Synthesis, Reactions, and Mass Spectral Studies of Some Cyclic Amine–Boranes and Their Catechol Derivatives[1,2]

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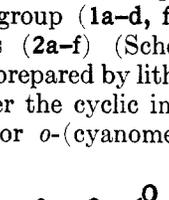
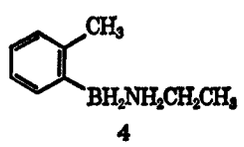
Several cyclic amine–boranes are prepared by lithium aluminum hydride reduction of appropriate aminoboronic acids or boronic acids containing potential amine functions. The cyclic amine–boranes are found to be more stable than an acyclic model compound. The mass spectral fragmentations of the cyclic amine–boranes and of their spirocatechol derivatives are discussed.

Hawthorne[3] has prepared a number of acyclic amine–boranes by lithium aluminum hydride reduction of boronic anhydrides in the presence of appropriate amines. The preparation of a number of cyclic amine–boranes, in which ring closure is effected through the formation of a boron–nitrogen dative bond,[4] has been accomplished by the hydroboration of aminoolefins.[5–7] Reaction of appropriate aminoboronic acids with catechol yields a second class of boronic acid derivatives in which a ring is formed as a result of coordination between the boron and nitrogen.[8] As a continuation of our interest in the preparation of aromatic boronic acid derivatives which are stabilized by incorporation of the boron within a cyclic system,[2] the synthesis of a number of cyclic amine–boranes was undertaken. A qualitative measure of the stability of the cyclic amine–boranes prepared was obtained by a comparison of the conditions for certain of their reactions with those conditions that afforded analogous products from an acylic model. The data obtained (see below) show that amine–boranes are stabilized by incorporation of the boron–nitrogen bond in a cyclic system. The closely related amine–boranes and their catechol derivatives which were prepared gave us a unique opportunity to study the mass spectral fragmentation of these two classes of compounds.

Lithium aluminum hydride reduction of an *o*-(aminoalkyl)arylboronic acid derivative (**1e**) and of boronic acids which potentially contain the *o*-(aminoalkyl) group (**1a–d, f**) gave a series of cyclic amine–boranes (**2a–f**) (Scheme I). 1,2-Boraztetralin (**2a**) can be prepared by lithium aluminum hydride reduction of either the cyclic imide of *o*-boronophenylacetamide (**3a**)[2a] or *o*-(cyanomethyl)benzeneboronic acid (**1a**),



3a, X = NH
b, X = O



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SCHEME I

1a, $n = 1$; X = —CN
b, $n = 1$; X = —CNHCH$_2$CH$_2$C$_6$H$_5$ (O)
c, $n = 0$; X = —CH=NOCH$_3$
d, $n = 0$; X = —CH=NCH$_2$CH$_2$C$_6$H$_5$
e, $n = 1$; X = —NC$_5$H$_{10}$ (catechol derivative)
f, $n = 0$; X = —CH=NC$_6$H$_5$

2a, $n = 2$; R = R′ = H
b, $n = 2$; R = H; R′ = CH$_2$CH$_2$C$_6$H$_5$
c, $n = 1$; R = R′ = H
d, $n = 1$; R = H; R′ = CH$_2$CH$_2$C$_6$H$_5$
e, $n = 1$; R—R′ = C$_5$H$_{10}$
f, $n = 1$; R = H; R′ = C$_6$H$_5$

the latter compound affording the higher yield of product. Reaction of the cyclic anhydride of *o*-boronophenylacetic acid (**3b**)[2a] with 2-phenylethylamine presumably gave **1b**, which was reduced with lithium aluminum hydride to yield 2-(2′-phenylethyl)-1,2-boraztetralin (**2b**).

