[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Condensed Cyclobutane Aromatic Systems. II. Dihalo Derivatives of Benzocyclobutene and Benzocyclobutadiene Dimer[1,2]

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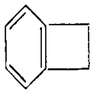
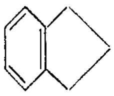
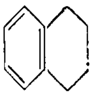
The reaction of α,α,α′,α′-tetrabromo-*o*-xylene with sodium iodide, first carried out by Finkelstein, has been reinvestigated. The structure of the dibromide produced and formulated by Finkelstein as 1,2-dibromobenzocyclobutene, has been confirmed. In addition, two new compounds have been isolated from the reaction mixture. These are 1,2-diiodobenzocyclobutene and a compound $C_{16}H_{12}BrI_3$. The latter two substances are shown to be secondary reaction products arising from reaction of the dibromide with sodium iodide. Zinc dehalogenation of either the dibromide or the diiodide gives not the simple benzocyclobutadiene C_8H_6 but a dimer $C_{16}H_{12}$. On the basis of aromatization evidence the dimer is assigned the structure 6a,10a-dihydrobenzo[a]biphenylene. Mechanisms of formation of the dibromide, the diiodide and the dimer are discussed.

Numerous bicyclic systems have been prepared which contain the structural feature of an alicyclic ring fused to an aromatic nucleus. The simplest known alicyclic-aromatic fused system is that of indane (I), or 1,2-benzocyclopentene. Although the higher homologs of indane such as tetralin (II) are well known, the lower indane homolog, benzocyclobutene (III), never has been reported.[3] In the course of his classical studies of cyclic systems, Perkin[4] wrote of attempts to prepare benzocyclobutene derivatives, although apparently no successful results followed. More recently, dibenzocyclobutadiene (biphenylene)[5] (IV) and several of its more highly condensed analogs[6,7] have been prepared. However, no authenticated case of a simple derivative of benzocyclobutene has yet been described. The considerable strain present in a molecule containing a cyclobutane ring fused to an aromatic ring may be partially compensated by the additional resonance gained if the entire system is conjugated and therefore aromatic, as in the case of biphenylene. Simple derivatives of benzocyclobutene would lack this stabilizing energy and might be expected to be incapable of existence, or at least highly unstable.[8]


III


I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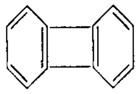
IV

As part of a broad program to prepare and study derivatives of benzocyclobutene, we have reinvestigated some very interesting unpublished work carried out almost 50 years ago by H. Finkelstein, working with J. Thiele.[9] During the course of a study of the reactions of a number of halides with iodide ion, Finkelstein observed that when α,α,α′-α′-tetrabromo-*o*-xylene (V) was refluxed with ethanolic sodium iodide, a very slow reaction occurred, accompanied by the gradual liberation of iodine. After two days of refluxing, about 0.7 mole of iodine had been liberated and the reaction was apparently completed. From the reaction mixture was isolated in 60% yield a crystalline, steam-distillable bromide. This product was contaminated by iodine-containing material which could not be removed by crystallization. However, a pure sample of this same bromide was obtained, in very poor yield, by distillation of α,α,α′,α′-tetrabromo-*o*-xylene with silver powder. The pure bromide, m.p. 52.5°, was reported to have the composition $C_8H_6Br_2$, as determined by elementary analysis and molecular weight determinations. Oxidation of the dibromide with nitric acid gave phthalic acid, whereas heating with bromine in a sealed tube at 130–165° regenerated α,α,α′,α′-tetrabromo-*o*-xylene. On the basis of these observations the dibromide was assigned the structure of 1,2-dibromobenzocyclobutene (VI). We have repeated the sodium iodide reaction of Finkelstein and have subjected the crude iodine-containing product to a series of repeated distillations and crystallizations to obtain the pure dibromide, m.p. 52.4–52.8°. Elementary analysis and molecular weight determinations confirmed the formula $C_8H_6Br_2$. Oxidation with nitric acid gave, in our hands, a quantitative yield of phthalic acid. Reaction of the dibromide with bromine at 150° for 12 hr. gave the original tetrabromide V in 48% yield. However, the dibromide does not react readily with bromine. A sample refluxed in pure bromine as the solvent for 46 hr. was recovered essentially unchanged. The possibility that the dibromide might actually possess the isomeric quinonoid structure VII was not consistent with this observation. In addition, it was found that no reaction occurred upon heating the dibromide at 100° for 15 hr. with maleic anhydride. N-Methylisoindole (VIII) possesses a quinonoid structure similar to that of structure VII but probably of more stable nature due to the fused aromatic pyrrole nucleus. This extremely reactive compound combines readily[10] with maleic anhydride in ether to give a Diels–Alder adduct.

