246. Monofunctional (Dimethylamino)silane as Silylating Agent

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Summary

The reaction of triorganyl(dimethylamino)silanes with surface-hydrated silicon dioxide has been studied. These silylating agents are easy to prepare from the corresponding chloro or bromosilanes with dimethylamine. The resulting products are thermally stable and relatively volatile. Reaction with surface-hydrated silicon-dioxide preparations at 150–250°C for 170 h yields a dense grafted layer. However, with (dimethylamino)silanes having strongly polar substituents, a retreatment of the surface-modified silica seems to be necessary in order to attain maximum coverage.

Introduction. – In recent studies, surface-modified silicon-dioxide preparations prepared by heating surface-hydrated silica with triorganyl(dimethylamino)silanes [1–5] were applied. In the present paper we describe the synthesis and properties of these silylating agents giving some typical examples.

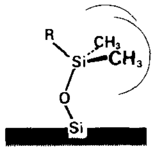
(Diethylamino)trimethylsilane, first prepared by *Sauer & Hasek* [6], is a reagent proposed for the selective silylation of the sterically less hindered OH-groups in steroids [7], and it was extensively applied to the silylation of amino acids by *Rühlmann* [8] [9] [10]. The silylation of primary OH-groups with (dimethylamino)triphenylsilane and (dimethylamino)dimethyl(naphthyl)silane has been shown to proceed quantitatively under mild conditions, permitting the colorimetric determination of low OH-contents in polymers [11]. In subsequent papers, the successful use of (dimethylamino)silanes was reported for the silylation of acid-leached glass capillaries [1], of silica gels for liquid-solid chromatography [3] [4], of glass micro-electrodes [12] [13], and for the immobilization of photosensitizers on silica carriers [14].

The preparation of a surface-hydrated silica, the necessary reaction partner, was recently described [5]. Heat treatment of high-purity fume silica, followed by a hydrothermal treatment in bidistilled H_2O at 95°C/70 h results in a silicon-dioxide preparation, which is a reproducible reaction partner in chemisorption experiments.

Having the necessary reaction partners at hand, it will also be shown in the present study that monofunctional (dimethylamino)silanes are highly efficient reagents for the preparation of dense grafted monolayers.

Results and Discussion. – *Triorganyl(dimethylamino)silanes.* For the synthesis of silica-gel samples covered with substituents (see **1**–**4**), the corresponding trialkyl(dimethylamino)silanes were prepared according to *Sauer & Hasek* by reacting the chloro or bromo derivative with dimethylamine, following *Eqn. 1* (X = Cl or Br) [6]. Precipitates of dimethylammonium chloride, easy to filter, were obtained by working in non-polar solvents.

$$R^1R^2R^3SiX + 2HN(CH_3)_2 = R^1R^2R^3SiN(CH_3)_2 + XH_2N(CH_3)_2 \qquad (1)$$



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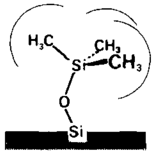
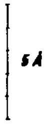
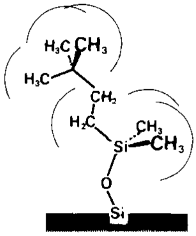
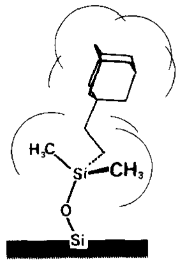


1a



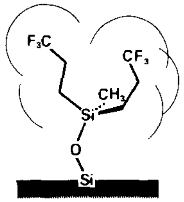


1i



1k

	R		R
1a	CH_3	**1i**	$(CH_3)_3CCH_2CH_2$
1b	C_2H_5	**1j**	cyclo-$C_6H_{11}CH_2CH_2$
1c	n-C_3H_7	**1k**	adamantyl-CH_2CH_2
1d	n-C_6H_{13}	**1l**	Ph
1e	n-$C_{10}H_{21}$	**1m**	$CH_3O(CH_2)_3$
1f	n-$C_{14}H_{29}$	**1n**	$CH_3(OCH_2CH_2)_2CH_2$
1g	n-$C_{18}H_{37}$	**1o**	$CH_3(OCH_2CH_2)_5CH_2$
1h	n-$C_{22}H_{45}$	**3**	n-$C_{22}H_{45}$, one CH_3, replaced by n-$C_{22}H_{45}$



