

Reaction of heteryl-silanes and -germanes with metal hydrides

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Abstract

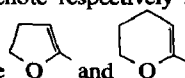
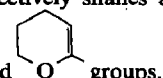
A series of heteryl-silanes and -germanes * containing a different number of dihydrofuryl and dihydropyranyl groups at the metal atom has been obtained by means of the lithium synthesis. Subsequent substitution of heteryl group for hydride ion occurs during the reaction of the compounds formed with LiAlH_4 . The hydrides and boron hydrides of lithium and sodium are able to eliminate the dihydrofuryl group from the most reactive bis[2-(4,5-dihydrofuryl)]methyl-silane (7). The reaction of tris-heteryl-silanes and -germanes with LiAlH_4 gives [2-(4,5-dihydrofuryl)]methylsilane (12), [2-(5,6-dihydro-4H-pyranyl)]methylsilane (14) and [2-(4,5-dihydrofuryl)]methylgermane (13) in good yields, which are otherwise difficult to obtain.

Introduction

As has been mentioned in our preliminary communication [1], lithium aluminium hydride can cleave the Si–C and Ge–C bonds in bis-heterylsilanes and -germanes (Het = 2-furyl, 2-tetrahydrofuryl- and [2-(4,5-dihydrofuryl)]-) to afford mono-heterylhydrosilanes and -germanes *.

The present study examines the influence of different factors on this reaction, such as the nature and number of heterocyclic groups and other substituents at the metal atom, and explores the possibility of obtaining heterylhydrosilanes and -hydrogermanes by this method. For this purpose we increased the variety of heteryl-containing substances used in this reaction.

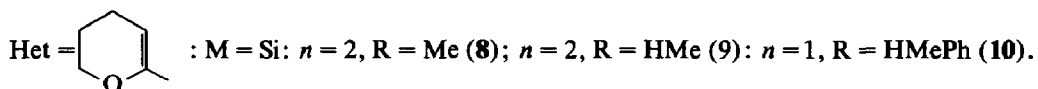
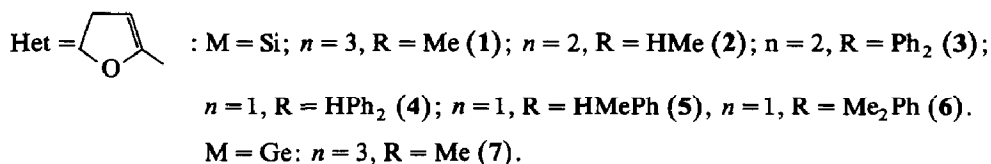
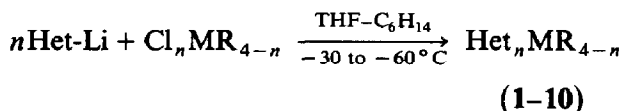
* The names heterylsilanes and heterylgermanes were used by us to denote respectively silanes and

germanes containing a heterocyclic substituent, in our case these are the  and  groups.

Results and discussion

Synthesis of heterylsilanes and -germanes

The synthesis of the known tris[2-(4,5-dihydrofuryl)]methylsilane (**1**), bis-[2-(4,5-dihydrofuryl)]methylsilane (**3**), and novel heterylsilanes and -germanes was carried out by the lithium method [2,3]; reaction of [2-(4,5-dihydrofuryl)]lithium or [2-(5,6-dihydro-4*H*-pyran)]lithium with chlorosilane or chlorogermane at low temperature:

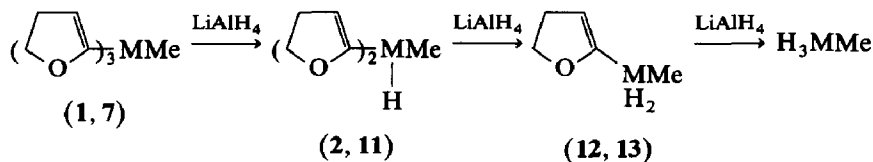


The reactions were carried out in a hexane-THF mixture. The synthesis of heterylhydrosilanes **2**, **4**, **5**, **9** and **10** place at -60°C (the other heterylsilanes and -germanes are obtained at -30°C) to avoid the reaction of heteryllithium at the Si-H bond. The yields, physico-chemical constants, the IR, ¹H NMR, and mass spectrometry data for the heterylsilanes and -germanes are presented in the Experimental.

Reactions of heterylsilanes and -germanes with LiAlH₄

Reactions of silane and germane containing three dihydrofuryl groups at the metal atom with lithium aluminium hydride were studied (Table 1).

