Reactions of Boron Tri-iodide with Nitrogen Donors. Some Comparisons of Boron Tri-iodide with Other Boron Halides

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The chemistry of the dehydrohalogenation reactions of boron tri-iodide–aromatic amine adducts is illustrated. The main difference between boron tri-iodide and other boron halides is the more extensive formation of 1,3-diaza-2,4-diboranaphthalene derivatives (from aromatic amine–boron halide adducts) for the iodide systems. The mechanism of orthoboronation is discussed.

THE instability of boron tri-iodide is well known, it decomposes even in the solid state to iodine and unspecified boron polymers.[1] It reacts as a Lewis acid [2] and some new adducts are reported in this paper.

The thermal dehydrohalogenation of adducts of boron tri-iodide with primary aromatic amines yields derivatives of 1,3-diaza-2,4-diboranaphthalene. These reactions involve an orthoboronation which has few

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[1] A. K. Holliday and A. G. Massey, *Chem. Rev.*, 1962, **62**, 303.

[2] G. K. Chantry, A. Finch, P. N. Gates, and D. Steele, *J. Chem. Soc.* (*A*), 1966, 896.

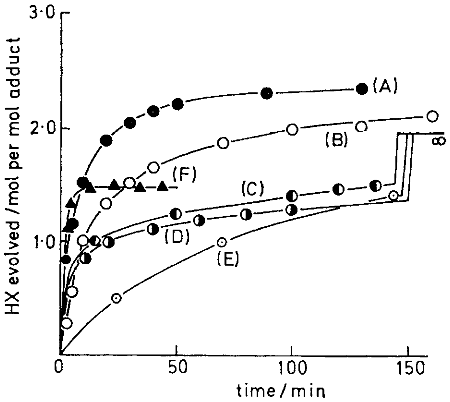
parallels in the corresponding boron trichloride systems. Dehydrohalogenation of primary aromatic amine–boron trichloride adducts usually yields cyclic borazines as the major reaction products.[3-5]

We have investigated the mechanism of orthoboronation and will suggest why its occurrence is more favoured in boron iodide systems than in the other boron halide systems.

RESULTS AND DISCUSSION

New Adducts.—The adducts of acetonitrile, *o*-toluidine, *N*-methylaniline, aniline, *p*-iodoaniline, and 2,6-di-iodoaniline, with boron tri-iodide have been prepared and their spectra showed them to have structures similar to those for the other BX_3 adducts, whose constitution has been thoroughly discussed.[5-7]

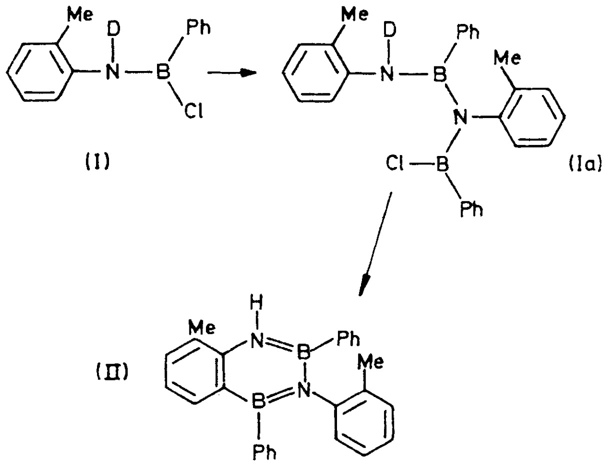
Dehydrohalogenation.—The rate of dehydrohalogenation of adducts of boron trichloride and boron tri-iodide is illustrated in the Figure. The marked increase in reactivity of the iodides is also reflected in a difference in the final products of dehydrohalogenation. Unfortunately the dehydrohalogenation kinetics of the boron tri-iodide adducts are too fast to measure quantitatively and the reaction appears to proceed without any kinetically distinguishable steps (Figure). However, a parallel system which dehydrohalogenates almost exclusively (>90%) to yield a diazadiboranaphthalene is that of the adduct *o*-toluidine–phenyldichloroborane. The rate of this reaction was measurable and intermediates could be isolated. The mechanism of this reaction is discussed and compared with the mechanism of borazine formation.



