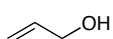
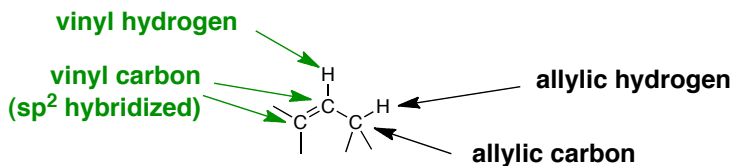


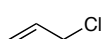
Chapter 10: Conjugation in Alkadienes and Allylic Systems

Conjugation: a series of overlapping p-orbitals

10.1: The Allyl Group - allylic position is the next to a double bond

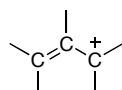


allyl alcohol



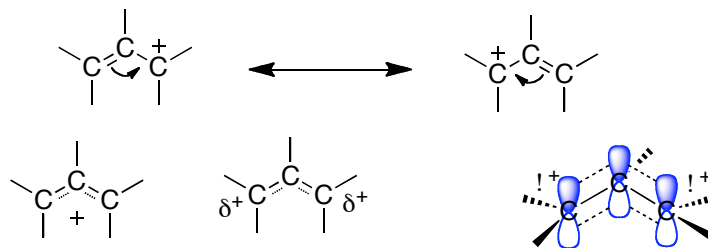
allyl chloride

10.2: Allylic Carbocations - carbocation with a vinyl group as a substituent (next to a double bond)



220

Allyl carbocations are stabilized by resonance



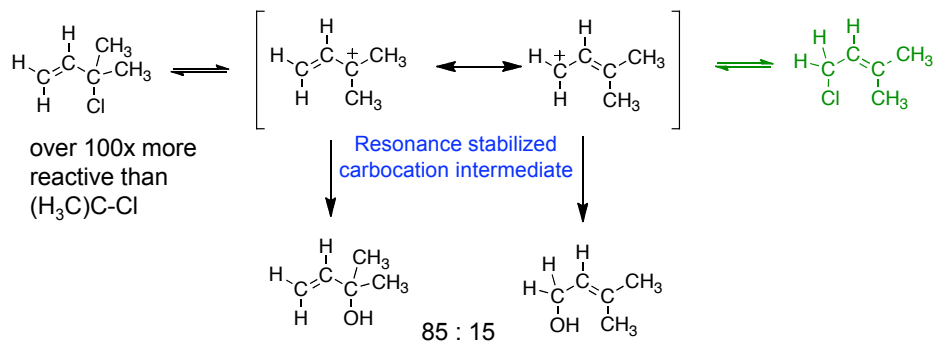
Recall from Chapter 1.8:

The atoms must remain fixed in all resonance forms. Resonance forms differ only by the placement of electrons

No one resonance form is entirely accurate. The actual structure is a hybrid of all the resonance forms. Resonance forms do not necessarily contribute equally to the resonance hybrid.

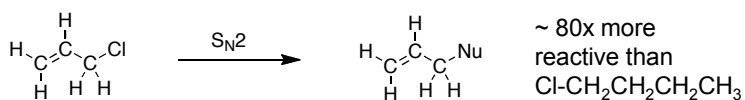
221

10.3: S_N1 Reactions of Allylic Halides - allylic halides and sulfonates are more reactive toward than simple alkyl halides toward nucleophilic substitution by the S_N1 mechanism



