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# Regiospecific synthesis of alpha-lithiated alkoxysilanes

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## Abstract

α-Lithioalkoxysilanes, [(RO)$R'_2$Si]CH(Li)(R″) (R = Me, Et; R′ = Me, Ph; R″ = H, $SiMe_3$), can be prepared by treating the appropriate alkoxysilane with *tert*-butyllithium in hydrocarbon solvents. For R = Me or Et, R′ = Me, and R″ = H or $SiMe_3$, the α-lithioalkoxysilanes are produced in high yield. Similar treatment of alkoxysilane **12**, $EtOPh_2SiCH_3$, afforded the corresponding α-lithioalkoxysilane **13** (R = Et, R′ = Ph and R″ = H), in moderate yield, along with substitution product **14**, *tert*-$BuPh_2SiCH_3$. Analogous reactions with *n*-butyl- and *sec*-butyllithium in hydrocarbon solvent produced significant or exclusive substitution at silicon, rather than α-lithiation. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Lithium; Silicon; Alkoxysilanes; Alpha-lithiated alkoxysilanes; Alpha-silyl carbanions; Alpha-lithiation

## 1. Introduction

As α-metallated silanes have become more sought after as reagents for organic synthesis, the number of available routes to these compounds has increased [1]. The most common means of preparation is metal-halogen exchange, as in the formation of the Grignard reagent from (chloromethyl)trimethylsilane and magnesium, first reported by Whitmore and Sommer in 1946 [2]. Unfortunately, the lack of availability of substituted α-chlorosilanes has curtailed the more general application of this strategy. Another important route to α-metallated, and particularly α-lithiated, silanes involves a metal-heteroatom exchange [1], where the heteroatom is sulfur, tin, silicon, or selenium. The most generally useful of these methods is the reductive lithiation of α-(phenylthio)silanes with 1-(dimethylamino)napthalenide reported in Ref. [3]. Alternatively, Chan and co-workers have taken particular advantage of the propensity of vinylsilanes to undergo addition with alkyllithium compounds to form a number of complex α-lithiated silanes [4].

Although these methods for producing α-lithiated silanes have proven highly valuable, a direct route would certainly be preferable. Unfortunately, tetraalkylsilanes have proven to be very sluggish towards lithium–hydrogen exchange [5], unless further activated by an additional anion-stabilizing group in the α-position [6]. These approaches have recently been reviewed [4b,7].

We previously reported that methoxytrimethylsilane, **1**, and methoxymethyltrimethylsilane, **5**, undergo a facile, high-yield lithium-hydrogen exchange with *tert*-butyllithium in pentane solvent to produce α-lithiosilanes, **3** and **6** [8]. Since then, only a few other researchers have reported the direct α-metallation of alkyl groups attached to silicon [9]. This high-yield preparation is in contrast to earlier reports by West and Gornowicz that the same reactants in THF or pentane–TMEDA solvents give a mixture of products due to competing substitution reactions at silicon [10]. It was of interest to know if similar, regiospecific lithiation of **1** and **5** in hydrocarbon solvent could be achieved with other less hindered bases, such as *n*-butyl- and *sec*-butyllithium. Previous attempts to lithiate **5** with these bases were carried out in THF. These resulted in exclusive substitution with *n*-butyllithium [6c], regiospecific lithiation at the methylene position with *sec*-butyllithium, to form (methoxy(trimethylsilyl)-methyl)lithium, **7** [6e], and regiospecific lithiation to give (methoxymethyldimethylsilyl)methyllithium, **6**, with

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with *tert*-butyllithium [6c]. We decided to further explore the generality of the lithiation reaction with other alkoxysilane substrates, **2**, **8**, **9** and **12**, using *tert*-butyllithium in hydrocarbon solvent. These substrates were of particular interest to us, since we were also exploring the utility of α-lithioalkoxysilanes in alkene synthesis via the Peterson methodology [11], particularly toward the synthesis of vinylsilanes [12].