The rate of evolution of hydrogen halide from aromatic amine–boron trihalide adducts in boiling benzene; (A), *o*-toluidine–tri-iodoborane; (B), aniline–tri-iodoborane; (C), *o*-toluidine–phenyldichloroborane; (D), *o*-toluidine–trichloroborane; (E), aniline–trichloroborane (from ref. 9, boiling toluene); (F), 2,6-di-iodoanilne–tri-iodoborane

Mechanism of Orthoboronation.—*o*-Toluidine–phenyldichloroborane forms *o*-toluidino(phenyl)chloroborane in the presence of triethylamine in benzene at 20 °C; refluxing *o*-toluidino(phenyl)chloroborane in the presence of an excess of triethylamine produces exclusively (>90%) 8-methyl-2,4-diphenyl-3-*o*-tolyl-1,3-diaza-2,4-diboranaphthalene. Thermal dehydrohalogenation follows the same reaction sequence, but much more slowly. Tris-*B*-phenyl-tris-*N*-*o*-tolylborazine is formed in trace amounts in both the thermal and base catalysed dehydrohalogenation.

The mechanism of rearrangement of *o*-toluidino(phenyl)chloroborane (I) was elucidated by studying the decomposition of *o*-toluidine–phenyldichloroborane which contained 55% *N*-deuterium. The first stage of dehydrohalogenation yielded (I) containing the same amount of *N*-deuterium.* The subsequent formation of (II) from (I) proceeds with total loss of deuterium (as triethylamine–deuterium chloride).



The only available source of ^1H would be the *o*-hydrogen displaced in ring boronation. It therefore appears that a C to N hydrogen transfer has occurred. Base molecules are known to reduce the yield of azaboranaphthalene relative to borazine;[8] it is likely therefore that the orthoboronation has some characteristics of an electrophilic displacement.

Hydrogen migration from the *ortho*-carbon to nitrogen accompanied by electrophilic attack at the *ortho*-carbon atom has been observed in the cyclisation of the adduct of phenyl acetylene and *B*-pentafluorophenyl-*N*-*p*-anisidyl borimide[9] and the mechanism of form-

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* The increase in *N*-deuterium content of (I) compared to the adduct, which would have established that *N*-hydrogen loss from the adduct was rate determining in the formation of (I), was not observable.

[3] W. Gerrard and E. F. Mooney, *J. Chem. Soc.*, 1960, 4028.

[4] R. G. Jones and C. R. Kinney, *J. Amer. Chem. Soc.*, 1939, **61**, 1378; W. Gerrard, H. R. Hudson, and E. F. Mooney, *J. Chem. Soc.*, 1962, 113.

[5] J. R. Blackborow and J. C. Lockhart, *J. Chem. Soc.* (*A*), 1969, 816.

[6] W. Gerrard, M. F. Lappert, and J. W. Wallis, *J. Chem. Soc.*, 1960, 2182.

[7] I. R. Beattie and T. Gilson, *J. Chem. Soc.*, 1964, 2292.

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

[9] P. I. Paetzold, G. Stohr, H. Maisch, and H. Lenz, *Chem. Ber.*, 1968, **101**, 2881.

ation of the 1,3-diaza-2,4-diboranaphthalene is considered a close parallel to that proposed for the cyclisation of the borimide adduct.

o-Toluidine–phenylchloroborane is considered to form the boronamine (Ia), which subsequently cyclises *via* electrophilic substitution of the terminal boron atom at the *ortho*-position of the *o*-toluidino-group. To accommodate hydrogen migration initial or concerted removal of the amino-hydrogen atom is conjectured.

