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CONVERSIONS OF [2-(4,5-DIHYDROFURYL)]-SILANES AND -GERMANES UNDER CATALYTIC HYDROGENATION CONDITIONS

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Summary

(2-Tetrahydrofuryl)-silanes and -germanes were obtained in high yield by the heterogeneous liquid-phase hydrogenation of [2-(4,5-dihydrofuryl)]trimethylsilane (I), bis[2-(4,5-dihydrofuryl)]dimethylsilane (II) and [2-(4,5-dihydrofuryl)]trimethylgermane with a Pd/Al_2O_3 catalyst. The dihydrofurylsilanes I and II were found to undergo disproportionation and dehydrogenation, the latter being involved in both intra- and inter-molecular disproportionation.

Introduction

(2-Tetrahydrofuryl)-silanes and germanes were unknown and all attempts to obtain these compounds using conventional organometallic chemistry methods such as hydrosilation/hydrogermylation of 2,3-dihydrofuran or metallation of 2-chlorotetrahydrofuran with n-BuLi followed by a reaction with chlorosilane, were unsuccesful [1]. It was demonstrated earlier that catalytic hydrogenation of [3-(2,5-dihydrofuryl)]-silanes and -germanes on palladium catalysts appeared to be the most convenient route to 3-tetrahydrofuryl derivatives of silicon and germanium which are difficult to obtain by other methods [2]. It follows then that liquid-phase hydrogenation of the appropriate silyl and germyl derivatives of 2,3-dihydrofuran may serve as a convenient method for the preparation of (2-tetrahydrofuryl)-silanes and -germanes. Furthermore, it was found that during the hydrogenation of [3-(2,5-dihydrofuryl)]-silanes and -germanes in the presence of a palladium catalyst other reactions such as isomerization, disproportionation, dehydrogenation leading to 3-furyl, 3-dihydrofuryl- and 3-tetrahydrofuryl-silanes (-germanes) can take place in addition to the prevailing hydrogenation process [2]. In the case of [2-(4,5-dihydrofuryl)]-silanes (-germanes) these conversions attract attention since they may serve as a source of various organosilicon (organogermanium) compounds *.

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* For a preliminary communication see ref. 3.

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Results and discussion

The starting compounds, [2-(4,5-dihydrofuryl)]trimethylsilane (I), bis[2-(4,5-dihydrofuryl)]dimethylsilane (II) [2-(4,5-dihydrofuryl)]trimethylgermane (III) were prepared by reacting [2-(4,5-dihydrofuryl)]lithium with trimethylchlorosilane, dimethyldichlorosilane and trimethylchlorogermane, respectively, according to ref. 4.

The reactions of I–III were carried out in a liquid phase in the presence of a Pd catalyst (5% wt. Pd/Al_2O_3) in solvents with different polarity. Previously it was shown that compounds I–III on making contact with the carrier (neutral Al_2O_3) in the solvents used, at 25–100°C, do not undergo any transformations.

Experiments show that in the absence of hydrogen, silane I in the presence of the catalyst Pd/Al_2O_3 was selectively (80–90% balance) converted into 2-trimethylsilylfuran (IV) and 2-(trimethylsilyl)tetrahydrofuran (V) (Table 1). Product V can arise only from disproportionation of I; furylsilane IV can be formed both by disproportionation and on dehydrogenation of I.

(IV) (I) (IV) (V)

The content of IV in the reaction mixtures is invariably higher than that of V, hence the dehydrogenation runs parallel to the disproportionation. In dilute ethanol solution at room temperature the two processes are slow. Elevation of temperature and, in particular, solution concentration enhance the formation of IV and V (Table 1). The ratio and rate of product formation arising from I in hexane were essentially the same as in the case of ethanol, thus solvent polarity does not appear to affect, to

TABLE 1

CONVERSIONS OF [2-(4,5-DIHYDROFURYL)]TRIMETHYLSILANE (I) ON 5% Pd/Al_2O_3 ([I]/[Pd] = 50/1)

Solvent	Initial concentration of I (*M*)	Temperature, (°C)	Time, (h)	Ratio of reaction mixture components, (%) (GLC data)		
				I	V	IV
EtOH	0.1	25	48	98.5	0.5	1
	1.0	25	48	3.1	17	52
	0.1	100	3	95	2	3
	0.1	100	15	81	4	15
	1.0	100	3	4	17	79
	1.0	100	15	–	18	82
THF	1.0	25	48	79	2	19
	1.0	100	3	76	3	21
	1.0	100	15	68	5	27
Et_2O	1.0	25	48	89	3	8
	1.0	100	3	80	3	17
	1.0	100	15	77	4	19
Hexane	1.0	25	48	48	16	36
	1.0	100	3	7	15	78
	1.0	100	15	–	17	83

