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

Condensed Cyclobutane Aromatic Systems. IV. Benzocyclobutene and 1-Bromobenzocyclobutene

BY M. P. CAVA AND D. R. NAPIER[1]

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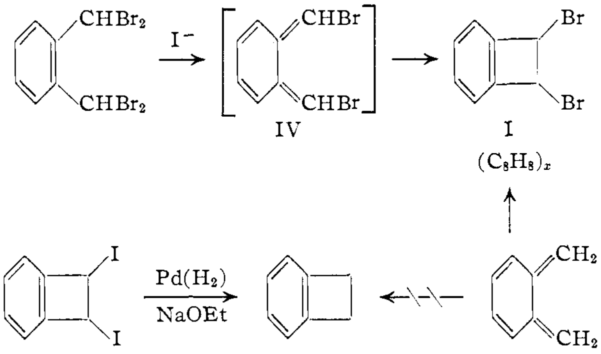
By catalytic hydrogenolysis of 1,2-diiodobenzocyclobutene the hitherto unknown benzocyclobutene has been obtained. Ziegler bromination of benzocyclobutene gave 1-bromobenzocyclobutene, which was dehydrobrominated by potassium *t*-butoxide to the dimer of benzocyclobutadiene.

In previous papers of this series[2,3] we have described the preparation and some properties of 1,2-dibromobenzocyclobutene (I) and 1,2-diiodobenzocyclobutene (II). The general stability of the dihalides I and II led us to believe that the unknown parent hydrocarbon, benzocyclobutene (III), should be amenable to synthesis. If the speculation[2] that the formation of the dibromide I from $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene proceeds *via* an *o*-quinonoid intermediate IV be correct, then generation of the simple olefin V might be expected to be followed by ring closure to benzocyclobutene (III). This expectation has not been realized. The reaction of *o*-methoxymethylbenzyl chloride with magnesium almost certainly generates the tetraene V, but only a high polymer of V could be isolated as a product of this reaction.[4] Similarly, the reaction of sodium with α,α'-dibromo-*o*-xylene, which may proceed at least partially *via* V, has been reported to give no benzocyclobutene even when carried out under conditions of high dilution.[5]



A successful route to benzocyclobutene (III) was found in the catalytic hydrogenolysis of 1,2-diiodobenzocyclobutene (II).[6] The reduction was carried out in ethanol solution using palladium-charcoal in the presence of sodium ethoxide, when benzocyclobutene was obtained in yields ranging from 20 to 38%, in addition to a considerable amount of a viscous polymer. Curiously enough, the use of sodium ethoxide, which was partially decomposed by aging, consistently raised the yield of benzocyclobutene to 49–55% at the expense of the polymeric product. This effect may be caused by a partial poisoning of the catalyst by the ethoxide decomposition products.

Benzocyclobutene was isolated as a colorless oil with a xylene-like odor, boiling at 150° (748 mm.) with no detectable decomposition. It melted at -24 to $-23°$. Its molecular weight was confirmed by its mass spectrum, which exhibited a parent peak at 104 m./e. units. Its ultraviolet spectrum, reproduced in Fig. 1, resembles closely that of indane,[7] both in the positions of the three maxima and in the rather high values of their extinction coefficients.

The infrared spectrum of benzocyclobutene (Fig. 2) illustrates several points of particular interest. The presence of a band at 10 μ has been correlated with the presence of a cycloalkane ring.[8] Such bands exist in the spectra[7] of indane and tetralin, although they are of such extremely low intensity as to be overlooked readily. The corresponding band (10.03 μ) in the benzocyclobutene spectrum, however, is a sharp band of at least medium intensity. The strongest bands in the benzocyclobutene spectrum and the most valuable for identification purposes are those occurring at 12.8 and 14.0 μ. *o*-Xylene and tetralin[7] both show a single very intense band near 13.5 μ, characteristic of an *o*-disubstituted benzene.[9] In the case of the more strained and more rigid indane[7] this band is split into two bands, only slightly separated (13.30 and 13.55 μ). A similar but much greater splitting of the 13.5 μ band occurs in the benzocyclobutene spectrum giving rise to the intense and very characteristic bands at 12.8 and 14.0 μ; as expected, no appreciable absorption remains in the 13.5 μ region.

