Nonafulvalenes. The Synthesis of 3,4:5,6:9,10:13,14-Tetrabenzoheptanonafulvalene and 1,2:3,4:9,10:13,14-Tetrabenzoheptanonafulvalene

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Summary The preparation of two heptanonafulvalenes is described.

DESPITE the fact that the *cis*-nonatetraenyl anion has been known for some time,[1] no nonafulvalenes and only one nonafulvene[2] have been prepared. The main obstacle to the synthesis of such compounds has been the ready rearrangement of cyclononatetraene to 8,9-dihydroindene.[3] The recent preparation of 3,4:5,6-dibenzocyclononatetraene,[4,5] which does not readily undergo such a rearrangement, encouraged us to investigate the synthesis of benzannelated nonafulvalenes. We now describe the synthesis of 3,4:5,6:9,10:13,14-tetrabenzoheptanonafulvalene (**5**) and 1,2:3,4:9,10:13,14-tetrabenzoheptanonafulvalene (**6**).

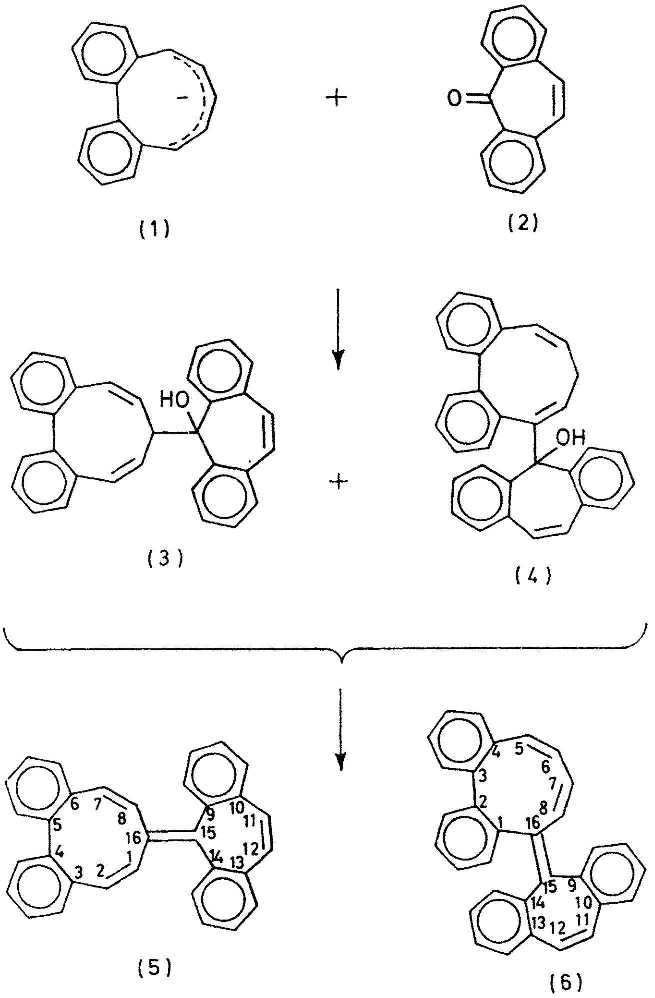
The anion (**1**)[4] (prepared by treatment of 3,4:5,6-dibenzocyclononatetraene with BuLi) was treated with an equimolar amount of 2,3:6,7-dibenzotropone (**2**) in tetrahydrofuran at 20°. The mixture was stirred at 20° for 6 h, then heated for 2 h at reflux, and the products were isolated by t.l.c. on silica. A mixture of alcohols (25%) was obtained, the mass spectrum of which showed a parent peak at *m/e* 424 ($C_{32}H_{24}O$). The n.m.r. spectrum indicated that the major components were (**3**) and (**4**) together with double-bond isomers.

The mixture of alcohols was boiled in benzene containing toluene-*p*-sulphonic acid, and the products separated by t.l.c. on silica. The resulting hydrocarbon fraction was re-chromatographed on $AgNO_3$ impregnated silica plates,[6] when two compounds (**5**) (29%) and (**6**) (59%)† were isolated. The structural assignments are based on the spectral properties.

The compound (**5**) (m.p. 55—57°) is a yellow crystalline solid, which has a mass spectral parent peak at *m/e* 406·1720 ($C_{32}H_{22}$ requires 406·1721). The u.v. spectrum (EtOH) has absorption maxima at 262 sh (ϵ 8700), 309 sh (4500), 323 (3800), 342 (2100), and 358 nm (2000). The n.m.r. spectrum (100 MHz, CCl_4) shows a multiplet at τ 2·62—3·48 (20 H) and a doublet at τ 3·95 (2H, *J* 10·5 Hz, 2-H, 7-H). The 1-H, 8-H protons appear to be shifted downfield, presumably due to deshielding by the fused benzo-groups on the 7-membered ring.

The compound (**6**) (m.p. 186—188° dec.) is an orange crystalline solid, which has a mass spectral parent peak at *m/e* 406·1721. The u.v. spectrum (EtOH) has absorption maxima at 250 (ϵ 12,200), 290 (12,300), and 325 nm (4200). The n.m r. spectrum (100 MHz, CCl_4) shows a multiplet at τ 2·38—3·42 (17H), a doublet at τ 3·66 (1H, *J* 7 Hz), a doublet at τ 3·91 (1H, *J* 12 Hz), and multiplets at τ 4·32 (2H, *J* 4·5 Hz) and 4·68 (1H, *J* 12, 4·5 Hz). This spectrum is in accord with the assigned structure, the doublet at τ 3·66 appearing to be due to an aromatic proton which is shielded as a consequence of steric crowding.

Both of the compounds (**5**) and (**6**) thus appear to be nonplanar, nonaromatic molecules, the dipolar forms making little contribution to the structures. Models of (**6**) indicate that the system is considerably crowded. Attempts to protonate (**6**) with CF_3CO_2H or $HClO_4$ gave no indication of the formation of a cation.



We thank the Science Research Council for a studentship (to K.A.K.).

(*Received, June 25th,* 1971; *Com.* 1051.)

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† These yields are based on the total amount of the mixture of alcohols.

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