[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO, CHICAGO, ILL.]

New Heteroaromatic Compounds. XX.[1] Derivatives of 4,3-Borazaroisoquinoline[2]

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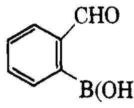
RECEIVED AUGUST 15, 1963

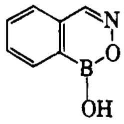
Condensation of *o*-formylphenylboronic acid with hydrazine, or monosubstituted hydrazines, gives derivatives of a new very stable heteroaromatic system, 4,3-borazaroisoquinoline. The preparation and properties of a number of these compounds are described. It is pointed out that the cyclic oxime[5] of *o*-formylphenylboronic acid is best regarded as a derivative of the analogous 4,3-boroxaroisoquinoline.

Previous papers of this series[1,6] have described the preparation and properties of a series of novel heteroaromatic compounds containing boron atoms as components of six-membered rings. These compounds are isoconjugate with "normal" aromatic systems, being derived from them by replacement of a pair of adjacent carbon atoms by boron and nitrogen or oxygen; their stability to oxidation or hydrolysis indicates that they too are aromatic and have large stabilization energies.

The compounds previously described have been related to aromatic hydrocarbons; here we describe the preparation of a number of similar analogs of a heteroaromatic system, namely, isoquinoline.

We were led into this field by a report[5] that the oxime of *o*-formylphenylboronic acid[7] (I) exists as the cyclic anhydride II. Snyder, Reedy, and Lennarz[5] did not comment on the properties of this material; however the arguments put forward in previous papers of this series suggest that it should be aromatic, being isoconjugate with 4-hydroxyisoquinoline. This relationship is indicated by writing the dipolar resonance structure III for II; in our system of nomenclature[8] the compound would be described as 4-hydroxy-4,3-boroxaroisoquinoline. We have re-examined the properties of this material and find that it does indeed show aromatic behavior; thus it is resistant to hydrolysis and appears to act as a protic acid rather than a Lewis acid—a point that will be discussed in more detail elsewhere.


I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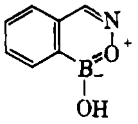
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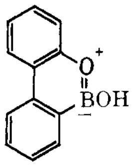
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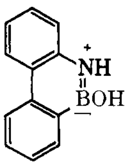
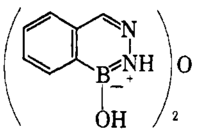
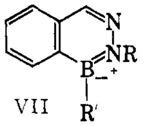
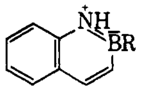
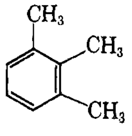

V

Now both theory and experiment suggest that boroxaro analogs of aromatic systems should be less stable than the corresponding borazaro compounds; thus 10-hydroxy-10,9-boroxarophenanthrene (IV) is less aromatic than the isoconjugate borazarophenanthrene (V).[9] Since the hydroxyboroxaroisoquinoline (II or III) appeared to show aromatic properties, it seemed likely that the corresponding borazaroisoquinoline would be exceptionally stable. Indeed, when we treated I with hydrazine, we obtained in quantitative yield a compound whose composition corresponded to that expected for the anhydride VI of 4-hydroxy-4,3-borazaroisoquinoline (VIIa) and which was almost unaffected by prolonged boiling with strong acid or alkali. The material behaved in solution as a protic acid rather than a Lewis acid, behavior characteristic of aromatic cycloborinic acids,[10] and the infrared spectrum indicated the presence of a very acidic NH proton, as would be expected if there is any significant contribution by the dipolar resonance structure VII.[11] Thus the stretching NH frequency in solid VI appears at 3340 cm.$^{-1}$, a value much lower than that observed in amides (3400–3420 cm.$^{-1}$) or in pyrrole (3410 cm.$^{-1}$).


