The Reaction of *o*-(Bromomethyl)benzeneboronic Anhydride with Primary Amines[1]

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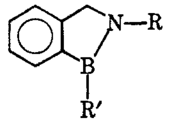
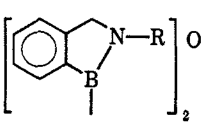
o-(Bromomethyl)benzeneboronic anhydride (I) has been treated with primary amines in a study of the 1,2-boraazaindanyl ring system. The B–N bonds in the systems encountered have proved to be comparatively ordinary, being formed or cleaved according to hydration–dehydration conditions in the case of monoamines, but forming readily in the case of diamines. No especial stabilization has been noted for the ring system, except from diamines, but several compounds have been shown to have stable C–B bonds nonetheless. A dimethanolate hemisulfate of 1,2,3,4,5,8-hexahydro-6,7-benzo-1,4,8-diazaborapentalene (VIII) has been synthesized by monobenzylation of ethylenediamine with I, and diindano[3,2-*b*;2′,3′-*f*]-13,16-diaza-5,7-diboraoxepane (VII) by bisbenzylation. A convenient synthesis of I has been developed and a remarkably stable boronic acid, N-(*o*-boronobenzyl)ethylenediamine-N′ hydrobromide, has been isolated.

Based upon earlier work,[2] primary amines may react with *o*-(bromomethyl)benzeneboronic anhydride (I) to provide *o*-(alkylaminomethyl)benzeneboronic anhydrides or acids which can then undergo rearrangement or cyclodehydration to heterocycles embodying the 1,2-boraazaindanyl ring system (II or III). Few members of the ring system have been reported[2–12] and simple examples are even rarer.[13] We have studied the hydrolytic and oxidative stabilities of the reaction products obtained from I and primary amines, and we have concluded that there is nothing particularly remarkable from the standpoint of stability about ring system II. We have noted no especial resonance stabilization attributable to the ring system, although ring closures were favored in some examples derived from ethylenediamine, to give polycyclic structures. The C–B bonds in our compounds did show enhanced stabilities over those in simple boronic acids, a result to be expected because of the favorable juxtaposition of the B and N atoms,[2] but the B–N bonds proved to be quite ordinary,[14] being opened or closed to ring system II all with comparative ease. Accordingly, we have formulated our examples as 1,2-boraazaindanes without dative bonds between B and N in contrast to Koster's label as boraazaindenes.[13] Our ultraviolet data, for example, suggest some interactions between B and N, but the spectra of our heterocyclic compounds are more nearly those of indans than indenes[15] and not greatly different from the spectra of boronophthalides[16] or boronic acids derived from secondary amines previously.[2] Other supporting evidence for these conclusions includes the interconversion of *o*-(*t*-butylaminomethyl)benzeneboronic acid and bis(2-*t*-butyl-1,2-boraazaindanyl-1) oxide, and our failure to encounter any 1-hydroxy-2-alkyl-1,2-boraazaindans (IIa) in the pure state.



II

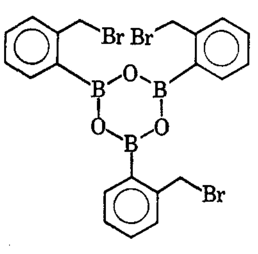
IIa, R′ = OH



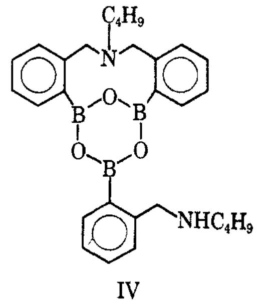
III, R = $t\text{-}C_4H_9$

With *t*-butylamine, I provided *o*-(*t*-butylaminomethyl)benzeneboronic acid (through hydrolysis of its anhydride) which was converted to the hydrochloride and to bis(2-*t*-butyl-1,2-boraazaindanyl-1) oxide (III). In contrast to these reactions with *t*-butylamine, when less hindered primary amines were employed, bisbenzylation of the N moieties was noted.