Factors governing the Product Ratio: Borazine: 1,3-*Diaza*-2,4-*diboranaphthalene*.—Traces of borazines or their amino-derivatives were found in many reactions in which diazadiboranaphthalenes were formed almost exclusively. It may be useful to consider that the formation of these products is a competitive process and it is probable that both products are derived from the same intermediary boronamine. In the one case, cyclisation–elimination leads to diazadiboranaphthalene formation and in the other case, addition of a further aminoborane unit followed by cyclisation–elimination leads to the borazine. The reason why *o*-toluidinophenylchloroborane gives a much higher yield of diazadiboranaphthalene than *o*-toluidinodichloroborane may be that the mesomeric effect of the phenyl group on the terminal boron of the intermediate (Ia) labilises the loss of halide (as Cl^-) from this boron atom more than a chloride group would do: subsequent electrophilic orthoboronation would then be enhanced by this process. A similar comparison between the adducts aniline–trichloroborane (yielding exclusively tris-*B*-chlorotris-*N*-phenylborazine) and aniline–tri-iodoborane (yielding exclusively 2,4-di-iodo-3-phenyl-1,3-diaza-2,4-diboranaphthalene) leads to the same conclusion. Iodine is more easily displaced (as I^-) from a boronamine (to yield a boronium ion) than chlorine.

An intermediate of type (Ia) required by our mechanism was isolated from the dehydrohalogenation of 2,6-*di-iodoaniline–tri-iodoborane*. The dehydrohalogenation proceeds at various concentrations in benzene with the stoicheiometric elimination of 1·5 mol of HI per mole of adduct leaving in solution the product of empirical formula $C_{12}H_7B_2N_2I_7$. This substance is very reactive and decomposes even in the solid state to tris-(2,6-di-iodoanilino)borane. However if formulated as $I_2C_6H_3NH(BI),N(I_2C_6H_3)BI_2$, it is exactly the intermediate required in our mechanism of formation of diazadiboranaphthalenes. The dehydrohalogenation proceeds very quickly. No intermediate 2,6-di-iodo-anilinodi-iodoborane was detected by analytical or kinetic means.

The greatly enhanced reactivity of the boron tri-iodide adducts compared to the corresponding boron trichloride adducts (Figure) and the known lability of I^- as a leaving group prompted us to look for diamine boronium cations as possible intermediaries. To avoid dehydrohalogenation we investigated *NN*-dimethylarylamine adducts of boron tri-iodide. Although no aromatic amine was found sufficiently basic to stabilise $(RNMe_2)_2B^+I_2I^-$ as a stable solid, the ^1H n.m.r. and conductivity of the adducts of the stronger bases showed that a high degree of ionisation occurred in solution, accompanied by rapid amine and halogen exchange. Such ionisation is only present in boron trichloride adducts of primary and tertiary *o*-toluidines and these are the only adducts of boron trichloride (to date) which undergo orthoboronation.[10]

The Chemistry of 2,4-*Di-iodo*-3-*phenyl*-1,3-*diaza*-2,4-*diboranaphthalene and its Derivatives*.—The boron–iodine bonds of the diboradiaza-compounds are so easily ruptured that self condensation with elimination of hydrogen iodide proceeds rapidly in the solid state. Aminolysis and halogen exchange reactions are illustrated in the Experimental section.

CONCLUSION

The chemistry of aromatic orthoboronation is complex. Although we have argued that the formation of the intermediate (Ia) is essential, it is not unreasonable that this may be formed much faster for the iodide systems and by a different mechanism than for the phenylboron dichloride system. It is certainly true that (Ia) is not a commonly encountered polyaminoborane in boron trichloride chemistry.[8] The difficulty in handling derivatives of boron tri-iodide is considerable and we feel a better understanding of aminoiodoborane compounds can more quickly come from a study of the exchange reactions involved in the solution chemistry of these species.

