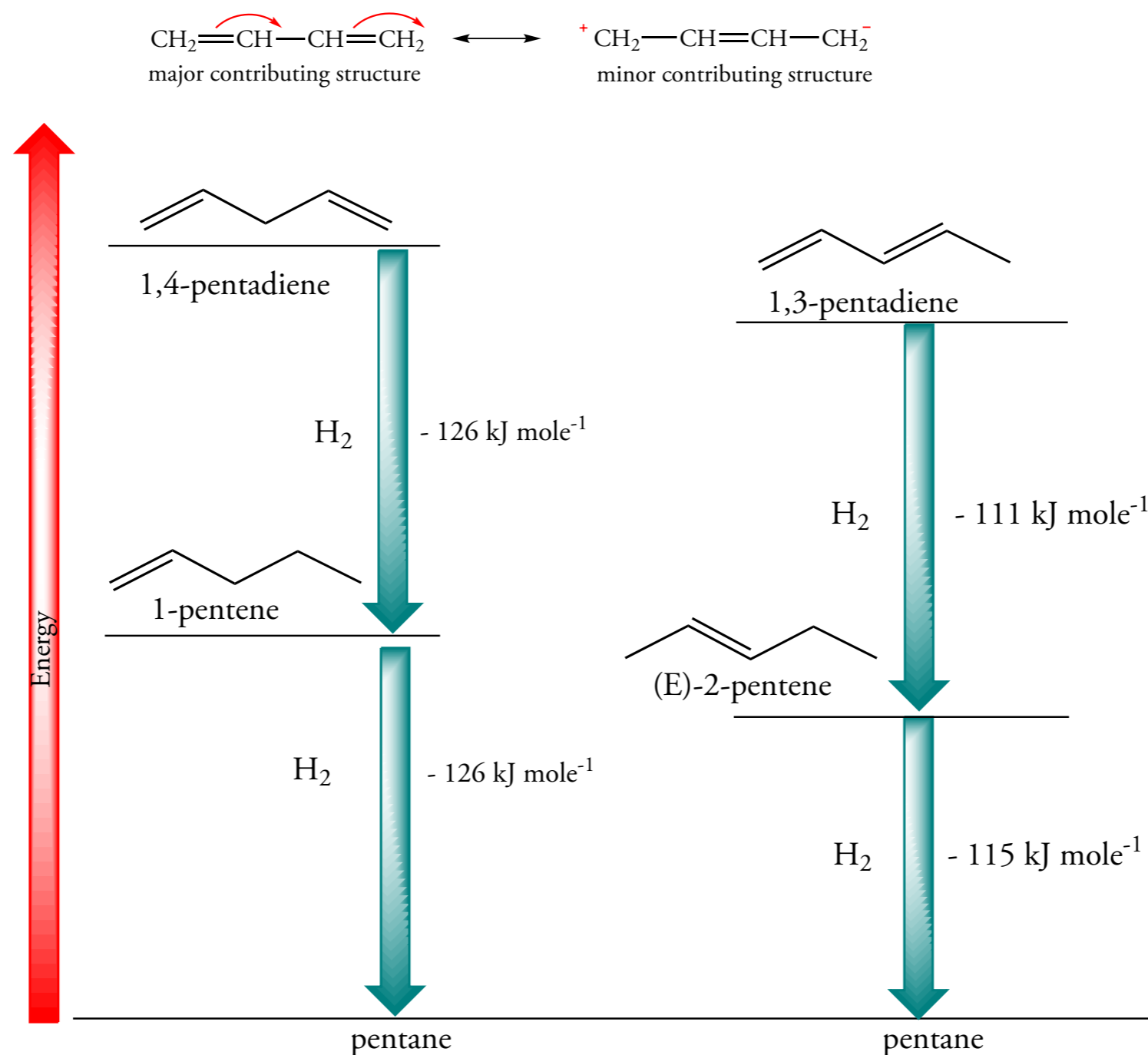
β -Carotene
(tetraterpene)

11.2 STABILITY OF CONJUGATED DIENES

Figure 11.2 Heats of Hydrogenation and Resonance Energy

(E)-1,3-pentadiene is more stable than 1,2-pentadiene for two reasons:

1. (E)-1,3-pentadiene is more substituted than 1,4-pentadiene.
2. The double bonds in (E)-1,3-pentadiene are conjugated, but the double bonds in 1,4-pentadiene are not.



11.3 MOLECULAR ORBITALS OF ETHENE AND 1,3-BUTADIENE

Figure 11.3 Orbital Overlap in Pi Bond

The side-by-side overlap of two 2p orbitals in ethene leads to two molecular orbitals. Constructive overlap gives the bonding π , molecular orbital. The destructive overlap of the two orbitals gives a higher energy, antibonding molecular orbital, π^* .

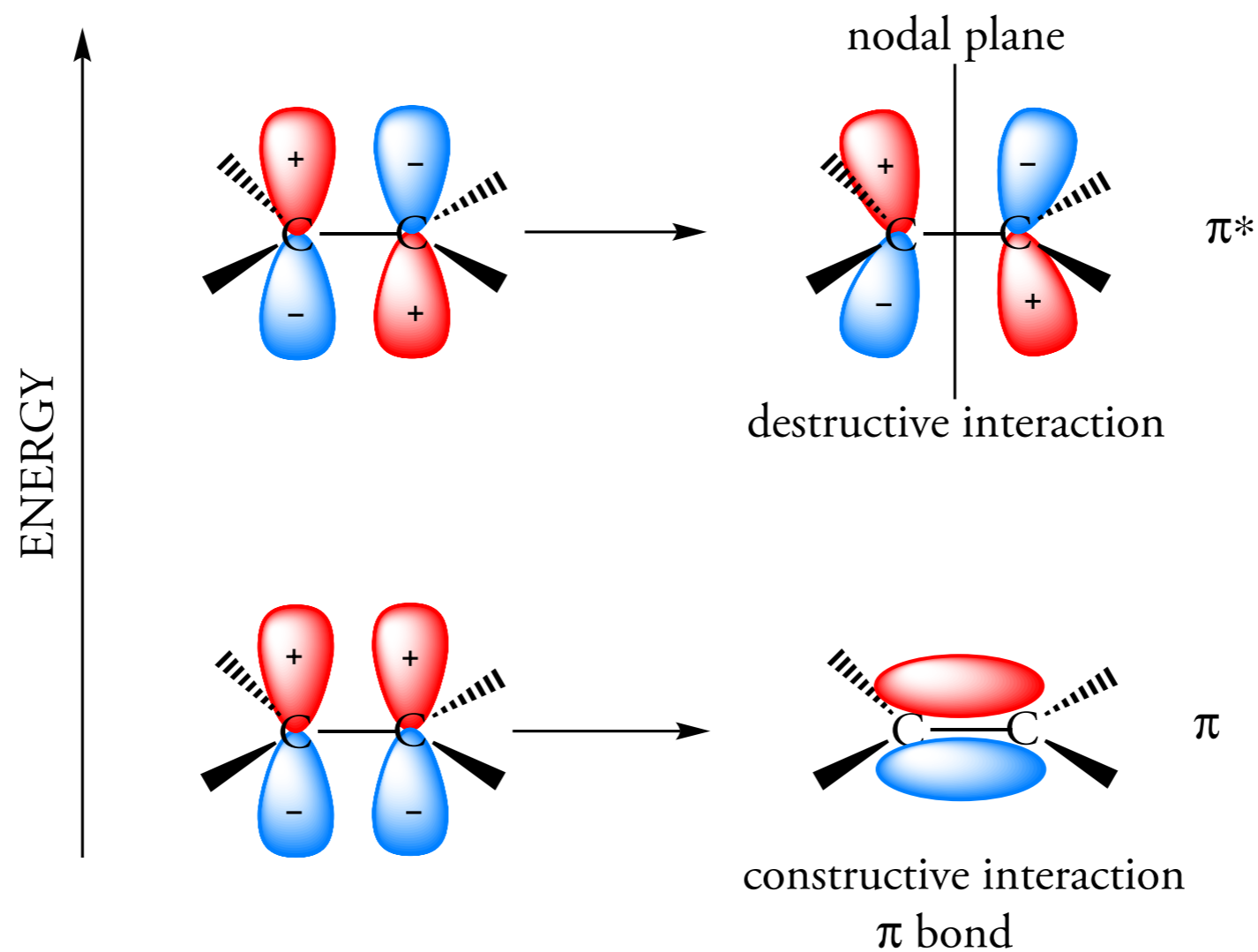


Figure 11.4 Symmetry of π Molecular Orbitals of Ethene

The π molecular orbitals of ethene have opposite symmetries with respect to the vertical plane that bisects the π bond. The bonding orbital is symmetric with respect to the vertical plane. However, the antibonding orbital is antisymmetric with respect to this plane. Thus, for the antibonding orbital, the vertical plane is also a nodal plane.

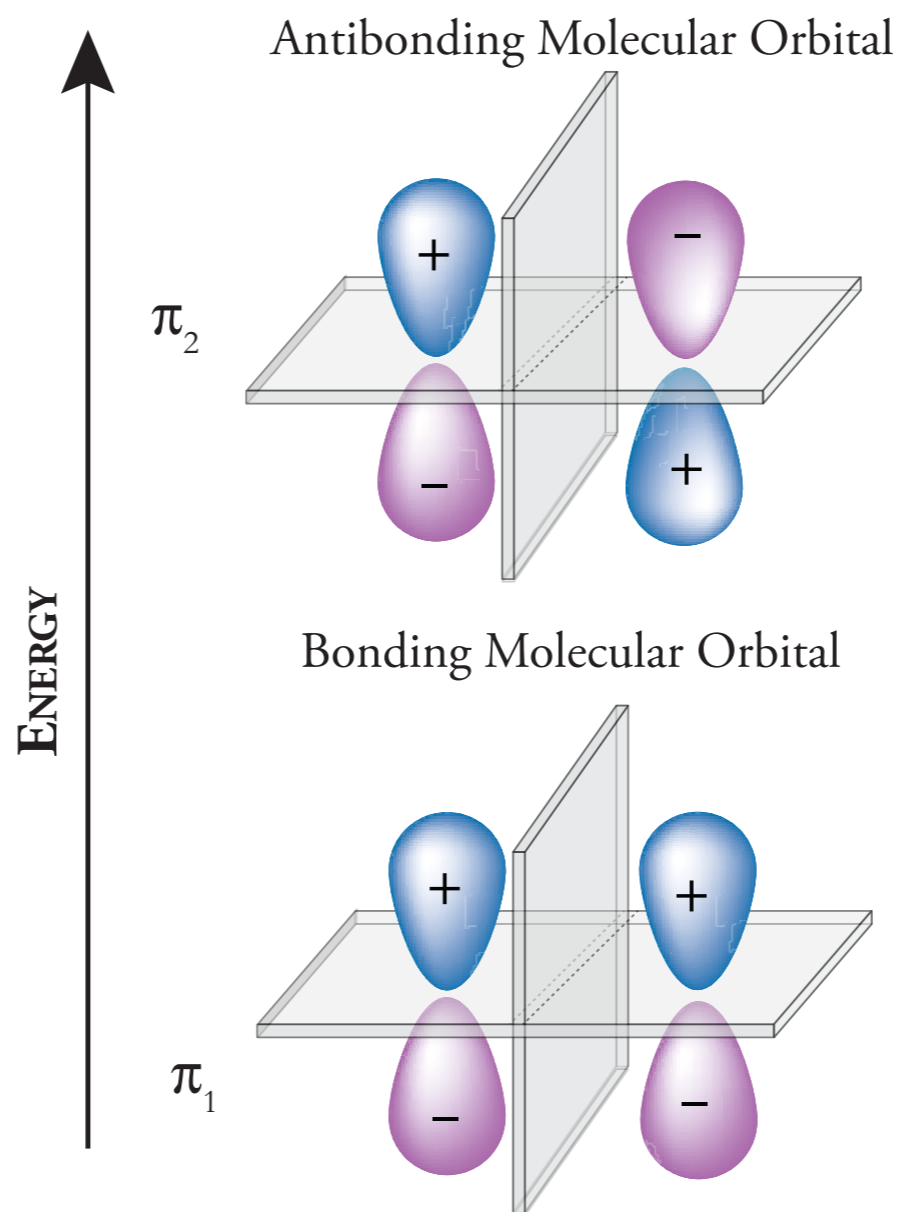


Figure 11.5 (a) Molecular Orbitals of 1,3-Butadiene

The unequal sizes of the 2p atomic orbitals from which the π MOs are made show the degree to which they contribute to the molecular orbital. A bonding interaction results from constructive overlap of 2p orbitals of the same sign. Nodal planes are shown between carbon atoms as vertical lines; this is where destructive overlap occurs. The energy of the orbitals increases as the number of nodal planes increases. The sign of the orbital inverts going from one side of a nodal plane to the other. Note that π_2 is the highest occupied MO (HOMO) and that π_3 is the lowest unoccupied MO (LUMO).

