methylenecyclobutane,[13a] cyclobutene,[13b] ethyl tetrolate,[14] benzalacetone[15] and ethyl vinylacetate.[16] The course of the reaction can be changed from predominating substitution to predominating addition by the addition of a trialkylammonium halide.[17]

Experimental

1-Phenyl-2-alkylcyclopropanes.—These were prepared by the method used by Davidson and Feldman[18] and had the same physical constants. A Prileschaev olefin determination with peroxyacetic acid on the ethyl analog showed the presence of 4 mole % of unsaturation.

Bromination of 1-Phenyl-2-isopropylcyclopropane.—In a typical experiment 30 g. (0.19 mole) of 1-phenyl-2-isopropylcyclopropane, 70 g. (0.39 mole) of N-bromosuccinimide and 3.0 g. (0.02 mole) of benzoyl peroxide were added to 80 ml. of carbon tetrachloride in 250-ml. round-bottom flask fitted with a condenser. The mixture was refluxed for four hours whence all of the N-bromosuccinimide was gone as shown by a starch–iodide test on the precipitate in the flask. The product was filtered and the carbon tetrachloride was removed under reduced pressure at room temperature. There was obtained 73 g. of a reddish oil. No appreciable reaction in 24 hr. was noted if the benzoyl peroxide was omitted, whether heat was provided by a heating mantle or a General Electric drying lamp (250 watt).

When vacuum distillation of the oil was attempted, decomposition began at about 50° so purification was done by chromatographic adsorption. A column 38 mm. in diameter was packed to a depth of 70 cm. with Merck 200-mesh alumina. A solution of 13.3 g. of the oil in 100 ml. of 1:2 benzene–acetone was placed on the column and eluted with 1:3 benzene–ligroin. The fourth and fifth 100-ml. fractions of the percolate contained 6.3 g. of a light yellow oil. A dark band which remained near the top of the column was removed with ethanol and contained 5.2 g. of a dark intractable oil which was discarded. The results did not differ markedly if as little as 3 g. or as much as 20 g. of the oil was used. The average yield of the light yellow dibromide was 57%.

Anal. Calcd. for $C_{12}H_{16}Br_2$: mol. wt., 320; C, 45.04; H, 5.05; Br, 49.99. Found: mol. wt. (Rast), 307; C, 45.21; H, 5.08; Br, 49.71.

Dehydrobromination of the Dibromide.—To a solution of 32.5 g. (0.10 mole) of the dibromide in 500 ml. of 95% ethanol was added 22.5 g. (0.13 mole) of silver nitrate dissolved in the minimum amount of water. After 24 hr. the silver bromide was filtered off and the alcohol was distilled off under reduced pressure at 25–40° leaving 15.2 g. of an oil which absorbed bromine rapidly. Chromatographic adsorption on alumina as described above for the dibromide using benzene as the eluent yielded 12.9 g. (74%) of a light yellow oil. When 5.3 g. of this oil was fractionated through a Podbielniak type column there was obtained 3.2 g. of 1-phenyl-4-methyl-1,3-pentadiene-1,3, b.p. 124.5–126.5° (11 mm.), $n^{20}D$ 1.5977 (lit. 1.5985).[19]

Anal. Calcd. for $C_{12}H_{14}$: C, 91.09; H, 8.93. Found: C, 91.18; H, 8,92.

1-Phenyl-4-methylpentadiene-1,3 was prepared in 65% yield by dehydration of styrylisopropylcarbinol with potassium bisulfate at 145°. This preparation had b.p. 140–141° (20 mm.), $n^{20°}D$ 1.5983. The two samples of diene had identical ultraviolet absorption spectra showing a broad band $\lambda_{max.}$ 290 mμ, log ϵ 4.41, in 95% ethanol.

Tetrabromides were made from the two samples of diene using the procedure of Cheronis and Entrikin[20]: the tetrabromide from the dehydration product of the carbinol gave m.p. 142–143.5°; that from the dehydrobromination product of the dibromide m.p. 141–142°; a mixture m.p. 142–142.5°. The tetrabromide from the dehydrobromination product was analyzed.