VI


VII


VIII


IX

VIIa, R = H, R' = OH VIIIa, R = OH
b, R = H, R' = CH_3 b, R = OCH_3
c, R = CH_3, R' = CH_3 c, R = H
d, R = CH_3, R' = OH
e, R = Ph, R' = OH
f, R = H, R' = H
g, R = CH_3, R' = H

The chemical properties of VI were analogous to those of the corresponding anhydride of 2-hydroxy-2,1-borazaronaphthalene[8] (VIIIa). Thus VI reacted with methylmagnesium iodide to form 4-methyl-4,3-borazaroisoquinoline (VIIb). The imino proton in this is even more acidic than that in VI, judging by its infrared spectrum which shows either in the solid, or in solution, a NH stretching vibration at 3280 cm.$^{-1}$. This would be expected if the acidity is due to resonance effects in the boron-containing ring since these would be inhibited by electron-releasing substituents attached to boron, and the inhibition by a −E substituent (*e.g.*, OR) should be greater than that by a −I substituent (*e.g.*, CH_3).

The acidity of the imino proton was further indicated by the ready methylation of VIIb to 3,4-dimethyl-4,3-borazaroisoquinoline (VIIc) with dimethyl sulfate in the presence of potassium hydroxide. No such reaction has been previously reported, other borazaro compounds having been N-alkylated only by treating their N-lithio derivatives with alkyl halides or sulfates. The same compound (VIIc) was also obtained by this route, from the N-lithio derivative of VIIb with dimethyl sulfate. The structure of VIIc was established by elemental analysis, by the similarity of its ultraviolet spectrum to that of VIIb, by the disappearance of the NH absorption from the infrared spectrum and

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[1] Part XIX: G. C. Culling and M. J. S. Dewar, *J. Org. Chem*, in press.

[2] This work was supported by the National Institutes of Health, U. S. Public Health Service, through Grant No. CY-5218. A preliminary account has appeared: M. J. S. Dewar and R. C. Dougherty, *J. Am. Chem. Soc.*, **84**, 2648 (1962).

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[4] Woodrow Wilson Fellow, 1960–1961; National Science Foundation Predoctoral Fellow, 1961–1963.

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

[6] For a recent paper and references, see M. J. S. Dewar, C. Kaneko, and M. K. Bhattachargee, *ibid.*, **84**, 4884 (1962).

[7] K. Torssell, *Arkiv Kemi*, **10**, 507 (1957).

[8] M. J. S. Dewar and R. Dietz, *J. Chem. Soc.*, 2728 (1959).

[9] M. J. S. Dewar and R. Dietz, *ibid.*, 1344 (1960).

[10] This point will be discussed in detail in a later paper of this series.

[11] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958.

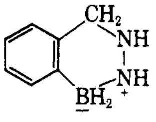
the appearance of a new CH band at 2495 cm.$^{-1}$, and by the fact that the proton n.m.r. spectrum showed the presence of two nonequivalent methyl groups.

Solutions of VIIc underwent autoxidation on standing in air to form 3-methyl-4-hydroxy-4,3-borazaroisoquinoline (VIId), the structure of which was indicated by elemental analysis, by its reconversion to VIIc on treatment with an excess of methylmagnesium bromide in ether, and by synthesis (see below). The conversion of VIIc to VIId certainly involves aerial oxidation since alcoholic solutions of VIIc are quite stable in the absence of air. This behavior is interesting, for the monomethylborazaroisoquinoline (VIIb) showed no signs of oxidation under similar conditions. The instability of VIIc is presumably a steric effect. Brown, Gintisth, and Domash[12] have shown that the compressional strain in hemimellitene (IX) is about 2.7 kcal./mole; IX and VIIc are homomorphs—indeed, the strain effect due to a *peri*-hydrogen must be greater than that due to an *o*-methyl group because of the possibility of free rotation in the latter case. Conversion of VIIc to VIId must therefore involve a relief of steric strain.

