acid, and the product was isolated by continuous extraction with ether. There was obtained 9.95 g. (75%) of a light tan solid, m.p. 165–176°. Crystallization from hexane gave XIII as a white solid, m.p. 178–179°.

Anal. Neut. equiv.: Calcd., 129; Found, 134, 136. F—NMR: 2515, 2735, 2975, 3190 c.p.s. (w,s,s,w; H_2O).

2,4-Bis(methoxycarbonyl)-6,6,7,7-tetrafluoro-3-oxabicyclo-[3.2.0]heptane (XIV).—A solution of 6.4 g. of XIII in 50 ml. of ether was treated with an ether solution of diazomethane. Evaporation left 6.90 g. (97%) of a white solid. Two crystallizations from methanol yielded white needles, m.p. 122–124°. Infrared: 3.31, 3.36, 5.73, 7.30, 7.47, 7.78, 7.92, 7.99, 8.34, 8.76, 8.85, 9.06, 9.17, 9.48, 9.54, 10.0, 10.40, 11.33, 12.19, and 13.48 μ.

Anal. Calcd. for $C_{10}H_{10}F_4O_5$: C, 41.96; H, 3.53; F, 26.55. Found: C, 42.39; H, 3.91; F, 26.72.

1,6-Dimethyl-3,3,4,4-tetrafluoro-9-oxatricyclo[4.2.1.0^{2,5}]-non-7-ene.—A mixture of 20 g. (0.16 mole) of TFCB and 20 g. (0.21 mole) of 2,5-dimethylfuran was sealed in a Carius tube and heated on a steam bath for 49 hr. After the volatile components evaporated, 16.9 g. (40%) of brown needles remained. Sublimation at 100°/1 mm. and crystallization from methanol gave 9.5 g. of white needles, m.p. 97.5–99°. Infrared: 7.16, 7.60, 7.54, 7.58, 7.96, 8.26, 8.63, 8.69, 9.15, 9.39, 9.62, 10.9, 11.61, 12.75, 12.87, 13.87, 13.95, and 14.08 μ.

Anal. Calcd. for $C_{10}H_{10}F_4O$: C, 54.08; H, 4.54; F, 34.22. Found: C, 54.08; H, 4.73; F, 34.45.

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Condensed Cyclobutane Aromatic Compounds. XIX. The Course of Dimerization of 1,2-Dibromobenzocyclobutadiene[1]

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The generation of 1,2-dibromobenzocyclobutadiene from 1,1,2-tribromobenzocyclobutene or 1,1,2,2-tetra-bromobenzocyclobutene leads to the formation of 5,6-dibromobenzo[*a*]biphenylene. A synthesis of the latter from compounds of known structure is described. The mechanism of the dehydrobromination of α,α,α′,α′-tetrabromo-*o*-xylene is discussed in the light of these observations.

It has been reported[2] that α,α,α′,α′-tetrabromo-*o*-xylene reacts with excess potassium *t*-butoxide to yield a mixture of 5,10-dibromobenzo[*b*]biphenylene (II) and 1,2,5,6-tetrabromo-3,4,7,8-dibenzotricyclo[4.2.0.0^{2,5}]octadiene (III). In attempting to explain this unusual transformation, it was suggested that the initial loss of hydrogen bromide from tetrabromide I would produce first an *o*-quinodimethane intermediate (IV). Intramolecular cyclization of IV, in analogy with a closely related and established reaction,[3] would give 1,1,2-tribromobenzocyclobutene (V). Under the strongly basic reaction conditions, rapid dehydrobromination of V could occur with the generation of 1,2-dibromobenzocyclobutadiene (VI). Linear dimerization of VI would lead directly to the observed product III and, by a more obscure process involving loss of bromine, to product II.

The recent synthesis of tribromide V[4] has now allowed this hypothesis to be tested. The reaction of V with potassium *t*-butoxide gave none of the expected products II and III, but instead an excellent yield of an orange compound, $C_{16}H_8Br_2$, shown to be 5,6-dibromobenzo[*a*]biphenylene (VII). The formation of VII is envisaged as proceeding *via* 1,2-dibromobenzocyclobutadiene (VI) which dimerizes not in a linear manner to give rise to II and III, but rather in the angular fashion observed previously in the dimerization of 1-bromobenzocyclobutadiene[5] and of benzocyclobutadiene itself.[6] The initial dimerization product VIII apparently lost the elements of molecular bromine during the course of the reaction and was aromatized to bromide VII. Although VIII could not be isolated directly by dehydrobromination of tribromide V, a colorless compound of composition VIII was obtained by the direct addition of bromide to the benzobiphenylene derivative VII. Reaction of tetrabromide VIII with potassium *t*-butoxide easily regenerated the orange bromide VII, strengthening the assumption that VIII is indeed an intermediate in the conversion of V into VII. The possibility that VIII in solution is in equilibrium with a small amount of dibromide VII and elemental bromine was discounted by warming a solution of VIII in *t*-butyl alcohol with phenol, a good bromine scavanger, when VIII was recovered unchanged. One must conclude therefore that the conversion of VIII into VII by *t*-butoxide ion involves attack upon one of the tertiary bromines in the molecule with concommitant elimination of the second tertiary bromine as bromide ion.