We now report on the details of the metallation of ethoxytrimethylsilane, **2**, (methoxydimethylsilyl)-(trimethylsilyl)methane, **8**, and (ethoxydimethylsilyl)(trimethylsilyl)methane, **9**, by *tert*-butyllithium in pentane solution to produce the corresponding α-lithiated alkoxysilanes, regiospecifically and in very high yield. We also describe our attempts to extend this methodology to the phenyl-substituted alkoxysilane, **12**, and the results of the treatment of **1** and **5** with other lithium bases, under similar conditions. Additionally, we report on an improved synthesis of (methoxydimethylsilyl)(trimethylsilyl)methane, **8**, from methoxytrimethylsilane, **1**, and an analogous synthesis of the ethoxy derivative, **9**, from **2**. Finally, we provide an account of our investigations concerning the mechanism of the lithiation of alkoxysilanes by *tert*-butyllithium.

## 2. Results and discussion

### 2.1. Lithiation of alkoxysilanes with organolithiums

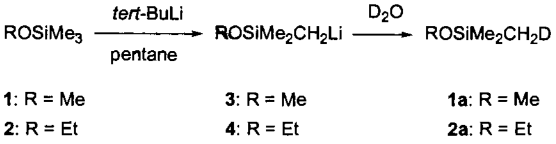
When a pentane solution of either methoxytrimethylsilane, **1**, or ethoxytrimethylsilane, **2**, reacted with one equivalent of *tert*-butyllithium at −78°C and was then allowed to warm to room temperature, a solution of the corresponding α-lithiated alkoxysilane, **3** or **4** respectively, was obtained (Scheme 1). In both cases, $^{13}$C-NMR spectra of the samples following quenching of the lithium compound with $D_2O$ indicated that lithiation had occurred regiospecifically and in greater than 98% yield at the carbon alpha to silicon. There was no evidence for substitution at silicon under these reaction conditions. However, our attempts to prepare **3** from **1** under similar conditions by use of other less sterically hindered bases, such as *n*-butyl- and *sec*-butyllithium, were unsatisfactory. These reactions, monitored via deuterium quenching experiments, revealed no deuteration at the carbon alpha to silicon in the $^{13}$C-NMR spectra, while the signal due to the methoxy carbon had disappeared.

A similar reaction of *tert*-butyllithium in cyclopentane with methoxymethyltrimethylsilane, **5**, resulted in nearly quantitative lithiation of the methyl carbon adjacent to silicon (Scheme 2). However, no lithiation resulted from treatment of **5** with *n*-butyllithium. With *sec*-butyllithium, lithiation occurred at the methyl carbon adjacent to silicon to form **6**, although this reaction was not as efficient as that with *tert*-butyllithium. However, the regiochemistry of the reaction with *sec*-butyllithium was particularly interesting, considering that the same reactants in THF led to metalation at the methylene carbon to give **7** in good yield [6e].

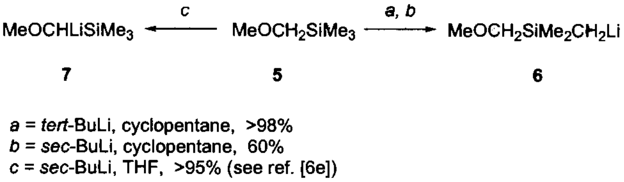
Both of the α-lithiated alkoxysilanes, **3** and **4**, reacted with trimethylchlorosilane in high yield to give (methoxydimethylsilyl)(trimethylsilyl)methane, **8**, and (ethoxydimethylsilyl)-(trimethylsilyl)methane, **9**, respectively (Scheme 3).

We previously reported [12a] the synthesis of **8** in 63% yield. During our attempts to optimize the conditions for this reaction, we found that improved yields of the desired product were obtained by a modification of our procedure for adding chlorotrimethylsilane. Instead of adding a solution of chlorotrimethylsilane in THF, as reported earlier, the chlorotrimethylsilane was added neat, followed by dropwise addition of one to two equivalents of diethyl ether. There was no visible evidence of reaction until about one equivalent of ether was added, when an exothermic reaction ensued. Subsequent work-up afforded the silane **8** in 87% yield (95% purity as seen by GC).

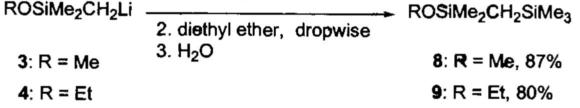
The alkoxysilanes **8** and **9** were metallated regiospecifically and in very high yield by *tert*-butyllithium in pentane at room temperature (Scheme 4). The reaction was essentially complete after 2 h, when 98% of the molecules from the $D_2O$ quenched aliquot contained a deuterium atom at the methylene position of **8**. No other carbon atoms became enriched with deuterium from this treatment. Similar experiments with **9** showed that this compound was also metallated regiospecifically.



