deposited large white crystals of XII on cooling in the refrigerator. After washing well with petroleum ether, the crude product (0.246 g., 94%), m.p. 207–208°, was recrystallized from benzene to give the analytical sample, m.p. 208–209°.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79. Found: C, 76.45; H, 5.05.

B. A mixture of naphtho[*a*]cyclobutene (0.026 g.), maleic anhydride (0.021 g.), and diethyl phthalate (0.2 g.) was heated for one hour at 200°. The cooled mixture was diluted with ether and the crystals which separated were washed well with ether to yield pure XII (0.023 g., 53%), m.p. 208–209°.

1,2,3,4-Tetrahydro-cis-2,3-anthracenedicarboxylic acid anhydride (XIII). A. Naphtho[*b*]cyclobutene (I, 0.100 g.) maleic anhydride (0.068 g.) and diethyl phthalate (1 ml.) were heated (250°) in a test tube for 1 hr. The cooled reaction mixture was washed and rubbed well with ether, then dried to give anhydride (0.101 g., 61%), m.p. 306–308°. Repetition of this experiment at 200° afforded the same product in only 2% yield. The adduct was recrystallized from acetic anhydride for analysis.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79. Found: C, 76.85; H, 4.70.

B. A mixture of 1,2-dihydronaphtho[2,3-*c*]thiophene 2,2-dioxide[1] (0.50 g.) and maleic anhydride (2.22 g.) was refluxed gently for 1 hr. The cooled reaction product was washed three times with benzene to remove unchanged maleic anhydride. Crystallization of the residue from acetic anhydride gave anhydride XII (0.31 g.), identical in melting point and infrared spectrum with the product obtained in Section A.

N-Phenyl-1,2,3,4-tetrahydro-cis-2,3-phenanthrenedicarboximide (X). A mixture of sulfone VII (1.00 g.) and *N*-phenylmaleimide (1.00 g.) was heated in an open flask. At about 220° evolution of sulfur dioxide was observed. When no further sulfur dioxide was evolved, the melt was cooled and taken up in absolute ethanol. An insoluble amorphous residue was removed by filtration, and the filtrate was concentrated and cooled to give white needles of imide X (1.05 g., 70%), m.p. 149.5–150.0°.

Anal. Calcd. for $C_{22}H_{17}O_2N$: C, 80.73; H, 4.20; N, 4.28. Found: C, 80.55; H, 4.98; N, 4.30.

The ultraviolet spectrum (ethanol) showed the following maxima: λ_{max} 227 (log ϵ 4.91), 273 (3.71), 283 (3.76), 291 (3.61), 312 (2.66), 320 (2.62), and shoulders at 264 and 304 mμ.

N-Phenyl-2,3-phenanthrenedicarboximide (XI). Imide X and 10% palladium-on-carbon (0.025 g.) were mixed and heated slowly to 360° under nitrogen (atmospheric pressure). After thirty minutes at 360°, the melt was cooled to 275° and the product sublimed out at 2 mm. pressure onto a cold finger. Two crystallizations from acetic acid afforded pale yellow needles (0.080 g., 80%), m.p. 259–260°. The ultraviolet spectrum in ethanol showed only one maxima: λ_{max} 288 mμ (log ϵ 4.64).

Anal. Calcd. for $C_{22}H_{13}O_2N$: C, 81.72; H, 4.05; N, 4.33. Found: C, 81.72; H, 4.26; N, 4.22.

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

Condensed Cyclobutane Aromatic Compounds. XVIII. Synthesis of the Remaining α-Brominated Benzocyclobutenes

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Bromination of 1-bromobenzocyclobutene with *N*-bromosuccinimide gave 1,1-dibromobenzocyclobutene. The same reagent converted either *cis*- or *trans*-1,2-dibromobenzocyclobutene into 1,1,2-tribromobenzocyclobutene and eventually into 1,1,2,2-tetrabromobenzocyclobutene, thus completing the synthesis of all of the possible α-brominated benzocyclobutenes.

Of the six possible bromo derivatives of benzocyclobutene having one or more bromine substituents on the four-membered ring, three already have been described. These compounds are 1-bromobenzocyclobutene (I),[1,2] *trans*-1,2-dibromobenzocyclobutene (II),[3,4] and *cis*-1,2-dibromobenzocyclobutene (III).[5] This paper describes the synthesis of the remaining three bromides (IV, V and VI) and offers evidence for the structures assigned to them.

