

Preparation of 2,8-Polymethylene-benzohomotropylum Cations

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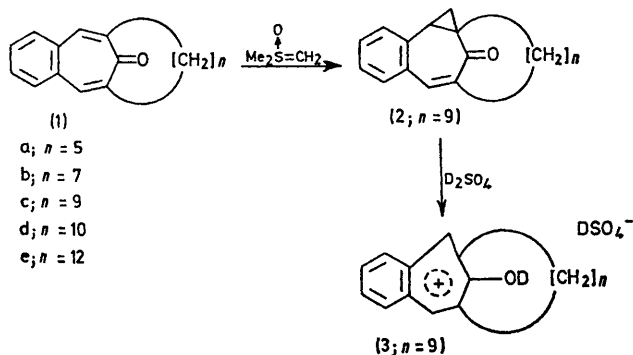
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Summary Evidence for the existence of 2,8-polymethylene-benzohomotropylum cations is described.

THERE has been considerable interest recently in the chemistry of homoaromaticity, homotropones, and homo-

tropylum cations.¹ We report here the preparation of 2,8-polymethylene-benzohomotropylum cations (**3**). (*Cf.* prior preparations of 2,7-polymethylene-4,5-benzotropylum perchlorates² and 2,7-polymethylenebis-4,5-benzotropylum 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 precipi-

† Satisfactory elemental analyses were obtained.

tate 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_2SO_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-benzohomotropylum cations. The benzo-homotropylum cation (**3**) is quite unstable and difficult to isolate.

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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.