Condensed Cyclobutane Aromatic Systems. III. The Dehydrobromination of 1,2-Dibromobenzocyclobutene

BY M. P. CAVA AND J. F. STUCKER

The orange crystalline compound $C_{16}H_9Br$, formed by the action of strong base on 1,2-dibromobenzocyclobutene, is shown to be 5-bromobenzo[a]biphenylene (VIII). Compound VIII has been converted to benzo[a]biphenylene and its structure confirmed by an independent synthesis from 4-bromo-2-naphthylamine.

In the preceding paper of this series[1] we have reported the nature of the reaction of 1,2-dibromobenzocyclobutene[2] (I) with sodium iodide and with zinc dust. We have now examined the behavior of I under dehydrohalogenating conditions.

It was observed by Finkelstein[2] that when the dibromide I was heated with 30% methanolic potassium hydroxide, an orange crystalline compound, m.p. 121°, was formed. Elementary analysis indicated the probable empirical formula $C_{16}H_9Br$. However, the analytical results were poor and the formula $C_{16}H_{11}Br$ could not be excluded. The orange bromide II did not add bromine, indicating the absence of a reactive olefinic double bond. It was recovered unchanged after boiling with sodium in ethanol, although sodium in amyl alcohol reduced it to a colorless oil, not further identified. Oxidation of II by chromic acid in acetic acid gave benzophenone-2,2'-dicarboxylic acid, isolated as the dilactone III. On the basis of these observations, Finkelstein suggested that II might be 3-bromo-1,2:4,5-dibenzopentalene (IV). No path was suggested for the formation of this product.


I, R = H; R' = Br
V, R = R' = H
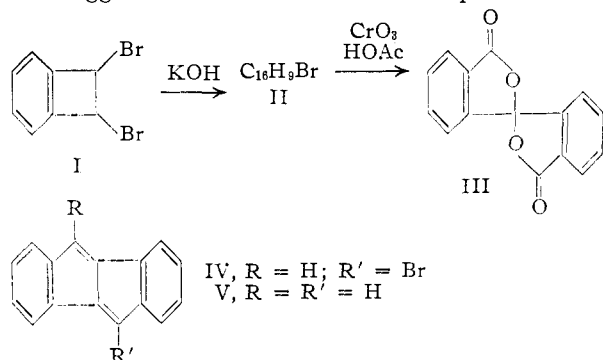
We have repeated and improved the preparation of the bromide II. Using iodine-free 1,2-dibromobenzocyclobutene and employing potassium t-butoxide in t-butyl alcohol as the base, a rapid exothermic reaction was observed, and the pure monobromide II, m.p. 126–127°, was isolated in 86% yield as long orange needles. Analysis definitely confirmed the expected empirical formula $C_{16}H_9Br$.
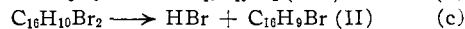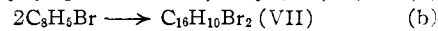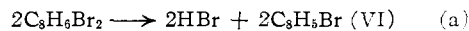
The original formulation of II as structure IV is not consistent with its oxidation to benzophenone-2,2'-dicarboxylic acid, particularly under acidic conditions. Indeed, the expected oxidation product of IV, benzil-2,2'-dicarboxylic acid, is known to be produced by oxidation of the parent hydrocarbon of IV, namely, 1,2:4,5-dibenzopentalene (V).[3]

(1) M. P. Cava and D. R. Napier, THIS JOURNAL, **79**, 1701 (1957).
(2) H. Finkelstein. Inaugural Dissertation, Strassbourg, 1910.
(3) C. T. Blood and R. P. Linstead, J. Chem. Soc., 2265 (1952).