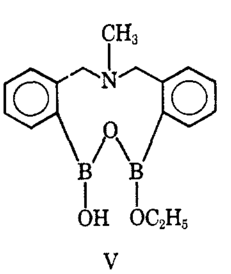
A mixed anhydride (IV) was obtained when *n*-butylamine was treated with I, even when excess amine was employed and I was added slowly. Such proclivity for bisbenzylation is doubtless attributable to the trimeric nature of I, with two benzyl functions in the immediate vicinity of any amine moiety undergoing reaction. A bisbenzylated product was obtained when methylamine was treated with I according to the method of Kuszewski.[11] From the work-up of the reaction mixture, a product was obtained which was assigned the structure V based upon the analyses,



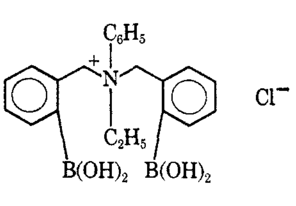
I



IV



V



VI

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[1] This investigation was supported in part by Public Health Service Research Grant CA-06587 from the National Cancer Institute.

[2] R. T. Hawkins and H. R. Snyder, *J. Am. Chem. Soc.*, **82**, 3863 (1960).

[3] W. Gerrard, *Chem. Ind.* (London), 832 (1966).

[4] P. M. Maitlis, *Chem. Rev.*, **62**, 223 (1962).

[5] R. F. Gould, Ed., "Boron-Nitrogen Chemistry," American Chemical Society, Washington, D. C., 1964.

[6] W. Gerrard, "The Organic Chemistry of Boron," Academic Press Inc., New York, N. Y., 1961.

[7] R. L. Letsinger and D. B. MacLean, *J. Am. Chem. Soc.*, **85**, 2230 (1963).

[8] H. C. Newson, W. D. English, A. L. McCloskey, and W. G. Woods, *ibid.*, **83**, 4134 (1961).

[9] H. R. Snyder, A. J. Reedy, and W. J. Lennarz, *ibid.*, **80**, 835 (1958).

[10] M. J. S. Dewar, K. C. Dougherty, and E. B. Fleischer, *ibid.*, **84**, 4882 (1962).

[11] J. R. Kuszewski, Ph.D. Thesis, University of Illinois, 1962.

[12] A. J. Reedy, Ph.D. Thesis, University of Illinois, 1957.

[13] R. Koster and K. Iwasaki, ref 5, Chapter 16.

[14] *Cf.* the psueudo-aromatic character ascribed to some related six-membered rings by M. J. S. Dewar, ref 5, Chapter 23.

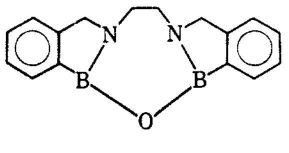
[15] R. A. Morton and A. J. A. de Gouveia, *J. Chem. Soc.*, 913 (1934).

[16] R. R. Haynes and H. R. Snyder, *J. Org. Chem.*, **29**, 3229 (1964).

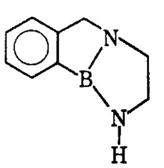
although other possibilities could not be rigorously excluded.

With aniline, because of a balance of steric requirements and nucleophilicity, conditions could be chosen to favor either mono- or bisbenzylation. Thus, we obtained *o*-(phenylaminomethyl)benzeneboronic acid as its salt in good yield, but we also were able to prepare and purify a bisbenzylated product through conversion to an etho chloride (VI). The precursor apparently was a phenyl analog of structure IV.

