

Cleavage of Si–C and Ge–C bonds in heterylsilanes and -germanes by organolithium reagents

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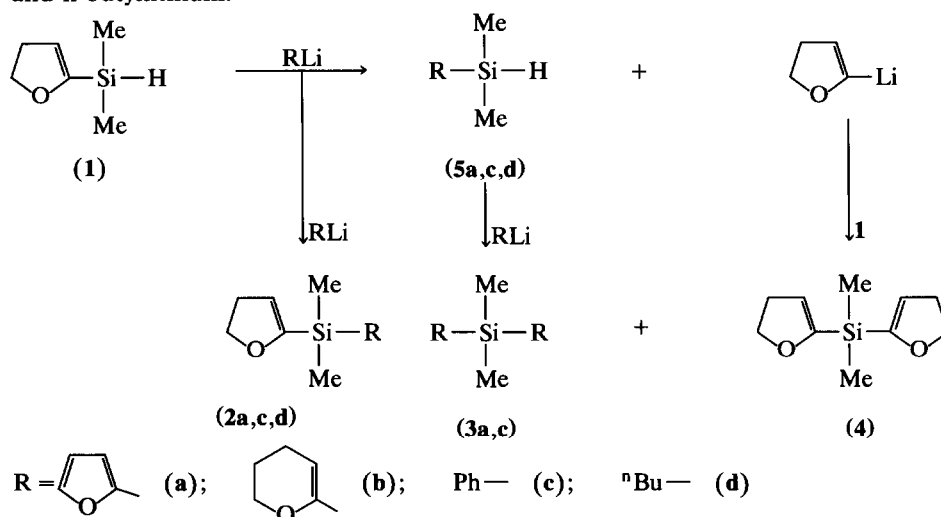
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Abstract

Organolithium reagents RLi can cleave Si–C and Ge–C bonds in heterylsilanes and -germanes substituting furyl, dihydrofuryl and dihydropyranyl groups for the organolithium residue R.

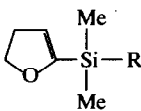
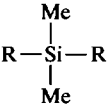
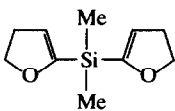
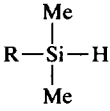
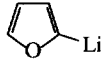
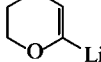
Reactions of organometallic C-nucleophiles (RLi, RMgX) with silicon-functional organosilanes ($\equiv\text{SiHal}$, $\equiv\text{SiH}$) are one of the pathways to the synthesis of compounds with a silicon–carbon bond [1]. At the same time, the cleavage of the Si–C bond with *n*-butyllithium and furyllithium in furylsilanes has been documented [2]. Moreover, we have found that the cleavage of the Si–C bond took place in the reaction of [2-(4,5-dihydrofuryl)]dimethylsilane (1) with 2-furyllithium [3]. Bis(2-furyl)dimethylsilane (3a) was detected in the reaction mixture. In order to learn more about the cleavage of the Si–C bond, we have studied the reactions of dihydrofurylhydrosilane (1) with [2-(5,6-dihydro-4*H*-pyranyl)]lithium, phenyllithium and *n*-butyllithium:



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Table 1

Reactions of [2-(4,5-dihydrofuryl)]silane (**1**) with organolithium reagents (0.1 M solution in THF/hexane (8:1), $-30^{\circ}\text{C}/30\text{ min} \rightarrow 25^{\circ}\text{C}/30\text{ min}$)

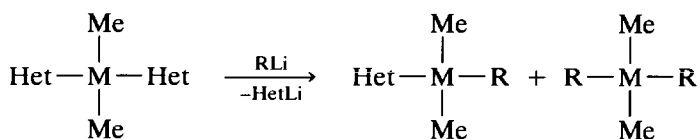
RLi	Reaction mixture components (%) ^a				
	Substrate 1				
	1	2	3	4	5
a 	5	27	22	15	8
b 	39	–	–	8	–
c PhLi	11	34	3	19	13
d ⁿ BuLi	18	35	–	21	21

^a GC data.