Anal. Calcd. for $C_{12}H_{14}Br_4$: C, 30.15; H, 2.95; Br, 67.49. Found: C, 29.00; H, 2.92; Br, 67.36.

Bromination of 1-Phenyl-2-ethylcyclopropane.—The procedure was the same as that used for the isopropyl analog. However, the reaction was slower, 11 hr. being required for the complete consumption of the N-bromosuccinimide. The dibromide could be purified by chromatographic adsorption giving product with $n^{25}D$ 1.5721 or by distillation, b.p. 97–98° (0.45 mm.), $n^{25}D$ 1.5736, 23% yield.

Anal. Calcd. for $C_{11}H_{14}Br_2$: C, 43.17; H, 4.61; Br, 52.22; *MR*D, 64.95. Found: C, 43.34; H, 4.72; Br, 52.21; *MR*D, 65.13; d^{25} 1.5464.

Reaction of 12.0 g. (0.0825 mole) of 1-phenyl-2-ethylcyclopropane with 13.2 g. (0.0825 mole) of bromine in 70 ml. of carbon tetrachloride yielded 18.4 g. (72.8%) of dibromide, b.p. 106–109° (0.7 mm.), $n^{25}D$ 1.5724; Br, 52.97. The infrared spectra of the two dibromides were identical.

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Organoboron Compounds. VI.[1] Preparation of a Heterocyclic Organoboron Compound

BY ROBERT L. LETSINGER AND IVAN H. SKOOG

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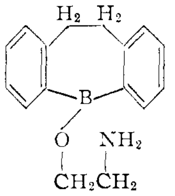
The techniques which were developed for the preparation of aminoethyl diphenylborinate[2] were used to synthesize 5-β-aminoethoxy-10,11-dihydrodibenzo[b,f]borepin (I). To our knowledge, this is the first example of the isolation of a heterocyclic compound which has only carbon and boron in the ring.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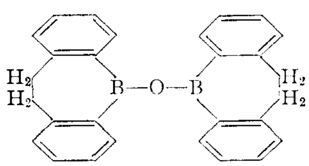
II

o,o'-Dilithiobibenzyl, prepared by a metal halogen interchange between butyllithium and dibromobibenzyl, was allowed to react with butyl borate in ether solution at about −70°. After hydrolysis, the products of the reaction were esterified with butyl alcohol and distilled. Compound I was obtained in 42% yield from the reaction of the impure butyl ester with ethanolamine. On hydrolysis and drying, compound I was converted to the oxide II in 96% yield.

The structure for I is based on the method of synthesis, analytical data, and the fact that bromine and hydrogen peroxide reacted with I to give good yields of *o,o'*-dibromobibenzyl and *o,o'*-dihydroxybibenzyl, respectively. Furthermore, bibenzyl was formed when the oxide II was heated with aqueous zinc chloride and with palladium-on-charcoal.

Experimental Part

o-Bromobenzyl Bromide.—Bromine (172 ml., 3.35 moles) was added dropwise over a three-hour period to 547 g. (3.35

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(13) (a) E. R. Buchman and D. R. Howton, THIS JOURNAL, **70**, 2517 (1948); (b) **70**, 3510 (1948).

(14) J. English, Jr., and J. D. Gregory, *ibid.*, **71**, 1115 (1949).

(15) P. L. Southwick, L. A. Pursglove and P. Numerof, *ibid.*, **72**, 1600 (1950).

(16) E. J. Corey, *ibid.*, **75**, 2251 (1953).

(17) E. A. Braude and E. S. Waight, *J. Chem. Soc.*, 1116 (1952).

(18) D. Davidson and J. Feldman, THIS JOURNAL, **66**, 489 (1944).

(19) W. S. Emerson, *J. Org. Chem.*, **10**, 466 (1945).

(20) N. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," Thomas Crowell Co., New York, N. Y., 1947, p. 315.

(1) For the previous paper in this series see R. L. Letsinger and N. Remes, THIS JOURNAL, **77**, 2489 (1955).

