3,4:5,6:9,10-Tribenzobicyclo[6,2,0]decapentaene. A (4*n* + 4*n*) π-Electron System

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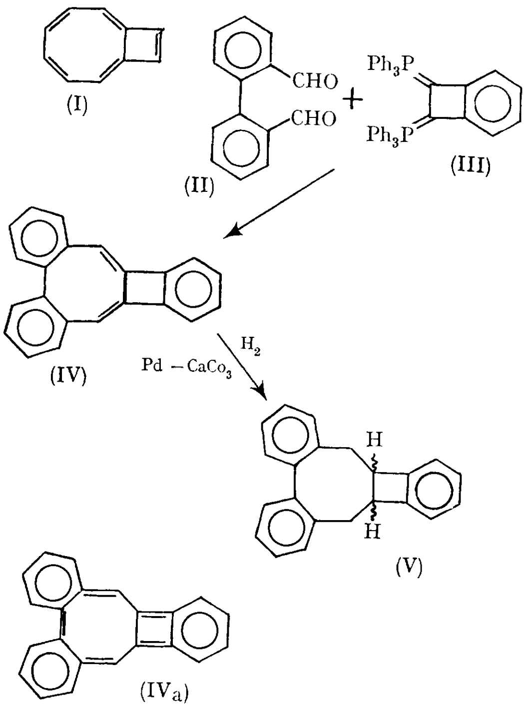
CONSIDERABLE interest has recently been shown in compounds containing fused $4n$ π-electron rings,[1] of which bicyclo[6,2,0]decapentaene (I) is an example. Resonance theory suggests that this system, unlike its isomers naphthalene and azulene, will show little aromatic stabilisation since two of the contributing canonical structures contain cyclobutadiene rings. Application of Dewar's perturbational molecular orbit (P.M.O.) method[2] leads to the same conclusion, a delocalization energy (D.E.) = 0 being calculated when (I) is compared with decapentaene. However it has been suggested[1a] that fused $(4n + 4n)$ π-electron systems, which overall possess $(4n + 2)$ π-electrons, may show aromatic properties. We now report the synthesis of 3,4 : 5,6 : 9,10-tribenzobicyclo[6,2,0]-decapentaene (IV), the first known derivative of the (4*n* + 4*n*) π-electron system (I).



A benzene solution of biphenyl dicarboxaldehyde (II) was added to a boiling benzene–ether solution of an equivalent of 1,2-bis(triphenylphosphoranyl)benzocyclobutene (III)[3] [prepared from *trans*-1,2-bis(triphenylphosphonio)benzocyclobutene by treatment with $NaNH_2$ in liquid NH_3]. A preliminary separation of the products on Al_2O_3, followed by preparative thin layer chromatography on silica, gave (among other products) a 2% yield of pale yellow crystals (m.p. 129—130°). The spectroscopic data are in accord with those expected for compound (IV).†‡ A high resolution mass spectrum gave a parent peak at 278·108 (calc. 278·109). The n.m.r. spectrum (CCl_4) showed a complex band at 2·7—3·2 (12 H) and a singlet at 3·48 (2H) τ;§ the u.v. spectrum (95% EtOH) had maxima at 279 (ε 46,000) and 352 nm. (9100);¶ the i.r. spectrum (KBr) had main bands at 3060, 1480, 1461, 1434, 1333, 1162, 1122, 950, 880, 872, 862, 767, 762, 750 and 742 cm.$^{-1}$

Hydrogenation of (IV) (5% Pd–$CaCO_3$, EtOAc) for 30 min. gave a 75% yield of colourless crystals (m.p. 173—179° from MeOH). The mass spectrum (parent peak 282·141) showed that 4 atoms of hydrogen had been added. The n.m.r. spectrum [CCl_4, 2·6—3·3 (m, 12H), 5·8—6·5 (m, 2H), 6·9—7·9 τ (m, 4H)] confirmed the 3,4 : 5,6 : 9,10-tribenzobicyclo[6,2,0]decatriene structure (V), probably a mixture of isomers. The u.v. spectrum [λ_{max} (EtOH) 261 (ε 2680), 268 (3530), 274 nm., (3580) and strong end-absorption] was also consistent with (V).**

The position of the vinylic protons of (IV) in the n.m.r. spectrum, together with the u.v. spectrum, suggests that (IV) does not possess 10 delocalised π-electrons distributed over the bicyclo[6,2,0]-decapentaene system. This is not surprising,as alternative resonance structures, such as (IVa), require disruption of the benzenoid systems. We are therefore modifying our synthetic procedure in order to obtain simpler derivatives of (I), as well as (I) itself.

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† Satisfactory elemental analyses were obtained for all new compounds.

‡ It was reported (ref. 3) that the related reaction between (II) and o-phthaldehyde did not give benzo-[*b*]biphenylene.

§ This is in agreement with the finding of Blomquist and Hruby[3] that in the n.m.r. spectrum of the *cis*-monobenzylidene derivatives of benzocyclobutene the vinylic proton appears at *ca.* τ 3·50, whereas in the *trans*-derivatives the vinylic proton appears at *ca.* τ 3·85. These authors' findings for the bisbenzylidene derivatives of benzocyclobutene are of less relevance, as the hydrogen–hydrogen interaction present in these derivatives is absent in (IV).

¶ By comparison biphenylene has two main u.v. bands at 250 (ε 79,000) and *ca.* 360 nm. (6,000)[4] and 1,2-dimethylenebenzocyclobutene has main bands at 230 (ε 6,000) and 329 nm. (14,130).[5]

** 1,2 : 3,4-Dibenzocyclo-octa-1,3-diene has u.v. maxima at 236 (ε 12,100), 264 (1050), and 273 nm. (590).[6]

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