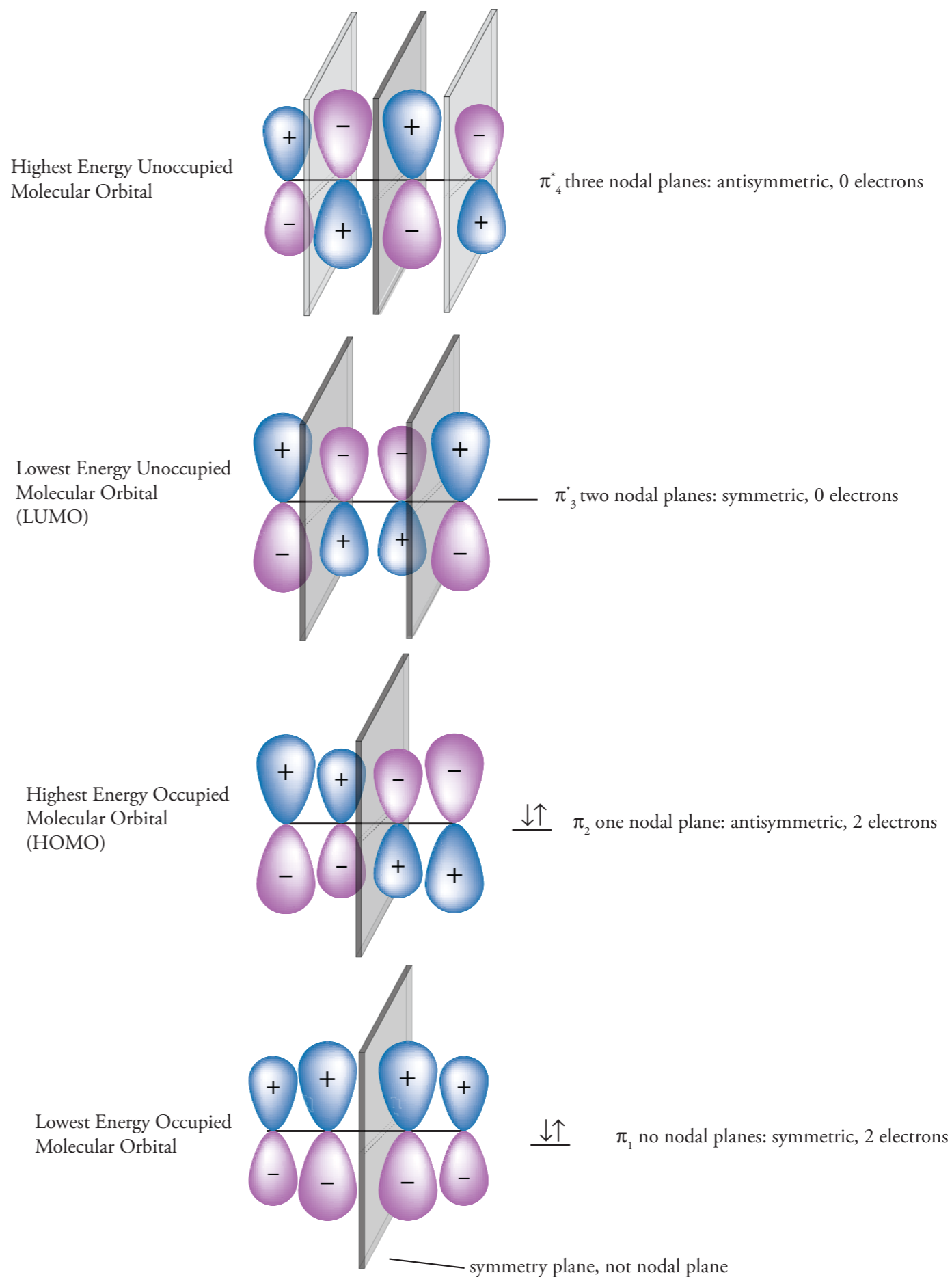


Figure 11.5 (b) Electron Densities of the Molecular Orbitals of 1,3-Butadiene

The π_1 molecular orbital contains two electrons. It has the lowest energy because it has no vertical nodal planes. Substantial double bond character exists between C-2 and C-3 atoms, a feature not represented by the Lewis structure of the major resonance contributor of butadiene. The π_2 molecular orbital, which has higher energy, also contains two electrons. π_2 is the highest energy occupied molecular orbital, HOMO. It is antisymmetric with respect to a nodal vertical plane between C-2 and C-3. Bonding interactions occur both between C-1 and C-2 and between C-3 and C-4. The antibonding π_3 and π_4 molecular orbitals have more vertical nodal planes, and have higher energy than the bonding molecular orbitals. The π_3 molecular orbital contains two antibonding interactions and one bonding interaction. π_3 is the lowest energy unoccupied molecular orbital, LUMO. The π_4 molecular orbital has three nodal planes, and no bonding interactions.

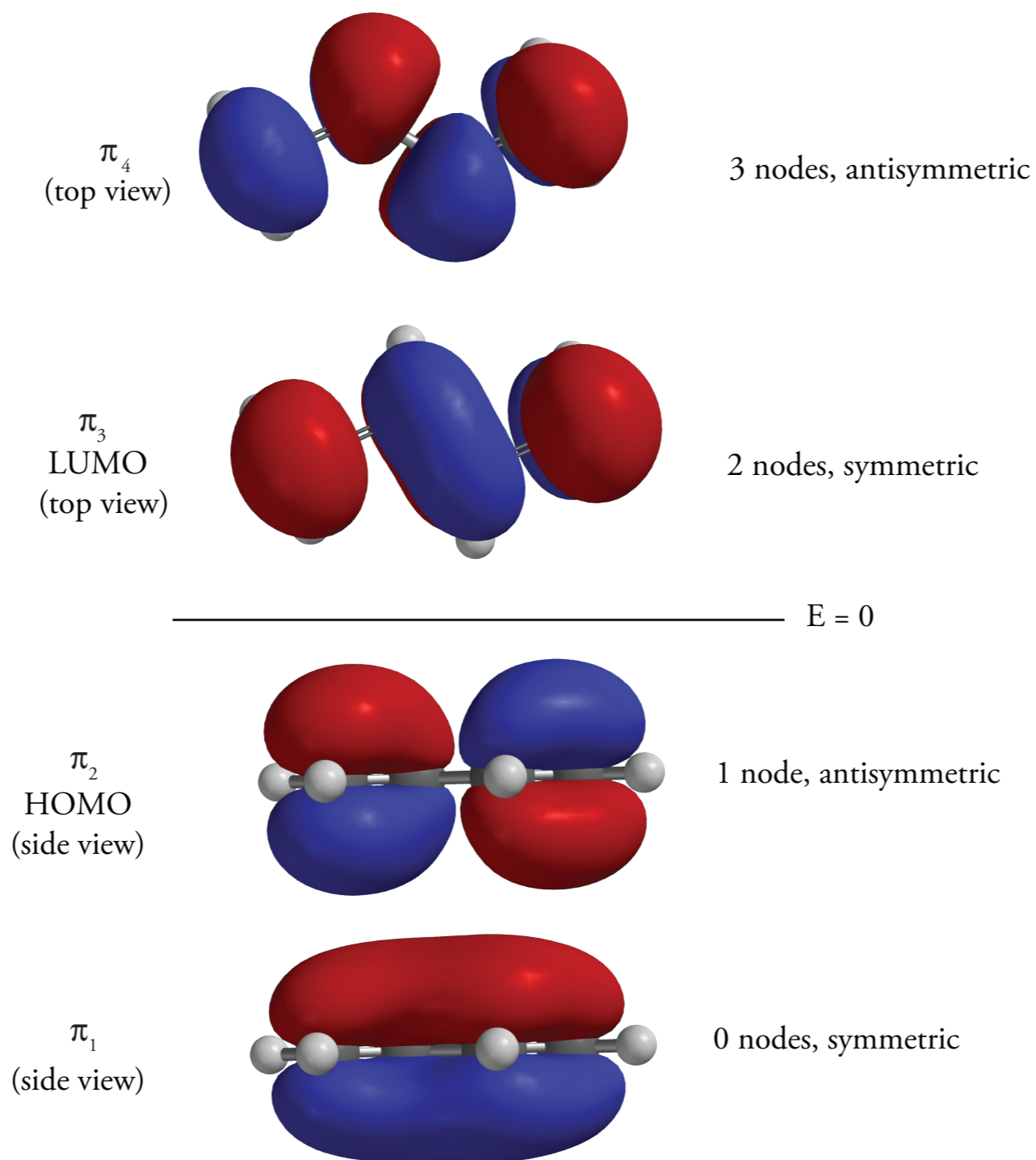
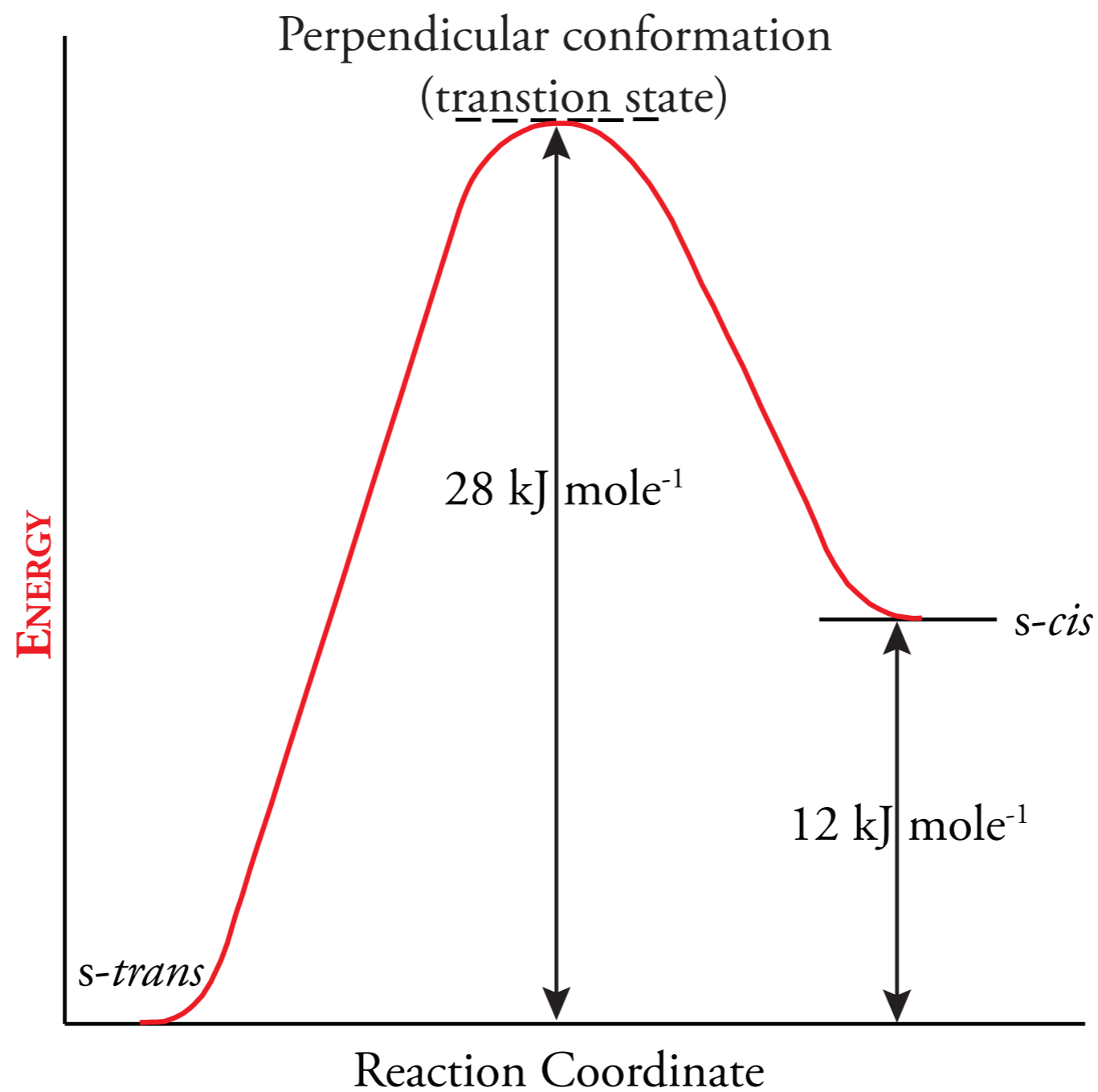