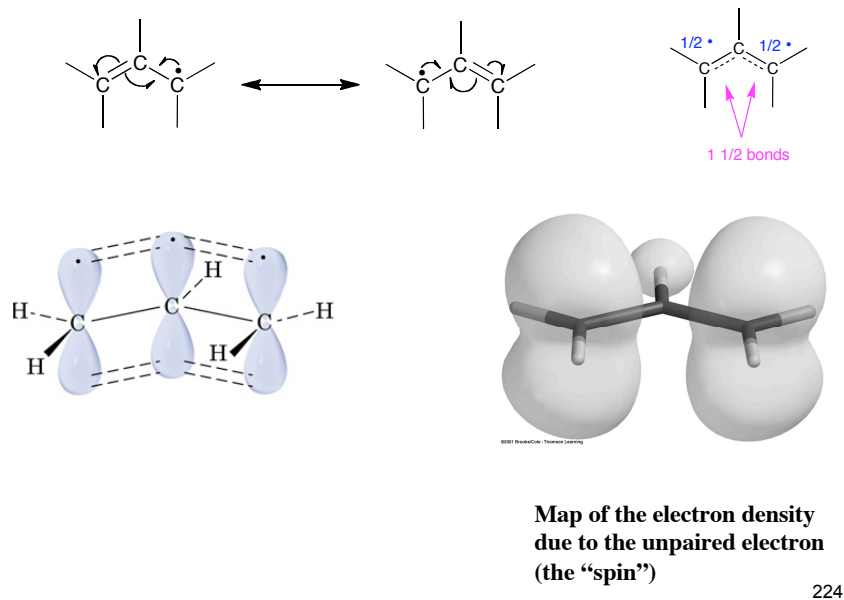
222

10.4: S_N2 Reactions of Allylic Halides - allylic halides and sulfonates are more reactive toward than simple alkyl halides toward nucleophilic substitution by the S_N2 mechanism

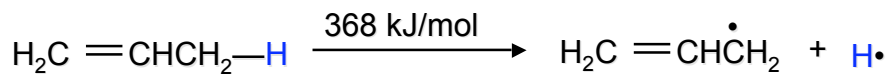
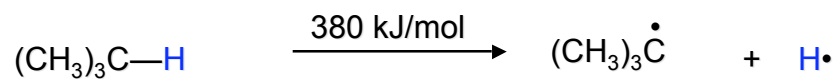
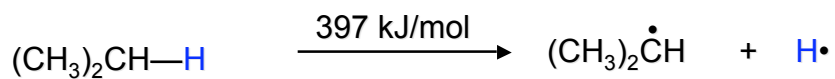
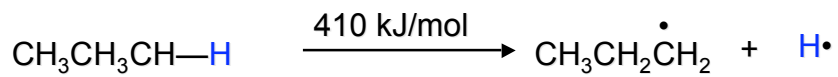


223

10.5: Allylic Free Radicals



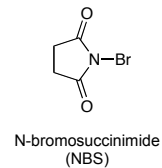
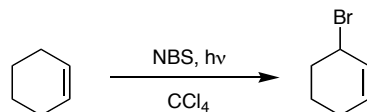
Free Radical Stabilities are Related to Bond-Dissociation Energies



C—H bond is weaker in propene because the resulting allyl radical is more stable than the alkyl radicals.

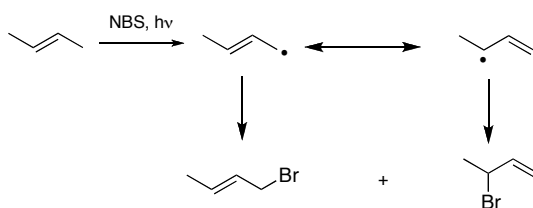
225

10.6: Allylic Halogenation - Allylic halogenation of an alkene takes place through a free radical mechanism.

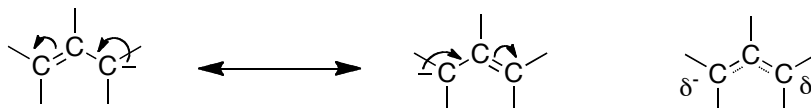


226

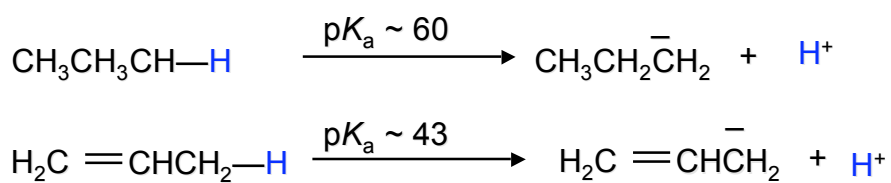
Limitation: Allylic halogenation is only useful when all of the allylic hydrogens are equivalent *and* the resonance forms of allylic radical are equivalent.



