activity of the asymmetric centers or has conferred new activity on additional chromophoric groups.

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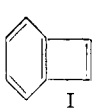
BENZOCYCLOBUTENE AND BENZOCYCLOBUTADIENE DIMER[1]

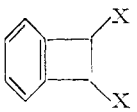
Sir:

Several fully aromatic hydrocarbons are known which may be considered to be dibenzo derivatives of the unknown cyclobutadiene.[2,3,4a,b] The simpler benzocyclobutadiene (I) has not been described, although molecular orbital calculations for the system have been made.[5] The closely related benzocyclobutene (II), the lower homolog of indane, also has not been described; doubts have been expressed concerning the stability of such a system[6] in which the considerable strain upon the ring is not compensated by any added resonance energy. We now wish to report the synthesis of the stable benzocyclobutene (II) and the generation of the unstable benzocyclobutadiene (I), isolated only as a dimer.

Treatment of $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene with excess sodium iodide in refluxing ethanol for two days has been reported[7] to give 1,2-dibromobenzocyclobutene (III). This reaction has been repeated and pure III isolated as colorless crystals, m.p. 52.4–52.8°. *Anal.* Calcd. for $C_8H_6Br_2$: C, 36.68; H, 2.31; Br, 61.02; mol. wt., 262. Found: C, 36.72; H, 2.35; Br, 60.83; mol. wt. (isothermal distillation), 258, 259. Dibromide III was unchanged by refluxing bromine after two days, and unaffected by maleic anhydride after fifteen hours at 90°. Nitric acid oxidized III to phthalic acid and bromine at 150° slowly converted III to $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene.



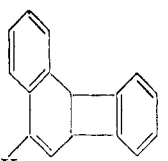
I



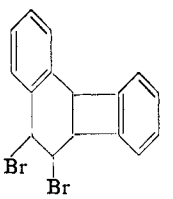
II, X = H
III, X = Br
IV, X = I

Refluxing a solution of III and excess sodium iodide in ethanol for eight days gave 1,2-diiodobenzocyclobutene (IV); m.p. 62.7–62.9°. *Anal.* Calcd. for $C_8H_6I_2$: C, 26.99; H, 1.70; I, 71.31; mol. wt., 356. Found: C, 26.84; H, 1.93; I, 71.05; mol. wt. (isothermal distillation), 350. Oxidation of IV with nitric acid gave phthalic acid. Hydrogenolysis of IV at room temperature in ethanol in the presence of palladium charcoal and sodium ethoxide gave, after distillation through a Nester spinning band column, pure II, b.p. 150.0° (748 mm.). *Anal.* Calcd. for C_8H_8: C, 92.26; H, 7.74. Found: C, 92.33, 92.47; H, 7.74, 7.72; $\lambda_{max.}^{EtOH}$ 260 mμ (log ε = 3.09), 265.5 mμ (log ε = 3.28), 271.5 mμ (log ε = 3.27); d^4_{25} = 0.957; $n^{25}D$ 1.5409. The mass spectrum of II exhibited a parent peak at 104 m./e.; the infrared spectrum contained a band at 10.05 μ characteristic of a cyclopropane ring.[8]

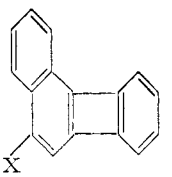
Dehalogenation of either III or IV with zinc in ethanol (containing hydroquinone) gave, in 70–80% yield, not the expected I, but a crystalline dimer (V), m.p. 74.5°. *Anal.* Calcd. for $C_{16}H_{12}$: C, 94.07; H, 5.92; mol. wt., 204. Found: C, 93.89; H, 5.93; mol. wt. (isothermal distillation), 200. Dimer V was aromatized by N-bromosuccinimide in benzene to 1,2-benzobiphenylene (VI), identical with an authentic sample.[4b] Only one mole of bromine added to V to give a dibromide (VII), m.p. 111.5–112.2°. *Anal.* Calcd. for $C_{16}H_{12}Br_2$: C, 52.78; H, 3.32; Br, 43.90. Found: C, 52.91; H, 3.46; Br, 43.70. Reaction of VII with potassium *t*-butoxide in *t*-butyl alcohol gave the monobromide (VIII), m.p. 124.3–124.6°. *Anal.* Calcd. for $C_{16}H_{11}Br$: C, 67.86; H, 3.92; Br, 28.22. Found: C, 67.59; H, 4.02; Br, 28.01. Aromatization of VIII by N-bromosuccinimide in benzene gave 3-bromo-1,2-benzobiphenylene (IX), m.p. 125–126°, identical in all respects with a sample synthesized from simple naphthalene precursors.[9] These reactions establish the structure of V, including the position of the double bond.



V, X = H
VIII, X = Br



VII



VI, X = H
IX, X = Br

The formation of dimer V appears to occur via a Diels–Alder condensation between two molecules of I, followed by spontaneous aromatization of the initially formed product to V.

(1) A part of this material was presented before the Division of Organic Chemistry at the 128th meeting of the American Chemical Society, Minneapolis, Minnesota, September, 1955.
(2) W. C. Lothrop, THIS JOURNAL, **63**, 1187 (1941).
(3) R. F. Curtis and G. Viswanath, *Chem. and Ind.*, 1174 (1954).
(4) (a) M. P. Cava and J. F. Stucker, *ibid.*, 446 (1955); (b) THIS JOURNAL, **77**, 6022 (1955).
(5) J. D. Roberts, A. Streitweiser, Jr., and Clare M. Regan, *ibid.*, **74**, 4579 (1952).
(6) W. Baker, *J. Chem. Soc.*, 258 (1945).
(7) H. Finkelstein, Dissertation, Strassbourg, 1910.
(8) L. W. Marrison, *J. Chem. Soc.*, 1614 (1951).
(9) M. P. Cava and J. F. Stucker, to be published shortly.

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SYNTHESIS OF POTENT ORAL ANABOLIC-ANDROGENIC STEROIDS

Sir:

In the course of studies on the synthesis of 11-oxygenated C-19 steroids[1] we have prepared a number of analogs (III, XI and XII) of this category which have been shown to possess oral anabolic and androgenic potency considerably higher than any other hitherto reported (see Table I).

The preparation of these compounds was in part accomplished by extension of the utility of 3-enamines formed selectively from polycarbonyl

(1) M. E. Herr and F. W. Heyl, THIS JOURNAL, **75**, 5927 (1953).