Stereochemistry of the Hydrogen–Deuterium Base-catalysed Exchange and Conformation of Cyclic Five-membered Sulphonium Cations

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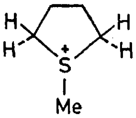
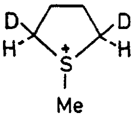
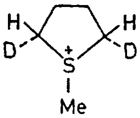
Summary Nuclear Overhauser experiments indicate that the ring protons of cation (**Ia**) which undergo fast base-catalysed exchange are *cis* to S–Me; values of J_{gem} for conformationally rigid thiolanium cations suggest a half-chair conformation for (I).

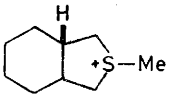
The differential reactivity in H–D exchange reactions of the diastereotopic α ring protons in 1-methylthiolanium iodide has been reported.[1] In view of the interest of this observation, in connection with the problem of the stereochemical properties of species possessing adjacent lone pairs and/or polar bonds,[2] it was important to establish the stereochemistry—*cis* or *trans* to the *S*-methyl group—of those protons which exchanged more rapidly.†

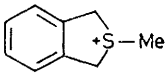
^{1}H N.m.r. evidence is not unambiguous[3] and we now offer evidence derived from nuclear Overhauser experiments. Two specifically deuteriated derivatives of (Ia), (Ib), and (Ic) (whose configurations are represented on the basis of the evidence below) have been prepared by taking advantage of the differential exchange rates of the diastereotopic protons. Irradiation at the *S*-methyl signal for compound (Ib) gives no important N.O. enhancement (+2 ± 1%).


(Ia)


(Ib)


(Ic)


(II)


(III)

The enhancement for (Ic) is +12 ± 1%. Since the magnitude of the N.O. enhancement depends on the distance

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† We appear to have grossly underestimated the reactivity of the slower pair of α ring H's.[1a,b] Recently, using a very accurate mass spectrometric method, Eliel[1c] has been able to set the reactivity ratio to 30 : 1 rather than > 400 : 1 as originally reported.[1a,b] Re-examination of the kinetics of exchange by an improved n.m.r. method allows us now to eliminate the discrepancy and roughly confirm Eliel's result.

between the mutually relaxing protons,[4] the structure of cations (Ib) and (Ic) are as depicted; the diastereotopic protons undergoing rapid exchange are those *cis* to the *S*-methyl group in agreement with earlier, tentative suggestion.[1a]

Coupled with this assignment is evidence on the preferred conformation of the cation. We had previously expressed a preference for the half-chair‡ rather than the envelope conformation after consideration of torsional and angular strain[1a] and we confirm this choice on the basis of values of the geminal coupling constants for α-methylene protons in the conformationally fixed cations (II) and (III). For cation (II), *trans* ring fusion determines the rigid half-chair conformation and the two J_{gem} values are 12 and 13 Hz. For cation (III), in which the *o*-phenylene junction at C(3)–C(4) allows only the envelope conformation, J_{gem} is 16·0 Hz. These values are consistent with the theory of geminal coupling constants for protons adjacent to a heteroatom,[6] as maximum staggering at positions 1, 2, and 5 is achieved in the envelope conformation. On this basis, (Ia), J_{gem} 13·0 Hz, is assigned the half-chair conformation.

The knowledge of the conformation of (I) as well as the stereochemistry of the rapidly exchanging protons allows a test of the Wolfe and Czimadia theory.[2]

Although, as previously argued,[1a,b] our findings conform to the theory, the recent data[7] on the effect of the solvent on the relative reactivity of diastereotopic protons (α to a sulphoxide function) severely limit the value of the present test.

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‡ The term "half-chair" actually implies a C_2 symmetry axis and is therefore improper for a sulphonium cation because of the pyramidal geometry around sulphur. Although the term "twist envelope" has been suggested as more appropriate,[5] we will continue to use the more descriptive term "half-chair."

[1] (a) G. Barbarella, A. Garbesi, and A. Fava, *Helv. Chim. Acta*, 1971, **54**, 341; (b) *ibid.*, 1971, **54**, 2297; (c) E. L. Eliel and O. Hofer, unpublished results, quoted by E. Eliel, *Angew. Chem. Internat. Edn.*, 1972, **11**, 748.

[2] A. Rauk, S. Wolfe, and I. G. Czimadia, *Canad. J. Chem.*, 1969, **47**, 113; S. Wolfe, A. Rauk, L. M. Tel, and I. G. Czimadia, *J. Chem. Soc.* (*B*), **1971**, **136**; S. Wolfe, L. M. Tel, J. H. Liang, and I. G. Czimadia, *J. Amer. Chem. Soc.*, 1972, **94**, 1361; S. Wolfe, *Accounts Chem. Res.*, 1972, **5**, 102.

[3] R. R. Fraser and F. I. Schuber, *Canad. J. Chem.*, 1970, **48**, 663.

[4] R. A. Bell and J. K. Saunders, *Canad. J. Chem.*, 1968, **46**, 3421.

[5] P. Haake, J. P. McNeal, and E. J. Goldsmith, *J. Amer. Chem. Soc.*, 1968, **90**, 715.

[6] J. A. Pople and A. A. Bothner-by, *J. Chem. Phys.*, 1965, **42**, 1339; R. Cahill, R. C. Cookson, and T. A. Crabb, *Tetrahedron*, 1969, **25**, 4681.

[7] T. Durst, R. R. Fraser, M. R. McClory, R. B. Swingle, R. Viau, and Y. Y. Wigfield, *Canad. J. Chem.*, 1970, **48**, 2148; R. R. Fraser, F. J. Schuber, and Y. Y. Wigfield, *J. Amer. Chem. Soc.*, 1972, **94**, 8794.