Although it was reported previously[1,2a] that attempted further bromination of monobromide I with *N*-bromosuccinimide failed, it has been found now that introduction of a second bromine is possible by using pure starting materials and a reaction time of several hours. The only product isolated, aside from starting material and a polymeric residue, was the liquid 1,1-dibromobenzocyclobutene (IV). The structure of IV was confirmed by hydrolysis with 5% sulfuric acid to benzocyclobutenone (VII), isolated in good yield as the known 2,4-dinitrophenylhydrazone.[6] The

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(1) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **80**, 2255 (1958).

(2) (a) E. Winkelmann, dissertation, University of Mainz, (1958); (b) L. Horner, W. Kirmse, and K. Muth, *Chem. Ber.*, **91**, 430 (1958).

(3) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **79**, 1701 (1957).

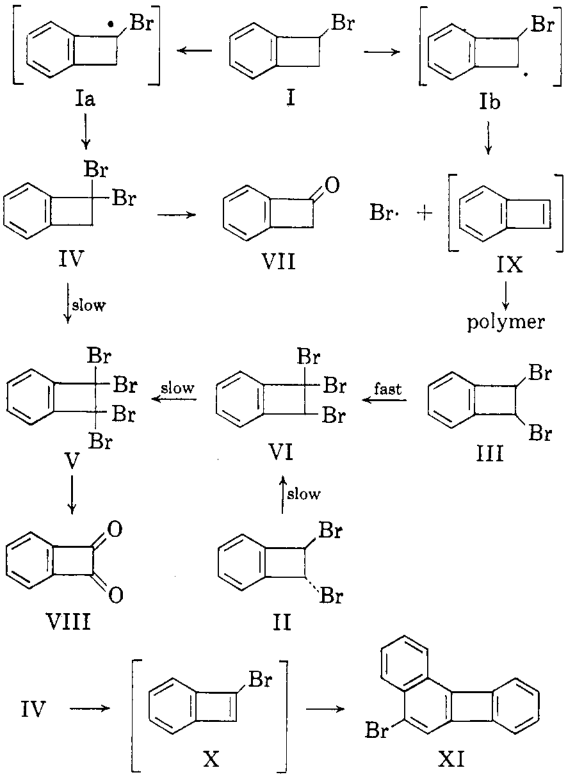
(4) H. Finkelstein, *Chem. Ber.*, **92**, XXXVII (1959).

(5) F. R. Jensen and W. E. Coleman, American Chemical Society Meeting, April 1958. Abstract of Papers, p. 79 N. The *cis*-dibromide III was obtained as a minor product of the reaction of either *cis*- or *trans*-1,2-diiodobenzocyclobutene with bromine.

(6) M. P. Cava and K. Muth, *J. Am. Chem. Soc.*, **82**, 652 (1960).

facile acid-catalyzed hydrolysis of IV finds analogy in the similar smooth conversion of 1,1-dichloro-3,4,5,6-tetramethylbenzocyclobutene to the corresponding ketone.[7]

Dehydrobromination of dibromide IV was effected readily by potassium *t*-butoxide to yield, *via* the benzocyclobutadiene X, 5-bromobenzo[*a*]biphenylene (XI) in 75% yield. This reaction is completely analogous with the previously observed dehydrobromination of *trans*-1,2-dibromobenzocyclobutene.[8]



As ordinarily prepared,[3,4] *trans*-1,2-dibromobenzocyclobutene is always contaminated[3] with some of the corresponding *trans*- and *cis*-1,2-diiodides.[9] Attempts to brominate further such material with *N*-bromosuccinimide in the presence of benzoyl peroxide for periods of up to a week led to essentially complete recovery of the starting material II. It was observed, however, that some decomposition of the accompanying diiodides occurred with the liberation of free iodine, a well-known inhibitor for free radical reactions. Consequently, a sample of pure dibromide II, freed from diiodides, was prepared by treatment of ordinary dibromide II with elemental bromine.[5] Bromination of this sample with excess *N*-bromosuccinimide was successful, although a reaction time of two days was needed. The reaction product, obtained in 65% yield, was a crystalline substance $C_8H_4Br_4$, m.p. 117–118°, which proved to be 1,1,2,2-tetrabromobenzocyclobutene (V). The assigned structure V was supported by treatment of the tetrabromide with silver trifluoroacetate, followed by water, to give the known benzocyclobutenedione (VIII).