TABLE 2

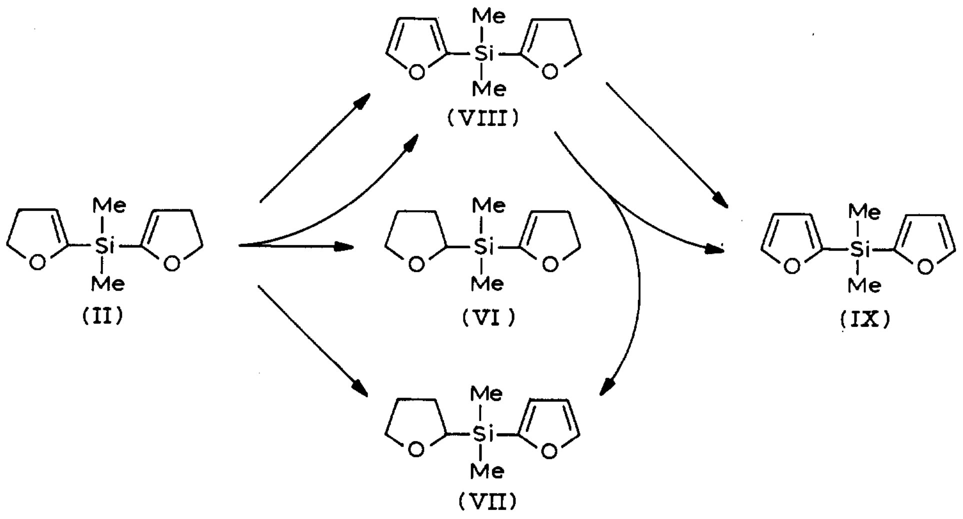
CONVERSIONS OF BIS[2-(4,5-DIHYDROFURYL)]DIMETHYLSILANE (II) ON 5% Pd/Al_2O_3 IN HEXANE ([II]/[Pd] = 50/1, 100°C) IN THE ABSENCE OF HYDROGEN

Initial concentration of II, (*M*)	Time, (h)	Ratio of reaction mixture components (%) (GLC data)				
		II	VI	VII	VIII	IX
0.1	1	84	2	4	10	–
	3	76	3	6	15	–
	12	33	8	33	20	6
	40	–	20	66	–	14
1.0	1	4	6	8	33	49
	3	–	6	17	19	58
	8	–	6	17	–	77

any appreciable extent, the interaction of I with the palladium catalyst. At the same time, dehydrogenation and disproportionation of I occur much slower in tetrahydrofuran and ether than in ethanol and hexane, which may be accounted for by the stronger solvation properties of the solvents towards the substrate interfering with the adsorption of I onto the catalyst.

Germane III in hexane with Pd/Al_2O_3 being used as a catalyst under conditions identical to those described for I was not found to undergo any changes. A decline in the [III]/[Pd] ratio from 50/1 to 10/1 also failed to promote any products of III in the reaction mixture.

Thus, dihydrofurylsilane (I), in the presence of a palladium catalyst, is subject to dehydrogenation and disproportionation leading to the appropriate furyl- and tetrahydrofuryl-silanes. A similar reaction would also be expected for bis(dihydrofuryl)-silane II.



SCHEME 1

In fact, our findings reveal that II in hexane in the presence of 5% Pd/Al_2O_3, 100°C, yields several products including [2-(4,5-dihydrofuryl)](2-tetrahydrofuryl)dimethylsilane (VI), (2-furyl)(2-tetrahydrofuryl)dimethylsilane (VII), (2-furyl)[2-(4,5-dihydrofuryl)]dimethylsilane (VIII) and bis(2-furyl)dimethylsilane (IX) (Table 2, Scheme 1).

