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THE TRANSITION STATE OF THE CLAISEN AND THE COPE REARRANGEMENTS

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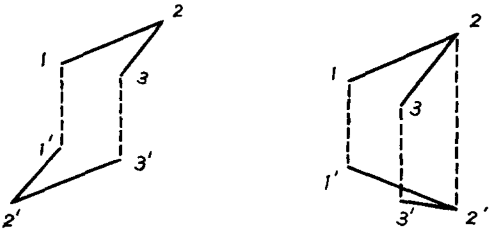
THE double allylic (the Claisen and the Cope) rearrangements are known to take place through an intramolecular, cyclic transtion state. The preferable form of the transition state has been demonstrated to be chairlike rather than boatlike.[1,2] Recently Hoffmann and Woodward discussed this problem from the point of view of the molecular orbital symmetry relationship,[3] giving an elegant explanation. However, in favour of those who are not much accustomed to such practices, we would like to present an alternative way of consideration, which will appear to be simpler and alike applicable to systems with no substantial symmetry.

We recollect here the method which was successfully employed to give an account of stereochemistry in the ring-closure of noncyclic conjugated olefins.[4] This method, being based on the estimation of the "overlap stabilization"[5] of molecular orbitals at the transition state, is applied this time to the Cope rearrangement of 1,5-hexadiene.

Fig. 1 illustrates two configurations of the transition state. The essential difference of the boat (ii) from the chair (i) may be characterized by a weak conjugation between the π-atomic orbitals at carbons 2 and 2′ which will cause an energy change.



(i) Chair-form (ii) Boat-form

Fig. 1. Schematic representation for the two forms of the transition state in the Cope rearrangement.
(The full and the dotted lines stand for a pπ-like and a pσ-like conjugation, respectively.)

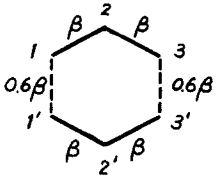
Qualitatively, that the boat form will possess a higher energy than the chair is most easily presumable by remembering that the 1,4-π-bond order of benzene is negative (-0.3333). More precisely, a simple Hückel perturbation calculation applied to the double allylic six π-electron systems leads to the energy increase due to the 2,2′-conjugation to be represented by

$$\Delta E = 2P_{22'}\gamma ,$$

where $P_{22'} = 2\sum_{j}^{occ} c_2^j c_{2'}^j$ is of the same form as the well-known "bond order" and to be a measure of "overlap stabilization"[5] in the present case, and γ stands for the resonance energy of the 2,2′-conjugation.

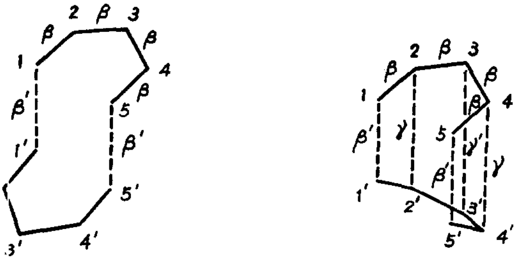
Habitual notations C_2^j and $C_{2'}^j$ denote the coefficients of $2p\pi$ atomic orbitals at carbons 2 and 2′, respectively, of jth molecular orbital, and the summation is carried out over occupied orbitals.

Since we have no information on the exact configuration of the transition state, we put a tentative assumption that the resonance integral for the 1,1′-(or 3,3′-)$p\sigma$-type conjugation is taken as 0.6β where β is that of the $p\pi$-type conjugation, obtaining $P_{22'} = -0.2075$. Since γ is negative, we thus see that the 2,2′-conjugation makes the system unstable.



If we assume that $\gamma = 0.2\beta$ and consider that $\beta = 2.5\sim3.0$eV, it follows that $\Delta E = 5\sim6$ kcal/mole. These values are consistent with Doering′s experimental evaluation (5.7 kcal/mole)[2], provided one neglects the contribution of "sigma" electrons to the difference in the total energy.

An analogous discussion is similarly made for the Claisen rearrangement, in which we have only to choose different parameters for the oxygen π orbital. The general feature of the result is not changed. Hoffmann and Woodward[3] discussed also the vinylogous Cope rearrangement of cis, cis-decatetraene. Fig. 2 indicates two configurations of the activated complex, (i) and (ii), schematically.



(i) exo-form (ii) endo-form

Fig. 2. The modes of the transition state interaction in a vinylogous Cope rearrangement.

($\beta' = 0.6\beta$; $|\gamma'| < |\gamma|$)

The calculation shows that 3,3′-interaction is bonding, while 2,2′- and 4,4′- are antibonding. The resultant energy change is obtained as

$$\Delta E = 2\left\{(P_{22'} + P_{44'})\gamma + P_{33'}\gamma'\right\} = -0.3244\,\gamma + 0.2413\,\gamma' > 0 \quad (|\gamma'| < |\gamma|)$$

leading to the conclusion that the form (i) is preferred.

The present treatment may conveniently be applied to many other, similar problems in organic chemistry.

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