10.7: Allylic Anions

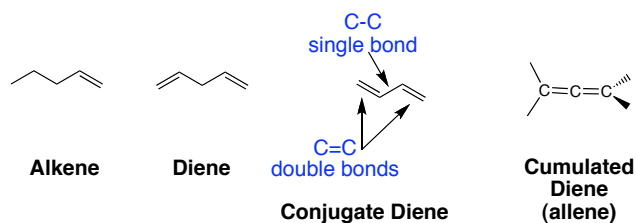


227



10.8: Classes of Dienes

Diene: molecule with two double bonds

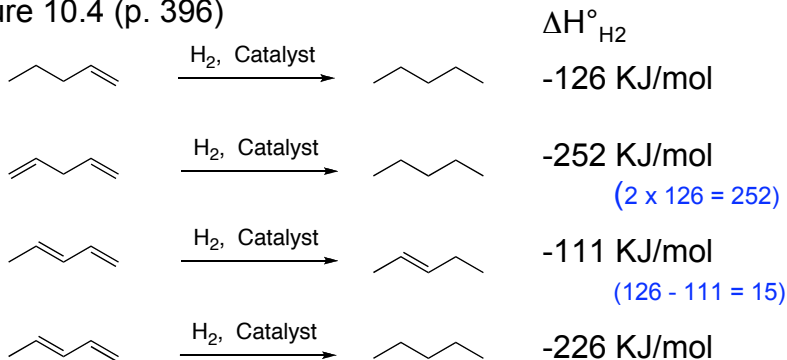


Conjugated diene: alternating double and single bonds 228

10.9: Relative Stabilities of Dienes

Recall from Chapter 6 that *heats of hydrogenation* ($\Delta H^\circ_{\text{H}_2}$) was used to measure the relative stability of isomeric alkenes

Figure 10.4 (p. 396)



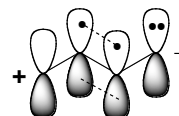
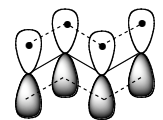
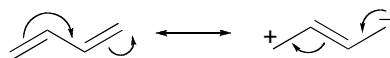
the double bonds of conjugated dienes are more stable than isolated double bonds.

229

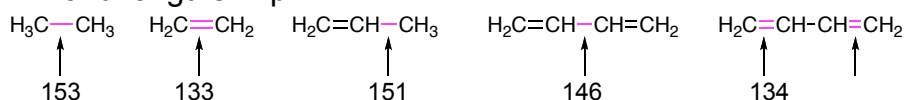
10.10: Bonding in Conjugated Dienes

When the carbons of a conjugate diene all lie in the same plane, the π -molecular orbitals overlap.

The four π -electrons of a conjugated diene are delocalized over the four p-orbitals



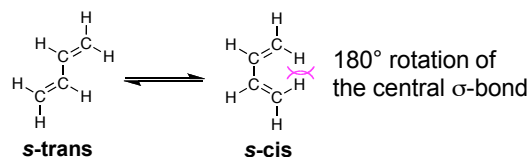
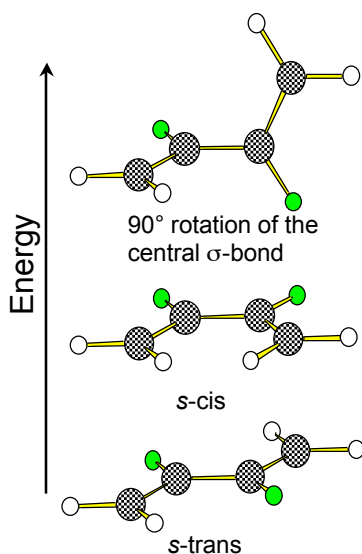
Bond lengths in pm



230

There are three conformations of butadiene.

