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**Preliminary communication** 

## **Reactions of borinic esters with (1,1-dichloroalkyl)lithium.** A facile synthesis of tertiary carbinols

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## Abstract

The reaction of various borinic esters with (1,1-dichloroalkyl)lithium, LiCRCl<sub>2</sub> (R = phenyl, methyl), followed by the treatment of base and hydrogen peroxide is a facile route to tertiary carbinols.

(Dichloromethyl)lithium, LiCHCl<sub>2</sub>, has recently been shown to be a highly efficient reagent to achieving C-C bond formation via organoboranes. This new methodology is useful for the synthesis of chiral secondary alcohols from boronic esters [1], for the synthesis of homologated primary and secondary alcohols from boronic esters, borinic esters and trialkylboranes [2], as well as for the synthesis of 1,4-alkanediols from 2-alkyl- and 2-alkoxy-1,2-oxaborolanes [3]. The homologation of boronic esters to the corresponding  $\alpha$ -chloro-boronic esters by (1,1-dichloroalkyl)lithium has also been described [4]. Here we present a novel route to tertiary carbinols by the reaction of various borinic esters with (1,1-dichloroalkyl)-lithium.

The reaction of borinic esters 1 with  $LiCRCl_2$  (2) proceeds via the ate complex 3 at -100 °C in THF, subsequent 1,2-migration of the two alkyls gives the intermedi-

ates 4 on warming to room temperature. The intermediates 4 were treated with alkaline hydrogen peroxide to give tertiary alcohols 5 (eq. 1). The 1,4-alkanediols and 9-bicyclo[3.3.1]nonanols were prepared by the reaction of either 2-alkyl-1,2-

Entry	Substrate 1	R of 2	Product "	Yield (%)
a	В-ОСН3	C <sub>6</sub> H <sub>5</sub>	C-C <sub>6</sub> H <sub>5</sub>	72
Ъ	B-OCH3	CH <sub>2</sub>	С-СН3	86
с	$(c-C_6H_{11})_2BOCH_3$	$C_6H_5$	$(c-C_6H_{11})_2CC_6H_5$   OH	74
d	(n-C <sub>6</sub> H <sub>13</sub> ) <sub>2</sub> BOCH <sub>3</sub>	CH <sub>3</sub>	$(\mathbf{n}-\mathbf{C}_{6}\mathbf{H}_{13})_{2}\mathbf{CCH}_{3}$   OH	67
e	$\sim$	C <sub>6</sub> H <sub>5</sub>	$\begin{array}{c} CH_2CH_2CH_2C(C_6H_5)(c-C_6H_{11})\\  \\ OH\\ OH\end{array}$	62
f		CH3	$\begin{array}{c} CH_2CH_2CH_2C(CH_3)(c-C_6H_{11})\\  \\ OH \\ OH \end{array}$	61
h	B-(CH <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	$\begin{array}{c} CH_2CH_2CH_2C(C_6H_5)(n-C_7H_{15})\\  \\ OH\\ OH\end{array}$	67

Synthesis of tertiaryl alcohols and 1,4-alkanediols

<sup>a</sup> All products were identified by <sup>1</sup>H NMR, 1R and MS spectroscopy. <sup>b</sup> Isolated yield.

oxaborolanes or 9-methoxy-9-borabicyclo[3.3.1]nonane with  $LiCRCl_2$  in the same way. The results are listed in Table 1.

In a typical procedure, a slurry of (1,1-dichloroalkyl)lithium in 20 ml of THF was prepared at -100 °C by a published procedure \*. Alkyl borinate [6] (10 mmol) or 2-alkyl-1,2-oxaborolane [3] (10 mmol) was added in one portion at -100 °C with stirring. After 15 min, the cold bath was removed and the mixture was allowed to warm to room temperature with stirring and kept overnight. Then 10 ml of 3*M* NaOH and 2.0 ml of 30% H<sub>2</sub>O<sub>2</sub> were added at ca. 0 °C. The mixture was stirred for 1 h at room temperature and 15 min at 50 °C. The aqueous phase was saturated with K<sub>2</sub>CO<sub>3</sub> and was extracted three times with ethyl ether (60 ml), and the combined organic layers were dried over K<sub>2</sub>CO<sub>3</sub>. The residue was concentrated under vacuum, and purified by column chromatography (silica gel, elution by ethyl acetate and petroleum ether) to give the pure product.

Table 1

<sup>\* (</sup> $\alpha, \alpha$ -Dichlorobenzyl)lithium was prepared from benzal chloride (11 mmol) and n-butyllithium (11 mmol) in THF at  $-100 \,^{\circ}$ C [5a]. (1,1-Dichloroethyl)lithium was prepared from 1,1,1-trichloroethane (11 mmol) and s-butyllithium [5b].

Trialkylcarbinol can alternatively be prepared from trialkylborane by carbonylation [7], cyanidation [8], or reaction with DCME (dichloromethyl methyl ether) [9], but these methods are of limited use in the synthesis of mixed trialkylcarbinols, since some mixed trialkylboranes are difficult to prepare. Mixed trialkylcarbinols can be produced by reaction of dialkylchloroboranes with lithium aldimines [10]. Our procedure provides a more efficient means of preparing some mixed trialkylcarbinols from alkenes.

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