It seems likely, however, that the reaction of α,-

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[1] For a preliminary account of this work, see M. P. Cava and D. R. Napier, THIS JOURNAL, **78**, 500 (1956).

[2] *Note on Nomenclature:* According to *Chemical Abstracts* nomenclature, the compounds designated by us as benzocyclobutene and benzocyclobutadiene would be called 5,6-dihydrocyclobutabenzene and cyclobutabenzene, respectively. In our discussion we shall retain the common names, as they point out more clearly the relation of the compounds to cyclobutadiene. Benzocyclobutadiene is then analogous in name to such substances as the benzanthracenes or benzophenanthrenes. The system referred to by us previously as 1,2-benzobiphenylene[1] will now be designated benzo[a]biphenylene.

[3] See reference 1 for a preliminary report of the preparation of III from compounds discussed in this paper.

[4] W. H. Perkin, Jr., *J. Chem. Soc.*, **53**, 1 (1888).

[5] W. C. Lothrop, THIS JOURNAL, **63**, 1187 (1941).

[6] M. P. Cava and J. F. Stucker, *ibid.*, **77**, 6022 (1955).

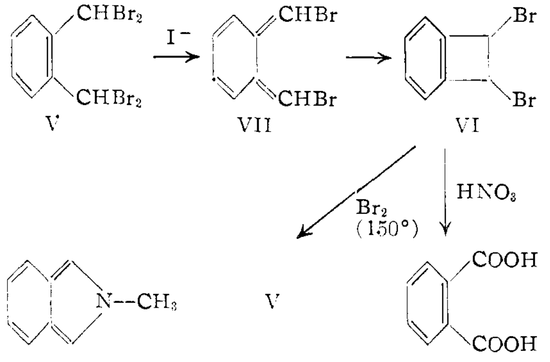
[7] R. F. Curtis and G. Viswanath, *Chem. and Ind.*, 1174 (1954).

[8] For a more complete discussion of this problem see W. Baker, (The Tilden Lecture 1944) *J. Chem. Soc.*, 258 (1945).

[9] H. Finkelstein, Inaugural Dissertation, Strassbourg, 1910.

[10] G. Wittig, H. Tenhaeff, W. Schoch and G. Koenig, *Ann.*, **572**, 1 (1951).

α,α',α'-tetrabromo-*o*-xylene with iodide ion proceeds as a vinylogous 1,2-dibromide elimination to give, as the initial reaction product, the quinonoid bromide VII. This species, present always in very low concentration, could undergo internal ring closure with aromatization to 1,2-dibromobenzocyclobutene.



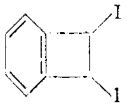
V VII VI

VIII V

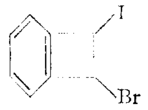
Attempts were made to isolate in pure form the iodine-containing material which was also present in the original reaction mixture. By the combined use of distillation and chromatography an iodine-rich sample of dibromide was obtained which, after extensive crystallization, yielded pure 1,2-diiodobenzocyclobutene (IX), m.p. 62.7–62.9°. This diiodide was very similar in solubility and crystal form to the dibromide. The infrared spectra of the two dihalides were complex but practically identical. Only one major difference was observed in the spectra: a fairly strong band exhibited by the dibromide at 12.6 μ was shifted to 12.8 μ in the case of the diiodide. The most striking differences in the properties of the two dihalides were those of their thermal and photochemical stabilities. The diiodide underwent extensive decomposition with the liberation of iodine during distillation under reduced pressure. Also, a colorless solution of the diiodide in petroleum ether became violet after very short exposure to sunlight; a similar solution of the dibromide remained colorless after long irradiation, no decomposition taking place. In addition the dibromide was quite stable when distilled at 140° under reduced pressure.