Further bromination of 1,1-dibromobenzocyclobutene (IV) with one equivalent of *N*-bromosuccinimide occurred slowly to give an oil from which only starting dibromide IV and the tetrabromide V were isolated. An incomplete large-scale bromination of *trans*-dibromide II afforded, in addition to unchanged II and tetrabromide V, an oil from which on repeated distillation and crystallization a new bromide $C_8H_5Br_3$, m.p. 40–41°, was isolated. This substance was assigned the structure 1,1,2-tribromobenzocyclobutene (VI), since it could be converted with difficulty by *N*-bromosuccinimide to tetrabromide V. In contrast to the low reactivity of bromides II, IV and VI toward *N*-bromosuccinimide, *cis*-1,2-dibromobenzocyclobutene (III) was attacked rapidly by this reagent, giving tribromide VI in 72% yield in a six minute reaction.

Considering the bromination results with the entire series II, III, IV and VI, the conclusion may be drawn that replacement of a hydrogen by bromine in these benzocyclobutene derivatives occurs readily only when the hydrogen being replaced is *cis* to another α-hydrogen, rather than to a bromine atom. In other words, the removal of a hydrogen atom by the succinimide radical is subject to very considerable steric hindrance by a *cis* substituent as large as bromine, at least in a rigid small-ring system such as that of benzocyclobutene.

The bromination of monobromide I to dibromide IV and polymer deserves brief comment. Abstraction of a hydrogen at C-1 leaves a radical (Ia), stabilized by the adjacent bromo substituent, which reacts normally with a bromine atom to give 1,1-dibromide IV. Hydrogen abstraction at C-2, however, leaves a radical (Ib) which can collapse readily (perhaps concertedly as it is generated) to give a bromine atom and the unstable benzocyclobutadiene (IX). Polymerization of IX would lead to the observed gummy residue. An argument similar to that above has been offered previously[1] in explanation of the formation of polymers during the monobromination of benzocyclobutene to bromide I.

EXPERIMENTAL[10]

1,1-Dibromobenzocyclobutene (IV). A mixture of 1-bromobenzocyclobutene[1] (9.40 g.), *N*-bromosuccinimide (9.80 g.),

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[7] H. Hart and R. W. Fish, *J. Am. Chem. Soc.*, **82**, 749 (1960).

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

[9] F. R. Jensen and W. E. Coleman, *J. Org. Chem.*, **23**, 869 (1958).

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

benzoyl peroxide (0.50 g.) and carbon tetrachloride (130 ml.) was refluxed for 3.5 hr. The cooled solution was filtered from succinimide, the solvent evaporated under vacuum, and the remaining oil distilled at 0.5 mm. to give the following fractions: (*a*) 3.97 g., b.p. 62–70° (I and IV); (*b*) 4.12 g., b.p. 70–85° (mainly IV); (*c*) a gummy residue of 3.18 g. Redistillation of fraction (*b*) gave pure dibromide IV (2.80 g., 23%) as an oil, b.p. 85° (0.5 mm.).

Anal. Calcd. for $C_8H_6Br_2$: C, 36.68; H, 2.31; Br, 61.02. Found: C, 36.89; H, 2.23; Br, 60.97.

Hydrolysis of 1,1-dibromobenzocyclobutene (IV). A small sample of dibromide IV was stirred rapidly overnight at room temperature with 5% sulfuric acid. Extraction with ether and evaporation of the dried extract left an oil identified as benzocyclobutenone by its infrared spectrum and by the melting point and infrared spectrum of its 2,4-dinitrophenylhydrazone.[6] In a quantitative experiment, 0.050 g. of IV gave 0.041 g. (72%) of benzocyclobutenone 2,4-dinitrophenylhydrazone.