Three 3,2-borazindans were also prepared *via* lithium aluminum hydride reductions. Reduction of N-(*o*-boronobenzal)methoxyamine (**1c**)[2b] and N-(*o*-boronobenzal)phenylethylamine (**1d**) yields 3,2-borazindan (**2c**) and 2-(2′-phenylethyl)-3,2-borazindan (**2d**), respectively. The third borazindane, 3,2-borazindan-2-spiro-1′-piperidine (**2e**) was prepared by reduction of the crude adduct obtained by reaction of the catechol derivative of *o*-(bromomethyl)benzeneboronic acid with piperidine, **1e**. An attempt to prepare 2-phenyl-3,2-borazindan (**2f**) by the lithium aluminum hydride reduction of N-(*o*-boronobenzal)aniline (**1f**) did not lead to the desired product. It is probable that **2f** formed but was lost during attempted isolation, as a result of hydrolysis to the corresponding aminoboronic acid.[2b]

The acyclic model, ethylamine–(N–B)-*o*-tolylborane (**4**), was prepared by lithium aluminum hydride reduction of a solution of *o*-toluneboronic anhydride and ethylamine in tetrahydrofuran.

Hawthorne reported that, upon dissolution of an alkylamine–(N–B)-alkylborane in a benzene solution of *o*-phenylenediamine at room temperature, hydrogen was evolved and the derived 1,3,2-benzodiazaborolidine was formed.[9] No reaction occurred when a benzene solution of ethylamine–(N–B)-*o*-tolylborane (**4**) and *o*-phenylenediamine was brought to reflux (~80°); however, 2-(*o*-tolyl)-1,3,2-benzodiazaborolidine (**5**)

(1) This work was supported in part by Grant AT(11-1)-314 from the Atomic Energy Commission, Report No. C00-314-14.

(2) For the previous papers, see (a) J. C. Catlin and H. R. Snyder, *J. Org. Chem.*, **34**, 1660 (1969); (b) H. E. Dunn, J. C. Catlin, and H. R. Snyder, *ibid.*, **33**, 4483 (1968).

(3) M. F. Hawthorne, *J. Amer. Chem. Soc.*, **80**, 4291 (1958).

(4) K. Niedenzu and J. W. Dawson, "Boron–Nitrogen Compounds," Academic Press, New York, N. Y., 1965, p 8.

(5) See ref 4, p 46.

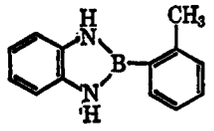
(6) G. B. Butler, G. L. Statton, and W. S. Brey, Jr., *J. Org. Chem.*, **30**, 4194 (1965).

(7) G. B. Butler and G. L. Statton, *J. Amer. Chem. Soc.*, **86**, 518 (1964).

(8) H. E. Dunn, Thesis, Doctor of Philosophy, University of Illinois, 1965; See also ref 2a.

(9) M. F. Hawthorne, *J. Amer. Chem. Soc.*, **83**, 831 (1961).

formed when a mixture of **4** and *o*-phenylenediamine was heated on the steam bath (~100°). The more strenuous conditions required for reaction of **4** with the



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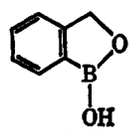

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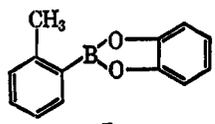
diamine suggest that amine–arylboranes are more stable than amine–alkylboranes. 1,2-Boraztetralin (**2a**) was found to be much less reactive toward *o*-phenylenediamine than the model compound, **4**. No reaction was observed even when a solution of 1,2-boraztetralin (**2a**) and the diamine was heated under reflux in xylene. The enhanced stability of **2a** is comparable with the increased stability of the cyclic boronic ester, boronophthalide, **6**.[10]

The increased stability of cyclic amine–boranes, relative to the acyclic model, **4**, is further indicated by a comparison of the conditions which lead to reaction of 1,2-boraztetralin (**2a**), 2-(2′-phenylethyl)-3,2-borazindan (**2d**), and ethylamine–(N–B)-*o*-tolylborane (**4**) with catechol. The acylic amine–borane **4** reacts with catechol in refluxing benzene to give the catechol derivative of *o*-toluneboronic acid (**7**). Neither



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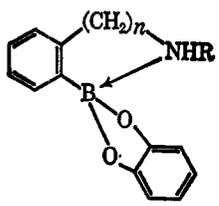
1,2-boraztetralin (**2a**) nor 2-(2′-phenylethyl)-3,2-borazindan (**2b**) reacts with catechol under these conditions; however, both **2a** and **2d** react with catechol in refluxing xylene to yield spirocatechol derivatives[11] **8a**



