Preparation of 2,8-Polymethylene-benzohomotropylium Cations

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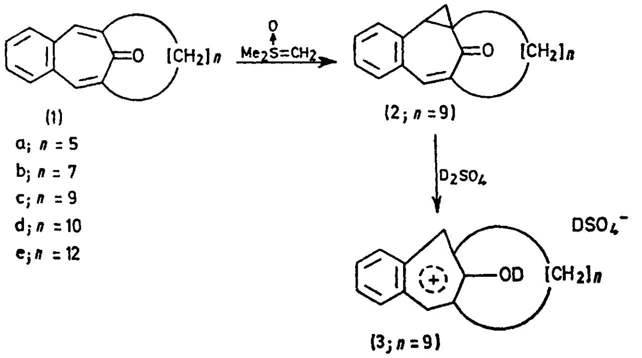
Summary Evidence for the existence of 2,8-polymethylene-benzohomotropylium cations is described.

THERE has been considerable interest recently in the chemistry of homoaromaticity, homotropones, and homotropylium cations.[1] We report here the preparation of 2,8-polymethylene-benzohomotropylium cations (**3**). (*Cf.* prior preparations of 2,7-polymethylene-4,5-benzotropylium perchlorates[2] and 2,7-polymethylenebis-4,5-benzotropylium perchlorates.[3])

The 2,7-polymethylene-4,5-benzotropones (**1a**)—(**1e**) were prepared by the reaction of phthalaldehyde with cyclic ketones.[4] Dropwise addition of a solution in tetrahydrofuran (THF) of dimethyloxosulphonium methylide (3·6 mmol), prepared as described previously,[5] to a well stirred solution of the ketone (**1c**) (5 mmol) in THF under nitrogen at 20° afforded a white precipitate. After 6 h, the precipitate was filtered off and the filtrate was evaporated to dryness under reduced pressure. The resulting white solid was crystallized from methanol to give the polymethylene-homobenzotropone (**2**)† (50%), m.p. 131—132°. Its i.r. [ν_{max} 1640 (C=O) and 1580 (C=C) cm^{-1}] and n.m.r. spectrum [δ 1·0—2·6 (18H, m, CH$_2$), 2·9—3·3 (2H, m, cyclopropyl-CH_2), 6·6 (1H, d, cyclopropyl-CH), and 7·1—7·4 p.p.m. (5H, m, aromatic and olefinic H)] were also consistent with the assigned structure. The homotropone (**2**) was treated with D$_2$SO$_4$ and the resulting green solution was immediately analysed by n.m.r. spectroscopy. The n.m.r. spectrum [δ 1·0—2·4 (18H, m, CH$_2$), 3·8—4·4 (2H, m, 3-H), and 7·6—8·0 p.p.m. (6H, m, remaining protons)] indicated complete delocalisation of the positive charge in (**3**). Our results agree with those reported by Sugimura *et al.*[6] on 4,5-benzohomotropylium cations. The benzohomotropylium cation (**3**) is quite unstable and difficult to isolate.



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† Satisfactory elemental analyses were obtained.

[1] R. Pettit and J. D. Holmes, *J. Amer. Chem. Soc.*, 1963, **85**, 2531; O. L. Chapman and R. A. Fugiel, *ibid.*, 1969, **91**, 215; J. L. Rosenberg, J. E. Mahrer, and R. Pettit, *ibid.*, 1962, **84**, 2842; R. F. Childs and S. Winstein, *ibid.*, 1967, **89**, 5348; W. Merk and R. Pettit, *ibid.*, 1968, **90**, 814.

[2] R. E. Harmon, R. Suder, and S. K. Gupta, *Canad. J. Chem.*, 1970, **48**, 195.

[3] R. E. Harmon, R. Suder, and S. K. Gupta, *Chem. Comm.*, 1969, 1170.

[4] von E. Kloster-Jensen, N. Tarkoy, A. Eschenmoser, and E. Heilbronner, *Helv. Chim. Acta*, 1956, **39**, 786.

[5] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 1965, **87** 1353.

[6] Y. Sugimura, N. Soma, and Y. Kishida, *Tetrahedron Letters*, 1971, 91.