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Palladium-catalyzed rearrangement of silanes containing oxygen or halogen α to silicon

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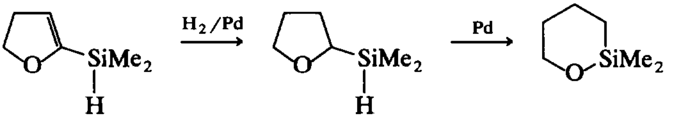
Abstract

Rearrangements of tetrahydrofuryl- and tetrahydropyranyl-hydrosilanes to oxasilaalkanes, of acetoxymethyl-hydrosilanes to acetoxysilanes, and halogenomethyl-hydrosilanes to halogenosilanes in the presence of palladium catalyst have been studied. The reaction has been shown to proceed more rapidly in tetrahydrofuran and hexane than in benzene or acetonitrile. The progressive replacement of the methyl groups on the silicon atom by phenyl groups slowed down the rearrangement, as did change from five-membered to six-membered heterocycles.

Introduction

We showed previously that under catalytic hydrogenation conditions (1 atm H_2, 25°C, 5% Pd/Al_2O_3, 0.1 *M* solution of substrate in hexane) 2-dimethylsilyl-4,5-dihydrofuran (**1**) is first completely converted into the corresponding tetrahydrofuryl derivative **2**, which then readily and quantitatively rearranges to give the six-membered oxasilacyclohexane **3** [1].



1 **2** **3**

We have now synthesized a series of 2-tetrahydrofuryl- and 2-tetrahydropyranyl-hydrosilanes and investigated their rearrangement in the presence of several catalysts, *e.g.* $(Ph_3P)_2PdCl_2$, $(Ph_3P)_4Pd$, $PdCl_2$, $(Ph_3P)_2PtCl_2$, $(NH_4)_2PtCl_6$, $H_2PtCl_6 \cdot 6H_2O$, $(Ph_3P)_3RhCl$, $(Ph_3P)_2Rh(CO)Cl$, $(Ph_3P)_3Rh(CO)H$, $RhCl_3 \cdot 3H_2O$, $(Ph_3P)_3RuCl_3$, $(Ph_3P)_2Ru(CO)_2Cl_2$, $(Ph_3P)_3Ir(CO)Cl$, $(NH_4)_2OsCl_6$, $(Ph_3P)_3Ni(CO)_2$, Pd (black), Pt (black), Pd/Al_2O_3, Pt/Al_2O_3, Rh/C, Rh (black),

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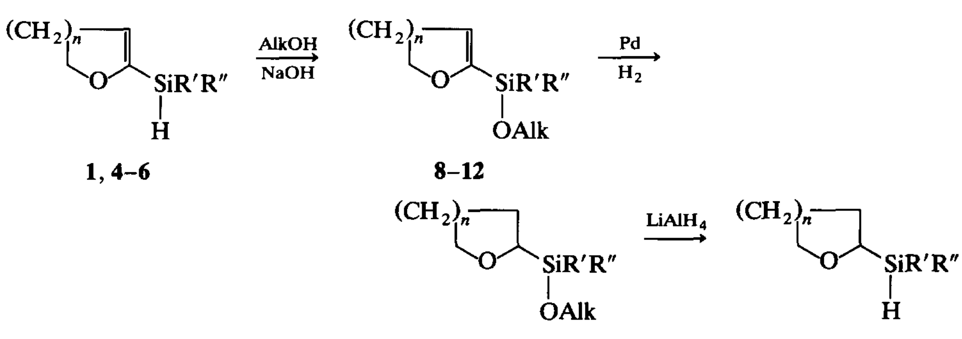
$AlCl_3$, $AlBr_3$ and $SnCl_4$. We also examined the influence of substituents at the silicon atom and of the nature of the solvent on the reaction rate.

Results and discussion

Hydrogenation of dihydrofuryl- and dihydropyranyl-hydrosilanes can not be regarded as an appropriate method for synthesizing tetrahydrofuryl- and tetrahydropyranyl-hydrosilanes since these species can rearrange under the reaction conditions [1]. A route was therefore devised involving conversion of the dihydrofurylhydrosilanes **1**, **4**, **5** and the dihydropyranylhydrosilanes **6**, **7** (made as previously described [2]) into the alkoxysilanes **8–12**, followed by hydrogenation of the latter to give the tetrahydro derivatives **13–17** in the presence of Pd/Al_2O_3 and reduction of the latter to hydrosilanes **2**, **18–21** by lithium aluminium hydride:



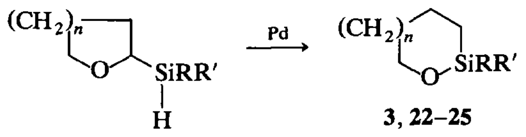
1, 4–6 **8–12** **13–17** **2, 18–21**

Alk = Me, Et

$n = 1$: **1, 2, 8, 13**: R′ = R″ = Me
4, 9, 14, 18: R′ = Me, R″ = Ph
5, 10, 15, 19: R′ = R″ = Ph

$n = 2$: **6, 11, 16, 20**: R′ = R″ = Me
7, 12, 17, 21: R′ = Me, R″ = Ph

When the 2-tetrahydrofurylhydrosilanes **2**, **18**, **19** and the 2-tetrahydropyranylhydrosilanes **20**, **21** were stirred with 5% Pd/Al_2O_3 in hexane at room temperature rearrangement occurred to give the corresponding oxasilacyclohexanes **3**, **22**, **23** and oxasilacycloheptanes **24**, **25** in high yields (70–100%).



2, 18–21 **3, 22–25**

$n = 1$: **2, 3**: R = R′ = Me
18, 22: R = Me, R′ = Ph
19, 23: R = R′ = Ph

$n = 2$: **20, 24**: R′ = R″ = Me
21, 25: R′ = Me, R″ = Ph

The rate of the reaction fell as the number of phenyl groups on the silicon atom increased. Under typical conditions (0.1 *M* solution of substrate in hexane, 25°C, [substrate] : [Pd] = 100 : 1) the rearrangement of the dimethyl derivative **2** requires 20 min and the methylphenyl derivative **18** 6 h, whereas complete conversion of the diphenyl derivative **19** requires 72 h at the boiling point of the mixture. The

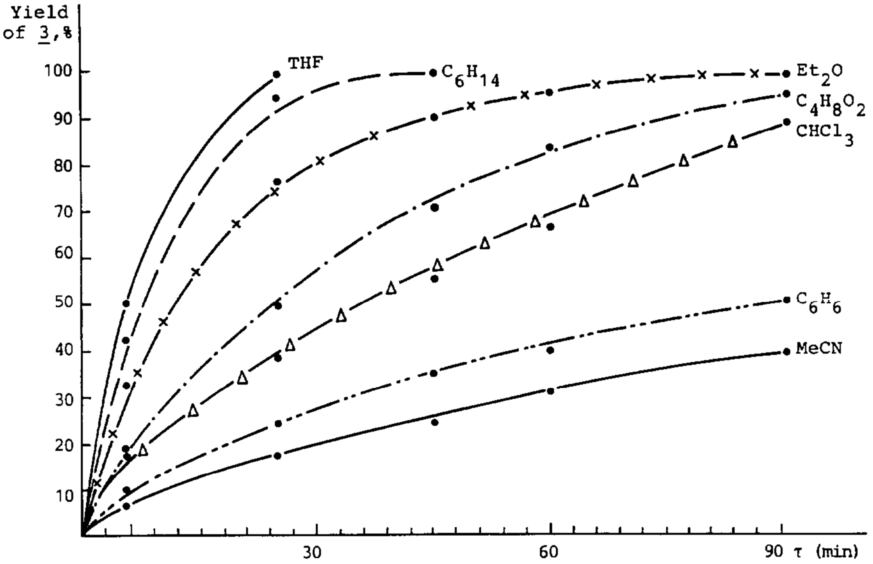
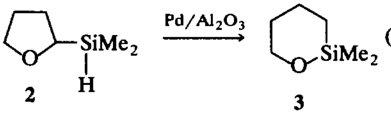


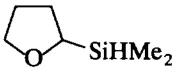
Fig. 1. Rearrangement



2 3

(0.1 *M* solution, [2]:[Pd] = 200:1).

reactivity of the tetrahydrofurylhydrosilanes **2**, **18**, **19** thus decreases in the following order:



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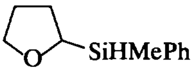

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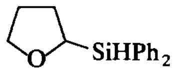
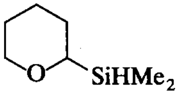


2 **18** **19**

A similar fall in reactivity is observed on introduction of a phenyl in place of a methyl group on going from the tetrahydropyranyl derivatives **20** and **21** (6 h for the conversion of **20**; 48 h for **21**):



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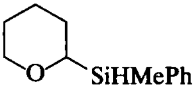


20 **21**

The conversions of tetrahydropyranylhydrosilanes **20** to **24** and **21** to **25** are much slower than that of the tetrahydrofuryl analogues **2** to **3** and of **18** to **22**.