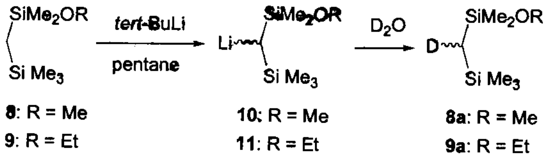
Scheme 1.



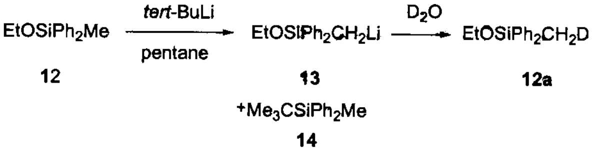
Scheme 2.



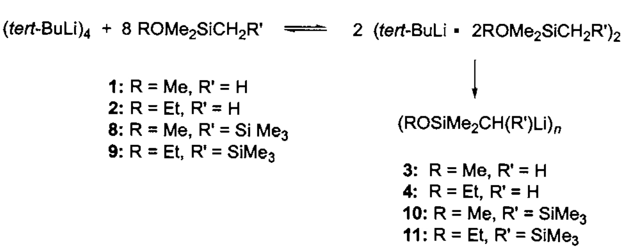
Scheme 3.



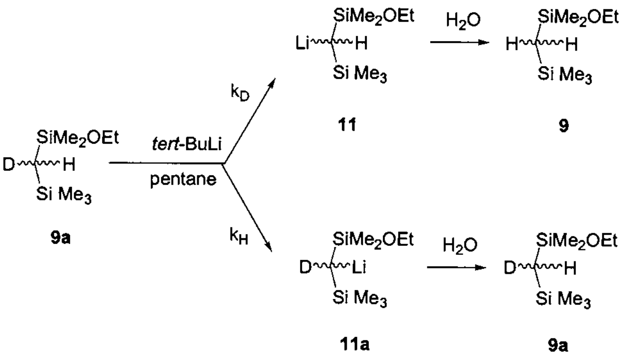
Scheme 4.



Scheme 5.



Scheme 6.



Scheme 7.

Attempts to extend this methodology to phenyl substituted alkoxysilanes were less successful. We found that diphenylmethylethoxysilane, **12**, reacted with *tert*-butyllithium to produce the corresponding α-lithioalkoxysilane, **13**, as indicated by the formation of **12a** when the reaction mixture was quenched with $D_2O$. However, a significant quantitity of the substitution product, *tert*-butylmethyldiphenylsilane, **14**, was also detected, indicating that substitution at silicon was competitive with lithiation at carbon. (Scheme 5)

### 2.2. Mechanism of lithiation

*tert*-Butyllithium is known to be tetrameric in hydrocarbon solvent [13,14]. However, we had previously found that when diethyl ether ($\leq$ two equivalents) was added to a hydrocarbon solution of *tert*-butyllithium-$^6$Li, it formed stable coordinated dimers, clearly observable by $^{13}$C- and $^6$Li-NMR [15]. There was a dynamic, temperature-dependent equilibrium between solvated dimers and unsolvated tetramers, the dimers being favored at low temperatures. We also reported an analogous interaction between methoxytrimethylsilane, **1**, and *tert*-butyllithium-$^6$Li, to form coordinated dimers (Scheme 6) [8]. Notable differences between these two reactions were the slower formation of the coordinated dimer and the shift in equilibrium towards the uncoordinated tetrameric *tert*-butyllithium when the silyl ether was used, relative to diethyl ether.

Cyclopentane mixtures of *tert*-butyllithium-$^6$Li and the alkoxysilanes, **2**, **8**, and **9**, were examined by $^{13}$C- and $^6$Li-NMR for the presence of coordinated dimers. No such dimers were detected between $-80$ and $+25$°C. The only lithium compounds observed in the $^{13}$C- and $^6$Li-NMR spectra were the *tert*-butyllithium starting material (uncoordinated tetramer) and the final α-lithiosilanes, **4**, **10** and **11** (aggregate size undetermined). Two possibilities could account for this observation: either the dimer concentration was too small to be observed by NMR, or the reaction proceeded via a different mechanism for these latter silanes. However, since the overall lithiation reactions were so facile, especially relative to tetraalkylsilanes, and so similar to the reaction between *tert*-butyllithium and **1** in terms of both reactivities and yields, it seemed reasonable to suppose that they all occurred via similar pathways, i.e. via formation of coordinated dimers.

