Preparation of 2, 7-Polymethylenebis-4,5-benzotropylium Perchlorates

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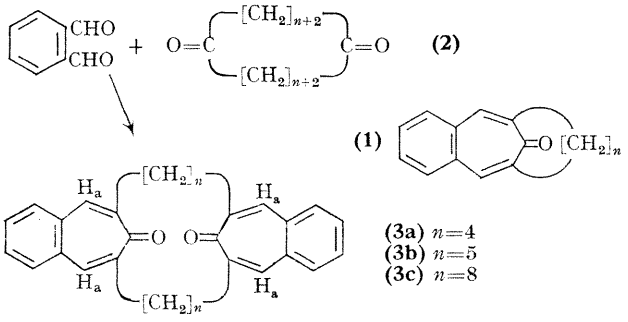
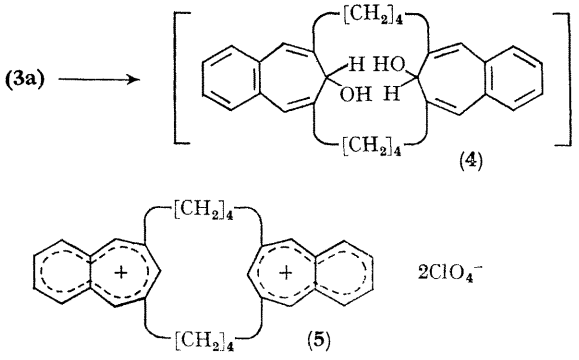
Summary The synthesis of 2,7-tetramethylene-4,5-bis-benzotropylium perchlorate, an interesting example of a compound containing two positive charges within the same molecule, has been accomplished.

WE report the synthesis 2,7-polymethylenebis-4,5-benzotropones (3) and 2,7-polymethylenebis-4,5-benzotropylium perchlorate (5). The latter compounds contain two positive charges within the same molecule. The preparation of simple 2,7-polymethylene-4,5-benzotropones (1) has been reported.[1]



(3a) $n=4$
(3b) $n=5$
(3c) $n=8$

The synthesis of 2,7-polymethylenebis-4,5-benzotropones (3) was achieved by the condensation of phthalaldehyde (2 mol.) and cyclic dimetric ketones (2) (1 mol) (reflux, EtOH) in the presence of a saturated solution of NaOH in MeOH and recrystallised (41—83%) from tetrahydrofuran. The i.r. spectra of these bisbenzotropones (3) (Table) showed the carbonyl absorption at 1595—1605 cm.$^{-1}$, suggesting that the seven-membered tropone ring is planar. (If the tropone ring is non-planar, electronic delocalization in it is inhibited



† The n.m.r. spectra were obtained with a Varian A-60 spectrometer. A Beckman IR-8 spectrophotomer was used to determine the i.r. spectra.

TABLE

Compound*	M.p. (°C)	Yield %	I.r.† (Nujol) cm.$^{-1}$ (C=C)	(C=O)	N.m.r.‡ $CD_3 \cdot CN(\delta)$
(3a)	347—350	83	1623	1595	1·2—2·9 (m, 16H, C*H*$_2$), 7·0 (s, 4H, *H*a), 7·2—7·6 (m, 8H, Ar*H*)
(3b)	265—266	54	1623	1595	1·0—2·9 (m, 20H, C*H*$_2$), 7·1 (s, 4H, *H*a), 7·3 (m, 8H, ArH)
(3c)	208—209	41	1626	1605	1·0—2·9 (m, 28H, C*H*$_2$), 7·4 (s, 4H, *H*a), 7·5—7·7 (m, 8H, ArH)

* All gave satisfactory analyses; † Beckman IR-8; ‡ Varian A-6°.

and the carbonyl absorption in the infrared spectrum should appear at 1650—1700 cm^{-1}.) In the case of simple 2,7-polymethylene-4,5-benzotropones (1), the results based on i.r. spectral analyses of the carbonyl absorption had indicated that if n is small (<7), the tropone ring is non-planar.[1]

Reduction of the carbonyl functions of (3a) was achieved with the help of lithium aluminium hydride. The resulting dihydroxy compound (4) isolated as an oil in 60% yield, was treated with an ethereal solution of 70% perchloric acid to afford crystalline 2,7-tetramethylenebis-4,5-benzotropylium perchlorate (5) in 50% overall yield for the two steps.

The perchlorate (5) [m.p. 231° (explodes)] was obtained as bright yellow crystals by recrystallization from acetonitrile–acetic acid. Elemental analyses (C, H, Cl) indicated the presence of two moles of acetic acid as solvent of crystallization; this was susbtantiated by the presence of a sharp carbonyl absorption at 1710 cm^{-1} in the i.r. spectrum. The u.v. spectrum (98%-H_2SO_4) gave a sharp absorption maxima at 294 nm (ϵ 125,000)[4] (*cf.* benzotropylium perchlorate 282 nm (ϵ 55,000)[2]).

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‡ The u.v. spectrum was taken on a Cary 14 spectrophotometer.

[1] von Else Kloster-Jensen, N. Tarkoy, A. Eschenmoser, and E. Heilbronner, *Helv. Chim. Acta*, 1956, **39**, 786.
[2] A. Eschenmoser, E. Heilbronner, and H. H. Rennhard, *Chem. and Ind.*, 1955, 415.