965. *Aminoditolylborane and the Preparation of Diarylborinic Acids.*

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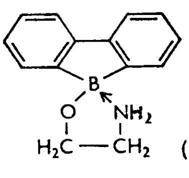
Aminodi-*o*-tolyl- and aminodimesityl-borane are monomeric in benzene solution, dimerization being prevented sterically by the *o*-methyl groups. The reaction between dichlorodiphenylaminoborane and an aryl Grignard reagent appears to be the best general method for the preparation of diarylborinic acids, which have been obtained as 2-aminoethyl esters in 51—93% yields.

AMINODIARYLBORANES, $Ar_2B{\cdot}NR_2$, have hitherto [1,2] been found to be dimeric when R = H, monomeric when R is an alkyl or aryl group, and both mono- and di-meric forms of $Ph_2B{\cdot}NHMe$ have been obtained.[3] We suggested [1] that in dimeric aminodiarylboranes $Ar_2B{\cdot}NR_2)_2$ any groups R bigger than hydrogen would cause substantial steric interference even with the hydrogen atoms in *ortho*-positions on the aryl groups. We now find that substitution of one or both *o*-hydrogen atoms by methyl groups also prevents dimerization; both aminodi-*o*-tolylborane and aminodimesitylborane are monomeric in benzene solution. Their dipole moments are small, being respectively $\mu = 1{\cdot}7$ and *ca.* 1·1 D. The moment of fluorodimesitylborane (1·7 D) is significantly smaller than that of chlorodiphenylborane (2·0 D), and we attribute part of the difference to the prevention of overlap between the boron 2*p*-orbital and the mesityl π-orbitals on account of the steric requirements of the mesityl groups.

The quantitative hydrolysis of aminodiarylboranes to diarylborinic acids, the simple preparation of the former from aminodichloroboranes ($Cl_2B{\cdot}NR_2$; R = alkyl or aryl) and a Grignard reagent,[2] and the easy preparation of dichlorodiphenylaminoborane from diphenylamine and trichloroborane,[4] lead us to consider the following reaction sequence the best preparative route to diarylborinic acids:

$$BCl_3 \xrightarrow{Ph_2NH} Cl_2B{\cdot}NPh_2 \xrightarrow{ArMgX} Ar_2B{\cdot}NPh_2 \xrightarrow{H_2O\text{-}NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH} Ar_2B{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2 \xrightarrow{HCl} Ar_2B{\cdot}OH$$

Since only a slight excess of Grignard reagent is used, this procedure is more economical than that of Povlock and Lippincott [5] in which a 50% excess of Grignard reagent is allowed to react with trimethoxyboroxine, and the yield of 2-aminoethyl diarylborinate is then only 21—63% (based on the boroxine) and some boronic acid is formed as well. By our method, yields of 2-aminoethyl esters have been in the range 51—93%, and boronic acids have never been detected among the products. The method was also used for the preparation of 2-aminoethyl biphenyl-2,2′-borinate (I).


(I)

EXPERIMENTAL

The preparation of diphenylborinic acid and its 2-aminoethyl ester, described below, illustrates the general method used for the preparation of the compounds listed in the Table.

2-*Aminoethyl Diphenylborinate.*—Phenylmagnesium bromide (0·25 mole) in ether was slowly added to dichlorodiphenylaminoborane [4] (0·1 mole) in benzene (100 c.c.). After the mixture had been refluxed for ½ hr., it was allowed to cool, then hydrolysed with dilute hydrochloric acid, and the pH adjusted to 6—7. After filtration the organic phase was evaporated, the residual yellow oil consisting of crude diphenylborinic acid was dissolved in ether (50 c.c.)

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[1] Coates and Livingstone, *J.*, 1961, 1000.

[2] Niedenzu and Dawson, *J. Amer. Chem. Soc.*, 1959, **81**, 5553.

[3] Mikhailov and Fedotov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1959, 1482.

[4] Becher, *Z. anorg. Chem.*, 1957, **289**, 277.

[5] Povlock and Lippincott, *J. Amer. Chem. Soc.*, 1958, **80**, 5409.

and 2-aminoethanol (22 c.c.) in an equal volume of water was added with stirring. The precipitated ester was separated from any residual diphenylamine by crystallization from ethanol; it (22·6 g.) had m. p. 188—189° (lit.[5] 189°).