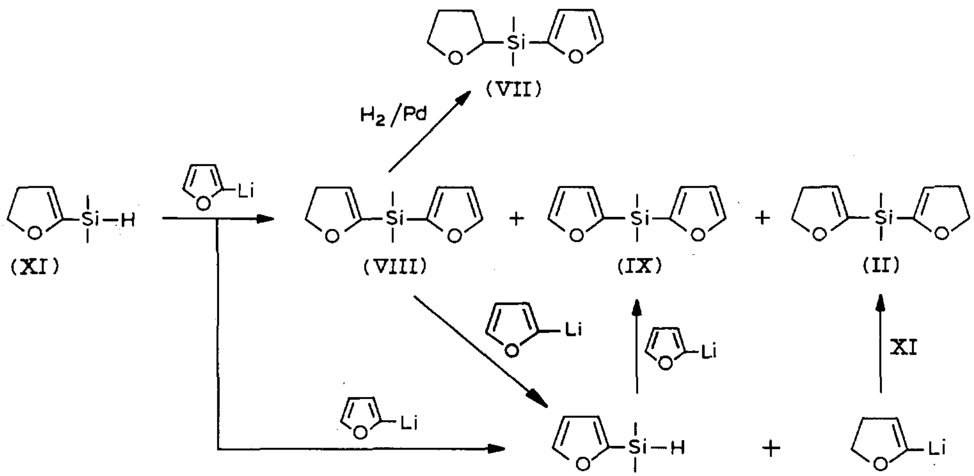
The tetrahydrofuryl containing products VI and VII can be obtained from II only by way of its disproportionation, silane VI being formed exclusively by intermolecular disproportionation of II. Silane VIII can be formed by this process and also from the dehydrogenation of II. The data of Table 2 indicate that dehydrogenation of II is prevalent over intermolecular disproportionation of II.

IX is predominantly formed by consecutive dehydrogenation: II → VIII → IX, these transformations being the prevalent ones at a 1 *M* concentration of II in solution. It is possible, especially in the latter case, that IX can also be formed directly from II.

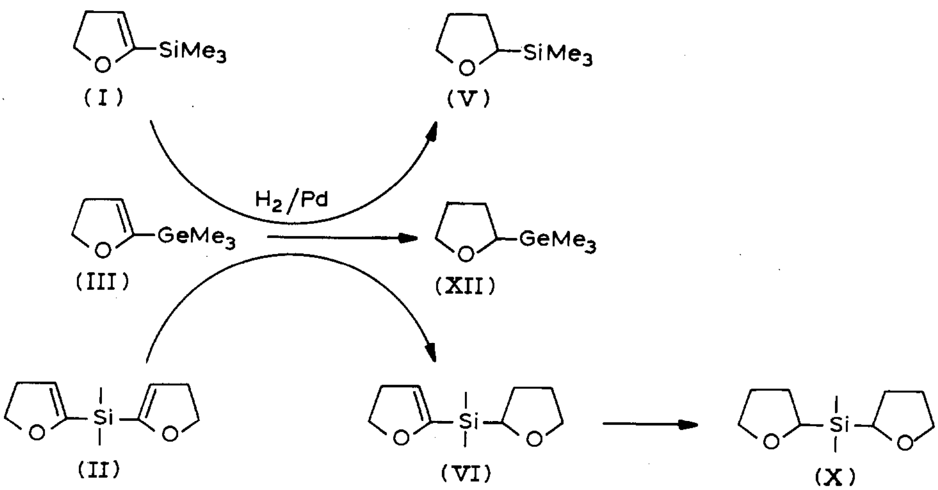
The silane VII can arise from II exclusively through its disproportionation, the increase in VII content in the reaction mixture on dilution (Table 2) suggesting the predominantly disproportionation intramolecular character of II leading to VII. Data in Table 2 also permit us to suggest the intermolecular disproportionation of VIII as a possible route to VII. The absence of bis(2-tetrahydrofuryl)dimethylsilane (X) from the reaction mixture indicates that silane VI is not involved in disproportionation under these conditions.

The structure of compounds IV–IX was confirmed by their ^{1}H NMR and mass spectra (see Experimental, Table 5, 6), as well as by an alternative synthesis (Scheme 2). Thus, by reacting [2-(4,5-dihydrofuryl)]dimethylsilane (XI) [5] with 2-furyllithium in ether a product identical to silane VIII was obtained in 57% yield. Interestingly, apart from VIII compounds II and IX are also produced in this reaction with yields of 21 and 10% respectively.

The formation of these compounds can occur either by cleaving the Si–C$_{furyl}$ bond of the starting hydrosilane XI with furyllithium [6] or with LiH, (which is



SCHEME 2



SCHEME 3

formed in the reaction) or by breaking the same bond in the product VIII (Scheme 2).

