12. *Reactions of Boron Halides, Phenylboron Dichloride, and* B-*Trichloroborazole with Some Organosilicon Amines.*

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Dialkylaminotrimethylsilanes react with boron trihalides and phenylboron dichloride to give a halogenotrimethylsilane and the corresponding aminoboron compound. *N*-Methylhexamethyldisilazane and *N*-trimethylhexamethylcyclotrisilazane react with boron trichloride and phenylboron dichloride to give a halogenosilane and the corresponding borazole. *B*-Trichloroborazole and diethylaminotrimethylsilane give *B*-trisdiethylaminoborazole, showing that such compounds can be made by a two-stage reaction of boron trichloride with silicon–nitrogen compounds.

THE use of silicon–nitrogen compounds as intermediates in the preparation of boron–nitrogen compounds from boron halides provides a useful route to compounds otherwise difficult to isolate. The method avoids the filtration difficulties involved when such compounds are prepared directly from the organic amines and covalent halides. This technique was first used with *N*-methyldisilazane and boron trifluoride [1] and trichloride.[2] The unstable adducts produced decomposed when warmed, to give the *B*-trihalogeno-*N*-trimethylborazole and halogenosilane.

During our work, dimethylaminotrimethylsilane was shown to react with boron trichloride and tribromide.[3] The mono- and bis(substituted amino)boron halides were produced for each halide, together with the trisaminoboron from boron trichloride and excess of aminosilane.

Dialkylaminotrimethylsilanes reacted with boron trichloride, tribromide, and tri-iodide to give the corresponding dialkylaminoboron dihalide in good yield.

$$\mathrm{R_2N{\cdot}SiMe_3 + BX_3 \longrightarrow R_2N{\cdot}BX_2 + Me_3SiX} \qquad (1)$$

(R = Et, Et, Bu^n, for X = Cl, Br, and I, respectively.)

Boron trichloride further reacted with two and three molar proportions of diethylaminotrimethylsilane to give bisdiethylaminoboron chloride and trisdiethylaminoboron.

$$\mathrm{2Et_2N{\cdot}SiMe_3 + BCl_3 \longrightarrow (Et_2N)_2BCl + 2Me_3SiCl} \qquad (2)$$

$$\mathrm{3Et_2N{\cdot}SiMe_3 + BCl_3 \longrightarrow (Et_2N)_3B + 3Me_3SiCl} \qquad (3)$$

Phenylboron dichloride reacted similarly with diethylaminotrimethylsilane to give bisdiethylamino(phenyl)boron.

$$\mathrm{2Et_2N{\cdot}SiMe_3 + PhBCl_2 \longrightarrow (Et_2N)_2BPh + 2Me_3SiCl} \qquad (4)$$

An attempt to produce ethylaminoboron dichloride by a similar method gave a good yield of the expected chlorotrimethylsilane, but the white crystalline product had not the correct analysis for $\mathrm{EtNHBCl_2}$. It appeared to have lost hydrogen chloride, possibly undergoing partial conversion into $\mathrm{(EtNBCl)_3}$. It is notable that such decomposition had not been observed for the compound $\mathrm{Me_3Si{\cdot}NH{\cdot}BCl_2}$.[4]

Hexamethyldisilazane is known to produce borazoles with all of the boron trihalides [3] and with organoboron dichlorides.[3,5] It also reacts with dialkylboron chlorides,[3] dimethylamino(phenyl)boron chloride,[5] and 2-chloro-1,3,2-benzodioxaborole [6] to give diborylamines.

We find that *B*-trichloro- and *B*-triphenyl-*N*-trimethylborazole can be prepared from

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[1] Sujishi and Witz, *J. Amer. Chem. Soc.*, 1957, **79**, 2447.

[2] Burg and Kuljian, *J. Amer. Chem. Soc.*, 1950, **72**, 3103.

[3] Noeth, *Z. Naturforsch.*, 1961, **16**, b, 618.