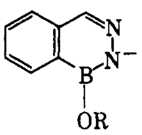
Attempts to N-methylate VIId with diazomethane were unsuccessful; a vigorous reaction took place with evolution of nitrogen, but the only products were unchanged VIIb and polyethylene. A similar reaction has been reported in the case of 10-methyl-10,9-borazarophenanthrene,[13] and many trivalent boron compounds show similar catalytic effects.[14] These reactions probably involve a nucleophilic attack on boron by the diazomethane, suggesting that the boron atoms in borazaroisoquinoline or borazarophenanthrene do retain some Lewis acidity. However, an alternative route to 3-substituted 4,3-borazaroisoquinolines seems to be provided by the reaction of I with substituted hydrazines; thus phenylhydrazine reacted with I to give an almost quantitative yield of 3-phenyl-4-hydroxy-2,1-borazaroisoquinoline (VIIe), while methylhydrazine likewise gave VIId. In the case of VIIe we were unable to replace the hydroxyl group by methyl by reaction with methylmagnesium bromide; a reaction took place, but the product was a low melting solid which proved difficult to characterize and which rapidly resinified in air. This behavior was not unexpected in view of the relative instability of VIIc; in 3-phenyl-4-methyl-4,3-borazaroisoquinoline the steric effects would be still greater. Similar indefinite products were obtained from the reaction of VIIb with phenylmagnesium bromide, presumably for the same reason.

The ready reaction of I with phenylhydrazine to form VIIe provides an explanation for the difficulties encountered by Snyder, *et al.*,[6] in attempts to prepare a dinitrophenylhydrazone of I. In this case cyclization to a borazaroisoquinoline should be much less facile, the borazaroisoquinoline ring being destabilized by the +E dinitrophenyl substituent. The products were probably mixtures of the open-chain dinitrophenylhydrazone and the borazaroisoquinoline. The destabilizing effect of +E substituents on nitrogen is well established in the case of 10,9-borazarophenanthrene[15]; such a substituent withdraws electrons from nitrogen, thus weakening the π-bond between nitrogen and boron and so reducing the mesomeric stabilization of the boron-containing ring.

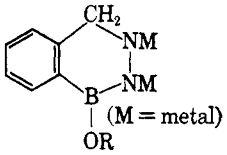
An interesting difference between 4,3-borazaroisoquinoline and 2,1-borazaronaphthalene became apparent in experiments designed to prepare the parent ring system (VIIg). The reduction of 2-methoxy-2,1-borazaronaphthalene (VIIIb) to 2,1-borazaronaphthalene (VIIIc) is a very facile process, taking place rapidly in the cold with only a small excess of lithium aluminum hydride.[8,16] Only unchanged starting material was recovered from the reaction of VI under the same conditions. Partial reduction took place after treating VI with a fivefold excess of lithium aluminum hydride for 18 hr.; decomposition of the reaction mixture with water gave unchanged VI together with 1,2,3,4-tetrahydro-4,3-borazaroisoquinoline (X), the boron-containing ring having undergone further reduction. The explanation of this difference in behavior between VI and VIIIb seems to lie in the greater acidity of the imino proton in the former (*vide supra*), due no doubt to the inductive effect of the adjacent nitrogen atom. The conversion of VIIIb to VIIIc involves a nucleophilic replacement of methoxy by hydride ion; it seems reasonable to suppose that this reaction takes place more rapidly than attack on the imino proton, but that the reverse is true in the case of VI. If VI is indeed first converted to the anion XI, nucleophilic attack on boron could well be inhibited by the negative charge on the adjacent nitrogen atom. This would account for the slowness of the conversion of VI to reduction products. Moreover, the second point of attack might well be the carbon atom in the 1-position; this would lead to a dihydroborazaroisoquinoline (XII) in which the boron-containing ring is no longer aromatic. The resulting decrease in mesomeric stabilization would then allow attack on boron to take place, with replacement of OR by hydrogen and further addition[13] of hydride, leading to a metal derivative of X.



X



XI



XII

The structure of X was indicated by the following evidence. Elemental analysis indicated unambiguously that it was a tetrahydro derivative of VIIf. The infrared spectrum contained a series of bands in the region 2190–2335 cm.$^{-1}$ which may be assigned to the symmetric and antisymmetric BH_2 stretching vibrations.[17] The compound was quite resistant to hydrolysis by water; boron hydrides show this behavior only if they are aromatic (which cannot be the case here), or if the boron is quadricovalent. Finally, the infrared spectrum in the 1500–1700 cm.$^{-1}$ region indicated quite clearly that the benzene ring was intact and that no unsaturated group was conjugated with it, there being only a single, sharp, strong absorption at 1598 cm.$^{-1}$.

