Dicyclo-octatetraeno[1,2 : 4,5]benzene,[1] a Tricyclic 18π-Electron System

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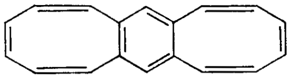
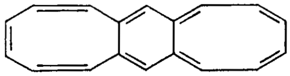
DICYCLO-OCTATETRAENO[1,2 : 4,5]BENZENE is a tricyclic hydrocarbon, which might be expected to represent a planar aromatic system. This follows from the fact that a contributing structure, (Ib), can be considered to be a perturbed [18]annulene.[2] We now describe the synthesis of (I), using the recently reported 7,8-dimethylenecyclo-octa-1,3,5-triene (II),[3] as well as 1,2-dibromomethylcyclo-octatetraene (VI).[3]



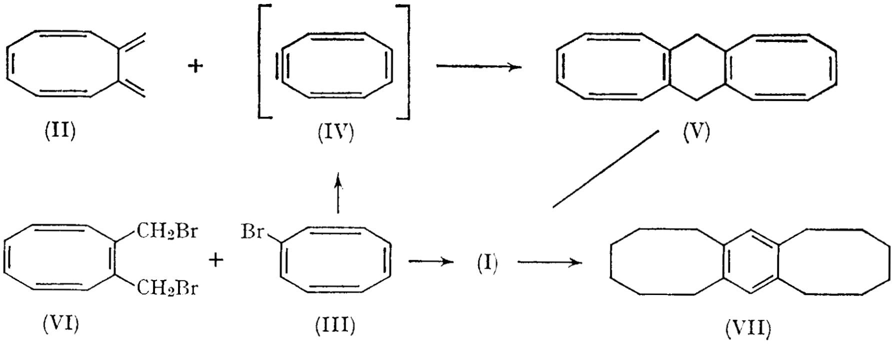
(Ia)



(Ib)

It has been shown by Krebs[4] that treatment of bromocyclo-octatetraene (III)[5] with potassium t-butoxide in ether at room temperature for 70 hr. leads to 1,2-dehydrocyclo-octatetraene (cyclo-octa-1,3,5-trien-7-yne) (IV) as a transient intermediate, which can be trapped in several ways. When this reaction is carried out in the presence of an equimolar amount of (II),[3] 22% of a mixture of the adduct (V) and the dehydrogenation product (I) is obtained (based on n.m.r., infrared, and mass-spectral evidence). Treatment of this mixture with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone in boiling benzene gave (I) in 47% yield.

A convenient one-step synthesis of (I), in 11% yield, was accomplished by treatment of an equimolar mixture of 1,2-dibromomethylcyclo-octatetraene (VI)[3] and bromocyclo-octatetraene (III)[5] with potassium t-butoxide under the same



conditions used previously. The mechanism of this reaction is now under investigation.

Dicyclo-octatetraeno[1,2 : 4,5]benzene (I) formed pale yellow prisms, m.p. 178—181° [subliming readily at 100° (0·5 mm.)]. λ_{max} (EtOH) 254 mμ (ϵ 24,700). In the mass spectrum, the base peak at *m/e* 230 corresponded to the molecular ion. Treatment with silver nitrate in ethanol led to a crystalline 1 : 1 adduct (77% yield), which decomposed slowly without melting above 200°. Catalytic hydrogenation of (I) over 5% palladium-calcium carbonate in methanol and ethyl acetate led to dicyclo-octeno[1,2 : 4,5]benzene (VII), m.p. 132—133°, in quantitative yield.

The n.m.r. spectrum of (I) in $CDCl_3$ (100 Mc./sec.) showed a singlet at τ 3·37 (2H) due to the six-membered-ring protons, as well as bands at τ 3·47, 3·56 (4H), 3·92, 4·03 (4H), and 4·12 (4H) due to the eight-membered-ring protons. By comparison, the n.m.r. spectrum of benzocyclo-octatetraene[3,6] exhibited bands at τ 2·76, 2·80, 2·82, 2·86 (2H), and 3·02, 3·06, 3·08 and 3·12 (2H) due to the six-membered-ring protons, as well as at τ 3·39, 3·51 (2H), 3·94, 4·06 (2H), and 4·13 (2H) due to the eight-membered-ring protons.

The n.m.r. data show that (I) does not represent a peripheral aromatic 18 π-electron system. This must be due to the fact that (Ib) is not a significant contributing structure, since it does not contain a benzenoid six-membered ring. Dicyclo-octatetraeno[1,2 : 4,5]benzene is presumably represented by (Ia), containing non-planar eight-membered rings.

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[1] This name is preferred to benzo[1,2:4,5]dicyclo-octene (nomenclature according to I.U.P.A.C. rules).

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