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BENZO[3,4]CYCLOBUTA[1,2-b]CYCLOHEPTATRIENE AND BENZO[3,4]CYCLOBUTA[1,2]TROPYLIUM CATION

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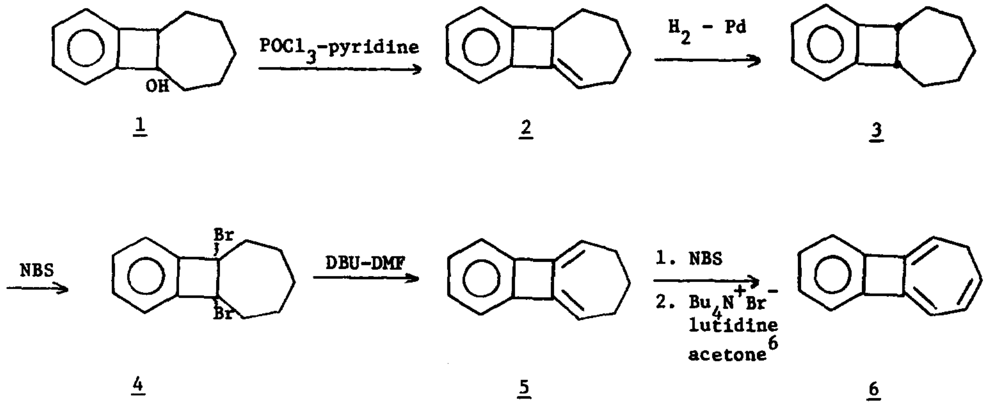
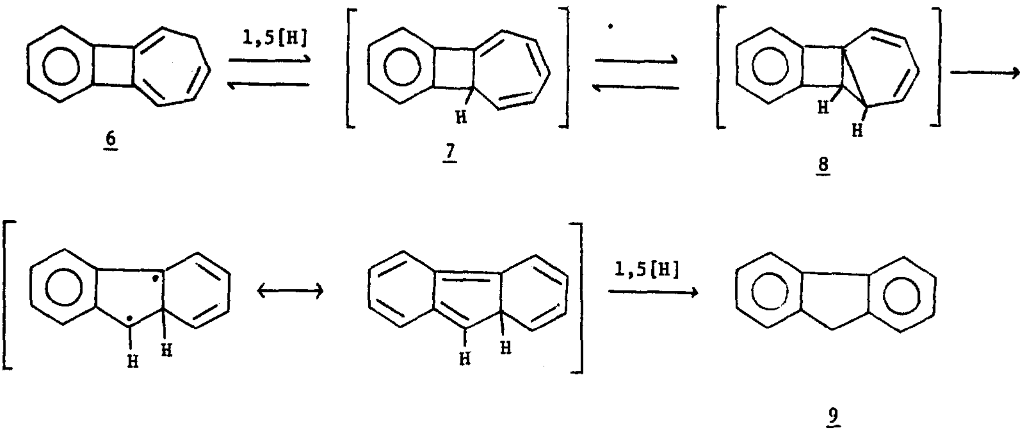
Recent interest in aromatic analogues of biphenylene in which one benzenoid ring is replaced by five membered 6π electron systems[1,2] prompts us to report our synthesis of the title triene 6 and the derived tropylium salt 11. The latter is a derivative of biphenylene in which a benzenoid ring is replaced by a seven membered 6π electron system. A benzo-annellated derivative of 11 has been described recently[3].



Scheme 1

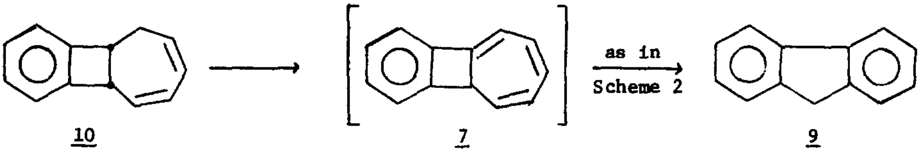
The preparation of triene 6 is outlined in Scheme 1. Alcohol 1 is readily available[4] and hydrocarbon 3 has already been prepared by other routes[5]. Yields were high, except for the last bromination-dehydrobromination step (20%). Satisfactory analytical and spectral data were obtained for all new compounds. The electronic spectrum of triene 6 (cyclohexane) showed a broad maximum at 237-256 nm (log ε 4.42), and further absorption at 315 (2.64), 328 (2.72), 343 (2.72), 358 (2.46), and 376 nm (1.99); pmr spectrum (90 MHz, CCl$_4$, TMS internal standard):

δ 7.10 (apparent s, 4H, aromatic), 5.90-5.16 (m, 4H, vinyl) and 3.21 (d of t, J = 1.5 and 4.5 Hz, 2H, methylene). When 6 was injected onto a vapour phase chromatographic column at 170°, fluorene 9 was eluted. A possible mechanism for this transformation is shown in Scheme 2. A related mechanism has been proposed to explain the formation of ethyl fluorene-2-carboxylate from the thermal decomposition of ethyl diazoacetate in the presence of biphenylene[7]. The mechanism in Scheme 2, however, does not involve intermediates possessing benzocyclobutadienoid double bonds.