The idea that salt formation (XI) was responsible for the over-reduction of VI was confirmed by the behavior of VIId. This reacted smoothly with a small excess (10%) of lithium aluminum hydride to give 3-methyl-4,3-borazaroisoquinoline (VIIg). The structure of VIIg was established by elemental analysis, by the similarity of its ultraviolet spectrum to those of other borazaroisoquinoline derivatives, by the similar resemblance of the infrared spectra in the region (1500–1700 cm.$^{-1}$) corresponding to skeletal vibrations, and by the appearance of a new band at 2542 cm.$^{-1}$, corresponding to a BH stretching vibration. The proton

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(12) H. C. Brown, D. Gintisth, and L. Domash, *J. Am. Chem. Soc.*, **78**, 5387 (1956).

(13) M. J. S. Dewar and P. M. Maitlis, *ibid.*, **83**, 187 (1961).

(14) See D. Seyferth, *Chem. Rev.*, **55**, 1155 (1955).

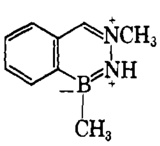
(15) M. J. S. Dewar and P. M. Maitlis, *Tetrahedron*, **15**, 35 (1961).

(16) M. J. S. Dewar, R. Dietz, V. P. Kubba, and A. R. Lepley, *J. Am. Chem. Soc.*, **83**, 1754 (1961).

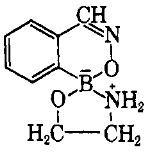
(17) *Cf.* L. J. Bellamy, W. Gerrard, M. F. Lappert, and R. L. Williams, *J. Chem. Soc.*, 2412 (1958).

n.m.r. spectrum showed two bands with relative areas 5:3; the BH proton was as usual invisible, being next to an atom with a large nuclear quadrupole moment. Although VIIg is less resistant to oxidation than X, it can be kept in the solid state at 0° for long periods. On standing, a solution of VIIg in ethanol underwent slow solvolysis or oxidation to VIId.

4-Methyl- and 4-hydroxy-4,3-borazaroisoquinolines are basic, like isoquinoline; thus VIIb dissolves in acids and can be reprecipitated by basification. We have not measured its dissociation constant; one might expect it to be a weaker base than isoquinoline itself because of the inductive effect of the positively charged nitrogen atom in the 3-position. With methyl iodide, VIIb gave a methiodide (XIII); this was unaffected by boiling water or dilute acids, providing further evidence for the aromaticity of the borazaroisoquinoline system, for the positive charge would be expected to increase greatly any tendency to hydrolysis to I.



XIII



XIV

We have carried out preliminary studies of electrophilic substitution in VI and VIIb; both compounds underwent nitration and bromination to give mixtures of products which proved very difficult to separate. Further work on this problem is in progress; the system is an interesting one in that it is difficult to predict with any certainty what the orientation of the products should be.

The ultraviolet spectra of derivatives of 4,3-borazaroisoquinoline are quite similar to that of isoquinoline (Fig. 1) as would be expected.[18] In both cases the α or L_b band is much more intense than it is in the isoconjugate hydrocarbon (naphthalene).

We have also re-examined 4-hydroxy-4,3-boroxaroisoquinoline (II) and find that it appears to be less aromatic than the corresponding borazaroisoquinoline, as would be expected. This was indicated by its failure to give identifiable products when treated with methylmagnesium bromide under the conditions used to prepare VIIb, and by its reaction with ethanolamine. Ethanolamine reacts with normal boronic or borinic acids to form esters which undergo internal coordination; a similar reaction seemed to take place when II was heated with toluene and ethanolamine in a Dean and Stark apparatus, water being evolved and a high melting (200–201°) solid being formed. The high melting point seemed to suggest that this had the cyclic structure XIV. No such reaction took place with the corresponding borazaroisoquinoline under these conditions; the formation of cyclic products such as XIV of course destroys the aromaticity of the boron-containing ring, and the greater ease of this process in the case of II shows it to be less aromatic than VI.

Note that the melting point reported here for II is much higher (264–265°) than that (150–155°) reported by Snyder, *et al.*[5] We observed a change in crystal form at 164°, using very slow heating. This kind of behavior is quite common in our experience for compounds of this type containing a hydroxyl linked to boron; on slow heating these often undergo dehydration to the corresponding ethers which have high melting points. Presumably Snyder and his collaborators used more rapid heating and so were able to observe the melting point of II itself; the wide melting point range was presumably due to dehydration during fusion.