[4] (*a*) Becke-Goehring and Krill, *Chem. Ber.*, 1961, **94**, 1059; (*b*) Andrianov, Astakhin, and Kochkin, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1926, 1852.

[5] Jenne and Niedenzu, *Inorg. Chem.*, 1964, **3**, 68.

[6] Lappert and Srivastava, *Proc. Chem. Soc.*, 1964, 120.

both *N*-methylhexamethyldisilazane and the six-membered silicon–nitrogen ring compound *N*-trimethylhexamethylcyclotrisilazane in good yields by use of the appropriate halide.

$$3(\mathrm{Me_3Si})_2\mathrm{NMe} + 3\mathrm{RBCl_2} \longrightarrow (\mathrm{RBNMe})_3 + 6\mathrm{Me_3SiCl} \quad (5)$$

$$\mathrm{Me_2Si{\cdot}NMe})_3 + 3\mathrm{RBCl_2} \longrightarrow (\mathrm{RBNMe})_3 + 3\mathrm{Me_2SiCl_2} \quad (\mathrm{R} = \mathrm{Cl\ and\ Ph}) \quad (6)$$

Hexamethylcyclotrisilazane has been reported[3] to react with di-n-propylboron chloride to give $\mathrm{Pr^n{}_2B(NH{\cdot}SiMe_2)}_n\mathrm{Cl}$ where $n = 1$ and 3, but our work represents the first example of complete fission of all the silicon–nitrogen bonds. Attempts to produce bromoborazoles by similar methods resulted only in extensive decomposition.

The chlorine atoms in *B*-trichloroborazole can be completely replaced on treatment with diethylaminotrimethylsilane, to give *B*-trisdiethylaminoborazole.

$$3\mathrm{Me_3Si{\cdot}NEt_2} + (\mathrm{ClBNH})_3 \longrightarrow 3\mathrm{Me_3SiCl} + (\mathrm{Et_2N{\cdot}BNH})_3 \quad (7)$$

When freshly prepared, the boiling point and refractive index are in excellent agreement with previous values,[7] and a detailed analysis of the infrared spectrum also confirms the identity of the products.[8] These aminoborazoles are known to undergo deamination and subsequent polymerisation, and this probably accounts for the slightly low carbon analysis obtained by us.

EXPERIMENTAL

Interaction of Diethylaminotrimethylsilane and Boron Trichloride (*eqn.* 1).—Diethylaminotrimethylsilane (12·8 g., 1 mol.) was added dropwise to boron trichloride (10·4 g., 1 mol.) at 0°. The reaction was exothermic, and after 1 hr. at room temperature the mixture was refluxed for 2 hr. Distillation gave chlorotrimethylsilane, b. p. 57°, and diethylaminoboron dichloride as a colourless liquid (9·3 g., 72%), b. p. 144—145°, n_D^{20} 1·4392 (Found: C, 31·5; H, 6·6; N, 9·0. Calc. for $\mathrm{C_4H_{10}BCl_2N}$: C, 31·2; H, 6·5; N, 9·1%).

Interaction of Diethylaminotrimethylsilane and Boron Tribromide (*eqn.* 1).—Diethylaminotrimethylsilane (15·1 g., 1 mol.) was slowly added to boron tribromide (26·2 g., 1 mol.) at 0°. After warming to room temperature and standing for 1 hr., fractionation gave bromotrimethylsilane, b. p. 80°, and diethylaminoboron dibromide (16·3 g., 80%), b. p. 184°, n_D^{20} 1·4914, as a red liquid (Found: C, 19·0; H, 3·9; N, 5·6. Calc. for $\mathrm{C_4H_{10}BBr_2N}$: C, 19·8; H, 4·1; N, 5·8%).