Although the mixture of dibromide and diiodide was very difficult to separate into its constituents, it was easily separated by chromatography from a third component of the original reaction mixture. This substance, which crystallized in long colorless needles, melted at 135–136° and had the composition $C_{16}H_{12}BrI_3$. The structure of this triiodide is being investigated and will be discussed in some detail in a future communication.

It would appear probable, at first consideration, that if the reaction of $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene with iodide ion produces both the dibromide VI and the diiodide IX, the iodobromide X also must be produced. However, in spite of extensive efforts to isolate the iodobromide from the primary reaction mixture, no indication of its presence ever was obtained.

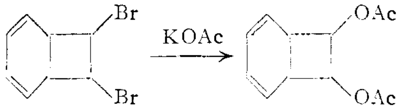


IX



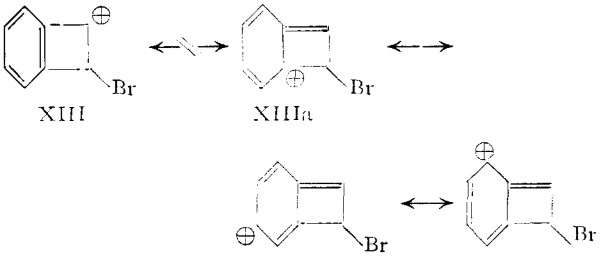
X

The bromine atoms of 1,2-dibromobenzocyclobutene behave very differently from those of the open chain analog, α,α'-dibromo-*o*-xylene. The latter, as a typical benzyl halide, undergoes solvolysis readily. Even the considerably less reactive and hindered $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene (V) can be solvolyzed fairly easily to *o*-phthalaldehyde in the presence of water.[11] In contrast, 1,2-dibromobenzocyclobutene is completely stable to boiling with aqueous alcohol, no detectable hydrolysis taking place. In addition, the compound was recovered unchanged after refluxing for two days with ethanolic potassium acetate, indicating that it must be very resistant to reaction by either the S$_N$1 or the S$_N$2 path. This decreased reactivity may be largely a result of the structural feature of a 1,2-dibromocyclobutane system, although the closely related dibromide XI reacts readily with alcoholic potassium acetate to give a good yield of the corresponding diacetate XII.[12]



XI XII

The inertness of 1,2-dibromobenzocyclobutene to solvolysis must indicate that in the carbonium ion XIII factors which normally operate to stabilize benzyl carbonium ions are lacking. In other words, the ion XIII is not stabilized to any appreciable extent by the canonical forms (XIIIa-c). These forms, which have in common a double bond *exo* to the aromatic ring into the four-membered ring, must be sufficiently strained structures so that their negative strain energy cancels out the positive resonance energy which they would normally contribute to the system.



XIII XIIIa

XIIIb XIIIc

When 1,2-dibromobenzocyclobutene was refluxed with ethanolic sodium iodide containing some iodine, the dibromide slowly disappeared. After heating for 8 days there was isolated 1,2-diiodobenzocyclobutene (IX) in 78.4% yield, the only other product obtained, in 10.1% yield, being the triiodide $C_{16}H_{12}BrI_3$. In other words, under the conditions in which the dibromide VI was originally produced, it is gradually transformed into a mixture of the two by-products which accompany its formation. It seems probable, therefore, that

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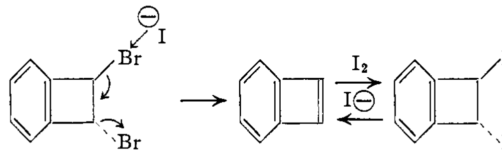
[11] J. Thiele and O. Gunther, *Ann.*, **347**, 106 (1906).

[12] It is quite possible, however, that this reaction proceeds *via* the ring tautomeric dibromocycloöctatriene.

1,2-dibromobenzocyclobutene is the first isolable reaction product of sodium iodide and $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene.