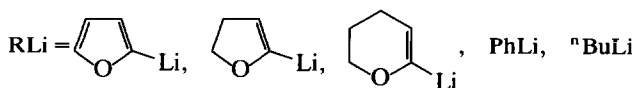
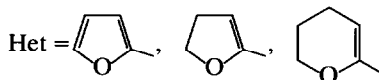
It was found that phenyllithium and *n*-butyllithium as well as (2-furyl)lithium along with the substitution of Si–H bond, are capable of cleaving the Si–C bond in the initial hydrosilane **1** with the substitution of dihydrofuryl group for the residue of the organolithium reagent. [2-(5,6-Dihydro-4*H*-pyranyl)]lithium is low reactive in this reaction and only minor amounts of bis-dihydrofuryl derivative (**4**) were detected in the reaction mixture (Table 1).

These experimental data and investigations of the cleavage of Si–C and Ge–C bonds by H-nucleophiles in heterylsilanes and -germanes [4,5] suggest the possibility of analogous reactions of C-nucleophiles with bis(2-furyl)dimethylsilane (**6a**), bis[2-(4,5-dihydrofuryl)]dimethylsilane (**4**), bis[2-(5,6-dihydro-4*H*-pyranyl)]dimethylsilane (**6b**) and bis[2-(4,5-dihydrofuryl)]dimethylgermane (**6c**).

2-Furyllithium, [2-(4,5-dihydrofuryl)]lithium, [2-(5,6-dihydro-4*H*-pyranyl)]lithium, phenyllithium and *n*-butyllithium were chosen as C-nucleophiles:



M = Si, Ge



Reactions of the heteryl derivatives **4**, **6a–c** with equimolar amounts of organolithium compounds were carried out in THF/hexane (8:1) at $-30^{\circ}\text{C}/30\text{ min}$, then the temperature was raised to ambient and the mixture was stirred for 30 min. The organolithium compounds (organolithium reagent + heteryllithium

Table 2

Reactions of bis-heterylsilanes (**4**, **6a-c**) and -germanes (**6c**) with organolithium reagents (0.1 M solution in THF/hexane (8:1), $-30^{\circ}\text{C}/30\text{ min} \rightarrow 25^{\circ}\text{C}/30\text{ min}$)