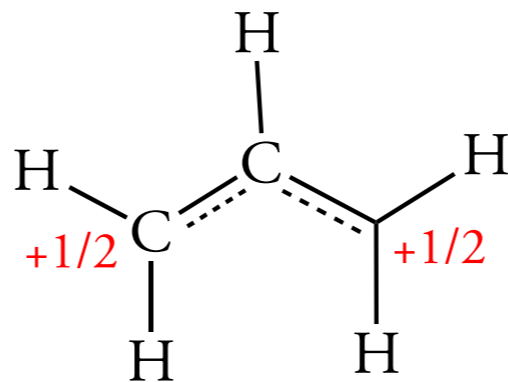
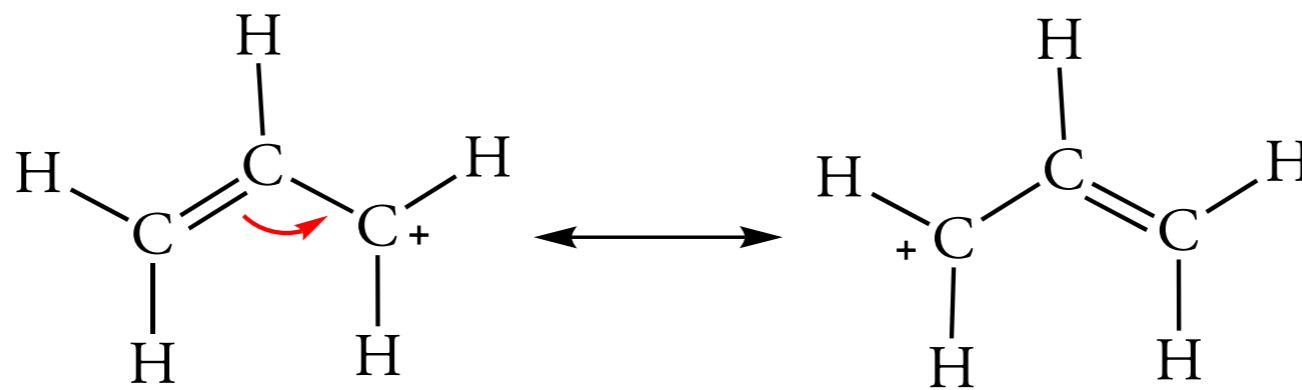
Figure 11.6 Interconversion of *s-trans* and *s-cis* 1,3-Butadiene

Rotation around the C-2 to C-3 bond interconverts the *s-trans* and *s-cis* conformational isomers. The *s-trans* conformation has all 2p orbitals aligned parallel to one another to form a resonance-stabilized system. In the transition state for rotation, the π bonds are perpendicular to each other. As a result they cannot interact, and their resonance stabilization is lost. The *s-cis* isomer is also planar, but it has a higher energy because of an unfavorable steric interaction between the hydrogens at C-1 and C-4.

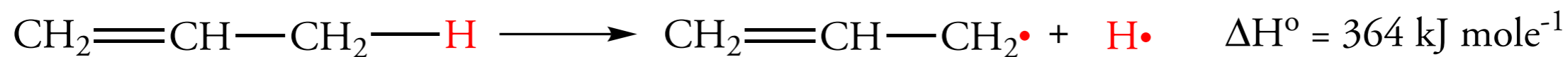
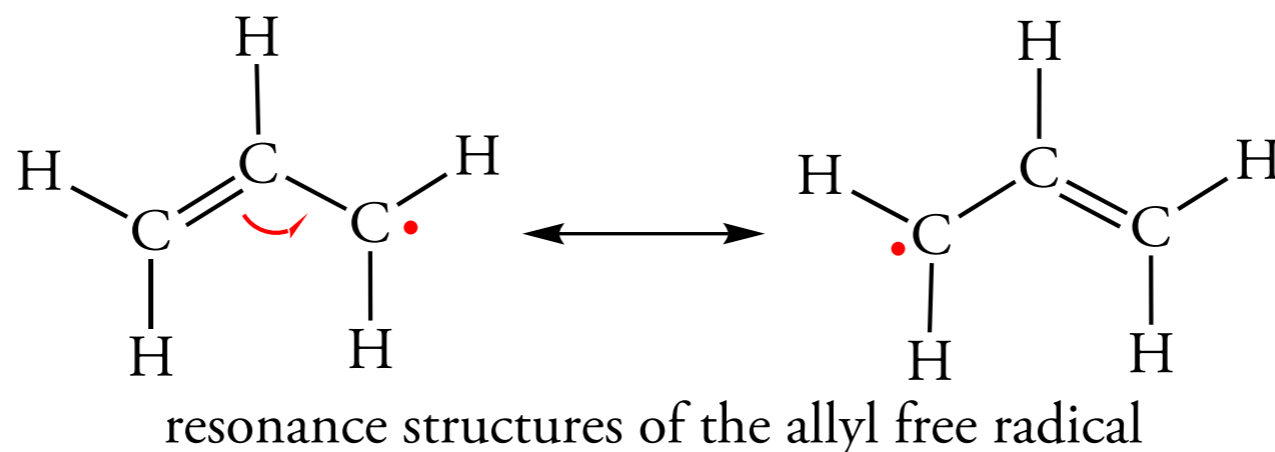


12.5 ALLYLIC SYSTEMS

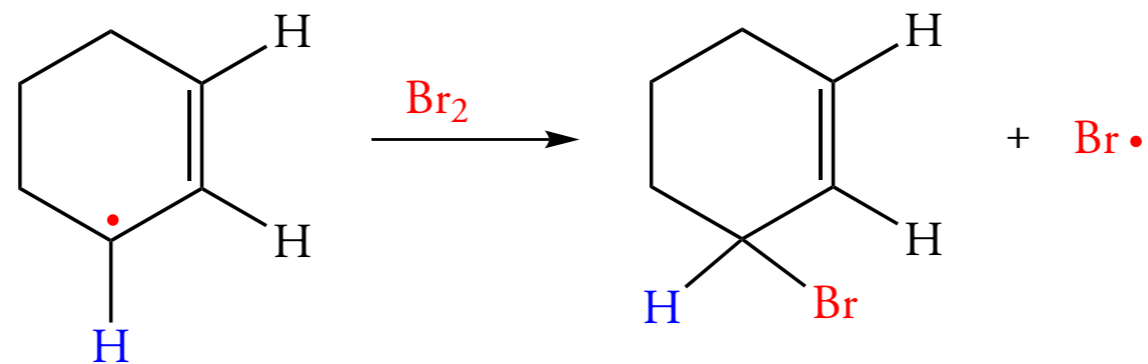
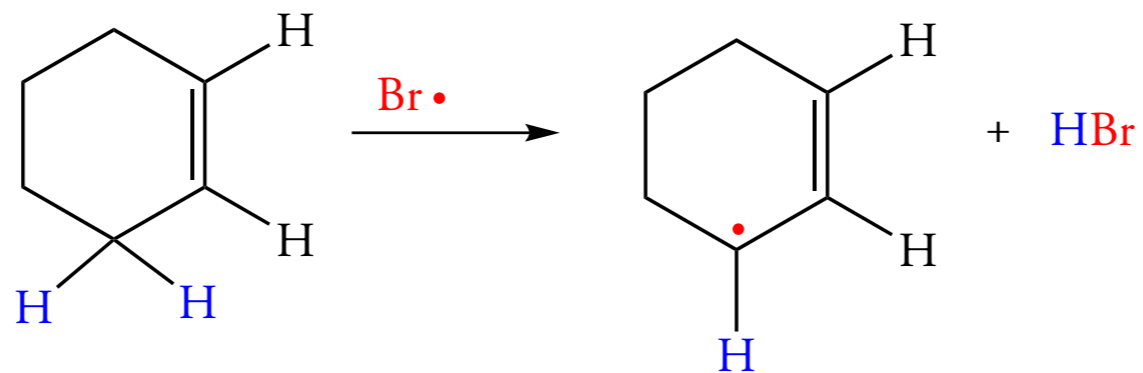
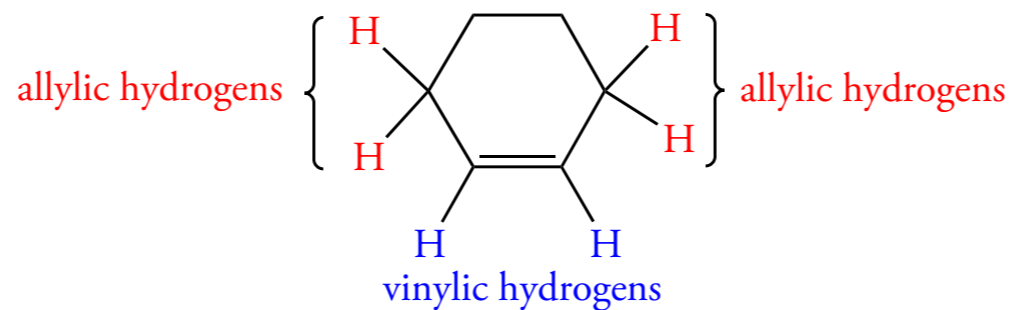
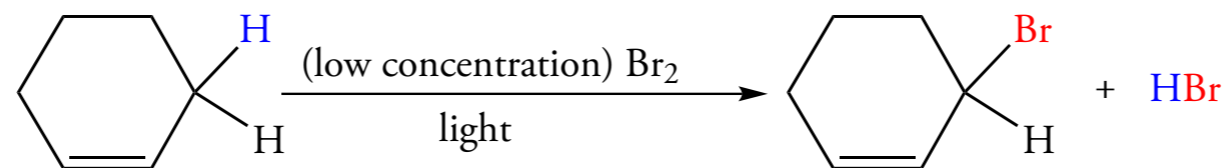
Allylic Carbocations



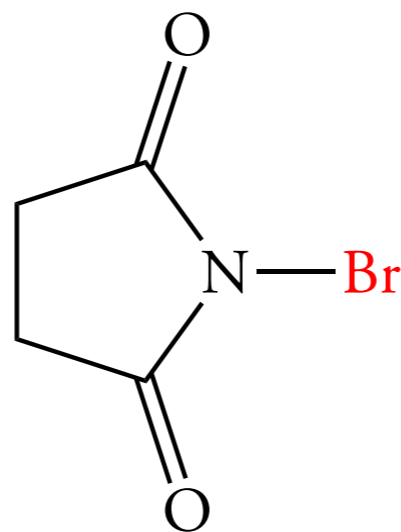
Allylic Free Radicals



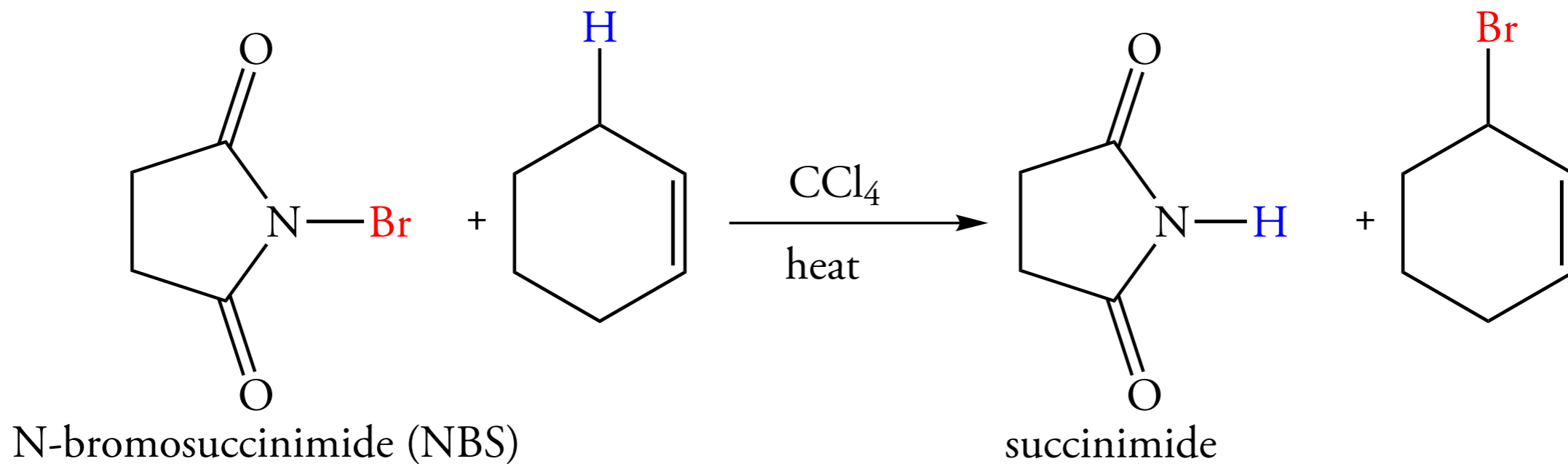
Free Radical Reactions at Allylic Centers



