white crystals. These were taken up in a mixture of benzene and petroleum ether (bp 60–70°), applied to a column of 2 lb of alumina, and chromatographed. Elution with benzene gave 25 g of impure dibenzyl carbobenzyloxyaminomalonate. Further elution with ether and absolute ethanol gave 47.2 g (47%) of *o*-(2,2-dicarbobenzyloxy-2-carbobenzyloxyaminoethyl)benzeneboronic acid as an oil, which was crystallized from aqueous *t*-butyl alcohol. An analytical sample was prepared by threefold recrystallization from 1,2-dichloroethane–petroleum ether, mp 110–111°.

Anal. Calcd for $C_{32}H_{30}BNO_8$: C, 67.73; H, 5.33; N, 2.47; B, 1.92. Found: C, 67.89; H, 5.33; N, 2.59; B, 1.83.

Preparation of α-Amino-*o*-boronobenzylmalonic Anhydride.—The 30% palladium-on-charcoal catalyst used in this experiment was washed with distilled water and absolute ethanol and dried *in vacuo*. Thus treated, the catalyst was highly pyrophoric. To a solution of 15.00 g (0.026 mol) of *o*-2,2-dicarbobenzyloxy-2-carbobenzyloxyaminoethyl)benzeneboronic acid in 200 ml of ethyl acetate under nitrogen, 3 g of 30% palladium-on-charcoal catalyst was added. The mixture was stirred while hydrogen was passed through rapidly for 7.5 hr. During this time, a precipitate of barium carbonate formed in a barium hydroxide trap connected to the apparatus; after being washed and dried *in vacuo*, this precipitate weighed 5.22 g (0.026 mol).

The hydrogenolysis mixture was filtered and washed with 100 ml of ethyl acetate. The residue remaining on the filter was extracted with 250 ml of water; the resultant aqueous solution was freed of a small amount of insoluble material by filtration through a fine sintered-glass funnel and evaporated *in vacuo*, giving 6.668 g (99.7%) of white crystals which could be recrystallized from water, mp 249–262°.

Anal. Calcd for $C_{10}H_{10}BNO_5$: C, 51.11; H, 4.29; N, 5.96; B, 4.60. Found: C, 51.09; H, 4.49; N, 5.94; B, 4.27.

Preparation of α-Amino-*o*-boronobenzylmalonic Anhydride Complex with Tetrahydrofuran.—A concentrated aqueous solution of α-amino-*o*-boronobenzylmalonic acid was treated with one-fourth its volume of tetrahydrofuran; the crystals which separated were dried overnight at room temperature *in vacuo*, mp 248–264°.

Anal. Calcd for $C_{14}H_{18}BNO_6$: C, 54.75; H, 5.91; N, 4.56. Found: C, 54.89; H, 5.96; N, 4.63.

Preparation of α-Amino-*o*-boronobenzylmalonic Anhydride Complex with *t*-Butyl Alcohol.—A concentrated aqueous solution of α-amino-*o*-boronobenzylmalonic acid was treated with ten times its volume of *t*-butyl alcohol and allowed to stand at 5° for 3 days; the crystals which separated were dried at room temperature *in vacuo* overnight, mp 250–253° dec, with gas evolution at 170–180°.

Anal. Calcd for $C_{14}H_{20}BNO_6$: C, 54.39; H, 6.52; N, 4.53. Found: C, 53.91; H, 6.48; N, 4.42.

Preparation of α-Amino-*o*-boronobenzylmalonic Acid Hydrate.—α-Amino-*o*-boronobenzylmalonic anhydride (0.2588 g, 0.0011 mol) was allowed to stand for 7 days in a desiccator saturated with water vapor. At the end of this time, the sample weighed 0.2997 g. The calculated value for the addition of 2 mol of water was 0.2992 g.

Anal. Calcd for $C_{10}H_{14}BNO_7$: C, 44.32; H, 5.21; N, 5.17. Found: C, 44.28; H, 5.16; N, 5.09.