8a, $n = 2$; R = H
b, $n = 1$; R = $C_2H_4C_6H_5$
c, $n = 1$; R = H

and **8b**. Contrary to expectation, 3,2-borazindan (**2c**) reacted with catechol in benzene solution at room temperature to form **8c**. Of the amine–boranes prepared in this work, **2a–e** and **4**, only 3,2-borazindan (**2c**) decomposed upon melting. It has been reported that both the thermal decomposition and the hydrolysis of simple amine–boranes are strongly influenced by traces of impurities;[12] it is possible that some impurity, perhaps inorganic, catalyzed the reaction of **2c** with catechol and also caused its decomposition near the melting point. That the catechol derivatives of the cyclic amine–boranes have spiro structures **8a–c** is indicated by their infrared spectra. The absence of the characteristic boron–oxygen stretch in the region 1350–1400 cm^{-1} indicates the boron to be tetrahedrally substituted.[13]

Ethylamine–(N–B)-*o*-tolylborane (**4**) is hydrolyzed in refluxing aqueous acetonitrile as is pyridine–(N–B)-phenylborane.[14] 1,2-Boraztetralin (**2a**), 3,2-borazindan-2-spiro-1′-piperidine (**2e**), and surprisingly, in view of its ready reaction with catechol and its low thermal stability, 3,2-borazindan (**2c**) are not hydrolyzed under these conditions. Refluxing aqueous acetone hydrolyzes 1,2-boraztetralin (**2a**).[2a] Presumably these conditions would also hydrolyze the other cyclic amine–boranes.

The ease with which amine–boranes react with olefins depends upon the strength of the boron–nitrogen coordination. The first step is dissociation of the amine–borane; the free borane then reacts with the olefin.[15] Ethylamine–(N–B)-*o*-tolylborane (**4**) does not react with cyclohexene at room temperature over a 24-hr period, but reaction occurs when a solution of **4** in cyclohexene is heated at reflux for 3 hr. 1,2-Boraztetralin (**2a**) does not react with cyclohexene even when the solution is heated at reflux for 12 hr, thus indicating again that the cyclic structure increases the stability of the amine–borane.

The difference between the ease of reaction of ethylamine–(N–B)-*o*-tolylborane (**4**) and the cyclic amine–boranes with *o*-phenylenediamine, catechol, and cyclohexene, and the difference in hydrolytic stability clearly indicate that cyclic amine–boranes are stabilized by incorporation of the boron and nitrogen atoms within a five- or six-membered nonaromatic ring.

Mass Spectral Studies.—With the preparation of a series of closely related amine–boranes and their catechol derivatives, we were in a unique position to study the mass spectral fragmentations of these heterocyclic compounds. The mass spectra of three cyclic amine–boranes (**2a, b,** and **d**) and two of their catechol derivatives (**8a** and **b**) were obtained. The results are of interest in part because these molecules contain functional groups which have not previously been studied under electron impact, and in part because they offer an opportunity to observe new modes of interaction between suitably located functional groups under electron impact.[16]

The major mass spectral fragmentations of 1,2-boraztetralin (**2a**) (Table I) involve loss of one, two, and three hydrogens (M − 1, 2, and 3). The base peak occurs at *m/e* 131 (M − 2). The next most intense peaks occur at *m/e* 104, 103, and 91.[17–19] (Support for the proposed structures comes from the presence of analogous fragments in the spectrum of **8a**.)

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

(11) Similar spiro compounds have been previously reported; see ref 8 and R. L. Letsinger and D. B. MacLean, *ibid.*, **85**, 2230 (1963).

(12) Reference 4, p 19, and H. Nöth and H. Beyer, *Chem. Ber.*, **93**, 928 (1960).

(13) R. L. Letsinger, Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p 3.

(14) M. F. Hawthorne, *J. Amer. Chem. Soc.*, **80**, 4291 (1958).

(15) M. F. Hawthorne, *ibid.*, **83**, 2541 (1961).