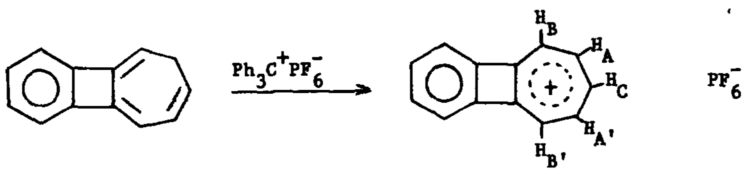


Scheme 2

Reaction of diene 10[5] with NBS in carbon tetrachloride, followed by dehydrobromination with $Bu_4N^+Br^-$ and lutidine in acetone[6] at 80° gave fluorene (42%). It is likely that triene 7 is an intermediate in this conversion. The 7 → 9 transformation is therefore a remarkably facile process.

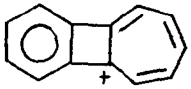


Treatment of triene 6 with trityl hexafluorophosphate in acetonitrile, followed by addition of ether gave the tropylium salt 11 as purple crystals, m.p. 131-2° dec. (35%); $\lambda_{max}^{CH_3CN}$ 226 (log ε 4.24), 233 (4.18), 279 (4.28), 328(4.30), 388 (3.67), 399 (3.67) and 510 nm (2.86).



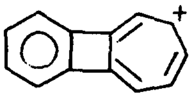
6 11

The pmr spectrum of 11 is shown in the Figure. On the basis of its appearance and chemical shift, the two proton multiplet centred at δ 8.20 is tentatively assigned to H_A and $H_{A'}$, and the three proton signal at δ 7.80 to 7.48 to the remaining protons in the seven membered ring. Canonical forms 12 and 13 should contribute to a greater extent than 14 and 15 (which have a benzocyclobutadienoid double bond) to the overall structure of cation 11. Hence H_A and $H_{A'}$ should be more strongly deshielded than H_B, $H_{B'}$ and H_C due to the higher positive charge at the carbon atoms bearing H_A and $H_{A'}$.



12

2 structures



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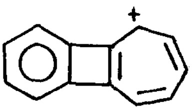

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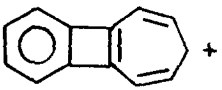
2 structures



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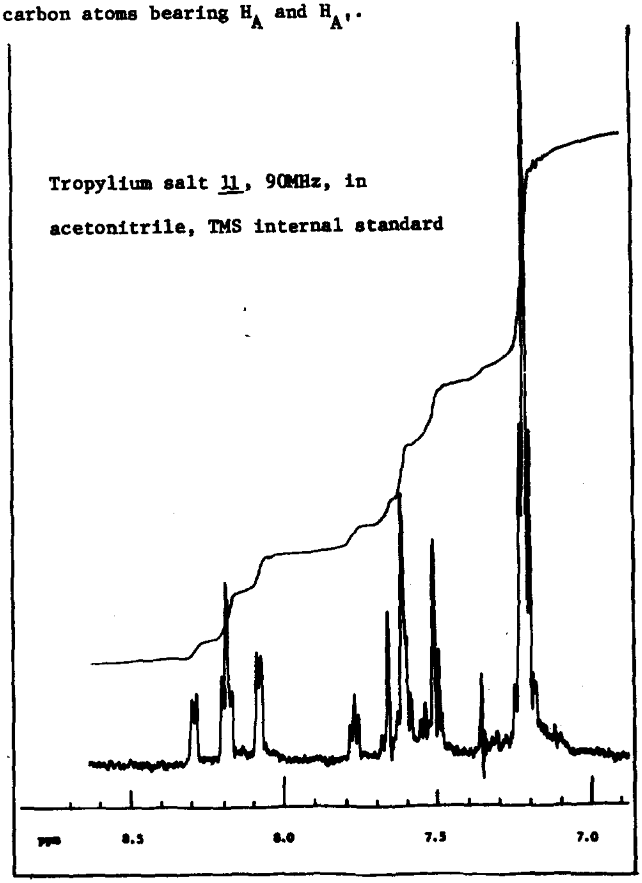
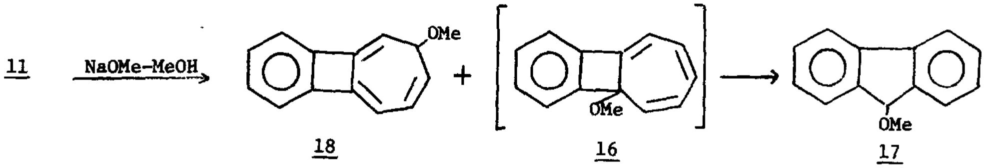


Tropylium salt 11, 90MHz, in

acetonitrile, TMS internal standard

Quenching of 11 with sodium methoxide-methanol gave 9-methoxyfluorene 17 (75%) and another methyl ether (25%) tentatively assigned structure 18. Lack of material has so far prevented unambiguous chemical characterisation of the latter product.



The formation of 9-methoxyfluorene can readily be explained in terms of methoxide ion attack at the tertiary centre of 11 to yield 16, which then suffers rearrangement of type outlined in Scheme 2.

Deuterium labelling experiments are in progress to confirm the mechanisms of the rearrangements described in this paper, and to assist in a full analysis of the pmr spectrum of cation 11.

Acknowledgement.

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References.

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