Interaction of Di-n-butylaminotrimethylsilane and Boron Tri-iodide (*eqn.* 1).—Di-n-butylaminotrimethylsilane (5·2 g., 1 mol.) was added to boron tri-iodide (10·2 g., 1 mol.) at 0°. After refluxing overnight, distillation gave iodotrimethylsilane, b. p. 108°, and *di-n-butylaminoboron di-iodide* as a red liquid (6·8 g., 67%), b. p. 115—116°/2 mm., n_D^{20} 1·5449 [Found: C, 25·3; H, 4·7; N, 3·6%; *M* (ebullioscopic in benzene), 406. $\mathrm{C_8H_{18}BI_2N}$ requires C, 24·5; H, 4·6; N, 3·6%; *M*, 394].

Interaction of Diethylaminotrimethylsilane and Boron Trichloride (*eqn.* 2).—Diethylaminotrimethylsilane (38·3 g., 2 mol.) was added to boron trichloride (15·5 g., 1 mol.). Distillation gave chlorotrimethylsilane, and bisdiethylaminoboron chloride (19·6 g., 77%), b. p. 43—44°/0·1 mm., n_D^{20} 1·4542 (Found: C, 51·0; H, 10·5; N, 14·4. Calc. for $\mathrm{C_8H_{20}BClN_2}$: C, 50·5; H, 10·6; N, 14·7%).

Interaction of Diethylaminotrimethylmethylsilane and Boron Trichloride (*eqn.* 3).—Diethylaminotrimethylsilane (64·9 g., 3 mol.) was added to boron trichloride (17·5 g., 1 mol.) at 0°. Fractionation gave chlorotrimethylsilane, and trisdiethylaminoboron as a clear liquid (29·3 g., 87%), b. p. 45—46°/0·02 mm., n_D^{20} 1·4456 (Found: C, 63·8; H, 12·8; N, 18·3. Calc. for $\mathrm{C_{12}H_{30}BN_3}$: C, 63·4; H, 13·3; N, 18·5%).

Interaction of Diethylaminotrimethylsilane and Phenylboron Dichloride (*eqn.* 4).—Diethylaminotrimethylsilane (13·2 g., 2 mol.) was added to phenylboron dichloride (7·2 g., 1 mol.) slowly at −78°. The mixture solidified after addition of about a half of the aminosilane, and subsequent refluxing yielded chlorotrimethylsilane (61%). Vacuum distillation of the residue gave bisdiethylamino(phenyl)boron as a colourless liquid (7·9 g., 75%), b. p. 56°/0·001 mm., n_D^{20} 1·4991 (Found: C, 71·4; H, 11·2; N, 11·8. Calc. for $\mathrm{C_{14}H_{25}BN_2}$: C, 72·4; H, 10·85; N, 12·05%).

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[7] Gerrard, Hudson, and Mooney, *J.*, 1962, **113**.

[8] Gerrard, Hudson, Mooney, Stripp, and Willis, *Spectrochim. Acta*, 1962, **18**, 149.

Interaction of Ethylaminotrimethylsilane and Boron Trichloride.—Ethylaminotrimethylsilane (43·3 g., 1 mol.) was slowly added to boron trichloride (43·3 g., 1 mol.) at 0°. Dense white fumes were evolved and a white mass was formed. After refluxing for 2 hr., chlorotrimethylsilane (74%) was slowly removed by distillation, leaving a white residue. The solid was filtered off, washed with dry ether (3 × 20 ml.), and recrystallised from benzene, to give suspected ethylaminoboron dichloride (27·2 g., 59%), m. p. 240—246° (Found: C, 22·8; H, 7·0; N, 13·8. Calc. for $C_2H_6BCl_2N$: C, 19·1; H, 4·8; N, 11·1%). It appears that partial elimination of hydrogen chloride has occurred (Calc. for C_2H_5BClN: C, 26·9; H, 5·6; N, 15·7%).