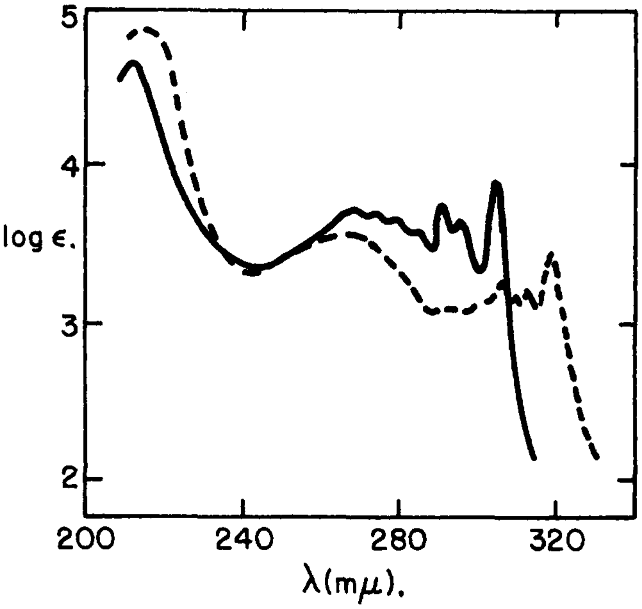


Fig. 1.—*Ultraviolet spectra of VIIg in ethanol* (———) *and of* isoquinoline in cyclohexane (– – – –).

Experimental

o-**Tolyboronic acid** was prepared by the method used by Washburn, *et al.*,[19] to make phenylboronic acid. Consistent yields of over 60% of pure material (m.p. 167°) were obtained on a 300-g. scale.

o-**Formylphenylboronic acid** was prepared by an improved modification of published[5,7] procedures. A small volume (200 ml.) of solvent was distilled from a solution of *o*-tolylboronic acid (40.0 g.) and N-bromosuccinimide (120.5 g.) (both dried for 24 hr. at 110°) in dry carbon tetrachloride (1.8 l.) to ensure complete absence of water. Benzoyl peroxide (6.0 g.) was then added and the solution boiled under reflux for 6 hr. When cold cyclohexene (5 ml.) was added to remove unreacted bromine and bromoimide, and the filtered solution was extracted with aqueous potassium hydroxide (4 × 300 ml. of 15%), the combined extracts were adjusted to pH 3 with concentrated hydrochloric acid, left for 90 min., and then extracted with ether. The residue from evaporation of the dried ($MgSO_4$) ether extract crystallized from water (250 ml.), giving *o*-formylphenylboronic acid (39.9 g., 78.5%), m.p. 120–123° (lit.[5,7] 123°).

Bis-(4,3-borazaro-4-isoquinolyl) Ether (VI).—A solution of *o*-formylphenylboronic acid (13.4 g.) in ether (200 ml.) was added to a stirred solution of hydrazine (10 ml. of 99%) in a mixture of alcohol (50 ml.) and ether (10 ml.). The residue from evaporation of the solution crystallized from water (100 ml.) giving **bis-(4,3-borazaro-4-isoquinolyl) ether** as colorless crystals (12.0 g., 95%), m.p. 243–243.5°; infrared spectrum (KBr disk, cm.$^{-1}$): 3340 s, 3300 m, 3070 m, 3030 m, 1603 m, 1563 s, 1502 s, 1463 m, 1445 s, 1389 s, 1182 s, 1374 m, 1351 s, 1306 m, 1287 w, 1220 w, 1157 m, 1133 m, 1127 m, 1107 w, 1094 w, 1056 w, 1038 w, 1014 m, 912 m, 893 m, 815 w, 798 m, 772 s, 754 m, 700 w.

Anal. Calcd. for $C_{14}H_{12}B_2N_4O$: C, 61.39; H, 4.42; B, 7.90; N, 20.46; mol. wt., 274; active hydrogen, 2 atoms. Found: C, 61.29; H, 4.48; B, 7.61; N, 20.22; mol. wt. (Rast), 273; active hydrogen (Zerewitinoff), 2.12 atoms.