Tris[2-(4,5-dihydrofuryl)]methylsilane (**1**) and tris[2-(4,5-dihydrofuryl)]methylgermane (**7**) were found to lose the dihydrofuryl groups more readily than their bis-dihydrofuryl analogues:



1, **2**, **12**: M = Si

7, **11**, **13**: M = Ge

The reaction proceeds stepwise. As a rule, exhaustive substitution is observed in THF and diethyl ether, the methylhydrosilane or methylhydrogermane without the heterocyclic group is the only product in this reaction. Monoheterylsilane **12** (the product of the substitution of two dihydrofuryl groups) could be obtained under the milder conditions of phase-transfer catalysis [4,5] in benzene, pentane or hexane. Thus, [2-(4,5-dihydrofuryl)]methylsilane (**12**) was obtained in 53% yield from a mixture of boiling silane **1** and LiAlH₄ in pentane in the presence of 18-crown-6.

Table 1

Reactions of heterylsilanes and -germanes with LiAlH_4

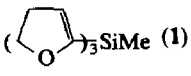
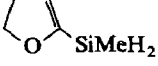
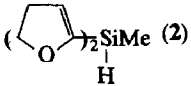

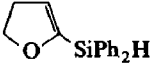
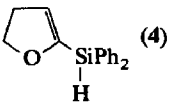
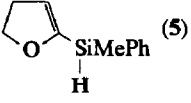


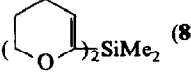
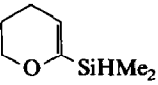
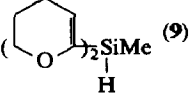
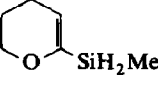

Compound	Solvent	$T, ^\circ\text{C}$	Time, h	Products, yield, % (GLC data)
 (1)	THF	25	0.5	H_3SiMe (> 95)
	Et_2O	25	3	H_3SiMe (> 95)
	C_5H_{12}	30	6	 (12) (53)
 (2)	THF	25	0.25	H_3SiMe (> 95)
	Et_2O	25	3	H_3SiMe (> 95)
	C_6H_6	80	4	12 (> 95)
 (3)	Et_2O	25	1	Ph_2SiH_2 (> 95)
	C_6H_6	25	4	 (4) (60) Ph_2SiH_2 (40)
 (4)	Et_2O	25	1	Ph_2SiH_2 (> 95)
	C_6H_6	80	4	Ph_2SiH_2 (75)
 (5)	THF	25	1	MePhSiH_2 (> 95)
	Et_2O	25	4	MePhSiH_2 (> 95)
	C_6H_6	80	200	MePhSiH_2 (~ 5)
 (6)	THF	25	4	Me_2SiPhH (> 95)
	Et_2O	25	200	Me_2SiPhH (~ 5)
 (7)	THF	25	0.25	H_3GeMe (> 95)
	Et_2O	25	3	H_3GeMe (> 95)
	C_6H_6	80	24	H_3GeMe (> 95)
 (8)	THF	25	24	H_2SiMe_2 (> 95)
	Et_2O	35	200	 (23) (25)
 (9)	THF	25	22	H_3SiMe (> 95)
	Et_2O	25	24	 (14) (> 95)
	C_6H_6	80	72	14 (65)

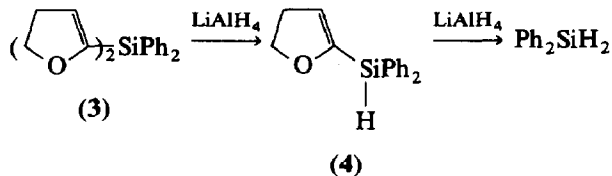
Table 1 (continued)

Compound	Solvent	T, °C	Time, h	Products, yield, % (GLC data)
 (10)	THF	25	4	MePhSiH ₂ (> 95)
	Et ₂ O	25	30	MePhSiH ₂ (> 95)

Our data indicate that bis-[2-(4,5-dihydrofuryl)]methylsilane (**2**) does not differ from tris-dihydrofurylsilane **1** in its reactivity toward LiAlH₄.

In the case of germane, the initial tris-dihydrofurylgermane **7** and the subsequent hydrogermanes **11** and **13** do not show significant differences in reactivity towards LiAlH₄, since all the components are present in equal amounts in the reaction mixture—even in apolar pentane or benzene (monoheterylgermane **13** was characterized only by GC-MS)—whereas a continuous reaction (24 h) affords only one product, viz., methylgermane.

