

ENDO AND EXO TRANSITION STATES IN THE DIELS-ALDER REACTION

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(Received 12 May 1967)

We have recently determined kinetic parameters for the unimolecular Diels-Alder retrogressions of exo and endo-dicyclopentadiene to monomer (1). The activation enthalpies and entropies are  $\Delta H^\ddagger$  (exo)  $37.4 \pm 0.3$  kcal/mole,  $\Delta S^\ddagger$  (exo)  $+ 1.1 \pm 0.6$  e.u.,  $\Delta H^\ddagger$  (endo)  $33.0 \pm 0.5$  kcal/mole, and  $\Delta S^\ddagger$  (endo)  $- 1.9 \pm 1.0$  e.u. Since our equilibration studies (1) indicate a difference in free energy of formation for the two dimers  $\Delta(\Delta G^\circ) = 0.0 \pm 1.0$  kcal/mole, the endo reaction pathway is therefore favored over the exo by 4.4 kcal/mole for either addition or retrogression. These results are the first quantitative measurements in a system where high conformity with the rule of endo addition is observed. All previous energy measurements pertain to the exceptional Diels-Alder reactions, those reactions which yield substantial amounts of both isomers (2,3).

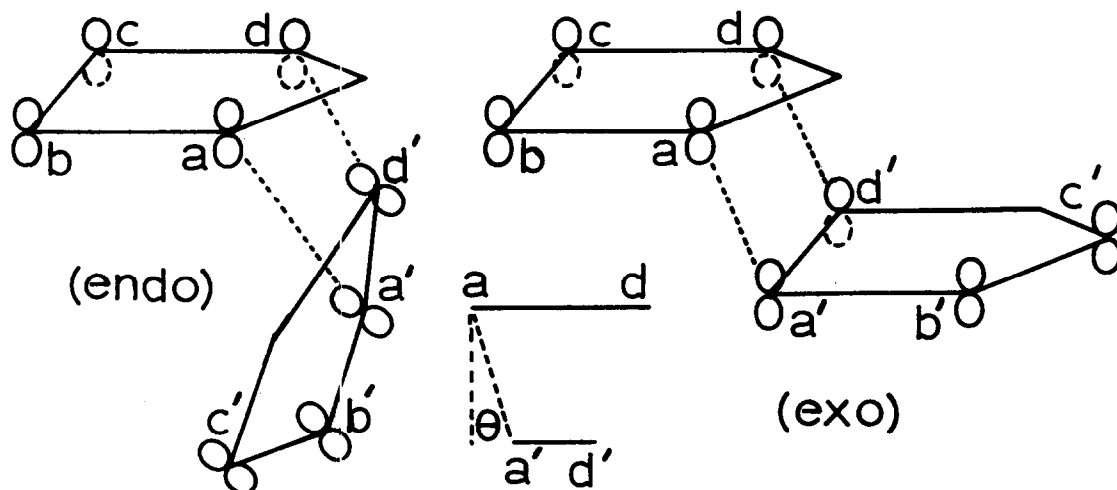
Predilection for endo addition has been ascribed to many factors (2,3,4). The earliest theory is embodied in the rule of "maximum accumulation of double bonds" formulated by Alder and Stein (5). A modern quantum chemical restatement in terms of orbital sign relationships (6) has reiterated the general opinion (7-11) that secondary attractive forces operating between centers which are not bonded in the adduct account for the rule of endo addition. We have also supported this view with some extended Hückel calculations (12).

Now, we suggest that such secondary relationships may be relatively unimportant, and that the stabilities of endo and exo transition states are governed by a less subtle factor, the geometrical overlap relationship of the

$\pi$ -orbitals at only the primary centers where bonds are actually developing. Our calculations indicate that this geometric factor is energetically sufficient to account for preferred endo addition in the Diels-Alder reaction, and we are therefore now able to rationalize the observed endo additions of monoolefinic dienophiles like cyclopropene (13), cyclopentene (14), and norbornylene (15). Such reactions are not accounted for by previous theories.