Preparation of *o*-Boronophenylalanine Anhydride.—α-Amino-*o*-boronobenzylmalonic acid hydrate (2.271 g, 0.008 mol) was heated at 220° (0.1 mm) for 3.75 hr. The yellow powder was extracted with 125 ml of hot water and the insoluble residue removed by filtration. The filtrate was treated with Darco and evaporated *in vacuo* to give 1.178 g (73.5%) of white crystals. An analytical sample was prepared by twofold recrystallization from a minimum amount of water, followed by drying at 100° *in vacuo* overnight, mp 252–262°.

Anal. Calcd for $C_9H_{10}BNO_3$: C, 56.59; H, 5.28; N, 7.33. Found: C, 56.49; H, 5.22; N, 7.44.

Registry No.—IX, 17604-89-6; X, 5115-46-8; XI, 17604-90-9; XIII, 17604-91-0; XIV, 17659-05-1; XVb, 17604-92-1; α-amino-*o*-boronobenzylmalonic anhydride complex with *t*-butyl alcohol, 17604-93-2; α-amino-*o*-boronobenzylmalonic acid, 77604-94-3; *o*-boronophenylalanine anhydride, 17604-95-4.

Arylboronic Acids. Imino Derivatives from *o*-Formylbenzeneboronic Acid[1]

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Received May 27, 1968

o-Formylbenzeneboronic anhydride reacts with aniline, *p*-toluidine, benzylamine, and *n*-propylamine to give Schiff bases which are isolated as the trimeric boronic anhydrides. These substances react with catechol to give the catechol derivatives of the boronic acids, in which the boron atom interacts with the neighboring nitrogen atom and becomes tetracovalent. When the free acid, *o*-formylbenzeneboronic acid, reacts with methoxyamine, the expected oxime ether is formed. Attempts to convert the product, N-*o*-boronobenzalmethoxyamine, into the boronic anhydride are complicated by the occurrence of a transformation of the Beckmann type, by which oximino ether groups are converted into nitrile groups, some of which are hydrolyzed to amide groups, with the result that a complex mixture of simple and mixed trimeric boronic anhydrides is formed. The previously known heterocyclic substance, 4-hydroxy-4,3-boroxaroisoquinoline, formed from the formylboronic acid and hydroxylamine, likewise undergoes a Beckmann transformation on heating and yields a mixture of trimeric simple and mixed anhydrides containing nitrile and amide groups.

Because of the ease of formation and the stability of the lactone ring in boronophthalide, I, one might expect *o*-formylbenzeneboronic acid, or its anhydride II, to react with primary amines to form substituted aminoboronophthalides rather than simple Schiff bases. The lactone ring of I forms so readily that the hydroxyboronic acid is unknown,[3,4] and the carbon–boron bond of I is stable to strong acids or strong bases[4] under conditions which effect the deboronation of most boronic acids.[5,6] It is surprising to find that the trimeric anhydride of II reacts with primary aromatic and aliphatic amines, such as aniline, *p*-toluidine, benzylamine, and *n*-propylamine, to give Schiff bases, readily obtained as the trimeric boronic anhydrides, III. The structures IIIa–d are indicated by the analyses, by the occurrence of –C=N– absorption in the region of 1622–1648 cm^{-1}, and by the occurrence of the boronic anhydride[7] B—O absorption in the 1315–1390-cm^{-1} region, as well as by the absence of absorption due to OH or NH

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[1] This work was supported in part by a grant from the Atomic Energy Commission, Report No. C00-314-12.

[2] Phillips Petroleum Fellow, 1962–1963.

[3] K. Torssell, *Arkiv Kemi*, **10**, 509 (1957).

[4] H. R. Snyder, A. J. Reedy, and W. J. Lennarz, *J. Amer. Chem. Soc.*, **80**, 835 (1958).

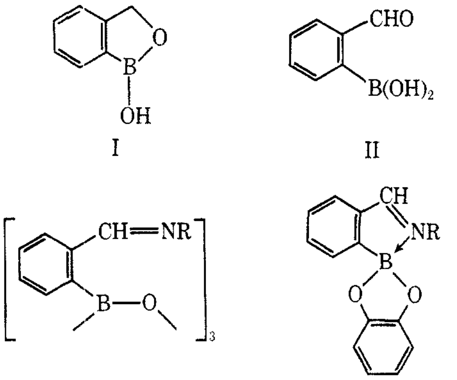
[5] M. F. Lappert, *Chem. Rev.*, **56**, 994 (1956).