Free Radical Reactions at Allylic Centers Catalyzed by N-Bromosuccinimide (NBS)

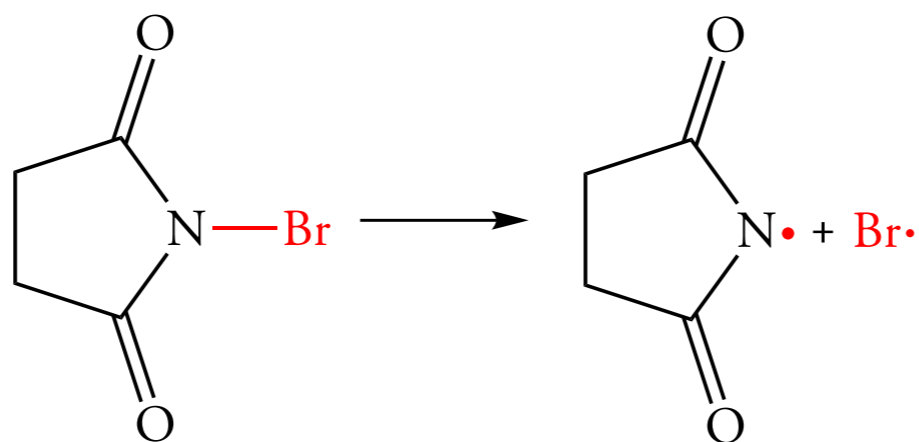


N-bromosuccinimide (NBS)

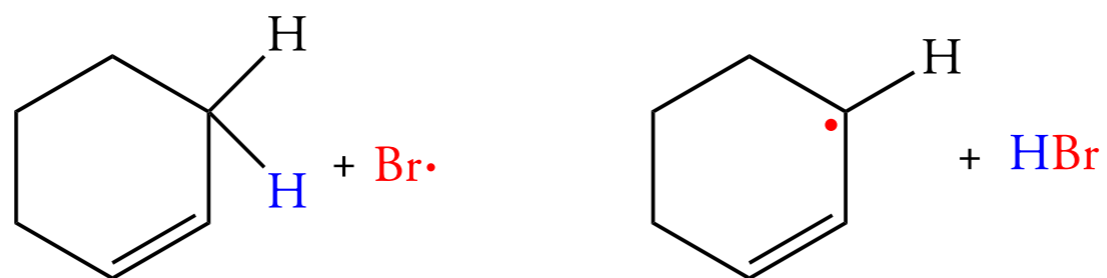


Mechanism of Reaction Catalyzed by (NBS)

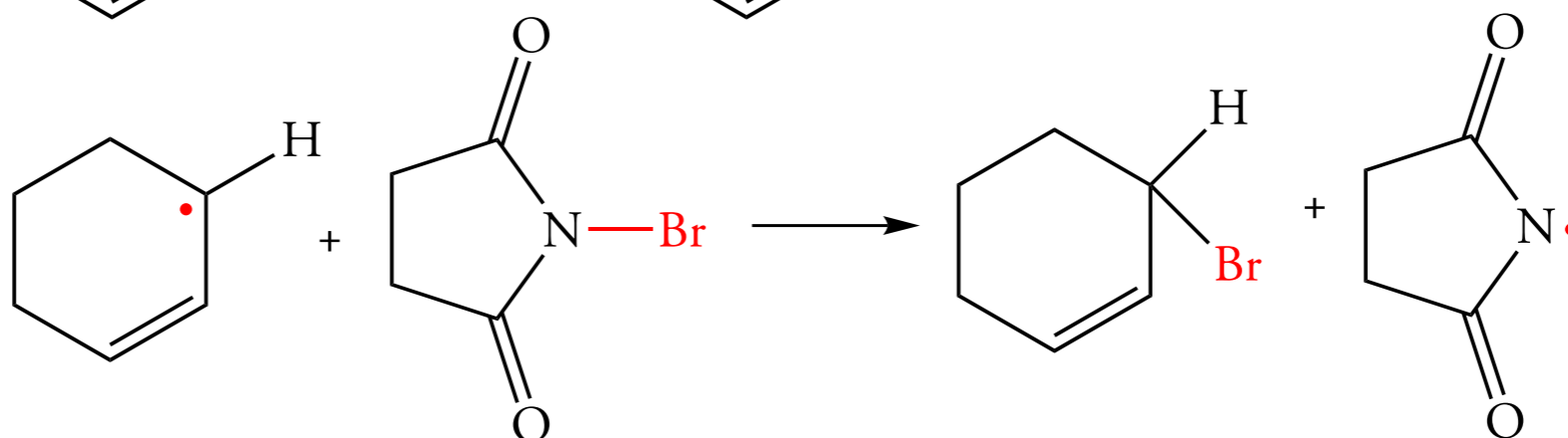
Step 1.
initiation



Step 2.
propagation



Step 3.
propagation



11.6 HÜCKEL MOLECULAR ORBITALS OF ALLYL SYSTEMS

Figure 11.7 Hückle Molecular Orbitals of Allyl Systems

The sizes of the 2p atomic orbitals represent the degree to which the orbitals contribute to the molecular orbitals in the allyl system. The constructive overlap of all three 2p orbitals in the lowest energy molecular orbital is bonding over the whole system. The nonbonding molecular orbital has a nodal plane at the center carbon atom. The electron configuration of the allyl radical is shown

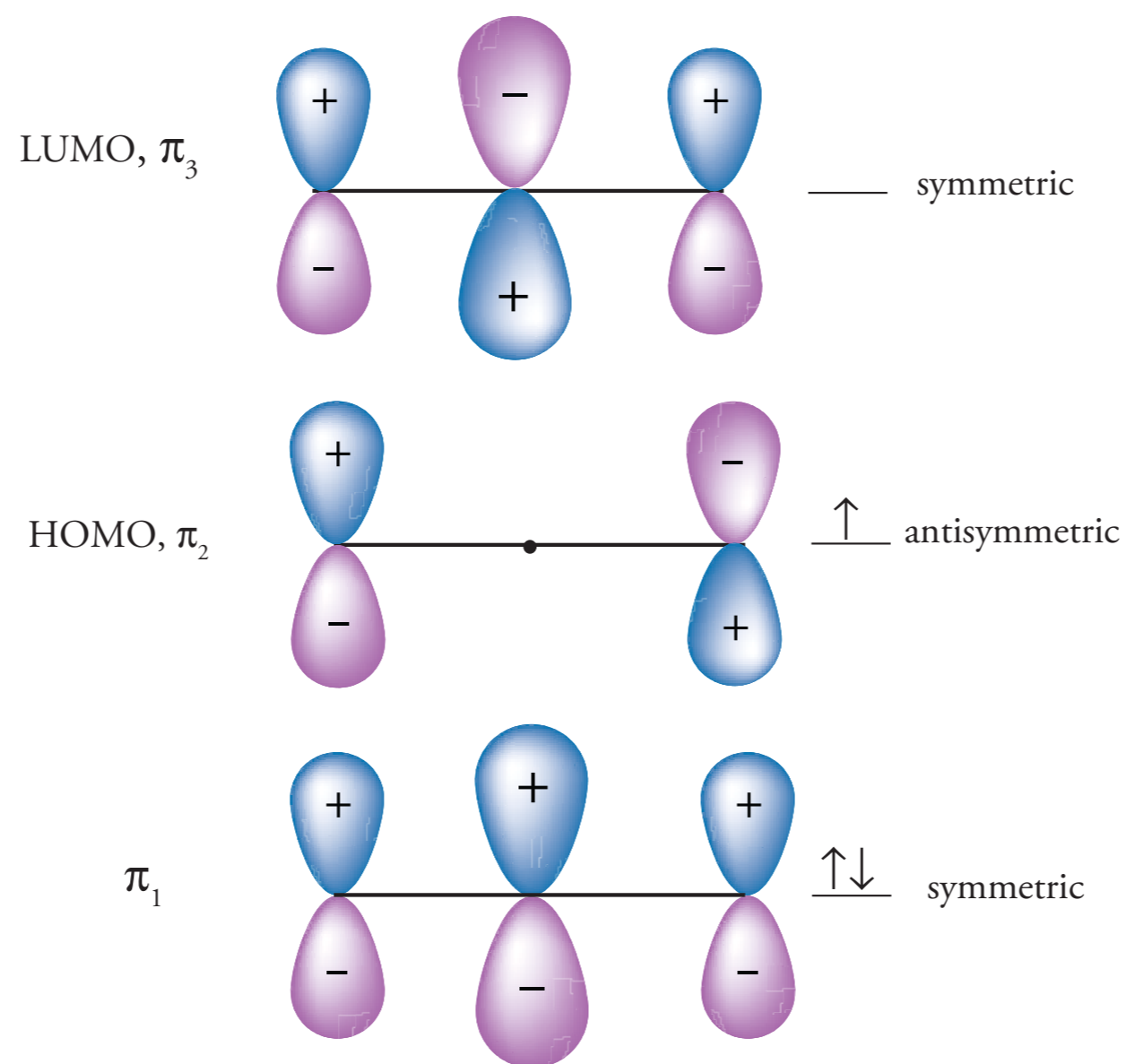


Figure 11.7b Molecular Orbitals of Allyl Carbocation

The three molecular orbitals in the allyl carbocation. The bonding orbital, π_1 , contains two electrons and the nonbonding orbital, π_2 , is empty. The antibonding orbital, π_3 , is also empty.

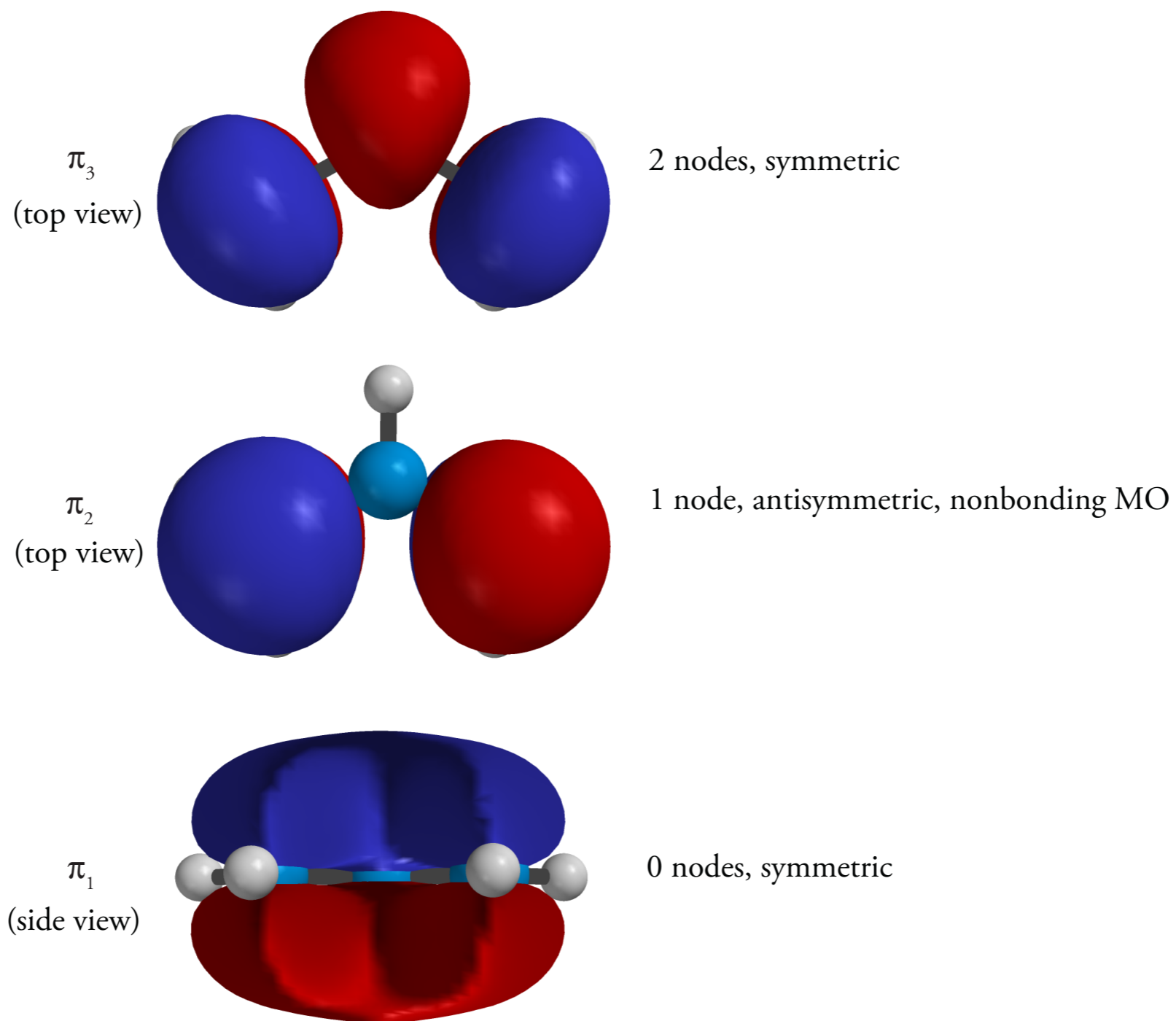
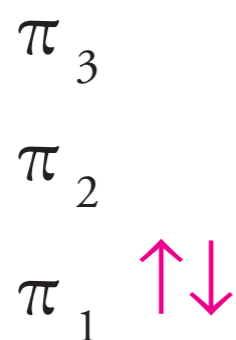


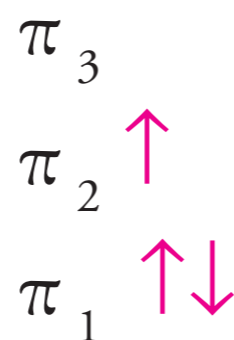
Figure 11. 8 Electron Configurations of Allyl Systems

The electrons of the π system occupy the lowest available orbitals.