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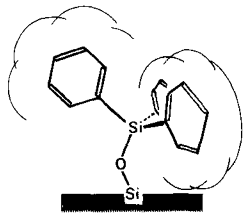

4

Two methods were applied for the preparation of halogenosilanes. 1) Alkylchlorodimethylsilanes were prepared by the catalytic hydrosilylation of vinyl compounds according to *Speier et al.* [15] following *Eqn. 2* with hexachloroplatinic acid as catalyst.

$$R'{-}CH{=}CH_2 + H{-}Si(CH_3)_2Cl = R'{-}CH_2{-}CH_2{-}Si(CH_3)_2Cl \qquad (2)$$

The vinyl components needed for the synthesis of **1b–j** were commercially available. The 1-vinyladamantane (→**1k**) was prepared in 63% yield by pyrolysis of the xanthate derived from 2-(1-adamantyl)ethanol according to *Stepanov & Stolyarov* [16]. The *Williamson* alkylation of monomethylated oligo(ethyleneglycols) with allyl bromide gave the oxa-1-alkenes necessary for the generation of **1m–o**. It is important to note that chlorosilanes attack ether C–O bonds, especially at higher temperatures [17] [18]. Therefore, chloro(oxaalkyl)silanes were not distilled, but used for the preparation of the dimethylamino derivative without any purification.

2) For the preparation of halogenosilanes with two bulky substituents, dichloro(methyl)silane was reacted with the corresponding *Grignard* compound to give the desired product in yields of 90% based on dichloro(methyl)silane *(Eqn. 3)*.

$$2\ R''MgBr + Cl_2(CH_3)SiH = R''_2(CH_3)SiH + 2\ MgBrCl \qquad (3)$$

Because of the negligible sterical hindrance of the H-atom, also the introduction of the second substituent R″ proceeded smoothly. Bromination of the resulting compound in CCl_4 with Br_2 gave the dialkyl(methyl)bromosilanes (yield 100%) needed for the synthesis of **2** and **3** *(Eqn. 4)*.

$$R''_2(CH_3)SiH + Br_2 = R''_2(CH_3)SiBr + HBr \qquad (4)$$

The physical properties of the prepared trialkyl(dimethylamino)silanes are summarized in *Table 3* in the *Exper. Part.* They are thermally stable and relatively volatile; even (dimethylamino)dimethyl (4,7,10,13,16-pentaoxaheptadecyl)silane (**1o**) could be purified by distillation and did not decompose on heating with silica gel up to *ca.* 300 °C. On the other hand, these substances reacted even with traces of H_2O, so they are best stored in sealed ampoules.

Surface Treatments. The surface-hydrated fume silica for the experiments was prepared according to the *Recommended Procedure* of [5], then it was stored and manipulated in a glove-box in a dry Ar atmosphere with humidity below 1 ppm. The samples contained, even after several months storage, physically adsorbed H_2O of about 0.2 $\mu mol \cdot m^{-2}$ as revealed by *Karl-Fischer* titration. Silylation of the surface and of the adsorbed H_2O required 3–5 $\mu mol \cdot m^{-2}$ of silylating agent depending on its structure. In our experiments, 10 $\mu mol \cdot m^{-2}$ of (dimethylamino)silane, corresponding to an excess of at least 100%, was reacted in a sealed ampoule with the silica. Surface silanols reacted according to *Eqn. 5.*

$$R^1R^2R^3SiN(CH_3)_2 + HO{-}[\;=\; R^1R^2R^3Si\text{-}O{-}[+ HN(CH_3)_2 \qquad (5)$$

Silylation of the adsorbed H_2O gave the corresponding hexaorganyldisiloxanes.

It has been shown that silylation with (dimethylamino)silanes in cyclohexane as solvent is an irreversible reaction [19]. It was now shown that under the actual experimental conditions in closed ampoules, the reaction of *Eqn. 5* does not stop at an equilibrium. In preliminary experiments, the same surface concentration was attained with higher-boiling (dimethylamino)silanes in sealed ampoules as in unsealed ampoules in an Ar stream [20].

