Routes to the Formation of 1,3,5-Triaryl- and 2,4,6-Trichloro-1,3,5-triarylborazines and Intermediate Compounds

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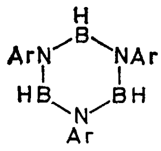
The effect of *ortho*-substitution has been investigated in routes to the formation of 1,3,5-triaryl- and 2,4,6-trichloro-1,3,5-triaryl-borazines. The presence of two substituents in the *ortho*-positions inhibits the formation of the equivalent borazine, both in reactions involving the heating of a mixture of arylamine and triethylamine–borane and in those which involve heating the 1 : 1 adduct of the arylamine and trichloroborane. Products isolated in these cases include diazaboranes (bisaminoboranes) [$(ArNH)_2BH$], aminodichloroboranes [$ArNHBCl_2$], and triazaboranes (boronamines) [ArNH·BX·NAr·BX·NArH] (X = Cl or H). A possible reaction path to the formation of borazines involving these intermediates is discussed.

Koster[1] *et al.* have reported the preparation of 1,3,5-triphenylborazine by heating a mixture of aniline and triethylamine–borane above 100°.

$$Et_3N,BH_3 + PhNH_2 \longrightarrow \tfrac{1}{3}(PhNBH)_3 + Et_3N + 2H_2$$

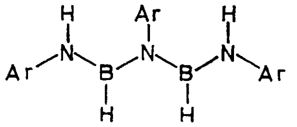
At 50—60° they obtained a mixture of bis(phenylamino)borane [$(PhNH)_2BH$] and tris(phenylamino)borane [$(PhNH)_3B$]. On treatment with more triethylamine–borane at 100° bis(phenylamino)borane gave the triazaborane [PhNH·BH·NPh·BH·NPhH].

Further investigation of this reaction using a variety of arylamines is now reported. Table 1 gives the results obtained on heating mixtures of the arylamines and triethylamine–borane. Except for the cases of 2,6-dichloroaniline and 2,6-xylidine the 1,3,5-triarylborazines (1a, b, c, d, and f) are the major products.

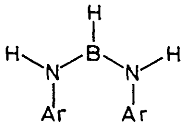

(I)

Ar
a; Ph
b; o-ClC_6H_4
c; o-CF_3·C_6H_4
d; C_6F_5
e; $2,6$-$Cl_2C_6H_3$
f; 2-Cl-6-FC_6H_3
g; $2,6$-$Me_2C_6H_3$

In the case of 2,6-dichloroaniline, the 1,3,5-triarylborazine (Ie) was only obtained in 3% yield, the major product being the triazaborane (IIa). In the case of 2,6-xylidine no borazine was obtained, the triazaborane (IIb) and the diazaborane (III) were the only products.


(II)

Ar = a; $2,6$-$Cl_2C_6H_3$
b; $2,6$-$Me_2C_6H_3$

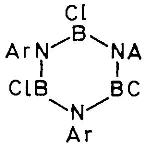

(III)

Ar = $2,6$-$Me_2C_6H_3$

The triazaboranes (IIa and b) when treated with triethylamine–borane in excess at 180—190° gave the corresponding 1,3,5-triarylborazines (1e and g).

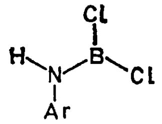
$$ArNH{\cdot}BH{\cdot}NAr{\cdot}BH{\cdot}NHAr + Et_3N,BH_3 \longrightarrow (ArNBH)_3 + Et_3N + 2H_2$$

The interaction of arylamine (1 mol) and trichloroborane (1 mol) gives 1 : 1 adducts (Table 2). The results of thermal decomposition of equimolar mixtures of arylamine and trichloroborane when heated in refluxing benzene or toluene are summarised in Table 3. All systems with one or no substituents in the *ortho*-position give the corresponding 2,4,6-trichloro-1,3,5-triaryl-borazine (IVa—d). If there are two substituents in the *ortho*-positions, *i.e.* in the case of the 2,6-xylidine, 2,4,6-trichloro- and tribromo-aniline–trichloroborane adducts, the corresponding borazine is not obtained. The 2,6-xylidine trichloroborane adduct gave a high yield of the aminodichloroborane (Va). The 2,4,6-trichloro- and tribromo-isomers gave lower yields of the aminodichloroborane (Vb and c) and corresponding greater amounts of the triazaborane (VIa and b).