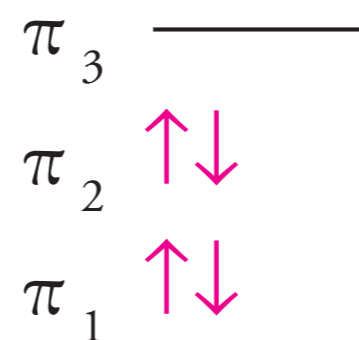
Allyl Cation
(2 π electrons)



Allyl Radical
(3 π electrons)



Allyl Carbanion
(4 π electrons)



11.7 ELECTROPHILIC ADDITION TO CONJUGATED DIENES

1,2- and 1,4-Electrophilic Addition Reactions

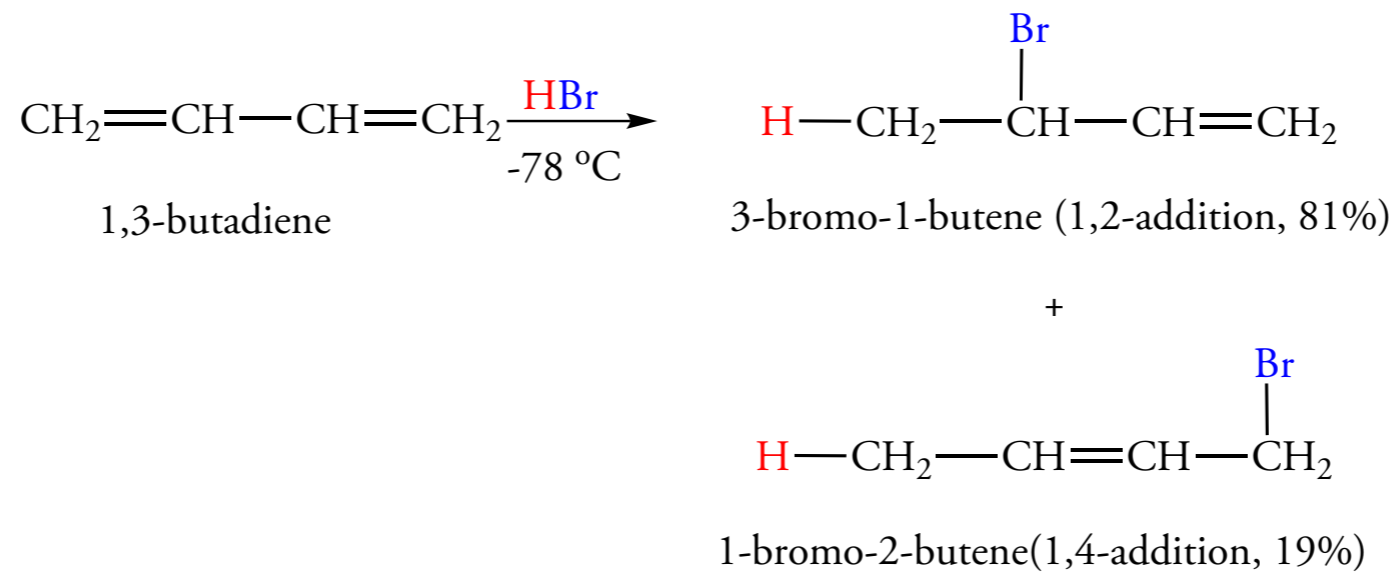
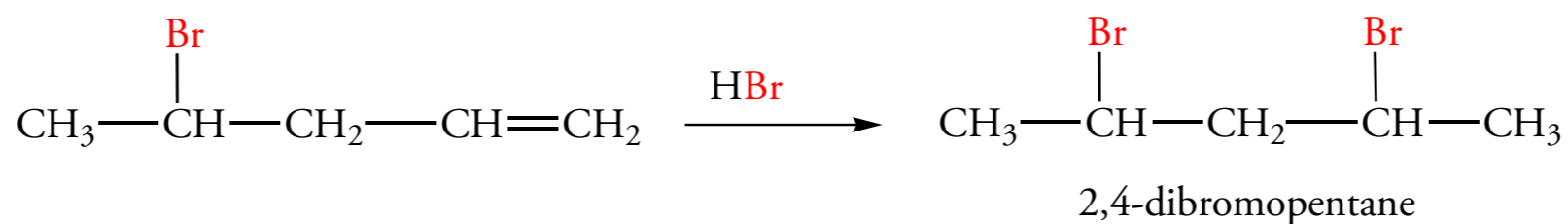
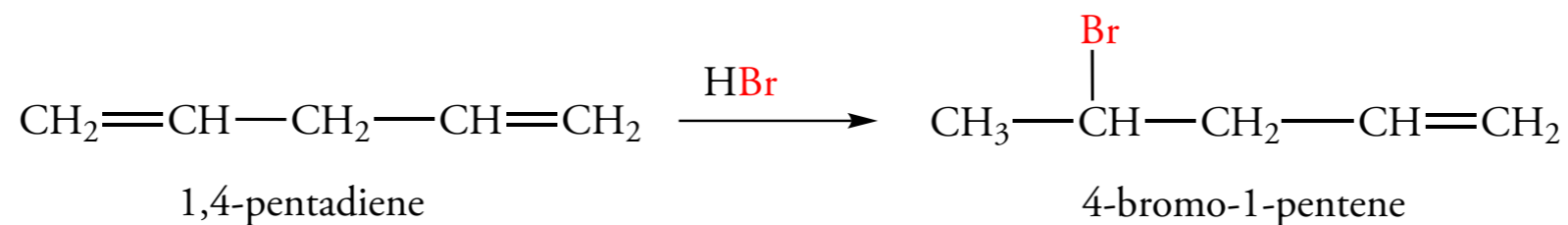
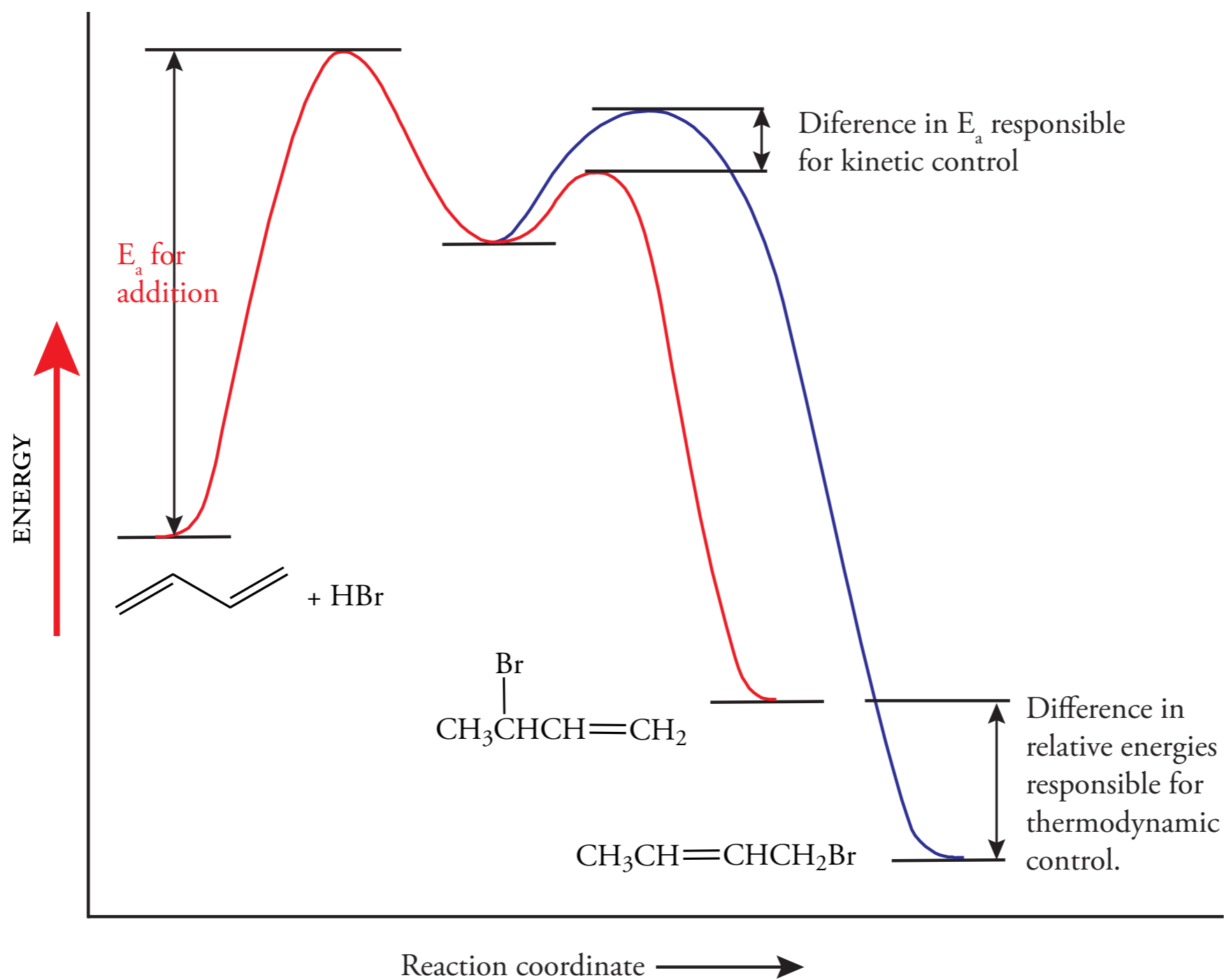
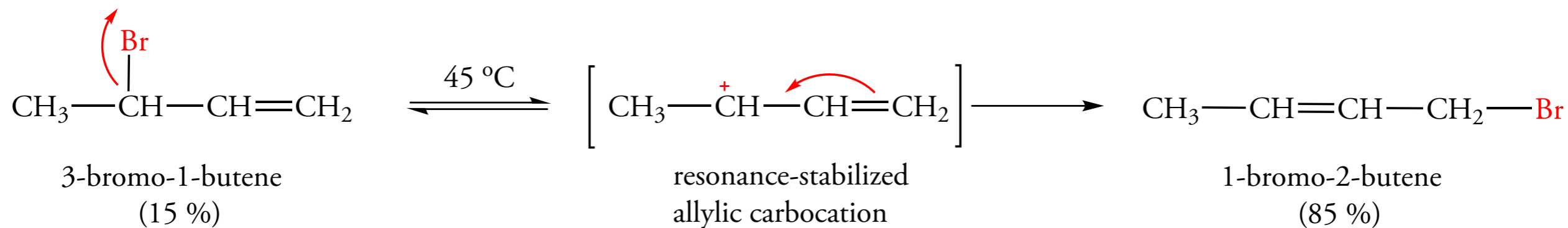
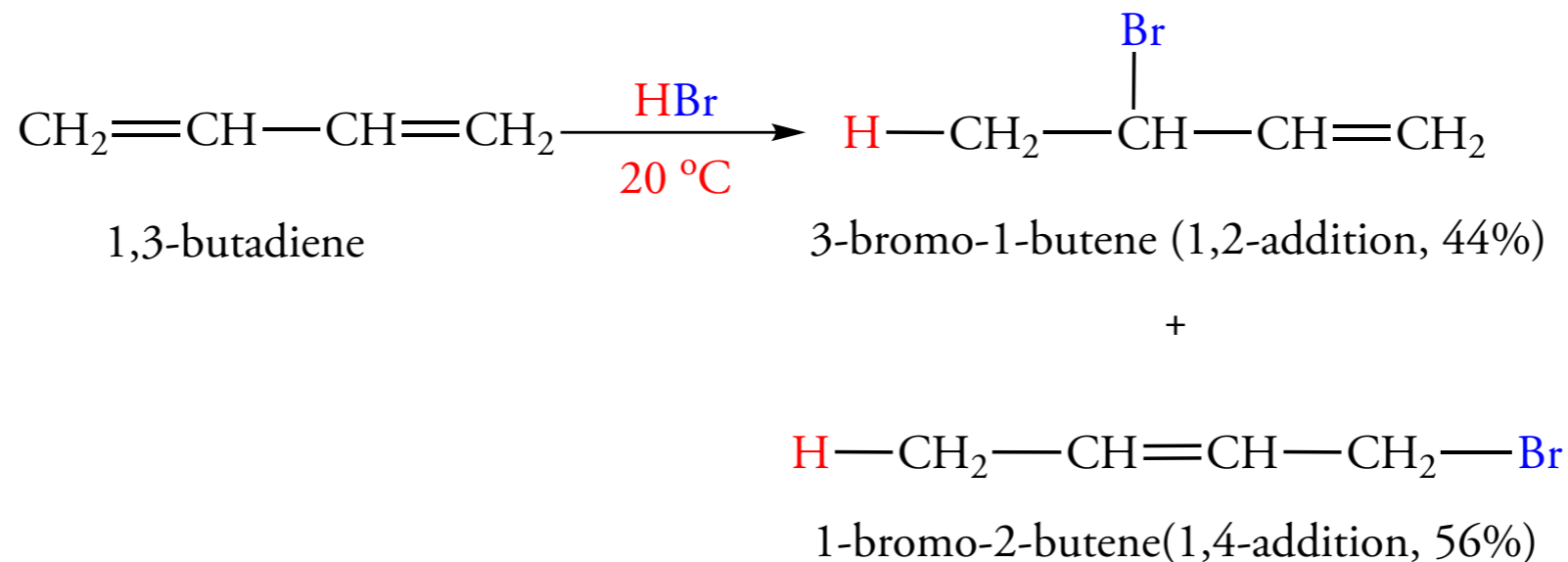