4-Methyl-4,3-borazaroisoquinoline (VIIb).—Methylmagnesium bromide (230 ml. of 3 *N* solution in ether, Arapahoe Chemicals Inc.) was added to a mixture of VI (20 g.) and tetrahydrofuran (350 ml. distilled from $LiAlH_4$) under nitrogen at such a rate that the solution boiled. After refluxing for a further 24 hr., the solution was poured onto ice (300 g.) and the neutralized (HCl) aqueous layer extracted with ether (2 × 200 ml.). Petroleum ether (50 ml., b.p. 90–100°) was added to the dried ($MgSO_4$) extract and the ether and dioxan distilled. The solution on cooling gave **4-methyl-4,3-borazaroisoquinoline (VIIb)** (17.6 g., 84%) m.p. 94–96°, raised by recrystallization from petroleum ether to 96.5–97.5°; infrared spectrum (KBr disk, cm.$^{-1}$): 3280 s, 3145 m, 3045 m, 3035 m, 3000 w, 2975 w, 2955 w, 2932 w, 1597 w, 1569 w, 1557 w, 1494 w, 1460 w, 1430 s, 1365 s, 1332 s, 1315 s, 1240 w, 1223 s, 1211 s, 1127 w, 1042 m, 1028 m, 1015 m, 963 w, 958 w, 902 s, 896 m, 837 s, 820 m, 785 sm, 764 s, 744 m.

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(18) *Cf.* M. J. S. Dewar, V. P. Kubba, and R. Pettit, *J. Chem. Soc.*, 3073 (1958).

(19) R. M. Washburn, E. Levers, C. F. Albright, and F. A. Billig, *Org. Syn.*, **39**, 3 (1959).

Anal. Calcd. for $C_8H_9BN_2$: C, 66.73; H, 6 30; B, 7.51; N, 19.46; mol. wt., 144. Found: C, 66.56; H, 6.35; B, 7.54; N, 19.75; mol. wt. (Rast), 136.

3-Methyl-4-hydroxy-4,3-borazaroisoquinoline (VIId).—A mixture of methylhydrazine (5 g.) and *o*-formylphenylboronic acid (10 g.) in 95% ethanol (150 ml.) was boiled 2 hr. under reflux. Water (150 ml.) was then added and the solution concentrated. On cooling, **3-methyl-4-hydroxy-4,3-borazaroisoquinoline (VIId)** (10.5 g., 100%) crystallized; after recrystallization from aqueous ethanol it melted at 154–156°, resolidified, and then melted again at 168°; infrared spectrum (KBr disk, cm.$^{-1}$): 3420 s (shoulder) 3220 s, 3070 s, 2970 m, 2940 m, 2835 w, 1614 s, 1588 w, 1548 m, 1487 s, 1465 w, 1450 m, 1432 s, 1422 s, 1407 s, 1388 s, 1372 s, 1365 m, 1328 w, 1312 w, 1275 w, 1234 m, 1211 s, 1175 w, 1160 m, 1132 s, 1099 m, 1055 w, 1032 s, 961 w, 927 w, 892 s, 880 w, 872 w, 872 w, 819 w, 717 s, 687 s, 652 w, 638 w.

Anal. Calcd. for $C_8H_9BN_2O$: C, 60.10; H, 5.67; N, 17.55. Found: C, 59.99; H, 6.08; N, 17.70.

Bis-(3-phenyl-3,4-borazaro-4-isoquinolyl) Ether.—A white precipitate formed immediately when phenylhydrazine (3 g.) was slowly added to a solution of *o*-formylphenylboronic acid (3 g.) in water (50 ml.). The mixture was heated to boiling and adjusted to pH 6 when **bis-(3-phenyl-3,4-borazaro-4-isoquinolyl) ether** (5.8 g., 100%) separated, m.p. 183.5–184.5°, raised by recrystallization from chloroform–petroleum ether to 185.5–186.5°; infrared spectrum (KBr disk, cm.$^{-1}$): 3052 m, 3018 m, 1622 w, 1597 w, 1494 s, 1478 m, 1452 m, 1445 s, 1406 s, 1383 s, 1359 s, 1334 s, 1307 s, 1293 m, 1338 w, 1204 w, 1164 w, 1155 w, 1140 w, 1126 w, 1110 w, 1075 w, 1032 m, 999 w, 964 w, 956 w, 911 m, 900 s, 893 s, 847 w, 767 w, 760 s, 757 w, 735 w, 728 m, 707 m, 695 m.

