Tetrahedron Letters No.4837-4841, 1966. Pergamon Press Ltd.
Printed in Great Britain.

EMPIRICAL CALCULATION OF ACTIVATION ENERGY AND TRANSITION STATE GEOMETRY FOR THE COPE REARRANGEMENT

Massimo Simonetta and Giorgio Favini(x)
Institute of Physical Chemistry, University of Milan
Milan, Italy

(Received 20 June 1966)

Considerable attention has been given in the last few years to the mechanism of the Cope Rearrangements. Experimental results have been extensively reviewed(1)(2), and theoretical interpretations have been suggested, based on orbital symmetries(3) or on a Hückel M.O. perturbation treatment(4). The two theoretical treatments agree in predicting the chair form of the transition state to be more stable than the boat form for 1,5-hexadienes. The result is in line with previous experiments on 3,4-dimethylhexa-1,5-diene(5).

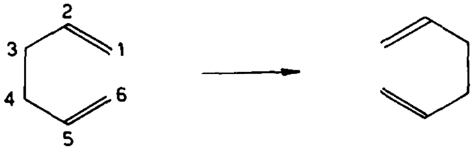
Both methods of calculation seem to have been devised for qualitative work, without any attempt to obtain quantitative information on the geometry of the transition state, and without inclusion of possible steric influences.

A different approach is here suggested, which is an extention of the method of computation of conformational energies successfully applied by Hendrickson(6) and Wiberg(7) to cycloal-

---

(x) Present address : Institute of Physical Chemistry
University of Catania - Catania, Italy

kanes. The variation of energy of a molecule along the reaction path is calculated as the sum of the following terms : bond angle bending strain, torsional strain, steric repulsion, π-delocalisation, compression of σ bonds in the conjugated parts of the molecule, making and rupture of a σ bond. The details of the calculation are now briefly summarised, for 1,5-hexadiene, as an example :



Calculations are performed at different degrees of advancement of the reaction (α), having defined α as the degree of breaking of the C_3-C_4 bond. Hybridisation at carbon atoms 1 , 3 , 4 and 6 is supposed to change along the reaction path from sp^2 to sp^3 or vice-versa .

The variation of the amount of s orbital in the hybrids is assumed linear in α .

Hybridisation at atoms 2 and 5 remains unchanged (sp^2) ; C_2 or C_s symmetry is also preserved along the chair-like or boat-like transition state reactions, respectively. The geometry at each stage is defined by the following parameters : $d_{1,2}$, $d_{2,3}$, $d_{2,5}$, $d_{3,4}$, $d_{6,1}$ carbon-carbon interatomic distances, and the dihedral angles ϑ_1 and ϑ_3 between the axis of local atomic ternary symmetry at C_1 and C_3 respectively and the axis of the p-orbital at C_2 , as illustred in FIG. 1

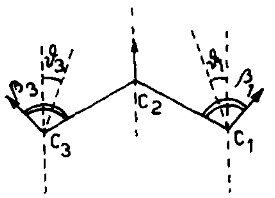


FIG. 1

Visualisation of ϑ_1 and ϑ_3 angles; the arrows indicate a p (at C_2) or quasi-p (at C_1 and C_3) orbital . For $\alpha = 0.5$, $\beta_1 = \beta_3 = 104.0°$

These parameters are not independent and can be expressed as functions of three of them (ϑ_1 , ϑ_3 , $d_{2,5}$) using empirical relationships between bond-distances and bond-order(8), bond-order and *effective overlap*(9). It is then possible to minimise , at each α, the energy with respect to ϑ_1 , ϑ_3 , and $d_{2,5}$ by machine computation and to find the activation energy and $\alpha^{\neq}$ (the degree of advancement at the transition state). The results are as follows :

	$\alpha^{\neq}$	$\Delta E^{\neq}$(Kcal/mole)	$\vartheta_1 = \vartheta_3$	$d_{2,5}$ (Å)
chair	0.5	30.5	+ 7.5°	2.7
boat	0.5	33.6	+13.5°	2.5

(The plus sign means inward rotation of the ternary axis). Activation energy values are of the right order of magnitude (see (2)), and in the right order, their difference being about 55% of an approximate experimental value, 5.7 Kcal/mole,(2) for the difference of activation free energy. The assumption that $\Delta S^{\ddagger}$ is about the same for the two arrangements has been justified by our results of entropy calculation. The method has been extended to consider more complex molecules and used to evaluate the rate enhancement of the Cope rearrangement obtained when one or two phenyl groups are bonded at C_3 and C_4 or when a strained ring is welded on the C_3-C_4 bond .

The calculation of the geometry of the transition state allows an evaluation of the activation and reaction entropies by using statistical mechanics techniques(10). For cis-1,2-divinylcyclobutane the experimental value is known, $\Delta S^{\ddagger} = -11.7$ e.u. at 358°K(11) while our calculation, along the boat-like transition state path, gives $\Delta S^{\ddagger} = -10$ e.u. at 423°K .

Acknowledgement : This work was supported by grants from the Italian C.N.R.

REFERENCES

1. E.Vogel, Angew.Chem. , Intern.Ed. 2, 1 (1963); S.J.Rhoads , "Molecular Rearrangements" - Edited by P.de Mayo, Interscience Publishers, New York, Part I p.655 (1963)
2. W.E.Doering, W.R.Roth, Angew.Chem. , Intern.Ed. 2, 115 (1963)
3. R.Hoffmann, R.B.Woodward, J.Am.Chem.Soc. 87, 4389 (1965); cfr. H.C.Longuet-Higgins, E.W.Abrahamson, ibid. 87, 2045 (1965)
4. K.Fukui, H.Fujimoto, Tetrahedron Letters No.2, 251 (1966)
5. W.E.Doering, W.R.Roth, Tetrahedron 18, 67 (1962)

6. J.B.Hendrickson, *J.Am.Chem.Soc.* **83**, 4537 (1961); *ibid.* **86**, 4854 (1964)

7. K.W.Wiberg, *J.Am.Chem.Soc.* **87**, 1060 (1965)

8. L.Pauling , *J.Am.Chem.Soc.* **69**, 542 (1947)

9. G.Favini, P.Gramaccioni, C.Mariani and M.Simonetta , to be published

10. K.E.Lewis, H.Steiner, *J.Chem.Soc.* 3080 (1964)

11. G.S.Hammond, C.D.DeBoer, *J.Am.Chem.Soc.* **86**, 899 (1964)