Examination of the stoichiometry of the dehydrobromination of 1,2-dibromobenzocyclobutene indicates that the monobromide II is produced according to the over-all equation

$$2C_8H_6Br_2 \longrightarrow C_{16}H_9Br + 3HBr$$
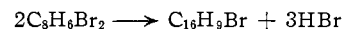
If the above equation is broken down into several steps, it can be rewritten as

$$2C_8H_6Br_2 \longrightarrow 2HBr + 2C_8H_5Br \text{ (VI)} \quad \text{(a)}$$
$$2C_8H_5Br \longrightarrow C_{16}H_{10}Br_2 \text{ (VII)} \quad \text{(b)}$$
$$C_{16}H_{10}Br_2 \longrightarrow HBr + C_{16}H_9Br \text{ (II)} \quad \text{(c)}$$

The first assumed intermediate C_8H_5Br (VI) should be the primary dehydrobromination product of 1,2-dibromobenzocyclobutene, namely, 1-bromobenzocyclobutadiene. In analogy with the previously observed behavior of the unsubstituted benzocyclobutadiene,[1] two molecules of VI would be expected to undergo condensation via a Diels–Alder reaction, the addition occurring in an angular manner rather than in a linear one. However, because of the added asymmetry of VI compared to benzocyclobutadiene, four different modes of Diels–Alder between two molecules of VI are theoretically possible, as illustrated by A, B, A' and B'. Path A would appear to be the most attractive one, since in the transition state of the

B:

VIIb

B':   IX
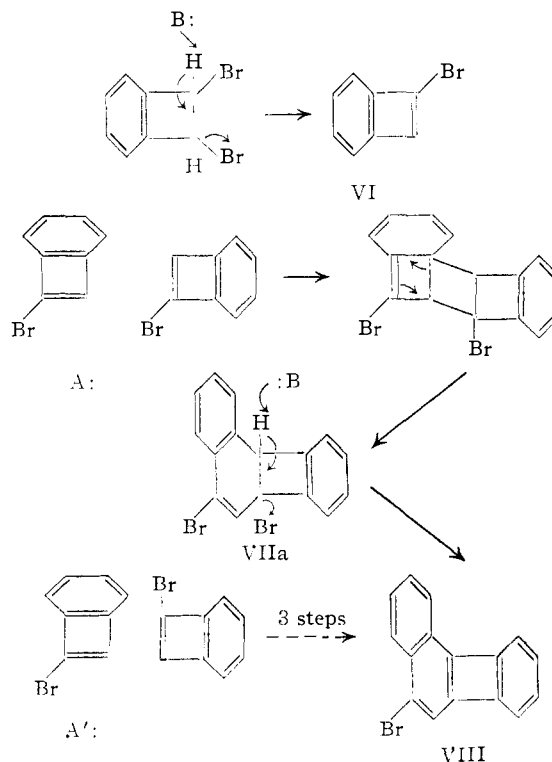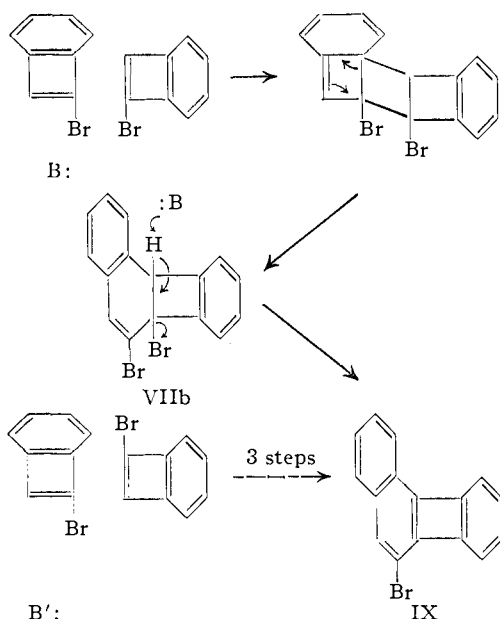
Diels–Alder reaction the bromine atoms of the two molecules of VI are in the positions offering the least possible amount of steric hindrance. The immediate condensation product from path A would give, after rearomatization, a dibromodihydrobenzo[a]biphenylene (VIIa). Dehydrobromination of VIIa, in the basic solution in which it is produced, would give the completely aromatic 5-bromobenzo[a]biphenylene (VIII). The somewhat less sterically favored path B would lead, by a sequence of completely analogous steps, to the isomeric 6-bromobenzo[a]biphenylene (IX). The routes A' and B', although the least likely sterically, would produce the same end products as routes A and B, respectively.