The mechanism of conversion of 1,2-dibromobenzocyclobutene into 1,2-diiodobenzocyclobutene deserves comment. Since the dibromide appears to be essentially incapable of either solvolysis or the normal Walden inversion type of reaction, the most likely remaining path is attack of the bromine by iodide ion. The reaction of a vicinal dibromide with iodide ion is indeed well known and occurs with the formation of an olefin and the liberation of iodine. In the usual case in which the bromine atoms of a vicinal dibromide can assume a completely transoid configuration to each other, maximum orbital overlap is achieved in the transition state for the elimination and the reaction proceeds readily. If, on the other hand, steric factors prevent the complete coplanarity of the atoms in the transition state, the reaction rate will be considerably decreased.[13]

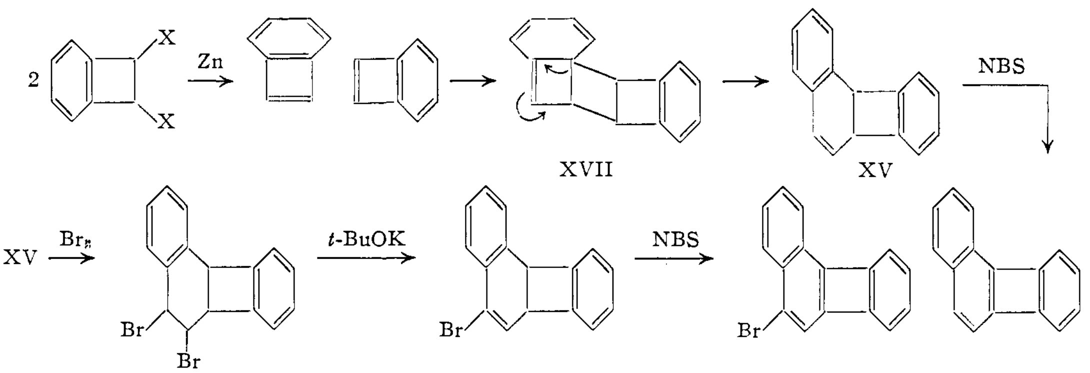
Although no direct physical proof of the configuration of 1,2-dibromobenzocyclobutene is yet available, the compound must almost certainly be the *trans*-dibromide. A *cis*-dibromide of this structure, because of the considerable inflexibility of the cyclobutane ring, would have to possess two bromine atoms directly over each other in such a manner as to create very great repulsion effects. However, this same rigidity of the cyclobutane ring would prevent the two bromine atoms of the *trans*-dibromide from being able to assume a position even approaching coplanarity with the carbon atoms bearing them in the transition state for their elimination by iodide ion. It is not surprising, therefore, that the reaction of 1,2-dibromobenzocyclobutene with iodide ion requires a number of days to go to completion. The most interesting and curious fact about this particular elimination, however, is that the major reaction product is not the expected olefin, benzocyclobutadiene (XIV), but rather the diiodide IX which would be formed by the addition of iodine to that olefin. This situation is just the reverse of that normally encountered, when in the presence of iodine and iodide ion no diiodide can be detected and only olefin can be found. The implication arising from these considerations is that the 1,2-double bond of benzocyclobutadiene is extremely reactive and undergoes addition reactions far more easily than a normal double bond. This would mean that not only does benzocyclobutadiene lack the stability expected of a new non-classical aromatic ring system,[14] but it is much more reactive, and therefore less stable, than such open chain analogs as styrene and stilbene.



VI XIV IX

The highly reactive character of benzocyclobutadiene was further illustrated by the results of the zinc dust dehalogenation of either the dibromide VI or the diiodide IX. Under ordinary conditions, using moderate concentrations of dihalide in ethanol and an atmosphere of air over the solution, reaction occurred to give an almost quantitative yield of an amorphous powder, corresponding in composition to a polymer of benzocyclobutadiene containing variable amounts of oxygen. When the dehalogenation was carried out under conditions of high dilution in the presence of hydroquinone as a polymerization inhibitor and under a nitrogen atmosphere, the major reaction product, formed in 70–80% yield, was a colorless crystalline hydrocarbon $C_{16}H_{12}$, m.p. 74.5°. This benzocyclobutadiene dimer XV was dehydrogenated slowly on boiling in benzene with N-bromosuccinimide to a yellow hydrocarbon $C_{16}H_{10}$, which proved to be identical with benzo[a]biphenylene[6] (XVI). No brominated derivative of XVI was isolated from the dehydrogenation mixture. The dimer XV was, therefore, a dihydro derivative of benzo[a]biphenylene (XVI). The dimerization of benzocyclobutadiene to such a structure can be rationalized as involving a Diels–Alder condensation between two molecules of the diene. The initially formed adduct XVII has lost the aromaticity of one of its benzene rings, but by a very simple electron shift that ring can rearomatize to give 6a,10a-dihydrobenzo[a]biphenylene (XV).