Although benzocyclobutene is stable to dilute mineral acids, strongly acidic reagents such as concentrated sulfuric acid or liquid hydrogen fluoride convert it readily to a viscous polymer. The infrared spectrum of this material exhibits a strong band at 14.2 μ, characteristic of a monosubstituted benzene ring,[9] suggesting that the polymer may consist, at least in part, of polystyrene units.

When benzocyclobutene was allowed to react with N-bromosuccinimide in the presence of peroxide, 1-bromobenzocyclobutene (VI) was obtained in 58% yield, the by-product of the reaction being a polymeric gum. The monobromide, however, was not the precursor of the polymer since it was completely unchanged when resubjected to the original

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(1) From the Ph.D. Dissertation of D. R. Napier, The Ohio State University, 1957.

(2) M. P. Cava and D. R. Napier, THIS JOURNAL, **79**, 1701 (1957).

(3) M. P. Cava and J. F. Stucker, *ibid.*, **79**, 1706 (1957).

(4) F. Mann and F. Stewart, *J. Chem. Soc.*, 2826 (1954).

(5) A. C. Cope and S. W. Fenton, THIS JOURNAL, **73**, 1668 (1951).

(6) For a preliminary account of this work, see M. P. Cava and D. R. Napier, *ibid.*, **78**, 500 (1956).

(7) Catalog of Ultraviolet and Infrared Spectra Data, American Petroleum Institute Research Project 44, National Bureau of Standards, Washington, D. C.

(8) L. W. Marrison, *J. Chem. Soc.*, 1614 (1951).

(9) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954.

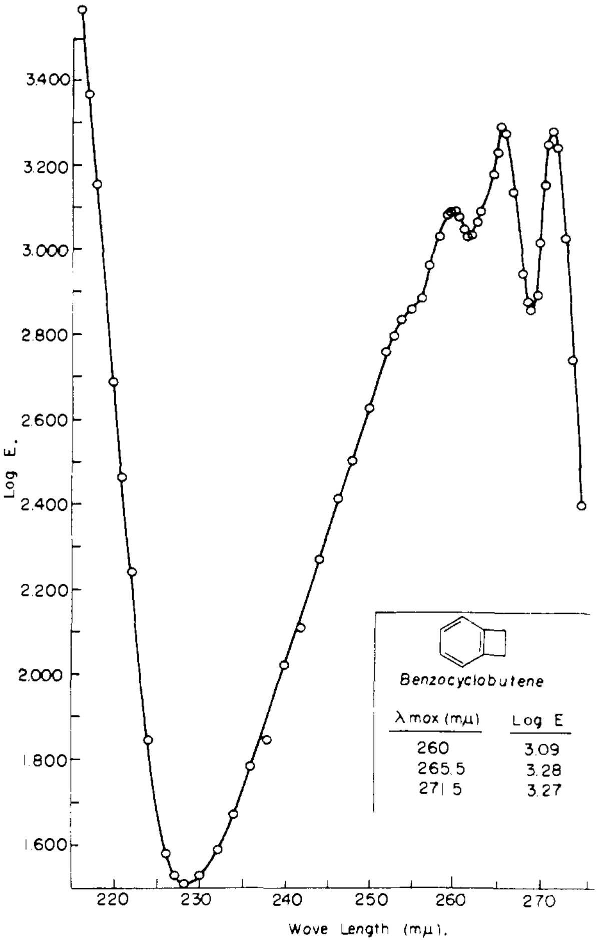


Fig. 1.

bromination conditions: indeed it was not further brominated by this treatment, as might be expected, to the known 1,2-dibromobenzocyclobutene (I).[2] It seems probable, therefore, that the polymer as well as the monobromide VI are produced *via* the same radical intermediate VII formed in the first stage of the bromination process.