Figure 11.9 Energy Profile for 1,2- and 1,4-Electrophilic Addition Reactions

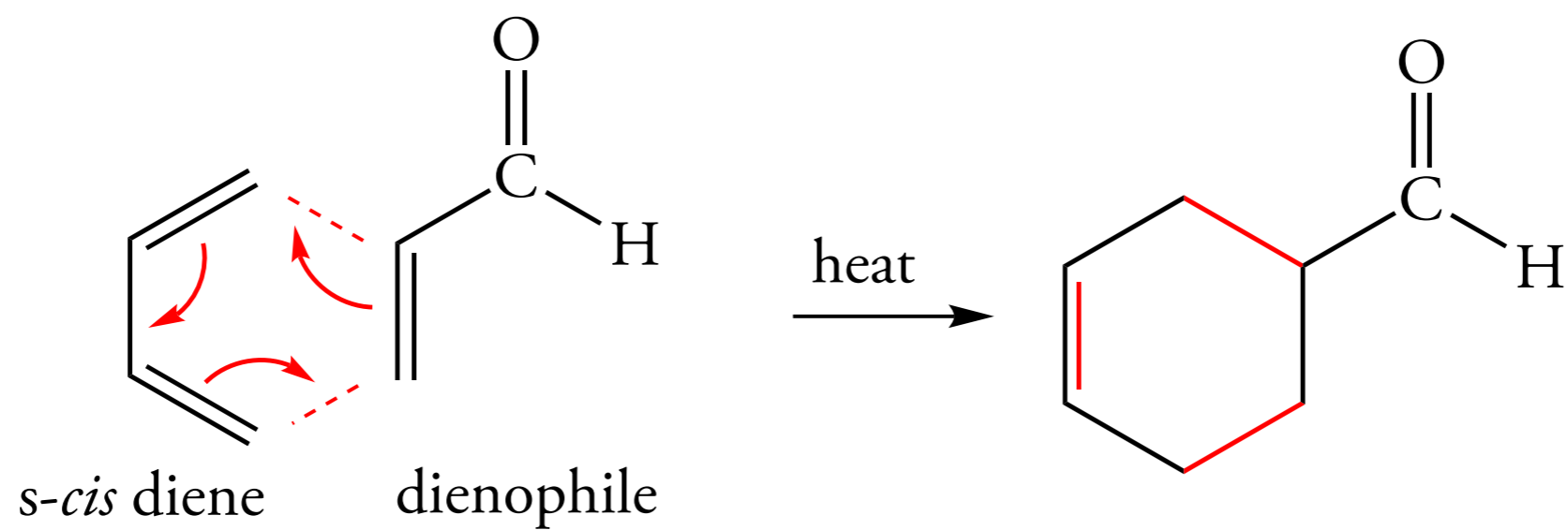
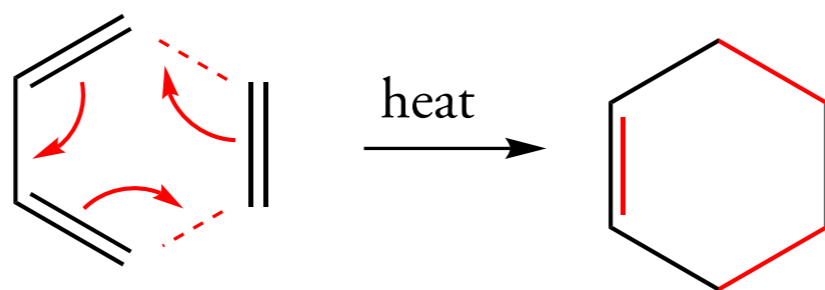
The energy of the transition state for 1,2-addition of HBr to 1,3-butadiene is lower than the energy of the transition state for 1,4-addition. 1,2-Addition predominates at low temperature because there is not enough energy for the system to reach the transition state for 1,4-addition. This energy difference is responsible for kinetic control of the addition reaction. The 1,4-addition product is more stable than the 1,2-addition product, but it forms more slowly. At higher temperatures, the transition state leading to the more stable product can be attained, and leads to 1,4 addition. Thus, at high temperatures the product composition reflects the relative stabilities of the products, not the relative energies of the transition states leading to them.



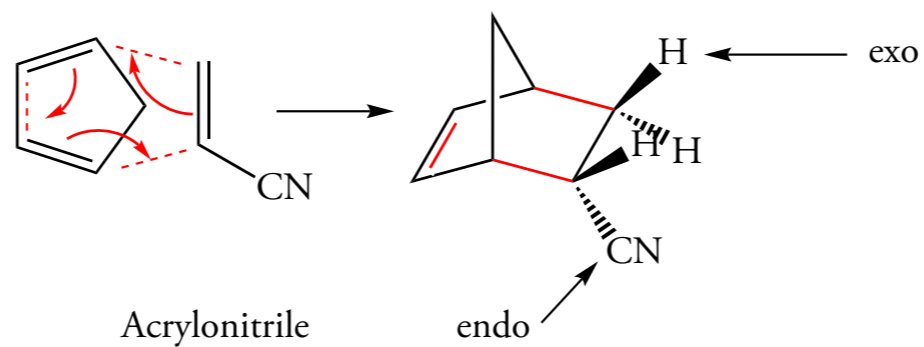
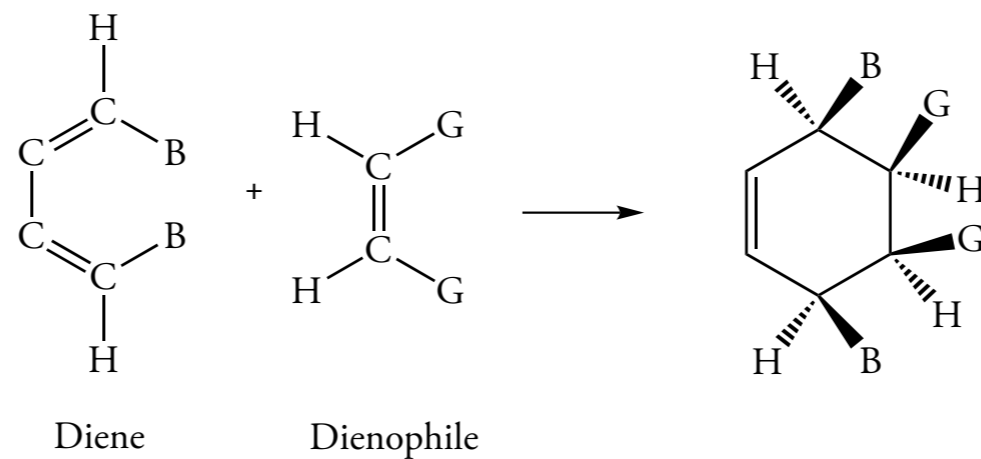
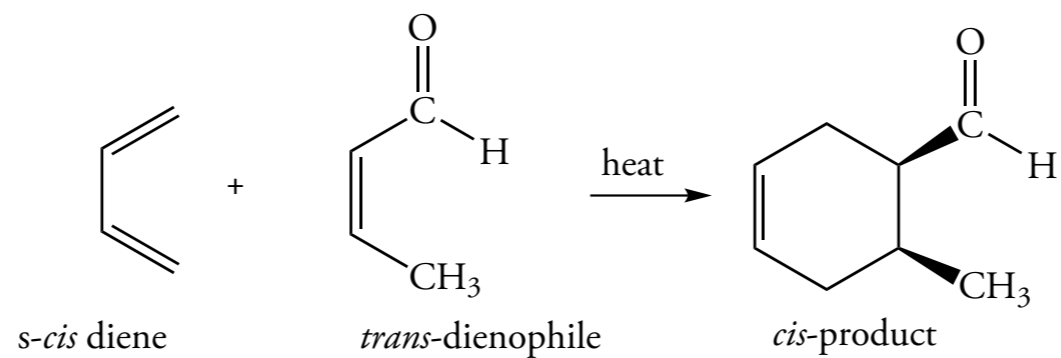
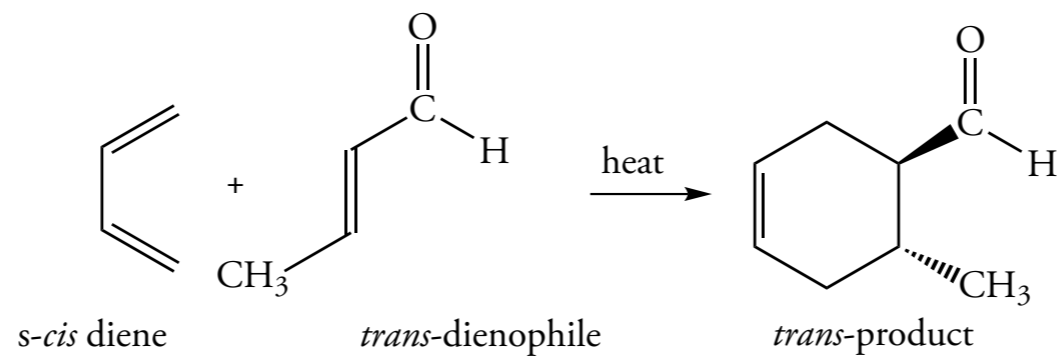
Kinetic Control vs Thermodynamic Control of 1,2- and 1,4-Electrophilic Addition Reactions