EXPERIMENTAL

Acetonitrile (Mallinkrodt) was purified as described previously.[11] Boron tri-iodide was obtained from Koch–Light and was not purified further. Amines were dried and purified by the usual method. Experiments involving boron tri-iodide were performed using Schlenk techniques under an atmosphere of dry nitrogen. Phenylboron dichloride was prepared by standard routes. Spectroscopic properties of compounds prepared are given in the Table where appropriate.

Preparation of Adducts.—*Acetonitrile–tri-iodoborane*. Boron tri-iodide (9·8 g, 0·0250 mol) dissolved in sodium dried cyclohexane (100 ml) was mixed with acetonitrile (1·05 g, 0·0256 mol) in cyclohexane (20 ml) at −20 °C. A white precipitate formed and was immediately filtered and washed with cyclohexane. The precipitate was vacuum dried in a blackened vessel and stored under nitrogen in a blackened tube (Found: B, 2·55; I, 88·0. Calc. for $C_2H_3BI_3N$: B, 2·5; I, 88·0%).

Arylamine Adducts.—Aniline (2·37 g, 0·0255 mol) was slowly added to a stirred solution of boron tri-iodide (10·0 g, 0·0255 mol) in cyclohexane at −20 °C. The resulting cream coloured precipitate was filtered and washed with cyclohexane (Found: B, 2·2; I, 78·7. $C_6H_7BI_3N$ requires: B, 2·2; I, 78·55%).

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[10] J. R. Blackborow and J. C. Lockhart, *J. Chem. Soc.* (*A*), 1971, 1343.

[11] J. R. Blackborow and J. C. Lockhart, *J. Chem. Soc.* (*A*), 1968, 3015.

Spectroscopic data

Compound	Characteristic i.r. bands/cm^{-1}	^{1}H N.m.r. (τ)	^{11}B N.m.r.[a]	Mass spectral data [b]
o-Toluidinophenylchloroborane	NH 3380 BCl 905	Ar 2·0, 3·3 NH 3·70 CH_3 7·92		229 (1B, 1Cl) $229^+ \longrightarrow 214^+ + 15$ [c]
Bis(*o*-toluidino) phenylborane	NH 3390 3415	Ar 2·5, 3·4 NH 5·00 CH_3 7·85		312 (3B), 300 (1B), 193 (1B)
BBB-Triphenyl-*NNN*-tri-*o*-tolylborazine	BN 1400 1450	Ar 2·5, 3·4 CH_3 7·9	−23·5 (16)	579 (3B), 489 (3B), 412 (3B)
8-Methyl-2,4-diphenyl-3-*o*-tolyl-1,3-diaza-2,4-diboranaphthalene	NH 3390	Ar 2·0, 3·0 NH 4·87 CH_3 7·80	−31·5 (18)	386 (2B), 312 (3B),[d] 300 (1B) 193 (1B)
8-Methyl-2,4-diphenyl-3-*o*-tolyl-1,3-diaza-2,4-diboranaphthalene oxide	NH 3395			402 (2B), 312 (3B),[d] 300 (1B) 193 (1B)
2,4-Di-iodo-3-phenyl-1,3-diaza-2,4-diboranaphthalene	NH 3400vw	Ar 2·0, 3·5		458 (2B) Calc. 457·9123 Found, 457·9134 423 (2B) 331 (2B)
2,4-Dichloro-3-phenyl-1,3-diaza-2,4-diboranaphthalene	NH 3400	Ar 2·5, 4·0 NH 4·95	28 (20)	329 (2B, 1Cl), 272 (2B, 2Cl)
2,4-Difluoro-3-phenyl-1,3-diaza-2,4-diboranaphthalene	NH 3525	Ar 2·6, 3·6 NH 5·30	−26 (18) −31	242 (2B), 93
2,4-Difluoro-3-phenyl-1,3-diaza-2,4-diboranaphthalene hydrofluoride	3260 1120 NH_2 3285 BF 1130 3140			242 (2B), 224
2,4-Di-iodo-8-methyl-3-*o*-tolyl-1,3-diaza-2,4-diboranaphthalene	NH 3400	Ar 2·3, 3·3 NH 4·00 CH_3 (m)		486 (2B), 465 (2B), 444 (2B)
8-Methyl-2,4-di-*o*-toluidino-3-*o*-tolyl-1,3-diaza-2,4-diboranaphthalene	NH 3365 3410 3450	Ar 2·6, 3·4 NH 3·97 CH_3 7·64 5·73 7·81 6·18 7·91 8·06		444 $444^+ \longrightarrow 337^+ + 107$ [c]
3-Methyl-2-aminophenylboronic anhydride	NH 3400 OH 3580			266 (2B) Dimer 133 (1B) $266^+ \longrightarrow 133^+ + 133$ [c]
2-Aminophenylboronic anhydride	NH 3460 OH 3400 3300			238 Dimer

