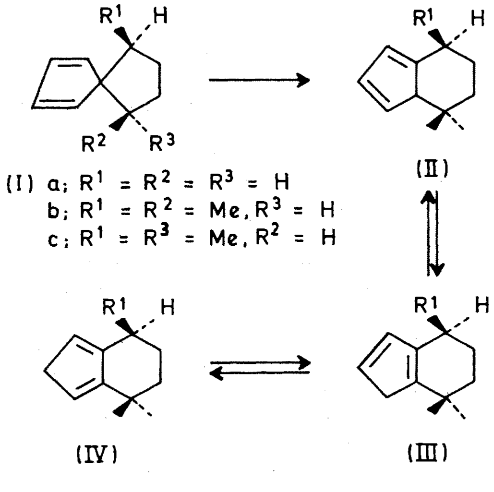
Stereospecificity and Stereochemistry of a Thermal Sigmatropic [1,5]-Shift of an Alkyl Group

By M. A. M. BOERSMA, J. W. DE HAAN, H. KLOOSTERZIEL,* and L. J. M. VAN DE VEN

(*Laboratories of Instrumental Analysis and of Organic Chemistry, University of Technology, Eindhoven, The Netherlands*)

Summary Thermal isomerization of *cis*- and *trans*-6,9-dimethylspiro[4,4]nona-1,3-diene involves a suprafacial, sigmatropic [1,5]-shift of *sp*³ carbon, with retention of configuration.

KINETIC data strongly suggest that thermal [1,5]-migrations of alkyl groups in cyclopentadiene derivatives are sigmatropic processes.[1–5] One of the compounds studied[3,5] is spiro[4,4]nona-1,3-diene (Ia) which yields (III) as the major product, allegedly in two steps—a [1,5]-sigmatropic shift of an alkyl group, (I) → (II), followed by the well-documented[6,7] and rapid [1,5]-sigmatropic shift of hydrogen, (II) → (III). Both shifts are of necessity suprafacial. Shifts of *sp*³ carbon may occur with inversion or retention of configuration. Symmetry selection rules[7] require the former to hold for thermal, suprafacial shifts of order [1,3] and the latter for those of order [1,5]. The former prediction has been confirmed.[8] The stereochemistry of thermal [1,5]-alkyl shifts has so far not been established.[9,10] We now present evidence that the reaction of type (I) → (II), (i) is stereospecific, thus confirming its sigmatropic nature and (ii) occurs with retention of configuration.



(I) a; $R^1 = R^2 = R^3 = H$
b; $R^1 = R^2 = Me, R^3 = H$
c; $R^1 = R^3 = Me, R^2 = H$

(II)

(IV)

(III)

Addition of 1 mol of *meso*-2,5-dibromohexane (m.p. 39°)[11] to 1 mol of cyclopentadiene and 2 mol of sodium amide in tetrahydrofuran yielded *cis*-6,9-dimethylspiro-[4,4]nona-1,3-diene (Ib). The n.m.r. spectrum (100 Hz) proves the *cis*-configuration: the four non-equivalent olefinic protons appear as a complex ABCD pattern. Similar treatment of (±)-2,5-dibromohexane (liq.) yielded the *trans*-compound (Ic), whose two pairs of mutually equivalent olefinic protons appear, by accidental equivalence, as one singlet.

Thermolysis of (Ib) (gas phase, 230—280°, 9—22 s) occurs by first-order kinetics and is approximately 1·5 times slower than for (Ia).[5] G.l.c. showed the formation of three products (II), (III), and (IV) in a ratio 3 : 92 : 5, respectively. Similarly (Ic) gives, at a rate 2·5 times faster than (Ia), another set of three products (II), (III), and (IV) in a ratio 12 : 81 : 7, respectively. The allocation of the double bonds in the two sets of three products, which is not pertinent to the present problem, rests upon spectral data of pure or enriched samples obtained by preparative g.l.c.