In a further series of experiments, the surface concentration of some $R^1R^2R^3SiO$ groups (in **1a**, **1g**, **1i**, **1l**, **1o**, and **2**) was measured after repeated treatments in sealed ampoules at 180 °C/120 h (see *Table 4, Exper. Part*). Analysis of variance *(Table 5, Exper. Part)* showed that the slight increase after repetition of the treatment is statistically significant at the 5% level. The increase seems to be more pronounced for silanes with polar substituents such as dimethyl(4,7,10,13,16-pentaoxaheptadecyl)siloxy-substituted **1o** and methylbis(3,3,3-trifluoropropyl)siloxy-substituted **2**, where the effect is in the order of 10%. It will be seen that a longer treatment does not increase the surface concentration. This phenomenon is analogous to that observed in the NH_3-catalyzed reaction of trialkylsilanols with silica, but of less important magnitude [21]. In subsequent experiments, only one treatment was carried out. However, if completely dense coverage is required as in [1], repeated silylation is recommended with silanes having polar substituents.

The effect of temperature on the silylation was studied with the same choice of (dimethylamino)silanes (formation of **1a**, **1g**, **1i**, **1l**, **1o** and **2**; see *Table 6, Exper. Part*). Silica was treated in a sealed ampoule with the corresponding reagent between 100 and 400 °C for 120 and 170 h. Occasional decomposition was observed even at lower temperatures during the formation of **1o**. Silanes with polar substituents (leading to **1o** and **2**) carbonized at 300 °C, other silanes were stable up to *ca.* 325 °C. In the case of (dimethylamino)trimethylsilane (→**1a**), decomposition was only observed at temperatures higher than 350 °C. Surface concentrations at 100 °C were systematically lower. Analysis of variance of the results between 125 and 275 °C and with the exclusion of **1o** shows (see *Table 7, Exper. Part*) that prolongation of the treatment does not affect the surface concentration. The effect of the temperature as well as the second-order effect are significant, meaning that the slight temperature effect is different for different substituents. *Fig. 1* shows that with silanes having bulky substituents the maximum concentration is attained only at 150 °C (**1g**, **1l**) whereas with increasing temperature, a slight increase of the trimethylsiloxy coverage (**1a**) and a slight decrease of the methylbis(3,3,3-trifluoropropyl)siloxy coverage (**2**) is observed.

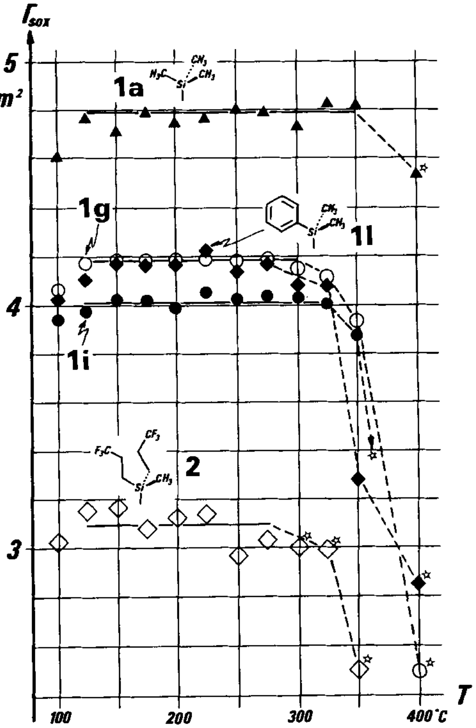

Fig. 1. *Surface concentration on trimethylsiloxy-* (**1a**), *dimethyl(octadecyl)siloxy-* (**1g**), *dimethyl(3,3-dimethylbutyl)siloxy-* (**1i**), *dimethyl(phenyl)siloxy-* (**1l**), *and methylbis(3,3,3-trifluoropropyl)siloxy-substituted* (**1o**) *silica as a function of the silylation temperature.* Points marked by * designate partly carbonized samples.

In a last series of experiments, silica was treated at optimum conditions with all the (dimethylamino)silanes prepared *(Table 8, Exper. Part)*. Results confirmed the conclusions of the foregoing experiments. For the preparation of dense layers, a reaction temperature of 160–200 °C is necessary for about 120 h. A longer reaction time is recommended for silanes having polar substituents.

Surface concentrations are summarized in *Table 1*. In *Fig. 2*, surface coverages of (n–C_zH_{2z+1})Me_2SiO substituents (see **1a–h**) are plotted as a function of the carbon number *z*. Decrease of concentration with chain length is only pronounced for the first members (from silanes having Me, Et and Pr substituents). Interestingly, oxaalkyl substituents (see **1m–o**) show the opposite behaviour. Phenyl- and 2-(cyclohexyl)ethyl-substituted silica (**1l** and **1j**, resp.) show about the same coverage.