[a] Relative to BF_3,Et_2O, in p.p.m., half height widths are given in parentheses. [b] Characteristic fragments *m/e*, isotopic atoms are given in parentheses. [c] Metastable transitions observed (±1%). [d] Oxidation product $(PhBO)_3$.

The adducts of *p*-iodoaniline, *N*-methylaniline, 2,6-di-iodoaniline, and *o*-toluidine with boron tri-iodide were prepared in a similar manner.

		Found	Calc.
p-Iodoaniline–tri-iodoborane	$C_6H_6BI_4N$	B, 1·75; I*, 61·1	B, 1·75; I*, 62·3%
N-Methylaniline–tri-iodoborane	$C_7H_9BI_3N$	I, 76·0	I, 76·35%
2,6-Di-iodoaniline–tri-iodoborane	$C_6H_5BI_5N$	B, 1·45; I*, 51·4	B, 1·45; I*, 51·7%
o-Toluidine–tri-iodoborane	$C_7H_9BI_3N$	B, 2·2; I, 76·5	B, 2·15; I, 76·35%

I* = hydrolysable iodide.

Dehydrohalogenation of Aniline–Tri-iodoborane.—Aniline tri-iodoborane (0·2 mol) was refluxed in boiling benzene (200 ml) under a stream of dry nitrogen. The HI evolved was measured by titration as described elsewhere.[12]

When the evolution of HI ceased the solvent was quickly evaporated to dryness and yielded a pale yellow crystalline *solid* (Found: B, 4·55; I, 50·2. $C_{12}H_{10}B_2I_2N_2$ requires B, 4·75; I, 55·3%.† The mass spectrum showed a major ion *m/e* 457·9137 [$C_{12}H_{10}B_2I_2N_2$ requires 457·9123 (±2 p.p.m.)] and minor *m/e* values (3%) due to mono-, di-, and tri-*B*-amino-derivatives of tris-*B*-iodo-tris-*N*-phenylborazine (identified by the boron isotope contributions); no tris-*B*-iodo-tris-*N*-phenylborazine was observed.

This yellow solid when redissolved in benzene slowly precipitated a yellow powder and an iodine coloured solution. The *powder* was insoluble in most solvents (Found: C, 43·2; H, 4·35; N, 8·7; B, 4·75; I, 34%; black residue after combustion 9% of total wt.). The *powder* was hydrolysed by methanol to yield HI. Reaction of the powder with *p*-tolylmagnesium bromide yielded a *p*-tolylaniline. The mass spectrum of the *powder* consisted of peaks at *m/e* 127, 128, and 219 (*N*-iodoaniline) as the major fragments.