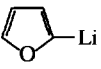
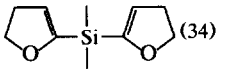
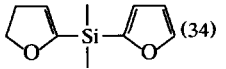
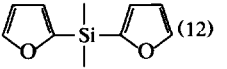
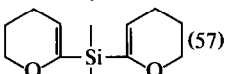
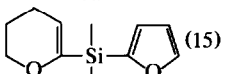
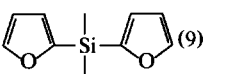
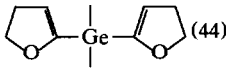
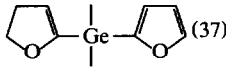
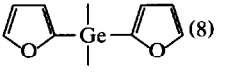
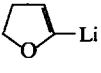
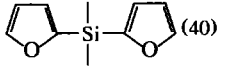
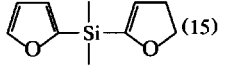
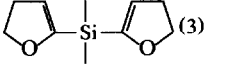
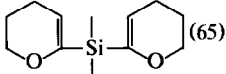
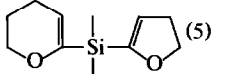
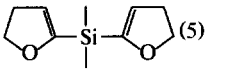
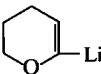
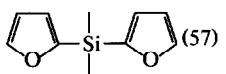
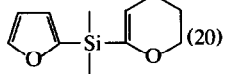
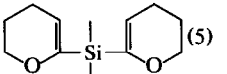
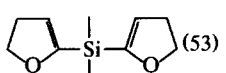
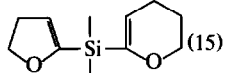
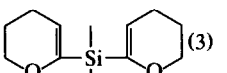
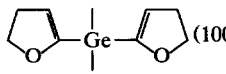
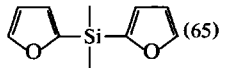
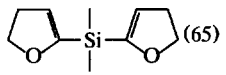
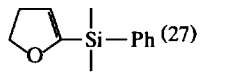
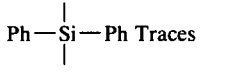
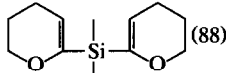
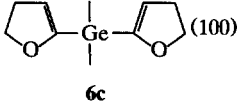
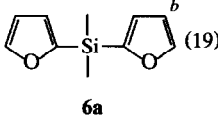
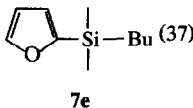
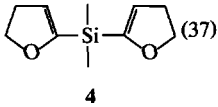
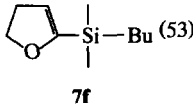
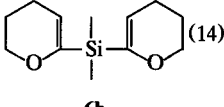
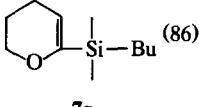
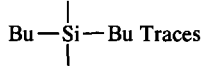
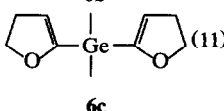
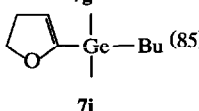
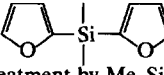
Entry	RLi	Reaction mixture components (%) ^a		
		$\begin{array}{c} \text{Me} \\ \\ \text{Het}-\text{M}-\text{Het} \\ \\ \text{Me} \end{array}$	$\begin{array}{c} \text{Me} \\ \\ \text{Het}-\text{M}-\text{R} \\ \\ \text{Me} \end{array}$	$\begin{array}{c} \text{Me} \\ \\ \text{R}-\text{M}-\text{R} \\ \\ \text{Me} \end{array}$
1		 (4) (34)	 (7a) (34)	 (6a) (12)
2		 (6b) (57)	 (7b) (15)	 (6a) (9)
3		 (6c) (44)	 (7h) (37)	 (8c) (8)
4		 (6a) (40)	 (7a) (15)	 (4) (3)
5		 (6b) (65)	 (7a) (5)	 (4) (5)
6		 (6a) (57)	 (7b) (20)	 (6b) (5)
7		 (4) (53)	 (7c) (15)	 (6b) (3)
8		 (6c) (100)	-	-
9	PhLi	 (6a) (65)	-	-
10		 (4) (65)	 (7d) (27)	 (8a) Traces
11		 (6b) (88)	-	-

Table 2 (continued)

Entry	RLi	Reaction mixture components (%) ^a		
		$\begin{array}{c} \text{Me} \\ \\ \text{Het}-\text{M}-\text{Het} \\ \\ \text{Me} \end{array}$	$\begin{array}{c} \text{Me} \\ \\ \text{Het}-\text{M}-\text{R} \\ \\ \text{Me} \end{array}$	$\begin{array}{c} \text{Me} \\ \\ \text{R}-\text{M}-\text{R} \\ \\ \text{Me} \end{array}$
12		 (100)	-	-
13	ⁿ BuLi	 (19)	 (37)	-
14		 (37)	 (53)	-
15		 (14)	 (86)	 Traces
16		 (11)	 (85)	-

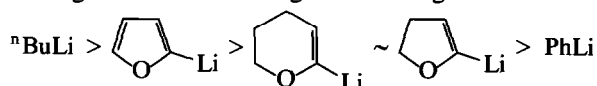
^a GC data. ^b The reaction mixture contains  (13%), a product of metallation of starting **6a** with ⁿBuLi and the following treatment by Me₃SiCl.

obtained in the reaction) present in the mixture were neutralized by the addition of the calculated amount of Me₃SiCl (Table 2).

Among the organolithium compounds used, ⁿBuLi was the most active; its reactions with all heteryl derivatives were characterized by the high degree of conversion of the latter (67–89%) and proceeded more selectively; only monosubstituted products were obtained (yield 37–89%).