The position of the olefinic double bond in the dimer was confirmed as follows. The dimer ab-



XIX XX XXI XVI

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[13] For a more detailed exposition of this principle and a striking application of it, see D. H. R. Barton and E. Miller, THIS JOURNAL, **72**, 1066 (1950).

[14] For the results of molecular orbital calculations for benzocyclobutadiene, see J. D. Roberts, A. Streitweiser, Jr. and C. M. Regan, *ibid.*, **74**, 4579 (1952).

sorbed readily only one mole of bromine to give a dibromide $C_{16}H_{12}Br_2$, m.p. 111.5–112.2° (XIX). Dehydrobromination of the dibromide by potassium *t*-butoxide proceeded smoothly to give, as the sole product, a monobromide, $C_{16}H_{11}Br$, m.p. 124.3–124.6° (XX). Dehydrogenation of the monobromide by N-bromosuccinimide in benzene gave as the only isolable product a yellow compound, $C_{16}H_9Br$, m.p. 126–126.5°. The identity of this substance with an authentic sample of 5-bromobenzo[a]biphenylene[15] (XXI) establishes unambiguously the position of the double bond in the central six-membered ring of benzocyclobutadiene dimer.

It is planned to study the generation of benzocyclobutadiene in the presence of other dienes and dienophiles in the hope of observing other Diels–Alder reactions of this molecule.

Acknowledgment.—We should like to thank the Research Corporation for a grant supporting this work.

Experimental[16]

Reaction of α,α,α',α'-Tetrabromo-*o*-xylene (V) with Sodium Iodide.—To a 5-l. 3-necked flask provided with a reflux condenser and an all-glass stirrer was added α,α,α',α'-tetrabromo-*o*-xylene (500 g.), sodium iodide (750 g.), absolute ethanol (2500 ml.) and water (1 ml.). The mixture was refluxed gently with stirring for 48 hr., during which time iodine was liberated gradually. The condenser was set for removal of the solvent and, with stirring, ethanol (1000 ml.) was distilled out. Water (1000 ml.) was added, and ethanol (1000 ml.) was distilled out. The mixture was cooled to room temperature and, with good stirring, a stream of sulfur dioxide was passed through until all of the iodine was reduced. With continued stirring, ice was added to bring the temperature down to 10°. After 3 hr. of stirring at 10°, the solution was decanted from the oily, granular, dark brown precipitate which was then filtered, washed with ice-water (500 ml.), cold 5% sodium bicarbonate (500 ml.) and again with ice-water (500 ml.). The crude moist product (325 g.) was dissolved in Skellysolve F and filtered through sodium sulfate. The brown filtrate (2000 ml.) was concentrated to 1 liter and passed through alumina (450 g.). The column was eluted with petroleum ether (30–60°) and the eluate collected in two fractions: A (1000 ml.) and B (1500 ml.). Fraction A was evaporated and the residual oil was distilled under reduced pressure. The material boiling at 95–100° (0.6 mm.) was recrystallized three times from petroleum ether (cooling each time to −5°) to yield 124 g. of crystals, m.p. 46–47°. This material on repeated distillation gave a fraction with constant boiling point of 124.5° (9.5 mm.), which was recrystallized from petroleum ether to yield 15 g. of 1,2-dibromobenzocyclobutane (VI), m.p. 52.4–52.8°, not changed by further recrystallization.

Anal. Calcd. for $C_8H_6Br_2$: C, 36.68; H, 2.31; Br, 61.02; mol. wt., 262. Found: C, 36.56, 36.72; H, 2.48, 2.35; Br, 60.87, 60.83; mol. wt. (isothermal distillation in benzene), 258, 259. Ultraviolet spectrum (ethanol): λ_{max} 273.5 (log E 3.66); λ_{max} 280 (log E 3.62).

