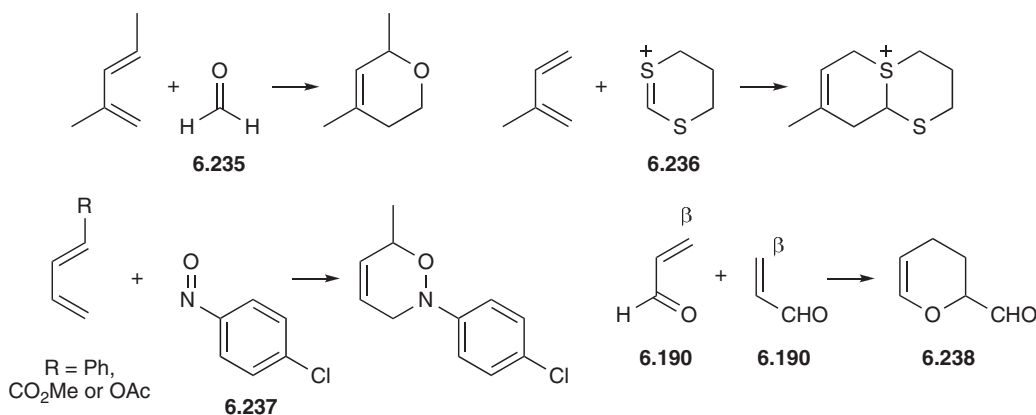


# FMO Analysis of Acrolein Dimerization

**The Regioselectivity of Hetero Diels-Alder Reactions.** In a few cases, carbonyl, nitrosyl, cyano, and a few other double bonds with one or more electronegative heteroatoms have acted as dienophiles in Diels-Alder reactions.<sup>794</sup> The carbonyl group has the HOMO and LUMO shown in Fig. 1.66 (see p. 58). The energies of both orbitals are relatively low, and most of their Diels-Alder reactions will therefore be guided by the interaction between the HOMO of the diene and the LUMO of the carbonyl or similar compound. The examples with formaldehyde **6.235**, the dithienium ion **6.236** and *p*-chloronitrosobenzene **6.237** illustrate that this works.<sup>795</sup>



There are also Diels-Alder reactions in which the heteroatom is part of the diene system.<sup>796</sup> The most notable of these is the dimerisation of acrolein **6.190** giving the adduct **6.238**.<sup>797</sup> This reaction had been a long-standing puzzle. As in the reaction of butadienecarboxylic acid **6.208** with acrylic acid **6.209** (see p. 304), the ‘electrophilic’ carbon atoms, labelled  $\beta$ , are the ones which have become bonded.

The first calculations of the frontier orbitals for acrolein gave the larger HOMO coefficient to the  $\alpha$  carbon of the C=C double bond of acrolein. This failed to explain the regiochemistry, but only because the simple Hückel theory that was used is notoriously weak in dealing with electron distribution in heteroatom-containing systems. Later calculations<sup>798,799</sup> gave a better set of coefficients, one of which<sup>375</sup> is shown in Fig. 6.34.



**Fig. 6.34** Frontier orbital energies and coefficients for acrolein

Both LUMO<sub>(diene)</sub>/HOMO<sub>(dienophile)</sub> and HOMO<sub>(diene)</sub>/LUMO<sub>(dienophile)</sub> interactions have to be considered, because both energy separations are the same for dimerisations. The former interaction is directly appropriate for the formation of the observed product, as shown on the left of Fig. 6.34, but the latter interaction, as shown on the right, has no obvious polarisation in the diene the C and O atoms have accidentally identical coefficients. However, the resonance integral,  $\beta$ , for the formation of a C O bond is smaller than the resonance integral for the formation of a C C bond. (This is only true when the atoms are more than 1.75 Å apart, but no one has suggested that the transition structure is likely to have a shorter distance than this, though several people have used longer distances.) Thus the  $(c\beta)^2$  term of Equation 3.13 is smaller at oxygen than at carbon in this orbital, and consequently this interaction also explains the regioselectivity. The regioselectivity in this reaction is delicately balanced,<sup>800</sup> but it also matches several cycloadditions between  $\alpha,\beta$ -unsaturated aldehydes, ketones and imines with C-, Z- and X-substituents on the dienophile, although some of the reactions may be stepwise, and not pericyclic.<sup>801</sup>