[6] A. D. Ainley and F. Challenger, *J. Chem. Soc.*, 2171 (1930).

[7] See R. L. Letsinger, Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., p 3.

groups or to the boronophthalide ring system.[8] All of the compounds react readily with catechol to give the catechol esters IV. The catechol derivatives exhibit a broad absorption band centered at 1220 cm^{-1}, sometimes a resolved doublet, which may be due to B–N stretching, and which does not occur in the spectra of IIIa–d. It appears that the interaction of nitrogen and boron is a more prominent feature of the structures of the catechol esters IV than of the boronic anhydrides III (Chart I).

CHART I



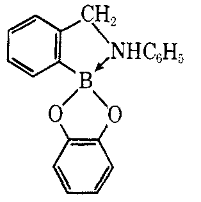
I II

IIIa, R = C_6H_5
b, R = p-$CH_3C_6H_4$
c, R = $C_6H_5CH_2$
d, R = $CH_3CH_2CH_2$

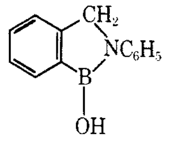
IVa, R = C_6H_5
b, R = p-$CH_3C_6H_4$
c, R = $C_6H_5CH_2$
d, R = $CH_3CH_2CH_2$

Part of the interest in the Schiff bases lies in their possible utility as intermediates for aminoboronic acids, to which they should be convertible by chemical or catalytic reduction. Since Hawkins and Blackham[9] have recently studied the more direct synthesis of such amino compounds by alkylation of aliphatic and aromatic amines with o-bromomethylbenzeneboronic anhydride, this possible utilization of the Schiff bases has been tested only in connection with the aniline compound (IIIa). The fact that pyridine and arylboronic anhydrides form 1:1 adducts which are nicely crystalline compounds of low solubility[10] suggested that the benzylamine derivative obtainable by reduction of IIIa might be an easily isolable solid, possibly polymeric since the interaction between the nitrogen atom and the boroxole ring could be intermolecular rather than intramolecular. In a hydrogenation over 30% palladium-on-charcoal catalyst, conducted in THF, o-boronobenzalaniline anhydride (IIIa) consumed almost the theoretical amount of hydrogen. The product, however, proved to be an oil, characterized as the nicely crystalline catechol derivative V.

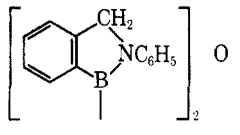
From a reduction of IIIa with lithium aluminum hydride in ether and THF, followed by treatment with water and eventual precipitation from ether with dry hydrogen chloride, the hydrochloride of o-boronobenzylaniline (mp 167° dec, lit.[9] mp 169–171° dec) was obtained. From a reduction with lithium aluminum hydride in THF, there was obtained a solid the composition of which indicated it to be largely N-phenylboronophthalimidine (VI) contaminated with a little o-boronobenzylaniline. Further dehydration of this solid by heating in cyclohexane gave a mixture of N-phenylboronophthalimidine and its dimeric anhyhydride (VII). Hawkins and Blackham[9] have noted the difficulty of isolating compounds of type VI and have suggested that they are to be formulated as shown rather than with an additional dative bond between the nitrogen and boron atoms (borazaindene structure). The rapid dehydration of VI in boiling cyclohexane would not have been predicted from the behavior of the oxygen analog (boronophthalide), since the latter is converted into its anhydride (VIII) only under more severe conditions.[11]



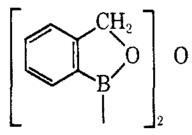
V



VI



VII



VIII

Reedy[4] obtained a cyclic product, 4-hydroxy-4,3-boroxaroisoquinoline (IX), by reaction of hydroxylamine hydrochloride with o-formylbenzeneboronic acid. He observed the substance to melt at 150–155°. Dewar and Dougherty[12] reported that on slow heating IX was observed to melt much higher (264–265°), with a change in crystalline form at 164°. In some of our experiments with slow heating, melting was observed at 148–150°, followed by decomposition (bubbling) at about 158°, with resolidification occurring at about 164°. It would appear possible, therefore, to prepare the dimeric anhydride of IX by simply heating at temperatures near 160°. However, a number of attempts, performed under a variety of conditions, gave products which were obviously mixtures and which, according to the infrared spectra, contained nitrile groups and usually also amide groups. Evidently the formation of the dimeric anhydride is accompanied or followed by a transformation of the Beckmann type, introducing cyano groups, some of which are converted into amide groups by water liberated as trimeric boronic anhydrides are formed.