Let us consider the Diels-Alder reactions of cyclopentadiene as concerted 4 + 2 cycloaddition reactions (16). Refer to the transition states depicted in figure 1. Note that the planes of the two rings are assumed parallel in the

FIG. 1



exo-transition state and to intersect at an angle of 60° in the endo-transition state. The nearly zero entropies of activation for the retro-reactions (1) require transition complexes in which the relative orientations of the diene and dienophile closely resemble the geometries of the two dimers. However, in accordance with the Hammond postulate (17), the exothermicity of the forward reactions indicates that little electron reorganization has taken place.

We estimate the difference in activation energies for the two reactions

in a similar manner to our previous work (12) as a perturbation on the reactant  $\pi$  orbitals with exchange integrals proportional to overlap integrals. The treatment follows that of Dewar (18) in its essential aspects. The orbital overlap can be trigonometrically resolved into a sum of  $\sigma - \sigma$  overlap and  $\pi - \pi$  overlap. The requisite formulas for the primary interactions,  $aa'$  and  $dd'$ , are  $S(\text{endo}) = (\cos^2\theta)(\cos^230^\circ) S_{\sigma\sigma} + (\sin^230^\circ) S_{\pi\pi}$  and  $S(\text{exo}) = (\cos^2\theta)(\cos^230^\circ) S_{\sigma\sigma} - (\sin^230^\circ) S_{\pi\pi}$ . The angle  $\theta$  is calculable after assumption of a distance between the interacting centers. Values of  $S_{\pi\pi}$  and  $S_{\sigma\sigma}$  were calculated from the formulas of Mulliken, et al. (19), and the values of the resultant overlap integrals are given in table 1, for a bonding distance of 1.54 A.

TABLE 1  
Overlap Integrals for Dicyclopentadiene Interactions\*

<u>Endo</u>					<u>Exo</u>						
		dienophile						dienophile			
diene	<u>a'</u>	<u>b'</u>	<u>c'</u>	<u>d'</u>	diene	<u>a'</u>	<u>b'</u>	<u>c'</u>	<u>d'</u>		
a	.2691	.0411	.0040	.0411	a	.1732	.0174	.0023	.0485		
b	.0643	.0605	.0209	.0270	b	.0128	.0000	.0000	.0050		
c	.0256	.0140	.0209	.0672	c	.0048	.0000	.0000	.0135		
d	.0411	.0049	.0061	.2691	d	.0485	.0015	.0020	.1732		

The relative sizes of the overlap integrals in the table are an indication of the dominating importance of the geometrical relationship of the primary interactions as compared to the secondary interactions. The interaction of the two cyclopentadiene systems leads to a second-order perturbation stabilization energy in which the effects of the primary overlap integrals are even more emphasized in comparison with the secondary overlap integrals. (The second-order perturbation involves a squared overlap term.) If all possible interactions are considered, the stabilization energy difference between endo and exo transition state is .079  $\beta$ , the primary interactions accounting for over 90% of this difference.

\*Refer to figure 1 for atom designations.

For this calculation we used Hückel molecular orbitals with exchange integrals proportional to overlap integrals. Taking a value for the resonance integral,  $\beta$ , of 60 kcal/mole (20) leads to a predicted energy difference between exo and endo transition states of 4.7 kcal/mole, in rough agreement with the experimental results. If one chooses longer interaction distances for the two systems, the energy difference decreases, but we consider the present result adequate to illustrate our point.

It should be noted that the geometrical primary effect which favors endo is still the most important factor, even if a highly unsymmetrical transition state is chosen for the Diels-Alder reaction (7). And we should mention that this interpretation predicts an even higher stereospecificity for the reaction of cyclopentadiene with cyclopentene, than for the reaction of cyclopentadiene with itself. We hope to confirm this point experimentally.