Table 1. *Surface Concentration Γ_{sox} [μmol · m^{-2}] of $R^1R^2R^3SiO$ Groups after Reaction of a Silicon Dioxide*[a]) *with the Corresponding (Dimethylamino)silane*

	R^1	R^2	R^3	*A*[b]) [µmol · m^{-2}]	*B*[c]) [µmol · m^{-2}]
1a	Me	Me	Me	4.77 ± 0.03	4.77 ± 0.04
1b	Et	Me	Me		4.52 ± 0.04
1c	Pr	Me	Me		4.31 ± 0.04
1d	C_6H_{13}	Me	Me		4.35 ± 0.04
1e	$C_{10}H_{21}$	Me	Me		4.30 ± 0.04
1f	$C_{14}H_{29}$	Me	Me		4.24 ± 0.05[d])
1g	$C_{18}H_{37}$	Me	Me	4.18 ± 0.03	4.20 ± 0.05[d])
1h	$C_{22}H_{45}$	Me	Me		4.16 ± 0.05[d])
1i	$(CH_3)_3CCH_2CH_2$	Me	Me	4.01 ± 0.03	4.02 ± 0.04
1j	cyclo-$C_6H_{11}CH_2CH_2$	Me	Me		4.25 ± 0.04
1k	adamantyl-CH_2CH_2	Me	Me		3.83 ± 0.04
1l	Ph	Me	Me	4.17 ± 0.03	4.18 ± 0.04
1m	$CH_3O(CH_2)_3$	Me	Me		3.41 ± 0.05[d])
1n	$CH_3(OCH_2CH_2)_2CH_2$	Me	Me		3.69 ± 0.05[d])
1o	$CH_3(OCH_2CH_2)_5CH_2$	Me	Me	4.07 ± 0.04[e])	4.10 ± 0.05[d])
2	$CF_3CH_2CH_2$	$CF_3CH_2CH_2$	Me	3.10 ± 0.03	3.14 ± 0.05[d])
3	$C_{22}H_{45}$	$C_{22}H_{45}$	Me		2.83 ± 0.05[d])
4	Ph	Ph	Ph		2.44 ± 0.05[d])

[a]) Prepared according to the *Recommended Procedure* in [5].

[b]) *A*: Average of results at 125–275°/120–170 h (see *Table 6, Exper. Part*).

[c]) *B*: Average after treatments at 180–200°/120–170 h (see *Table 8, Exper. Part*).

[d]) Average after treatments at 180–200°/170 h (see *Table 8, Exper. Part*).

[e]) Not considering results at 125°/150 h and 150°/150 h.

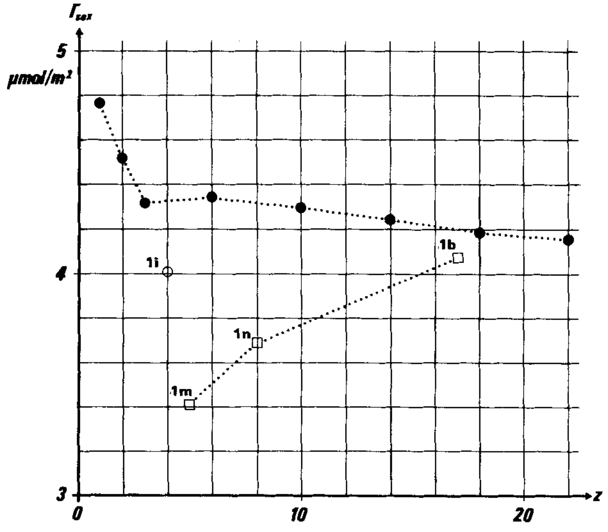

Fig. 2. *Surface concentration of R(Me)$_2$SiO groups after treatment at 180°C/170 h.* Data of substituents with R = n-C_zH_{2z+2} (full circles; **1a–k**) are plotted as a function of the carbon number *z*; those with R = oxaalkyl (open squares; **1m–o**) as a function of the number of heavy atoms in the oxaalkyl chain. Surface concentration of **1i**, where R is a branched alkyl radical, is also shown.

