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A Simple Model For Substituent Effects In Cycloaddition Reactions. II.

The Diels-Alder Reaction

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The perturbational treatment of substituent effects in cycloadditions[1] is applied to the Diels-Alder reaction. The HOMO's (highest occupied molecular orbital) and LUMO's (lowest unoccupied molecular orbital) of the diene and dienophile are used in the construction of orbitals for the transition state model. The influence of electron withdrawing and releasing substituents on the orbital energies of the addends and hence on the symmetry orbitals is evaluated by first order HMO-perturbation theory[2].

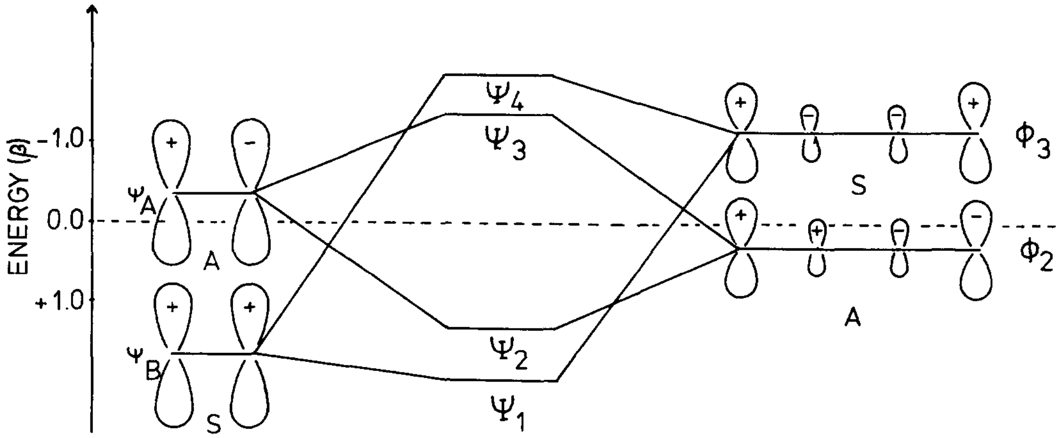

Fig. 1 Formation of symmetry orbitals from the HOMO's and LUMO's of an electron poor dienophile and an electron rich diene.

The model adopted for the transition state assumes that the molecules are oriented in two separate planes. This model was used to prove the concertedness of Diels-Alder reactions[3]. As depicted in Fig. 1, the HOMO of the dienophile interacts with the LUMO of the diene[4] to form the orbitals Ψ_1 and Ψ_4. Ψ_2 and Ψ_3 result from the interaction of ψ_A and

Φ_2. The resulting stabilization is a function of the separation of the interacting orbitals.

Two different types of Diels-Alder reactions can be distinguished experimentally[5]. The reaction occurs easily if the diene is electron rich and the dienophile electron poor (normal DA) or vice versa (inverse DA). The orbital arrangement of a normal Diels-Alder addition is shown in Fig. 1. The orbital energies of the dienophile are lowered (in comparison to those of ethylene), but the orbitals of the diene are raised in energy (in comparison with those of butadiene)[2]. Because of the smaller separation of ψ_A and Φ_2, the stabilizing effect of their interaction is higher than the one from the interaction of ψ_B and Φ_3. Using the orbital arrangement of Fig. 1 the influence of substituents in the dienophile on the reaction rate can easily be understood. Electron withdrawing substituents will lower both ψ_A and ψ_B in energy. The LUMO-ethylene - HOMO-diene interaction will increase and this more rapidly than the concomittant decrease in the interaction $\psi_B - \Phi_3$; a net energy gain results. An illustrative case has been described by Sauer, Wiest and Mielert[6]: The more cyanogroups attached to ethylene as dienophile the greater the reactivity towards cyclopentadiene. Conversely electron releasing substituents will increase both ψ_B and ψ_A in energy. As a consequence the stabilization from the interaction $\psi_A - \Phi_2$ is reduced, but the decrease in the separation $\psi_B - \Phi_3$ will stabilize the transition state. However, the separation $\psi_B - \Phi_3$ is lessened relatively to a smaller extent than $\psi_A - \Phi_2$ is increased. Therefore the net effect will be a destabilization of the transition state by electron releasing substituents.

In the normal Diels-Alder addition the interaction LUMO-dienophile and HOMO-diene is the dominant stabilizing factor. For the inverse type the relative positions of the orbitals are interchanged (Fig. 2). The orbitals of the dienophile are higher in energy than

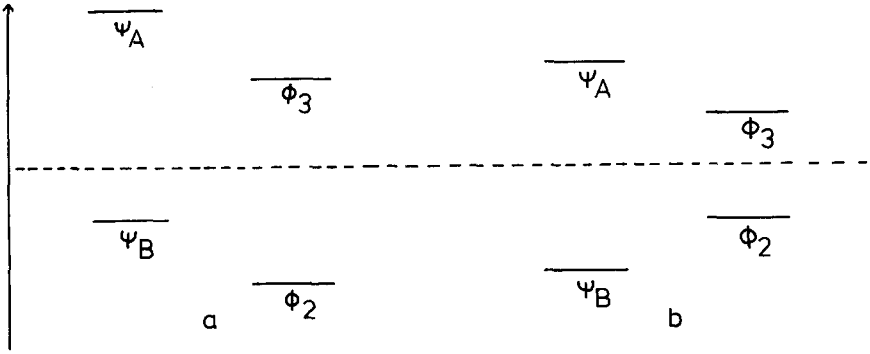

Fig. 2 HOMO - LUMO orbital arrangement for an inverse (a) and a neutral (b) Diels-Alder reaction

those in ethylene; in the diene they are lower than in butadiene[2]. The predominant interaction now becomes HOMO-dienophile and LUMO-diene. Such additions should be accelerated by electron releasing substituents in the dienophile.

A third type of orbital arrangement for a Diels-Alder reaction which might be called neutral can be visualized (Fig. 2). How should substituents in the dienophile affect these additions? The HOMO - LUMO separations are similar. As electron withdrawing and releasing substituents either lower or raise both ψ_B and ψ_A each kind of substituent will strengthen one HOMO - LUMO interaction but weaken the other. The strengthening effect should be more pronounced and therefore electron attraction and release should increase the reactivity. However, the influence of substituents on the rate should be smaller than for normal or inverse Diels-Alder additions. 1,3-dipolar cycloadditions, where an orbital arrangement similar to b in Fig. 2 seems to be realized[1], do indeed show smaller substituent effects than the normal Diels-Alder reaction[7].

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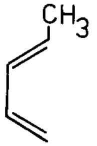
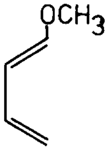
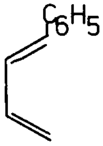
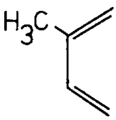
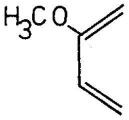
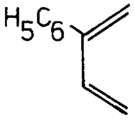
	175		86100		652
	74.1		2960		323

Table 1: Reaction rates for the addition of monosubstituted dienes to tetracyanoethylene in CH_2Cl_2 at 20° C[8].

Substitution of the diene component also should have a marked influence. The more electron releasing the diene substituent in normal Diels-Alder reactions, the higher the rate accelerating effect[8]. The difference in reactivity between 1- and 2-substituted dienes (Table 1) also supports our MO-model. As shown in Fig. 1, where the magnitude of the MO-coefficients at the different positions of the HOMO's and LUMO's has been symbolized by the size of the p-lobe, a substituent should have a higher influence at the 1- than at the 2-position. The kinetic data of Table 1 reflect this expectation.

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