Silane VII, identical to that resulting from II, was obtained on catalytic hydrogenation of VIII (0.1 *M* solution in hexane, 25°C, 1 atm H_2, 5% Pd/Al_2O_3 used as catalyst, [VIII]/[Pd] = 50/1).

Silane VI identical to that obtained from II with 5% Pd/Al_2O_3 being used as catalyst in the absence of hydrogen, was prepared by hydrogenation of II (see below, Scheme 3).

TABLE 3

HYDROGENATION OF 2-[(4,5-DIHYDROFURYL)]TRIMETHYLSILANE (I) AND 2-[(4,5-DIHYDROFURYL)]TRIMETHYLGERMANE (III)

(0.1 *M* solution, catalyst 5% Pd/Al_2O_3, 25°C, 1 atm H_2)

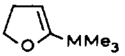
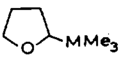
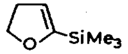
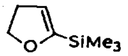
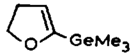
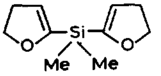
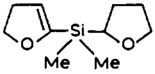
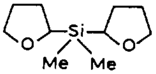
Starting compound	Solvent	[substrate]/[Pd]	Time, (h)	Ratio of reaction mixture components (%) (GLC data)	
					
	EtOH	20/1	0.3	86	14
			1.0	19	81
			1.3	2	98
			1.5	–	100
	hexane	50/1	2.5	74	26
			4.0	47	53
			5.0	23	77
			6.5	11	89
	hexane	10/1	1	93	7
			3	56	44
			10	27	73
			12	16	84
			15	–	100
		50/1	48	100	–

TABLE 4

HYDROGENATION OF BIS [2-(4,5-DIHYDROFURYL)]DIMETHYLSILANE (II)

(0.1 *M* solution in hexane, catalyst 5% Pd/Al_2O_3, 25°C, 1 atm H_2)

[II]/[Pd]	Time, (h)	Ratio of reaction mixture components, (%) (GLC data)		
				
50/1	2.5	80	20	2
	10	31	66	3
	20	–	96	4
25/1	0.5	26	52	22
	1.0	–	27	73
	1.5	–	–	100

Hydrogenation of dihydrofuryl silanes I and II was examined using the same catalyst, Pd/Al_2O_3 (5%), catalyst, as that used in the reactions of these silanes without hydrogen. Silane I in ethanol and hexane undergoes selective ($>$ 95% balance) hydrogenation under mild conditions (25°C, 1 atm H_2) to the corresponding tetrahydrofuryl derivative (V) (Table 3, Scheme 3). Germane III undergoes hydrogenation in hexane to give (2-tetrahydrofuryl)trimethylgermane (XII) at a much slower rate than its silicon counterpart, I.

Germane III can be converted to XII (∼ 60% balance) only when the ratio [III]/[Pd] is 10/1. Bis(dihydrofuryl)silane II, depending on the amount of catalyst present, can undergo hydrogenation to VI or to bis(tetrahydrofuryl)silane X (Scheme 3, Table 4).

Consequently, the study of catalytic reactions with [2-(4,5-dihydrofuryl)]silanes (I, II) and [2-(4,5-dihydrofuryl)]germane (III) has shown that their hydrogenation on palladium can be useful as a preparative procedure for obtaining (2-tetrahydrofuryl)-silanes and -germanes. Without hydrogen the silicon-containing dihydrofurans, in the presence of a palladium catalyst, can undergo dehydrogenation and disproportionation to give otherwise unattainable furyl- and tetrahydrofuryl-silanes.

Experimental

^1H NMR spectra were obtained on a Bruker WH-90/DS spectrometer using $CDCl_3$ as solvent and TMS and cyclohexane as internal standards. Mass spectra were recorded on a Kratos MS-25 GC/MS system (70 eV).

The catalytic procedures were described earlier [2]. These reactions were monitored by GLC analysis of the reaction mixtures using a Chrom-5 instrument with flame-ionization detector, glass column (2.4 × 3 mm) packed with 10% SE-30 and 2.5% Reoplex-400 on Chromosorb W-AW (60–80 mesh), helium was used as carrier gas (50 ml/min). The column temperature was 100°C for the catalytic reactions of silane I and germane III or 130°C for the analysis of a mixture of silane II and its reaction products. The hydrogenation products; silanes V, VI, X and germane XII were isolated by distillation. Compounds VII and VIII resulting from dehydrogenation and disproportionation of silane II were separated by preparative GLC.

