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NEW HETEROAROMATIC COMPOUNDS—XXXIV*

BISBORATRIAZAROLES

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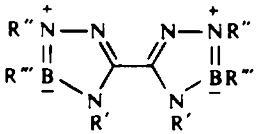
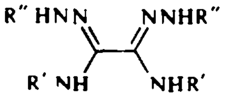
Abstract—A number of *bis*-2,1,3,4-boratriazaroles have been prepared by reacting boronic acids or their derivatives with *bis*-amidrazones and their properties studied.

WE HAVE RECENTLY SHOWN[1] that boronic acid derivatives condense readily with amidrazones to form derivatives of 2,1,3,4-boratriazarole,[2] a ring system which is much more stable to hydrolysis that previously reported compounds with boron in five-membered rings. We have now extended this synthesis to compounds containing two such rings, by condensing boronic acids with *bis*amidrazones. Analogous condensation of *bis*boronic acids should lead to potentially interesting polymers; the properties of the *bis*boratriazaroles are of interest in this connection since they should provide a guide to the structures most likely to show thermal and hydrolylic stability.

The first series of *bis*boratriazaroles (**1**) were prepared in excellent yield by heating oxamidrazones (**2**) with boronic acids (**3**) in isopropyl ether, the water formed being removed by distillation. The compounds showed chemical stability of the same order as the monoboratriazaroles previously described.[1] Thus **1a** could be prepared in 58% yield by boiling its components together in water and all could be recovered unchanged from boiling EtOH aq.



1: **a**: $R' = R'' = H$; $R''' = Ph$
b: $R' = R'' = H$; $R''' = n\text{-}Bu$
c: $R' = H$; $R'' = R''' = Ph$
d: $R' = R''' = Ph$; $R'' = H$



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$R'''B(OH)_2$

3

Next we tried substituting cyclic *bis*amidrazones for **2**. We had previously failed[1] to obtain a boratriazole from 2-pyridylhydrazine (**4**) and boronic acids; this failure was attributed[1] to the aromaticity of the pyridine ring which reduces the stability

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* Part XXXIII: Michael J. S. Dewar, Ronald Golden, and Philip A. Spanninger, *J. Am. Chem. Soc.* **93** 3298 (1971)

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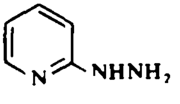
of the tautomeric form **5** required to form the boratriazarole. It is of course well known that α-aminopyridine exists predominantly as the aminopyridine rather than iminodihydropyridine. However calculations[3] have suggested that the difference in energy between the tautomers should be less in the diaminodiazines than in the aminopyridines and less again in the corresponding benzo derivatives. We therefore examined the reactions of 2,4-*bis*(hydrazino)pyrimidine[4] (**6**) and 2,3-*bis*(hydrazino)-quinoxaline[5] (**7**) with phenylboronic acid (**3**; R‴ = Ph) under the conditions used for the synthesis of **1**. In each case condensation took place to form a *bis*boratriazarole, **8** or **9**.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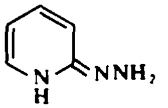
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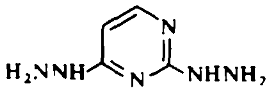
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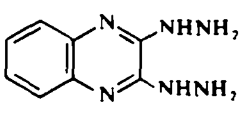
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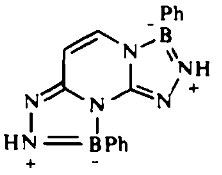
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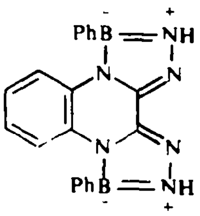
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The aromaticity of **8** and **9** is indicated by their mass spectra in which 99% of the total ionization is concentrated in the peak corresponding to the parent molecular ion. Moreover a relatively large peak was also observed corresponding to the doubly charged molecular ion; this seems to be characteristic[6] of "borazaromatic" compounds. On the other hand **8** and **9** are much less stable to hydrolysis than **1**, being destroyed by warm alcohol; this of course might be expected since in each case hydrolysis leads to an increase in aromaticity of the six-membered nitrogen-containing ring. We were also unable to prepare a boratriazarole from 2-hydroazino-pyrimidine (**10**); calculation[3] indicates that the analogous amine should be much less easily tautomerized than the diamines corresponding to **6** or **7**.

TABLE 1. PROPERTIES OF BORATRIAZAROLES

Compound	m.p.[a]	Yield (%)[b]	Elemental Analysis (%)							
			Calc.				Obsd.			
			C	H	N	B	C	H	N	B
1a	293-5	80	58·33	4·86	29·16	7·64	58·57	4·93	29·31	7·67
1b	127	82	48·39	8·87	33·87	8·87	48·20	8·82	34·01	8·61
1c	236-7	quant.	70·91	5·00	19·09	5·00	70·75	4·88	18·90	5·11
1d	224-5	quant.	70·91	5·00	19·09	5·00	70·70	5·11	19·26	5·00
8	223-5	51	61·54	4·48	26·92	7·05	61·31	4·69	26·76	6·74
9	239–41	63	66·29	4·42	23·20	6·07	65·55	4·35	22·74	5·79

[a] In sealed tube under nitrogen, uncorrected.
[b] Based on product before sublimation

EXPERIMENTAL

The compounds described here were prepared by similar techniques, illustrated by the preparation of **1a**.

*2,2'-Diphenyl-5-*bis(2,1,3,4-*boratriazarole*) (**1a**). Oxamidrazone (**2**, 10 mmole) and phenyl boronic acid (**3**,R''' = Ph; 20 mmole) were boiled overnight under reflux in diisopropyl ether in a N_2 atmosphere, H_2O being removed with a Dean-Stark trap. The mixture remained heterogeneous but changed in appearance. Next day, when nearly 40 mmole of H_2O had separated, the mixture was cooled and **1a** collected m.p. 285-90° raised by sublimation at 160° in a vacuum to 293-5°.

Table 1 lists physical properties and analytical data for the compounds reported.

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