The formulation of the orange bromide II as either VIII or IX is in accord with its oxidation by chromic acid to the dilactone III, since the parent hydrocarbon benzo[a]biphenylene (X) is oxidized also to III under similar conditions.[4] Furthermore, the infrared spectrum of II is very similar to that of the hydrocarbon X. Especially outstanding in the spectrum of II are two strong bands at 13.42 and 13.63 μ, almost identical to those exhibited by X at 13.41 and 13.64 μ.[4] The complex ultraviolet spectra of II and X are even more similar. The two spectra are almost superimposable, that of II being shifted to slightly longer wave lengths than that of X,[4] however, and exhibiting an additional short wave length maximum at 225 mμ.

Definite proof that II was represented by either VIII or IX was obtained by replacement of its bromine atom by hydrogen. Several attempts to remove the bromine atom by a catalytic hydrogenolysis were unsuccessful, reductive cleavage of the ring system proceeding simultaneously with the removal of the halogen. However, treatment of the bromide II with n-butyllithium effected a metal exchange reaction and, after decomposition of the lithio derivative with methanol, benzo[a]-biphenylene (X), identical in all respects with an authentic sample,[4] was isolated in 19% yield.

(4) M. P. Cava and J. F. Stucker, THIS JOURNAL, **77**, 6022 (1955).

$$C_{16}H_9Br \xrightarrow{n\text{-BuLi}} C_{16}H_9Li \xrightarrow{CH_3OH}$$

X
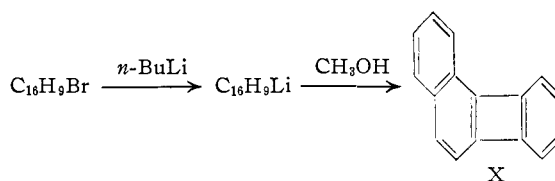
The one structural element of II which now remained in doubt was the position of the bromine atom in the central ring of the benzo[a]biphenylene nucleus. This problem was resolved by an unambiguous synthesis of 5-bromobenzo[a]biphenylene (VIII).

1-Amino-2-nitro-4-bromonaphthalene (XI)[5] was deaminated to 2-nitro-4-bromonaphthalene (XII) in 76% yield by a new deamination procedure using hypophosphorous acid, the previously described deaminations of XI[6,7] giving, in our hands, poor yields of difficultly purified material. Reduction of XII gave 4-bromo-2-naphthylamine[8] (XIII), converted by thionyl chloride to 4-bromo-2-thionyl-aminonaphthalene (XIV). Reaction of XIV with β-phenylhydroxylamine gave, in 41% yield, 4-bromo-2-(benzeneazo)-naphthalene (XV). Ammonium sulfide reduction of XV to the hydrazo compound (XVI), followed by hydrochloric acid treatment of XVI gave a 65% yield of 4-bromo-1-(2-aminophenyl)-2-naphthylamine (XVII). The o,o'-diamine structure of XVII was confirmed by heating its hydrochloride to 220°, when loss of ammonia occurred with the formation of 5-bromo-7-benzo[c]carbazole (XVIII). This behavior parallels exactly the known conversion of 1-(2-aminophenyl) - 2 - naphthylamine (XIX) to 7-benzo[c]carbazole.[9] Further confirmation of the structure of the bromodiamine XVII was obtained by reducing the unsubstituted 2-benzeneazonaphthalene (XX) with ammonium sulfide and rearranging the resulting hydrazo compound (XXI) with hydrochloric acid, when the known diamine XIX was obtained in 72% yield. These experiments constitute, incidentally, the first direct demonstration that the acid-catalyzed rearrangement of N-phenyl-N'-(2-naphthyl)-hydrazines gives o-benzidine type products.