(16) (a) For a comprehensive review of mass spectrometry, see H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967. (b) M. I. Bruce, *Advan. Organometal. Chem.*, 273 (1968). We wish to thank a referee for bringing this review to our attention.

(17) The tropylium ion structures for the *m/e* 91 and 103 peaks are suggested by analogy to the structure assigned in other work to the hydrocarbon fragment occurring at *m/e* 91; see ref 16a, p 76.

(18) The structural formulas, *i.e.*, the bicyclic structure of the *m/e* 104 fragment, are formal representations; see ref 16a, p 6.

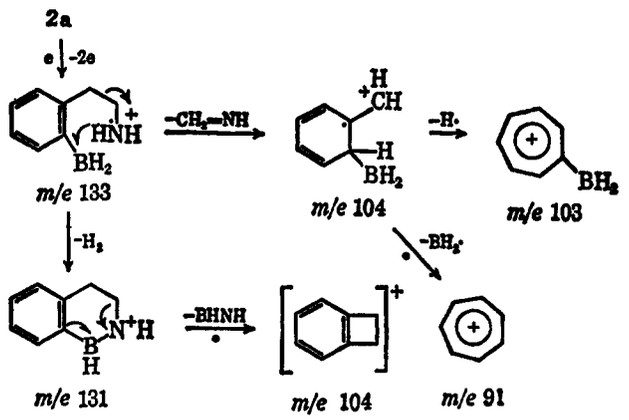
(19) Fragmentation pathways supported by metastable peaks are indicated by asterisks.

TABLE I

THE MASS SPECTRA OF 1,2-BORAZTETRALIN (**2a**), 2-(2′-PHENYLETHYL)1,2-BORAZTETRALIN (**2b**), AND 2-(2′-PHENYLETHYL)-3,2-BORAZINDAN (**2d**)

2a		2b				2d			
m/e	%[a,b]	*m/e*	%[a,b]	*m/e*	%[a,b]	*m/e*	%[a,c]	*m/e*	%[a,c]
134	4	238	8	119	2	225	2	115	2
133	44	237	39	118	17	224	17	114	1
132	78	236	26	117	7	223	100	106	5
131	100	235	10	116	5	222	72	105	52
130	87	234	7	115	6	221	31	104	3
129	32	233	2	114	3	220	19	103	10
128	60	194	2	113	4	219	6	102	3
127	16	160	2	106	10	218	3	101	3
126	3	159	3	105	100	217	4	100	2
117	2	158	2	104	10	180	1	93	2
116	12	157	2	103	10	145	1	92	24
115	16	146	2	102	3	144	2	91	14
114	5	145	8	101	3	143	1		
113	3	144	63	100	2	133	1		
105	16	143	18	92	4	132	10		
104	65	142	4	91	22	131	6		
103	29	134	3			130	29		
102	10	132	8			129	8		
101	18	131	47			128	4		
100	9	130	22			127	1		
92	3	129	6			118	2		
91	24	128	8			117	16		
90	2	127	2			116	8		

[a] The peaks are reported as per cent height relative to the largest peak in the spectrum. No peak below *m/e* 90 is reported. [b] No peak is reported which has a relative height of less than 2%. [c] No peak is reported which has a relative height of less than 1%.