11.8 THE DIELS-ALDER REACTION



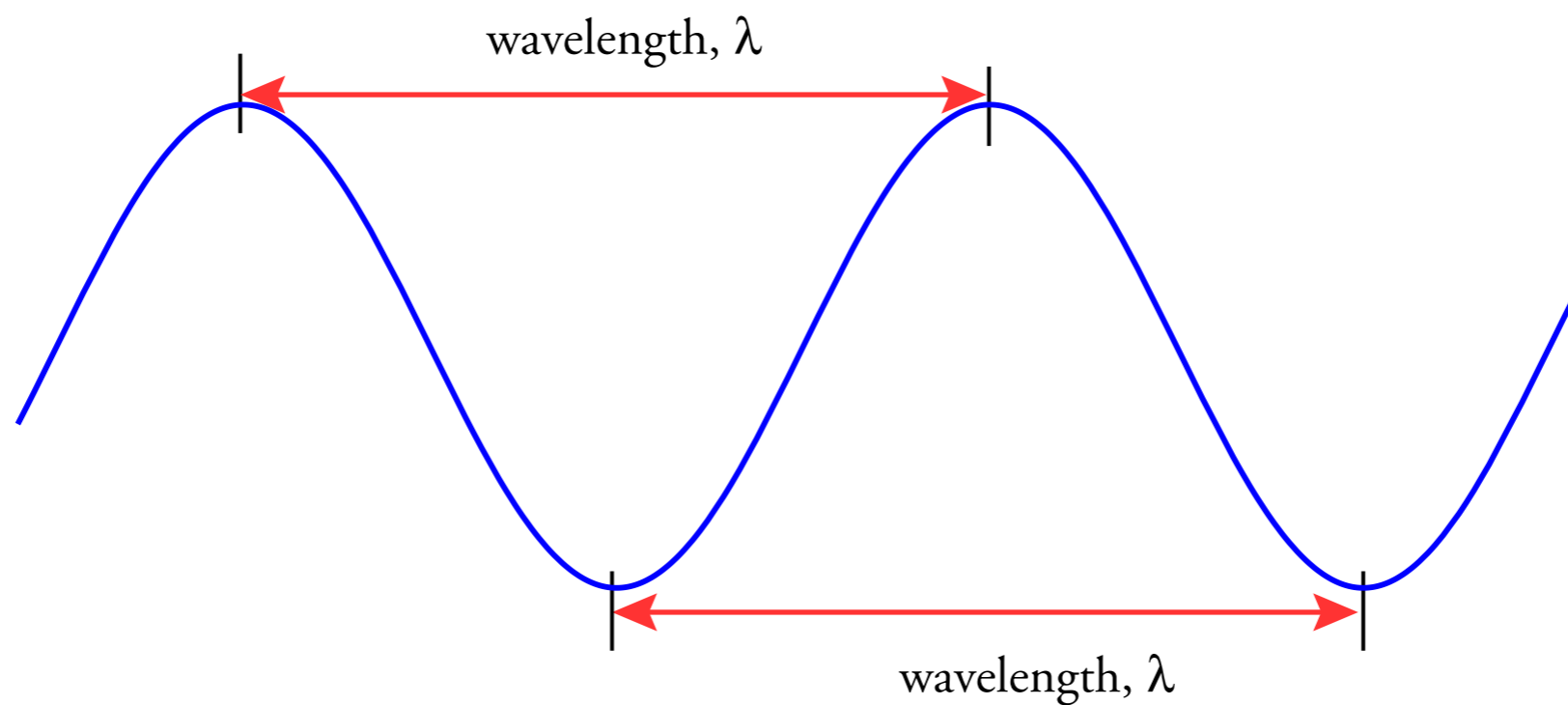
11.8 THE DIELS-ALDER REACTION, II



11.9 THE ELECTROMAGNETIC SPECTRUM

Figure 11.10 Electromagnetic Radiation

The wavelength, λ , of electromagnetic radiation is the distance between any two peaks or troughs of the wave.



$$E = h\nu \quad E = \frac{hc}{\lambda} \quad E = hc\left(\frac{1}{\lambda}\right)$$

11.9 THE ELECTROMAGNETIC SPECTRUM, II

Figure 11.11 Electromagnetic Spectrum

The regions of the spectrum used in organic chemistry. Usually the wavelength or the reciprocal of the wavelength, the wavenumber, is used to identify absorptions of organic molecules. The visible spectrum is only a tiny sliver of the entire electromagnetic spectrum.

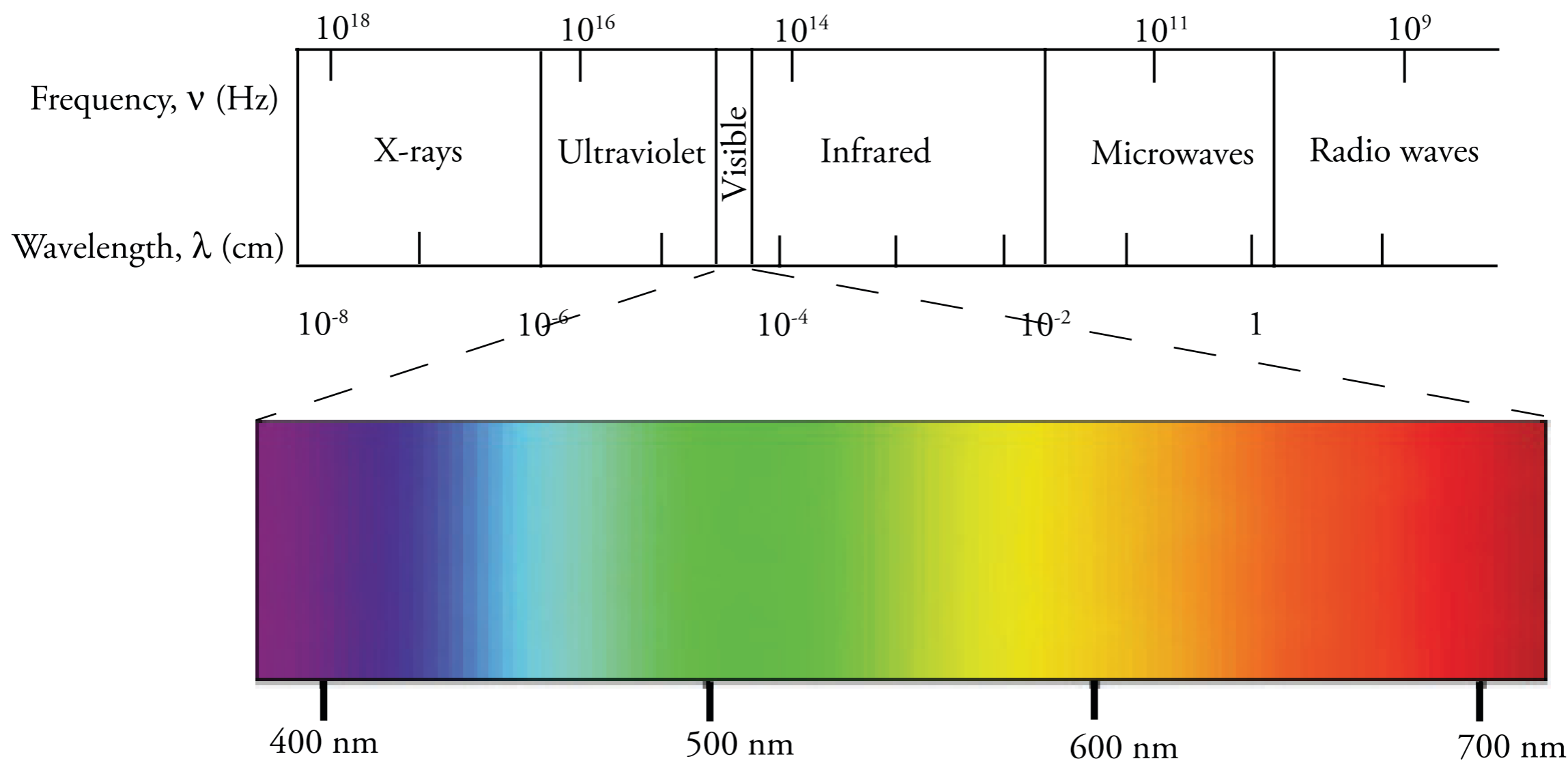
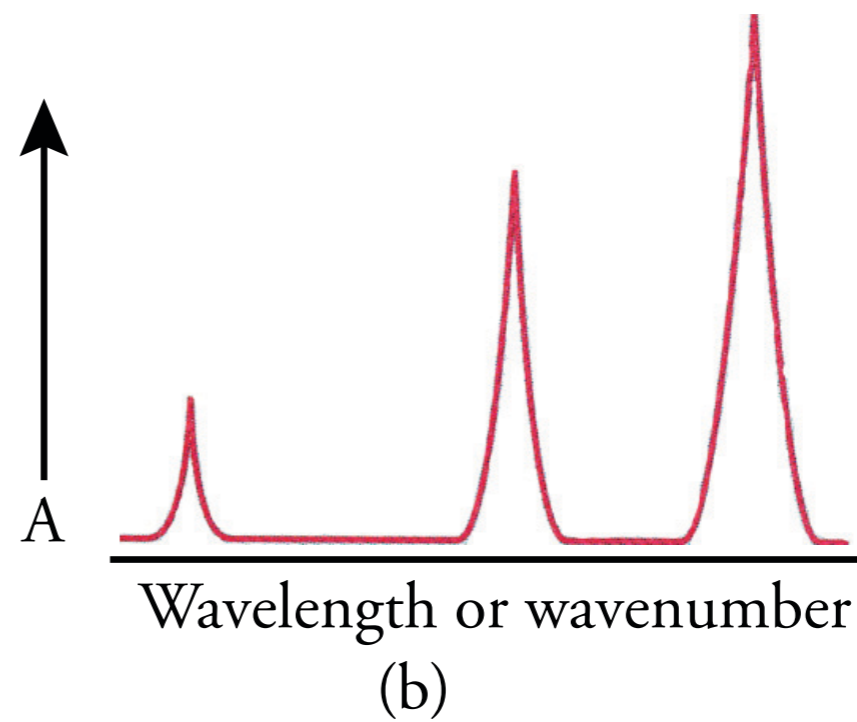
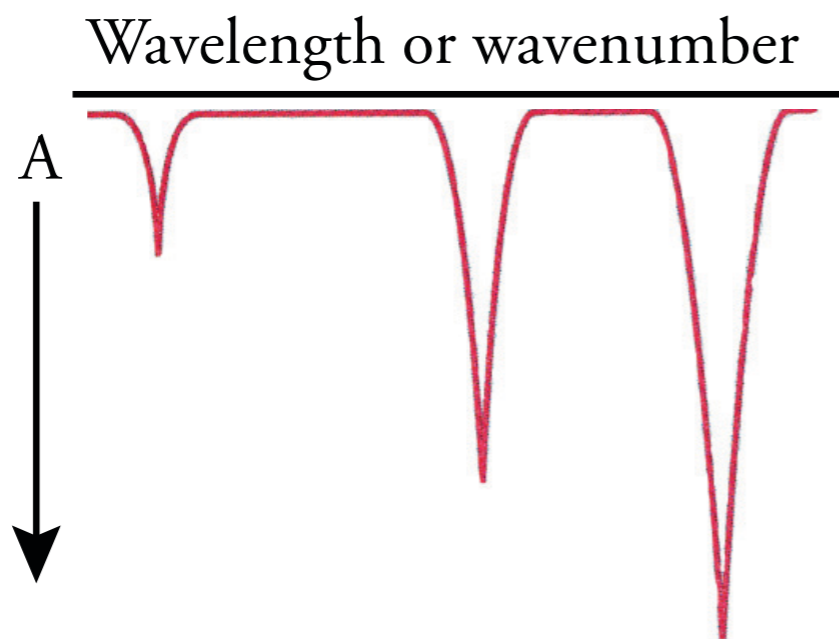


Figure 11.12 Features of a Spectrum

The portion of the spectrum where no absorption occurs is the base line. This horizontal line may be located at the top or bottom of a graph. Absorption then is recorded as a peak down from the base line. In an infrared spectrum, (a), the base line is at top of the spectrum. In an NMR spectrum, (b), the base line is at the bottom of the spectrum.



11.10 ULTRAVIOLET-VISIBLE SPECTROSCOPY OF ALKENES AND CONJUGATED SYSTEMS

Figure 11.13 UV Spectrum of Isoprene

The ultraviolet spectrum of isoprene dissolved in methanol is representative of the spectra of conjugated dienes.

The position of maximum absorption, λ_{max} , occurs at 222 nm.