XX   XXI

72% $\downarrow$ HCl

NH₂ H₂N

XIX
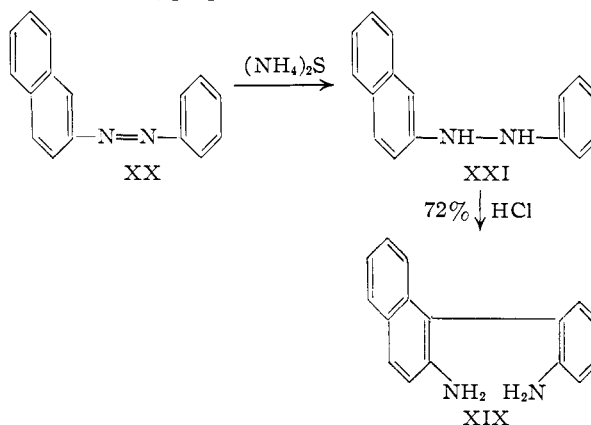
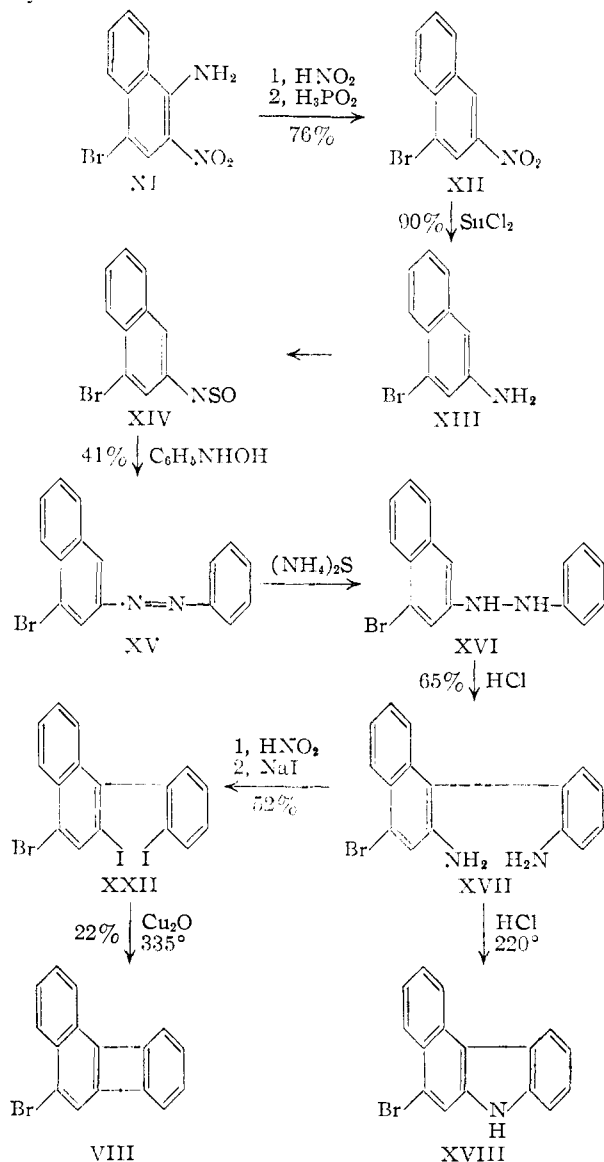(5) H. H. Hodgson and S. Birtwell, *J. Chem. Soc.*, 321 (1943).

(6) C. Liebermann and F. Scheiding, *Ber.*, **8**, 1108 (1875).

(7) H. H. Hodgson, S. Birtwell and E. Marsden, *J. Chem. Soc.*, 112 (1944).

(8) H. H. Hodgson and R. L. Elliott, *ibid.*, 1850 (1935).

(9) W. Fuchs and F. Niszel, *Ber.*, **60**, 209 (1927).

