A stable α-chloroalkyllithium compound: 2-lithiumchloromethyl-1-methyl-*o*-carborane

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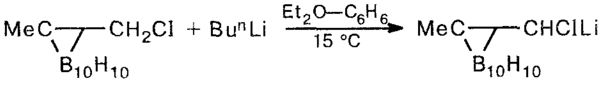
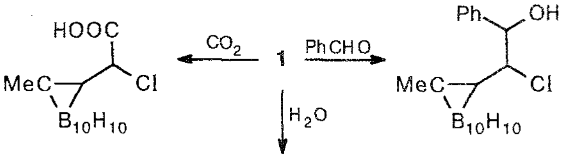
At present it is customary to assume that α-chloroalkyl lithium derivatives, RCHClLi and RR'CClLi, are stable in solution only at low temperatures (<−85 °C).[1] By contrast, we showed that 2-lithiumchloromethyl-1-methyl-*o*-carborane (**1**), prepared for the first time, is stable in a benzene—ethereal solution at ambient temperature.

When a benzene solution of Bu^nLi is added to an ethereal solution of 2-chloromethyl-1-methyl-*o*-carborane (**2**) at 15 °C, metallation of the CH_2Cl group readily occurs to yield two liquid layers. The lower orange-colored layer contains solvated **1**.



2 **1**

Compound **1** does not change when its solution is stored for 1 h at 25 °C. The poor solubility of **1** in a benzene—ether mixture points to substantial polarity of the C—Li bond. Treatment of compound **1** with CO_2, PhCHO, or H_2O affords acid **3**, chlorohydrin **4**, or the starting carborane **2**, respectively.



3 **2** **4**

The structures of products **3** (m.p. 86—87 °C) and **4** (m.p. 129—130 °C) were confirmed by elemental analysis and ^1H NMR and IR spectra.

The stability of compound **1** is due to the considerable strength of the C—Cl bond, which is caused by the great electron-withdrawing effect of the *o*-carboranyl group[2] and charge delocalization.

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Synthesis and stereochemistry of *O*-(1-trifluoromethylalkyl)methylphosphonochloridates

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Previously we described the synthesis of polyfluorinated esters of aryl- and alkylphosphonic and -chlorophosphonic acids by catalytic phosphorylation of primary 1,1-dihydropolyfluoroalkanols[1,2] and secondary

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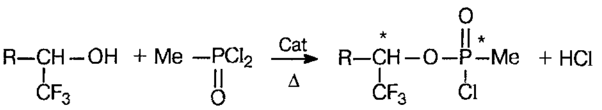
Table 1. Composition of the products of the catalytic phosphorylation of compounds **1a—d**

Compound	R	Diastereomers ratio determined by ^{31}P NMR
2a	Bu^n	50 : 50
2b	Bu^t	52 : 48
2c	n-C_6H_{13}	50:50
2d	$PhCH_2$	64:36

Note. LiCl was used as the catalyst.

α-(polyfluoroalkyl)benzyl alcohols.[3—5] To continue these studies, we prepared a number of methylphosphonochloridates starting from secondary 1-(trifluoromethyl)alkanols.



1a—d **2a—d**

R = Bu^n (**a**), Bu^t (**b**), n-C_6H_{13} (**c**), $PhCH_2$ (**d**)

Thus, for example, heating compounds **1a—d** with methylphosphonic dichloride without a solvent at 120—160 °C for 1—3 h in the presence of 1—5 mol. % LiCl or $MgCl_2$ as a catalyst affords the corresponding chlorophosphonates **2a—d** in 70—84 % yield. It should be noted that this reaction is the first example of catalytic phosphorylation of secondary alkyl(trifluoromethyl)carbinols with methylphosphonic dichloride. According to ^{31}P NMR spectroscopy and GLC, the resulting *O*-(1-trifluoromethylalkyl)methylphosphonochloridates **2a—d** are mixtures of diastereomers (Table 1).

It should be noted that in the case of **2d**, the ratio between the diastereomers obtained in the reaction noticeably deviates from the statistical value. The diastereomeric excess amounts to 28 %, according to ^{31}P NMR, and 30 and 34 %, according to the data of GLC and GC—MS, respectively. Previously, the predominant formation of one of the diastereomers has been observed only in the catalytic phosphorylation of α-(polyfluoroalkyl)benzyl alcohols with methylphosphonic dichloride.[4—6]

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The use of XeF_2 for preparation of azepins

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In recent years, apart from the traditional use of xenon difluoride (XeF_2) as a mild fluorinating agent, the increasing attention has been attracted to methods based on the generation of other highly reactive reagents using

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