The reaction of **4**, **6a–c** with lithium derivatives of heterocycles proceeds otherwise: it is characterized by the lesser conversion of the **4**, **6a–c** (35–60%) and in all cases by small amounts (3–12%) of products resulting from the exhausted substitution of the heteryl group in the starting compounds for the heteryl group of the organolithium reagent.

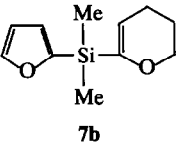
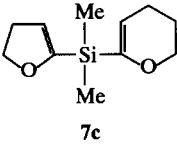
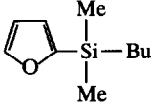
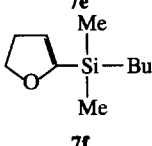
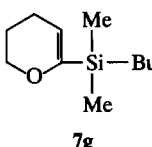
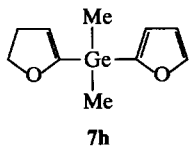
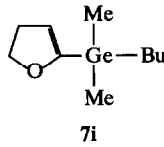
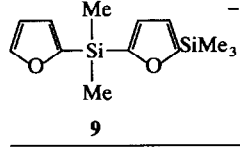
Phenyllithium appears to be the weakest reagent; it reacts only with the most reactive bis(dihydrofuryl)silane (**4**). All the organolithium reagents studied can be arranged in the following diminishing order of reactivity:



The most active in the reactions with organolithium reagents bis(dihydrofuryl)silane (**4**) has been studied in the reactions with Grignard reagents. Methylmag-

Table 3

¹H NMR and mass spectra of compounds obtained by reactions of heterylsilanes and -germanes

Compound	¹ H NMR spectrum (ppm)	Mass spectrum <i>m/z</i> (rel. intensity, %)
	0.36 (s, 6H, CH ₃); 1.67–2.11 (m, 4H, 4', 5'-CH ₂); 3.82–4.04 (m, 2H, 6'-CH ₂); 4.96–5.17 (m, 1H, 3'-CH); 6.39 (m, 1H, 4'-CH); 6.71 (m, 1H, 4-CH); 7.65 (m, 1H, 5-CH)	208 (M ⁺ , 27); 193 ((M-Me) ⁺ , 3); 125 ((M-C ₅ H ₇ O) ⁺ , 100)
	0.22 (s, 6H, CH ₃); 1.73–2.07 (m, 4H, 4', 5'-CH ₂); 2.58 (d.t., 2H, 4-CH ₂); 3.84–4.00 (m, 2H, 6'-CH ₂); 4.27 (t, 2H, 5-CH ₂ , <i>J</i> = 10.1 Hz); 5.02–5.14 (m, 1H, 3'-CH); 5.30 (t, 1H, 3-CH, <i>J</i> = 2.1 Hz)	210 (M ⁺ , 23); 195 ((M-Me) ⁺ , 2); 141 ((M-C ₄ H ₅ O) ⁺ , 4); ((M-C ₅ H ₇ O) ⁺ , 7); 28(100)
	0.22 (s, 6H, CH ₃); 0.56–1.44 (m, 9H, C ₄ H ₉); 6.39 (m, 1H, 4-CH ₂); 6.63 (m, 1H, 3-CH); 7.67 (m, 1H, 5-CH)	182 (M ⁺ , 7); 167 ((M-Me) ⁺ , 5); 125 ((M-Bu) ⁺ , 100)
	0.12 (s, 6H, CH ₃); 0.50–1.50 (m, 9H, C ₄ H ₉); 2.56 (m, d.t., 2H, 4-CH ₂); 4.25 (t, 2H, 5-CH ₂ , <i>J</i> = 9.3 Hz); 5.17 (t, 1H, 3-CH, <i>J</i> = 2.4 Hz)	184 (M ⁺ , 6); 169 ((M-Me) ⁺ , 3); 127 ((M-Bu) ⁺ , 15); 115 ((M-C ₄ H ₅ O) ⁺ , 8); 97(100)
	0.24 (s, 6H, CH ₃); 0.57–1.61 (m, 9H, C ₄ H ₉); 1.81–2.39 (m, 4H, 4,5-CH ₂); 3.97–4.15 (m, 2H, 6-CH ₂); 5.02–5.19 (m, 1H, 3-CH)	198 (M ⁺ , 4); 183 ((M-Me) ⁺ , 3); 141 ((M-Bu) ⁺ , 21); 115 ((M-C ₄ H ₄ O) ⁺ , 4); 75(100)
	–	240 (M ⁺ , 23); 225 ((M-Me) ⁺ , 26); 173 ((M-C ₄ H ₃ O) ⁺ , 5); 171 ((M-C ₄ H ₅ O) ⁺ , 19); 28(100)
	–	230 (M ⁺ , 4); 215 ((M-Me) ⁺ , 3); 173 ((M-Bu) ⁺ , 37); 161 ((M-C ₄ H ₅ O) ⁺ , 8); 143(100)
	–	264 (M ⁺ , 58); 249 ((M-Me) ⁺ , 46); 199 (100), 125 ((M-C ₄ H ₂ OSiMe ₃) ⁺ , 12)