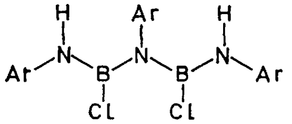

(IV)

Ar = a; m-ClC_6H_4–
b; o-BrC_6H_4–
c; m-BrC_6H_4–
d; p-FC_6H_4–

$$ArNH_2.BCl_3 \longrightarrow {}^1/_3(ArNBCl)_3 + 2HCl$$


(V)

Ar = a; $2,6$-$Me_2C_6H_3$-
b; $2,4,6$-$Cl_3C_6H_2$-
c; $2,4,6$-$Br_3C_6H_2$-


(VI)

Ar = a; $2,4,6$-$Cl_3C_6H_2$
b; $2,4,6$-$Br_3C_6H_2$

Preparation of the triazaborane from the aminodichloroborane was confirmed by heating the pure aminodichloroborane under reflux and recovering the calculated amounts of boronamine (VIa and b), trichloroborane and hydrogen chloride (Table 4).

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[1] R. Koster, H. Bellut, and S. Hattori, *Ann. Chim.*, 1968, **720**, 1.

TABLE 1

Reactions of primary arylamines with triethylamine–borane

$ArNH_2$			Et_3N,BH_3			Product														
									Found						Calculated					
Ar	g	mol	g	mol	Reaction time	Nature	Yield (%)	M.p.	C	H	B	Cl	F	N	C	H	B	Cl	F	N
Ph	42·8	0·46	52·9	0·46	140°, 50 min 180°, 2 h	(Ia) [a]	70	158—160°	69·45	5·95	10·5			13·6	70·0	5·9	10·5			13·6
o-ClC_6H_4	42·5	0·33	38·3	0·33	140°, 50 min 180°, 2 h	(Ib) [a]	80	126—128 [b]	51·6	3·7	7·85			10·0	52·45	3·7	7·9			10·2
o-$CF_3{\cdot}C_6H_4$	32·2	0·20	23·0	0·20	140—150°, 80 min 180°, 2 h	(Ic) [c]	31	134—135·5	49·3	3·1	5·3		35·3	7·9	49·2	2·95	6·3		33·35	8·2
C_6F_5	30·6	0·17	19·2	0·17	145°, 2 h 180°, 1 h	(Id) [d]	56	138—140	37·35	0·05	5·5		49·4	7·2	37·4	0·5	5·6		49·25	7·3
2,6-$Cl_2C_6H_3$	26·7	0·16	19·0	0·16	140°, 2 h	(IIa) [e]	75	191—192	42·3	2·5	4·1	41·2		8·2	42·8	2·6	4·3	42·1		8·3
					185°, 30 min	(Ie) [e]	3	216—218 [g]			5·4	40·1		7·9			6·3	41·3		8·15
2,6-$Me_2C_6H_3$	37·1	0·31	35·2	0·31	140°, 2 h	(IIb) [f]	4	218—220	75·3	8·0	5·6			10·7	75·2	8·15	5·65			11·0
					185°, 30 min	(III) [f]	90	73—76	76·0	8·5	4·4			11·2	76·2	8·4	4·3			11·1
2-Cl-6-FC_6H_3	37·8	0·26	30·0	0·26	145°, 2 h 180°, 2 h	(If) [a]	71	165—166			7·0	22·8		9·0			7·0	23·0		9·0

[a] Purified by recrystallisation from n-hexane. [b] Lit. (G.P. 1,169,445) m.p. 118—119°. [c] Purified by recrystallisation from n-hexane followed by sublimation (130°, 0·01 mmHg). [d] Purified by distillation (b.p. 162—168°, 0·8 mmHg) followed by sublimation (120°, 0·05 mmHg). [e] Products separated by fractional crystallisation from light petroleum [compound (Ie) is the more soluble]. [f] Products separated by fractional crystallisation from light petroleum [compound (III) is the more soluble, and was purified by sublimation (70°, 0·05 mmHg)]. [g] Crude material, probably contaminated with some of (IIa).