Since the silyl ether coordinated dimers were not observed in the NMR spectra (except with **1**), they either reacted as rapidly as they were formed, or the tetramer/dimer equilibrium was shifted significantly toward the tetramer at all temperatures. To differentiate between these two possibilities, we measured the deuterium isotope effect for the lithiation of $EtOMe_2SiCHDSiMe_3$, **9a**. This was **9**, which had been singly deuterated at the carbon alpha to both silicons (Scheme 7). If the dimers were reacting rapidly, proton abstraction from the coordinated dimer formed by **9a** would be expected to proceed at about the same rate as deuterium abstraction. A significant isotope effect, on the other hand, would indicate that the metallation was slow and that the position of dimer/tetramer equilibrium was responsible for the low concentration of dimers in the reaction mixtures.

We found that lithium replaced proton atoms 7.8 times faster than deuterium atoms. This significant isotope effect indicated that metallation must be rate-determining. If the metallation in Scheme 6 is slow relative to the initial equilibrium, yet no dimers are observed, then the equilibrium must be shifted towards the uncoordinated *tert*-butyllithium tetramers.

This interpretation is further supported by the rates of reaction as a function of ether. The *tert*-butyllithium dimer coordinated with diethyl ether, produced by an equilibrium analogous to that in Scheme 6 but shifted completely to the right, was stable for O:Li ratios of $\leq$ two equivalents. However, it reacted at higher O:Li ratios, presumably via reaction with free, uncoordinated ether [15]. Reaction of **1** with *tert*-butyllithium proceeded even at O:Li ratios $<2$. For this case, free alkoxysilane was present even at lower O:Li ratios, since the equilibrium did not lie completely to the right [8]. By contrast, coordinated dimers formed from the alkoxysilanes **2**, **8**, or **9** and *tert*-butyllithium were never observed, but the reaction occurred immediately upon mixing for all O:Li ratios. The increased steric requirements of these alkoxysilanes were apparently sufficient to significantly shift the equilibrium to the left, leaving free alkoxysilane available for reaction once the dimers were formed.

## 3. Experimental

### 3.1. General

All experiments were carried out under an argon atmosphere. Glassware was assembled hot from the drying oven. Reagents were transferred by standard syringe or double-ended needle techniques. Methoxytrimethylsilane, **1**, was either prepared by the literature procedure [10] or purchased from Aldrich Chemical Co. In either case, traces of methanol were removed by distillation from sodium metal [16]. Ethoxytrimethylsilane, **2**, and diphenylmethylethoxysilane, **12**, purchased from Hüls Scientific, were also distilled from sodium metal. Commercial *n*-, *sec*- and *tert*-butyllithium solutions in pentane, hexanes or cyclopentane, purchased from Aldrich, were titrated prior to use [17]. Halide-free *tert*-butyllithium-$^6$Li was prepared from bis(*tert*-butyl)mercury and 95.5% isotopically-enriched $^6$Li metal (US Services) as described earlier [13] and sublimed prior to use. Pentane was dried over $LiAlH_4$ before transferring to a dry storage vessel under high vacuum. Diethyl ether was distilled from $LiAlH_4$. All NMR spectra were obtained on a Varian VXR-300 NMR spectrometer (299.9 MHz for $^1$H, 75.4 MHz for $^{13}$C and 44.1 MHz for $^6$Li). Chemical shifts are expressed in ppm relative to TMS.

### 3.2. Reaction of alkoxysilanes, *1* and *5*, with *sec*-butyllithium and *n*-butyllithium

#### 3.2.1. Reaction of *1* with *sec*-butyllithium

To a solution of methoxytrimethylsilane, **1**, (0.69 ml, 0.52 g, 5.0 mmol) dissolved in cyclopentane (10 ml) at −78°C was added *sec*-butyllithium (5.0 mmol) and stirred for 2 h. The cooling bath was then removed and the solution was allowed to warm to r.t. (1 h). Three aliquots (3 ml each) were removed at hourly intervals, added to deuterium oxide (3 ml) and agitated to ensure thorough mixing. In each case, the organic layer was separated and dried over anhydrous magnesium sulfate (30–45 min). A small portion of each was mixed with $CDCl_3$ (1:1 ratio by volume) and examined by $^{13}$C-NMR. The lack of a 1:1:1 triplet ($^{13}$C–$^2$H coupling), just upfield from the singlet at −1.0019 ppm, revealed that no lithiation had occurred at the alpha carbon. The only 1:1:1 triplet observed was attributed to the $D_2O$ quenching of *sec*-butyllithium. Additionally, the signal at 49.33 ppm, representing the methoxy carbon of **1**, had disappeared, indicating that the base had caused substitution at silicon.