In the mass spectrum of 2-(2′-phenylethyl)-1,2-boraztetralin (**2b**) and 2-(2′-phenylethyl)-3,2-borazindan (**2d**) the major fragmentations involve the 2′-phenylethyl moiety (see Table I). The peaks in the spectrum of borazindan **2d** occur 14 *m/e* units lower than the corresponding peaks in the spectrum of **2b** (see Table II). The only difference in structures **2b** and **2d** is that the former contains two methylene carbons in the heterocyclic ring while the latter contains only one methylene group. As in the case of 1,2-boraztetralin (**2a**), **2b** and **2d** easily lose one, two, and three protons. The largest fragmentation peak in the spectra of both 2-(2′-phenylethyl)-1,2-boraztetralin (**2b**) and 2-(2′-phenylethyl)-3,2-borazindan (**2d**) is due to the 2′-phenylethyl group (*m/e* 105). The 2′-phenylethyl group is lost from the appropriate M − 1 fragment (metastable peaks); in each case the other "half" of the molecule is also observed (*m/e* 131 and 117). N-Substituted amine–boranes **2b** and **2d** have fragments *m/e* 144 and 130, respectively, which are presumed to be due to loss of a tropylium ion from the M − 2 fragments; a peak corresponding to the tropylium ion is also observed in both spectra.[17] In the spectrum of **2b** there is a fragment at *m/e* 159 which corresponds to the formal loss of C_6H_6 from the molecular ion; the corresponding fragment in the spectrum of **2d** occurs at *m/e* 144, not *m/e* 145 as would be predicted. 2-(2′-Phenylethyl)-1,2-boraztetralin (**2b**) and 2-(2′-phenlyethyl)-3,2-borazindan (**2d**) can undergo the formal loss of ethylenimine (43 mass units) with phenyl migration. In the spectrum of **2d** there is a metastable peak corresponding to the loss of ethylenimine. 2-(2′-Phenylethyl)-3,2-borazindan (**2d**) also yields a major fragment at *m/e* 92; none of the other

TABLE II

MAJOR FRAGMENTS IN THE MASS SPECTRA OF **2b** AND **2d**

m/e		
2b	**2d**	Δ
237	223	14
236	222	14
194	180 (*)	14
159	144	15
144	130	14
131	117	14
105 (*)	105 (*)	0
91	91	0

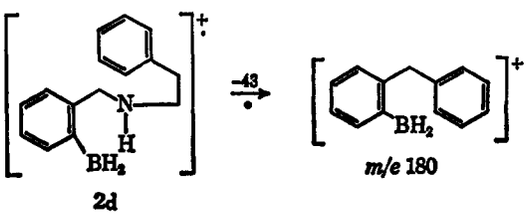


TABLE III

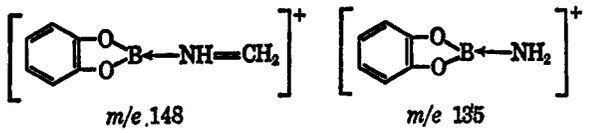
THE MASS SPECTRA OF THE CATECHOL DERIVATIVE OF 1,2-BORAZTETRALIN (8a) AND 2-(2′-PHENYLETHYL)3,2-BORAZINDAN (8b)

8a		8b	
m/e	%[a]	m/e	%[a]
240	18	330	7
239	100	329	27
238	30	328	7
237	3	239	12
211	4	238	76
210	24	237	20
209	24	236	4
208	5	210	15
165	8	209	100
149	5	208	25
148	20	165	5
147	8	119	4
146	5	117	3
145	3	105	7
144	4	104.5	20
136	3	104	6
135	4	91	7
128	3		
119.5	4		
117	6		
104	8		
103	7		
92	4		
91	9		
90	3		

[a] The peaks are reported as per cent height relative to the largest peak in the spectrum. No peak which has a relative height of less than 3% and no peak below m/e 90 is reported.

compounds studied had an important fragment with this mass-to-charge ratio.

The mass spectrum of the catechol derivative of 1,2-boraztetralin (**8a**) (see Table III) contains the m/e 104 and 91 fragments which were observed in the spectrum of 1,2-boraztetralin (**2a**). In each case the other "half" of **8a** is also seen (m/e 148 + 91 = 135 + 104 = 239 = mol wt). The fragments m/e 209 and 210 in the spectrum of **8a** are analogous to the m/e 103 and 104 fragments in the spectrum of **2a**. A peak is observed at 119.5 due to the doubly charged molecular ion.



The mass spectrum of the catechol derivative of 2-(2′-phenylethyl)-3,2-borazindan (**8b**) (Table III) is similar to that of 2-(2′-phenylethyl)-3,2-borazindan (**2d**), except that the fragmentations of **2d** are complicated by cleavage of the boron–hydrogen bonds.

