559. *The Fission of Silicon–Sulphur Bonds in Organosilicon Compounds by Boron Trichloride and Phenylboron Dichloride*

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Silicon–sulphur bonds in organosilicon compounds appear invariably to undergo fission on attack by boron trichloride or phenylboron dichloride. Alkylchlorosilane is produced and the use of the appropriate organosilicon intermediate has given rise to trialkyl thioborate, bis-n-alkylthio chloroboronate, bis-n-alkylthio phenylboronate, triarylborthiin (triarylborsulphole) dithiaboracyclopentanes and boron sulphide.

The fission of silicon–sulphur bonds in organosilicon compounds by the action of covalent halides has revealed their use as synthetic intermediates in the preparation of a variety of sulphur compounds.[1,2] The present work describes the action of boron trichloride and phenylboron dichloride on a number of organosilicon sulphur compounds.

We find that cleavage of the silicon–sulphur bond invariably occurs in the reactions studied, with elimination of the appropriate alkylhalogenosilane and formation of the boron–sulphur derivative. The reactions were generally exothermic, and were frequently conducted at −78°.

Boron trichloride reacted with three equivalents of n-butylthiotrimethylsilane to give trimethylchlorosilane and tri-n-butyl trithioborate (reaction **1**).

$$3Me_3SiSBu^n + BCl_3 \longrightarrow 3Me_3SiCl + (Bu^nS)_3B \tag{1}$$

A similar reaction in a 2 : 1 molar ratio (reaction **2**) gave the expected di-n-butyl chlorodithioboronate, though in this case the yield was not good owing to disproportionation of the product during distillation.

$$2Me_3SiSBu^n + BCl_3 \longrightarrow 2Me_3SiCl + (Bu^nS)_2BCl \tag{2}$$

Further, the 1 : 1 reaction of boron trichloride and n-butylthiotrimethylsilane gave none of the expected n-butyl dichlorothioborinate, but only the corresponding chloroborinate and trithioborate.

A similar fission of the silicon–sulphur bond in ethylthiotrimethylsilane was achieved by phenylboron dichloride (reaction **3**) to give the bisethylthio phenylboronate.

$$PhBCl_2 + 2EtSSiMe_3 \longrightarrow 2Me_3SiCl + PhB(SEt)_2 \tag{3}$$

Hexamethyldisilthiane reacted very vigorously with boron trichloride. In a 3 : 2 molar ratio reaction (reaction **4**), removal of trimethylchlorosilane left boron sulphide as the pale yellow product.

$$3Me_3SiSSiMe_3 + 2BCl_3 \longrightarrow 6Me_3SiCl + B_2S_3 \tag{4}$$

The same reaction was carried out in a 3 : 1 molar ratio, in an effort to prepare tris-(trimethylsilyl) trithioborate (reaction **5**). The removal of trimethylchlorosilane left a pale yellow oil which appeared to be the expected product. In an effort to purify this by vacuum distillation, however, decomposition took place to give boron sulphide and hexamethyldisilthiane (reaction **6**).

$$3Me_3SiSSiMe_3 + BCl_3 \longrightarrow (Me_3SiS)_3B + 3Me_3SiCl \tag{5}$$

$$2(Me_3SiS)_3B \longrightarrow B_2S_3 + 3Me_3SiSSiMe_3 \tag{6}$$

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[1] E. W. Abel, D. A. Armitage, and R. P. Bush, *J.*, **1964**, **2455**.

[2] E. W. Abel, D. A. Armitage, and R. P. Bush, *J.*, **1965**, **62**.

Hexamethylcyclotrisilthiane reacted with phenylboron dichloride, the six-membered ring structure being preserved in the product, triphenylborthiin (reaction 7).

$$(Me_2SiS)_3 + 3PhBCl_2 \longrightarrow 3Me_2SiCl_2 + (PhBS)_3 \qquad (7)$$

In an effort to obtain a four-membered boron–sulphur ring, phenylboron dichloride was treated with tetramethylcyclodisilthiane. No four-membered boron ring was isolated, the boron–sulphur product again being triphenylborthiin.

