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Anions Derived from 3,4:5,6-Dibenzocyclononatetraene

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Summary Deprotonation of 3,4:5,6-dibenzocyclononatetetraene (1) gives a nonplanar, nonaromatic anion (3), which rearranges to the planar, aromatic anion (5). compounds which can potentially exist as delocalised, aromatic systems. Thus the cyclononatetraenyl anion occurs as a delocalised, aromatic species in both the all-cis,^{1a} and mono-trans forms,^{1b} whereas oxonin,^{1e} N-substituted azonines,^{1d} and probably thionin, ^{1e} are nonplanar, localised

A RANGE of behaviour has been observed in medium-ring

systems.² Both 4,5:6,7-dibenzoxonin and the corresponding thionin, systems in which the interactions of the phenyl rings would be expected to be large, are also nonaromatic.³ Since it is possible that a delicate balance might exist between localised and delocalised anions derived from the related 3,4:5,6-dibenzocyclononatetraene (1), we have examined the deprotonation of this compound.

3,4:5,6-Dibenzocyclononatetraene (1), m.p. 37-38°,† was obtained in 13% yield by the reaction of 2,2'-biphenyl-



dicarboxaldehyde with the bis-ylide derived from 1,3-bis-(triphenylphosphonio)propane dibromide,⁴ by analogy with the preparation of the corresponding heterocycles.³ The n.m.r. [CDCl₃, 7 2.60-3.0 (m, 8H, ArH), 3.69 (br d, 2H,H^c, $J_{cb} = 12$ Hz), 4·45 (m, 2H, H^b, J = 6, 12 Hz), 7·30 (t, 2H, H^a, $J_{ab} = 6$ Hz)] and u.v. [λ_{max} (tetrahydrofuran) 245 nm (ϵ 6500)] spectra are in accord with structure (1). Compound (1) rearranges on Spence-H alumina to (2), m.p. 235-238°, † which appears from the spectral properties to be mainly the isomer with a *cis* ring junction.

Treatment of (1) in [2H8]tetrahydrofuran with n-butyllithium in hexane at room temperature (20°) in vacuo gave a deep red solution. The n.m.r. showed signals at τ 3.09

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(m, 4H), 3.35 (m, 4H), 4.49 (dd, 2H, H^b, J = 8, 11 Hz), 5.67 (d, 2H, H^c, $J_{bc} = 11$ Hz) and 7.04 (t, 1H, H^a, J = 8Hz), and we assign the nonplanar, partially delocalised structure (3) to the anion in solution. The chemical shifts and coupling constants are very similar to those of the cycloheptadienyl anion.⁵ Quenching the solution with water gave a ca. 2:1 mixture of (1) and 1,2:3,4-dibenzocyclononatetraene (4), t identified by their spectral properties. Preliminary experiments indicate that on quenching the anion (3) with D_2O no deuterium is incorporated at position 2.

When solutions of the anion (3) are kept at room temperature, the n.m.r. spectrum due to (3) slowly disappears, with the concommitant appearance of a new spectrum. This spectrum shows signals at $\tau 1.66$ (dd, 2H, ArH, J = 2, 8 Hz), 2.00 (dd, 2H, ArH, J = 2, 8 Hz), 2.65–3.10 (m, 6H, ArH and H^b), 3.42 (d, 2H, H^c, J = 4 Hz) and 3.65 (t, 1H, H^a, J = 4 Hz). The chemical shifts and the size of the coupling constants are those expected for the planar, delocalised, aromatic anion (5).§ The low-field signals are due to the aromatic protons H^d, H^g, which experience the deshielding effect of the adjacent aromatic rings in the planar anion, and the protons H^a , H^b , and H^c all show a downfield shift, largely due to the induced diamagnetic ring current in (5). Quenching a solution of (5) with water gave 1*H*-cyclopenta-[l]-phenanthrene (6), m.p. 146-148° (lit.⁷ 150-152°), in ca. 25% yield, identified by spectral properties.

The conversion of (3) into (5) was studied over the temperature range 30°-52° and, assuming first-order kinetics, $\Delta F^{\ddagger} = 8.9 \text{ kcal mole}^{-1} \text{ and } K (30^{\circ}) = 7.6 \times 10^{-5}$ s^{-1} . Since the major barrier to delocalisation must be the twisting of the biphenyl system into the plane of the 9membered ring, ΔF^{\ddagger} is a measure of the minimum delocalisation energy for the 1,2:3,4-dibenzocyclononatetraenyl anion (5).

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† Satisfactory elemental analysis and mass spectral data have been obtained for all new crystalline compounds.

It has not, as yet, been possible to separate (1) from (4).

We have previously suggested that a similar transformation might occur in the formation of the 3,4:5,6:9,10-tribenzobicyclo-[6,2,0] decapentaenyl dianion, (ref. 6) but subsequent experiments (in collaboration with K.P.C. Vollhardt) have indicated that the behaviour is more complex in this case.

 \P A 50% increase in the concentration of (1) had little effect on the rate of conversion of (3) into (5).

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