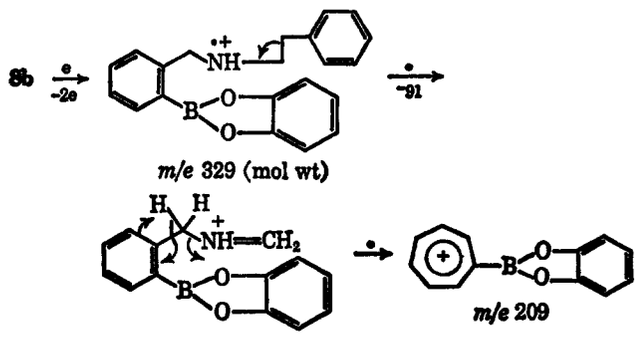


TABLE IV

PREPARATION OF AMINE–BORANES

Precursor	Amine–borane	Crystallization solvent	Yield, %	Mp, °C	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N	Mol wt[a] Calcd	Mol wt[a] Found
1a[b]	**2a**	H_2O, EtOH	83	150–151	72.24	9.09	10.53	72.11	9.32	10.54	133	133
1b[c]	**2b**	Benzene	29	120–122	80.68	8.41	5.91	80.51	8.51	5.95	237	237
1c[d]	**2c**	Benzene	17	88–90[e]	70.65	8.47	11.77	70.42	8.49	10.62	119	117
1d[f]	**2d**	EtOH–H_2O	43	122.5–123	80.72	8.07	6.23	80.68	8.01	5.87	233	233
1e	**2e**	Benzene–hexane	48	81–83	77.07	9.70	7.49	77.03	9.85	7.02		
Ethylamine + o-tolylboronic anhydride	**4**	H_2O	50	69–70	72.54	10.80	9.40	72.20	11.01	8.90, 9.34		

[a] Molecular weights were obtained by mass spectrum. [b] See ref 2a for the preparation of **1a**. [c] See ref 2a for the preparation of an analogous compound. [d] See ref 2b. [e] Melted with decomposition. [f] See ref 2b for the preparation of analogous compounds.

TABLE V

PREPARATION OF CATECHOL DERIVATIVES OF AMINE–BORANES

Amine–borane	Catechol derivative	Reaction solvent	Crystallization solvent	Yield, %	Mp, °C	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N	Mol wt[a] Calcd	Mol wt[a] Found
4	**7**	Benzene	Benzene–hexane	33	90–92	74.35	5.28		74.06	5.26			
2a	**8a**	Xylene	Chloroform	50	257–259	70.35	5.90		70.43	5.84		239	239
2d	**8b**	Xylene	Benzene	63	198–200	76.59	6.08	4.25	77.41	6.15	4.06	329	329
2c	**8c**	Benzene[b]	Benzene	62	272–274	69.33	6.22		69.07	5.91		225	225

[a] Molecular weights were obtained by mass spectrum. [b] Room temperature for 0.5 hr.

The major electron-induced fragmentations of the catechol derivative of 2-(2′-phenylethyl)-3,2-borazindan (**8b**) involve the stepwise cleavage of the 2′-phenylethyl moiety. The *m/e* 209 fragment is identical with that in the spectrum of **8a**, and in both cases arises from the loss of CH_2NH. A doubly charged species was observed at *m/e* 104.5 (*m/2e* 209); no doubly charged peak was observed corresponding to the molecular ion.

In the mass spectra of the amine–boranes (**2a, b,** and **d**) and their catechol derivatives (**8a** and **b**), there are many fragments which are either analogous or identical in these closely related compounds (see Table II). Support for assignments made is obtained by comparing related spectra.

Experimental Section[20]

Preparation of Amine–Boranes.—A solution of the appropriate aminoboronic acid, or potential aminoboronic acid, in tetrahydrofuran (THF) was slowly added to an excess of lithium aluminum hydride in THF. The resulting mixture was refluxed for 1 hr, and the excess $LiAlH_4$ was decomposed by the careful addition of water. The mixture was filtered and the residue was washed with THF. Evaporation of the combined THF solutions gave the desired amine–boranes which were purified by crystallization (see Table IV).