Mono- and bisbenzylated products could also be obtained from ethylenediamine as evidenced by the preparation of VII and VIII, the latter as a methanolate salt. Even under conditions which involved the addition of I to ethylenediamine, the latter in large excess, bisbenzylation was noted. For example when I in methanol was added to ethylenediamine with the ratio of moles of amine to equivalents of bromide being 6:1, about 17% of the *o*-boronobenzyl groups charged appeared as VII; when the ratio was 9.3:1, smaller amounts were obtained; and, when the ratio was 27.6:1, the bisbenzylated product (VII) was still detectable. Bisbenzylation results such as these suggest the advisability of going to a monomeric bromide such as di-*n*-butyl *o*-(bromomethyl)benzeneboronate, presently unknown, for the preparation of monobenzylated amines.



VII



VIII

The crude reaction products obtained from I and ethylenediamine proved to be complex mixtures of mono- and bis-*o*-boronobenzylated ethylenediamines which could not be separated or purified by the usual techniques. The tricyclic compound (VIII) was converted by chromatography upon acid-washed alumina to the hemisulfate which was separated and recrystallized as the methanolate, in 20% over-all yield based upon I. Attempts to form the hemisulfate more directly from 1 equiv of sulfuric acid in methanol were unsuccessful. From the same crude reaction products, VII could be isolated by vacuum sublimation, in 17% over-all yield based upon I. The structures were assigned on the basis of analytical and spectral data.

A remarkably stable boronic acid, N-(*o*-boronobenzyl)ethylenediamine-N′ hydrobromide, was also obtained during preparation of VII and VIII, in very low yield. It survived conditions known to dehydrate or deboronate simpler boronic acids,[17,18] but it was available in such limited quantities that it was not examined extensively.

Ultraviolet Data.—The substances synthesized in these studies showed secondary benzenoid bands in the ultraviolet near 258, 264, and 270 mμ, in methanol solution. As expected, only those compounds derived from aniline showed any significant deviations from this pattern. The spectra proved to be more nearly that of indan than indene, with consonant intensities (log *a* 2.6–3.6). Compounds with the 1,2-boraazaindanyl ring system showed ultraviolet spectra essentially indistinguishable from those of ring-opened compounds, and there was no evidence for a double bond between B and N.

Experimental Section

Melting points were determined with a calibrated Thomas-Hoover Unimelt and are uncorrected. Microanalyses were performed in these laboratories, or by Geller Microanalytical Laboratories, Charleston, W. Va., F & M Scientific Corp., Avondale, Pa., or Elek Microanalytical Laboratories, Torrance, Calif. Infrared spectra were determined with Beckman IR-5 or IR-7 spectrophotometers; ultraviolet spectra were taken with a Beckman DK-2 spectrophotometer; proton magnetic resonance spectra were determined with Varian spectrometers through the kind cooperation of Dr. E. G. Paul, University of Utah, and Dr. R. C. Anderson, Utah State University; and microthermistor molecular weights were determined with a Mechrolab 301 vapor pressure osmometer.

Preparation of *o*-(Bromomethyl)benzeneboronic Anhydride (I).—*o*-Toluenebоronic anhydride was brominated by a modification of the method of Snyder, *et al.*,[19] which employed a Hanovia ultraviolet immersion lamp to speed the reaction. Stoichiometric amounts of bromine in carbon tetrachloride were added rapidly to *o*-tolueneboronic anhydride dissolved in the same solvent. Catalytic quantities of benzoyl peroxide were added and the stirred solution was illuminated for 20 min. The reaction proceeded noticeably within 7 min and only a light yellow color persisted after 20 min. The solution was refluxed for 2 hr to ensure removal of hydrogen bromide, and then concentrated and allowed to crystallize. The off-white product was recrystallized from a minimum amount of carbon tetrachloride to ensure suitable purity for these reactions.