The rate of the rearrangement of **2** to **3** is influenced by the solvent used (Fig. 1), but no correlation has been observed between solvent polarity and the rate. The reaction is more rapid in tetrahydrofuran and hexane than in benzene and acetonitrile. It is reasonable to assume that the latter pair of solvents competes with hydrosilane **2** for adsorption on the surface of palladium and inhibits the rearrangement.

Palladium containing catalysts show the highest activity in the rearrangement. In the presence of Pd/Al_2O_3 the yield of **3** was 95% after 45 min. Palladium black was even more active, giving 95% yield after 15 min. Catalysis by palladium(II) chloride gave 40% of **3** from the complete consumption of the initial hydrosilane during 1 h.

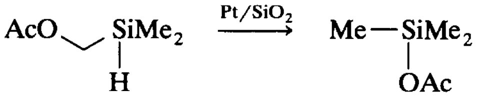
The complex catalyst $(Ph_3P)_2PdCl_2$ (0.1 *M* solution of **2** in hexane, [**2**]:[cat.] = 100:1, 25°C) also showed good activity (95% yield of **3** in 24 h). Contrary to our expectations, the palladium(0) complex $(Ph_3P)_4Pd$ did not catalyze rearrangement of **2** to **3**.

The reaction catalyzed by platinum (black) gave 17% of **3** in 6 h. The platinum complex $(Ph_3P)_2PtCl_2$ showed a considerably lower catalytic activity (18% yield in 24 h) than its palladium analogue $(Ph_3P)_2PdCl_2$.

Catalysis by Rh/C and Rh-black was very ineffective (yield of **3**, 5%). The rhodium complexes $(Ph_3P)_3Rh(CO)H$ and $(Ph_3P)_2Rh(CO)Cl$ catalyzed the rearrangement only at higher temperatures (after 3 h at 60°C the yield of **3** was *ca.* 20%). Complexes of ruthenium, iridium, osmium and nickel showed no catalytic activity, and $H_2PtCl_6 \cdot 6H_2O$, $RhCl_3 \cdot 3H_2O$, Pt/Al_2O_3 and Lewis acids were also inactive in this reaction.

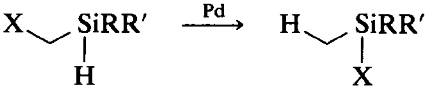
Hydrosilane **2** underwent no change either during UV irradiation (254 nm) for 3 h or upon rapid heating to 400°C in the gas phase.

The tetrahydrofuryl- and tetrahydropyranyl-hydrosilanes that rearranged in the presence of palladium have oxygen *α* to the silicon atom. There are reports in the literature of similar rearrangement of acyclic silanes having electronegative substituents *α* to silicon initiated thermally [3–8] or by peroxides [7] or by Lewis acids [8–11]. We have found that dimethylacetoxysilane **28** undergoes rearrangement to trimethylacetoxysilane **29** under mild conditions in the presence of Pt on silica gel (0.1 *M* solution in hexane, [**28**]:[Pt] = 50:1, 25°C) the yield of acetoxysilane **29** after 1 h being *ca.* 40%.



28 **29**

In the presence of Pd/Al_2O_3 the hydrosilane **28** decomposes even at −78°C. Palladium on Al_2O_3 can be used for the rearrangement of halomethylhydrosilanes **30a–f** to the methylhalosilanes (**31a–f**) under mild conditions (0.1 *M* solution in hexane or methylene chloride; [substrate]:[Pd] = 50:1, 25–80°C, 5–90 min), and yields are good (for **30a–c**, 80–100%; for **30f**, 40%).



30a–f **31a–f**

a: X = Cl, R = R′ = Me; **b**: X = Br, R = R′ = Me; **c**: X = Cl, R = Me, R′ = Ph; **d**: X = Cl, R = R′ = Ph; **e**: X = Cl, R = H, R′ = n-C_6H_{13}; **f**: X = Cl, R = H, R′ = Ph.

Replacement of the methyl groups by phenyl (as in the case of the cyclic analogues) lowers the reactivity of the hydrosilanes; thus the order of reactivity is **30** (RR′: Me_2 (**30a**) > MePh (**30c**) > Ph_2 (**30d**)). In thermal rearrangement of $AcOCH_2SiHRR'$ the opposite order was found [6]. Bromomethyldimethylsilane (**30b**) rearranges more slowly in the presence of Pd/Al_2O_3 than its chloromethyl analogue (**30a**).