Table 2. *Comparison of Surface Concentration*[a]) *of Trimethylsiloxy and (3,3-Dimethylbutyl)dimethylsiloxy Substituents on Different Fully Hydrated Silicas*[b])

Starting silica[c])	Treatment[d])	s[e]) $[m^2 \cdot g^{-1}]$	ref.	**1a** ($R^1 = R^2 = R^3 = Me$) $[\mu mol \cdot m^{-2}]$	**1i** ($R^1 = (CH_3)_3CCH_2CH_2$, $R^2 = R^3 = Me$) $[\mu mol \cdot m^{-2}]$
Aerosil-OX50	– /H	47.0	[22]	4.68 ± 0.07	3.90 ± 0.12
	T/H	45.6	[22]	4.67 ± 0.07	3.86 ± 0.12
Aerosil-200	– /H	186	[22]	4.73 ± 0.07	3.82 ± 0.12
	T/H	172	[22]	4.77 ± 0.07	3.93 ± 0.12
Aerosil-300	– /H	241	[22]	4.78 ± 0.07	3.80 ± 0.12
	T/H	221	[22]	4.79 ± 0.07	3.87 ± 0.12
Fractosil-500	– /H	59.0	[22]	4.64 ± 0.06	3.75 ± 0.08
Fractosil-200	– /H	110	[22]	4.66 ± 0.06	3.77 ± 0.08
Lichrosorb-SI100	– /H	170	[22]	4.66 ± 0.06	3.85 ± 0.08
Lichrosorb-SI100	– / –	274–296	[20]	–	3.90 ± 0.10
Cab-O-Sil M5	T/H	188–200	[5]	4.72 ± 0.05	–
	T/H	120–194	[5]	4.73 ± 0.02	–
Cab-O-Sil M5	T/H	179	this work	4.77 ± 0.03	4.02 ± 0.04
Mean				4.72 ± 0.11	3.86 ± 0.18

[a]) Confidence limits are at the 95% confidence level.

[b]) Silylation with (dimethylamino)silanes at 180° for 170 h or similar conditions.

[c]) Fume silicas were from *Degussa (Aerosil)* and from *Cabot Corp. (Cab-O-Sil)*, precipitated silicas for chromatographic purposes were from *Merck (Fractosil, Lichrosorb)*.

[d]) T = temperature treatment (900°/120 h), H = hydrothermal treatment (boiling H_2O/70 h).

[e]) s = specific surface area.

Finally, in *Table 2*, surface concentrations of trimethylsiloxy (see **1a**) and (3,3-dimethylbutyl)dimethylsiloxy substituents (see **1i**) from [5] [20] [22] and the present work are compared on different surface-hydrated silicon dioxides. It is seen that on fully hydrated surfaces (see [5]), the surface concentration scatters only by about ±3%. Moreover, in order to attain maximum coverage, heat treatment can be omitted, only the hydrothermal treatment for at least 70 h is necessary. By silylation at 180°C/170 h with (dimethylamino)silanes, maximum coverage is also attained on silicas which are fully hydrated by the method of preparation (precipitated silicas).

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Experimental Part

1. General. – The structure of all synthesized substances was confirmed by UV, IR, ^{1}H-, and ^{13}C-NMR spectra as well as by elemental analysis (for exceptions see text). All melting points are uncorrected. The *densities* (corrected for vacuum) are averages of at least 2 determinations at 20.0 ± 0.1°; the confidence limit of the average at the 95% confidence level is $\Delta_{95} = 0.002$ g·cm^{-3}. The *refraction index* was measured in a *Zeiss* refractometer (system *Abbé*) thermostated at 20.0 ± 0.1°; $\Delta_{95} = 0.0003$. Silicon-dioxide samples were stored and handled in a *dry-box* from *Mecaplex AG* (Grenchen, Switzerland; mod. *GB-80*) in an Ar atmosphere containing < 1 ppm of O_2 and H_2O. The dry-box was equipped with: O_2 analyzer from *Thermox Instr. Inc.* (Pittsburgh, Penn., USA; mod. *Thermox I*); hygrometer from *Show Ltd.* (Bradford, UK; mod. *Sensitive*); a balance from *Mettler Instr. AG* (Zurich, Switzerland; mod. *A3*) with a weighing precision of 0.1 mg. *Heat treatments* at

100–450 °C (± 5 K short-range changes) were made in an oven from *Salvis AG* (Luzern, Switzerland; mod. *TSK 340*) and those at 500–1500 °C (± 20 K) in an oven from *Gerhardt GmbH* (Bonn, FRG; mod. *BMF 14*); the temperature in this oven was controlled with a Pt/Pt-Rh thermocouple.