Preparation of Catechol Derivatives of Amine–Boranes.—Equivalent molar amounts of catechol and the appropriate amine–borane were heated under reflux for 1 hr in either benzene or xylene. When benzene was used as solvent, the reaction mixture was evaporated *in vacuo*. The reactions in xylene were chilled and the catechol derivatives were collected by filtration. The catechol derivatives were purified by crystallization (see Table V).

Preparation of the Catechol Derivative of *o*-(Bromomethyl)-benzeneboronic Acid.—The water was azeotropically removed from a carbon tetrachloride solution of 5.9 g of *o*-toluneboronic anhydride and 5.5 g of catechol. Carbon tetrachloride was added as required to keep the total volume at about 300 ml. The flask was then equipped with a reflux condenser and addition funnel. A solution of 2.56 ml of bromine in 100 ml of carbon tetrachloride was added slowly to the solution of the catechol derivative of toluneboronic acid which was heated under reflux and irradiated overnight with a Hanovia 215-W ultraviolet light (No. 30400). The dark solution was concentrated *in vacuo* and poured into an equal volume of hexane. The solution was treated with Darco and filtered. Upon concentration nearly to dryness at room temperature, 8.2 g (56%) of crude product was obtained. After having been recrystallized several times from hexane, the sample melted from 104 to 105°.

Anal. Calcd for $C_{13}H_{10}BO_2Br$: C, 54.02; H, 3.47. Found: C, 53.91; H, 3.48.

o-(Bromomethyl)benzeneboronic anhydride can also be converted into the catechol derivative by azeotropic removal of water from a solution of *o*-(bromomethyl)benzeneboronic anhydride and catechol.

Preparation of 3,2-Borazindan-2-spiro-1′-piperidine (2e).—To a solution of 2.89 g of the catechol derivative of *o*-(bromomethyl)benzeneboronic acid in 25 ml of THF was added 2 ml of piperidine. The slurry which formed was allowed to stand for 0.5 hr. Then the THF solution was added to a stirred slurry of 0.78 g of $LiAlH_4$ in 100 ml of THF. The piperidine hydrogen bromide was then washed with two 25-ml portions of THF which were also added to the $LiAlH_4$ slurry and the reaction mixture was heated at reflux for 1 hr. The excess $LiAlH_4$ was decomposed with water, the mixture was filtered, and the filtrate was evaporated. The residue obtained upon evaporation of the filtrate was extracted with two 50-ml portions of ether. Evaporation of the combined ether extracts yielded 0.9 g (48%) of 3,2-borazindan-2-spiro-1′-piperidine which, after recrystallization from benzene–hexane and washing with ethanol, melted at 81–83° (see Table IV).

Reaction of Ethylamine–(N–B)-*o*-Tolylborane with *o*-Phenylenediamine.—A mixture of 0.15 g of ethylamine–(N–B)-*o*-tolylborane and 0.11 g of *o*-phenylenediamine was heated on the steam bath for 0.5 hr. 2-(*o*-Tolyl)-1,3,2-benzodiazaborolidine (**5**, 0.17 g), after having been recrystallized from benzene–hexane, melted at 81–82°.

Anal. Calcd for $C_{13}H_{13}BN_2$: C, 75.06; H, 6.30. Found: C, 75.18; H, 6.22.

Registry No.—**2a,** 19214-72-3; **2b,** 19214-73-4; **2c,** 19214-74-5; **2d,** 19214-75-6; **2e,** 19214-76-7; **5,** 19206-12-3; **7,** 19206-13-4; **8a,** 19214-77-8; **8b,** 19214-78-9; **8c,** 19214-79-0; catechol derivative of *o*-(bromomethyl)benzeneboronic acid, 19206-14-5.

(20) Microanalyses were performed by Josef Nemeth and his associates. Infrared spectra were determined by the staff of the Spectroscopy Laboratory of the Department of Chemistry and Chemical Engineering of the University of Illinois, using a Perkin-Elmer Model 21 infrared spectrophotometer (equipped with sodium chloride optics). All melting-point determinations were uncorrected and were obtained on a Kofler microstage melting-point apparatus. Evaporations done *in vacuo* were carried out on a rotary evaporator unless specified otherwise. The mass spectra were obtained by Mr. Joseph Wrona on an Atlas CH4 spectrometer.