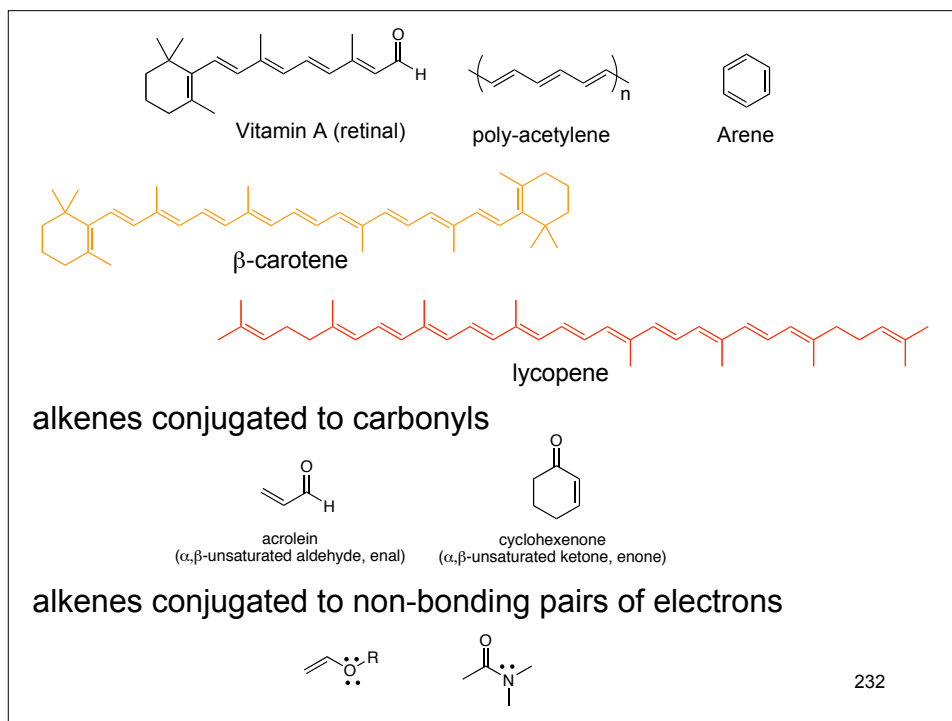
The (lower case) s prefix designates a conformation around single (σ) bond.



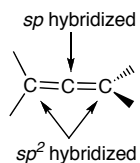
The perpendicular conformation is 16 KJ/mol higher in energy than the s-cis

The s-cis conformation is 12 KJ/mol higher in energy than the s-trans

231

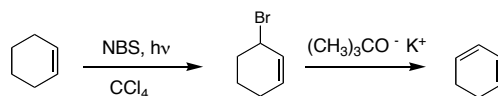


10.11: Bonding in Allenes (please read)



10.12: Preparation of Dienes

Preparation of conjugated dienes (1,3-dienes) from alkenes:
allylic bromination followed by dehydrohalogenation



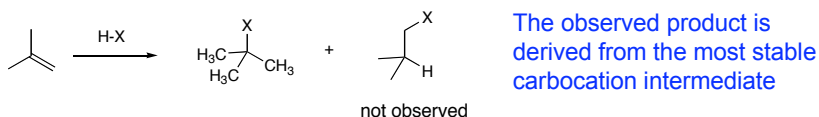
233

10.13: Addition of Hydrogen Halides to Conjugated Dienes

Isolated dienes: double bonds react independently.

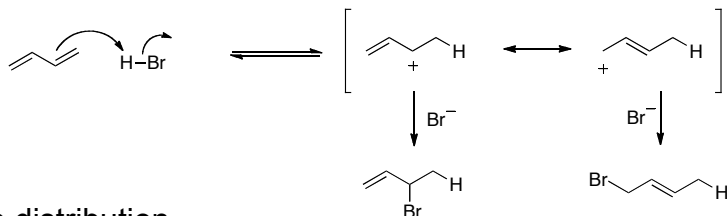
Conjugated dienes: the π -bonds of a conjugated diene react as a single unit.