TABLE 5

^{1}H NMR SPECTRAL DATA FOR PRODUCTS ARISING FROM CATALYTIC CONVERSIONS OF [2-(4,5-DIHYDROFURYL)]-SILANES AND -GERMANES

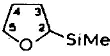
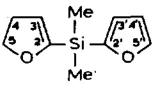
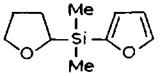
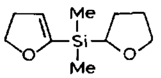
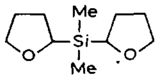
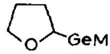
Compound		δ (ppm)
	(V)	0.06 (s, 9H, $SiMe_3$), 1.85 (m, 4H, 3,4-CH_2), 3.23 (m, 1H, 2-CH), 3.75 (m, 2H, 5-CH_2)
	(VIII)	0.41 (s, 6H, $SiMe_2$), 2.60 (dt, 2H, 4-CH_2), 4.22 (t, 2H, 5-CH_2), 5.31 (t, 1H, 3-CH), 6.40 (m, 1H, 4'-CH), 6.75 (m, 1H, 3'-CH), 7.68 (m, 1H, 5'-CH)
	(VII)	0.50 (d, 6H, *J* 3.4 Hz, $SiMe_2$), 1.90 (m, 4H, 3,4-CH_2), 3.82 (m, 3H, 2,5-CH_2), 6.41 (m, 1H, 4'-CH), 6.75 (m, 1H, 3'-CH), 7.67 (m, 1H, 5'-CH)
	(VI)	0.27 (d, 6H, *J* 3.6 Hz, $SiMe_2$), 1.87 (m, 4H, 3,4-CH_2), 2.60 (dt, 2H, 4'-CH_2), 3.41 (m, 1H, 2-CH), 3.81 (m, 2H, 5-CH_2), 4.21 (t, 2H, 5'-CH_2, 6.27 (t, 1H, 3'-CH)
	(X)	0.08 (m, 6H, $SiMe_2$), 1.84 (m, 8H, 3.3', 4,4'-CH_2), 3.34 (m, 2H, 2,2'-CH), 3.73 (m, 4H, 5,5'-CH_2)
	(XII)	0.34 (s, 9H, $GeMe_3$), 1.81 (m, 4H, 3,4-CH_2), 3.49 (m, 1H, 2-CH_2), 3.72 (m, 2H, 5-CH_2)

TABLE 6

MASS SPECTRAL DATA FOR CATALYTICALLY-OBTAINED COMPOUNDS

Compound	*m/e* (rel. abundance, (%))
V	129 ($M^+ -$Me, 2), 116(38), 101(100), 73(62), 59(36)
VIII	194 (M^+, 55), 179(8), 161(7), 153(7), 151(17), 150(12), 149(84), 138(11), 137(7), 127(6), 126(13), 125(100), 123(10), 121(16), 120(30), 111(12), 109(12), 99(11), 98(8), 97(17), 95(22), 91(8), 85(13), 83(9), 81(8), 79(6), 77(14), 75(17), 71(8), 69(30), 68(5), 67(12), 66(7), 65(10), 59(21), 55(14), 53(22), 51(9), 45(34), 43(44)
VII	168 ($M^+ - C_2H_4$, 56), 167(29), 154(31), 140(10), 139(14), 135(17), 126(11), 125(100), 111(10), 99(14), 97(10), 95(14), 94(49), 91(14), 77(17), 71(13), 63(10), 59(13), 43(10)
VI	170 ($M^+ - C_2H_4$, 24), 169(35), 115(9), 151(16), 142(19), 129(31), 127(21), 126(22), 125(41), 113(20), 111(21), 109(15), 101(53), 99(35), 97(100), 96(19), 95(13), 75(94), 71(18), 69(21), 59(25), 45(10), 43(15)
X	157 ($M^+ - C_2H_4 -$Me, 2), 129(24), 117(9), 116(92), 113(8), 103(7), 102(10), 101(100), 100(6), 99(52), 87(6), 77(8), 75(50), 71(76), 61(14), 59(54), 58(7), 55(11), 47(11), 45(21), 43(85)
XII [a]	175 ($M^+ -$Me, 3), 164(5), 162(26), 161(6), 160(19), 158(15), 145(15), 143(12), 141(9), 121(24), 119(100), 118(26), 105(13), 104(12), 103(12), 101(10), 91(14), 89(39), 87(30), 85(19), 75(10), 71(47), 43(35)

[a] Peaks of germanium-containing ions are given for ^{74}Ge isotope.