Anal. Calcd. for $C_{26}H_{20}B_2N_4O$: C, 73.98; H, 4.78; B, 5.13; N, 12.33; mol. wt., 422. Found: C, 73.76; H, 4.72; B, 5.05; N, 12.50; mol. wt. (Rast), 399.

3,4-Dimethyl-4,3-borazaroisoquinoline (VIIc). (a) From VIId.—Methylmagnesium bromide (20 ml. of 3 *N* solution in ether) was added to a stirred mixture of VIId (4 g.) in ether (100 ml.) under nitrogen at 0°. The solution was boiled under reflux, then evaporated, and the residue sublimed at 50° (0.5 mm.), giving **3,4-diethyl-4,3-borazaroisoquinoline** (2.3 g., 78% allowing for recovery), m.p. 18–20°; infrared spectrum (liquid, 0.025 mm., cm.$^{-1}$): 3055 m, 3030 m, 2970 m, 2945 s, 2910 m, 2895 m, 2818 w, 1619 s, 1544 m, 1538 m, 1482 s, 1444 s, 1361 s, 1344 s, 1336 s, 1318 s, 1276 s, 1248 s, 1226 m, 1172 w, 1140 m, 1076 s, 1033 w, 1000 w, 958 s, 900 s, 887 m, 863 w, 804 w, 767 w, 748 s, 644 w.

Anal. Calcd. for $C_9H_{11}BN_2$: C, 68.42; H, 7.02; N, 17.73. Found: C, 68.39; H, 7.00; N, 17.40.

The residue from the sublimation, after recrystallization from aqueous ethanol, gave unchanged VIId (1.0 g.).

(**b**) **From VIIb.**—Dimethyl sulfate (3 ml.) was added to a mixture of potassium hydroxide (3 g.), water (12 ml.), and VIIb (2 g.). The mixture was then heated under reflux for 2 hr. and the VIIc isolated with ether and sublimed, giving 350 mg. of material identical (infrared spectrum) with that prepared above.

2,4-Dimethyl-4,3-borazaroisoquinolinium Iodide (XIII).—A mixture of VIIb (4 g.), methyl iodide (20 g.), and ether (75 ml.) was stirred at room temperature for 75 hr. The solid **2,4-dimethyl-4,3-borazaroisoquinolinium iodide (XIII)** (7.4 g., 93%) was collected, m.p. 223–235° dec. A sample was crystallized from water (charcoal) for analysis; infrared spectrum (KBr disk, cm.$^{-1}$): 3450 s, 3180–2890 s, 1662 s, 1599 s, 1564 s, 1501 s, 1477 m, 1440 s, 1418 m, 1408 m, 1376 w, 1330 s, 1307 s, 1243 m, 1218 s, 1182 s, 1132 w, 1098 m, 1043 m, 1018 w, 977 w, 963 w, 936 m, 873 m, 769 s, 710 w, 654 w.

Anal. Calcd. for $C_9H_{12}BN_2I$: C, 37.50; H, 4.20; N, 10.06; I, 44.63. Found: C, 37.80; H, 4.49; N, 9.81; I, 44.40.

1,2,3,4-Tetrahydro-4,3-borazaroisoquinoline (XII).—A suspension of lithium aluminum hydride (2.5 g.) in ether (150 ml.) was added to one of VI (5 g.) in ether (100 ml.) and the mixture stirred 18 hr. at room temperature. After decomposing the excess hydride, the ether solution was dried ($MgSO_4$) and evaporated. Sublimation of the residue at 90° (0.5 mm.) gave **1,2,3,4-tetrahydro-4,3-borazaroisoquinoline (XII)**, m.p. 132° dec.; infrared spectrum (KBr disk, cm.$^{-1}$): 3420 s, 3270 s, 3180 s, 3055 m, 3000 m, 2935 m, 2860 w, 2780 w, 2335 s, 2310s, 2275 m, 2190 w, 1598 s, 1482 m, 1470 m, 1462 m, 1440 s, 1265 s, 1233 w, 1193 s, 1176 m, 1105 m, 1093 w, 1072 s, 1048 m, 1032 m, 880 m, 873 m, 793 w, 753 s, 698 w.