The silicon–sulphur bonds in 2,2-dimethyl-1,3-dithia-2-silacyclopentane undergo fission with boron trichloride and phenylboron dichloride to give 2-chloro- and 2-phenyl-1,3-dithia-2-boracyclopentanes (reaction 8).

(8)

(R = Ph and Cl)

EXPERIMENTAL

All reactions were carried out under anhydrous conditions, and the alkylchlorosilanes evolved were characterised by boiling point and refractive index. Phenylboron dichloride,[3] alkylthiotrimethylsilanes,[4] hexamethyldisilthiane[5] and hexamethylcyclotrisilthiane[6] were prepared by reported methods.

Preparation of Tetramethylcyclodisilthiane.—Hexamethylcyclotrisilthiane was heated at 200° under reflux for 24 hr. The resulting tetramethylcyclodisilthiane was purified by sublimation (20°/0·01 mm.).

Preparation of 2,2-*Dimethyl*-1,3-*dithia*-2-*silacyclopentane.*—The lead derivative of ethane-1,2-dithiol was prepared by the interaction of approximately equimolar amounts of lead acetate and the dithiol in aqueous ethanol. After copious washing with water the cream-coloured powder was thoroughly dried over phosphorus pentoxide, and then heated under reflux with dimethyldichlorosilane (slight excess). The mixture was filtered and the precipitate washed with dimethyldichlorosilane. Distillation of the combined filtrate and washings produced 2,2-dimethyl-1,3-dithia-2-silacyclopentane[7] (57%), m. p. 10°, b. p. 188°, n_D^{20} 1·5534 (Found: C, 32·2; H, 6·5. Calc. for $C_4H_{10}S_2Si$: C, 32·0; H, 6·7%).

Interaction of n-Butylthiotrimethylsilane and Boron Trichloride (*Reaction* 1).—The thiosilane (13·83 g.) was added to boron trichloride (3·35 g.) at −78°. After the reaction mixture had been allowed to warm to room temperature, distillation gave trimethylchlorosilane (82%) and tri-n-butyl trithioborate[8] (5·6 g., 71%), b. p. 140°/0·01 mm., n_D^{20} 1·5227 (Found: C, 51·3; H, 9·9. Calc. for $C_{12}H_{27}S_3B$: C, 51·8; H, 9·7%), as a colourless oil.

Interaction of n-Butylthiotrimethylsilane and Boron Trichloride (*Reaction* 2).—The thiosilane (10·75 g.) and boron trichloride (3·92 g.) were carefully mixed at −78°, and allowed to warm to room temperature. Volatile material was removed at 20°/15 mm., and trapped, to give on distillation trimethylchlorosilane (94%). Vacuum distillation of the residual oil gave di-n-butyl chlorodithioborinate (1·00 g., 13·5%), b. p. 85°/0·01 mm., n_D^{20} 1·5052 (Found: C, 42·9; H, 8·7. Calc. for $C_8H_{18}S_2BCl$: C, 42·7; H, 8·0%). A considerable amount of boron trichloride was evolved during the distillation, and the residual oil was distilled to yield tri-n-butyl trithioborate (3·42 g.), b. p. 140°/0·01 mm., n_D^{20} 1·5215.

Interaction of Ethylthiotrimethylsilane with Phenylboron Dichloride (*Reaction* 3).—The dichloride (3·40 g.) was added to the thiosilane (5·72 g.) without any rise in temperature being noted. When heat was applied trimethylchlorosilane (78%) was distilled off in 3 hr. Subsequent vacuum distillation of the residual liquid gave *diethyl phenyldithioboronate* (2·5 g.,

[3] J. E. Burch, W. Gerrard, M. Haworth, and E. F. Mooney, *J.*, 1960, 4916.

[4] E. W. Abel, *J.*, 1960, 4406.

[5] E. W. Abel, *J.*, 1961, 4933.

[6] T. Nomura, M. Yokoi, and K. Yamasaki, *J. Amer. Chem. Soc.*, 1955, **77**, 4484.

[7] F. P. Richter and B. A. Orkin, U.S.P. 2,590,039/1952 (*Chem. Abs.*, 1952, **46**, 5892); M. Schmidt and M. Wieber, *Z. Naturforsch.*, 1963, **18**b, 846.