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(1) For a preliminary communication of this subject, see M. P. Cava and K. Muth, *Tetrahedron Letters*, No. 42, 140 (1961).

(2) F. R. Jensen and W. E. Coleman, *Tetrahedron Letters*, No. 20, 7 (1959).

(3) M. P. Cava, A. A. Deana, and K. Muth, *J. Am. Chem. Soc.*, **81**, 6458 (1959).

(4) M. P. Cava and K. Muth, *J. Org. Chem.*, **27**, 757 (1962).

(5) M. P. Cava and J. F. Stucker, *J. Am. Chem. Soc.*, **79**, 1706 (1957).

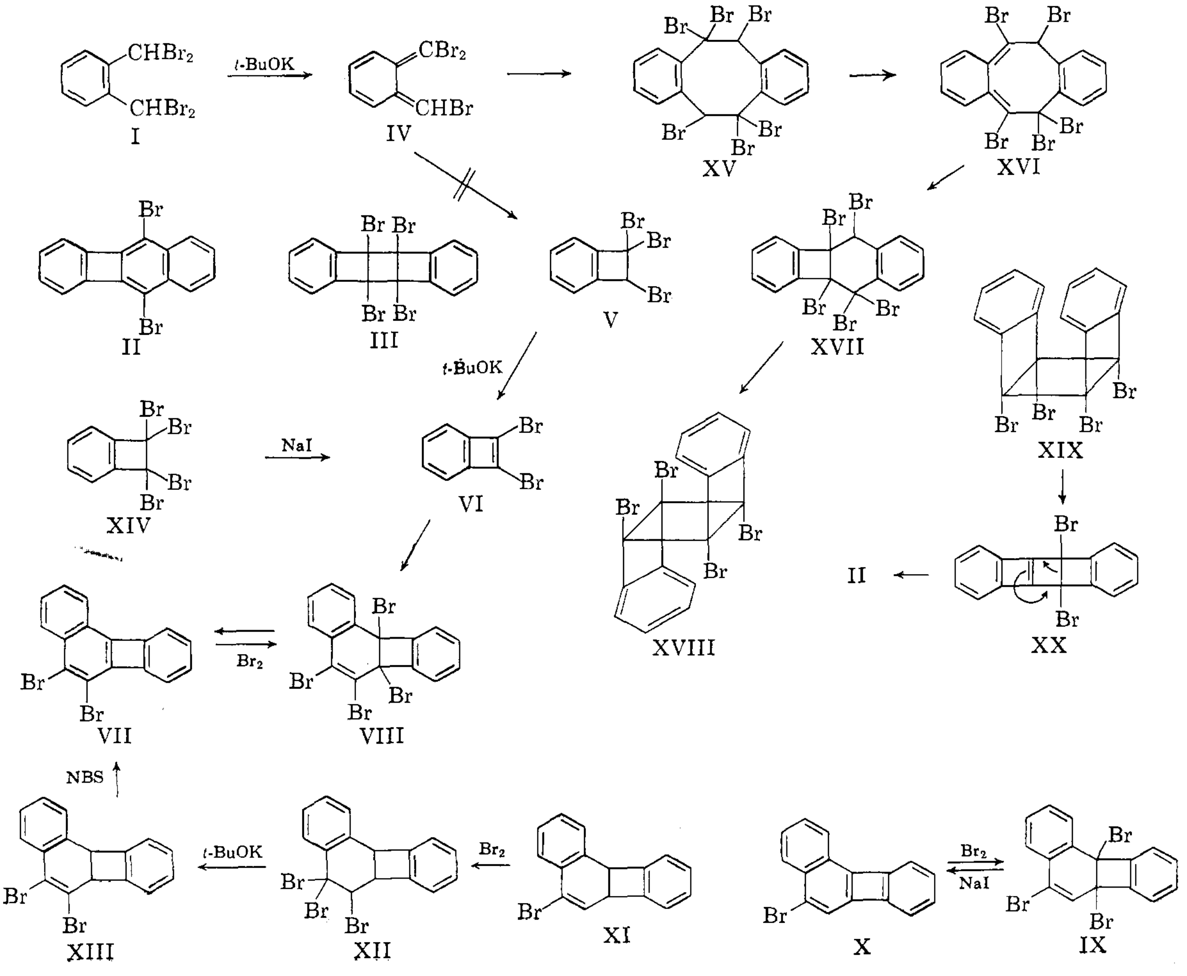
(6) M. P. Cava and D. R. Napier, *ibid.*, **79**, 1701 (1957).