The yellow crystalline solid (0·1 mol) reacted with aniline (0·1 mol) to yield anilinium hydroiodide and a benzene soluble pale yellow crystalline solid (Found: C, 53·05; H, 4·5; N, 9·2; B, 4·7; I, 28·3. $C_{18}H_{16}B_2IN_3$ requires C, 51·2; H, 3·8; N, 9·7; B, 5·1; I, 30·1%).† The mass spectrum of this material showed a major peak at *m/e* 423 (*P*, 100 *P* − 1, 41·5, *P* − 2, 14·0, *P* + 1, 17·6%) and a metastable transition *m/e* 207·0 corresponding to $423^+ \longrightarrow 296^+ + I$ (127). The ^{1}H n.m.r. showed aromatic protons (τ 2·9—3·5) and a singlet NH (τ 5·13). ^{11}B n.m.r. showed a very broad peak at −25 p.p.m. [BF_3–$(C_2H_5)_2O$ = 0 p.p.m.] with half height width 18 p.p.m.

N-*Methylaniline–Tri-iodoborane and its Decomposition.*—

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† Attempted purification of these yellow crystalline products by recrystallisation or sublimation results in decomposition.

[12] J. R. Blackborow and J. C. Lockhart, *J. Chem. Soc.* (*A*), 1971, 49.

The addition of *N*-methylaniline (0·05 mol in 30 ml CH_2Cl_2) to boron tri-iodide [0·05 mol in light petroleum (100 ml b.p. 40—60 °C)] at −20 °C produced a yellow solution and a precipitate. The filtrate from this reaction yielded after evaporation of the solvent a yellow crystalline compound (Found: I, 76·0. $C_7H_9BI_3N$ requires I, 76·35%). The crystals decomposed within minutes at room temperature to yield a brown liquid and evolution of HI. The liquid was heated to 50° at 20 mmHg for 10 min to remove all the HI (Found: I, 66·5; B, 2·8. $C_7H_8BI_2N$ requires I, 67·3; B, 2·9%). The yellow precipitate from the initial reaction was refluxed in benzene; the cooled solution was filtered and the residue had the same i.r. absorption as *N*-methylanilinium hydroiodide. From the filtrate a small amount of brown crystalline solid was obtained. Mass spectrum showed a parent m/e of 350 (1 boron) [*Bis*(N-*methylanilino*)-*iodoborane* calculated m/e 350 (1 boron)].

Preparation and Reactions of o-*Toluidine–Phenyldichloroborane*.—The adduct was prepared in a similar manner to those described above (Found: B, 4·1; Cl, 26·7. $C_{13}H_{14}BCl_2N$ requires B, 4·05; Cl, 26·55%). o-*Toluidinophenylchloroborane* was prepared by adding triethylamine (2·5 g, 0·025 mol) to *o*-toluidine–phenyldichloroborane (6·6 g, 0·025 mol) dissolved in dichloromethane–benzene (100 ml 50/50 v/v). After 30 min the solvent was reduced to 30 ml and at 0 °C light petroleum (10 ml, b.p. 40—60 °C) was added. The triethylamine hydrochloride was removed by filtration and the removal of the solvent from the filtrate gave pure *o*-toluidinophenylchloroborane (Found: B, 4·8; Cl, 16·0. $C_{13}H_{13}BClN$ requires B, 4·7; Cl, 15·45%).

o-Toluidinophenylchloroborane (2·3 g, 0·007 mol) refluxed in triethylamine (4·0 g, 0·04 mol) and benzene (10 ml) (*and in the total absence of oxygen*) gave precipitation of triethylamine hydrochloride; after filtration and vacuum evaporation of the filtrate a yellow oil remained (Found: C, 79·9; H, 6·95; N, 7·1. $C_{26}H_{24}B_2N_2$ requires C, 80·9; H, 6·25; N, 7·25%). Sublimation of the product produced decomposition.

This product 8-methyl-2,4-diphenyl-3-*o*-tolyl-1,3-diaza-2,4-diboranaphthalene reacts with oxygen. One product $C_{26}H_{24}B_2N_2O$ was identified in the mass spectrometer, but there appear to be others.

