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STEREOSELECTIVITY ASSOCIATED WITH NONCYCLOADDITION TO UNSATURATED BONDS

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THE predominance of socalled trans addition to olefins is experimentally well established. Various instances are afforded in both ionic and radical noncyclic additions. An unequivocal account for this fact, however, seems to have not yet been given[1]. It appears to me useful to apply the "frontier electron" concept to discussing problems of this sort[2]. In this theory every actual chemical interaction is assumed to take such a pathway to occur that thereby the charge-transfer interaction (in heterolytic interactions) or the electron-exchange interaction (in homolytic interactions) may be facilitated as possible. Accordingly the transition state might be specified as an electronic state in which, in heterolytic interactions, the highest occupied molecular orbital (HO) of one component and the lowest vacant molecular orbital (LV) of the other come to play the most significant role, whereas in homolytic interactions the half occupied molecular orbital works in their place[3]. Therefore, the intramolecular electron distribution of these particular molecular orbitals would govern the orientation of reaction through the conjugation stabilization at the transition state, while the direction of extension of these particular orbitals would designate the spatial direction of approach in mutual attack*. When we apply the theory to the problem of addition reaction, the former provides the position of both the primary and the secondary attacks in acyclic additions[4,5], and the latter will supply the knowledge on the steric course involved in these processes.

With a view to explaining the trans addition I adopt the following model. The attacking species is denoted by XY. The component of primary attack, X, is supposed to approach a conjugated olefin molecule having k π electrons toward its terminal carbon** from the direction perpendicular to the plane of molecule, as is illustrated in the figure. In adopting simply the Hückel molecular orbital treatment, we only take into account as the basis atomic orbitals an interacting orbital, ϕ_x, at the attacking component, X,

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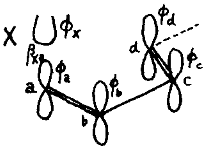
* By the consideration of the direction of orbital extension we are automatically able to avoid getting into erroneous points of view like, for instance, the opinion of Bader _et al_. (A. R. Bader, R. P. Buckley, F. Leavitt, M. Szwarc, _J. Am. Chem. Soc._ _79_, 5621 (1957)) in which the direction of approach of methyl radical in additions to olefins was assigned to be along the carbon-carbon double bond axis.

** An unsubstituted conjugated olefin has the maximum frontier electron density at the terminal carbon[4].

and a 2pπ atomic orbital at each carbon atom. The interaction between X and the carbon, a, may be represented by a resonance integral, β_{xa}.



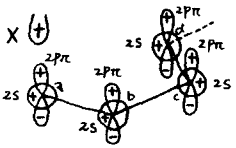
The usual secular equation for determining orbital energies of the whole system will be obtained as

$$\Delta(\varepsilon)=\left|\begin{array}{cccccc} \alpha_x-\varepsilon & \beta_{xa} & 0 & \cdots & 0 & 0 \\ \beta_{xa} & \alpha-\varepsilon & \beta & \cdots & 0 & 0 \\ 0 & \beta & \alpha-\varepsilon & \cdots & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & 0 & \cdots & \alpha-\varepsilon & \beta \\ 0 & 0 & 0 & \cdots & \beta & \alpha-\varepsilon \\ & \multicolumn{5}{c}{\underbrace{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}_{k}} \end{array}\right| \left.\vphantom{\begin{array}{c}0\\0\\0\\0\\0\end{array}}\right\}k \;=0 \qquad (1)$$

where ε, α_x, α, and β are the one-electron orbital energy, the coulomb integrals of ϕ_x and the carbon 2pπ orbital, and the resonance integral of the π bond, respectively. The jth molecular orbital is expressed by

$$\psi_j=c_x^{(j)}\phi_x+c_a^{(j)}\phi_a+c_b^{(j)}\phi_b+\text{-----} \qquad (2)$$

where ϕ_a, ϕ_b, etc. are the 2pπ atomic orbitals at carbons a, b, etc. Here I take the sign of basis atomic orbitals as follows:



In addition to each π atomic orbital we have to consider the carbon 2s atomic orbitals which will participate in forming afterwards an sp^3 hybridised orbital at the position of attack. Then we will have negative β and β_{xa} as usual. We are able to assume that ϕ_x is originally occupied by sero, one, and two electrons, corresponding respectively to electrophilic, radical, and nucleophilic primary attacks. The secondary attack of the second component, Y, will correspondingly be nucleophilic, radical, and electrophilic. The "frontier orbital", designated as FO, is therefore (2n+2)-th molecular orbital for the system of k=4n+2, while (2n+1)-th molecular orbital for k=4n. A simple algebraic manipulation easily leads to the following theorem:*

$$C_x^{(FO)}C_b^{(FO)}<0,\quad C_x^{(FO)}C_d^{(FO)}>0,\quad C_x^{(FO)}C_f^{(FO)}<0,\ \text{and so forth.} \qquad \cdots\cdots (3)$$

This signifies that in the frontier orbital the coefficients have alternately definite signs which reverse alternately. If we endow C_x with the plus sign, then the wave function of this particular molecular orbital will be characterised by the following figure:**

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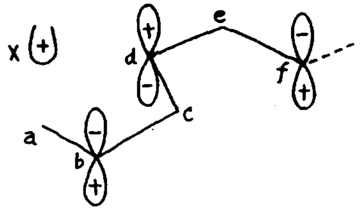
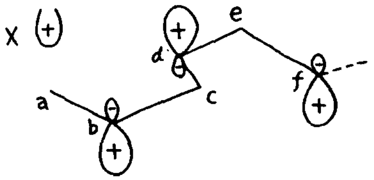
* To prove this theorem it is recommended to employ eq.(5) of K. Fukui, C. Nagata, T. Yonesawa, H. Kato, K. Morokuma, J. Chem. Phys. 31, 287 (1959).

** The coefficients Ca, Cc, Ce, etc. have no definite sign and relatively small absolute values provided ε_{FO} lies near to α. As is easily seen, if $\alpha_x=\alpha$ and $\beta_{xa}=\beta$, we have Ca=Cc=Ce=-----=0, and Cb=-1, Cd=+1, Cf=-1, and so forth.



The 2s orbital at carbon atom a must have the plus sign in order to be overlapped by the atomic orbital, ϕ_x, in the bonding molecular orbitals of the olefinic chain, giving rise in turn to the plus sign of the 2s orbitals at carbons b, d, f, and so forth by way of the chain of sp^3 sigma bonds. Hence the hybridised orbital to appear at the positions of attack in case of bonding must have the following direction of extension:



The result evidently shows that

i) 1,2-Addition will take place by a <u>trans</u> mechanism*,

ii) 1,4-Addition will take place by a <u>cis</u> mechanism,

and so on. The conslusion is very succinct. It is hoped to

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* Hosoya and Nagakura (Preprint of Symposium on Molecular Structure, Japan, 1962, p. 48 (in Japanese)) considered the participation of carbon 3s orbital causing the deformation of LV due to the approach of a point plus charge. They obtained an LV which extended to the direction trans to the location of the point charge.

compare this result with duly projected experiments which may act as examples of 1,4- or more distant addition reactions.

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