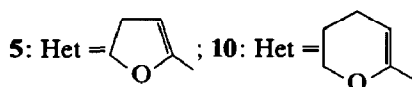
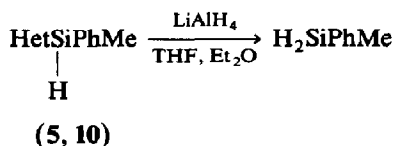
Bis[2-(4,5-dihydrofuryl)]diphenylsilane **3** reacts with LiAlH₄ more rapidly than its methyl analogue, bis[2-(4,5-dihydrofuryl)]dimethylsilane [**1**] to give diphenylsilane, the only product of the reaction in ether after ca. 1 h. The reaction proceeds stepwise in benzene, but not selectively, thus the process cannot be inhibited at the hydrosilane **4** formation step.



An independent experiment with hydrosilane **4** showed similar reactivity for silanes **3** and **4** in this reaction.

[2-(4,5-Dihydrofuryl)]dimethylphenylsilane **6** is more inert to LiAlH₄ than the heterylsilanes **3** and **4** (Table 1). Removal of the dihydrofuryl group occurs only in THF after 4 h at ambient temperature.

Dihydropyranylsilane (**10**) can also lose the heterocycle in the reaction with LiAlH₄:



At the same time, dihydropyranylsilane **10** is more stable than its dihydrofuryl analogue **5** (complete conversion of **5** silane was observed in THF after 1 h, that of silane **10**: after 4 h; silane **5** in Et₂O: after 4 h, **10** silane: after 24 h).

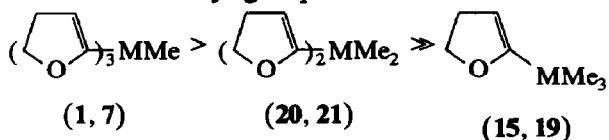
Bis[2-(5,6-dihydro-4H-pyranyl)]methylsilane (**9**) is the most reactive of dihydro-pyranylsilanes in the reaction with LiAlH_4 . It was converted into methylsilane in THF after 22 h, whereas in ether this reaction gives the monoheteryl derivative, [2-(5,6-dihydro-4H-pyranyl)]methylsilane (**14**), in quantitative yield after 24 h (identified by GC-MS).

Bis[2-(5,6-dihydro-4H-pyranyl)]dimethylsilane also reacts with LiAlH_4 ; the reaction is accompanied by the cleavage of Si-C bond in the heterocycle (see Table 1).

The monoheterylsilanes and -germanes ([2-(4,5-dihydrofuryl)]trimethylsilane (**15**), (2-furyl)trimethylsilane (**16**), (2-tetrahydrofuryl)trimethylsilane (**17**), [2-(5,6-dihydro-4H-pyranyl)]trimethylsilane (**18**) and [2-(4,5-dihydrofuryl)]trimethylgermane (**19**)) containing three alkyl substituents at the metal atom are stable to LiAlH_4 and do not lose the heterocycle even during continuous refluxing in THF.

The results of the reactions of heterylsilanes and -germanes with LiAlH_4 , indicate that their reactivity depends on the number and nature of heteryl groups on the Si or Ge atom.

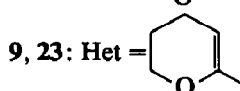
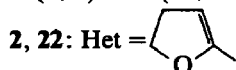
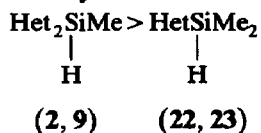
The reactivity of silanes and germanes tends to decrease with the decreasing number of heteryl groups.



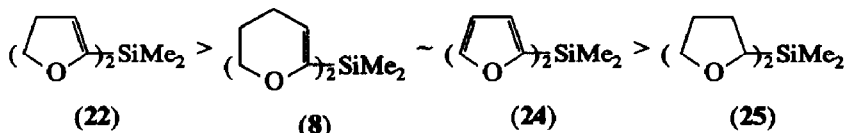
1, 15, 20: M = Si

7, 19, 21: M = Ge

Heterylsilanes containing one Si-H bond behave similarly:



Our data on the stability of bisdihydropyranylsilane **8** towards LiAlH_4 (Table 1) have extended the existing series of bis-heterylsilanes. Arranged in the order of ease of heterocycle elimination they are:



An increase in the stability of the silane towards LiAlH_4 with decrease in the number of phenyl groups in the molecule was found for the series of phenyl-containing dihydrofurylsilanes:

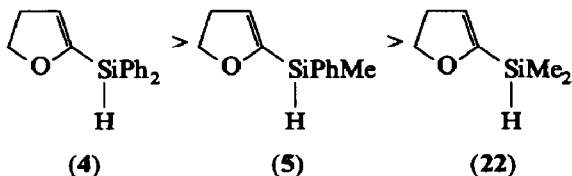
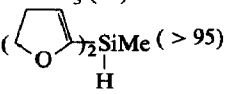
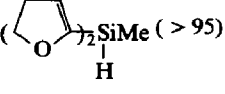
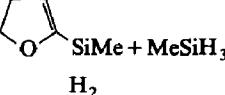
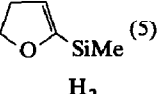
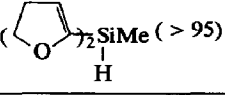


Table 2

Reaction of bis[2-(4,5-dihydrofuryl)]methylsilane (**2**) with LiBH_4 , NaBH_4 , LiH , and NaH

Metal hydride	Solvent	$T, ^\circ\text{C}$	Time, h	Product, % (GLC data)
LiBH_4	THF	25	24	MeSiH_3 (75)
	C_6H_6	80	5	 (> 95)
NaBH_4	THF	25	24	MeSiH_3 (59)
	C_6H_6	80	5	 (> 95)
LiH	THF	25	24	 + MeSiH_3 1 : 1.4
	C_6H_5	80	5	 (5)
NaH	THF	25	24	MeSiH_3 (20)
	C_6H_6	80	5	 (> 95)

A study of the results indicates that the replacement of the dihydrofuryl group by a hydride ion occurs predominantly in silanes and germanes, which are able (after elimination of the heteryl group) to conjugate Si or Ge with the substituent containing the π -system (heteryl or aromatic group). Consequently, if the number of substituents at silicon or germanium is large, a better leaving group is a heteryl substituent substituted by a hydride ion.

Reaction of bis[2-(4,5-dihydrofuryl)]methylsilane (**2**) with metal hydrides

The eliminations of the heteryl group from heterylsilanes by other metal hydrides viz., lithium hydride, sodium hydride, lithium boron hydride, sodium boron hydride, have been studied. Bis[2-(4,5-dihydrofuryl)]methylsilane (**2**), which has the highest reactivity in the reactions with LiAlH_4 , was selected for the investigation.

It has been found that the metal hydrides mentioned can eliminate the dihydrofuryl group from the hydrosilane **2**, but they are less reactive and less selective than LiAlH_4 (see Table 2). Bis[2-(4,5-dihydrofuryl)]methylsilane (**2**) does not undergo any changes in the reaction with LiBH_4 and NaBH_4 under phase-transfer catalysis (0.1 M solution **2** in benzene, 5% 18-crown-6, [2]:[metal hydride] = 1:2, 5 h, 80°C). The product of the substitution of one dihydrofuryl group, the hydrosilane **12**, is obtained in small amounts ($\sim 5\%$) under the same conditions but only with LiH and NaH . The reactions with NaH , LiBH_4 and NaBH_4 give products which have undergone exhaustive substitution of the dihydrofuryl groups in silane **2** viz., methylsilane in 20, 75 and 59% yield, respectively (reaction in the more polar THF at ambient temperature after 24 h proceeds differently). In contrast, under the same

conditions the reaction with LiH leads to a stepwise substitution of dihydrofuryl groups, and after 24 h the reaction mixture consists of the products of substitution of one or two dihydrofuryl groups by hydride ion in the ratio 1 : 1.4.

Thus, these experiments show that the replacement of furyl, dihydrofuryl, dihydropyranyl or tetrahydrofuryl groups in heterylsilanes and -germanes by hydride ion can serve as a convenient and, in some cases, the only method for the preparation of heterylsilanes (Table 2) and heterylgermanes; which are otherwise difficult to obtain [1].

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). GLC analysis was carried out with a Chrom-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).

[2-(4,5-Dihydrofuryl)]lithium was prepared by the addition of 5–6 *N* n-BuLi solution in hexane to tetrahydrofuran solution of dihydrofuran (the ratio of THF to hexane = 2 : 1) at -30°C with subsequent stirring for 30 min: the temperature was then raised to ambient temperature and the mixture was stirred for 1 h.

[2-(5,6-Dihydro-4*H*-pyranyl)]lithium was obtained by the addition of 5–6 *N* n-BuLi solution in hexane to tetrahydrofuran solution of dihydropyran (the ratio of THF to hexane = 1 : 1) at -30°C , with subsequent stirring for 30 min, the temperature of the reaction was raised to boiling point and the reaction mixture was stirred for 1 h.

