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Preliminary communication

HOMOLOGATION OF BORONIC ESTERS WITH TRIMETHYLSILYLCHLOROMETHYLLITHIUM

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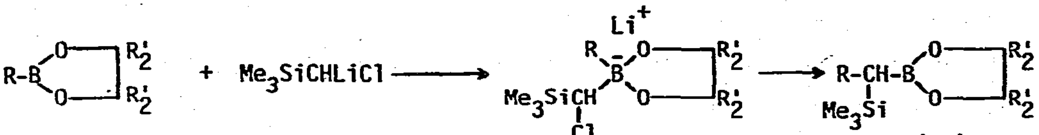
Summary

Trimethylsilylchloromethyllithium adds to boronic esters to form ate complexes which rearrange with displacement of chloride to form the homologous α-trimethylsilyl boronic esters in high yields.

Homologation is a well established operation in trialkylborane chemistry. Among the earlier of numerous examples are carbonylation of R_3B with CO [1,2] and conversion of R_3B to RCH_2BR_2 with $Me_2S^+CH_2^-$ [3]. A variety of α-halo carbanions, $Y\bar{C}H$-X, insert YCH into the carbon-boron bond of R_3B [4], and $(PhS)_2CH^-$ readily converts R_3B to $RCH(SPh)BR_2$ [5-7]. If similar reactions could be carried out with boronic esters, $RB(OR')_2$, there would be the synthetic advantage of full utilization of the single R group. Ate complexes derived from α-halo boronic esters do rearrange in the desired fashion [8-10], but the ate complex derived from $(PhS)_2CHB(OR')_2$ by S-methylation followed by treatment with butyllithium yielded more cleavage products than it did $C_4H_9CH(SPh)B(OR')_2$ [11]. We began the present work with a number of fruitless attempts to homologate $RB(OR')_2$ with PhSCHLiX, where X = SR, SR_2^+, NMe_3^+, or Cl, but in all cases the ate complex if formed dissociated to PhSCH, which dimerized to the isolated product PhSCH=CHSPh.

Trimethylsilylchloromethyllithium, $Me_3SiCHLiCl$, is easily prepared from commercially available reagents [12] and is not prone to carbene formation. (We thank Professor George Rubottom of the University of Idaho for suggesting this reagent.) The analogous $Me_3SiCHLiBr$ has been reported to homologate trialkylboranes by Larson and coworkers [13].

Reaction of boronic esters (I) with $Me_3SiCHLiCl$ consistently yielded 75-87% of the homologous α-trimethylsilyl boronic esters (II).



(I) (a) R' = H; (b) R' = CH_3

(II)

Typical results are summarized in Table I.

Table I. Homologation of Boronic Esters (I) to α-Trimethylsilyl Boronic Esters (II).

R	R'	(II) b.p., °C/Torr	NMR: SiCHB, δ	% Yield
n-Butyl	H	80-84/4	0.35	87
sec-Butyl	H	86-90/5	0.16	85
Cyclopentyl	H	96-99/4	0.5	80
Cyclohexyl	H	72-75/1	0.3	81
Benzyl	H	80-85/0.1	0.73	77
$PhSCH_2$-	H	108-110/0.05	0.83	80
Allyl	CH_3	90-94/4	0.33	78
$CH_3CH=CH$-	CH_3	86-90/3.5	1.50	75

In the typical experimental procedure, 2.25 g (18.4 mmol) of chloromethyltrimethylsilane in 24 mL of anhydrous tetrahydrofuran was stirred at -78°C under argon during the dropwise injection of 20.3 mmol of sec-butyllithium in cyclohexane, followed by injection of ∿20 mmol of tetramethylethylenediamine [12]. After 45 min, the mixture was warmed to -55°C and 14 mmol of the boronic ester (I) in 5 mL of tetrahydrofuran was injected. After 10 min at -55°C (or immediately for R = $PhSCH_2$) the cooling bath was refilled with Dry Ice and the mixture was allowed to reach room temperature slowly as the bath warmed. After stirring overnight, the mixture was treated with aqueous hydrochloric acid and extracted with ether/dichloromethane 5:1. The ethylene glycol esters (IIa) were treated with additional ethylene glycol before distillation. Pinacol esters (IIb) were fully stable to the work-up conditions. All structures were confirmed by elemental analyses (C, H, B, Si) and proton NMR spectra (in CCl_4). The prominent CH_3Si peak appeared at δ 0, peaks characteristic of R and R' were observed, and the broad $BC\underline{H}Si$ doublets or partially resolved triplets appeared as listed in Table I.

Although we have prepared $Me_3SiCH_2BO_2C_2(CH_3)_4$ and found that it can be deprotonated easily with lithium 2,2,6,6-tetramethylpiperidide [14], substituted α-trimethylsilyl boronic esters have proved resistant to the usual deprotonation conditions, and their other chemistry remains to be explored.

Acknowledgment

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