Chloromethyldimethylsilane (**30a**) also readily rearranged (10 min, 25°C) in the presence of $AlCl_3$, but the reactions were not selective, and the yield of trimethylchlorosilane (**31a**) was *ca.* 60% at the 100% conversion of the initial hydrosilane (**30a**).

The amino-substituted silane $Me_2NCH_2SiHMe_2$ underwent no reaction in the presence of Pd/Al_2O_3 during 100 h in refluxing in pentane (silane/Pd ratio 10/1).

We have demonstrated that palladium-containing species catalyze the rearrangement under mild conditions of hydrosilanes containing cyclic ether groups, an acetoxy group, of a halogen (Cl, Br) atom in the position α to silicon, giving silicon-functional compounds.

Experimental

^1H NMR spectra were recorded on a Bruker WH-90/DS spectrometer in $CDCl_3$ with 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 column (1.2 m × 3 mm) packed with 5% OV-17/Chromosorb W-AW (60–80 mesh) were used with helium (50 ml/min) as carrier gas.

[2-(4,5-Dihydrofuryl)]dimethylsilane (**1**), [2-(4,5-dihydrofuryl)]dimethylmethoxysilane (**8**), (2-tetrahydrofuryl)dimethylmethoxysilane (**13**), (2-tetrahydrofuryl)dimethylsilane (**2**) and 1-oxa-2-sila-2,2-dimethylcyclohexane were prepared as described [1]. [2-(4,5-Dihydrofuryl)]methylphenylsilane (**4**), [2-(4,5-dihydrofuryl)]diphenylsilane (**5**), [2-(5,6-dihydro-4*H*-pyranyl)]dimethylsilane (**6**) and [2-(5,6-dihydro-4*H*-pyranyl)]methylphenylsilane (**7**) were prepared by published procedures [2]. The properties of these compounds were in full agreement with published data.

Acyloxymethyldimethylsilane (**28**) was made by a reported method [6].

The complexes $(Ph_3P)_3RuCl_3$, $(Ph_3P)_2Ru(CO)_2Cl_2$, $(Ph_3P)_3RhCl$, $(Ph_3P)_3Rh(CO)H$, $(Ph_3P)_2PdCl_2$, $(Ph_3P)_4Pd$, $(Ph_3P)_2PtCl_2$, $(Ph_3P)_3Ir(CO)Cl$, $(NH_4)_2OsCl_6$, $(NH_4)_2PtCl_6$, $(Ph_3P)_3Ni(CO)_2$ and Lewis acids ($AlCl_3$, $AlBr_3$, $SnCl_4$) were purchased from Fluka. Pd-black, Pt-black and Rh-black were prepared as described in ref. 12.

Synthesis of dihydrofuryl- and dihydropyranyl-alkoxysilanes (general procedure)

A mixture of the appropriate [2-(4,5-dihydrofuryl)]- or [2-(5,6-dihydro-4*H*-pyranyl)]hydrosilane and alcohol was boiled in the presence of solid NaOH. Products were isolated by distillation in vacuum. Product **5** was isolated by column chromatography (eluent 2% ethyl acetate in hexane).

[2-(4,5-Dihydrofuryl)]methylphenylmethoxysilane (9). Compound **9** was obtained (66% by GLC) by boiling a solution of [2-(4,5-dihydrofuryl)]methylphenylsilane (**4**) (0.6 g, 3 mmol) and MeOH (0.16 g, 4 mmol) for 30 min. B.p. 98°C/3 mmHg. ^1H NMR ($CDCl_3$, ppm): δ 0.51 (s, 3H, Si–CH_3), 2.61 (d.t., 2H, 4–CH_2, J_{3-4} 2.3 Hz, J_{4-5} 9.5 Hz), 3.53 (s, 3H, O–CH_3), 4.32 (t, 2H, 5–CH_2, J 9.5 Hz), 5.34 (t, 1H, 3–CH, J 2.3 Hz). MS m/e (rel. intensity, %): 220 (M^+, 36), 205 ($(M\text{–Me})^+$, 5), 175 (100), 151 ($(M\text{–}C_4H_5O)^+$, 73).

