

10.2: Background

In the lecture portion of your organic chemistry course, you likely learned that in a cycloaddition reaction two *[Math Processing Error]* bonds are converted into two *[Math Processing Error]* bonds. As shown in Figure 1, the most well-known of the cycloaddition reactions is the [4+2] or Diels-Alder cycloaddition. In this reaction, a *[Math Processing Error]* electron diene reacts with a *[Math Processing Error]* electron dienophile in a concerted reaction forming a cyclohexene molecule. As shown in Figure 1, this reaction is successful because the frontier molecular orbitals of the diene (HOMO) and the dienophile (LUMO) overlap with the correct symmetry and similar energies.

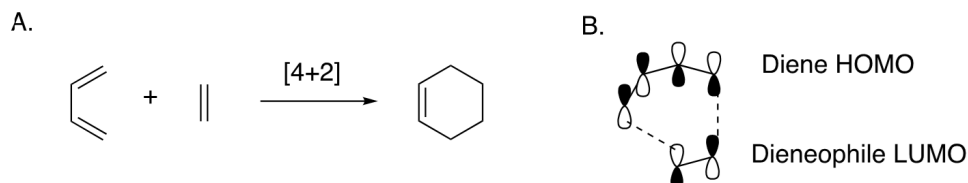


Figure 1A. Diels-Alder Cyclization. **B.** The overlap of Frontier Molecular Orbitals allowing for the formation of the cyclohexene ring.

While similar [2+2] cycloaddition reactions are possible, they are thermally forbidden and require light to proceed. This difference is related to the symmetry of the frontier molecular orbitals. Unlike in a Diels-Alder reaction where the frontier molecular orbitals of the diene and the dienophile overlap in phase to form the ring, the HOMO and LUMO of the 2+2 cycloaddition don't have the correct symmetry to overlap in phase (Figure 2). For this reaction to occur, photoexcitation of electrons from the HOMO to the LUMO must occur.

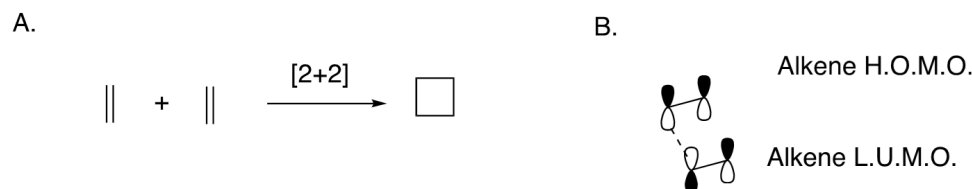


Figure 2A. The formation of a cyclobutene ring via a [2+2] cycloaddition. **B.** The HOMO of one alkene does not have the same symmetry of the LUMO of another alkene. The result is no net bonding without photoexcitation of one alkene.

The cyclobutanes created in a [2+2] cycloaddition are found natural products. One example of this is in the dimerization of cinnamic acid to yield different stereoisomers of truxillic acid, as shown in Figure 3. Truxillic acid is found in the leaves of the coca plant, and a derivative of truxillic acid, known as incarvilleate, has shown promise as a powerful analgesic.^{7,8}

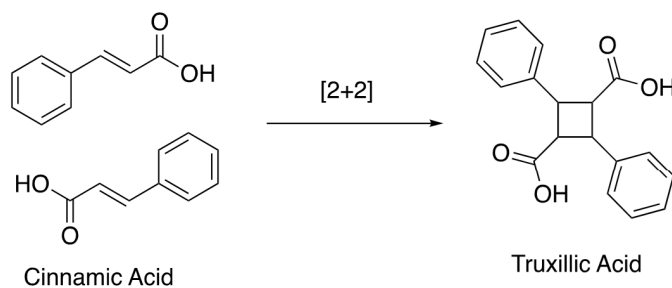


Figure 3. [2+2] cycloaddition of cinnamic acid yielding truxillic acid.

In the computational exercise that follows, you will calculate the molecular orbitals of cinnamic acid to determine which orbitals will overlap to yield the desired cyclobutane-containing truxillic acid. Moreover, you will use the energy values of the molecular orbitals generated to estimate the wavelength of light needed to cause the photoexcitation.

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