***o*-(*t*-Butylaminomethyl)benzeneboronic Acid Hydrochloride.**—A solution of 20.0 g of *t*-butylamine (274 mmoles) in 30 ml of methanol was added to a solution of 20.0 g of I (101 mequiv) in 120 ml of benzene and the mixture was refluxed 6 hr. All the methanol was distilled off and a precipitate of *t*-butylamine hydrobromide was removed by filtration (10.0 g, 65% of theory). The filtrate (benzene solution) was agitated with 100 ml of 5 *N* sodium hydroxide. The caustic layer was separated and set aside; although it was shown to contain boron compounds, the amount was small. The hydrolyzed benzene layer was treated with 100 ml of 3 *N* hydrochloric acid to give a white precipitate which was removed by filtration and dried under vacuum. The product weighed 15.1 g (61% yield) and was suitable for conversion to other derivatives. Recrystallization provided an analytical sample, mp 200° dec (dehydration).

Anal. Calcd for $C_{11}H_{19}BClNO_2$: N, 5.75; equiv wt, 242. Found: N, 5.78; equiv wt (by $AgNO_3$ titration), 242.

***o*-(*t*-Butylaminomethyl)benzeneboronic Acid.**—Each gram of the above hydrochloride was neutralized with 1 ml of 5 *N* sodium hydroxide with warming. The liberated amine was taken into benzene and recrystallized by addition of isooctane. An analytical sample was prepared by repeated recrystallization from benzene–isooctane, mp 135–137° dec (dehydration).

Anal. Calcd for $C_{11}H_{18}BNO_2$: C, 63.80; H, 8.76; N, 6.76; mol wt, 207. Found: C, 63.88; H, 8.81; N, 6.52; mol wt, 210.

Bis(2-*t*-butyl-1,2-boraazaindanyl-1) Oxide.—The free boronic acid was dehydrated by sublimation at 250–280° and about 0.5 mm. Sublimation at lower temperatures produced mixtures of uncertain composition. Pure material was obtained by repeated sublimations at the higher temperatures, mp 139.5° dec.

Anal. Calcd for $C_{22}H_{30}B_2N_2O$: C, 73.38; H, 8.40; N, 7.78; mol wt, 360. Found: C, 73.19; H, 8.63; N, 7.71; mol wt (Rast), 358.

The pure sample showed no evidence for OH or NH in its infrared spectrum. An nmr spectrum of this oxide in $CDCl_3$ showed singlets at δ 1.3 (*t*-butyl) and 4.2 (benzyl), and a multiplet around 7.2 (aryl) in the proper ratios, with no unexpected resonances. The oxide could be hydrated to the acid; indeed, the two could be interconverted repeatedly, by many of the

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(17) M. F. Lappert, *Chem. Rev.*, **56**, 959 (1956).

(18) R. T. Hawkins, W. J. Lennarz, and H. R. Snyder, *J. Am. Chem. Soc.*, **82**, 3053 (1960).

(19) H. R. Snyder, M. S. Konecky, and W. J. Lennarz, *ibid.*, **80**, 3611 (1958).

usual techniques of hydration–dehydration. In addition, a pure sample of oxide reverted predominately to acid when it was stored in a loosely stoppered vial with access to atmospheric moisture over a 2-year period.

Mixed Anhydride IV.—A solution of 10.0 g of I (51 mequiv) in 50 ml of methanol was added over a 30-min period to 25 ml of *n*-butylamine (261 mmoles) dissolved in 10 ml of methanol. The solution was maintained at gentle reflux (56°) during the addition and throughout an additional 30 min. The yellow solution was evaporated (rotary evaporator) to a thick residue which was dissolved in 20 ml of 1:4 hydrochloric acid. The yellow-green solution was neutralized in the cold with 10% sodium hydroxide to apparent pH 8. Extraction by carbon tetrachloride either batchwise or in a Raab extractor, followed by filtration and removal of the solvent under vacuum, led to light-colored solids. Recrystallization from 75% aqueous ethanol (4.85 ml per gram) gave the mixed anhydride IV (yield 41% based upon I). An analytical sample was obtained by two more recrystallizations from 95% ethanol, mp 178° (open capillary when introduced at 171°).