If the Beckmann transformation in the decomposition of IX or its dimeric anhydride depends on the existence of the boron–oxygen–nitrogen bonds in the molecule, the thermal behavior of o-boronobenzalmethoxyamine (X) might be entirely different. The oxime ether (X) was easily prepared in excellent yield, and analysis of the first crop from recrystallization from chloroform was in excellent agreement with that expected. However, all attempts to convert the oxime ether (X) into the trimeric boronic anhydride with the oximino ether groups intact failed. As in the dehydration of IX, complex mixtures containing cyano, amide, and probably oximino ether groups were formed and

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[8] R. R. Haynes, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1963.

[9] R. T. Hawkins and A. U. Blackham, *J. Org. Chem.*, **32**, 597 (1967).

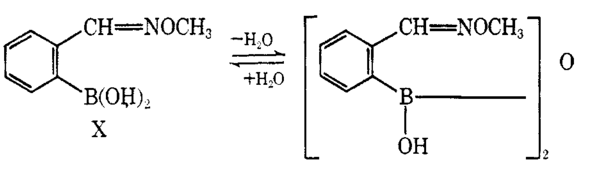
[10] H. R. Snyder, M. S. Konecky, and W. J. Lennarz, *J. Amer. Chem. Soc.*, **80**, 3611 (1958).

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

[12] M. J. S. Dewar and R. C. Dougherty, *J. Amer. Chem. Soc.*, **86**, 433 (1964).

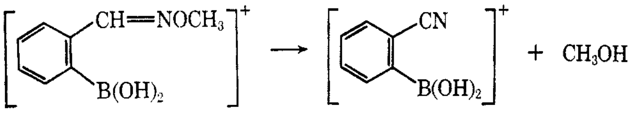
the mixtures resisted attempted separation (there can be ten different simple and mixed trimeric anhydrides with three different substituents on the benzene ring). Evidently the Beckmann transformation can result from the coordination of the ether oxygen atom of X with the boron atom.

Evidence for an unstable dimeric semianhydride of X was obtained from the nmr spectral examination of crystals from a second crop in the chloroform recrystallization. The nmr spectrum of the first crop showed peaks at τ 1.71, 2.55, and 6.00, with relative areas of 4:3:3. When the sample was shaken with deuterium oxide, the relative areas reduced to 2:3:3. The spectrum of a sample from the second crop had peaks centered at τ 1.75, 2.55, and 6.00, with relative areas of 2:4:3. When the sample was shaken with water, the spectrum became identical with that of the first-crop sample, and the spectrum after exposure to deuterium oxide was indistinguishable from that of first-crop material treated with deuterium oxide. These results can be explained on the assumptions that the second-crop material is the dimeric semianhydride (XI), and that the resonances near 1.71 are due to boronic acid protons, the proton on the carbon atom adjacent to the aromatic ring, and one of the aromatic protons, the resonances at 2.55 are due to the remaining aromatic protons, and those at 6.00 are due to the methyl protons.



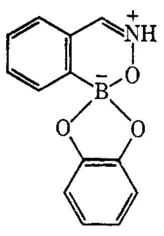
X XI

The mass spectrum of X obtained with no heating of the sample exhibits the parent mass at 179 along with a mass peak at 147 and a metastable peak at 121.[13] The appearance of these peaks suggests this ionic reaction.



As the sample of X is heated, the mass peak at 179 disappears and peaks corresponding to molecular ions of trimers appear, but there is no indication of the simple trimeric anhydride (mass 483) of X; only mass peaks corresponding to trimers which have lost one, two, or three molecules of methanol are observed (mass peaks at 451, 419, and 387). As expected, there is no indication in the mass spectra of the very unstable semianhydride XI. The mass spectrum of 4-hydroxy-4,3-boroxaroisoquinoline IX, obtained at low ionizing voltage, on the other hand, does contain a peak (mass 276) corresponding to a dimeric anhydride as well as one (mass 147) corresponding to the monomer. Even the catechol derivative of X undergoes loss of methanol in the mass spectrometer, the spectrum showing the parent mass at 253, a mass peak at 221 (loss of methanol), and a metastable peak at 193. The fragmentation pattern evidently is the same as the first stage of that of X.