Electrophilic Addition to Conjugated Alkenes: The addition of HX to butadiene. Recall that the addition of HX to alkenes follows Markovnikov's Rule



The addition of HX to a conjugated diene occurs to give a resonance stabilized allyl carbocation

234



The distribution of products is dependent upon temperature

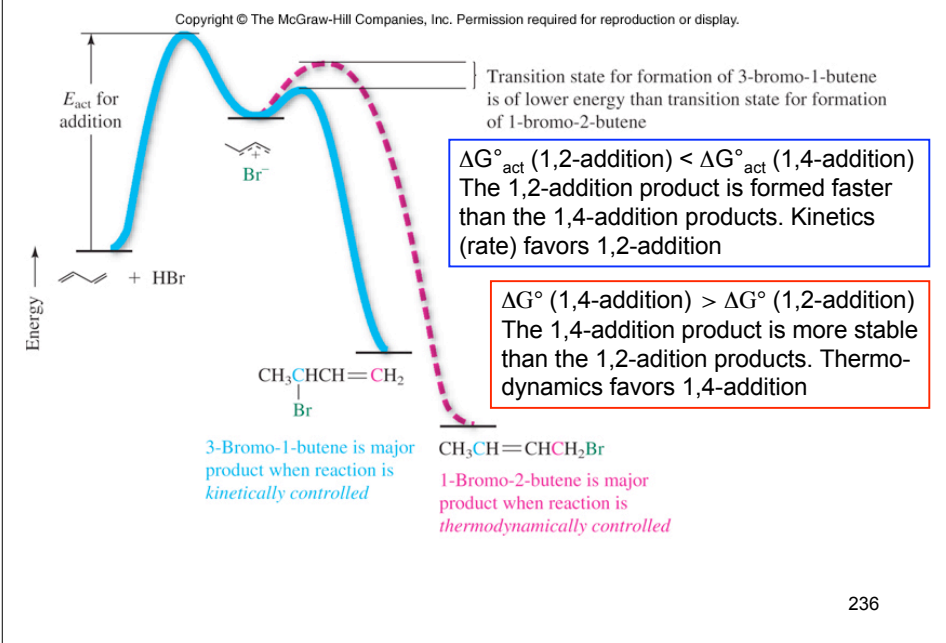
	25 °C	44%	56%
	-80 °C	81%	19%

At low temperature the reaction is under *kinetic control*, the major product is the one that forms fastest.

The reaction is under *thermodynamic control* at higher temperature, the major product is the most stable.