TABLE 2

Preparation of arylamine–trichloroborane 1 : 1 adducts ($ArNH_2,BCl_3$)

		Found %							Required %						
Ar	Yield %	C	H	B	Cl *	Cl †	Br	N	C	H	B	Cl *	Cl †	Br	N
o-ClC_6H_4	51·8			4·4	44·0	56·8		5·7			4·4	43·5	57·9		5·7
p-ClC_6H_4	80·7			4·4	43·8	56·4		5·6			4·4	43·5	57·9		5·7
p-BrC_6H_4	64·4			3·6	39·8			4·7			3·7	36·8			4·8
2,4,6-$Cl_3C_6H_2$	64·9	23·0	1·35	3·5	33·7	69·5		4·4	23·2	1·28	3·5	33·9	69·7		4·5
2,4,6-$Br_3C_6H_2$	83·1	16·0	0·9	2·6	23·5		53·8	3·1	16·1	0·9	2·4	23·8		53·6	3·1
2,6-$Me_2C_6H_3$	66·8	40·2	4·4	4·2	44·4			5·7	40·3	4·7	4·5	44·6			5·9

* Chlorine easily hydrolysed by water. † Total chloride.

TABLE 3

Thermal decomposition of arylamine–trichloroborane adducts

$ArNH_2,BCl_3$			Solvent		Reflux time	Product																				
									Found									Calculated								
Ar	g	mol		mls	(h)	Nature	Yield g	Yield %	C	H	B	Br	Cl *	Cl †	F	N	M	C	H	B	Br	Cl *	Cl †	F	N	M
m-ClC_6H_4	*a*		Toluene	1000	24	(IVa)	87·8 [f]	42·6	41·8	2·2	6·1		20·9	41·2		7·9		41·9	2·8	6·3		20·7	41·3		8·2	
o-BrC_6H_4	45	0·05	Chloro-benzene	150	24	(IVb)	25·8 [f]	76·5	33·2	1·8	5·1	36·7	16·2			6·4		33·3	1·9	5·0	36·9	16·4			6·5	
m-BrC_6H_4	*b*		Toluene	1000	24	(IVc)	172 [f]	46·4	33·2	2·1	5·0	36·7	16·3			6·5		33·3	1·9	5·0	36·9	16·4			6·5	
p-FC_6H_4	*c*		Toluene	250	6	(IVd)	71·8 [f]	61·1	46·2	2·6	7·0		22·7		12·0	8·8		46·4	2·6	7·0		22·8		12·2	9·0	
2,6-$Me_2C_6H_3$	26·2	0·11	Toluene	100	6	(Va)	19·7 [f]	88·7	47·4	4·8	5·3		35·3			6·9	195	47·6	5·0	5·4		35·1			6·9	202
2,4,6-$Br_3C_6H_2$	*d*		Benzene	200	4	(Vb)	40·8 [g]	71·2	17·8	0·6	2·6	59·5	17·5			3·6	392	18·0	0·8	2·7	59·8	17·7			3·5	410
2,4,6-$Cl_3C_6H_2$	*e*		Benzene	250	6	(Vc)	45·6 [h]	65·8	26·1	1·2	3·8		25·6	63·7		4·9	272	26·0	1·1	3·9		26·0	64·0		5·0	277

