Synthesis of Benzo[3,4]cyclobuta[1,2-*a*]benzo[*d*]tropylium Cation, a Homobiphenylene Cation

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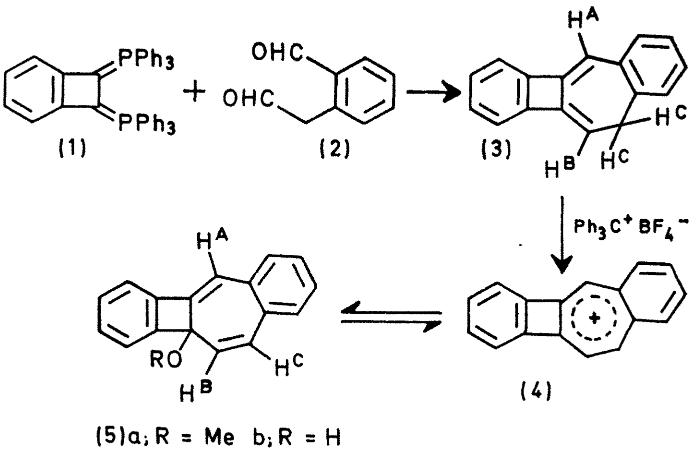
Summary The synthesis and some properties of the benzo[3,4]cyclobuta[1,2-*a*]benzo[*d*]tropylium cation (**4**) are described.

WHEREAS the synthesis of the norbiphenylene anion, an analogue of biphenylene in which one of the phenyl rings has been replaced by the 6π-electron cyclopentadienyl anion, has been described,[1] the only reported attempts to prepare the corresponding tropylium analogue have been unsuccessful.[2,3] We now report the synthesis of the benzo[3,4]-cyclobuta[1,2-*a*]benzo[*d*]tropylium cation (**4**), a homobiphenylene cation in which one of the phenyl rings in biphenylene has been replaced by the benzotropylium cation.



A Wittig reaction between 1,2-bis(triphenylphosphoranyl)-benzocyclobutene (**1**)[4] and homophthalaldehyde (**2**)[5] gave, among other products, (**3**) (2%), m.p. 136—137°. The structure (**3**) is based on its physical and chemical properties.† The n.m.r spectrum (CCl_4) showed signals at τ 2·95 (m, 8H, benzenoid), 3·50 (s, 1H, H^A), 4·36 (t, 1H, *J* 5·5 Hz, H^B), and 6·37 (d, 2H, *J* 5·5 Hz, H^C), and the electronic spectrum [λ_{max} (EtOH) 246 (ϵ 30,000), 325 (11,000), 341 (11,700), and 359 nm (9000)] resembled that of other dimethylene-benzocyclobutenes.[6]

Treatment of a solution of (**3**) in CD_3CN with trityl fluoroborate gave a deep green solution containing the cation (**4**). The n.m.r. spectrum showed a doublet at τ 1·09, signals in the aromatic region (τ 1·7—3·2), and no signals at higher field except for those of the residual solvent protons. The aromatic region contains signals due to triphenylmethane, but attempts to separate the salt from this hydrocarbon were unsuccessful. The solution of (**4**) was therefore quenched with methanol to give the liquid methyl ether (**5a**) (60%). Structure (**5a**) was based on spectral properties.† The n.m.r. spectrum (CCl_4) showed signals at τ 2·72—3·05 (8H, m, benzenoid), 3·44 (d, 1H, *J* 10 Hz, H^C), 3·45 (s, 1H, H^A), 3·94 (d, 1H, *J* 10·5 Hz, H^B), and 7·00 (3H, s, OCH_3), and the electronic spectrum showed λ_{max} (EtOH) 250 (ϵ 16,700) and 317 nm (6300).

Treatment of the ether (**5a**) with conc. H_2SO_4 regenerated the cation (**4**), the n.m.r. spectrum being similar to that obtained by the trityl fluoroborate method, except that the phenyl protons of triphenylmethane were absent. The electronic spectrum of the cation (**4**) showed $\lambda_{max}(H_2SO_4)$ 263 (ϵ 17,500), 295 (11,300), 344 (19,700), 428 (4100), 456 (5300), and 598 nm (750).‡ The electronic spectrum indicates that (**4**) is more extensively conjugated than the benzotropylium cation.[7]

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† Satisfactory analytical or high resolution mass spectral data have been obtained for all new compounds isolated.

‡ These are minimal molar absorptivity values, being based on complete conversion of the ether (**5a**).

The $\langle\!\langle pK \rangle\!\rangle$ of the cation (**4**), determined by the method of Meuche *et al.*,[8] was found to be $-1{\cdot}3$. Comparison with the $\langle\!\langle pK \rangle\!\rangle$ values for the benzotropylium cation $(+1{\cdot}7)$[7] and the 1,2:4,5-dibenzotropylium cation $(-1{\cdot}9)$[7] indicates that the fusion of the benzocyclobutadiene group has a similar destabilising effect on the tropylium cation as the fusion of a benzene ring. The difference in the $\langle\!\langle pK \rangle\!\rangle$ values shows that the cation (**4**) is less readily formed (*ca.* 4·0 kcal mol^{-1}) from the alcohol (**5b**) than is the benzotropylium cation from its corresponding alcohol.

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