Deprotonation of a Trimethylsilylmethaneboronic Ester

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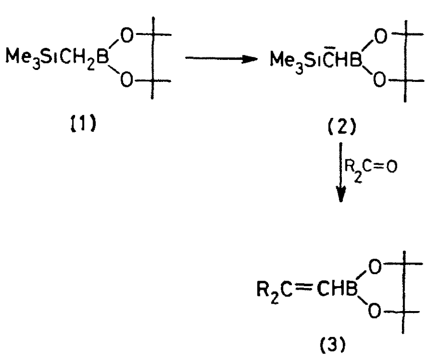
Summary. Deprotonation of pinacol trimethylsilylmethaneboronate yields an anion which reacts with carbonyl compounds to form alkeneboronic esters, or with alkyl halides to form α-trimethylsilylalkaneboronic esters.

Deprotonation of *gem*-diboronic esters[1] or α-phenylthiomethaneboronic esters[2] yields carbanions useful in synthesis. We have now extended this chemistry to the readily accessible pinacol trimethylsilylmethaneboronate (**1**).

Trimethylsilylmethylmagnesium chloride,[3] added concurrently with trimethyl borate to diethyl ether stirred at −78 °C followed by aqueous work-up led to trimethylsilylmethaneboronic acid (65—75% yield), which was esterified with pinacol[2] to yield (**1**), b.p. 70—72 °C (12 Torr). Treatment of (**1**) with lithium 2,2,6,6-tetramethylpiperidide and tetramethylethylenediamine in tetrahydrofuran at 0 °C[2] yielded a solution of the anion (**2**), which was alkylated efficiently by alkyl halides (see Table). Carbonyl compounds condensed with (**2**) with exclusive elimination of the silicon component to form alkene–boronic esters (**3**) (see Table). Products were isolated by distillation and characterised by ^{1}H n.m.r. spectra and elemental analyses



TABLE

Reactions of pinacol trimethylsilylmethaneboronate anion (**2**)

Reactant	Product	% Yield
n-$C_5H_{11}Br$	n-C_5H_{11}–$CH(SiMe_3)BO_2C_2Me_4$	85
$PhCH_2Br$	$PhCH_2$–$CH(SiMe_3)BO_2C_2Me_4$	83
$PhCH_2CH_2I$	$PhCH_2CH_2$–$CH(SiMe_3)BO_2C_2Me_4$	79
n-$C_6H_{13}CHO$	n-$C_6H_{13}CH{=}CHBO_2C_2Me_4$ (mostly *cis*)	73
PhCHO	$PhCH{=}CHBO_2C_2Me_4$ (mostly *cis*)	84
$CH_2[CH_2]_4$-C=O	$CH_2[CH_2]_4C{=}CHBO_2C_2Me_4$	87
$Bu^n_2C{=}O$	$Bu^n_2C{=}CHBO_2C_2Me_4$	74

The exclusive elimination of silicon was unexpected in view of the ease of elimination of boron in other systems.[4] However, ^1H n.m.r. spectra of the distilled alkeneboronic esters revealed no methylsilyl peak at δ 0, implying complete loss as hexamethyldisiloxane.

A further unexpected result was the predominance of the *cis* isomer in the alkeneboronic esters derived from aldehydes. The α-proton of *cis* pinacol 2-phenylethene-boronate, $PhCH{=}C\mathit{H}BO_2C_2Me_4$, appeared in the n.m.r. spectrum at δ 5·53, *J* 16 Hz and of the *trans* isomer at δ 6·12, *J* 18 Hz,[5] in a *ca.* 2 : 1 ratio. Similarly, for pinacol oct-1-eneboronate, the *cis* α-proton is at δ 5·34, *J* 14 Hz and the *trans* α-proton at δ 5·44,[5] *J* 18 Hz, ratio 2 : 1. This stereochemistry contrasts with that of the condensation of diborylmethide ions with aldehyde, which yields >90% *trans* alkeneboronic esters.[5]

We thank the National Science Foundation for support.

(*Received, 2nd October* 1979; *Com.* 1056.)

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