[a] m-$ClC_6H_4{\cdot}NH_2$ (146·4 g, 1·2 mol), BCl_3 (144·7 g, 1·2 mol). [b] m-$BrC_6H_4{\cdot}NH_2$ (294 g, 1·7 mol), BCl_3 (350 g, 3·0 mol). [c] p-$FC_6H_4{\cdot}NH_2$ (84·5 g, 0·76 mol), BCl_3 (175 g, 1·49 mol). [d] 2,4,6-$Br_3C_6H_2{\cdot}NH_2$ (46 g, 0·14 mol), BCl_3 (123 g, 1·05 mol). [e] 2,4,6-$Cl_3C_6H_2{\cdot}NH_2$ (50 g, 0·25 mol), BCl_3 (99·8 g, 0·85 mol). [f] Crystalline product obtained by concentration of reaction mixture. [g] Liquid, b.p. 160°, 0·1 mmHg leaving an intractable residue (12·2 g) probably a mixture of $(Br_3C_6H_2{\cdot}NBCl)_3$ and (VIb). [h] Liquid, b.p. 134°, 1·0 mmHg and a residue (18·3 g) probably a mixture of $(Cl_3C_6H_2{\cdot}NBCl)_3$ and (VIa).

* Chlorine easily hydrolysed by water. † Total chlorine.

TABLE 4

Pyrolysis of arylaminodichloroboranes

$ArNHBCl_2$			Pyrolysis		Products																					
					HCl		BCl_3		Triazaborane ($ArNH{\cdot}BCl{\cdot}NAr{\cdot}BCl{\cdot}NArH$)																	
											Found								Calculated							
Ar	g	mol	Time (h)	Conditions	g	mol	g	mol	g	%	C	H	B	Br	Cl *	Cl †	N	M	C	H	B	Br	Cl *	Cl †	N	M
2,4,6-$Cl_3C_6H_2$	8·5	0·03	0·5	200°, 760 mmHg	0·3	0·008	1·3	0·011	7·0 [a]	100	32·0	1·2	3·2		11·1	55·4	6·3	700	31·8	1·2	3·2		10·5	53·1	6·3	679
			0·5	250°, 0·1 mmHg																						
2,4,6-$Br_3C_6H_2$	12·3	0·03	1·0	250°, 0·8 mmHg	0·44	0·012	1·1	0·009	10·9 [b]	100	20·3	0·9	1·9	67·8	6·2		3·9	1058	20·1	0·8	2·0	66·7	6·6		3·9	1078

[a] B.p. 219—221°, 0·01 mmHg. [b] B.p. 280°, 0·01 mmHg.

* Chlorine easily hydrolysed by water. † Total chlorine.

These results are analogous to those of Turner and his co-workers [2] who reported the formation of a mixture of

$$\mathrm{ArNH_2,BCl_3} \longrightarrow \mathrm{ArNH{\cdot}BCl_2} + \mathrm{HCl}$$
$$3\mathrm{ArNH{\cdot}BCl_2} \longrightarrow \mathrm{ArNH{\cdot}BCl{\cdot}NAr{\cdot}BCl{\cdot}NHAr} + \mathrm{HCl} + \mathrm{BCl_3}$$

aminodichloroborane and the triazaborane when the 1:1 adduct of 2,6-xylidine and trichloroborane was heated in toluene under reflux.

Attempts were made to interact these triazaboranes with trichloroborane in the hope that ring closure to give the borazine might be effected. The trichlorophenyltriazaborane (VIa) did not form an adduct with trichloroborane at −80° and was recovered unchanged. Similarly the tribromophenyltriazaborane (VIb) when heated in benzene under reflux with triethylamine–trichloroborane adduct showed no reaction.

