Tetrakis(dialkoxyboryl)silanes

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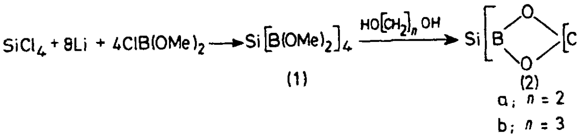
Summary Tetrakis(dimethoxyboryl)silane has been synthesized from silicon tetrachloride, lithium, and dimethoxyboron chloride, and the boron–silicon bonds have been found highly susceptible to oxidative or hydrolytic cleavage, yet sufficiently stable to survive transesterification of the boronic ester with ethylene glycol.

KNOWN compounds containing boron–silicon bonds are limited in variety.[1] Our synthesis of tetrakis(dialkoxyboryl)methanes[2,3] and related syntheses of tetrakis(trimethylsilyl)silane[4] and tetrakis(diphenylboryl)stannane[5] suggested the possibility of making tetrakis(dialkoxyboryl)silanes.



Our synthesis of tetrakis(dimethoxyboryl)silane (**1**) follows the route used for the carbon analogue,[2,3] except that the thermal instability of (**1**) prohibits distillation and it was therefore necessary to devise a new isolation technique. Transesterification of (**1**) with diols yielded cyclic boronic esters (**2**).

The experimental procedure described for tris(dimethoxyboryl)methane[3] was followed, with silicon tetrachloride in place of chloroform and lithium dispersion washed free of mineral oil. Crude (**1**) was dissolved in ether and the gummy by-product was filtered off, the solution was concentrated *in vacuo*, and the cycle was repeated with 1:1 ether–light petroleum, yield 63% of solid (**1**), which was stable to storage under nitrogen at −15 °C for a year. *Caution:* The gummy by-product is pyrophoric on standing, and pure (**1**) ignites on contact with water in the presence of air. Although (**1**) decomposed on attempted distillation, 1 g was successfully sublimed below 50 °C (0·1 Torr), m.p. 58—60 °C, δ 3·54 (s, OMe).

Treatment of a 10% solution of (**1**) in tetrahydrofuran with ethylene glycol precipitated tetrakis(ethylenedioxyboryl)silane (**2a**) (72%), which was handled in a glove box and sublimed at 180 °C (0·1 Torr); δ 4·27 (s, OCH_2); satisfactory C, H, B, and Si analyses; m.p. > 400 °C (sealed tube), apparently because of polymerization. (The carbon analogue melts at 182 °C[6]). Propane-1,3-diol and (**1**) in ether yielded (**2b**) (41%); ^1H n.m.r. spectrum as expected; ^{11}B n.m.r. resonance at −37·1 p.p.m. from BF_3–Et_2O; satisfactory C, H, B, and Si analyses; m.p. > 400 °C.

Benzaldehyde is reduced by (**1**) but not by (**2a**) in a few days at 25 °C to a mixture of products. Methanol attacks (**1**) vigorously, but 5% methanol in dichloromethane left (**1**) unchanged after 1·5 h under reflux. Although (**2a**) is less reactive than (**1**), (**2a**) also ignites on contact with water.

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