[8] M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1961, **83**, 1345; B. M. Mikhailov and T. A. Shchegoleva, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1959, 1868.

56%), b. p. 82—84°/0·05 mm., n_D^{19} 1·5779 (Found: C, 56·7; H, 6·40. $C_{10}H_{15}BS_2$ requires C, 57·15; H, 7·15%). This particular ester appears to be previously uncharacterised but the class of compound $PhB(SR)_2$ is already known.[9]

Interaction of Hexamethyldisilthiane with Boron Trichloride (*Reaction* 4).—The disilthiane (6·14 g.) was added to boron trichloride (2·7 g.) at −78°. After the mixture had warmed to room temperature, distillation gave trimethylchlorosilane (86%), and a yellow solid. After being washed with anhydrous ether, and subsequent pumping (20°/0·01 mm.) to constant weight, the boron sulphide (Found: B, 18·7. Calc. for B_2S_3: B, 18·4%) was obtained as an off-white powder, which reacted violently with water to liberate hydrogen sulphide.

Interaction of Boron Trichloride with Hexamethyldisilthiane (*Reaction* 5).—To boron trichloride (1·6 g.) was added hexamethyldisilthiane (7·3 g.) slowly at −78°. After being slowly warmed to room temperature the mixture was pumped at 25°/0·01 mm. After distillation the condensate yielded trimethylchlorosilane (72%). The residual yellow oil decomposed upon attempted vacuum distillation to yield hexamethyldisilthiane (85%, reaction 6) and boron sulphide (98%, reaction 6).

Interaction of Hexamethylcyclotrisilthiane with Phenylboron Dichloride (*Reaction* 7).—The dichloride (11·05 g.) was added to the silthiane (6·25 g.) at room temperature. When the reaction mixture was heated to 180° dimethyldichlorosilane (82%) distilled off during 6 hr. The residue became completely solid upon cooling, and after being twice recrystallised from anhydrous benzene gave triphenylborthiin[10] (2 g., 25%), m. p. 233—235° (Found: C, 60·3; H, 4·3. Calc. for $C_{18}H_{15}B_3S_3$: C, 60·0; H, 4·16%).

Interaction of Tetramethylcyclodisilthiane with Phenylboron Dichloride.—The dichloride (7·07 g., 2 mols.) was added to tetramethylcyclodisilthiane (4·0 g., 1 mol.) in toluene (30 c.c.) at room temperature. The mixture was then heated, dimethyldichlorosilane (81%) being removed by distillation. After removal of toluene (30°/0·01 mm.), the pale yellow residue was crystallised from benzene to give triphenylborthiin (2·0 g., 38%), m. p. 234—236°, having an infrared spectrum identical with that of the product of the previous experiment. No trace of any four-membered boron-sulphur ring was found at any stage of the work-up.

Interaction of Boron Trichloride with 2,2-*Dimethyl*-1,3-*dithia*-2-*silacyclopentane* (*Reaction* 8, R = Cl).—The silacyclopentane (19·35 g.) was added to boron trichloride (15·15 g.) in light petroleum (b. p. 100—120°; 50 c.c.) at −78°. A vigorous reaction took place, and subsequent distillation yielded dimethyldichlorosilane (97%), light petroleum, and finally 2-chloro-1,3-dithia-2-boracyclopentane[11] (11·2 g., 59%), b. p. 65°/10 mm., n_D^{23} 1·5760 (Found: C, 17·6; H, 2·9. Calc. for $C_2H_4S_2BCl$: C, 17·4; H, 2·9%).

Interaction of Phenylboron Dichloride with 2,2-*Dimethyl*-1,3-*dithia*-2-*silacyclopentane* (*Reaction* 8, R = Ph).—The addition of the dichloride (5·54 g.) to the silacyclopentane (5·23 g.) caused considerable evolution of heat and the mixture boiled under reflux. Subsequent distillation gave dimethyldichlorosilane (77%), and 2-phenyl-1,3-dithia-2-boracyclopentane[11] (4·4 g., 70%), b. p. 83—84°/0·01 mm., n_D^{20} 1·6373 (Found: C, 53·3; H, 4·8%; *M*, 180. Calc. for $C_8H_9BS_2$: C, 53·4; H, 5·0%; *M*, 180).

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