Possible Reaction Paths.—The interaction of triethylamine–borane and arylamines may involve the initial formation of the 1 : 1 adduct $\mathrm{ArNH_2,BH_3}$. Decomposition of 1 : 1 adducts $\mathrm{ArNH_2,BX_3}$ (where X = Cl or H) may be envisaged as following reaction paths involving initially elimination of HX to form $\mathrm{ArNH{\cdot}BX_2}$ which then undergoes further condensation reactions with elimination of HX or $\mathrm{BX_3}$.

$$\mathrm{ArNH_2{\cdot}BX_3} \longrightarrow \mathrm{ArNH{\cdot}BX_2} + \mathrm{HX}$$
$$2\mathrm{ArNH{\cdot}BX_2} \longrightarrow \mathrm{ArNH{\cdot}BX{\cdot}ArNH} + \mathrm{BX_3}$$
$$2\mathrm{ArNH{\cdot}BX_2} \longrightarrow \mathrm{ArNH{\cdot}BX{\cdot}ArN{\cdot}BX_3} + \mathrm{HX}$$
$$\mathrm{ArNH{\cdot}BX{\cdot}ArN{\cdot}BX_3} + \mathrm{ArNH{\cdot}BX_2} \longrightarrow \mathrm{ArNH{\cdot}BX{\cdot}ArN{\cdot}BX{\cdot}ArNH} + \mathrm{BX_3}$$

Ring closure to form the borazine may now be effected as follows:

$$\mathrm{ArNH{\cdot}BX{\cdot}ArN{\cdot}BX{\cdot}ArNH} + \mathrm{BX_3} \longrightarrow \mathrm{(ArNBX)_3} + 2\mathrm{HX}$$

In the cases where X = H, ring closure to give the borazine by reaction with $\mathrm{Et_3N,BH_3}$ has been demonstrated. Although not demonstrable experimentally similar ring-closure reactions may occur in those cases involving X = Cl which give yields of the borazine from the 1 : 1 adduct. In the cases where there is 2,6-disubstitution in the aryl group the inhibition of borazine formation may be due to steric hindrance.

EXPERIMENTAL

Reactions of Primary Arylamines with Triethylamine–Borane.—The arylamines were added dropwise to stirred triethylamine–borane at 140—150°; hydrogen and triethylamine were evolved. The mixtures were then heated at 180—185°, then any unchanged triethylamine–borane removed at 100°, 10 mmHg.

Preparation of Arylammonium Tetrachloroborates.—The amine hydrochloride was suspended in dry dichloromethane and the suspension cooled to −80°, an excess of trichloroborane added and the mixture allowed to stand for up to 30 min. The filtered solid was then washed with chilled dichloromethane and dried under reduced pressure.

Preparation of Arylamine–Trichloroborane 1 : 1 *Adducts.*—Solutions of the appropriate amine in dichloromethane were added to solutions of an excess of trichloroborane in dichloromethane at −80°. The mixtures were then set aside at −80° for periods up to 1 h. The white precipitates were filtered off, washed with dichloromethane, and dried under reduced pressure.

Thermal Decomposition of Arylamine–Trichloroborane 1 : 1 *Adducts.*—The arylamine–trichloroborane 1 : 1 adducts were heated for 24 h in refluxing toluene or chlorobenzene. The reaction mixture was then concentrated by distilling off the bulk of the solvent.

Pyrolysis of Arylaminodichloroboranes.—These compounds were heated under reflux under the conditions given in Table 4. The resulting boronamine was isolated by distillation.

Reaction between $\mathrm{ArNH{\cdot}BH{\cdot}NAr{\cdot}BH{\cdot}NHAr}$ (Ar = 2,6-$\mathrm{Cl_2C_6H_3}$) *and Triethylamine–Borane.*—The triazaborane (12·4 g, 0·025 mol) and triethylamine–borane (4·4 g, 0·04 mol) were heated at 180—190° for 9 h. Triethylamine (identified by its i.r. spectrum) distilled into a receiver. After the removal of some unchanged triethylamine–borane by distillation *in vacuo*, the product was recrystallised from n-hexane, to give colourless crystals of 1,3,5-tris-(2,6-dichlorophenyl)borazine (10·5 g, 81%), m.p. 221—223°. Further purification by recrystallisation (light petroleum) gave a sample, m.p. 222·5—224·5° (Found: C, 42·9; H, 2·4; B, 5·0; Cl, 41·05; N, 8·2%; *M*, 545. $\mathrm{C_{18}H_{12}B_3Cl_6N_3}$ requires C, 41·95; H, 2·35; B, 6·3; Cl, 41·3; N, 8·2%; *M*, 507). After the compound (0·1613 g) had been heated with water under reflux for 1 h, 0·1592 g (98·7%), m.p. 220—222·5°, was recovered.