[2-(4,5-Dihydrofuryl)]diphenylethoxysilane (10). Compound **10** (11.0 g, yield 84%) was obtained by boiling for 6 h a mixture of 2-(4,5-dihydrofuryl)]diphenylsilane (**5**) (11.1 g, 0.044 mol) and ethanol (2.1 g, 0.044 mol). ^{1}H NMR ($CDCl_3$, ppm): δ 1.24 (t, 3H, O-CH_2-CH_3, J 7.0 Hz), 2.61 (d.t., 2H, 4-CH_2, J_{3-4} 2.5 Hz, J_{4-5} 9.6 Hz), 3.87 (q, 2H, O-CH_2-CH_3, J 7.0 Hz), 4.36 (t, 2H, 5-CH_2, J 9.6 Hz), 5.33 (t, 1H, 3-CH_3, J 2.5 Hz), 7.20–7.78 (m, 5H, C_6H_5). MS m/e (rel. intensity, %): 296 (M^+, 36), 251 ((M-C_4H_5O)$^+$, 13), 45 (100). IR (cm^{-1}): 1592 (ν(C=C)). n_D^{20} = 1.5622.

*[2-(5,6-Dihydro-4*H*-pyranyl)]dimethylmethoxysilane (11).* Compound **11** (3.0 g, yield 58%) was obtained by boiling 4.24 g (0.03 mol) of [2-(5,6-dihydro-4*H*-pyranyl)]dimethylsilane (**6**) with 1.28 g (0.04 mol) of MeOH for 1 h. B.p. 65–66°C/12 mmHg. ^{1}H NMR (CDCl, ppm): δ 0.18 (s, 6H, Si–CH_3), 1.73–2.18 (m, 4H, 4.5–CH_2), 3.47 (s, 3H, O–CH_3), 3.80–4.04 (m, 2H, 6–CH_2), 5.09–5.17 (m, 1H, 3–CH). MS m/e (rel. intensity, %): 172 (M^+, 21), 157 ((M-Me)$^+$, 10), 89 ((M–C_5H_7O)$^+$, 100). IR (cm^{-1}): 1620 (ν(C=C)). n_D^{20} = 1.4444.

*[2-(5,6-Dihydro-4*H*-pyranyl)]methylphenylmethoxysilane (12).* Compound **12** (2.2 g, yield 47%) was obtained by boiling a mixture of [2-(5,6-dihydro-4*H*-pyranyl)]methylphenylsilane (**7**) (4.1 g, 0.2 mol) and methanol (0.96 g, 0.03 mol) for 1 h. B.p. 129–130°C/2 mmHg. ^{1}H NMR ($CDCl_3$, ppm): δ 0.44 (s, 3H, Si–CH_3), 1.64–2.22 (m, 4H, 4.5–CH_2), 3.51 (s, 3H, O–CH_3), 3.82–4.07 (m, 2H, 6–CH_2), 5.07–5.24 (m, 1H, 3–CH), 7.22–7.71 (m, 5H, C_6H_5). MS m/e (rel. intensity, %): 234 (M^+, 28), 219 ((M-Me)$^+$, 5), 151 ((M–C_5H_7O)$^+$, 100). IR (cm^{-1}): 1620 (ν(C=C)). n_D^{20} = 1.5245.

Synthesis of tetrahydrofuryl- and tetrahydropyranyl-alkoxysilanes (general procedure)

A solution of the dihydrofuryl- or dihydropyranyl-alkoxysilanes and 5% Pd/Al_2O_3 ([substrate]:[catalyst] = 100:1) in pentane or hexane was stirred at room temperature under 1 atm of hydrogen. After complete conversion of the starting tetrahydro-compounds the reaction mixture was filtered, the evaporated filtrate, and the residue distilled in vacuum. Pure **15** was isolated by column chromatography (eluent 2% ethyl acetate in hexane).

(2-Tetrahydrofuryl)methylphenylmethoxysilane (14). Compound **14** (2.5 g, yield 56%) was obtained by stirring 2.2 g (0.01 mol) of (2-[4,5-dihydrofuryl])methylphenylmethoxysilane (**9**) with 200 mg of Pd/Al_2O_3 in 25 ml hexane for 6 h. B.p. 100°C/3 mmHg. ^{1}H NMR ($CDCl_3$, ppm): δ 0.42 (s, Si–CH_3), 1.54–2.18 (m, 4H, CH_2–CH_2), 3.53 (d, 3H, O–CH_3, J 1.7 Hz), 3.38–3.97 (m, 3H, CH–O–CH_2), 7.16–7.71 (m, 5H, C_6H_5). MS m/e (rel. intensity, %): 151 ((M–C_4H_7O)$^+$, 96), 104 (100). n_D^{20} = 1.5110.