The facile addition of molecular bromide to the cyclobutadienoid double bond of the benzo[*a*]biphenylene system appears to be a quite general process. Indeed, a colorless bromine addition product IX was obtained from 5-bromobenzo[*a*]biphenylene (X)[3]; compound X was regenerated from IX by the action of sodium iodide. It is noteworthy that the initial attack of the biphenylene X by oxidizing agents occurs also at the cyclobutadienoid bond of the aromatic system.[7]

Confirmation of structure VII for the base transformation product of 1,1,2-tribromobenzocyclobutene was obtained by an independent synthesis. Addition of bromine to 5-bromo-6a,10a-dihydrobenzo[*a*]biphenylene (XI)[6] gave 5,5,6-tribromo-6a,10a-dihydrobenzo[*a*]biphenylene (XII), which was dehydrobrominated by potassium *t*-butoxide to 5,6-dibromo-6a,10a-dihydrobenzo[*a*]biphenylene (XIII). Dehydrogenation of XIII by reaction with *N*-bromosuccinimide gave the orange dibromide VII.

The generation of 1,2-dibromobenzocyclobutadiene(VI) under neutral conditions could be effected from 1,1,2,2-tetrabromobenzocyclobutene (XIV),[5] as evidenced by the isolation of VII. Tetrabromide XIV reacted slowly with sodium iodide in warm dimethylformamide to give compound VII in fair yield.

Finally some comment may be made concerning the course of the dehydrobromination of $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene (I). Since the cyclobutadiene derivative VI cannot be an intermediate in this reaction, it appears likely that the primary quinoid product IV may dimerize initially to the dibenzocyclooctadiene derivative XV. Loss of hydrogen bromide from XV would give the quinoid structure XVI, the intramolecular cyclization of which would give the benzocyclobutene derivative XVII. In a similar sequence of dehydrobromination followed by ring closure XVII would give either of the two stereoisomers XVIII and XIX. Both isomers may well form, one of these (probably XVIII) being identical with the observed product III. Loss of bromine from the other isomer, in a process quite analogous to the conversion of VIII to VII by *t*-butoxide ion would generate the benzocyclobutadiene derivative (XX), which is formally a Dewar type ring tautomer of the observed biphenylene derivative II. Indeed, the stable isomer of the pair XVIII and XIX, namely Jensen and Coleman's compound III, has been reported to be



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(7) M. P. Cava and K. W. Ratts, *J. Org. Chem.*, **27**, 752 (1962).

convertible to the biphenylene II in a similar reaction by iodide ion, although at an exceedingly slow rate. Attempts to obtain experimental confirmation for the mechanistic scheme outlined above are in progress.

Experiments[8]

5,6-Dibromobenzo[*a*]biphenylene (VII). A. From 1,1,2-Tribromobenzocyclobutene (V).—A solution of tribromide V[5] (1.71 g.) in *t*-butyl alcohol (5 ml.) was added at room temperature to a stirred solution of potassium *t*-butoxide prepared by dissolving potassium (1.40 g.) in *t*-butyl alcohol (50 ml.). The orange solution was stirred for an additional 90 min., and then diluted with water (50 ml.). The precipitate was filtered, washed with water, dried, and crystallized from cyclohexane to give orange needles of VII (0.670 g., 85%), m.p. 149–150°.

Anal. Calcd. for $C_{16}H_8Br_2$: C, 53.33; H, 2.22; Br, 44.44. Found: C, 53.39; H, 2.02; Br, 44.31.

B. From 1,1,2,2-Tetrabromobenzocyclobutene (XIV).—A mixture of tetrabromide XIV[5] (0.500 g.), sodium iodide (1.0 g.), and dimethylformamide (11 ml.) was heated for 20 hr. on the steam bath. The cooled solution was diluted with water (50 ml.), and the free iodine present was reduced by the addition of excess sodium sulfite. The suspension was extracted with benzene and the organic layer washed with water, dried, concentrated, and chromatographed on alumina. Elution of the orange band yielded, after evaporation and two crystallizations from cyclohexane, needles of VII (0.085 g., 41%), identical in melting point and infrared spectrum with material obtained from tribromide V.