It would not be surprising if 4-hydroxy-4,3-boroxaroisoquinoline (IX) were unreactive toward catechol under the conditions employed in the preparation of the other catechol derivatives reported here, because of the greater aromaticity of the system and the resulting loss of Lewis acidity at the boron atom.[12] Nevertheless, the substance (IX) did react rapidly to give a derivative of the expected composition in good yield. The infrared spectrum of the derivative reveals no strong band in the 1315–1390-cm^{-1} region; there is strong absorption at 1200 cm^{-1}, and also a broad band at 2680 cm^{-1}. The spectrum seems best accommodated by structure XII, with the proton located either on the nitrogen atom as shown or, less probably, on any of the three oxygen atoms.



XII

Experimental Section[14]

Preparation of Schiff Bases. o-Boronobenzalaniline Anhydride.—A mixture of 4.50 g of *o*-formylbenzeneboronic acid[15] and 100 ml of benzene was refluxed for 2 hr in a flask fitted with a Dean-Stark water separator, during which time the theoretical amount of water was removed. To the remaining solution was added 2.79 g of freshly distilled aniline. The mixture was again refluxed and the theoretical amount of water codistilled. A white solid separated and the reaction mixture was allowed to cool to room temperature. The product weighed 4.64 g (74.7% yield, mp 223–225° dec). An analytical sample (mp 229.5–230.5°) was prepared by recrystallizing the product twice from chloroform-cyclohexane and drying (0.1 mm over phosphorus pentoxide) at 52.6° for 20 hr.

Anal. Calcd for $(C_{13}H_{10}BNO)_3$: C, 75.43; H, 4.87; N, 6.77. Found: C, 75.36; H, 4.97; N, 6.87.

o-Boronobenzal-p-toluidine anhydride, mp 232–235°, was prepared similarly but in much more dilute solution. An analytical sample was prepared by recrystallizing twice from nitromethane, with heating for 10 hr at 0.1 mm to remove residual nitromethane.

Anal. Calcd for $(C_{14}H_{12}BNO)_3$: C, 76.06; H, 5.47; N, 6.36. Found: C, 75.65; H, 5.48; N, 6.36.

o-Boronobenzalbenzylamine anhydride, mp 181–185°, was prepared similarly and recrystallized from toluene for analysis.

Anal. Calcd for $(C_{14}H_{12}BNO)_3$: C, 76.08; H, 5.47; N, 6.34; mol wt, 663. Found: C, 76.28; H, 5.63; N, 6.26; mol wt (mass spectrum), 663.

o-Boronobenzalpropylamine anhydride, mp 168–178°, was prepared similarly and recrystallized from toluene for analysis.

Anal. Calcd for $(C_{10}H_{12}BNO)_3$: C, 69.42; H, 6.99; N, 8.10. Found: C, 69.37; H, 6.93; N, 8.12.

Reactions with Catechol. Catechol Derivative of o-Boronobenzalaniline.—A mixture of 3.00 g of *o*-boronobenzalaniline anhydride, 1.59 g of catechol, and 15 ml of absolute ethanol immediately turned orange. It was heated to reflux for 1 min, filtered, and chilled. A red-orange crystalline product (3.36 g) was obtained (yield 77.5%). After recrystallization from absolute ethanol and drying (0.1 mm) over calcium chloride at 56° for 3 hr, brilliant orange crystals (mp 156–159°) were obtained.

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(13) K. Biemann, "Mass Spectrometry: Organic Chemical Applications," McGraw Hill Book Co., Inc., New York, N. Y., 1962, pp 154–156.

(14) Microanalysis was performed by Mr. Josef Nemeth and his associates. All melting points are uncorrected. Infrared spectra were determined by the staff of the Spectroscopy Laboratory of the Department of Chemistry and Chemical Engineering using a Perkin-Elmer Model 21 infrared spectrophotometer (with sodium chloride optics). The mass spectra were determined by Mr. Joseph Wrona on an Atlas CH4 spectrometer.