The residue from the first distillation of (A) was combined with fraction B, concentrated to 800 ml. and chromatographed through alumina (144 × 2.5 cm.), using 30–60 petroleum ether as eluent. The first 1350 ml. of eluate yielded 130 g. of material on crystallization (m.p. 46–47°); a second fraction (1250 ml.) yielded 15 g. (m.p. 51.6–52.2°) which was recrystallized 20 times from petroleum ether to yield 0.5 g. of pure 1,2-diiodobenzocyclobutene (IX), m.p. 62.7–62.8°.

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 in benzene), 350. Ultraviolet spectrum (ethanol), λ_{max} 287 (log E 3.73).

The alumina column on which the original sodium iodide reaction mixture was chromatographed was eluted with 1:9 benzene-Skellysolve F (1000 ml.). Evaporation of the eluate left long white needles (5.3 g.) which, after three crystallizations from methylene chloride-Skellysolve F, melted at 136–138° dec.

Anal. Calcd. for $C_{16}H_{12}BrI_3$: C, 28.90; H, 1.82; Br, 12.02; I, 57.26; mol. wt., 664. Found: C, 28.98; H, 1.81; Br, 11.65; I, 57.45; mol. wt. (isothermal distillation in methylene chloride), 664, 532. Ultraviolet spectrum (ethanol), λ_{max} 289 (log E 3.94).

Treatment of Dibromide VI with Maleic Anhydride.—Dibromide VI (1.00 g.) and maleic anhydride (3.0 g.) were mixed and heated 15 hr. on the steam-bath. Hot water was added to dissolve the unreacted maleic anhydride. The mixture was cooled and the white crystals filtered and dried. Unreacted dibromide (0.975 g.) was recovered, m.p. 51.5°, not depressed by a sample of the starting material (m.p. 51.5°).

Oxidation of Dibromide VI.—Dibromide VI (1.00 g.) and nitric acid (d. 1.42, 20 ml.) were heated together on the steam-bath for 40 minutes, after which time bromine vapors no longer were evolved. The clear solution was evaporated to dryness, the last traces of nitric acid being removed by adding benzene and evaporating again to dryness. The solid residue of crude phthalic acid (m.p. 190–210°) weighed 0.650 g. (theoretical yield 0.644 g.). A small portion was sublimed to give phthalic anhydride (m.p. 128–129°). The mixed melting point with an authentic sample (m.p. 132°) was 128–130°, and the infrared spectra of both samples were identical.

Reaction of Dibromide VI with Bromine. (a).—A mixture of dibromide VI (1.00 g.) and bromine (12 ml.) was refluxed 46 hr. After evaporation of the bromine, the residue (1.05 g.) was dissolved in Skellysolve F and filtered through alumina. Evaporation of the solvent and two recrystallizations of the residue from Skellysolve F gave unchanged dibromide, m.p. 49–50°. The infrared spectrum of this material was identical with that of an authentic sample.

(b).—A solution of dibromide VI (1.00 g.) and bromine (2.2 ml.) in chloroform (12 ml.) was placed in a Carius tube. The tube was sealed and heated at 150° for 12 hr. The tube was cooled and opened and the solution evaporated to dryness. The residue was dissolved in benzene and filtered through alumina. Evaporation of the filtrate left a residue (1.42 g.) which, after one crystallization from methylene chloride-Skellysolve F, gave α,α,α',α'-tetrabromo-*o*-xylene (0.775 g., 48%), m.p. 110–113°. A further recrystallization from the same solvent gave pure tetrabromide, m.p. 114–115°. The mixed melting point with authentic material (m.p. 115.5°) was 113.5–115°; in addition, the infrared spectra of both samples were identical.

Treatment of Dibromide VI with Potassium Acetate.—A mixture of dibromide VI (m.p. 52.1–52.6°, 0.50 g.), potassium acetate (2.0 g.) and ethanol (6 ml.) was refluxed for 50 hr. Careful addition of water (75 ml.) to the cooled solution gave fine crystals, which were filtered off and dried. The unchanged dibromide (0.45 g.) melted at 52.1–52.6°; the melting point was not depressed by authentic starting material.