Anal. Calcd for $C_{29}H_{37}B_3N_2O_3$: C, 70.50; H, 7.55; B, 6.56; N, 5.67; mol wt, 494; equiv wt, 247. Found: C, 70.85; H, 7.46; B, 6.90; N, 5.59; mol wt (Rast), 470; equiv wt, 253 (as amine).

The anhydride was too insoluble in the usual solvents to obtain useful nmr data; the infrared spectrum (Nujol, cm^{-1}) showed 3210 (NH), 1330, 1300 (BO), 742, 732 (*ortho*), and 686 (boroxine ring).[19,20]

Attempted Hydrolysis of IV.—A sample of IV was dispersed in boiling water for 20 hr (1.0 g/20 ml). About half dissolved but 41% of the sample was recovered unchanged. An additional 42% of the sample was recovered by removing the water in a rotary evaporator. This resistance to hydrolysis is noteworthy.

Bisbenzylated Product (V) from Methylamine.—Prepared according to the procedure of Kuszewski,[11] the boron-containing substance was repeatedly recrystallized from aqueous ethanol. The analytical sample melted at 134–138° with solidification and remelting at 162–165°. This bisbenzylated product was tentatively assigned the structure V, the infrared spectrum being consistent for that.

Anal. Calcd for $C_{17}H_{21}B_2NO_3$: C, 66.08; H, 6.85; N, 4.53. Found: C, 66.36; H, 6.49; N, 4.40.

o-(Phenylaminomethyl)benzeneboronic Acid Hydrochloride.—A solution of 11.410 g of I (57.9 mequiv) in 50 ml of methanol was added over a 25-min period to a refluxing solution of 26.56 g of aniline (285 mmoles) in 10 ml of methanol. After an additional 105 min at reflux, equal volumes of water and chloroform were added, and the reaction mixture was washed, separated, and extracted into chloroform. After 4 hr of extraction in a Raab apparatus, the chloroform was removed on the hotplate and the excess amine was removed under vacuum. This left an oil which could not be hydrated by aqueous alcohol, so all solvents were removed to yield a dark tar which was treated with gaseous hydrogen chloride in ether solution. A sticky precipitate was obtained which slowly crystallized upon digestion in 95% ethanol. Two crops were obtained, totaling 6.075 g (40% yield based upon I). Repeated recrystallization from aqueous ethanol and then from water provided an analytical sample, mp 169–171° dec.

Anal. Calcd for $C_{13}H_{15}BClNO_2$: C, 59.25; H, 5.74; Cl, 13.45; N, 5.32. Found: C, 59.14; H, 5.69; Cl, 13.87; N, 5.18.

Bisbenzylated Product (VI) from Aniline.—When 2 moles of aniline per 1 equiv of I were mixed in the cold (little detectable reaction) and then refluxed, bisbenzylated products were obtained. One of them was successfully converted to its ethochloride derivative which was recrystallized from ethanol. The infrared spectrum was consistent for a quaternary salt (no absorption in the 2500–2700-cm^{-1} region characteristic of tertiary amine salts, bands at 1400 and 1420 characteristic of CH_2 adjacent to quaternary nitrogen, and absorption at 3250 characteristic of BOH[19,20]) and so were the proton magnetic resonance spectra (nmr in dimethyl sulfoxide and also D_2O δ 1.17 triplet, area 2.9, CH_3; 3.6 quartet, area 1.8, CH_2; 5.14 singlet, area 4.0, $ArCH_2N$; 7.2–7.6, multiplet, area 13, aryl protons; and 8.74, singlet, area 4.0, BOH[18]). Accordingly, the product was assigned the structure VI. The analytical sample melted at 172.5–173.0° dec with apparent dehydration.

Anal. Calcd for $C_{22}H_{26}B_2ClNO_4$: C, 62.10; H, 6.16; B, 5.08; Cl, 8.33; N, 3.29. Found: C, 61.98; H, 6.16; B, 4.53; Cl, 8.31; N, 3.34.