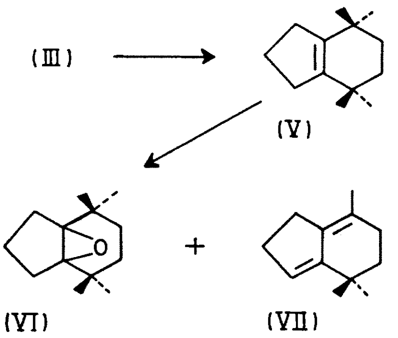
The isomerizations of (Ib) and (Ic) proceed, within the detection limits of the g.l.c. analysis, with complete stereospecificity (estimated to be better than 99% for both reactions).

In order to determine the relative positions of the methyl groups in the two sets of products, each of the major products (III) formed from (Ib) and (Ic) and isolated by preparative g.l.c., was partially hydrogenated (1 mol of H_2, room temperature, Pd–C, Et_2O). The two corresponding 2,5-dimethylbicyclo[4,3,0]non-1(6)-ene compounds (V) were isolated in 74 and 56% yields, respectively.† Each of the

---

† Low temperature n.m.r. spectra (CS_2, 100 MHz, −100°) of the two isomers (V) yielded no conclusive information on the relative positions of the methyl groups.

two compounds (V) upon treatment with *m*-perchlorobenzoic acid ($CHCl_3$, 0°, 10 min) yielded an epoxide (VI), as well as a dehydrogenation product, probably (VII).



The n.m.r. spectrum (100 MHz) of (VI) obtained from (Ib) showed only one methyl doublet (δ 1·03 p.p.m., J 6·8 Hz) in a number of solvents. We conclude, therefore, that it contains two equivalent methyl groups in a *cis*-configuration.‡ The n.m.r. spectrum (in benzene) of (VI) obtained from (Ic) showed two methyl doublets of equal intensity (δ 1·05 p.p.m., J 6·7 Hz and δ 0·85 p.p.m., J 6·7 Hz, respectively). This magnetic non-equivalence of the methyl groups proves their *trans*-configuration in (VI) and thus in the product (III) obtained from (Ic).§ It is thus concluded that the stereospecific rearrangement of (I) to (II) involves a [1,5]-sigmatropic shift of an alkyl group, with retention of configuration.

(*Received, July* 13*th*, 1970; *Com.* 1144.)

---

‡ The relative position of the methyl groups with respect to the oxygen atom cannot be deduced from the n.m.r. spectra.

§ The alternative interpretation of the n.m.r. spectra of the two products (VI) would imply formation of the two possible epoxides from *cis*-dimethyl-(V) in a 1 : 1 ratio as well as accidentally identical chemical shifts for the non-equivalent methyl groups of the epoxide from *trans*-dimethyl-(V). G.l.c. shows the former implication to be improbable; n.m.r. spectra in several solvents rule out the latter. This interpretation is thus rejected as highly improbable.

[1] J. W. de Haan and H. Kloosterziel, *Rec. Trav. chim.*, 1965, **84**, 1594; 1968, **87**, 298.
[2] W. C. Herndon and J. M. Manion, *J. Org. Chem.*, 1968, **33**, 4504.
[3] V. A. Mironov, A. P. Ivanov, Ya. M. Kimelfeld, L. I. Petrovskaya, and A. A. Akhrem, *Tetrahedron Letters*, 1969, 3347.
[4] J. M. E. Krekels, J. W. de Haan, and H. Kloosterziel, *Tetrahedron Letters*, 1970, 2751.
[5] L. M. Dané, J. W. de Haan, and H. Kloosterziel, *Tetrahedron Letters*, 1970, 2755.
[6] W. R. Roth, *Tetrahedron Letters*, 1964, 1009.
[7] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie–Academic Press, Weinheim, 1970.
[8] J. A. Berson and G. L. Nelson, *J. Amer. Chem. Soc.*, 1967, **89**, 5503.
[9] J. A. Berson and M. R. Willcott, III, *J. Amer. Chem. Soc.*, 1966, **88**, 2494.
[10] Ref. 7, p. 125.
[11] J. Wislicenus, *Ber.*, 1901, **34**, 2565.