(15) P. Tschampel and H. R. Snyder, *J. Org. Chem.*, **29**, 2168 (1964).

Anal. Calcd for $C_{19}H_{14}BNO_2$: C, 76.29; H, 4.72; N, 4.68. Found: C, 76.13; H, 4.69; N, 4.75.

The catechol derivative of *o*-boronobenzal-*p*-toluidine, yellow-orange crystals, mp 161–163°, was prepared similarly.

Anal. Calcd for $C_{20}H_{16}BNO_2$: C, 76.69; H, 5.15. Found: C, 76.84; H, 5.18.

The catechol derivative of *o*-boronobenzalbenzylamine, yellow crystals, mp 164–166°, was prepared similarly.

Anal. Calcd for $C_{20}H_{16}BNO_2$: C, 76.69; H, 5.15; N, 4.62. Found: C, 76.72; H, 5.16; N, 4.40.

The catechol derivative of *o*-boronobenzalpropylamine, pure light yellow crystals, mp 154–155°, was prepared similarly.

Anal. Calcd for $C_{16}N_{16}BNO_2$: C, 72.48; H, 6.09; N, 5.29. Found: C, 72.51; H, 6.19; N, 4.99.

Catalytic Reduction of *o*-Boronobenzalaniline Anhydride.—From 4.00 g (6.44 mmol) of *o*-boronobenzalaniline anhydride, 150 ml of tetrahydrofuran, and 0.4 g of 30% palladium on carbon (Engelhard Lot C03051), shaken in a Parr apparatus (initial pressure 21.4 psi at 27°) for 33 min, there was obtained a gold oil indicated to be a mixture of *o*-boronobenzylaniline anhydride and tetrahydrofuran by its nmr spectrum in carbon tetrachloride; hydrogen consumption was 94%. The product was characterized as the catechol derivative (mp 197–200°).

Preparation of *o*-Boronobenzylaniline Hydrochloride by Lithium Aluminum Hydride Reduction of *o*-Boronobenzalaniline Anhydride.—To 20 ml of dry ether and 0.038 g (1 mmol) of lithium aluminum hydride was added a slurry of 0.500 g (0.805 mmol) of *o*-boronobenzalaniline anhydride in 20 ml of ether, and the mixture was refluxed for 2 hr. Since it appeared that no reaction had taken place, 12 ml of dry tetrahydrofuran was added and the mixture was refluxed for 2 hr and cooled. After treatment with water and 50 ml of a 20% solution of sodium potassium tartrate, the mixture was separated and the aqueous layer extracted with three 100-ml portions of ether. The solvent was removed *in vacuo* from the dried extract to give a yellow oily emulsion which could not be induced to crystallize. To the oily emulsion was added 10 ml of ether. Dry hydrogen chloride was bubbled through the solution and 0.53 g of a white precipitate formed (mp 167° dec, lit.[9] mp 169–171° dec). The nmr spectrum in deuterium oxide indicated that reduction had taken place and that the product was the hydrochloride of *o*-boronobenzylaniline.

Preparation of the Catechol Derivative of *o*-Boronobenzylaniline.—To 0.200 g (0.318 mmol) of *o*-boronobenzylaniline anhydride which contained a small amount of tetrahydrofuran were added 2 drops of water, 5 ml of absolute ethanol, and 0.105 g (0.954 mmol) of catechol. The reaction mixture was heated 1 min, then cooled and chilled. The clear quartzlike crystals which formed weighed 0.025 g. On cooling 48 hr, the mother liquor deposited a second crop (0.039 g, total yield 22%).

The analytical sample was obtained by drying the first crop (0.1 mm) over phosphorus pentoxide at 56.2° for 1 hr (mp 197–200°).

Anal. Calcd for $C_{19}H_{16}BNO_2$: C, 75.78; H, 5.36; N, 4.65. Found: C, 75.76; H, 5.38; N, 4.39.