These results emphasize a necessity for a closer consideration of the geometrical relationship of the signs of the interacting orbitals in the transition state of a cycloaddition reaction (6,16). Secondary orbital sign relationships may not be important. It is incorrect to state that "the electronic energies as determined solely by bonding interactions would be the same, or very nearly the same" (9) for both modes of addition. If steric constraints exist for reactants the effect of a geometrical change at a primary bonding site may be of paramount importance.

Finally, we would like to point out again that these considerations offer an explanation other than a rather nebulous steric effect (2) for the preferred formation of endo adducts in various reactions of cyclic monoolefins (13-15) with cyclopentadiene. The principle which we have stated is also useful in understanding the stereospecificity of the Diels-Alder reactions which yield the insecticides isodrin, aldrin, and other similar products (21).

#### Acknowledgement

The authors wish to thank the staff of the computer center of Texas Technological College for their assistance, and for the generous allotment of computer time.

## References

1. W. C. Herndon, C. R. Grayson and J. M. Manion, J. Org. Chem. 32, 526 (1967).
2. For a review of the stereochemistry of the Diels-Alder reaction see J. G. Martin and R. K. Hill, Chem. Rev. 61, 537 (1961).
3. A leading reference to exceptions to the endo rule is J. A. Berson, Z. Hamlet and W. A. Mueller, J. Am. Chem. Soc. 84, 297 (1962).
4. A. Wassermann, Diels-Alder Reactions, Ch. 5, Elsevier Publishing Co., New York (1965); A. S. Onishchenko, Diene Synthesis, Ch. 1, Daniel Davey and Co., Inc., New York (1965).
5. K. Alder and G. Stein. Ann. 504, 222 (1933); 514, 1 (1934); Angew. Chem. 50, 514 (1937).
6. R. Hoffmann and R. B. Woodward, J. Am. Chem. Soc. 87, 4388 (1965).
7. R. B. Woodward and T. J. Katz, Tetrahedron 5, 70 (1959).
8. J. A. Berson, A. Remanick, and W. A. Mueller, J. Am. Chem. Soc. 82, 5501 (1960).
9. C. K. Ingold, Structure and Mechanism in Organic Chemistry, p. 718, Cornell University Press, Ithica, N. Y. (1953).
10. M. G. Ettliger and E. S. Lewis, Texas J. Sci. 14, 58 (1962).
11. C. Walling, Ch. 47 in The Chemistry of Petroleum Hydrocarbons, Vol. III, B. T. Brooks, editor, Reinhold Publishing Co., New York (1955).
12. W. C. Herndon and L. H. Hall, Theoret. chim.Acta 7, 4 (1967).
13. K. B. Wiberg and W. J. Barley, J. Am. Chem. Soc. 82, 6375 (1960).
14. S. J. Cristol, W. K. Seifert, and S. B. Soloway, J. Am. Chem. Soc. 82, 2351 (1960); P. Wilder, Jr., C. F. Culberson and G. T. Youngblood, J. Am. Chem. Soc. 81, 655 (1959).
15. S. B. Soloway, J. Am. Chem. Soc. 74, 1027 (1952).
16. R. Hoffmann and R. B. Woodward, J. Am. Chem. Soc. 87, 2046 (1965).
17. G. S. Hammond, J. Am. Chem. Soc. 77, 334 (1953).
18. M. J. S. Dewar, J. Am. Chem. Soc. 72, 4493 (1950).

19. R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, J. Chem. Phys. 17, 1248 (1949).
20. The value of the resonance integral in the Hückel-type molecular orbital treatment is a moot point. A. Streitwieser, Jr. (Molecular Orbital Theory for Organic Chemists, Chapters 7, 8, and 9, John Wiley and Sons, Inc., New York (1961)) lists a wide range of values. 60 kcal/mole is very close to that derived from vertical resonance energies, polarographic reduction, ultraviolet spectra, and phosphorescence spectra. It also conforms to the value one would obtain using the Mulliken formulation (R. S. Mulliken, J. Am. Chem. Soc. 72, 4493 (1950)).
21. R. L. Metcalf, Organic Insecticides, p. 237, Interscience Publishers, Inc., New York (1955).