The ^{1}H NMR and mass spectra parameters of compounds resulting from the catalytic reactions with I–III are summarized in Tables 5, 6. The ^{1}H NMR and mass spectra of (2-furyl)trimethylsilane (IV) and bis(2-furyl)trimethylsilane (IX) are consistent with those published in the literature [6].

All synthetic procedures were conducted in absolute solvents under a nitrogen atmosphere.

[2-(4,5-Dihydrofuryl)]trimethylsilane (I) and bis[2-(4,5-dihydrofuryl)]dimethylsilane (II)

I and II were prepared as described, [4] except that ether was used as solvent instead of THF, the yields amounting to 72 and 68%, respectively. The physicochemical constants and the parameters of ^{1}H NMR spectra for I and II coincide with the data reported, [1]; mass spectrum of I, m/e (rel. abundance, %): 142 (M^+, 24), 127 (M^+- Me, 13), 109 (13), 99 (26), 97 (88), 85 (6), 83 (5), 75 (20), 73 (100), 69 (15), 61 (8), 59 (12), 53 (8), 45 (32), 43 (35); mass spectrum of II: 196 (M^+, 53), 167 (8), 154 (4), 153 (29), 152 (3), 151 (19), 140 (6), 139 (9), 133 (4), 128 (3), 127 (11), 126 (6), 125 (27), 123 (19), 122 (4), 121 (20), 113 (10), 111 (31), 109 (16), 99 (27), 98 (15), 97 (100), 95 (10), 85 (11), 83 (13), 75 (45), 69 (35), 67 (13), 59 (14), 55 (12), 53 (16), 45 (21), 43 (33).

[2-(4,5-Dihydrofuryl)]trimethylgermane (III)

Trimethylchlorogermane (4.7 g, 0.03 mol) dissolved in THF (10 ml) was dropped to a solution of [2-(4,5-dihydrofuryl)]lithium (43.6 ml, 0.031 mol) in hexane/THF (1/1) mixture cooled to -30°C. The reaction mixture was stirred for 15 min, then brought to room temperature and stirred for another 30 min. After removing solid LiCl by filtration the solvents were evaporated and the residue was distilled in vacuo to give 4.0 g of III (Yield: 71%), b.p. 62°C 32 mm, $n_D^{20} = 1.4601$. IR spectrum: 1600 cm^{-1} (ν(C=C)); ^{1}H NMR spectrum, δ, ppm: 0.30 (s, 9H, GeMe$_3$), 2.58 (dt, 2H, 4-CH$_2$), 4.29 (t, 2H, 5-CH$_2$), 5.04 (t, 1H, 3-CH); mass spectrum, m/e (rel. abundance, %) *: 188 (M^+, 17), 173 (35), 143 (100), 119 (36), 113 (7), 91 (11), 89 (32), 87 (25), 83 (5), 74 (13).

[2-(4,5-Dihydrofuryl)](2-furyl)dimethylsilane (VIII)

To a solution of 2-furyllithium (0.03 mol) obtained from a 1.15 N n-BuLi solution in hexane (26.1 ml) and furan (2.2 ml, 0.03 mol) dissolved in diethyl ether (25 ml) at -30°C a solution of XI (3.8 g, 0.03 mol) in diethyl ether (5 ml) was added. The mixture was brought to room temperature, the solvents were evaporated and the residue was distilled in vacuo to give VIII (0.9 g, yield 57%), b.p. 63°C/1 mm, $n_D^{20} = 1.4338$; the ^{1}H NMR and mass spectra of VIII were identical to those recorded for VIII prepared on disproportionation and dehydrogenation of II (Table 5, 6).

(2-Tetrahydrofuryl)(2-furyl)dimethylsilane (VII)

To a solution of VIII (19.4 mg, 0.0001 M) in cyclohexane-d_{12} the catalyst 5% Pd/Al$_2$O$_3$ (8 mg; [VIII]/[Pd] = 25/1) was added and the reaction mixture was stirred under hydrogen (1 atm) at room temperature for 1 h to give VII (GLC yield > 95%). The ^{1}H NMR and mass spectra recorded for VII without its isolation

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* The peaks for germanium-containing ions are given for the ^{74}Ge isotope.

from deuterated solvent were identical to those for the VII obtained by disproportionation of II on palladium catalyst in the absence of hydrogen (Table 5 and 6).

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