(2-Tetrahydrofuryl)diphenylethoxysilane (15). Compound **15** (7.2 g, yield 71%) was obtained by stirring 10 g (0.034 mol) of (2-[4,5-dihydrofuryl])diphenylethoxysilane (**10**) with 723 mg of Pd/Al_2O_3 in 100 ml pentane for 10 h. ^{1}H NMR ($CDCl_3$, ppm): δ 1.09–1.49 (m, 3H, O–CH_2–CH_3), 1.64–2.22 (m, 4H, 3,4–CH_2), 3.57–4.02 (m, 5H, 2–CH, 5–CH_2, O–CH_2–CH_3), 7.21–7.79 (m, 10H, C_6H_5). MS m/e (rel. intensity, %): 227 ((M–C_4H_7O)$^+$, 59), 183 (100). n_D^{20} = 1.5549.

(Tetrahydropyranyl)dimethylmethoxysilane (16). Compound **16** (4.1 g, yield 78%) was obtained by stirring 5.6 g (0.03 mol) of [2-(5,6-dihydro-4*H*-pyranyl)]dimethylmethoxysilane (**11**) with 638 mg of Pd/Al_2O_3 in 50 ml hexane for 4 h. B.p. 65°C/12 mmHg. ^{1}H NMR ($CDCl_3$, ppm): δ 0.14 (s, 6H, Si–CH_3), 1.14–1.97 (m,

6H, 3,4,5-CH_2), 2.91–3.71 (m, 2H, 6-CH_2), 3.44 (s, 3H, O–CH_3), 3.80–4.08 (m, 1H, 2-CH). MS *m/e* (rel. intensity, %): 159 ((M–Me)$^+$, 12), 89 ((M–C_5H_9O)$^+$, 100). n_D^{20} = 1.4352.

(Tetrahydropyranyl)methylphenylmethoxysilane (17). Compound **17** (3.2 g, yield 68%) was obtained by stirring of 5 g (0.02 mol) of [2-(5,6-dihydro-4*H*-pyranyl)]methylphenylmethoxysilane (**12**) with 426 mg of Pd/Al_2O_3 in 50 ml hexane for 6 h. B.p. 104–106°C/1 mmHg. ^{1}H NMR ($CDCl_3$, ppm): δ 0.38 (s, 3H, Si–CH_3), 1.27–1.97 (m, 6H, 3,4,5–CH_2), 2.73–3.78 (m, 2H, 6–CH_2), 3.50 (s, 3H, O–CH_3), 3.82–4.16 (m, 1H, 2–CH), 7.22–7.73 (m, 5H, C_6H_5). MS *m/e* (rel. intensity, %): 221 ((M–Me)$^+$, 23), 151 ((M–C_5H_9O)$^+$, 100). n_D^{20} = 1.5088.

Synthesis of tetrahydrofuryl- and tetrahydropyranylhydrosilanes (general procedure)

The tetrahydrofuryl- and tetrahydropyranyl-hydrosilanes **18**, **20**, **21** were obtained by reduction of the corresponding alkoxy derivatives with lithium aluminium hydride under phase-transfer conditions (0.1 *M* solution in non-polar solvent, 60°C, 5 mol% 18-crown-6, [substrate]:[$LiAlH_4$] = 1 : 2) [13,14]. After complete consumption of the alkoxysilane the mixture was filtered, the filtrate evaporated, and the residue distilled in vacuum. The hydrosilane **19** was made by the standard method of reduction in diethyl ether. The mixture was treated with 5% aqueous HCl, the organic layer was separated, and the aqueous solution was twice extracted with diethyl ether. The organic extracts were combined, dried, and evaporated, and from the residue silane **19** was isolated by column chromatography (eluent 2% ethyl acetate in hexane).

(2-Tetrahydrofuryl)methylphenylsilane (18). Compound **18** (1 g, yield 62%) was obtained by heating 2 g (0.01 mol) of (2-tetrahydrofuryl)methylphenylmethoxysilane (**14**), 0.8 g (0.02 mol) of $LiAlH_4$ and 50 mg 18-crown-6 in 20 ml hexane for 6 h. B.p. 85–88/3 mmHg. ^{1}H NMR ($CDCl_3$, ppm): δ 0.40 (dd, 3H, Si–CH_3, *J* 2 Hz), 1.51–2.18 (m, 4H, 3,4–CH_2), 3.40–3.96 (m, 3H, 2–CH, 5–CH_2), 4.24–4.49 (m, 1H, Si–H), 7.16–7.73 (m, 5H, C_6H_5). MS *m/e* (rel. intensity, %): 177 ((M–Me)$^+$, 0.5), 121 ((M–C_4H_7O)$^+$, 60), 104 (100). IR (cm^{-1}): 2113 (ν(Si–H)). n_D^{20} = 1.4952.