N-*Deuterio*-o-*toluidine*.—This compound must be prepared without a trace of deuterium in the aromatic ring; to this end all reactions were carried out in basic solution. Deuterium chloride was generated *in situ* by allowing deuterium oxide to drip on to the acetonitrile–boron trichloride adduct. The gaseous acid was passed into *o*-toluidine in benzene (40% soln.) until precipitation of *o*-toluidinium deuteriochloride was complete. The solvent was then removed under vacuum and the solid deuteriochloride dissolved in an excess of sodium deuterioxide solution. The free amine was extracted with ether and dried over calcium chloride. Removal of the solvent ether yielded *N*-deuterio-*o*-toluidine containing 33% deuterium. This procedure was repeated and *N*-deuterio-*o*-toluidine containing *ca.* 55% of *N*-deuterium then was obtained. I.r. spectra revealed no absorption in the C–D stretching region.

The *o*-toluidine–phenyldichloroborane, *o*-toluidinophenylchloroborane, and diazadiboranaphthalene derivatives were prepared with the deuteriated amine as described above. The naphthalene derivative showed no trace of the presence of deuterium.

Reactions of 2,4-*Di-iodo*-3-*phenyl*-1,3-*diaza*-2,4-*diboranaphthalene and its Derivatives*.—*Halogen exchange reactions.* Aniline–tri-iodoborane was refluxed under nitrogen until 2·0 mol of hydrogen iodide had been evolved (monitored by continuous titration as described elsewhere).[12]

A slurry of freshly prepared silver chloride in benzene was added and the combined solutions refluxed for a further 30 min. The solution was then filtered and the filtrate evaporated to yield a colourless solid (Found: Cl, 22·1. $C_{12}H_{10}B_2Cl_2N_2$ requires Cl, 25·85%). This crude 2,4-*dichloro*-3-*phenyl*-1,3-*diaza*-2,4-*diboranaphthalene* could not be purified by further experimentation. The Table gives spectroscopic results on this crude product. 2,4-*Difluoro*-3-*phenyl*-1,3-*diaza*-2,4-*diboranaphthalene* was prepared using the same procedure with cadmium fluoride as the fluorinating agent.

Evaporation of 60% of the solvent from the filtrate of the fluorination reaction and addition of light petroleum (b.p. 40—60 °C) yields pale yellow microcrystals which are stable under nitrogen when dry (Found: C, 59·85; H, 4·3; N, 11·4; B, 8·6; F, 15·35. $C_{12}H_{10}B_2F_2N_2$ requires C, 59·6; H, 4·15; N, 11·6; B, 8·95; F, 15·7%). These crystals were dissolved in a minimum of dichloromethane: slow evaporation of the solvent (over two days) induced crystallisation on the vessel and a precipitation of a brown powder. The crystals were 2,4-*difluoro*-3-*phenyl*-1,3-*diaza*-2,4-*diboranaphthalene hydrofluoride* (Found: C, 55·0; H, 4·1; N, 11·1. $C_{12}H_{11}B_2F_3N_2$ requires C, 55·2; H, 4·25; N, 10·4%).

Hydrolysis Reactions.—2,4-Di-iodo-3-phenyl-1,3-diaza-2,4-diboranaphthalene (5 g) was dissolved in methanol–water then shaken with benzene. Gaseous hydrogen iodide was passed through the benzene layer and precipitation of a yellow solid occurred. The solution was filtered and evaporation of the filtrate yielded a white solid [Found: C, 62·4; H, 5·05; N, 11·1; B, 8·45. $(C_6H_6BNO)_n$ requires C, 60·6; H, 5·1; B, 9·05% o-*aminophenylboronic anhydride*]. The yellow precipitate was identified from its i.r. spectrum as *anilinium hydroiodide*. Removal of organic matter from the aqueous layer (at pH 8) with benzene and ether yielded on evaporation a white solid with essentially the same i.r. spectrum as boric acid. The products of hydrolysis of 2,4-*dichloro*-3-*phenyl*-1,3-*diaza*-2,4-*diboranaphthalene* were found to contain *anilinium hydrochloride*, o-*aminophenylboronic anhydride*, and *boric acid*.

