

Chapter 16. Dienes.

1. Allenes (1,2-Dienes).
 - a) orbitals of two π bonds are orthogonal — don't overlap
 - b) 1,3-disubstituted allenes are chiral
 - c) chemically the two π bonds don't influence each other too much
2. 1,3-Dienes
 - a) conjugation
 - i) two contiguous π bonds interact with one another
 - ii) four orbitals (two π , two π^* , or four p orbitals) make four new MOs
 - a) can be represented as + + + +, + + - -, - + + -, and + - + - where orbitals of the same arithmetic sign overlap constructively and those of opposite arithmetic sign overlap destructively
 - b) called ψ_{0-3}
 - c) have 0–3 nodes in order of increasing energy
 - iii) only ψ_0 and ψ_1 are occupied
 - iv) energy gap between HOMO and LUMO of 1,3-diene is smaller than in alkenes, so 1,3-dienes absorb lower-energy wavelengths
 - v) carried to more conjugated polyenes, eventually absorbance occurs in visible range — beta-carotene
 - b) conformation
 - i) in ψ_0 there is a bonding interaction between p orbitals on C(2) and C(3) of the 1,3-diene
 - ii) rotation about this σ bond causes this interaction to go away at the 90° dihedral angle mark
 - iii) we would predict that rotation about the central bond costs energy — it does, but not a lot, only about 4–5 kcal/mol
 - iv) the two planar forms are called s-cis and s-trans (*not* cis and trans, which are reserved for configurational stereochemistry about rings and π bonds)
 - v) s-trans is lower in energy than s-cis by about 2–3 kcal/mol due to steric interaction between H atoms on C(1) and C(4)
 - c) electrophilic addition reactions
 - i) 1,3-dienes undergo typical electrophilic addition reactions of alkenes
 - ii) electrophile always adds to terminal C to form allylic carbocation
 - iii) nucleophile can add to carbocation at either allylic position to give 1,2- or 1,4-addition product
 - iv) addition to terminal C gives more substituted alkene, so is favored thermodynamically (under conditions where products are in equilibrium with one another via cation)
 - v) turns out addition to internal C is favored kinetically because nucleophile is closer to internal C after electrophile reacts with terminal C
 - d) Diels–Alder reaction

- i) 1,3-dienes react with alkenes to give cyclohexenes
- ii) mechanism is concerted [4+2] cycloaddition, just like carbene addition to alkenes is concerted [1+2] cycloaddition
- iii) 1,3-diene must be s-cis
 - a) higher-energy conformation is required
 - b) 1,3-dienes locked into s-cis conformation react much more quickly
 - c) 1,3-dienes locked into s-trans conformation don't react at all
- iv) reaction usually proceeds faster when alkene is electron-deficient (such as with a carbonyl group attached), 1,3-diene is neutral or electron-rich (such as with a heteroatom attached)
- v) as a result of concerted mechanism, stereochemistry of alkene is preserved in product
- vi) as a result of concerted mechanism, out groups in 1,3-diene become cis in product, as do the in groups
- vii) substituted 1,3-dienes react by ortho-para rule (regiochemistry) and out-endo-cis rule (stereochemistry)
- viii) retron for D-A reaction is cyclohexene
 - a) disconnect C(3-4) and C(5-6) bonds (π bond is C(1-2))
 - b) erase π bond at C(1-2)
 - c) put new π bonds at C(2-3), C(1-6), and C(4-5)
 - d) even when a cyclohexane ring does not have a π bond, a π bond may be introduced retrosynthetically