#### 3.2.2. Reaction of *1* with *n*-butyllithium

The procedure described in Section 3.2.1 was repeated with methoxytrimethylsilane, **1**, (0.69 ml, 0.52 g, 5.0 mmol) and *n*-BuLi (12.0 mmol). Analysis of the $^{13}$C-NMR spectra revealed that no lithiation had occurred at the alpha carbon site and **1** had undergone exclusive substitution at silicon.

#### 3.2.3. Reaction of *5* with *sec*-butyllithium

The procedure described in Section 3.2.1 was repeated, using methoxymethyltrimethylsilane, **5**, (0.79 ml, 0.59 g, 5.0 mmol) and *sec*-butyllithium (11.0 mmol). The $^{13}$C-NMR spectra of all aliquots quenched with deuterium contained a 1:1:1 triplet just upfield of the methyl carbon singlet at −3.37 ppm, showing that lithiation had occurred at the methyl carbon alpha to silicon, although integration of the two signals revealed that lithiation had not been quantitative. Also, the absence of a similar triplet near the methylene carbon signal at 67.52 ppm was evidence that no lithiation had occurred at the methylene carbon adjacent to silicon.

#### 3.2.4. Reaction of *5* with *n*-butyllithium

The procedure described in Section 3.2.1 was repeated, using methoxymethyltrimethylsilane, **5**, (0.79 ml, 0.59 g, 5.0 mmol) and *n*-butyllithium (12.0 mmol). $^{13}$C-NMR analysis showed that no lithiation had occurred at carbons adjacent to silicon.

### 3.3. Preparation of (methoxydimethylsilyl)(trimethylsilyl)methane, *8*

To a solution of methoxy(trimethyl)silane, **1**, (27.6 ml, 20.9 g, 200 mmol) dissolved in pentane (75 ml) at −78°C was added *tert*-BuLi (200 mmol). After stirring for 2 h at −78°C, the reaction mixture was allowed to warm to r.t. and additionally stirred for 2 h. The reaction mixture was then cooled to 0°C before adding freshly distilled chlorotrimethylsilane (25.3 ml, 21.7 g, 220 mmol). Diethyl ether (40 ml) was then added dropwise, with ice-water flowing through the condenser to minimize loss of solvent upon commencement of the exothermic reaction. The ice bath was then removed and the reaction mixture stirred for 0.5 h before transferring to a separatory funnel containing ice–water mixture (500 ml). After separation and extraction of the aqueous layer with pentane (2 × 40 ml), the combined organic layers were dried with anhydrous $MgSO_4$. Removal of the solvent under reduced pressure afforded 30.6 g (87%) of **8** (95% pure by NMR). It was then distilled at reduced pressure through a glass bead-packed fractionating column.

B.p.$_{83}$ 78–81°C (lit. [18] b.p.$_{26}$ 54–55°C). $^1$H-NMR ($CDCl_3$): $\delta = 0.42$ (s, 2H, $SiC\mathit{H}_2Si$), 0.60 (s, 9H, $Si(C\mathit{H}_3)_3$), 0.65 (s, 6H, $CH_3OSi(C\mathit{H}_3)_2$), 3.93 (s, 3H, $OC\mathit{H}_3$) (lit. [10]). $^{13}$C-NMR($CDCl_3$): $\delta = -0.10$ (2 $Si(\mathit{C}H_3)_2$), 1.00 (3 $Si(\mathit{C}H_3)_3$), 4.00 ($\mathit{C}H_2$), 49.78 ($O\mathit{C}H_3$).