Synthesis of heterylsilanes and -germanes (General Procedure)

[2-(4,5-Dihydrofuryl)]lithium or [2-(5,6-dihydro-4*H*-pyranyl)]lithium was added to the chlorosilane solution in THF (in the case of silane 3 to Ph_2SiH_2 solution in a 1 : 1 mixture of THF–hexane) at low temperature (-30°C for 3, 4, 6, 7, and 8, -60°C for 5, 9, and 10). The mixture was stirred for 30 min and the temperature was raised to ambient temperature followed by stirring for 1 h. After 12 h. the reaction mixture was filtered, evaporated and the product obtained was distilled in vacuum (3 and 4 were isolated by column chromatography, eluent 2% ethyl acetate in hexane). The ^1H NMR and mass spectral data for these compounds are given in Table 3.

Tris[2-(4,5-dihydrofuryl)]methylsilane (1) and bis[2-(4,5-dihydrofuryl)]methylsilane (2) were prepared by published procedures [2,3] and their structures are in full agreement with published data.

Bis[2-(4,5-dihydrofuryl)]diphenylsilane (3) and [2-(4,5-dihydrofuryl)]diphenylsilane (4)

The mixture of 0.3 mol of dihydrofuryllithium and 55.3 g (0.3 mol) of diphenylsilane was treated with saturated aqueous solution of NH_4Cl ; the organic layer was separated and the aqueous solution was extracted with 50 ml of THF. The organic extracts were combined, dried, and the solvent was removed by evaporation. The mixture of products was separated on a chromatographic column packed with silica

Table 3

¹H NMR and mass spectra of heterylsilanes and -germanes

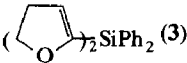
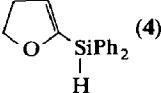
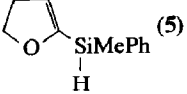
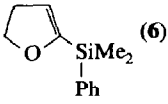
Compound	¹ H NMR spectrum, ppm	Mass spectrum <i>m/z</i> (rel. intensity, %)
 (3)	2.62 (d.t., 4H, 4-CH ₂); 4.38 (t, 4H, 5-CH ₂ , <i>J</i> 9.5 Hz); 5.40 (t, 2H, 3-CH, <i>J</i> = 2.3 Hz); 7.16– 7.77 (m, 10H, C ₆ H ₅)	320 (<i>M</i> ⁺ , 59), 263 (9), 262 (6), 249 (7), 223 (17), 222 (12), 221 (51), 220 (6), 219 (9), 217 (8), 215 (11), 214 (13), 213 (13), 212 (6), 211 (10), 207 (6), 200 (7), 199 (38), 197 (6), 195 (6), 187(6), 185(8), 184 (10), 183 (26), 182 (9), 181 (22), 180 (8), 174 (5), 173 (12), 167 (7), 165 (7), 160 (5), 155 (8), 147 (8), 143 (11), 142 (6), 136 (5), 131 (7), 130 (7), 129 (14), 128 (7), 123 (16), 117 (9), 115 (12), 107 (8), 106 (14), 105 (100), 103 (7), 102 (7), 92 (6), 91 (21), 79 (13), 78 (12), 77 (22), 67 (7), 53 (28), 51 (12), 45 (22), 41 (14), 39 (20), 27 (6).
 (4)	2.61 (d.t., 2H, 4-CH ₂); 4.33 (t, 2H, 5-CH ₂ , <i>J</i> 9.15 Hz); 5.13 (s, 1H, Si-H); 5.39 (t, 1H, 3-CH, <i>J</i> 2.45 Hz); 7.16–7.69 (m, 10H, C ₆ H ₅)	252 (<i>M</i> ⁺ , 57), 224 (10), 223 (13), 222 (15), 221 (13), 208 (12), 207 (9), 195 (5), 184 (10), 183 (51), 182 (20), 181 (48), 180 (15), 179 (6), 178 (7), 176 (6), 175 (34), 174 (27), 173 (25), 172 (5), 155 (6), 147 (17), 146 (11), 145 (10), 144 (22), 143 (12), 131 (9), 130 (13), 129 (16), 128 (9), 117 (5), 115 (7), 107 (12), 106 (14), 105 (100), 104 (5), 103 (9), 102 (15), 98 (7), 97 (10), 96 (5), 91 (10), 79 (18), 78 (16), 77 (16), 67 (5), 55 (5), 54 (6), 53 (40), 52 (5) 51 (14), 50 (7), 45 (17), 41 (6), 39 (13).
 (5)	0.47 (d, 6H, Si-CH ₃ , <i>J</i> 3.5 Hz); 2.56 (d.t., 2H, 4-CH ₂); 4.28 (t, 2H, 5-CH ₂ , <i>J</i> 9.27 Hz); 4.58 (sq., 1H, Si-H); 5.31 (t, 1H, 3-CH, <i>J</i> 2.15 Hz); 7.16–7.69 (m. 5H, C ₆ H ₅)	190 (<i>M</i> ⁺ , 98), 176 (15), 175 (100), 173 (16), 161 (23), 160 (13), 159 (19), 147 (23), 146 (12), 145 (45), 137 (9), 135 (5), 134 (6), 131 (11), 129 (5), 123 (6), 122 (13), 121 (95), 120 (14) 119 (14), 113 (9), 112 (15), 111 (17), 107 (6), 106 (9), 105 (56), 97 (28), 91 (12), 85 (8), 79 (7), 78 (6), 77 (6), 69 (7), 67 (7), 53 (12), 45 (8), 43 (12)
 (6)	0.38 (s, 6H, Si-CH ₃); 2.56 (d.t., 2H, 4-CH ₂ , <i>J</i> 2.75 Hz); 4.27 (t, 2H, 5-CH ₂ , <i>J</i> 9.4 Hz); 5.2 (t, 1H, 3-CH, <i>J</i> 2.75 Hz); 7.18–7.67 (m, 5H, C ₆ H ₅)	204 (<i>M</i> ⁺ , 34), 189 (10), 176 (9), 161 (19), 160 (11), 159 (67), 149 (10), 137 (5), 136 (9), 135 (69), 133 (6), 131 (10), 129 (6), 121 (5), 119 (9), 117 (5), 111 (7), 107 (11), 105 (34), 97 (6), 93 (8), 91 (16), 83 (5), 79 (9), 78 (6), 77 (11), 75 (6), 69 (11), 67 (13), 66 (6), 65 (6), 61 (6), 59 (11), 57 (5), 55 (10), 53 (30), 51 (14), 50 (6), 45 (17), 44 (5), 43 (52), 42 (6), 41 (14), 39 (28), 32 (21)