2. Apparatus. – *Elemental analyses* were made with an apparatus from *Perkin Elmer* (Norwalk, CT, USA; mod. *240 B*). *Nitrogen-adsorption isotherms* were measured with a slightly modified automatized apparatus from *Carlo Erba S.p.A.* (Milano, Italy; mod. *Sorptomatic 1800*). Modifications, the calibration procedure, and the method of evaluation of surface areas are described in [5]. *Gas-chromatographic analyses* were performed with chromatographs from *Packard-Becker* (Delft, Holland; mod. *419*). The *spectrometers* used were an IR spectrometer from *Perkin Elmer* (mod. *521*), a UV/VIS spectrometer from *Varian-Techtron Pty. Ltd.* (Melbourne, Australia; mod. *635*), and a NMR spectrometer from *Spectrospin AG* (Zurich, Switzerland; mod. *Bruker WP 80*). *Fine distillations* were made in an apparatus from *Fischer Labortech.* (Bad Godesberg; FRG; 'Spaltrohrkolonne' *FB-HMS 300*). *Sedimentations* were made with a centrifuge from *DuPont Instr.* (Newtown, CT, USA; mod. *Sorwall RC-SB*, Refrigerated Superspeed Centr.).

3. Materials. – The research-grade *solvents* EtOH, THF and CH_2Cl_2 from *Merck* (Darmstadt, FRG) as well as dioxane, Et_2O, 2,5,8-trioxanonane, 1,2-dichloroethane, pyridine, *N,N*-dimethylformamide, benzene, toluene, isopentane, hexane, MeOH and i-PrOH from *Fluka AG* (Buchs, Switzerland) were all freshly distilled before use. Common *reagents* were from *Merck* or *Fluka*. Research-grade HBr, SbF_3, $SbCl_5$ were from *Merck*; NaH (dispersion in paraffin oil, *ca.* 50%), iodomethane, 1,2-dibromoethane, benzyl bromide, 1-docosanol, dichloro(methyl)silane, chloro(dimethyl)silane were from *Fluka*; 2-(1-adamantyl)ethanol was from *Aldrich Chem. Co.* (Millwaukee, WI, USA). Me_2NH (research-grade) from *Fluka* was distilled over molecular sieves (*Union Carbide*, type 3Å) before use. Silica gel for preparative chromatography was from *Merck* (Kieselgel *60*, 70–230 mesh). *Bidistilled water* was prepared by distilling deionized water over $KMnO_4$ in a pyrex-glass still from *Büchi* (Flawil, Switzerland; mod. *Fontavapor 285*).

4. Standard Silicon Dioxide. – Commercial fume silica, *Cab-O-Sil M5*, from *Cabot Corp.* (Mass, USA) was treated following the *Recommended Procedure* of [5]: In a vitrous silica crucible, 150 g of fume silica was heated to 900° for 120 h. The resulting powder was then digested in 1600 ml of bidistilled water at 95° for 70 h. After cooling, the supernatant was decanted, the wet paste was dispersed in a vessel by shaking, then frozen at $-20°$ before evaporating the ice at $0°/10^{-3}$ Torr for 48 h. After drying at $120°/10^{-2}$ Torr for 48 h, the product was stored in a glove-box under Ar. Specific surface area, $s = 179 \pm 2\ m^2 \cdot g^{-1}$ (average of 5 determinations; space requirement of N_2, $\mathring{a}(N_2) = 16.2\ Å^2$); apparent density, $d_{app} = 0.16\ g \cdot cm^{-3}$.

5. Starting Products of the Type R–CH=CH$_2$. – 5.1. *Ethylene* (**1b′**, purity 99.7%) and *propene* (**1c′**, 99.8%) from *Matheson* (Lyndhurst, NJ, USA) were used without further purification. The olefins *1-hexene* (**1d′**), *1-decene* (**1e′**), *1-tetradecene* (**1f′**), *1-octadecene* (**1g′**) from *Merck*, and *1-docosene* (**1h′**) from *Riedel de Haën* (Hannover, FRG) were distilled in a *Vigreux* column where a first fraction and a residue of 25% each was rejected. The middle fraction used for synthesis had a purity > 99.5% (GC). *3,3-Dimethylbutene* (**1i′**) and *vinylcyclohexane* (**1j′**) from *Fluka* (research-grade) were distilled before use to give products with purity > 99.7% (GC).