1-Bromobenzocyclobutene (VI) was obtained as a colorless oil with an odor reminiscent of bromobenzene. Like 1,2-dibromobenzocyclobutene,[2] it differs from typical benzyl halides in exhibiting no lachrymatory properties; preliminary experiments indicate that the bromine atom is not displaced readily by anions.

The dehydrobromination of 1-bromobenzocyclobutene was effected by potassium *t*-butoxide. The resulting benzocyclobutadiene (VIII) was isolated in 84% yield as its dimer IX.[2] The high yield of dimer IX in this reaction, in which no precautions were taken to inhibit the polymerization of the intermediate benzocyclobutadiene, is to be contrasted with the results of the zinc debromination of 1,2-dibromobenzocyclobutene (I),[2] when the lack of such precautions leads to polymer formation. It seems likely now that the normal self-reaction product of benzocyclobutadiene is the dimer IX, but that polymerization may occur readily in the presence of a Lewis acid such as zinc bromide.

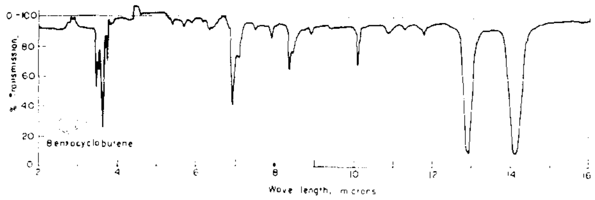
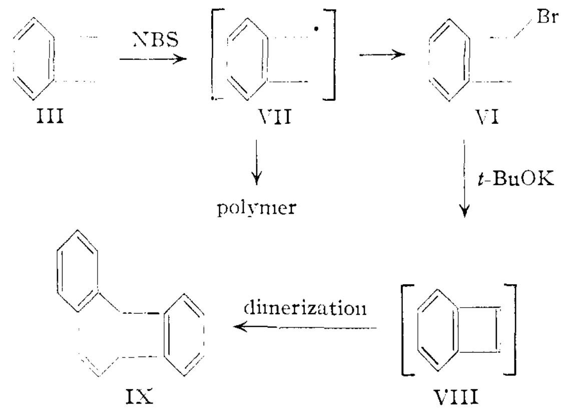


Fig. 2



Acknowledgment.—We wish to thank the Research Corporation for a grant supporting a portion of this work.

Experimental[10]

Benzocyclobutene (III).—Palladium-charcoal catalyst (10 g., 10% palladium) was placed in a hydrogenation bottle. After flushing the bottle with nitrogen, there was added a solution of 1,2-diiodobenzocyclobutene[2] (II) (27.0 g., 0.076 mole) in absolute ethanol (300 ml.) and an aged sample[11] of sodium ethoxide (20 g.). The suspension was shaken with hydrogen for 19 hours under an initial pressure of 3.54 atm. At the end of this period 0.080 mole of hydrogen had been absorbed. The pressure was raised to 3.54 atm. and after 48 hours shaking an additional 0.0615 mole of hydrogen was taken up. At this point, fresh catalyst (4.0 g.) was added and after 5 hours of further shaking (initial pressure 3.54 atm.) the total amount of hydrogen absorbed (0.152 mole) had reached the theoretical value and the reduction was stopped. The suspension was filtered through Super-Cel, diluted with water (400 ml.) and extracted twice with 300-ml. portions of petroleum ether (30–60°). The hydrocarbon extract was filtered through sodium sulfate, concentrated to 75 ml., and passed through a column of alumina (1 × 10 cm.). The column was eluted with 30–60° petroleum ether (350 ml.), and the eluate concentrated carefully to 25 ml. On distillation through a small column (glass bead packing) the benzocyclobutene (3.89 g., 49%) was collected at 75–80° (50 mm.). When five times the above quantity of diiodide was reduced the yield of hydrocarbon rose to 55%. Pure **benzocyclobutene** was obtained by redistillation through a Nester spinning band column (b.p. 94.2–94.5° at 142–143 mm.). This material possessed the following properties: b.p. 150° (748 mm.), m.p. −23 to −24°, d^{4}_{25} 0.957, n^{25}_{D} 1.5409. The mass spectrum showed a parent peak at 104 m./e.; the calculated molecular weight was 104. The ultraviolet spectrum, determined in 95% ethanol, is shown in Fig. 1, together with values of the observed maxima.