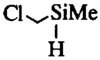
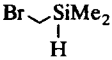
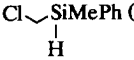
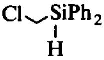
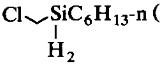
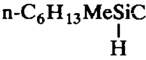
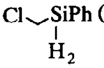
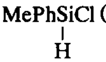
(2-Tetrahydrofuryl)diphenylsilane (19). Compound **19** (1.9 g, yield 37%) was obtained from 6 g (0.02 mol) of (2-tetrahydrofuryl)diphenylethoxysilane (**15**) and 379 mg (0.009 mol) of $LiAlH_4$ in 100 ml diethyl ether after 4 h heating. ^{1}H NMR ($CDCl_3$, ppm): δ 1.67–2.27 (m, 4H, 3,4–CH_2), 3.58–4.02 (m, 3H, 2–CH, 5–CH_2), 4.84 (d, 1H, Si–H, *J* 2.0 Hz), 7.19–7.72 (m, 10H, C_6H_5). MS *m/e* (rel. intensity, %): 254 (M^+, 0.3), 183 ((M–C_4H_7O)$^+$, 100). IR (cm^{-1}): 2112 (ν(Si–H)).

(2-Tetrahydropyranyl)dimethylsilane (20). Compound **20** (1.1 g, yield 69%) was obtained by heating a mixture of 2 g (0.011 mol) of (2-tetrahydropyranyl)dimethylmethoxysilane (**16**), 0.8 g (0.02 mol) of $LiAlH_4$, and 50 mg of 18-crown-6 in 20 ml of pentane for 5 h. B.p. 151°C/760 mmHg. ^{1}H NMR ($CDCl_3$, ppm): δ 0.11 (d, 6H, Si–CH_3, *J* 2.3 Hz), 1.16–1.98 (m, 6H, 3,4,5–CH_2), 3.00–4.10 (m, 4H, Si–H, 2–CH, 6–CH_2). MS *m/e* (rel. intensity, %): 129 ((M–Me)$^+$, 25), 59 ((M–C_5H_9O)$^+$, 100). IR (cm^{-1}): 2120 (ν(Si–H)). n_D^{20} = 1.4459.

(2-Tetrahydropyranyl)methylphenylsilane (21). Compound **21** (yield 72%, GC data) was obtained from 1.4 g (0.006 mol) of (2-tetrahydropyranyl)methylphenylmethoxysilane (**17**), 240 mg (0.012 mol) of $LiAlH_4$ and 8 mg of 18-crown-6 in 14 ml of hexane after 4 h heating. ^{1}H NMR ($CDCl_3$, ppm): δ 0.41 (d, 3H, Si–CH_3, *J* 1.9 Hz), 1.33–2.09 (m, 6H, 3,4,5–CH_2), 3.76–4.09 (m, 3H, 2–CH, 6–CH_2), 4.14–4.38

Table 1

Rearrangement of halomethylhydrosilanes **30a–f**

Substrate	Time (min)	T (°C)	Product	Yield (%) (GLC data)
 $\mathrm{Cl}\smile\underset{\substack{\vert\\ \mathrm{H}}}{\mathrm{Si}}\mathrm{Me}_2$ **(30a)**	5	25	Me_3SiCl **(31a)**	> 95
 $\mathrm{Br}\smile\underset{\substack{\vert\\ \mathrm{H}}}{\mathrm{Si}}\mathrm{Me}_2$ **(30b)**	60	80	Me_3SiBr **(31b)**	> 95
 $\mathrm{Cl}\smile\underset{\substack{\vert\\ \mathrm{H}}}{\mathrm{Si}}\mathrm{MePh}$ **(30c)**	60	25	$Me_2PhSiCl$ **(31c)**	> 95
 $\mathrm{Cl}\smile\underset{\substack{\vert\\ \mathrm{H}}}{\mathrm{Si}}\mathrm{Ph}_2$ **(30d)**	90	100	$MePh_2SiCl$ **(31d)**	> 95
 $\mathrm{Cl}\smile\underset{\substack{\vert\\ \mathrm{H}_2}}{\mathrm{Si}}\mathrm{C}_6\mathrm{H}_{13}\text{-n}$ **(30e)**	90	60	 $\text{n-C}_6\mathrm{H}_{13}\mathrm{Me}\underset{\substack{\vert\\ \mathrm{H}}}{\mathrm{Si}}\mathrm{Cl}$ **(31e)**	80
 $\mathrm{Cl}\smile\underset{\substack{\vert\\ \mathrm{H}_2}}{\mathrm{Si}}\mathrm{Ph}$ **(30f)**	30	60	 $\mathrm{MePh}\underset{\substack{\vert\\ \mathrm{H}}}{\mathrm{Si}}\mathrm{Cl}$ **(31f)**	40

(m, 1H, Si–H), 7.20–7.67 (m, 5H, C_6H_5). MS *m/e* (rel. intensity, %): 206 (M^+, 2), 191 ($(M\text{–}CH_3)^+$, 10), 121 ($(M\text{–}C_5H_9O)^+$, 100).