Preparation of Crude Reaction Mixtures from Ethylenediamine.—A solution of 9.588 g of I (48.7 mequiv) in 30 ml of methanol was added over a 45-min period to a stirred solution of 20.0 ml of ethylenediamine (293 mmole) in 5 ml of methanol. The temperature was maintained between 35 and 50° during this time by controlling the rate of addition. After an additional 15 min of stirring and cooling time, the reaction product was stripped (rotary evaporator) to remove the solvent and most of the excess diamine. To the thick, dark orange residue was added 100 ml of 10% sodium bicarbonate. The aqueous solution was charged to a Raab extractor and extracted with chloroform for 14 hr. The chloroform extract was filtered, if necessary, and concentrated almost to dryness on a hot plate. Then it was warmed under vacuum (yield typically 3.0–3.5 g). This crude reaction mixture, an amber powder when pulverized, contained boron (flame test), about 4% ionic bromide (*via* silver nitrate precipitation), and yielded a mixture of N-benzyl- and N,N′-dibenzylethylenediamines in substantial amount upon acid-catalyzed deboronation. The amines were identified by means of infrared spectroscopy after neutralization and isolation. In addition, suitable derivatives were prepared for unequivocal identification.

1,2,3,4,5,8-Hexahydro-6,7-benzo-1,4,8-diazaborapentalene (VIII) Dimethanolate Hemisulfate.—A column was prepared for elution chromatography by packing it with acid-washed alumina containing 0.267% by weight of free sulfuric acid. The crude reaction mixture (500 mg) was charged to the column (25.0 g of alumina) wetted with benzene. Cuts eluted by benzene, chloroform, or mixtures of these, were discarded. The hemisulfate was eluted slowly by methanol or better by water. The eluting solvent was removed in a rotary evaporator and the residue was recrystallized from methanol (460 mg of residue digested with a large excess of hot methanol, then solvent concentrated to about 20 ml). The resulting white crystals were removed by filtration, rinsed well, and dried under vacuum at room temperature (yield 358 mg, 76% by weight based upon crude reaction mixture, or 20% based upon I). The salt was very soluble in water, not especially hygroscopic, and did not change in appearance when exposed many months to normal atmospheric conditions on the desk top. Recrystallization from methanol provided an analytical sample which showed poorly defined melting behavior (probably due to loss of methanol); when the sample was introduced near 190° in an evacuated capillary, the observed range was 190–202° dec.

Anal. Calcd for $C_{11}H_{20}BN_2O_4S_{0.5}$: C, 48.73; H, 7.44; B, 3.99; N, 10.33; O, 23.60; S, 5.91. Found: C, 47.92; H, 7.71; B, 3.01; N, 10.00; O, 23.02; S, 5.94.

Nmr (H_2O) showed a singlet with underlying multiplet at δ 3.31, a singlet at 4.03, and an unresolved multiplet at 7.2–7.5, these being CH_3 of methanol and CH_2 of unsymmetrical ethylene, $ArCH_2N$, and aryl H plus protonated nitrogen, respectively, with areas estimated to be 11:2:5. The nmr spectra in H_2O and also in D_2O (the D_2O spectrum was also consonant with the above interpretation) suggest that the structure assigned is correct and that the B–N bonds of the substance are hydrolytically stable. Infrared (KBr, cm^{-1}) showed 3400 strong, broad (OH), 3150 strong, broad; 2950 shoulder; 2835 medium (all protonated amine); 1603 medium, broad (aryl); 1450, 1340, 1272, 1252, 1222 all medium; 1200 shoulder; 1119 very strong (SO_4 ion); 1028 strong (CO); 982, 970 weak doublet; 814 very weak; 756 strong (*ortho*), 725, 660 shoulder; and 621 strong (SO_4 ion).[20]

All attempts to acetylate or benzoylate the salt were unsuccessful because of no reaction or deboronation. For example, a typical benzoylation under Schotten–Baumen conditions resulted in extensive deboronation, with at least 27% N-benzyl-N,N′-dibenzoylethylenediamine being recovered and with no evidence for any boron-containing derivative. The deboronated derivative was identified by means of its melting point (187°)[21] and infrared spectrum compared with those of an authentic sample. The deboronated free amine, N-benzylethylenediamine, was also converted to three other derivatives

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[20] (a) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, Chapter 2; (b) D. W. Aubrey, M. F. Lappert and H. Pyszora, *J. Chem. Soc.*, 1931 (1961).