Anal. Calcd. for C_8H_8: C, 92.26; H, 7.74. Found: C, 92.33; H, 7.74.

The residue from the first distillation of the benzocyclobutene, combined with similar material eluted from the alumina column by methylene chloride, formed a viscous

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[10] Analyses carried out by Galbraith Laboratories, Knoxville, Tenn.

[11] This material was obtained by placing fresh dry sodium ethoxide in a glass jar, which was sealed with wax and allowed to stand on the laboratory shelf for six months, after which time it had become pale orange and somewhat moist in appearance.

gum, the infrared spectrum of which was very similar to that of the benzocyclobutadiene polymer obtained as a by-product in the zinc dehalogenation of the diiodide II and the dibromide I.[2] Its weight corresponded to a yield of 40%, calculated as $(C_8H_6)_x$.

In place of aged sodium ethoxide, freshly prepared sodium ethoxide could be employed in the hydrogenolysis: the yields of benzocyclobutene were, however, consistently lower (20–38%). The use of other bases (pyridine, sodium carbonate, sodium hydroxide) in place of the ethoxide led to yields of benzocyclobutene below 20%.

Thermal Stability of Benzocyclobutene.—Refluxing the hydrocarbon for one hour under nitrogen at atmospheric pressure produced no change in the boiling point of the liquid or in its infrared spectrum; at room temperature, no change in the refractive index or infrared spectrum of a sample was detected after one year.

Acid Sensitivity of Benzocyclobutene.—(a) Benzocyclobutene (0.50 g.) was dissolved in methanol (58.5 ml.) and concentrated hydrochloric acid (5 ml.) added. The resulting solution (1 *N* in acid) was allowed to stand for 48 hours, diluted with water (200 ml.) and the hydrocarbon isolated by extraction with petroleum ether (30–60°). The infrared spectrum of the recovered benzocyclobutene (0.49 g.) was identical with that of the starting material.

(b) Benzocyclobutene (3.0 g.) was added dropwise to liquid hydrogen fluoride (50 ml.) contained in a polyethylene beaker. A milky suspension resulted which was allowed to evaporate at room temperature under the hood. The residue was dissolved in methylene chloride and filtered through alumina. Evaporation of the solvent left a somewhat sticky, transparent glass (3.0 g.). The infrared spectrum exhibited a strong band at 14.2 μ (monosubstituted benzene).[9]

1-Bromobenzocyclobutene (VI).—A mixture of benzocyclobutene (17.0 g.), N-bromosuccinimide (29.2 g.), benzoyl peroxide (0.01 g.) and carbon tetrachloride (75 ml.) was refluxed with stirring for 2.5 hours. Petroleum ether (30–60°, 30 ml.) was added and the solution decanted onto a column (1 × 10 cm.) of alumina. The column was eluted with petroleum ether (30–60°, 1000 ml.) and the eluate concentrated carefully to a volume of about 15 ml. Distillation through a spinning band column gave the pure **1-bromobenzocyclobutene** (17.4 g., 58%) as a colorless oil, b.p. 90° (10.5 mm.), n^{26}_{D} 1.5907.

Anal. Calcd. for C_8H_7Br: C, 52.49; H, 3.86; Br, 43.66. Found: C, 52.67; H, 4.01; Br, 43.49.