Rearrangement of (2-tetrahydrofuryl)- and (2-tetrahydropyranyl)hydrosilanes (general procedure)

5% Pd/Al_2O_3 ([substrate] : [catalyst] = 100 : 1) was added to 0.1 *M* hydrosilane in hexane and the mixture was stirred at room temperature. After disappearance of the initial hydrosilane the mixture was filtered and evaporated, and the residue distilled in vacuum. Pure **18** was isolated by column chromatography (eluent 2% ethyl acetate in hexane).

1-Oxa-2-sila-2-methyl-2-phenylcyclohexane (22). Compound **22** (1.7 g, yield 60%) was obtained by stirring 2.85 g (0.015 mol) of **18** and 0.3 g of Pd/Al_2O_3 for 6 h. B.p. 85–88°C/3 mmHg. ^1H NMR ($CDCl_3$, ppm): δ 0.24 (s, 3H, CH_3), 0.67–1.11 (m, 2H, 3–CH_2), 1.47–2.11 (m, 4H, 4,5–CH_2), 3.80–4.04 (m, 2H, 6–CH_2), 7.22–7.71 (m, 5H, C_6H_5). MS *m/e* (rel. intensity, %): 192 (M^+, 13), 177 ($(M\text{–}CH_3)^+$, 100). $n_D^{20} = 1.4950$.

1-Oxa-2-sila-2,2-diphenylcyclohexane (23). Compound **23** (0.3 g, yield 59%) was obtained by stirring 0.508 g (0.002 mol) of **19** and 171 mg of Pd/Al_2O_3 for 15 h. ^1H NMR ($CDCl_3$, ppm): δ 0.73–2.22 (m, 6H, 3,4,5–CH_2), 3.44–4.18 (m, 2H, 6–CH_2), 7.22–7.73 (m, 10H, C_6H_5). MS *m/e* (rel. intensity, %): 254 (M^+, 42), 177 ($(M\text{–}C_6H_5)^+$, 100).

1-Oxa-2-sila-2,2-dimethylcycloheptane (24). Compound **24** (0.9 g, yield 68%) was obtained by stirring 1.4 g (0.01 mol) of **20** with 213 mg of Pd/Al_2O_3 for 6 h. Mass spectrum, *m/e* (rel. intensity, %): 144 (M^+, 4), 130(12), 129(100), 101(53), 99(17), 97(5), 87(6), 75(22), 61(23), 58(8), 45(10), 43(8), 32(12). The ^{1}NMR data coincide with literature data [15].

1-Oxa-2-sila-2-methyl-2-phenylcycloheptane (25). Compound **25** (1.3 g, yield 65%) was obtained by stirring 2.06 g (0.01 mol) of **21** with 213 mg of Pd/Al_2O_3 for 48 h. B.p. 114°C/2 mmHg. ^1H NMR ($CDCl_3$, ppm): δ 0.34 (s, 3H, CH_3), 0.73–2.04 (m, 8H, 3,4,5,6-CH_2), 3.80–4.07 (m, 2H, 7-CH_2), 7.22–7.67 (m, 5H, C_6H_5). MS m/e (rel. intensity, %): 206 (M^+, 3), 191 ($(M-CH_3)^+$, 100).

Rearrangement of acetoxymethyldimethylsilane (28)

A mixture of 40 mg of **28**, 5 mg of Pt/SiO_2, and 3 ml of pentane ([**28**]:[Pt] = 50:1) was stirred for 1 h at room temperature. The yield of trimethylacetoxysilane (**29**) was 40% (by GLC).

Rearrangement of halomethylhydrosilanes (general procedure)

The hydrosilane (0.3 mmol) was mixed with 12.5 mg of 5% Pd/Al_2O_3 ([hydrosilane]:[Pd] = 50:1) in 3 ml of pentane and the mixture was stirred in a Pierce microautoclave. The products were analysed by GLC. (For results and conditions see Table 1.)

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