Diazotization of the bromodiamine (XVII), followed by the reaction of the tetrazonium salt with sodium iodide, gave, in 52% yield, 4-bromo-1-(2-iodophenyl)-2-iodonaphthalene (XXII). Pyrolysis of XXII with active cuprous oxide[4] at 335° and 3.5 mm. gave an orange sublimate, from which 5-bromobenzo[a]biphenylene (VIII) was isolated in 22% yield as its beautifully crystalline, deep brown 2,4,7-trinitrofluorenone complex. Regeneration of the *5-bromobenzo[a]biphenylene* from the complex gave orange needles which, in elementary composition, infrared spectrum and ultraviolet spectrum were *indistinguishable from the dehydrobromination product of 1,2-dibromobenzocyclobutene.*

NH₂ → 1, HNO₂ 2, H₃PO₂ 76% → XII

XI

90% ↓ SnCl₂

XIV ← XIII

41% ↓ C₆H₅NHOH

XV →(NH₄)₂S→ XVI

65% ↓ HCl

XXII ←1, HNO₂ 2, NaI 52%— XVII

22% ↓ Cu₂O 335°

VIII   ↓ HCl 220°   XVIII

Experimental[10]

5-Bromobenzo[a]biphenylene (VIII).—To a hot solution of potassium *t*-butoxide, prepared by dissolving potassium (7 g.) in *t*-butyl alcohol (130 ml.), was added slowly 1,2-dibromobenzocyclobutene (14.7 g.). The yellow-orange solution was refluxed for 40 minutes; water (120 ml.) was added, fol-

(10) Analyses were carried out by Galbraith Laboratories, Knoxville, Tennessee.

lowed by sufficient acetic acid to neutralize the excess base. The solution was cooled and the orange crystalline precipitate was filtered off, washed with water and dried in a vacuum desiccator. The crude product was extracted for 7 hr. in a Soxhlet apparatus with Skellysolve F, when a small amount of an amorphous brown powder remained behind in the extraction thimble. The Skellysolve extract was evaporated to dryness and the residue was crystallized from aqueous ethanol to give orange needles of 5-bromobenzo[α]biphenylene (6.80 g., 86.1%), m.p. 125–126°. Vacuum sublimation followed by recrystallization from aqueous ethanol raised the melting point to 126–127.5°.

Anal. Calcd. for C₁₆H₉Br: C, 68.33; H, 3.20; Br, 28.47. Found: C, 68.19; H, 3.23; Br, 28.69.

The infrared spectrum was determined in carbon bisulfide solution and exhibited medium or low intensity bands at 3.30, 7.01, 7.09, 7.37, 8.02, 8.37, 9.09, 9.82, 10.25, 10.44, 11.00, 11.48, 11.55 and 12.08 μ. In addition, four bands of high intensity were observed at 8.82, 13.20, 13.42 and 13.63 μ.

The ultraviolet spectrum was determined in 95% ethanol and the following maxima were found: λ 225 mμ (log E 4.36), 264 (4.72), 283 (4.47), 294 (4.49), 381 (4.75), 400 (4.91).

The 2,4,7-trinitrofluorenone complex of VIII was prepared by mixing equimolar saturated benzene solutions of 2,4,7-trinitrofluorenone and the bromide. After two recrystallizations from benzene–methanol the complex formed deep brown shining needles, m.p. 202–203°.

Anal. Calcd. for C₂₉H₁₄N₃BrO₇: C, 58.39; H, 2.35; N, 7.05; Br, 13.42. Found: C, 58.70; H, 2.43; N, 7.06; Br, 13.20.