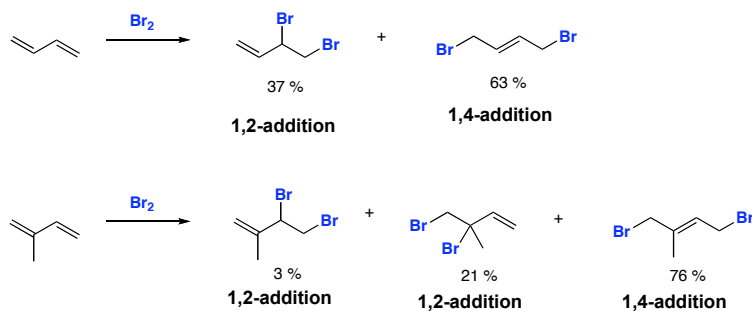
235

Figure 10.8



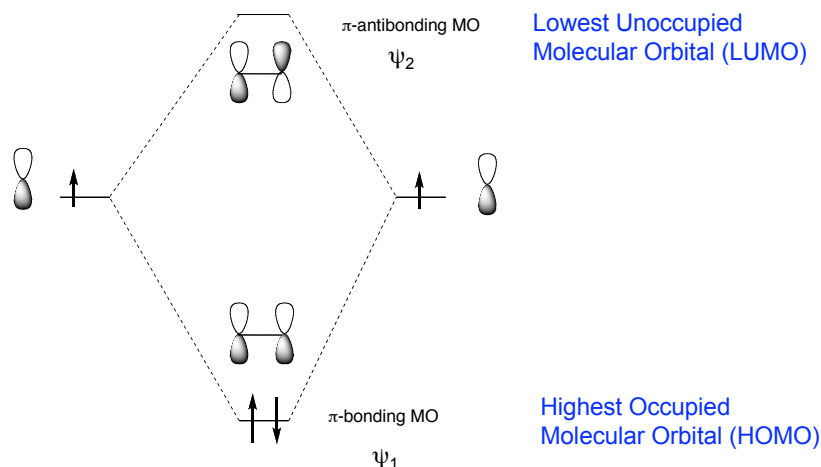
10.14: Halogen Addition to Dienes

Electrophilic additions of other electrophile to dienes give similar results



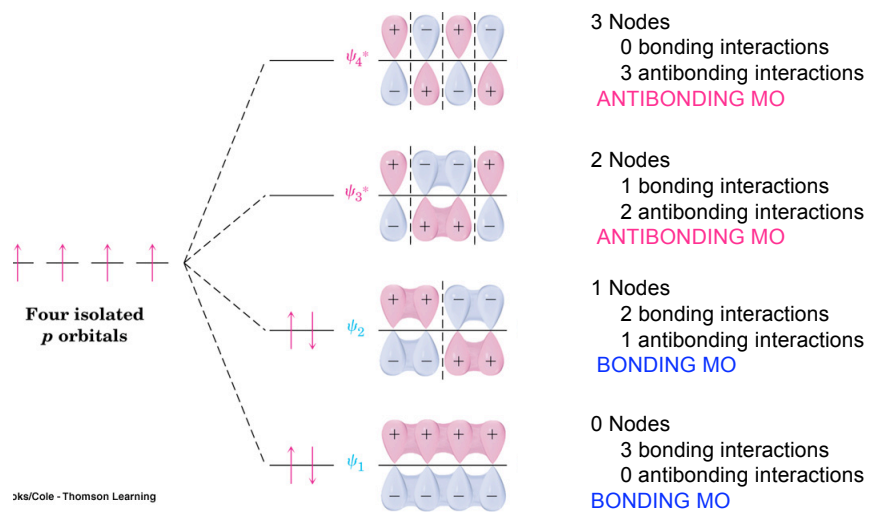
237

10.16: The π Molecular Orbitals of Ethylene and 1,3-Butadiene
 π -MO's of ethylene (from Chapter 2)



238

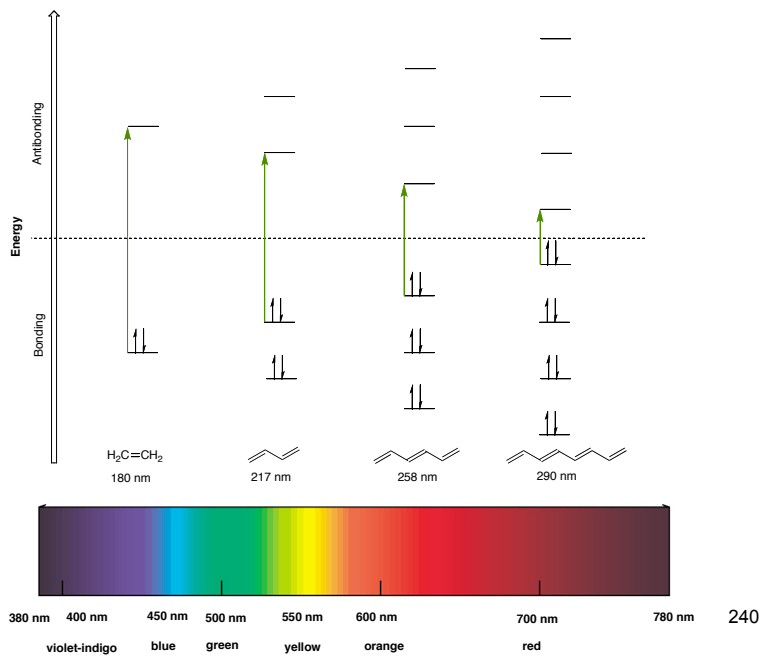
π -molecular orbitals of butadiene



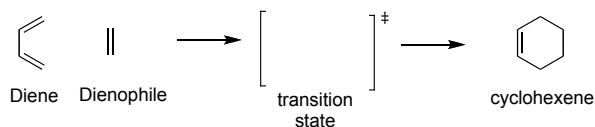
ψ_2 is the Highest Occupied Molecular Orbital (HOMO)
 ψ_3 is the Lowest Unoccupied Molecular Orbital (LUMO)

239

Molecular orbitals of conjugated polyenes



10.15: The Diels-Alder Reaction (a very important reaction) - Reaction between a conjugated diene and an alkene (dienophile) to give a cyclohexene.