Diphenylborinic Acid.—The 2-aminoethyl ester (22·6 g.) in a mixture of acetone (50 c.c.) and methanol (50 c.c.) was hydrolysed by addition of hydrochloric acid (12·5 c.c. of concentrated acid in 100 c.c. of water). After addition of ether (100 c.c.) the organic layer was separated, dried ($MgSO_4$), and evaporated, yielding diphenylborinic acid (16·1 g.), b. p. 210—213°, condensing as anhydride, m. p. 116° (from hexane) (lit.,[6] 116°).

Preparation of diarylborinic esters and acids, $R_2B\cdot OR'$.

R	Ester, $R' = \cdot CH_2\cdot CH_2\cdot NH_2$						Acid, $R' = H$					
	M. p.	Yield (%)	Found (%)		Reqd. (%)		M. p.	Yield (%)	Found (%)		Reqd. (%)	
			C	H	C	H			C	H	C	H
C_6H_5	188—189°	93	74·1	7·1	74·6	7·2	Liquid	88	78·9	6·0	79·2	6·1
o-$CH_3\cdot C_6H_4$	184	80	76·1	7·9	75·9	7·9	78—79°	75	79·9	7·1	80·1	7·2
p-$CH_3\cdot C_6H_4$	186	80	75·4	7·0	75·9	7·9	105	71	78·9	7·2	80·1	7·2
o-$CH_3O\cdot C_6H_4$ [a]	164—165	58	67·4	7·0	67·3	7·0	[b]	—	—	—	—	—
p-$Br\cdot C_6H_4$	236—237	56	43·3	3·6	43·8	3·7	84—86	50	42·0	4·6	42·4	4·6
p-$Cl\cdot C_6H_4$	226—227	82	56·8	4·6	57·1	4·8	77	75	57·0	3·5	57·4	3·6
p-$C_6H_5\cdot C_6H_4$ ...	219	57	81·9	6·4	82·8	6·4	[b]	—	—	—	—	—
1-$C_{10}H_7$	204	51	80·9	6·1	81·2	6·2	117	45	84·7	5·1	85·0	5·3
$C_6H_5\cdot C\vdots C$ [a]	172—174	58	78·8	7·1	79·1	7·4	98—100	52	83·3	4·6	83·4	4·8
3,4-$(CH_3)_2C_6H_3$ [a]	204—206	72	76·1	8·4	76·8	8·6	[b]	—	—	—	—	—

[a] Not previously described. [b] Acids were prepared only when needed for further study.

*Aminodi-*o*-tolylborane.*—Chlorodi-*o*-tolylborane (4·5 g., 0·02 mole; b. p. 100—102°/0·01 mm., prepared from di-*o*-tolylborinic acid and boron trichloride [6]) in ether was slowly added to a solution of ammonia (about 0·5 g.) and triethylamine (2·1 g.) in ether (100 c.c.) at about −40°. There was an immediate white precipitate. The mixture was refluxed for ½ hr., then filtered from triethylammonium chloride. Vacuum-distillation yielded a colourless liquid *product* 2·93 g., b. p. 86—88°/$<10^{-3}$ mm. (Found by hydrolysis: *o*-tolyl$_2$B, 91·9; NH_2, 7·6, 7·4. $C_{14}H_{16}BN$ requires *o*-tolyl$_2$B, 92·3; NH_2, 7·7%).

Aminodimesitylborane.—Fluorodimesitylborane [7] (6 g.) in ether (50 c.c.) was slowly added to an excess of anhydrous ammonia in ether (50 c.c.). There was immediate precipitation of the borane–ammonia complex. The mixture was refluxed for 48 hr., during which the ammonia complex gradually dissolved and ammonium fluoride (0·4 g.) was deposited. The ether solution was filtered and evaporated, yielding aminodimesitylborane (5·5 g., 93%), m. p. 118—120° (from light petroleum) {Found by hydrolysis: $[(CH_3)_3C_6H_2]_2B$, 93·4, 93·5; NH_2, 5·96, 5·92. $C_{18}H_{24}BN$ requires $[(CH_3)_3C_6H_2]_3B$, 94·1; NH_2, 6·0%)}.

2-*Aminoethyl Biphenyl*-2,2′-*borinate* (I).—n-Butyl-lithium (0·08 mole) in ether was added to 2,2′-dibromobiphenyl [8] (10 g., 0·032 mole) in ether (100 c.c.), and the mixture stirred for 4 hr. before dichlorodiphenylaminoborane (0·032 mole) in dry benzene was slowly added. After addition of water (50 c.c.) the pale yellow organic layer was separated and a solution of 2-aminoethanol (10 c.c.) in water (50 c.c.) was added. The precipitated *ester*, crystallised from ethanol, had m. p. 170—171° (3·9 g., 61%) (Found: C, 75·3; H, 6·2. $C_{14}H_{14}BNO$ requires C, 75·1; H, 6·3%).

