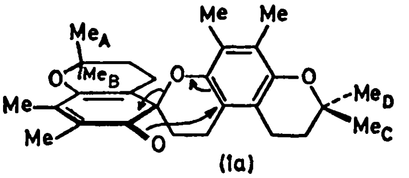
Effects of Transition-state Geometry on the Rates of a [3,3] Sigmatropic Rearrangement

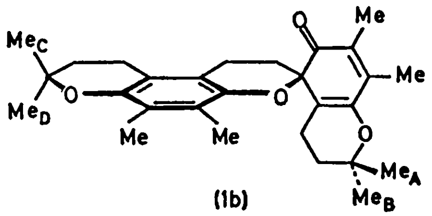
By C. J. DIXIE and I. O. SUTHERLAND
(*Department of Chemistry, The University, Sheffield* S3 7HF)

Summary The free energy of activation for the [3,3] sigmatropic rearrangement of the spirodienones (**3**) → (**4**) is significantly increased by restraints which impose twisting distortions on the boat-like transition state.

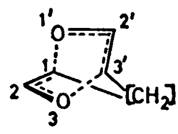
THE degenerate rearrangement (**1a**) → (**1b**) of the spirodienone (**1**), that becomes fast on the n.m.r. time scale at 70°, has been formulated[1] as a [3,3] sigmatropic rearrangement [see arrows and numbering in (**1a**)], although this mechanism has recently been criticised.[2] The transition state for this rearrangement is necessarily boat-like and twisted in that the partial bonds between atoms 1 and 1′ and 3 and 3′ are not parallel owing to the restraints imposed by the bridging methylene groups [see (**2**; $n = 2$) for geometrical relationships between the participating π-systems]. This twisting becomes more severe if positions 3′ and 1 are bridged by only a single methylene group (**2**; $n = 1$) and this would be expected to result in a decrease in the rate of reaction.



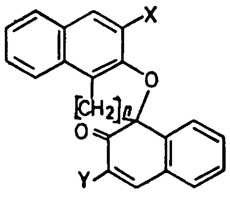
(1a)



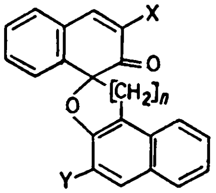
(1b)



(2)

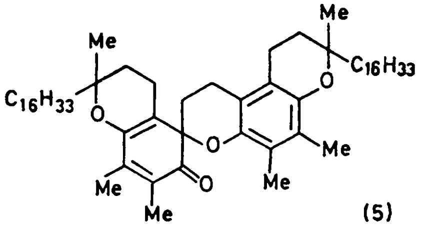


(3)



(4)

a; X = Y = H, n = 1
b; X = Y = H, n = 2
c; X = H, Y = Br, n = 1
d; X = H, Y = Br, n = 2
e; X = Y = OMe, n = 2



(5)

In view of the scarcity of information[3] regarding the effects of steric restraints of this type upon the rates of sigmatropic rearrangements the n.m.r. spectra of the spirans[4] (**3a**) and (**3b**) were studied for possible temperature dependence, but these spectra remained unchanged up to 200° indicating that the degenerate rearrangements (**3a**) $\rightleftarrows$ (**4a**) and (**3b**) $\rightleftarrows$ (**4b**) remained slow on the n.m.r. time scale ($k < ca.$ 1 s^{-1}) (*cf.* ref. 2). The rearrangement was therefore studied using the monobromo-derivatives (**3c**) and (**3d**), synthesised by the addition of bromine to the olefinic double bonds of (**3a**) and (**3b**) followed by base-catalysed elimination of HBr. The rates of attainment of the equilibria between the brominated spirodienones, (**3c**) $\leftrightarrows$ (**4c**) and (**3d**) $\leftrightarrows$ (**4d**), could then be followed by monitoring suitable n.m.r. signals for each isomer of each pair. The results show that the rearrangement of the five-membered spirodienone system (**3c**) $\leftrightarrows$ (**4c**) (k $1{\cdot}4 \times 10^{-5}\,s^{-1}$ in $C_6D_5NO_2$ at 138°, $\Delta G^{\ddagger}$ 33·5 kcal mol^{-1}) is very much slower than that of the six-membered spirodienone system (**3d**) $\leftrightarrows$ (**4d**) (k $0{\cdot}35 \times 10^{-5}\,s^{-1}$ in $C_6D_5NO_2$ at 50°, $\Delta G^{\ddagger}$ 27·0 kcal mol^{-1}). From the relative free energies of activation for these two processes we conclude that the free energy of the transition state (**2**) is significantly changed by the distortion from a boat-like geometry[5] in which the 1–1′ and 3–3′ partial bonds are parallel (the transition states are considered since the ground states in both cases are reasonably free from steric strain).

The above results are also consistent only with a concerted mechanism for the rearrangement process, rather than the acid-catalysed mechanism recently suggested[2] for the [3,3] rearrangement of the spirodienone (**5**), and the rates of the rearrangements of (**3c**) and (**3d**) are not affected by carrying out the reaction in nitrobenzene containing trichloroacetic acid (0·2M). The reaction rate is accelerated, however, by methoxy-substituents, and the degenerate rearrangement of (**3e**) may just be followed by changes in the n.m.r. spectrum of the methoxy-groups (line-broadening *ca.* 2 Hz at 180 °C, $\Delta G^{\ddagger}$ 25·2 kcal mol^{-1}). Substituent effects of this type have been noted in other concerted [3,3] sigmatropic rearrangements.[6] The uncatalysed rearrangement of the spiro-dienone (**1**) is also possibly concerted in view of the reported doublet signal for the geminal methyl groups [Me_A—Me_D, see (**1**)] at temperatures where the degenerate [3,3] rearrangement (**1a**) $\leftrightarrows$ (**1b**) is fast. The methyl groups are therefore only exchanged as $Me_A \leftrightharpoons Me_C$ and $Me_B \leftrightharpoons Me_D$ in accord with the chiral nature of a concerted rearrangement mechanism, rather than a mechanism involving potentially achiral (diradical or dipolar) intermediates which would result in exchange of the methyl groups between all four sites A—D.

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[1] H. A. Lloyd, E. A. Sokoloski, B. S. Strauch, and H. M. Fales, *Chem. Comm.*, 1969, 299.

[2] M. Chauhan, F. M. Dean, K. Hindley, and M. Robinson, *Chem. Comm.*, 1971, 1141.

[3] T. Miyashi, M. Nitta, and T. Mukai, *J. Amer. Chem. Soc.*, 1971, **93**, 3441; J. E. Baldwin and M. S. Kaplan, *ibid.*, p. 3969; 1972, **94**, 668; S. Mageswaran, W. D. Ollis, I. O. Sutherland, and Y. Thebtaranonth, *Chem. Comm.*, 1971, 1494.

[4] R. Pummerer and E. Cherbuliez, *Ber.*, 1919, **52**, 1392.

[5] M. J. S. Dewar and D. H. Lo, *J. Amer. Chem. Soc.*, 1971, **93**, 7201, R. Hoffmann and W.-D. Stohrer, *ibid.*, p. 6941.

[6] R. W. Jemison, W. D. Ollis, I. O. Sutherland, and J. Tannock, forthcoming publications.