Reaction of Dibromide VI with Sodium Iodide.—A mixture of dibromide VI (46.0 g.), iodine (15 g.) and absolute ethanol (500 ml.) was refluxed gently with stirring for 8 days. Ethanol (250 ml.) was distilled out, water (700 ml.) was added and sulfur dioxide was passed through the solution until all of the iodine was reduced. The mixture was extracted twice with 4:1 petroleum ether (30–60°)-benzene (700 ml. total). The hydrocarbon layer was evaporated under reduced pressure to remove all of the benzene, and the residue dissolved in a minimal volume of petroleum ether (30–60°) and adsorbed on a column of alumina (20 × 3 cm.). The column was eluted with petroleum ether until evaporation of an eluate sample left no residue. Elution of the column with methylene chloride removed 3.6 g. of triiodide, m.p. 135–137°. The petroleum ether eluate was concentrated to a small volume and rechromatographed on a column of alumina (50 × 4 cm.). The column was eluted first with petroleum ether (30–60°; 5000 ml.) which, on evaporation left 48.7 g. (78%) of 1,2-diiodobenzocyclobutene (IX). After one recrystallization from petroleum ether the diiodide melted at 62.7–62.9°. Elution of the alumina column with methylene chloride removed 7.5 g. of triiodide, bringing the total yield of triiodide to 10.1 g. (10%).

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[15] M. P. Cava and J. F. Stucker, THIS JOURNAL, **79**, 1706 (1957).

[16] Analyses carried out by Galbraith Laboratories, Knoxville, Tennessee. Melting points are corrected.

Zinc Dehalogenation of Dibromide VI and Diiodide IX.—Zinc dust (10 g.) was shaken with saturated aqueous ammonium chloride and then washed with water, followed by 95% ethanol. This activated zinc dust (10 g.) and hydroquinone (2 g.) were added to 95% ethanol (200 ml.) in a 500-ml. 3-necked flask equipped with a reflux condenser, nitrogen inlet tube and addition funnel. To the rapidly stirred refluxing mixture there was added slowly over 6 hr. a solution of dibromide VI (3.00 g.) in 95% ethanol (150 ml.) nitrogen being constantly passed through the system. After refluxing for an additional 30 hr., the suspension was filtered and the filtrate concentrated to 100 ml. Water (75 ml.) was added and the milky suspension extracted with Skellysolve F (200 ml.). The extract was concentrated to 100 ml. and poured through a column of alumina (15 × 2 cm.), the column being eluted with Skellysolve F (500 ml.). Concentration of the eluate and cooling to −50° gave, in two crops, **benzocyclobutadiene dimer XV** (0.97 g., 83%), m.p. 70°. Further recrystallization or sublimation at 100° (1 mm.) raised the melting point to 74.7–74.9°.

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 in methylene chloride), 200. Ultraviolet spectrum (ethanol): λ_{max} 215 (log *E* 4.50); λ_{max} 266 (log *E* 3.96); λ_{max} 273 (log *E* 3.93).

Elution of the alumina column with methylene chloride and evaporation of the eluate left a viscous gum. The dropwise addition of a concentrated solution of the gum in methylene chloride to a large volume of methanol precipitated a white amorphous powder, m.p. 125–145°. Qualitative tests showed this material to be halogen-free, although upon analysis very low carbon values were observed. The polymer contained, apparently, some oxygen.

Anal. Calcd. for $(C_8H_6)_x$: C, 94.07; H, 5.92. Found: C, 89.95, 90.15; H, 5.93, 5.96.

The reaction of diiodide IX with zinc dust under similar conditions gave the same mixture of amorphous polymer and benzocyclobutadiene dimer (70%), separated as described above.