Reduction of 5-Bromobenzo[a]biphenylene (VIII) to Benzo[a]biphenylene (X).—To a suspension of lithium (0.080 g.) in dry ether (10 ml.) was added slowly with magnetic stirring 1-bromobutane (0.50 ml.) under a nitrogen atmosphere. After 10 minutes, a solution of 5-bromobenzo[a]biphenylene (0.200 g.) in a mixture of ether (10 ml.) and benzene (2 ml.) was added slowly. After a further 45 minutes methanol (1 ml.) was added. The yellow solution was washed by shaking with dilute hydrochloric acid, dilute potassium hydroxide and finally with water. Evaporation of the dried ethereal layer gave a residual oil which was treated with a concentrated benzene solution of 2,4,7-trinitrofluorenone. A voluminous charcoal-black complex (0.070 g., 19.1%) separated, which after two recrystallizations from benzene–methanol melted at 200–203°. A benzene solution of the complex was chromatographed on alumina and the yellow eluate was evaporated. Sublimation of the residue under vacuum gave small yellow needles, m.p. 72.2–73.0°. The melting point was not depressed upon admixture with authentic benzo[a]biphenylene,[4] m.p. 72.2–72.8°. In addition, the ultraviolet and infrared spectra of the sample were identical with the previously observed spectra[4] of benzo[a]biphenylene.

Oxidation of 5-Bromobenzo[a]biphenylene.—To a solution of 5-bromobenzo[a]biphenylene (0.400 g.) in acetic acid (20 ml.) was added chromic oxide (1.10 g.). After refluxing for 1 hr., during which time bromine vapors were evolved, the acetic acid was removed by distillation under reduced pressure, leaving a dark green gum. Concentrated hydrochloric acid (40 ml.) was added and the solution was heated on the steam-bath for a few minutes. After cooling, white crystals separated which were filtered off and sublimed at a bath temperature of 215° under a pressure of 3 mm. of mercury. The sublimate, after recrystallization from ethanol, formed white crystals (0.039 g., 14.7%), m.p. 208–210°. The melting point was not depressed after mixing with an authentic sample of the dilactone of benzophenone-2,2′-dicarboxylic acid, m.p. 208–210°, prepared by the oxidation of 2,2′-dimethylbenzophenone. In addition the infrared spectra in chloroform of both samples of the lactone were identical.

Conversion of 2-Benzeneazonaphthalene (XX) to 1-(2-Aminophenyl)-2-naphthylamine (XIX).—To a hot solution of 2-benzeneazonaphthalene[11] (0.215 g.) in ethanol (8 ml.) was added slowly, with continued warming on the steam-bath, aqueous 16% ammonium sulfide until the color of the solution became light yellow and the solution remained cloudy while hot. After cooling, the hydrazo compound separated

(11) H. E. Fierz-David, L. Blangey and E. Merian, *Helv. Chim. Acta,* **34,** 846 (1951).

as an oil which crystallized on rubbing. Water was added carefully to precipitate all of the dissolved material, which was then filtered and washed well with cold water. The crude hydrazo compound was added at room temperature to 20% aqueous hydrochloric acid (3.5 ml.). After 5 minutes the mixture was warmed for 5 minutes on the steam-bath, water (10 ml.) added and the solution filtered. The filtrate was almost neutralized with sodium hydroxide solution and then made basic by the addition of excess sodium carbonate solution. The gum which separated was rubbed until solid, filtered, washed well with water and crystallized from aqueous ethanol. The colorless needles of 1-(2-aminophenyl)-2-naphthylamine (0.156 g., 72%) melted at 154–155°. The melting point was not depressed after mixing with an authentic sample[4] of diamine, and the infrared spectra of both samples were identical.