Dehydrobromination of 1,1-dibromobenzocyclobutene (IV). Dibromide IV (0.050 g.) was heated with a solution of excess potassium *t*-butoxide in *t*-butyl alcohol (2 ml.) until the reflux temperature was reached. After standing overnight at room temperature, the orange needles (0.021 g., 75%) of 5-bromobenzo[*a*]biphenylene (XI) were filtered and dried. The melting point (125–126°) and infrared spectrum were identical to those of an authentic sample.[8]

cis-1,2-Dibromobenzocyclobutene (III). Ordinary iodide-containing *trans*-1,2-dibromobenzocyclobutene[3] was treated with excess bromine in carbon tetrachloride at room temperature. Unchanged bromine and liberated iodine were removed by shaking with sodium bisulfite solution and the organic phase, after washing with dilute base, was dried and the solvent removed by distillation. The residual dark oil was purified by distillation under reduced pressure until only a black tar remained in the pot. The distillate was then twice more subjected to the entire purification process as outlined above. Most of the pure *trans*-1,2-dibromide was separated by crystallization from petroleum ether (30–60°). Fractional crystallization of the remaining material yielded the *cis*-dibromide (III) as long colorless needles, m.p. 101–101.5°.

Anal. Calcd. for $C_8H_6Br_2$: C, 36.68; H, 2.31; Br, 61.02. Found: C, 36.87; H, 2.08; Br, 61.12.

1,1,2,2-Tetrabromobenzocyclobutene (V). A mixture of pure *trans*-1,2-dibromobenzocyclobutene (II, 5.00 g.), benzoyl peroxide (0.25 g.), *N*-bromosuccinimide (7.00 g.) and carbon tetrachloride (50 ml.) was refluxed for one day. Additional *N*-bromosuccinimide (7.00 g.) and benzoyl peroxide (0.25 g.) were added and refluxing was continued for a second day. The reaction mixture was filtered and the concentrated filtrate was passed through a small column of alumina. Evaporation of the eluate and crystallization of the solid residue from petroleum ether afforded white crystals of tetrabromide V (5.20 g., 65%), m.p. 117–118°.

Anal. Calcd. for $C_8H_4Br_4$: C, 22.86; H, 0.94; Br, 76.19. Found: C, 23.15; H, 1.00; Br, 76.01.

Benzocyclobutenedione (VIII) *from tetrabromide* V. To a stirred solution of tetrabromide V (0.184 g.) in benzene (3 ml.) was added, at room temperature over a three hour period, a solution of silver trifluoroacetate (0.450 g.) in a small volume of benzene. After removal of the precipitated silver bromide, the benzene solution was shaken well with water several times, dried and evaporated. Crystallization of the residue from chloroform-petroleum ether afforded diketone VIII (0.027 g., 41%), identical in melting point and infrared spectrum with authentic material.[11]

1,1,2-Tribromobenzocyclobutene (VI). A mixture of *cis*-1,2-dibromobenzocyclobutene (III, 0.500 g.), *N*-bromosuccinimide (0.374 g.), benzoyl peroxide (0.050 g.) and carbon tetrachloride (15 ml.) was refluxed gently for 6 min. The succinimide which formed was filtered off, and the concentrated filtrate was passed through a short column of alumina. Evaporation of the filtrate and low temperature crystallization of the residue from petroleum ether afforded white cubes of tribromide VI (0.467 g., 72%), m.p. 40–41°.

Anal. Calcd. for $C_8H_5Br_3$: C, 28.15; H, 1.47; Br, 70.38. Found: C, 28.36; H, 1.22; Br, 70.31.

Bromination of dibromide (IV). Dibromide IV (0.500 g.) was refluxed for 7 hr. with *N*-bromosuccinimide (0.780 g., 2.2 equivalents) and benzoyl peroxide (0.050 g.) in carbon tetrachloride (10 ml.). The product was worked up by chromatography on alumina, followed by low temperature crystallization from pretroleum ether. Tetrabromide V (0.255 g., 35%), m.p. 116–117°, m.p. 116–117°, was isolated in several crops. Infrared examination of the residual oil indicated that it consisted mainly of unchanged bromide IV.

Partial bromination of dibromide (II). Bromination of dibromide II (0.500 g.) with 1.1 equivalent of *N*-bromosuccinimide in the usual manner for a period of 18 hr. gave a small amount (0.053 g.) of tetrabromide V in addition to unchanged II. A similar incomplete bromination of 70 g. of dibromide II gave, after extensive fractional distillation and crystallization, about 3 g. of tribromide VI in addition to much unchanged II and some tetrabromide V.

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(11) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **79,** 3606 (1957).