Table 3 (continued)



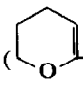
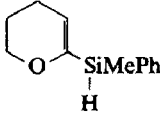
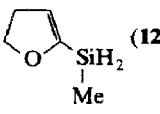
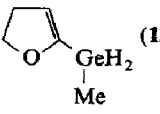
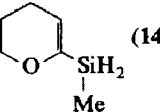
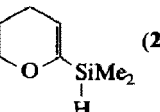
Compound	¹ H NMR spectrum, ppm	Mass spectrum <i>m/z</i> (rel. intensity, %)
 (7)	0.58 (s, 3H, Ge-CH ₃); 2.59 (d.t., 6H, 4-CH ₂ , <i>J</i> _{4,3} 2.5 Hz); 4.31 (t, 6H, 5-CH ₂ , <i>J</i> 9.5 Hz), 5.29 (t, 3H, 3-CH, <i>J</i> 2.5 Hz)	296 (<i>M</i> ⁺ , 26), 295 (9), 294 (19), 292 (14), 251 (6), 225 (9), 223 (13), 221 (12), 219 (7), 199 (6), 197 (18), 196 (7), 195 (21), 193 (18), 191 (9), 179 (7), 178 (17), 177 (5), 169 (11), 167 (26), 166 (8), 165 (22), 163 (23), 161 (6), 158 (5), 157 (5), 156 (5), 155 (5), 153 (5), 152 (5), 151 (9), 150 (7), 149 (8), 143 (12), 141 (11), 139 (14), 138 (25), 137 (12), 135 (9), 133 (6), 129 (6), 127 (6), 125 (5), 121 (6), 117 (6), 115 (20), 114 (5), 113 (45), 112 (12), 111 (38), 110 (33), 109 (34), 107 (7), 105 (9), 101 (5), 99 (9), 97 (17), 95 (9), 93 (10), 91 (40), 89 (42), 88 (9), 87 (32), 85 (20), 83 (10), 82 (7), 81 (9), 79 (16), 77 (9), 75 (6), 74 (5), 73 (5), 71 (6), 69 (34), 68 (7), 67 (7), 65 (5), 55 (16), 53 (16), 51 (5), 43 (6), 42 (10), 41 (100), 40 (14), 39 (74), 38 (8), 30 (6), 29 (17), 28 (43), 27 (25)
 (8)	0.18 (s, 6H, Si-CH ₃); 1.64–2.16 (m, 8H, 4,5-CH ₂); 3.60–4.02 (m, 4H, 6-CH ₂); 4.98– 5.16 (m, 2H, 3-CH)	224 (<i>M</i> ⁺ , 17), 196 (5), 167 (5), 151 (5), 141 (7), 127 (6), 125 (13), 113 (6), 111 (15), 109 (6), 101 (10), 99 (8), 97 (7), 91 (6), 87 (5), 85 (10), 83 (16), 79 (5), 77 (21), 76 (8), 75 (100), 69 (5), 67 (8), 61 (12), 59 (20), 58 (5), 55 (13), 53 (8), 47 (10) 45 (16), 43 (17), 41 (13), 39 (15), 32 (7), 29 (8), 28 (38), 27 (21)
 (9)	0.23 (d, 3H, Si-CH ₃); 1.67–2.20 (m, 8H, 4,5- CH ₂); 3.80–4.11 (m, 4H, 6-CH ₂); 5.09–5.33 (m, 2H, 3-CH)	210 (<i>M</i> ⁺ , 27), 153 (5), 151 (5), 139 (5), 137 (6), 127 (15), 126 (9), 125 (13), 113 (9), 112 (11), 111 (25), 109 (8), 105 (6), 103 (5), 101 (17), 99 (22), 98 (21), 97 (26), 96 (7), 95 (9), 91 (11), 87 (17), 85 (15), 83 (17), 81 (6), 79 (8), 78 (5), 77 (25), 75 (6), 71 (14), 69 (21), 68 (6), 67 (21), 66 (6), 65 (7), 63 (10), 62 (7), 61 (100), 59 (6), 55 (32), 54 (6), 53 (16), 45 (46), 44 (6), 43 (34), 42 (6) 41 (30), 40 (6), 39 (26), 32 (10), 29 (10), 28 (20), 27 (12)