[21] Lit. mp 186–187° [C. D. Lunsford, R. E. Lutz, and E. E. Bowden, *J. Org. Chem.*, **20**, 1513 (1955)]; mp 186.5–187.0° [S. C. Dickerman and A. J. Besozzi, *ibid.*, **19**, 1855 (1954)]; mp 188° [S. R. Adinsell, *J. Am. Chem. Soc.*, **63**, 852 (1941)].

recorded in the literature (bisacetamide, dihydrochloride, and dipicrate), with the correct melting points being observed.

Diindano[3,2-*b*;2′,3′-*f*]-13,16-diaza-5,7-diboraoxepane (VII).—Sublimation of the crude reaction mixture at 200° (0.015 mm) yielded crude pentacycle VII (35% by weight of crude, 17% yield based upon I). Several more sublimations provided an analytical sample which melted in a sealed capillary under nitrogen at 198–211° dec.

Anal. Calcd for $C_{16}H_{16}B_2N_2O$: C, 70.15; H, 5.89; N, 10.23; mol wt, 280. Found: C, 69.85; H, 6.10; N, 10.27; mol wt, 246 (Rast), 313 (osmometer).

In the infrared the substance showed no OH or NH absorption, but it did show a strong band attributable to BO at 1350 with two bands in the 757–729-cm^{-1} region, either of which, or both, could be assigned to *ortho* substitution. Acid-catalyzed deboronation of II yielded 37% N,N′-dibenzylethylenediamine, identified by its infrared spectrum.[22]

N-(*o*-Boronobenzyl)ethylenediamine-N′ Hydrobromide.—The analytically pure hydrobromide was obtained from those preparations of crude reaction mixtures wherein high purity I was used. Sometimes the yield was nil; it was never greater than 2% based upon I. This procedure was followed with the salt appearing as a white precipitate during the extraction with chloroform. The crystals were collected on a sintered-glass funnel, rinsed, and dried under vacuum: mp 305–306° dec, when introduced in an open capillary at 299°.

Anal. Calcd for $C_9H_{16}BBrN_2O_2$: C, 39.31; H, 5.87; Br, 29.06; N, 10.19. Found: C, 39.38; H, 5.54; Br, 29.57; N, 10.47.

The infrared spectrum was consistent for a boronic acid containing a primary amine hydrobromide moiety (primary ammonium band overlapping CH stretch).[20a] As evidenced by infrared spectra, a sample of this salt slowly sublimed unchanged at 306° (0.012 mm). No dehydration was noted, and the recovery was at least 89%.

A solution of 38 mg of N-(*o*-boronobenzyl)ethylenediamine-N′ hydrobromide (0.138 mmole) in 1.0 ml of water was agitated with 18 mg of silver oxide (0.155 mequiv, or 112% of theory)[23] for 15 min at 25°. Then the water was removed under vacuum from the resulting gray solids and the residue was extracted thrice with 1.0-ml portions of hot methanol. The methanol was filtered and concentrated to a yellow oil weighing 12 mg. This proved to be a free amine with an infrared spectrum very like that of materials from which the hemisulfate was obtained, and probably was unencumbered VIII. Unfortunately, it was not successfully purified, although it could be converted to the hemisulfate. The infrared spectrum of the oil was not that of N-benzylethylenediamine and the oil contained boron; hence no heavy metal-catalyzed deboronation was noted under these conditions.