(2) R. L. Letsinger and I. H. Skoog, *ibid.*, **77**, 2491 (1955).

moles) of *o*-bromotoluene illuminated by a mercury arc lamp. The mixture was stirred throughout the addition period and for one additional hour. Distillation yielded 492 g. (59%) of *o*-bromobenzyl bromide; b.p. 127-133° (15 mm.).

o,o'-**Dibromobibenzyl.**—Phenyllithium (890 ml. of a 1.06 *N* ether solution) was added slowly to a solution of 492 g. (1.97 moles) of *o*-bromobenzyl bromide in 500 ml. of ether. During the addition of the phenyllithium the ether refluxed spontaneously. The next day the pale yellow solution was hydrolyzed with 300 ml. of water, the resulting layers were separated and the ether layer washed, dried, and distilled. The bromo compound distilled at 193-200° at 5 mm. and solidified on cooling. After recrystallization from 125 ml. of ethanol it melted at 83°; weight 191 g. (60% yield). The reported melting point is 84.5°.[3]

5-(2-Aminoethoxy)-10,11-dihydrodibenzo[b.f]borepin (I).—A solution of 100.0 g. (0.294 mole) of *o,o'*-dibromobibenzyl in 600 ml. of ether was added slowly to 0.632 mole of butyllithium in 578 ml. of ether at 5°; then the mixture was refluxed for one hour. During this period a white precipitate separated from the solution. This mixture was transferred to a dropping funnel and slowly added to 67.5 g. (0.294 mole) of tributyl borate in 700 ml. of ether maintained at −70°. The next morning the mixture was hydrolyzed with 400 ml. of 2 *N* hydrochloric acid. Distillation of the ether layer with 700 ml. of toluene and 10 ml. of butyl alcohol gave the high boiling fractions shown in Table I. Fractions 1, 2 and 3, which contained the desired heterocyclic organoboron compound, then were distilled separately with ethanolamine and toluene. In each case, after the excess ethanolamine had been removed but before all of the toluene had distilled, the solution was allowed to cool. The weights of the resulting precipitates also are included in Table I. The total amount of aminoethoxydihydrodibenzoborepin thus obtained was 30.82 g. (42%). Recrystallization of 2.16 g. of this material from 30 ml. of ethanol and 20 ml. of water yielded 1.33 g. of the purified ester, m.p. 195-196°.

TABLE I

Fract.	B.p., °C., 2 mm.	Wt., g.	Aminoethyl ester, g.
1	131-157	7.07	0.00
2	157-166	41.23	19.52
3	166-200	18.30	10.30

Anal.[4] Calcd. for $C_{16}H_{18}ONB$: B, 4.308; N, 5.58; equiv. wt., 251. Found: B, 4.32; N, 5.72; equiv. wt. (by titration with hydrochloric acid), 245.

It is interesting that no precipitate formed when an ether solution of fraction 3 was saturated with ammonia. In the case of butyl diphenylborinate,[2] a solid ammonia complex separated under these conditions.

Anhydride of Hydroxydihydrodibenzoborepin (II).—The aminoethyl ester (0.500 g.) was dissolved in a mixture of 10 cc. of ethanol and 10 cc. of 6 *N* hydrochloric acid. On addition of 30 cc. of 1 *N* hydrochloric acid, a white solid separated. It was filtered and dried in a vacuum oven at 40° for two hours; weight 0.381 g. (96% yield), m.p. 145-146°. A portion (0.2337 g.) was dissolved in a solution of 15 cc. of ethanol, 15 cc. of water and 2 g. of mannitol; then titrated with standard sodium hydroxide with the aid of a Beckman *p*H meter; equivalent weight: found 199; calcd. for II, 199.

In another experiment, 6.11 g. of the aminoethyl ester was acidified, then extracted with ether and distilled with toluene (200 cc.). The anhydride distilled at 265-270° (2 mm.) and weighed 3.84 g. (79%). Apparently, some decomposition occurred for this material melted over a range from 131-136°; however, the neutralization equivalent found by titration (203) agreed fairly well with the value calculated for II (199).