Anal. Calcd. for $C_7H_{11}BN_2$: C, 62.75; H, 81.27; B, 8.08; N, 20.91. Found: C, 62.60; H, 8.51; B, 7.73; N, 20.68.

3-Methyl-4,3-borazaroisoquinoline (VIIg).—Lithium aluminum hydride (0.8 g.) in ether (30 ml.) was added dropwise to a stirred solution of VIId (6 g.) in ether (150 ml.) at room temperature. After stirring for 18 hr. the solution was evaporated and the residue distilled (bath temp. 90–100°, 0.3 mm.) giving **3-methyl-4,3-borazaroisoquinoline** as an oil (3.8 g., 71%), m.p. 8–10°, which was homogeneous to gas–liquid chromatography on silicone rubber (retention time, 1.3 min.; column length, 8 ft.; temperature, 170°); infrared spectrum (liquid, 0.025 mm., cm.$^{-1}$): 3085 m, 3055 s, 2982 w, 2955 w, 2920 m, 2890 w, 2830 w, 2542 s, 2500 w, 2440 w, 2400 w, 1613 m, 1545 m, 1538 m, 1483 s, 1466 w, 1447 s, 1394 m, 1375 s, 1360 w, 1345 w, 1324 m, 1283 s, 1245 s, 1230 s, 1176 m, 1153 m, 1119 m, 1069 m, 1037 m, 1020 m, 962 w, 930 s, 910 s, 851 s, 772 s, 742 s, 628 s, 626 m.

Anal. Calcd. for $C_8H_9BN_2$: C, 66.73; H, 6.30; N, 19.46. Found: C, 66.70; H, 6.00; N, 19.64.

4-Hydroxy-4,3-boroxaroisoquinoline (II) was prepared by a modification of the method of Snyder, *et al.*[5] Hydroxylamine hydrochloride (3.6 g.) and *o*-formylphenylboronic acid (5 g.) were dissolved in water (200 ml.) and the solution adjusted to pH 6 with sodium hydroxide. The crystals of II were collected (4.9 g., 100%), m.p. 264–265° (slow heating, phase change at 164°) (lit.[5] 150–155°); infrared spectrum (KBr disk, cm.$^{-1}$): 3200–3000 s, 1622 s, 1596 w, 1565 m, 1556 s, 1506 s, 1495 s, 1454 s, 1444s, 1415 s, 1344 m, 1298 s, 1230 s, 1225 s, 1178 w, 1147 s, 1110 w, 1062 m, 1024 m, 956 m, 917 s, 892 s, 854 m, 784 w, 770 s, 694 w, 630 w.

4-(2′-Aminoethoxy)-4,3-boroxaroisoquinoline (XIV).—A solution of II (1 g.) and ethanolamine (1 ml.) in toluene (75 ml.) was boiled 2 hr. under reflux in a Dean and Stark apparatus. On cooling, 4-(2′-aminoethoxy)-4,3-boroxaroisoquinoline (XIV) separated in almost theoretical yield (1.3 g.), m.p. 200–201° after crystallization from ethanol–petroleum ether; infrared spectrum (KBr disk, cm.$^{-1}$): 3645 m, 3410 s, 3170 s, 3070 s, 3015 m, 2970 m, 2898 m, 1618 s, 1565 m, 1465 w, 1448 m, 1442 m, 1362 w, 1347 m, 1328 s, 1312 m, 1276 s, 1242 s, 1215 s, 1128 s, 1084 s, 1076 s, 975 m, 960 s, 950 s, 944 s, 928 m, 905 m, 885 w, 865 w, 812 m, 763 m, 752 s, 747 s, 733 s, 676 w.

Anal. Calcd. for $C_9H_{11}BN_2O_2$: C, 56.59; H, 5.81. Found: C, 56.90; H, 5.75.