Infrared Spectra.—Both aminoboranes showed very strong absorptions at 1450 (*o*-tolyl compound) and 1419 (mesityl compound) cm.$^{-1}$ (measured in benzene solution), which we attribute to a B–N stretching vibration. These frequencies, which show the isotopic splitting commonly observed in spectra of boron compounds, are higher than those of corresponding bands in other monomeric aminodiarylboranes,[1] which lie in the range 1360—1410 cm.$^{-1}$. This is to be expected since the *o*-methyl groups would reduce interaction between the boron 2*p*-orbital and the aryl π-electrons, and this should increase the order of the B–N bond.

The N–H frequencies of the *o*-tolyl compound, measured as a contact film, were 3390 and 3490 cm.$^{-1}$.

Dipole Moments.—These were measured for benzene solutions, refractivities being measured

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[6] Abel, Dandegaonker, Gerrard, and Lappert, *J.*, 1956, 4697.

[7] Brown and Dodson, *J. Amer. Chem. Soc.*, 1957, **79**, 2305.

[8] Gilman and Gaj, *J. Org. Chem.*, 1957, **22**, 447.

*Aminodi-*o*-tolylborane*

Wt. fraction (w)	Spec. volume (v)	$10^8\,\Delta n$	ΔC (cm.)
0·1668	1·1424	17·92	0·140
0·1858	1·1410	21·73	0·220
0·2802	1·1391	33·81	0·351
0·3093	1·1387	59·17	—

$dC/dw = 1{\cdot}867$, $dv/dw = -0{\cdot}291$, $dn/dw = 0{\cdot}1034$, ${}_{\mathrm{T}}P = 127{\cdot}8$, ${}_{\mathrm{E}}P = 64{\cdot}6$, ${}_{\mathrm{O}}P = 60{\cdot}0$ c.c., $\mu = 1{\cdot}7$ D.

Aminodimesitylborane

Wt. fraction (w)	Spec. volume (v)	$10^8\Delta n$	ΔC (cm.)
0·0676	1·1421	37·90	0·218
0·1177	1·1417	66·78	0·342
0·1698	1·1401	86·64	0·383
0·2733	1·1395	97·47	0·421

$dC/dw = 0{\cdot}9771$, $dv/dw = -0{\cdot}1264$, $dn/dw = 0{\cdot}0799$, ${}_{\mathrm{T}}P = 119{\cdot}1$, ${}_{\mathrm{E}}P = 90{\cdot}5$, ${}_{\mathrm{O}}P = 24{\cdot}1$ c.c., $\mu =$ *ca.* 1·1 D.

Chlorodiphenylborane

Wt. fraction (w)	Spec. volume (v)	$10^8\,\Delta n$	ΔC (cm.)
0·0079	1·1419	59·57	0·174
0·0123	1·1404	93·79	0·478
0·0268	1·1367	111·5	0·940
0·0342	1·1329	119·1	1·267

$dC/dw = 2{\cdot}527$, $dv/dw = -0{\cdot}3425$, $dn/dw = 0{\cdot}1155$, ${}_{\mathrm{T}}P = 143{\cdot}2$, ${}_{\mathrm{E}}P = 60{\cdot}3$, ${}_{\mathrm{O}}P = 79{\cdot}9$ c.c., $\mu = 2{\cdot}0$ D.

Fluorodimesitylborane

Wt. fraction (w)	Spec. volume (v)	$10^8\Delta n$	ΔC (cm.)
0·0045	1·1417	—	0·066
0·0102	1·1402	—	0·174
0·0143	1·1396	—	0·233
0·0257	1·1378	—	0·321

$dC/dw = 7{\cdot}4861$, $dv/dw = -0{\cdot}1839$, ${}_{\mathrm{T}}P = 148{\cdot}3$, ${}_{\mathrm{E}}P$ (calc. from bond refractivities for 5893 Å) $= 84{\cdot}9$, ${}_{\mathrm{O}}P = 59{\cdot}2$ c.c., $\mu = 1{\cdot}7$ D.

at 6620 Å. Atom polarization was arbitrarily taken as 5% of the electron polarization at 6620 Å. Moments were calculated from observed weight fractions, densities, refractivities, and changes of capacity by Halverstat and Kumler's method.[9]

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[9] Halverstat and Kumler, *J. Amer. Chem. Soc.*, 1942, **64**, 2988.