4-Bromo-2-nitronaphthalene (XII).—To concentrated sulfuric acid (85 ml.) was added slowly with stirring, powdered sodium nitrite (6.00 g.) at 15–20°. To the resulting solution was added, at 15–20°, 4-bromo-2-nitro-1-naphthylamine[5] (13.35 g.) in small portions. Acetic acid (85 ml.) was run in slowly at 15–20° (heat is evolved) and the resulting solution was allowed to stand for 30 minutes at the same temperature. The resulting diazonium solution was added slowly with shaking to a freshly prepared solution of hydrated cupric sulfate (13.0 g.) in 32% hypophosphorous acid (100 ml.), the temperature of the mixture being maintained at 10–20° during the reaction. During the addition of the diazonium solution there was added to the hypophosphorous acid solution, in several portions, ethanol (50 ml.), and after the addition of diazonium solution was completed, a further amount of ethanol (50 ml.) was added. After 1 hr. sufficient water was added to increase the total volume to one liter and the suspension was heated to 55° to coagulate the solid product. After cooling, the precipitate was filtered, washed well with water, sucked almost dry and dissolved in a hot mixture of ethanol (100 ml.) and acetone (350 ml.). The hot solution was filtered to remove a dark flocculent impurity and the filtrate reheated and water added to the hot solution until crystals appeared. After cooling, the pale brown crystals (9.60 g., 76%) were filtered and dried; m.p. 129–130° (reported[6] 131°).

4-Bromo-2-naphthylamine (XIII).—The amine was prepared by reduction of the above nitro compound with stannous chloride.[8] The crude dark amine was purified by passing its solution in methylene chloride through alumina, concentrating the eluate to a small volume and carefully adding petroleum ether (30–60°). The yield from 29 g. of nitro compound was 20.8 g. (90%), m.p. 70–71° (reported[8] 72°).

4-Bromo-2-(benzeneazo)-naphthalene   (XV).—Thionyl chloride (2.8 ml.) was added dropwise with swirling and external cooling to a solution of 4-bromo-2-naphthylamine (7.27 g.) in benzene (50 ml.). The resulting suspension was refluxed for 45 minutes, when all of the precipitate of amine hydrochloride dissolved. The deep orange-brown solution was evaporated under vacuum with gentle heating until all of the benzene and excess thionyl chloride was removed. The brownish yellow crystalline residue of the thionyl amine XIV (m.p. 82–83°) was dissolved in benzene (65 ml.) and added in small portions with swirling to a solution of pure N-phenylhydroxylamine (9.1 g.) in benzene (260 ml.) in which anhydrous sodium sulfate (30 g.) was suspended. After 14 hr. at room temperature the red-orange solution was filtered and the filtrate concentrated to about 60 ml. and chromatographed on a column of alumina (2 × 60 cm.). A broad orange-red band was eluted by benzene. The solvent was evaporated on the steam-bath and the solid residue was crystallized from aqueous ethanol. The azo compound (4.20 g., 41%) formed a voluminous mass of orange needles, m.p. 122–123.5°.

Anal. Calcd. for C₁₆H₁₁N₂Br: C, 61.74; H, 3.54; N, 9.00; Br, 25.72. Found: C, 61.75; H, 3.65; N, 9.15; Br, 25.52.

4-Bromo-1-(2-aminophenyl)-2-naphthylamine   (XVII).—To a hot solution of 4-bromo-2-benzeneazonaphthalene (4.20 g.) in ethanol (75 ml.) was added 16% aqueous ammonium sulfide (35 ml.) during a period of 10 minutes. After adding just enough water to make the solution slightly cloudy, seed crystals (obtained by cooling and scratching a few drops of the solution) were added. After cooling, the white crystalline hydrazo compound was filtered, washed with water and extracted three times with warm dilute hydrochloric acid. The combined filtered acid extracts were made basic with

aqueous ammonia and the white curdy precipitate filtered off. After two crystallizations from 1:1 ethanol–methanol, the diamine (2.75 g., 65%) formed small shining needles, m.p. 111.7–112.3°.

Anal. Calcd. for C₁₆H₁₃N₂Br: C, 61.34; H, 4.15; N, 8.95; Br, 25.56. Found: C, 61.52; H, 4.32; N, 8.79; Br, 25.40.