5,6,6a,10a-Tetrabromo-6a,10a-dihydrobenzo[*a*]biphenylene (VIII).—To a solution of dibromide VII (0.150 g.) in chloroform (4 ml.) was added a solution of bromine (0.080 g.) in chloroform (1 ml.). The mixture was refluxed for 2 min., and then evaporated to dryness under reduced pressure. Crystallization of the residue from cyclohexane afforded white crystals of compound VIII (0.145 g., 68%), m.p. 155° dec.

Anal. Calcd. for $C_{16}H_8Br_4$: C, 36.92; H, 1.54; Br, 61.54. Found: C, 37.16; H, 1.73; Br, 61.58.

Reconversion of VIII into VII.—Compound VIII (0.060 g.) was refluxed for 5 min. with potassium *t*-butoxide solution prepared from potassium (0.013 g.) and *t*-butyl alcohol (5 ml.). Dilution of the orange solution with water (15 ml.) was followed by neutralization with acetic acid and extraction with petroleum ether. Chromatography of the crude product in benzene over alumina, followed by crystallization from cyclohexane afforded 0.025 g. (61%) of pure VII.

5,6a,10a-Tribromo-6a,10a-dihydrobenzo[*a*]biphenylene (IX).—To a stirred solution of monobromide X[3] (0.200 g.) in chloroform (12.5 ml.) was added slowly at 0° a solution of bromine (0.040 g.) in chloroform (2.5 ml.). The mixture was allowed to come to room temperature slowly, and the solvent was evaporated at room temperature *in vacuo*. Crystallization of the residue from cyclohexane afforded substance IX (0.239 g., 65%) as very pale yellow cubes, m.p. 144–145° dec.

Anal. Calcd. for $C_{16}H_9Br_3$: C, 43.54; H, 2.04; Br, 54.42. Found: C, 43.58; H, 2.31; Br, 54.27.

Reconversion of IX into X.—A mixture of compound IX (0.030 g.), sodium iodide (0.150 g.), and dimethylformamide (2 ml.) was heated for 20 min. on the steam bath. The cooled solution was diluted with water (6 ml.), filtered, and sodium sulfite was added to reduce the free iodine present. The yellow solution was extracted several times with petroleum ether, and the residue from the evaporated extracts was crystallized from ethanol to yield pure bromide X (0.018 g., 95%), m.p. 127–128°, identical in infrared spectrum with authentic material.

5,5,6-Tribomo-6a,10a-dihydrobenzo[*a*]biphenylene (XII).—A solution of compound XI[6] (0.240 g.) and bromine (0.136 g.) in chloroform (10 ml.) was allowed to stand for 10 min. at room temperature and then heated to reflux for 2 min. Evaporation of the solvent and crystallization of the residue from cyclohexane gave white crystals of XII (0.270 g., 73%), m.p. 140–142° dec.

Anal. Calcd. for $C_{16}H_{11}Br_3$: C, 43.34; H, 2.48; Br, 54.18. Found: C, 43.47; H, 2.70; Br, 54.42.

5,6-Dibromo-6a,10a-dihydrobenzo[*a*]biphenylene (XIII).—To a stirred solution of potassium *t*-butoxide prepared from potassium (0.025 g.) and *t*-butyl alcohol (5 ml.) was added, at room temperature and under nitrogen, a solution of compound XII (0.221 g.) in *t*-butyl alcohol (2 ml.). After standing for 1 hr., the solution was diluted with water (40 ml.), neutralized with a little acetic acid, and extracted thoroughly with benzene. Evaporation of the dried extract and crystallization of the residue from petroleum ether afforded voluminous white needles of XIII (0.095 g., 53%), m.p. 130–131°.

Anal. Calcd. for $C_{16}H_{10}Br_2$: C, 53.04; H, 2.76; Br, 44.25. Found: C, 53.04; H, 2.81; Br, 44.28.

Conversion of XIII into VII.—A mixture of compound XIII (0.063 g.), *N*-bromosuccinimide (0.060 g.), and benzene (8 ml.) was irradiated under reflux for 15 hr. by a 100-w. tungsten bulb. The yellow solution was filtered through alumina, the filtrate evaporated, and the residue crystallized from cyclohexane to yield crystals of crude 5,6-dibromobenzo-[*a*]biphenylene (VII; 0.031 g., 52%), m.p. 141–142°. The product was purified by conversion in benzene to its 2,4,7-trinitrofluorenone complex (violet-black needles, m.p. 172–173° dec.) and regeneration from the latter by chromatography over alumina. The purified sample of VII (m.p. 148–150°) was identical with material prepared from bromides V and XIV.

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[8] Analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and by Schwarzkopf Laboratories, Woodside, N. Y. All melting points are uncorrected.