

CALCULATION OF TRANSITION STATE ENERGIES BY MEANS OF SIMPLE
QUANTUM MECHANICAL LC-METHODS

(Transition State Energies of 1,3-Dipolar Additions)

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R. HUISGEN et al.^{1,2} have shown that the well known addition of diazoalkanes to alkenes resulting in pyrazolines follows the mechanism of the so-called 1,3-dipolar addition. In the course of that mechanism there occur simultaneously with the successive formation of the two new σ -bonds (fig. 1) changes in the hybridisation at the four centres of the reaction and at the central N-atom of the diazoalkane. Roughly interpreted the C-atoms change from sp^2 - to sp^3 -states and the N-atoms change from sp - to sp^2 -states. J.D. ROBERTS³ has calculated quantum chemically that the energy Q, arising from the change of hybridisation at the central N-atom, lies in the range

$|2 \alpha_N + 0,83 \beta_{NN}| < Q < |2 \alpha_N + 2,00 \beta_{NN}|$; energy quanta of this order should be available under the usual reaction conditions. R. HUISGEN et al.² have presented kinetic data concerning the 1,3-dipolar addition of 1,1-diphenyldiazomethane to various alkenes.

Fig. 1 shows the model used in our work, of the transition state of these reactions. For simplicity this model is idealized geometrically to some extent by the assumptions: (1) that the lengths of the C-C-bond in the alkene and the C-N- and N-N-bonds in the diazoalkane are equal to d and do not alter during the formation of the activated complex;

(2) that the newly formed σ -bonds have equal lengths r ;
 (3) that the valence angles at the four centres of the reaction are at all stages of the transition state equal to ϕ . So the four centres of the reaction and the central N-atom occupy the corners of an irregular but symmetric pentagon. The valence angle at the central N-atom is called φ .

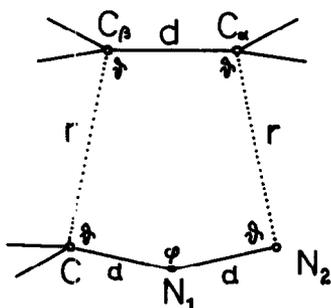


Fig. 1: Slightly idealized model of the transition state in 1,3-dipolar addition of diazoalkanes to alkenes.

Two different wave functions $\psi_d(\gamma)$ and $\psi_1(\gamma)$ are used to describe the transition state. Both represent the electrons involved and are simple product functions. In detail, $\psi_d(\gamma)$ represents the electrons of the two reactants without allowance being made for the formation of the two new σ -bonds along r , but $\psi_1(\gamma)$ describes them when the two σ -bonds are formed. Two energies $E_d(\gamma)$ and $E_1(\gamma)$ correspond to both these wave functions. The contributions of π -electrons to these energies are calculated using the simple Hückel method, and those of the σ -electrons are estimated by means of Morse potential functions. Fig. 2 shows the relationship between $E_d(\gamma)$ and $E_1(\gamma)$ respectively, and the angle γ . The intersection of the two curves (point C in fig. 2, corresponding to the energy E_C) is to a first approximation re-

If an angle γ is defined by

$$\gamma = \phi - 90^\circ \quad (1)$$

there follows by elementary geometry

$$\varphi = 180^\circ - 4\gamma \quad (2)$$

$$r = d \frac{2 \cos 2\gamma - 1}{2 \sin \gamma} \quad (3)$$

As shown by eqns. (1), (2) and (3) γ may be used as well as r as a measure of the reaction coordinate whereby

$0 \leq \gamma \leq 18^\circ$ corresponds with $\infty \leq r \leq d$.

Two different wave func-

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