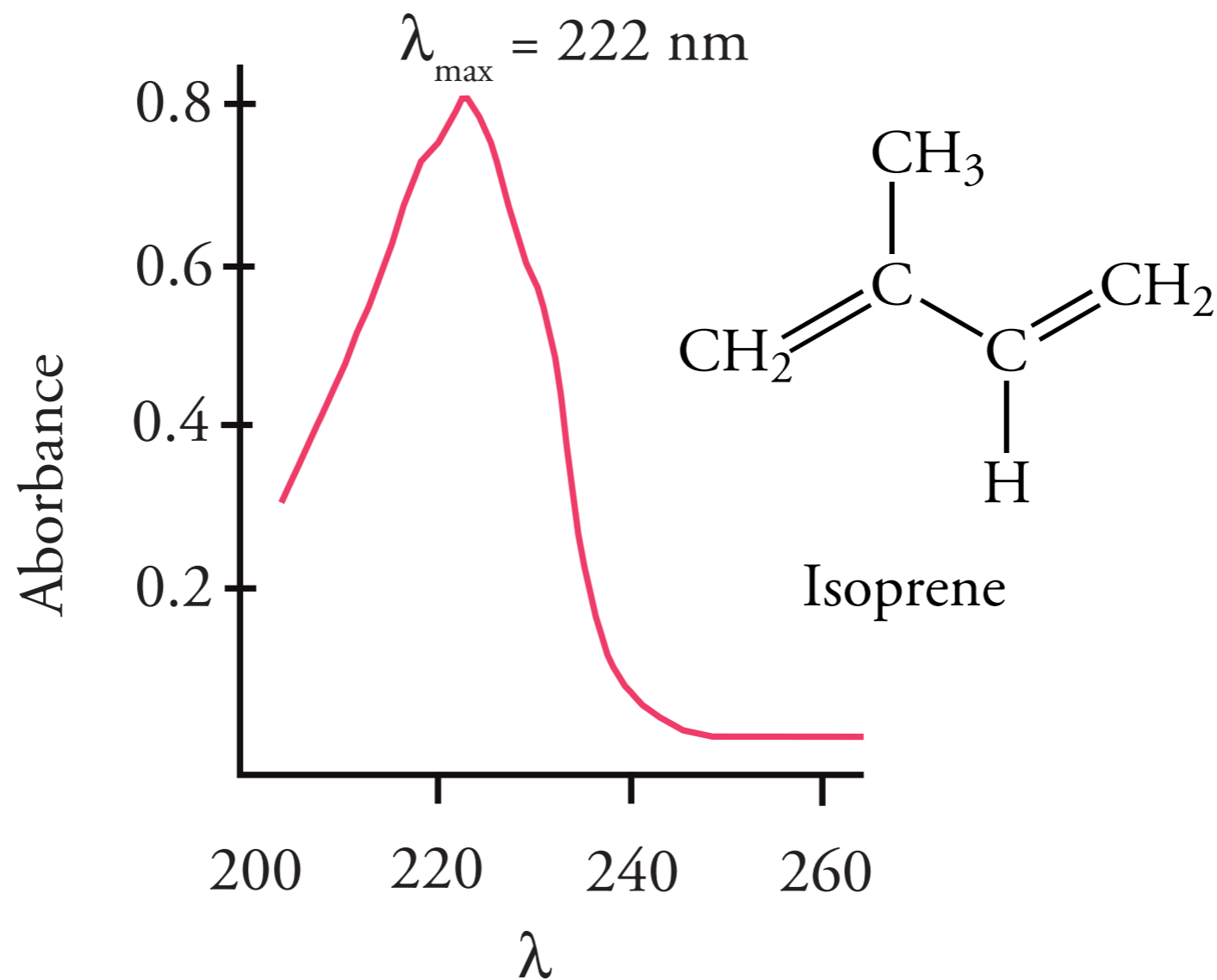


Figure 11.14 Molecular Orbitals and Electronic Transitions

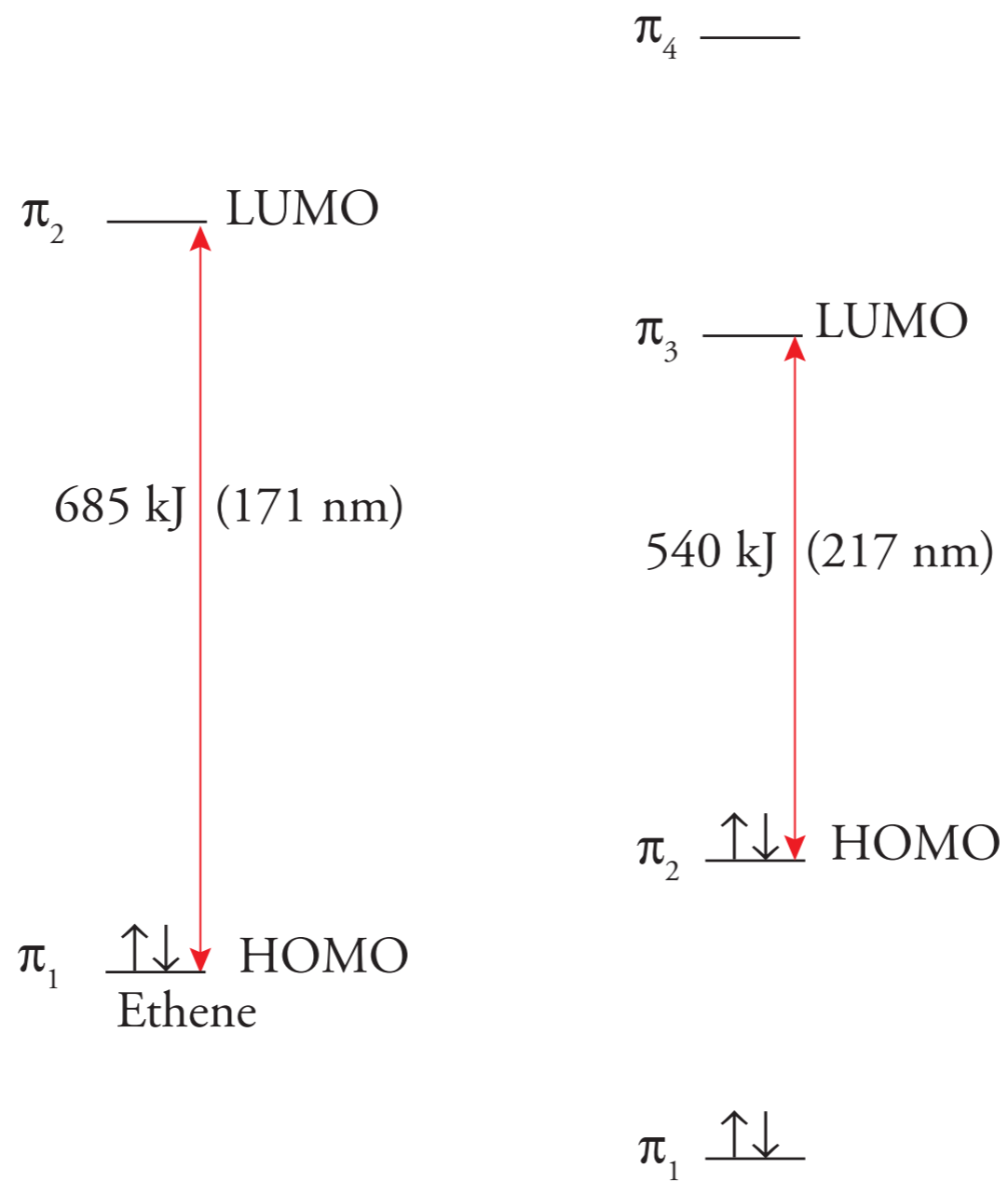


Figure 11.15 UV-Visible Spectrum of p-Nitrophenol

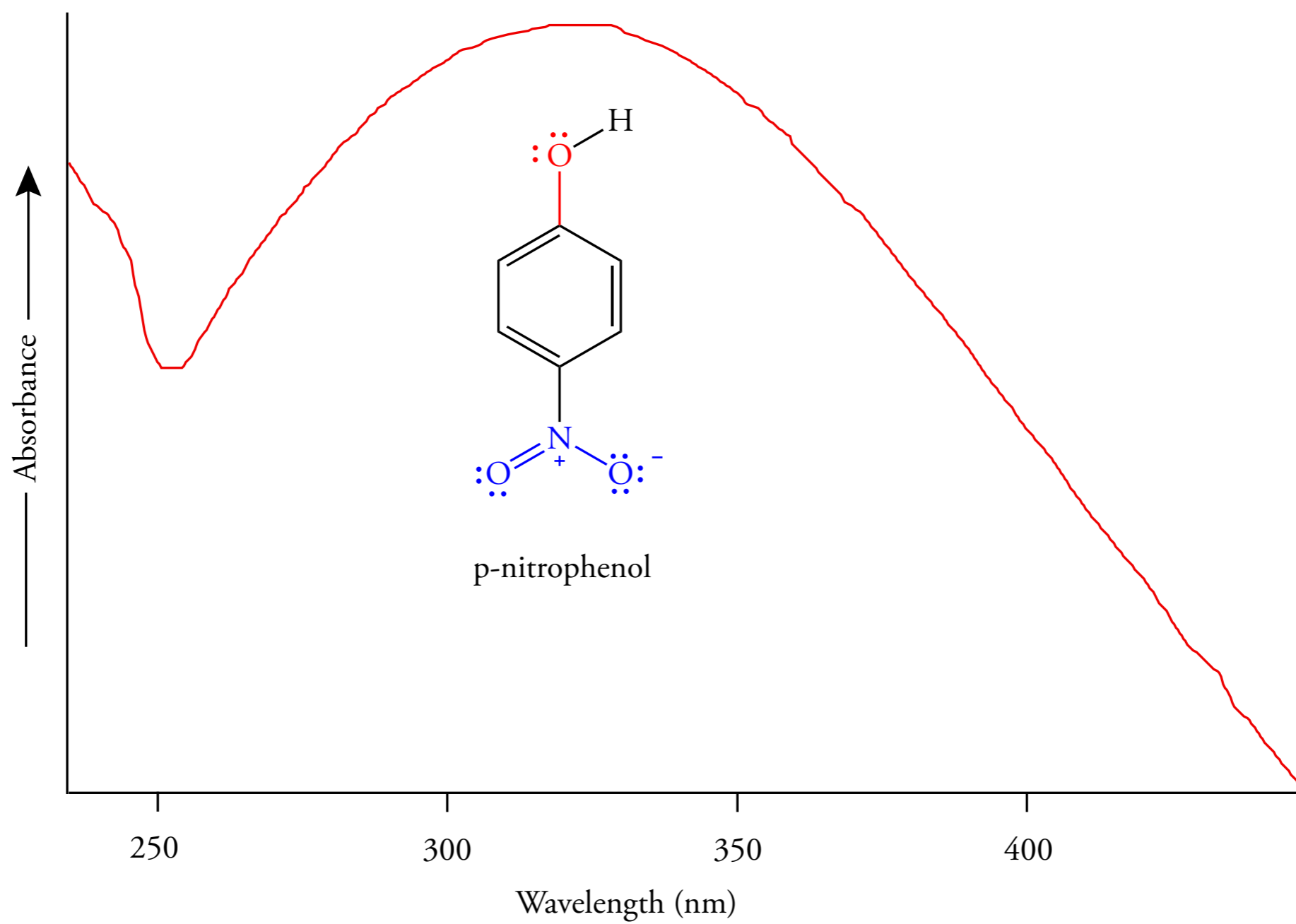
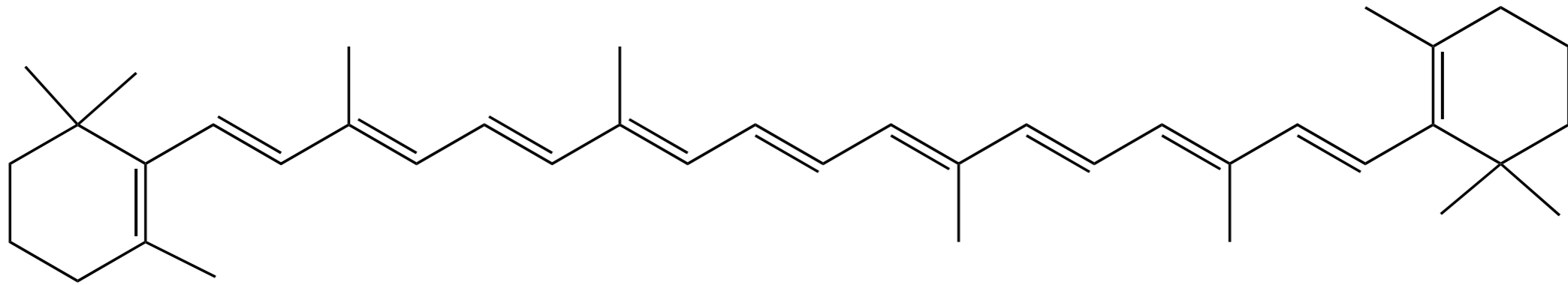


Figure 11.16 Visible Spectrum of β -Carotene



β -Carotene

