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Preliminary communication

Formation of boron–carbon bonds through silyl derivatives*

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SUMMARY

The synthesis of new *B*-substituted boron heterocycles can be achieved in high yields by using silyl ether derivatives of hydroxyboron compounds as intermediates. This method has numerous advantages over previous techniques; in particular it permits the use of organolithium reagents.

Recently considerable theoretical[1] and biological[2] interest has been shown in the chemistry of the organic boron compounds. Up to now boron–carbon bonds have been formed by the action of Grignard reagents on a *B*-halogen substituted derivative[3] or on the n-butyl ether of a *B*-hydroxylated heterocycle[4]. However, in the case of many boron heterocycles, especially borazarothienopyridines[4] and borazarofuropyridines[5], the halogen compounds are unknown and obtaining the desired products through the alkyl ethers is somewhat difficult. Indeed, these butyl ethers are unstable and must be prepared by refluxing the hydroxy compounds with butanol and then reacting the crude ether with Grignard reagent; this latter must be used in excess owing to the presence of contaminating n-butanol. Moreover, under these conditions the yields are often poor and the use of an organolithium reagent is precluded.

We have found that the replacement of the alkyl ethers by trimethylsilyl ethers has a number of advantages over previous methods. These silyl derivatives are obtained quantitatively by treating bis(trimethylsilyl)acetamide (BSA) with hydroxyboron derivatives. They are crystalline stable products in the absence of moisture. A few of these derivatives are compounds Ia–Id. The boron–carbon bond is obtained by the action of a

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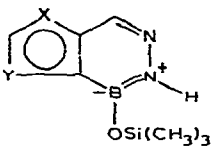
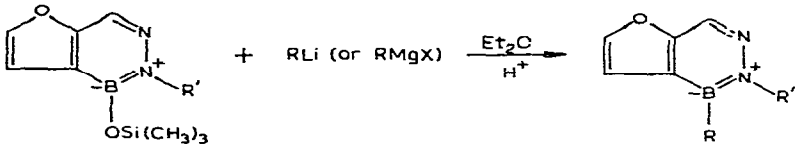


Ia (X = O, Y = CH; m.p. 58–60°)
Ib (X = S, Y = CH; m.p. 65°)
Ic (X = CH, Y = S; m.p. 79°)
Id (X = CH=CH, Y = CH; m.p. 95–96°)

Grignard reagent or, when this is difficult to prepare, by treating an organolithium compound with the above-mentioned silyl ethers:



By this method highly strained compounds such as (V) and (VI) could be prepared in high yields:

	R'	R	m.p. (°C)	Yield (%)
II	H	C_6H_5	104–105	81
III	H	p-$(CH_3)_2N$–C_6H_4	174–177	81
IV	CH_3	CH_3	liq.	80
V	C_6H_5	C_6H_5	95–96	89
VI	C_6H_5	CH_3	liq.	85

Preparation of [4-p-dimethylamino]-4,5-borazarofuro[2,3-c] pyridine (III). 4-Hydroxy-4,5-borazarofuro[2,3-*c*] pyridine[5] (0.0169 mol) was dissolved in 50 ml of acetonitrile. A solution of BSA (0.025 mol) in 20 ml of acetonitrile was added dropwise. The mixture was refluxed for 2 h. The solution was evaporated *in vacuo*. Recrystallization from ether gave white crystals of (Ia).

The ether solution of the organolithium reagent (0.016 mol), prepared by standard methods from *p*-bromodimethylaniline and lithium, was added slowly at 0° to a solution of (Ia) (0.0144 mol) in ether. The mixture was refluxed for 2 h. The solution was poured into 100 ml of ice and water, acidified with HCl, and extracted with several portions of ether. The combined extracts were dried and evaporated *in vacuo*. Recrystallization from ether gave brown crystals of (III) m.p. 174–177°.

Satisfactory analyses were obtained for all the compounds investigated; full experimental details and discussion will be reported later.

The stability of the silyl compounds compared with the alkyl ethers must be due

to the delocalization of the lone pair of oxygen in an empty atomic orbital of π symmetry of silicon[6].

In conclusion, the easy formation of carbon–boron bonds through silyl ethers is of general interest in heterocyclic boron chemistry. Further studies on the extension of this method to compounds containing a boron–oxygen bond[7] and to the synthesis of boron analogues of nucleotides are in progress.

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