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MECHANISM OF THE DIELS-ALDER REACTION

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WOODWARD and Katz[1] have recently proposed a new mechanism for the Diels-Alder reaction, based on a remarkable rearrangement undergone by a hydroxy derivative of the dimer of cyclopentadiene. This mechanism requires the reaction to occur in two stages, the two bonds linking diene to dienophil being formed separately.

If such a mechanism operates, one would expect little difference in reactivity between a monosubstituted ethylene $CH_2=CHX$ and a corresponding disubstituted ethylene XCH=CHX; for only one of the substituents X can be well placed to stabilise the transition state. The situation would be similar to that in radical addition reactions to ethylene derivatives where compounds of the type CHX=CHX do not react more readily than analogous vinyl derivatives $CH_2=CHX$.

If on the other hand the reaction takes place by a one-step mechanism, as many authors have suggested,[2] <u>both</u> substituents in CHX=CHX can stabilise

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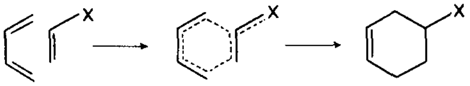
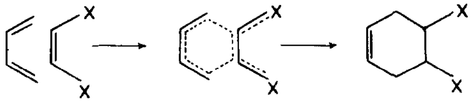
[1] R.B. Woodward and Thomas J. Katz, <u>Tetrahedron</u> **5**, 70 (1959).

[2] cf. Evans, <u>Trans. Faraday Soc.</u> **35**, 824 (1939).

the corresponding symmetrical transition state, equally well, i.e.





Here one would expect XCH = CHX to be much more reactive than CH_2=CHX, the difference in reactivity between them being similar to the difference in reactivity between CH_2=CHX and ethylene itself.

Some years ago I examined the Diels-Alder reactions of isoprene with acrolein and with maleic anhydride. The second order rate constants for reactions in anisole at 100°C were:

acrolein, 1.82×10^{-4} ; maleic anhydride, 1.29×10^{-2} $ml^{-1}s^{-1}$.

Since the conjugative effect of formyl is greater than that of anhydride carbonyl, the difference in reactivity between maleic and acrylic anhydrides would presumably be still greater. Moreover extrapolation of the data reported by Rowley and Steiner[3] for the reaction between butadiene and ethylene gives a calculated second order rate constant at 100°C of 3×10^{-6} $ml^{-1}s^{-1}$. Since isoprene is if anything more reactive than butadiene, it seems clear that the differences in rate constants between ethylene and acrolein, and between acrolein and maleic anhydride, are very similar ($\sim$ 70).

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[3] Rowley and Steiner, *Disc. Faraday Soc.* **10**, 198 (1951).

These observations provide very strong evidence for the one-step mechanism for the Diels-Alder reaction, proceeding through a cyclic pseudo-aromatic[2] transition state.

Full details of this work, in which the rates of the isoprene-maleic anhydride and isoprene-acrolein reaction were measured over a range of temperature in a variety of solvents, will be published shortly. The effect of solvent on the rates of reaction also seemed to favour the one-step mechanism.

It may be added that the evidence given by Woodward and Katz is not directly relevant to the mechanism of the Diels-Alder reaction. 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 molecules of diene.

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.