2,4-*Di-iodo*-8-*methyl*-3-o-*tolyl*-1,3-*diaza*-2,4-*diboranaphthalene* hydrolysed in a similar manner to that described above, produced *o*-toluidinium hydroiodide, boric acid (identified by the i.r. spectra), and 2-amino-3-methylphenylboronic anhydride (i.r. D.M.S. card 3318) [Found: C, 63·7; H, 6·3; N, 10·4. Calc. for $(C_7H_8BNO)_n$: C, 63·3; H, 6·10; N, 10·5%].

Thermal Dehydrohalogenation Reactions.—The amine halogenoborane adduct was added to boiling benzene under nitrogen as described previously [12] and the liberation of hydrogen halide continuously monitored with sodium hydroxide solution; the rate of evolution of hydrogen halide is shown in the Figure.

Preparation of 2,4-*Di-iodo*-8-*methyl*-3-o-*tolyl*-1,3-*diaza*-2,4-*diboranaphthalene*.—*o*-Toluidine–tri-iodoborane (3·1 g, 0·006 mol) was dehydrohalogenated (as described above) until two moles of hydrogen iodide per mole of adduct had been evolved. The solvent was removed with suction to yield a viscous brown highly reactive oil (Found: I, 48·3. $C_{14}H_{14}B_2I_2N_2$ requires I, 52·3%). Mass spectral and ^1H n.m.r. analysis showed the oil was a mixture of the

(2,4-di-iodo)-, (2,4-*o*-toluidino, iodo)-, and (2,4-di-*o*-toluidino)-8-methyl-3-*o*-tolyl-1,3-diaza-2,4-diboranaphthalenes. Attempted purification of this product caused decomposition.

Aminolysis of the Crude Di-iodo-derivative.—Hydrogen iodide (0·01 mol) was removed from *o*-toluidine–tri-iodoborane (2·5 g, 0·005 mol) in a solution of boiling benzene, *o*-toluidine (1·0 g. 0·01 mol) was added. After 15 min the solvent was reduced to 25 ml and petroleum spirit (b.p. 40—60 °C, 3 ml) was added. The solution was filtered and the precipitate identified as *o*-toluidinium hydroiodide (i.r. spectrum). The filtrate was reduced to 5 ml and petroleum spirit (20 ml) added. Further filtration produced a filtrate from which white-green crystals were obtained on removing the bulk of the solvent (Found: C, 75·2; H, 6·9; N, 12·8. $C_{28}H_{30}B_2N_4$ requires: C, 75·7; H, 6·80; N, 12·6%), *8-methyl-*2,4-*di-o-toluidino-*3-*tolyl-*1,3-*diaza-*2,4-*diboranaphthalene.*

Dehydrohalogenation of 2,6-*Di-iodoaniline–boron Tri-iodide.*—The rate of dehydrohalogenation of the adduct (0·1 mol in 100 ml benzene) is shown in the Figure. After evolution of HI had ceased the bulk of the benzene (90 ml) was removed by suction, and light petroleum added (20 ml). Precipitation occurred after further removal of the bulk of the solution.

The precipitate was washed with light petroleum by decantation and vacuum dried, a yellow crystalline solid was obtained [Found: B, 2·0; I*, 37·3. $C_{12}H_7B_2N_2I_7$ requires: B, 2·2; I*, 38·5%; i.r. stretch 3400 cm^{-1} (NH); (I* = hydrolysable iodine)].

Physical Measurements.—I.r. spectra were recorded as Nujol mulls or neat oils. N.m.r. spectra were recorded on a Bruker Spectrospin spectrometer. Mass spectral data were collected from an MS9 high resolution spectrometer.

Thanks are due to Mr. J. Akitt for some n.m.r. spectra and Mr. P. Kelly for mass spectral data.

[2/1357 *Received*, 14*th June*, 1972]