### 3.4. Preparation of (ethoxydimethylsilyl)-(trimethylsilyl)methane, **9**

To a solution of ethoxy(trimethyl)silane, **2**, (15.6 ml, 11.8 g, 100 mmol) dissolved in pentane (40 ml) at −78°C was added *tert*-BuLi (58.8 ml, 100 mmol, 1.7 M). After stirring for 2 h at −78°C, the reaction mixture was allowed to warm to r.t. and stirred again for 2 h. The reaction mixture was cooled to 0°C before adding freshly distilled chlorotrimethylsilane (13.3 ml, 11.4 g, 105 mmol). Diethyl ether (20 ml) was then added dropwise, the ice bath removed and the reaction mixture stirred for 0.5 h before transferring to a flask containing water (100 ml). After extraction with pentane and drying the combined organic layers with anhydrous $MgSO_4$, the solvent was removed under reduced pressure, affording 15.23 g (80%) of **9** (95% pure by NMR). It was further purified by fractional distillation under reduced pressure.

B.p.$_6$ 35–37°C (lit. [10] b.p.$_{55}$ 75–85°C). $^1$H-NMR ($CDCl_3$): $\delta = -0.12$ (s, 2H, $SiC\mathit{H}_2Si$), 0.04 (s, 9H, $Si(C\mathit{H}_3)_3$), 0.06 (s, 6H, $CH_2OSi(C\mathit{H}_3)_2$), 1.17 (t, $J = 7.0$ Hz, 3H, $C\mathit{H}_3CH_2O$), 3.63 (q, $J = 7.0$ Hz, 2H, $CH_3C\mathit{H}_2O$) (lit. [10]). $^{13}$C-NMR ($CDCl_3$): $\delta = 0.56$ ($CH_2OSi(\mathit{C}H_3)_2$), 1.10 ($Si(\mathit{C}H_3)_3$), 4.51 ($Si\mathit{C}H_2Si$), 18.50 ($\mathit{C}H_3CH_2O$), 57.85 ($O\mathit{C}H_2$).

### 3.5. Reaction of **9** with tert-butyllithium

To a solution of diphenylmethylethoxysilane, **9**, (1.9 ml, 1.9 g, 8.0 mmol) dissolved in pentane (10 ml) at r.t. was added *tert*-BuLi (8 mmol). Several aliquots (2 ml each) were removed and added to deuterium oxide (3 ml). In each case, the organic layer was separated, dried over molecular sieves and examined by $^{13}$C-NMR. An aliquot removed after 5 h of stirring revealed the presence of the deuterated compound, **9a**, along with undeuterated starting material, **9**, and substitution product, **11.**

### 3.6. NMR studies of mixtures of alkoxysilanes **2**, **8** and **9** with tert-butyllithium-$^6$Li

Mixtures of *tert*-butyllithium-$^6$Li and alkoxysilanes **2**, **8** and **9**, respectively, in cyclopentane (8% cyclopentane-$d_{10}$, Wilmad; 92% cyclopentane, 99.9% Wiley organics) were prepared as described earlier [8] for NMR analysis, to detect presence of coordinated dimers at different temperatures. Variable-temperature $^{13}$C- and $^6$Li-NMR experiments were carried out as described earlier [8] at several temperatures between −80°C and +25°C. No coordinated dimers were detected, the only aggregates observed being ($tert$-Bu$^6$Li)$_4$ and $([ROR'_2Si]CH(^6Li)(R''))_n$. The aggregate size of the α-lithiosilanes was not determined.

### 3.7. Deuterium isotope effect: reaction of tert-butyllithium with $EtOMe_2SiCHDSiMe_3$ (**9a**)

#### 3.7.1. Preparation of deuterio-(ethoxydimethylsilyl)(trimethylsilyl)methane, **9a**

A mixture of (ethoxydimethylsilyl)(trimethylsilyl)-methane, **9**, (0.95 g, 5 mmol) and *tert*-butyllithium (3.24 ml, 5.5 mmol, 1.7 M) in pentane (8 ml) was stirred at r.t. for 6 h before being transferred to a dry flask containing deuterium oxide (5 ml). After stirring, the layers were separated and dried over molecular sieves. A $^{13}$C-NMR of the crude product indicated that it contained 86% mono-deuterated product, **9a**.

#### 3.7.2. Lithiation of **9a**

A solution of **9a** in pentane was stirred with *tert*-butyllithium (5 h) and quenched with $H_2O$. $^{13}$C-NMR spectroscopy revealed the presence of **9** and **9a**, formed from the lithiated species, **11** and **11a**, respectively. The product distribution of **9**:**9a** was 1:7.8.

## Acknowledgements

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