Registry No.—I, 7481-16-5; *o*-(*t*-butylaminomethyl)-benzeneboronic acid hydrochloride, 7491-62-5; *o*-(*t*-butylaminomethyl)benzeneboronic acid, 7481-22-3; bis(2-*t*-butyl-1,2-boraazaindanyl-1) oxide, 7481-21-2; IV, 7492-95-7; VI, 7481-20-1; VIII hemisulfate, 7481-17-6; VII, 7481-18-7; N-(*o*-boronobenzyl)ethylenediamine-N′ hydrobromide, 7481-19-8.

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[22] "Sadtler Standard Spectra," Midget ed., Sadtler Research Laboratories, Philadelphia, Pa., 1956, No. 6271.

[23] This was at the suggestion of Professor H. R. Snyder, University of Illinois.

An Approach to the Synthesis of Tetrabenzo[*a*,*c*,*g*,*i*]heptalene

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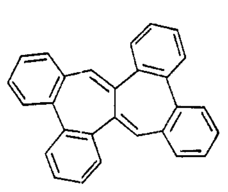
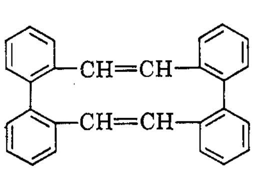
Diphendialdehyde and 2,2′-bis(cyanomethyl)biphenyl condense, in the presence of sodium ethoxide, to the tetrahydro derivative (IVa) of tetrabenzo[*a*,*c*,*g*,*i*]heptalene. 9,10-Dicyanophenanthrene was a by-product of this reaction. From diphendialdehyde and 2,2′-diaminobiphenyl, 9,20-diazatetrabenzo[*a*,*c*,*g*,*i*]cyclododecene (XIV) was obtained.

Calculations on the electronic structure and on the "pseudo-aromatic" character of heptalene have not yet led to unequivocal results.[1,2] As it has been predicted[1a] that higher benzologs of heptalene, such as tetrabenzo[*a*,*c*,*g*,*i*]heptalene (A), may be of particular theoretical interest, it seemed worthwhile to attempt to synthesize compound A, which is closely related to tetrabenzo[*a*,*c*,*g*,*i*]cyclododecene (B).



A



B

Diphendialdehyde (I) and 2,2′-bis(cyanomethyl)-biphenyl (II) condensed under the influence of sodium ethoxide to a product of the formula $C_{30}H_{20}N_2O$ which is composed of 1 mole each of I and II, minus 1 mole of water. Two formulas (IIIa and IVa) appeared possible *a priori*. The compound contained, indeed, two slightly different nitrile groups (doublet at 2240 and 2225 cm^{-1}) and a secondary hydroxyl; the acetyl derivative absorbed at 1745 cm^{-1} and was thus an ester, and not an amide, and the product could be oxidized to a ketone ($C_{30}H_{18}N_2O$) which absorbed at 1675 cm^{-1} and was thus of the arylalkyl ketone type. The nitrile doublet is explained by the fact that one of the nitrile groups is hydrogen bonded to the hydroxyl; thus, the acetyl derivative and the ketone show only *one* nitrile frequency.

A decision between IIIa and IVa and in favor of IVa was possible on the strength of the following observations: (a) the ultraviolet spectrum of the con-

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[1] (a) G. Berthier, B. Pullman, and J. Baudet, *J. Chim. Phys.*, **49**, 641 (1952); (b) E. D. Bergmann in "Non-benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, p 141.

[2] (a) T. Nakajima in "Molecular Orbitals in Chemistry, Physics and Biology," P. O. Loewdin and B. Pullman, Ed., Academic Press Inc., New York, N. Y., 1964, p 451; (b) G. Wagnière and M. Gouterman, *Mol. Phys.*, **5**, 621 (1962); (c) H. J. Dauben and D. J. Bertelli, *J. Am. Chem. Soc.*, **83**, 4659 (1961).