5-Bromo-7-benzo[c]carbazole (XVIII).—In a test-tube was placed the above diamine XVII (0.100 g.) and a small amount of concentrated hydrochloric acid. The tube was immersed in an oil-bath, the temperature of which was slowly raised to 220°. The residue in the tube was washed with dilute hydrochloric acid to remove unchanged diamine and crystallized from aqueous ethanol to give the carbazole (0.017 g., 18%) as white crystals, m.p. 168–170°.

Anal. Calcd. for C₁₆H₁₀NBr: C, 64.86; H, 3.38; N, 4.73; Br, 27.03. Found: C, 64.69; H, 3.52; N, 4.56; Br, 27.40.

4-Bromo-1-(2-iodophenyl)-2-iodonaphthalene (XXII).—To an ice-cold solution of 4-bromo-1-(2-aminophenyl)-2-naphthalene (5.40 g.) in water (40 ml.) and concentrated hydrochloric acid (20 ml.) was added slowly a solution of sodium nitrite (2.80 g.) in ice-water (15 ml.). The diazonium solution was allowed to stand for 15 minutes in an ice-bath. There was added then to it an ice-cold solution of sodium iodide (25 g.) in water (150 ml.). After standing for 1 hr. at 0° the mixture was allowed to warm to room temperature and sodium bisulfite was added to destroy any free iodine present. The brown precipitate was filtered, washed with cold water and dried at room temperature in a vacuum desiccator. The dry brown powder was extracted for 4 hr. in a Soxhlet apparatus with Skellysolve F. The brown extract was evaporated to dryness and the residue dissolved in benzene and chromatographed on alumina, the column being eluted with benzene. The red eluate was evaporated to dryness, dissolved in cyclohexane and the solution was completely adsorbed on excess dry alumina. The resulting moist alumina was placed in a paper thimble and extracted for 13 hr. with Skellysolve F in a Soxhlet apparatus. Evaporation of the extract left the diiodo compound (4.81 g., 52%) as light orange crystals, m.p. 151–153°. Two recrystallizations from aqueous ethanol gave almost colorless crystals, m.p. 158.8–159.3°.

Anal. Calcd. for C₁₆H₉BrI₂: C, 35.87; H, 1.76; Br, 14.68; I, 47.75. Found: C, 35.89; H, 1.68; Br, 14.95; I, 47.48.

5-Bromobenzo[a]biphenylene (VIII).—A finely ground mixture of 4-bromo-1-(2-iodophenyl)-2-iodonaphthalene (0.400 g.) and active[4] cuprous oxide (8.0 g.) was placed in a test-tube shaped sublimer provided with a side arm. The mixture was covered with additional active cuprous oxide (4.0 g.) and a cold finger condenser was fitted into the tube. After flushing the apparatus out with nitrogen and reducing the pressure to 3.5 mm., the lower portion of the tube was immersed in a salt-bath preheated to 335°, and heating was continued at this temperature for 30 minutes. The sublimate on the cold finger was washed off with benzene and the concentrated benzene wash was added to an excess of a saturated solution of 2,4,7-trinitrofluorenone in benzene. The dark brown complex which separated was filtered off and washed with a little methanol. Exactly the same experiment was repeated three times (total amount of bromodiiodide used = 1.600 g.) and the combined brown complex was recrystallized from benzene–methanol to give the pure complex (0.315 g., 22%) as glistening deep brown needles, m.p. 202–204°. A portion of the complex (0.210 g.) was dissolved in benzene and the benzene solution was passed through a column of alumina. The yellow-orange benzene eluate was crystallized from aqueous ethanol to give 5-bromobenzo[a]biphenylene (0.080 g., 80% based on complex used) as orange needles, m.p. 124–125°. Sublimation of the product under reduced pressure raised the melting point to 126–127°. The melting point was not depressed after mixing with a sample prepared by the dehydrobromination of 1,2-dibromobenzocyclobutene. In addition, the infrared and ultraviolet spectra of both samples were identical in every respect.

Anal. Calcd. for C₁₆H₉Br: C, 68.33; H, 3.20; Br, 28.47. Found: C, 68.30; H, 3.47; Br, 28.42.

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