The Conformational Requirement of αβ-Unsaturated Dieneophiles

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Summary A stabilizing 2-4′-*endo*-interaction in the transition state is supported by the observed faster rate of reaction of hexachlorocyclopentadiene with αβ-unsaturated dieneophiles capable of assuming a cisoid conformation.

IT is well known that, in the Diels–Alder reaction, the diene component must attain a cisoid conformation for reaction to occur.[1] The conformational requirement of the dieneophile is important in an understanding of the Alder *endo*-rule.

A molecular orbital treatment of the thermal dimerization of butadiene by Hoffmann and Woodward[2] has provided an explanation for the preference for *endo*-addition in terms of a symmetry allowed second-order interaction between atoms 3 and 3′ (Figure 1).‡ More recently, calculations by Salem[3] have suggested that the 3–3′ interaction is negligible and that *endo*-preference is due, instead, to a favourable 2–4′ interaction (Figure 2).‡

The latter hypothesis may be tested by a comparison of the reactivities of αβ-unsaturated dieneophiles which can

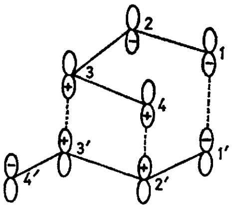

FIGURE 1. *Suggested* endo-*transition state showing* 3–3′ *interaction*

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‡ The figures depict the highest occupied diene orbital (top) and the lowest unoccupied dieneophile orbital (bottom) (refs. 2 and 3). Clearly, the reverse arrangement is also possible.

readily attain the required cisoid conformation with analogues for which this geometry is disfavoured. The choice of diene is important. In order to minimize the complications introduced by side-reactions, the diene component must react preferentially as a diene, it must react selectively with the intended double bond of the dieneophile, it must be reactive enough so that self-condensation of the dieneophile is minimized, and it must be such that the retro-reaction is unimportant.

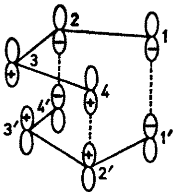


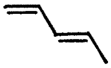
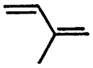
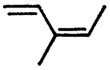
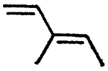
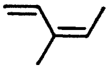
FIGURE 2. *Suggested* endo-*transition state showing* 2–4′ *interaction*

Hexachlorocyclopentadiene (C_5Cl_6) meets the above requirements and was thus chosen for this study. Although it differs from the typical Diels–Alder diene in that it reacts preferentially with electron-rich dieneophiles,[4] we believe that conclusions drawn on the point in question may well be generalized.

Competition experiments were carried out by contacting the dieneophiles with C_5Cl_6 for 4 hr. at 80°. Reaction occurred at the terminal olefinic bond§ giving *endo*-products exclusively. Separate experiments showed that no isomerization or reversal occurs even at 150° and 24 hr.

Our data (Table) do not rule out a 3–3′ interaction nor do they apply to the *endo* preference of non-conjugated dieneophiles.[5] The observed rate enhancements suggest that, in reacting with C_5Cl_6, additional stability in the transition state is achieved when the dieneophile exists in a cisoid conformation. This lends support to a 2–4′ interaction in the Diels–Alder reaction.

Relative rates of reaction of hexachlorocyclopentadiene with selected dienes

Cisoid	non-Cisoid	$k_{\text{cisoid}}/k_{\text{non-cisoid}}$
		2
		3
trans-Octa-1,3,7-triene	*cis*-Octa-1,3,7-triene	4
		11
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§ This selectivity as well as the spectral and chemical properties of the products will be discussed in a forthcoming paper.

[1] J. G. Martin and R. K. Hill, *Chem. Rev.*, 1961, **61**, 537.

[2] R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, 1965, **87**, 4388.

[3] L. Salem, *J. Amer. Chem. Soc.*, 1968, **90**, 553.

[4] J. Sauer and H. Wiest, *Angew. Chem. Internat. Edn.*, 1962, **1**, 269; the atypical nature of C_5Cl_6 may be enhanced by the possibility of spiroconjugation, see H. E. Simmons and T. Fukunaga, *J. Amer. Chem. Soc.*, 1967, **89**, 5208.

[5] An alternative theory has recently been suggested: W. C. Herndon and L. H. Hall, *Tetrahedron Letters*, 1967, 3095.