The infrared spectra of the materials obtained by these two procedures were virtually identical. Both showed strong absorption in the region of 7-8 μ, characteristic of organoboron compounds, and a weak maximum at 2.7 μ. This latter peak is in the region characteristic of the hydroxyl group and suggests that the compound might be the borinic acid rather than the anhydride. However, it seems unlikely that the acid would distil under the conditions employed. Furthermore, diphenylborinic anhydride[2] showed a weak maximum at 2.7 μ; and Neu found that diphenylborinic acid also dehydrated very easily to yield the anhydride.[5]

Reactions of I. (a) Bromine.—To 0.400 g. of I in 30 ml. of acetic acid was added a solution of 5 ml. of bromine in 20 ml. of water which contained potassium bromide. After 10 minutes, the solution was diluted with 100 ml. of water and excess bromine was reduced with sodium bisulfite. The white precipitate was separated by filtration, and dried; weight 0.501 g. (92.5% yield), m.p. 78-81°. After recrystallization from alcohol and water, the sample (0.366 g. recovered) melted at 82-83°. The melting point was not depressed when the sample was mixed with *o,o'*-dibromobibenzyl prepared from *o*-bromobenzyl bromide.

(b) Hydrogen Peroxide.—Ten milliliters of a 30% hydrogen peroxide solution was added to a solution of 0.400 g. of I in 10 ml. of acetic acid and 5 ml. of water at room temperature. After five minutes the solution was diluted with 70 ml. of water and cooled in an ice-bath. White crystals of *o,o'*-dihydroxybibenzyl separated; weight 0.222 g. (65% yield), m.p. 114-115°. The melting point was unchanged after the substance had been recrystallized from water and alcohol. This material burned without any green coloration, showing that boron was absent. The melting point reported for *o,o'*-dihydroxybibenzyl is 115°.[6]

Reactions of II. (a) Palladium.—The anhydride II (0.6127 g.) was heated at 280-320° for two hours with 0.47 g. of 5% palladium-on-charcoal in a stream of carbon dioxide. The gas evolved, presumably hydrogen, amounted to 16.6 ml. During the heating period a white solid (0.142 g.) slowly collected on the condenser which was situated above the surface of the reaction mixture. This substance was shown to be bibenzyl by its melting point (49-50° after recrystallization from aqueous ethanol) and the melting point of its trinitrobenzene adduct (102°). When a sample of II was heated in the same apparatus under the same conditions in the absence of the palladium-charcoal catalyst, no biphenyl was formed.

The residue from the palladium reaction was taken up in hot alcohol and filtered. Evaporation of the ethanol left a residue which solidified when petroleum ether was added. This substance, after drying for 10 hours at 90°, weighed 0.1462 g. and softened at 260-270°. It gave a positive flame test for boron, was soluble in alcohol and in benzene, and could be sublimed in vacuum.

(b) Zinc Chloride.—A portion of the oxide (0.063 g.) was heated under reflux for four hours with 5 ml. of water and 0.36 g. of zinc chloride. After cooling, 20 ml. of water was added and the mixture extracted with ether. The residue after distillation of the ether gave, on warming with an ethanol solution of 1,3,5-trinitrobenzene, a precipitate which melted at 102° after recrystallization from ethanol. The melting point was not depressed when the sample was mixed with the compound obtained from trinitrobenzene and commercial bibenzyl.

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[3] J. Kenner and J. Wilson, *J. Chem. Soc.*, 1108 (1927).

[4] The boron analyses were made by J. Thoburn; the nitrogen analyses by V. Stryker.

[5] R. Neu, *Ber.*, **87**, 802 (1954).

[6] J. Thiele and O. Kolzinger, *Ann.*, **305**, 99 (1899).

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The Dienone–Phenol Rearrangement. IV. A New Example of the Abnormal Path[1]

BY ELLIOT N. MARVELL AND JOHN L. STEPHENSON

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The majority of the examples of the dienone–phenol rearrangement are encompassed by the Arnold mechanism.[2] However 2,2-dimethyl-1-oxo-

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[1] Published with the approval of the Monographs Publications Committee, Oregon State College, as Research Paper No. 275, School of Science, Department of Chemistry. Taken from a thesis submitted by John Stephenson in partial fulfillment of the requirements for the Master of Science degree, Oregon State College, 1955.

[2] R. T. Arnold, J. S. Buckley and J. Richter, THIS JOURNAL, **69**, 2322 (1947).