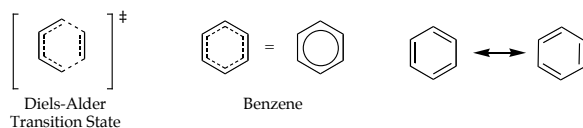


Mechanism:

concerted - reaction (bond breaking and bond forming) takes place in a single step.

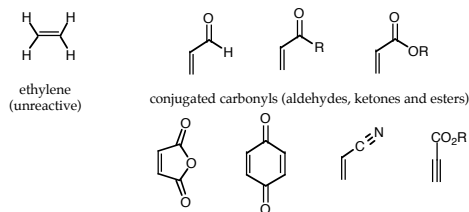
Cycloaddition - non-cyclic reactant react to form a cyclic product

Pericyclic - cyclic “aromatic-like” transition state



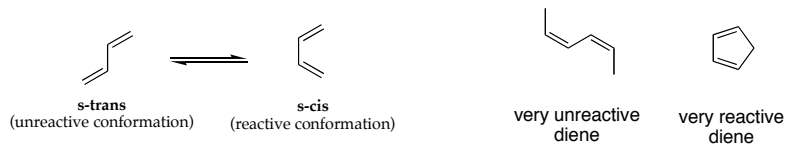
241

The Diels-Alder reaction is favored by electron withdrawing groups on the dienophile and electron donating groups on the diene.



Good dienophiles

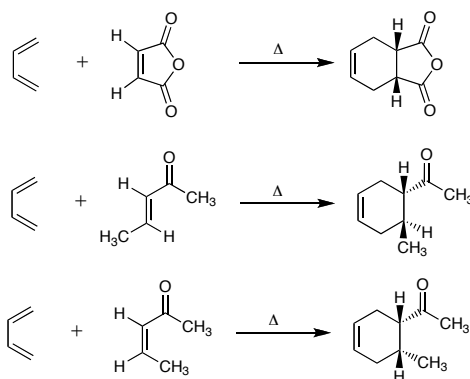
The diene must adopt an s-cis conformation to be reactive:



242

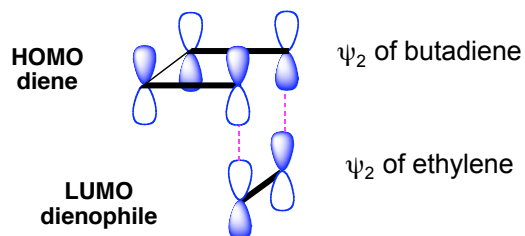
Stereochemistry of the Diels-Alder Reaction:

The stereochemistry of the alkene reactants (dienophile) is preserved in the product.

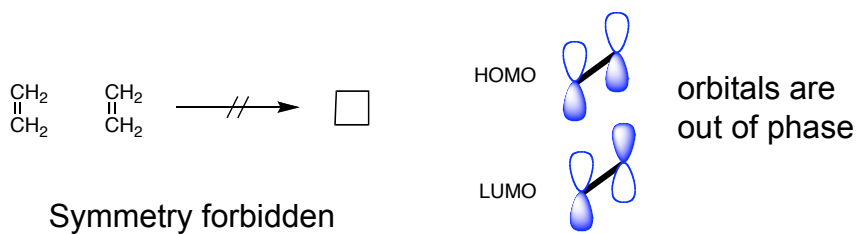


243

10.17: A π Molecular Orbital Analysis of the Diels-Alder Reaction



The orbitals between the diene and dienophile involved in bond formation are in phase - symmetry allowed.



244