Attempted Bromination of 1-Bromobenzocyclobutene.—A mixture of monobromide VI (0.64 g., 0.0035 mole), N-bromosuccinimide (0.7 g., 0.0392 mole), benzoyl peroxide (0.005 g.) and carbon tetrachloride (10 ml.) was refluxed for 2 hours. The mixture was cooled and filtered through alumina, using petroleum ether (30–60°) as the eluting agent. Evaporation of the eluate gave a colorless oil (0.62 g.), the infrared spectrum and refractive index of which were identical to those of the original monobromide.

Dehydrobromination of 1-Bromobenzocyclobutene.—The monobromide VI (1.00 g.) was added to 12 ml. of a 0.98 molar solution of potassium *t*-butoxide in *t*-butyl alcohol. After refluxing the mixture for 7 hours, water (40 ml.) was added and the hydrocarbon extracted out with two 40-ml. portions of petroleum ether (30–60°). The extract, after filtration through sodium sulfate, was evaporated to dryness and the residue sublimed at 100° (1 mm.) to give 0.475 g. (84%) of **benzocyclobutadiene dimer (IX)**, m.p. 68–74°. After one recrystallization from petroleum ether (30–60°) the melting point (74–74.5°) was not depressed upon admixture with an authentic sample.[2] In addition, the infrared spectra of both samples were identical.

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Condensed Cyclobutane Aromatic Systems. V. The Synthesis of Some α-Diazoindanones: Ring Contraction in the Indane Series

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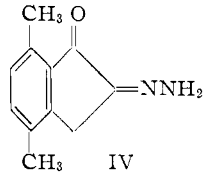
A new and convenient method is described for the conversion of cyclic α-diketones to the corresponding α-diazoketones, employing monotosylhydrazones of the diketones as intermediates. By this procedure, a number of cyclic diazoketones, including some diazoindanones, have been prepared. In addition, several diazoindanones have been obtained using the reaction of Forster, *i.e.*, treatment of an α-oximinoketone with chloramine. The Wolff rearrangement of 2-diazo-1-indanone, 4,7-dimethyl-2-diazo-1-indanone and 4-methyl-7-chloro-2-diazo-1-indanone has been effected under the influence of ultraviolet light to give benzocyclobutene-1-carboxylic acid, 3,6-dimethylbenzocyclobutene-1-carboxylic acid and 3-methyl-6-chlorobenzocyclobutene-1-carboxylic acid. The structure of the simple benzocyclobutene-1-carboxylic acid was confirmed by an unambiguous synthesis from 1-bromobenzocyclobutene.

Although acyclic α-diazoketones, especially α-diazomethyl ketones, usually are prepared readily from acid chlorides and diazoalkanes,[2] this method of synthesis is intrinsically inapplicable to the synthesis of cyclic α-diazoketones.

Excluding from consideration the special case of the aromatic *o*-diazoöxides, only a very limited number of cyclic α-diazoketones has been reported. Most of these have been prepared by the mercuric oxide oxidation of the monohydrazone of an α-diketone. Examples are found in the preparation of 3-diazocamphor (Ic),[3] diazoöxindole (IIc)[4] and 7-diazo-8-acenaphthenone (IIIc),[5] the yield in the latter case being very low.



IV

The primary purpose of the investigation reported here was to synthesize the hitherto unknown 2-diazo-1-indanone (Xa) and some substituted analogs of Xa for ring contraction studies. The monohydrazone approach was investigated in some detail in the 4,7-dimethylindane series. 4,7-

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[1] From the Ph.D. Dissertations of R. L. Litle and D. R. Napier, The Ohio State University, 1957; for a preliminary report of a portion of this work, see: M. P. Cava and R. L. Litle, *Chemistry & Industry*, 367 (1957). The remaining material of this paper was presented before the Division of Organic Chemistry at the 132nd Meeting of the American Chemical Society, New York, N. Y., September, 1957.

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[3] J. Bredt and W. Holz, *J. prakt. Chem.*, [2] **95**, 133 (1917).

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[5] L. Berend and J. Hermes, *ibid.*, [2] **60**, 1 (1899).