Table 3 (continued)

Compound	¹ H NMR spectrum, ppm	Mass spectrum <i>m/z</i> (rel. intensity, %)
 (10)	0.42 (d, 3H, Si-CH ₃ , <i>J</i> 2.3 Hz); 1.62–2.02 (m, 4H, 4,5-CH ₂), 3.82–4.04 (m, 2H, 6- CH ₂); 4.34–4.56 (m, 1H, Si-H); 5.00–5.19 (m, 1H, 3-CH); 7.20– 7.67 (m, 5H, C ₆ H ₅)	204 (<i>M</i> ⁺ , 42), 190 (7), 189 (37), 177 (6), 175 (13), 163 (6), 161 (13), 159 (11), 149 (23), 147 (9), 145 (8), 143 (6), 137 (35), 131 (6), 126 (10), 125 (6), 123 (34), 122 (14), 121 (100), 120 (10), 119 (7), 111 (19), 107 (6), 106 (7), 105 (39), 99 (6), 98 (16), 95 (8), 93 (8), 91 (11), 83 (6), 79 (9), 78 (7), 77 (9), 71 (6), 69 (8), 67 (10), 66 (6), 65 (6), 61 (15), 55 (10), 53 (21), 51 (7), 45 (16), 43 (27), 39 (7),
 (12)	0.33 (t, 9H, Si-CH ₃ , <i>J</i> 3.9 Hz), 2.48–2.79 (m, 2H, 4-CH ₂), 3.91– 4.11 (m, 2H, Si-H), 4.36 (t, 2H, 5-CH ₂ , <i>J</i> 9.1 Hz), 5.40 (t, 1H, 3-CH, <i>J</i> 2.6 Hz)	114 (<i>M</i> ⁺ , 48), 113 (10), 111 (8), 99 (11), 97 (7), 85 (12), 84 (12), 83 (13), 75 (6), 73 (23), 71 (15), 69 (30), 68 (5), 67 (7), 61 (11), 59 (8), 58 (24), 55 (16), 54 (6), 53 (9), 47 (5), 46 (6), 45 (100), 44 (7), 43 (35) 42 (6), 41 (8), 39 (10)
 (13)		160 (<i>M</i> ⁺ , 20), 159 (5), 158 (20), 156 (12), 117 (18), 115 (33), 114 (5), 113 (37), 112 (7), 111 (22), 110 (5), 109 (6), 93 (15), 91 (70), 90 (25), 89 (100), 88 (32), 87 (83), 86 (8), 85 (21), 83 (6), 76 (7), 75 (19), 74 (32), 73 (23), 72 (21), 71 (28), 70 (29), 69 (62), 68 (7), 55 (22), 54 (18), 53 (10), 45 (5), 43 (7), 42 (20) 41 (48), 40 (10), 39 (60), 38 (11), 37 (6), 31 (11), 30 (7), 29 (17), 28 (79), 27 (20)
 (14)		128 (<i>M</i> ⁺ , 51), 127 (12), 113 (20), 111 (7), 100 (8), 99 (58), 98 (6), 97 (10), 95 (6), 87 (14), 85 (23), 84 (7), 83 (64), 74 (5), 73 (15), 72 (16) 71 (23), 70 (7), 69 (17), 68 (7), 67 (16), 66 (13), 61 (65), 60 (6), 59 (7), 58 (9), 55 (60), 54 (7), 53 (17), 47 (8), 46 (7), 45 (100), 44 (19), 43 (18), 41 (5), 39 (15)
 (23)	0.07 (d, 6H, Si-CH ₃ , <i>J</i> 3.5 Hz); 1.47–2.04 (m, 4H, 4,5-CH ₂); 6.9–3.97 (m, 3H, 6-CH ₂ , Si-H); 4.67– 5.00 (m, 1H, 3-CH)	142 (<i>M</i> ⁺ , 42), 141 (12), 127 (43), 125 (10), 113 (23), 111 (8), 109 (8), 101 (15), 99 (48), 97 (20), 87 (11), 85 (16), 83 (20), 75 (85), 67 (12), 61 (63), 59 (100), 58 (16), 55 (19), 53 (12), 45 (16), 43 (25)