Aromatization of Benzocyclobutadiene Dimer (XV) to Benzo[a]biphenylene (XVI).—The dimer XV (0.400 g.) was added to a solution of N-bromosuccinimide (0.400 g.) in benzene (50 ml.). The solution was refluxed for 36 hr., while illuminated by a 100-w. tungsten bulb. The yellow solution was cooled and filtered through a column of alumina (12 × 0.75 inch), the column being eluted with benzene until the eluate was colorless. The yellow eluate was evaporated on the steam-bath to 100 ml. and 2,4,7-trinitrofluorenone (0.400 g.) was added. The solution was concentrated to 75 ml. and methanol (150 ml.) was added. After cooling for 1 hr. at 0° the black complex (299 mg.), m.p. 203–204°, was filtered off and washed with petroleum ether. Concentration of the mother liquor yielded a second crop of complex (133 mg.), m.p. 204–205° and, after the addition of more 2,4,7-trinitrofluorenone, a third crop (50 mg.), m.p. 198–202°, was obtained. The total yield was 0.482 g. (48%). A solution of recrystallized complex (0.150 g.) in benzene was filtered through a column of alumina (10 × 0.75 inch) and the yellow eluate was evaporated in a stream of nitrogen. The residue was sublimed at 110–120° (0.5 mm.) to give voluminous yellow needles, m.p. 71.2–72.4° (slow melting point in a preheated bath). The mixed melting point with authentic benzo[a]-biphenylene[6] (m.p. 72–72.8°) was 71.2–72.9°. In addition the infrared and ultraviolet spectra of both samples were identical.

Reaction of Bromine with Dimer XV.—To a solution of dimer XV (1.03 g.) in chloroform (100 ml.), cooled to 0°, there was added dropwise a solution of bromine (0.808 g.) in chloroform (50 ml.). After evaporation of the chloroform on the steam-bath, the residue was dissolved in Skellysolve F, the solvent was concentrated to a volume of 40 ml. and cooled at −5° for 15 hr. Colorless needles (1.55 g.), m.p. 104.5–106.5°, separated; concentration of the filtrate gave a further quantity (0.150 g.) of similar material, the total yield being 1.70 g. (94%). After three recrystallizations from petroleum ether, analytically pure dibromide (XIX) was obtained, m.p. 111.5–112.2° dec.

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.

Dehydrobromination of Dimer Dibromide XIX.—To a solution of dibromide XIX (1.29 g.) in *t*-butyl alcohol (50 ml.) and benzene (15 ml.), was added a 1.15 *N* solution (20 ml.) of potassium *t*-butoxide in *t*-butyl alcohol. After standing at room temperature for 19 hr., the solution was diluted with water and extracted with several portions of ether-benzene mixture. The solvent was filtered through sodium sulfate and evaporated to dryness. The solid residue was dissolved in petroleum ether (30–60°), the solvent concentrated to 40 ml. and cooled to −5°. There was obtained, in three crops, 0.840 g. (84%) of **monobromide (XX)**, m.p. 124°. Recrystallization from petroleum ether (30–60°) gave long needles, m.p. 124.3–124.6°.

Anal. Calcd. for $C_6H_{11}Br$: C, 67.86; H, 3.92; Br, 28.22. Found: C, 67.59; H, 4.02; Br, 28.01.

Aromatization of Dimer Monobromide (XX) to 5-Bromobenzo[a]biphenylene (XXI).—To a solution of N-bromosuccinimide (0.400 g.) in benzene (50 ml.) was added the monobromide XX (0.400 g.). The solution was refluxed for 15 hr., while illuminated by a 100-w. tungsten bulb. The yellow solution was cooled and filtered through a column of alumina (8 × 0.75 inch), the column being eluted with benzene until the eluate was colorless. The yellow eluate was evaporated on the steam-bath to 100 ml. and 2,4,7-trinitrofluorenone (0.400 g.) was added. The solution was concentrated to 50 ml. and methanol (150 ml.) was added. After cooling for 1 hr. at −5° the fine brown crystals (184 mg.), m.p. 202–203°, were filtered off and recrystallized from benzene-methanol to give lustrous brown-black needles, m.p. 203–204°. A solution of pure complex (100 mg.) in benzene was filtered through a column of alumina and the yellow eluate was evaporated in a stream of nitrogen. Sublimation of the solid residue at 140–150° (0.75 mm.) gave an orange crust (m.p. 125–125.5°) which, after crystallization from aqueous ethanol, afforded voluminous orange-yellow needles, m.p. 126–126.5°. The mixed melting point with an authentic sample of 5-bromobenzo[a]biphenylene (m.p. 126–127.5°)[15] was 126–127°. In addition, the infrared and ultraviolet spectra of both samples were identical.

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