Reaction between $\mathrm{ArNH{\cdot}BH{\cdot}NAr{\cdot}BH{\cdot}NHAr}$ (Ar = 2,6-$\mathrm{Me_2C_6H_3}$) *and Triethylamine–Borane.*—Triethylamine–borane (3·1 g, 0·03 mol) and the triazaborane (4·9 g, 0·01 mol) were heated at 180—190° for 8·5 h. Triethylamine (identified by its i.r. spectrum) was collected as a distillate. The glassy residue remaining after the unchanged triethylamine–borane had been distilled off was crystallised from light petroleum (b.p. 60—80°), to give crystals of 1,3,5-tris-(2,6-dimethylphenyl)borazine (2·1 g, 54%), m.p. 151—154° (lit.,[3] 154—155°). The i.r. spectrum of the product was practically identical to that given by Turner *et al.*[3]

The Attempted Reaction between $\mathrm{ArNH{\cdot}BCl{\cdot}NAr{\cdot}BCl{\cdot}NHAr}$ (Ar = 2,4,6-$\mathrm{Br_3C_6H_2}$-) *and Triethylamine–trichloroborane Complex.*—The triazaborane (10·0 g, 0·01 mol) was dissolved in benzene (100 ml) and freshly prepared triethylamine–trichloroborane (1·7 g, 0·01 mol) was added to it. The mixture was heated under reflux for 1 h and any gases evolved were passed through potassium hydroxide solution (Found: Cl, 0%). The benzene was removed by evaporation under reduced pressure to leave a white solid (12·1 g), presumably a mixture of the triazaborane and the triethylamine complex (Found: B, 2·4; Cl, 10·2%). A portion (5·8 g) of this material was heated to 200° under reduced pressure to remove the complex by sublimation. The residue weighed 5·4 g (Found: B, 1·9; Cl, 6·4; N, 3·9. $\mathrm{C_{18}H_8B_2Cl_2Br_9N_3}$ requires B, 1·9; Cl, 6·2; N, 3·9%).

Attempted Reaction of $\mathrm{ArNH{\cdot}BCl{\cdot}NAr{\cdot}BCl{\cdot}NHAr}$ (Ar = 2,4,6-$\mathrm{Cl_3C_6H_2}$- *and Trichloroborane.*—A solution of tri-

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[2] R. K. Bartlett, H. S. Turner, R. J. Warne, M. A. Young, and I. J. Lawrenson, *J. Chem. Soc.* (*A*), 1966, 479.

[3] R. K. Bartlett, H. S. Turner, R. J. Warne, M. A. Young, and I. J. Lawrenson, 'DMS Index,' Butterworths, Card No. 13,327 (1966).

chloroborane (8·8 g, 0·07 mol) in dichloromethane (20 ml) was cooled to −80° and added to a solution of the triazaborane (1·9 g, 0·003 mol) in dichloromethane (25 ml) also cooled to −80°. The mixture was allowed to warm up slowly to room temperature and then trichloroborane and dichloromethane were evaporated under reduced pressure. The residue solid (1·8 g) was determined by analysis to be the unchanged triazaborane (Found: B, 3·0; hydrolysed Cl, 10·6; total Cl, 52·8, N, 6·4. $C_{18}H_8B_2Cl_{11}N_3$ requires B, 3·2; hydrolysed Cl, 10·5; total Cl, 53·1; N, 6·3%).

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