gel L 40/100, to give 10.6 g of **3** (yield 22%) and 12.7 g of **4** (yield 17%), $n_D^{20} = 1.5807$. IR (cm^{-1}): **3** 1592 ($\nu(\text{C}=\text{C})$); **4** 2120 ($\nu(\text{Si}-\text{H})$), 1592 ($\nu(\text{C}=\text{C})$).

[2-(4,5-Dihydrofuryl)]methylphenylsilane (5).

5 (30 g, yield 26%), b.p. 88–90 °C/3 mm Hg., $n_D^{20} = 1.5350$ was prepared from methylphenylchlorosilane (94.0 g, 0.6 mol) and dihydrofuryllithium (0.6 mol). IR (cm^{-1}): 2140 ($\nu(\text{Si}-\text{H})$), 1598 ($\nu(\text{C}=\text{C})$).

2-(4,5-Dihydrofuryl)dimethylphenylsilane (6).

6 (2.8 g, yield 47%) was obtained from a mixture of dimethylphenylsilane (4.1 g, 0.03 mol) and dihydrofuryllithium (0.03 mol), $n_D^{20} = 1.5311$. IR (cm^{-1}): 1596 ($\nu(\text{C}=\text{C})$).

Tris[2-(4,5-dihydrofuryl)]methylgermane (7).

7 (21 g, yield 38%) was obtained from a mixture of methylchlorogermane (29.5 g 0.19 mol) and dihydrofuryllithium (0.57 mol), b.p. 135–137 °C/1 mm Hg, IR (cm^{-1}): 1602 ($\nu(\text{C}=\text{C})$).

Bis-2-(5,6-dihydro-4H-pyranyl)dimethylsilane (8).

8 (5.9 g, yield 53%) was obtained from a mixture of dimethyldichlorosilane (6.4 g, 0.05 mol) and dihydropyranlyllithium (0.1 mol), b.p. 120 °C/3 mm Hg, $n_D^{20} = 1.4981$. IR (cm^{-1}): 1620 ($\nu(\text{C}=\text{C})$).

Bis-2-(5,6-dihydro-4H-pyranyl)methylsilane (9).

9 (5.2 g, yield 49%) was prepared from methylchlorosilane (5.7 g, 0.05 mol) and dihydropyranlyllithium (0.1 mol), b.p. 119 °C/4 mm Hg, $n_D^{20} = 1.5098$. IR (cm^{-1}): 1620 ($\nu(\text{C}=\text{C})$), 2140 ($\nu(\text{Si}-\text{H})$).

2-(5,6-Dihydro-4H-pyranyl)methylphenylsilane (10).

10 (16.4 g, yield 45%) was obtained from a mixture of methylphenylchlorosilane (28.2 g, 0.18 mol) and dihydropyranlyllithium (0.18 mol), b.p. 109 °C/2 mm Hg, $n_D^{20} = 1.5380$. IR (cm^{-1}): 2125 ($\nu(\text{Si}-\text{H})$).

Reactions of heterylsilanes and -germanes with metal hydrides (General Procedure)

Metal hydride (0.6 mmol) and 10 μl of the corresponding alkane (as internal standard) were added to 0.3 mmol of substrate in 3 ml of solvent. 18-Crown-6 (5 mol%) was used as the catalyst in the phase-transfer reaction in benzene, pentane or hexane solution. The reaction products were analyzed by GLC. The temperature and time of reaction, and the yields of silanes and germanes are presented in Tables 1 and 2; NMR and mass spectra are given in Table 3.

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