Interaction of N-*Methylhexamethyldisilazane and Boron Trichloride* (*eqn.* 5).—*N*-Methylhexamethyldisilazane (38·9 g., 1 mol.) was added dropwise to boron trichloride (26·1 g., 1 mol.) at 0°. A vigorous exothermal reaction occurred, with formation of a bulky white precipitate and white fumes. After 1 hr. at room temperature the mixture became a yellow liquid. After refluxing for 2 hr. chlorotrimethylsilane (94%) was removed, and the residue cooled. This solidified, and after washing with dry ether (6 × 20 ml.) and drying (0·1 mm./4 hr.) it yielded *B*-trichloro-*N*-trimethylborazole (15·0 g., 89%), m. p. 160—161·5° (Found: C, 16·1; H, 4·0. Calc. for CH_3BClN: C, 16·0; H, 4·0%).

Interaction of N-*Trimethylhexamethylcyclotrisilazane and Boron Trichloride* (*eqn.* 6).—The cyclotrisilazane (17·60 g., 1 mol.) was dissolved in dry toluene (12 ml.) and slowly added to boron trichloride (23·80 g., 3 mol.) at 0°. This mixture was set aside overnight, and fractionation gave dichlorodimethylsilane (24·4 g., 93%), b. p. 70—72°, n_D^{20} 1·4074. Crystallisation from the remaining liquor gave *B*-trichloro-*N*-trimethylborazole (6 g., 40%), m. p. 160—162° (Found: C, 16·0; H, 4·9. Calc. for CH_3BClN: C, 16·0; H, 4·0%).

Interaction of N-*Methylhexamethyldisilazane and Phenylboron Dichloride* (*eqn.* 5).—Addition of the disilazane (6·35 g., 1 mol.) to the halide (5·17 g., 1 mol.) in toluene at room temperature followed by fractional distillation gave chlorotrimethylsilane (90%). White crystals were precipitated when the toluene solution cooled, giving *N*-trimethyl-*B*-triphenylborazole (3·1 g., 74%), which was recrystallised from benzene–light petroleum and dried for 6 hr. at 0·01 mm., m. p. 259—264° (Found: C, 70·5; H, 7·3. Calc. for C_7H_8BN: C, 71·75; H, 6·8%). The infrared spectrum agreed with that of an authentic sample.

Interaction of N-*Trimethylhexamethylcyclotrisilazane and Phenylboron Dichloride* (*eqn.* 6).—Phenylboron dichloride (21·70 g., 3 mol.) was added to the cyclosilazane (11·88 g., 1 mol.) in toluene (10 ml.) at room temperature. A little cloudiness soon cleared, and refluxing gave dichlorodimethylsilane (80%). Crystallisation occurred on cooling, and filtration, washing, and recrystallisation of this borazole (5·6 g., 32%) gave *N*-trimethyl-*B*-triphenylborazole, m. p. 263—266° (Found: C, 71·6; H, 7·5. Calc. for C_7H_8BN: C, 71·75; H, 6·85%).

Interaction of Diethylaminotrimethylsilane and B-*Trichloroborazole* (*eqn.* 7).—Diethylaminotrimethylsilane (21·4 g., 3 mol.) was added slowly to *B*-trichloroborazole (9·09 g., 1 mol.) in dry toluene at room temperature. An exothermic reaction occurred and fractionation gave chlorotrimethylsilane (92%). After distilling off the toluene, vacuum distillation of the residue gave crude *B*-trisdiethylaminoborazole (7·5 g., 54%). Redistillation gave the product as a colourless liquid, b. p. 110°/0·001 mm., n_D^{20} 1·4727 (Found: C, 46·9; H, 12·2. Calc. for $C_4H_{11}BN_2$: C, 49·1; H, 11·3%), which darkened on standing, possibly owing to deamination and polymerisation previously reported.[7] An orange polymeric residue (2·5 g.) remained after the redistillation.

The authors are grateful to the D.S.I.R. for financial support, and to Midland Silicones Ltd. for generous gifts of chlorosilanes.

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[*Received, June* 10*th*, 1964.]