nesium iodide was found to be too weakly nucleophilic in the reaction under study, and even during prolonged boiling in THF, it is not capable of substituting the more easily leaving dihydrofuryl group in bis[2-(4,5-dihydrofuryl)]dimethylsilane (4).

Experimental

^1H NMR spectra were recorded with a Bruker WH-90/DS spectrometer in CDCl_3 using TMS as internal standard. Mass spectra were recorded with a Kratos MS-25 GC-MS (70 eV). GC analysis was carried out with a Chroma-5 apparatus equipped with a flame-ionization detector. Glass columns (1.2 m \times 3 mm) packed with 5% OV-17/Chromosorb W-AW (60–80 mesh) were used for analysis; the carrier gas was helium (50 ml/min).

$^n\text{BuLi}$ (5–6 N) was prepared by a modified literature procedure [6]. PhLi was purchased from Fluka.

2-Furyllithium was prepared by the addition of 5–6 N $^n\text{BuLi}$ solution in hexane to a solution of furan in tetrahydrofuran (THF/hexane, 2:1) at -30°C with subsequent stirring for 30 min. The temperature of the reaction was raised to boiling and the reaction mixture was stirred for 30 min at this temperature.

[2-(4,5-Dihydrofuryl)]lithium and [2-(5,6-dihydro-4H-pyranyl)]lithium were prepared as described in [5].

[2-(4,5-Dihydrofuryl)]dimethylsilane (1) [7], (2-furyl)dimethylsilane (6a) [8], bis[2-(4,5-dihydrofuryl)]dimethylsilane (4) [9], bis[2-(5,6-dihydro-4H-pyranyl)]dimethylsilane (6b) [5] and bis[2-(4,5-dihydrofuryl)]dimethylgermane (6c) [4] were prepared according to published procedures.

The physico-chemical constants of [2-(4,5-dihydrofuryl)](2-furyl)dimethylsilane (7a) [3], [2-(4,5-dihydrofuryl)]phenyldimethylsilane (7d) [5] and bis(2-furyl)dimethylgermane (8c) [10,11] obtained in reactions with organolithium compounds correspond to published data.

Reactions of heterylsilanes and -germanes with organolithium reagents (general procedure)

Organolithium reagent RLi (5 mmol) was added to a 0.1 M solution of silane or germane (5 mmol) in THF at -30°C with subsequent stirring for 30 min. The temperature was then raised to ambient and the mixture was stirred for 30 min. Then the organolithium compounds (organolithium reagent + compound obtained in the reaction with heteryllithium) present in the reaction mixture were neutralized by addition of Me_3SiCl . The reaction mixture was filtered and evaporated. The nucleophilic substitution products were isolated from reaction mixture by distillation *in vacuo* and tested by GC-MS and NMR. [2-(4,5-dihydrofuryl)](2-furyl)dimethylgermane (7h), [2-(4,5-dihydrofuryl)]butylmethylgermane (7i) and (5-trimethylsilyl-2-furyl)(2-furyl)dimethylgermane (9) were identified by GC-MS-spectra (Table 3).

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