The infrared spectrum (KBr) showed no absorption at 1620 cm^{-1}, confirming the absence of the CH=N group. The N—H stretch appeared at 3155 cm^{-1}, substantially lower than the range 3300–3500 characteristic of most secondary amines.[16]

N-(Phenyl)boronophthalimidine and Its Anhydride by Reduction of *o*-Boronobenzalaniline Anhydride.—A THF solution of 1.04 g of *o*-boronobenzalaniline anhydride was added slowly to a stirred slurry of 0.38 g of $LiAlH_4$ in THF. Upon completion of the addition, the reaction mixture was heated at reflux for 1 hr; the excess $LiAlH_4$ was decomposed (water); and the mixture obtained was filtered. The residue was washed with THF. The filtrate and the wash solution were combined and evaporated. The solid thus obtained was extracted with three 50-ml portions of ether which upon evaporation gave 0.59 g of product. Recrystallization from benzene–hexane gave a compound whose analysis (C, 73.47; H, 5.91) indicated it to be a mixture of *o*-boronobenzylaniline (C, 68.78; H, 6.22) and N-(phenyl)-boronophthalimidine (C, 74.70; H, 5.79). Azeotropic distillation of cyclohexane–water gave a mixture of the N-(phenyl)-boronophthalimidine and its anhydride (*Anal.* Calcd for $C_{26}H_{22}B_2N_2O$: C, 78.07; H, 5.54. Found: C, 76.72; H, 5.61.). The mass spectrum indicated a molecular weight of 400 which is that calculated for the anhydride of N-(phenyl)boronophthalimidine.

Preparation of the Catechol Derivative of 4-Hydroxy-4,3-boroxaroisoquinoline.—A solution prepared from 0.147 g of 4-hydroxy-4,3-boroxaroisoquinoline, 0.11 g of catechol, and 2 ml of absolute ethanol turned yellow as it was heated to reflux. The hot solution was filtered, then cooled to give yellow crystals (0.145 g, yield 60.6%), mp 207–211° dec. The analytical sample was recrystallized twice from absolute ethanol and dried at 0.1 mm at 56° for 2 hr, then at 100° for 1 hr.

Anal. Calcd for $C_{13}H_{10}BNO_3$: C, 65.33; H, 4.22; N, 5.86. Found: C, 65.15; H, 4.32; N, 5.66.

Preparation of N-(*o*-Boronobenzal)methoxyamine.—The pH of a solution prepared from 3.95 g of *o*-formylbenzeneboronic acid, 3.00 g of methoxyamine hydrochloride, and 100 ml of water was adjusted to 7 by adding approximately 10 ml of 10% sodium hydroxide solution. This mixture was refluxed for 15 min, cooled to room temperature, stoppered, and placed in the refrigerator overnight. The beautiful long transparent needles weighed 4.38 g (yield 93%). An analytically pure sample was obtained by recrystallization from chloroform (mp 87–87.5°).

Anal. Calcd for $C_8H_{10}BNO_3$: C, 53.68; H, 5.63; N, 7.83; mol wt, 179. Found: C, 53.55; H, 5.61; N, 7.72; mol wt (mass spectrum) 179.

Preparation of the Catechol Derivative of N-(*o*-Boronobenzal-methoxyamine.—In an apparatus equipped with a Dean–Stark water separator, water and benzene were codistilled from a solution of 2.56 g of N-(*o*-boronobenzal)methoxyamine in 100 ml of benzene. The reaction mixture was allowed to cool to 70° and 1.57 g of catechol was added. Codistillation was continued for 1.25 hr. The remaining solvent was removed *in vacuo*, and 2.7 g (yield 75%) of crude product was obtained. It was dissolved in toluene, treated with Darco, filtered, and caused to crystallize by the addition of low petroleum ether (bp 30–60°). The white needles obtained melted at 98–99°.

An analytical sample was obtained by recrystallizing the white needles twice from toluene and drying at 0.1 mm at 56° over calcium chloride for 8 hr (mp 102–103°).

Anal. Calcd for $C_{14}H_{12}BNO_3$: C, 66.43; H, 4.78; N, 5.54. Found: C, 66.76; H, 4.82; N, 5.30.

Registry No.—IIIa, 17604-35-2; IIIb, 17604-69-2; IIIc, 17743-98-5; IIId, 17659-03-9; IVa, 17604-19-2; IVb, 17604-20-5; IVc, 17604-21-6; IVd, 17604-22-7; V, 17692-14-7; X, 17604-70-5; XII, 17668-52-9; catechol deivative of N-(*o*-boronobenzal)methoxyamine, 17604-34-1.

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[16] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1958, p 249.