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THE MECHANISM OF THE DIELS-ALDER REACTION

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DEWAR'S observation[1] that maleic anhydride reacts with isoprene seventy-one times faster than acrolein in anisol solution at 100° adds a potentially useful punctilio to the body of qualitative and quantitative evidence which long since showed that maleic anhydride is an exceptionally reactive participant in the Diels-Alder reaction.[2,3,4,5]

But the observation is far from providing "very strong evidence for the one-step mechanism for the Diels-Alder reaction, proceeding through a cyclic pseudo-aromatic transition state". Fortunately, recourse to subtle theoretical analysis of the question is unnecessary, since maleic anhydride is well known to be exceptionally reactive in numerous reactions which clearly involve initial attack upon one terminus of its double bond.[6] Of particular relevance

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[1] M. J. S. Dewar, Tetrahedron Letters No. 4, 16 (1959).

[2] M. C. Kloetzel, Organic Reactions Vol. IV, p. 1. John Wiley, New York (1948).

[3] K. Alder, XIVth International Congress of Pure and Applied Chemistry, Experientia Supplementum II, p. 86. Birkhäuser, Basel (1955).

[4] B. Eisler and A. Wassermann, J. Chem. Soc. 1943 (1953).

[5] G. B. Kistiakowsky and J. R. Lacher, J. Amer. Chem. Soc. 58, 123 (1936).

[6] L. H. Flett and W. H. Gardner, Maleic Anhydride Derivatives, Reactions of the Double Bond. John Wiley, New York (1952).

is the fact that in copolymerization experiments a terminal styryl radical reacts very much more readily with maleic anhydride than with any other monomer yet studied (including, for example, methylvinylketone, acrylonitrile, and methyl acrylate).[7,8]

We would hardly cavil at the essential distinction drawn in Dewar's succinct transliteration of a central point made in our paper on the mechanism of the Diels-Alder reaction:[9]

> "In the transition state for their isomerisation, the diene and dienophil are linked by a full bond. In the transition state for their Diels-Alder mechanism, the components are linked by a partial bond. The two transition states are quite dissimilar. It might be added that if they were not dissimilar, then the rearrangement observed by Woodward and Katz could not occur; for the transition state could equally well dissociate into two meleoules of diene."

There remains the assertion, unadorned by experiment or argument:

> "Since the transition state for the rearrangement observed by Woodward and Katz is necessarily different to the transition state for the Diels-Alder reaction, the two reactions are unrelated and no conclusions concerning the mechanism of one can be drawn from that of the other."

We can only regard as bizarre, that view which holds that a process involving the cleavage of one bond of a molecule is unrelated to a process which involves the breaking of that same bond and one other. In our work it was established experimentally beyond question that the cleavage of one of the two bonds which must be broken in a particular instance of the reverse

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[7] C. Walling, Free Radicals in Solution p. 97. John Wiley, New York (1957).

[8] F. R. Mayo and C. Walling, Chem. Rev. **46**, 191 (1950).

[9] R. B. Woodward and T. J. Katz, Tetrahedron **5**, 70 (1959).

Diels-Alder reaction is not concerted with the breaking of the other. This demonstration provides a necessary factual basis, not hitherto accessible either from theory or experiment, for our unsymmetrical mechanism.