

Formation of a Benzocyclopropenium Ion: Ionisation of 1,1-Dichloro-2,5-diphenylcyclopropabenzene

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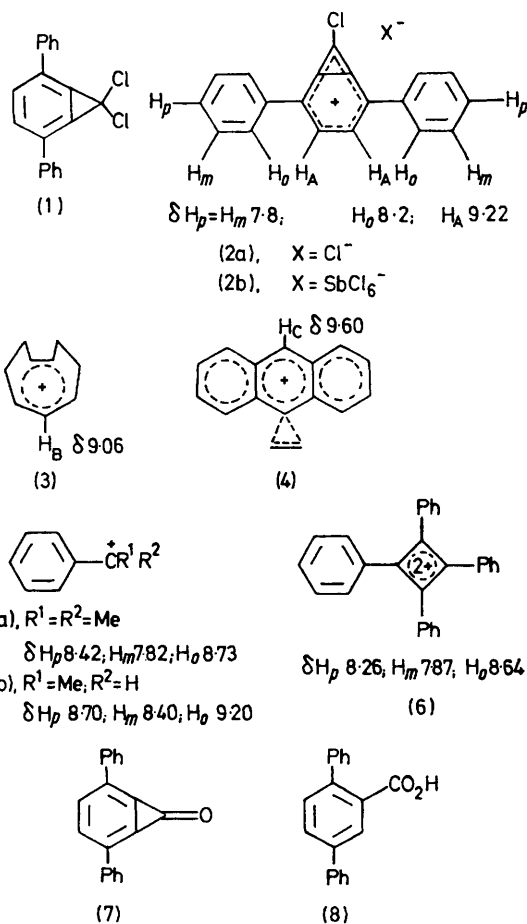
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Summary Dissolution of the cyclopropabenzene (1) in fluoro-sulphonic acid results in ionisation and formation of the aromatic cation (2a); with antimony pentachloride, compound (1) affords an orange solid which is proposed as the salt (2b).

THEORETICAL considerations have predicted that the cation derived from cyclopropabenzene should be stabilised by π -electron delocalisation despite the strain associated with the ring-system.¹ However, the stabilities of the parent benzocyclopropenium ion and its associated derivatives are uncertain and, although there is a body of evidence to support their existence, both as fragment ions in the mass spectra of various cyclopropabenzene² and as reactive intermediates in solution,³ no cation from a cyclopropabenzene has been observed directly.

Dissolution of (1)⁴ in freshly distilled fluoro-sulphonic acid at *ca.* -40° (under nitrogen and in a dry box) gives rise to a solution which is extremely sensitive to moisture and temperature. However, the ¹H n.m.r. spectrum of the solution, measured at -17° with minimal decomposition,[†] provides direct evidence for the benzocyclopropenium ion (2a) and consists of a singlet at δ 9.22 (2H) and multiplets at 8.2 (4H) and 7.8 (6H), respectively. The singlet is assigned to the centre ring protons H_A which are deshielded by about 1.5 p.p.m. compared with (1). While there are no close analogues of (2) available for comparison, the chemical shift of H_A is consistent with that observed for H_B (δ 9.06) and H_C (δ 9.60) in the ions (3)⁵ and (4),⁶ respectively. The multiplets at δ 8.2 (4H) and 7.8 (6H) in the spectrum of (2) are assigned to the H_o, and the H_m + H_p protons of the phenyl substituents, respectively. The occurrence of the *ortho* protons of (2) at lower field than those in the *meta* or *para* positions is consistent with the data recorded for the benzylic cations (5)⁷ and the tetraphenyl-



[†] A peak at δ 8.5 in the spectrum of (2) results from slight decomposition.

cyclobutadiene dication (6).⁸ Furthermore, the presence of H_o , H_m , and H_p at higher field than their counterparts in (5) and (6) indicates a lower degree of charge delocalisation into the phenyl substituents of (2) than in (5) or (6). This conclusion appears reasonable since (5) and (6) are expected to derive much more stabilisation from the pendant aromatic rings than is a benzocyclopropenium ion.

Attempts to isolate derivatives of cation (2) from reactions of (1) with suitable Lewis acids have met with mixed success. Addition of antimony pentachloride to a dichloromethane solution of (1) gives a moisture sensitive orange precipitate which, unlike (1), decomposes rapidly to terphenic acid (8).⁴ The orange solid, which can be stored in sealed ampoules under nitrogen, is proposed as the salt (2b)† and, when dissolved in precooled chlorosulphonic acid,

gives rise to a ¹H n.m.r. spectrum identical with that of (2a). Attempts to determine the mass spectrum of (2b) were frustrated by its rapid decomposition. However, the spectra obtained gave ions at *m/e* 256 (base) and 274 (25%) compatible with the oxocyclopropabenzene (7) and the acid (8), respectively. Since the mass spectrum of (8) shows no significant fragment ion at *m/e* 256, these data strongly suggest that the reaction of (2b) with moisture proceeds to (8) via (7).

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† An alternative formulation of (2b) would be a charge-transfer complex. However, the stability of the compound has thus far prevented conductivity determinations.

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