5.2. *1-Vinyladamantane* (**1k′**) was prepared following a slightly modified procedure of *Stepanov & Stolyarov* [16] in two steps:

5.2.1. In a vessel of 200 ml, a solution of 5.0 g (27.7 mmol) of 2-(1-adamantyl)ethanol in 20 ml of anh. Et_2O was added dropwise at 0° to a cooled suspension of 0.72 g (30 mmol) of NaH in 25 ml of Et_2O. After 15 min at r.t. and 30 min refluxing, the mixture was diluted with 10 ml of anh. THF, and at 0°, a solution of 4.42 g (58 mmol) of CS_2 in 10 ml of THF was added dropwise. After refluxing for 2.0 h, the yellow suspension was cooled, and 7.95 g (58 mmol) of CH_3I was added at 0° (the suspension turned white). After boiling at reflux for 8 h, the mixture was cooled, filtered, washed with 3 × 30 ml of H_2O and dried over Na_2SO_4. After evaporation of the solvent, distillation of the residue gave, at $123–125°/10^{-2}$ Torr, 5.5 g (73%) of O-*2-(1-adamantyl)ethyl* S-*methyl xanthate*, yellow ill-smelling oil $n_D^{20} = 1.5687$, $d^{20} = 1.279$ ([16]: $n_D^{20} = 1.5691$). The crude product was used without further purification.

5.2.2. In a slow Ar stream, 2.00 g (7.39 mmol) of the above xanthate was heated to 260° until no more product distilled (*ca.* 20 min). The distillate was dissolved in 50 ml of pentane, and the solution was extracted with 3 × 10 ml of sat. $NaHCO_3$ and 3 × 10 ml of sat. NaCl, then dried over Na_2SO_4, and filtered on a column of 40 g of silica gel. After elution with further 100 ml of pentane and evaporation of the solvent through a *Vigreux* column, distillation of the residue gave, at 105°/9 Torr, 760 mg (63%) of **1k′**, colorless oil (purity (GC)

99.1%) n_D^{20} = 1.5050, d^{20} = 0.823 g·cm^{-3} ([16]: n_D^{20} = 1.5052). Anal. calc. for $C_{12}H_{18}$ (162.27): C 88.82, H 11.18; found: C 88.79, H 11.20.

5.3. *4-Oxa-1-pentene* (**1m′**) was prepared according to [23].

5.4. *4,7-Dioxa-1-octene* (**1n′**). At 60°, 25.3 g (1.10 mol) of Na was dissolved under Ar in 419 g (5.50 mol) of 2-methoxyethanol. At 60°, 133.1 g (1.10 mol) of allyl bromide was added dropwise, and the mixture was heated to 70° overnight. After cooling, 700 ml of Et_2O was added, the mixture was extracted with 3 × 800 ml of H_2O, then dried over Na_2SO_4. After evaporation of the Et_2O (*Vigreux* column), distillation of the residue gave, at 32°/18 Torr, 73.2 g (57%) of **1n′** as colorless oil (purity (GC) 99.5%), n_D^{20} = 1.4131, d^{20} = 0.892 g·cm^{-3}. Anal. calc. for $C_6H_{12}O_2$ (116.16): C 62.04, H 10.41; found: C 61.95, H 10.46.

5.5. *4,7,10,13,16-Pentaoxa-1-heptadecene* (**1o′**). 5.5.1. *13-Phenyl-3,6,9,12-tetraoxatridecan-1-ol.* A solution of NaOMe was prepared by dissolving 33.1 g (1.44 mol) of Na in 500 g of MeOH. This solution to 1120 g (5.77 mol) of tetra(ethylene glycol). The MeOH was distilled off at 90°, then the rest of MeOH was eliminated by passing an Ar stream through the mixture at 120° for 5 h. Then, 246 g (1.44 mol) of benzyl bromide was added dropwise at 100° during 3 h. After cooling, the mixture was extracted with Et_2O for 15 h in a *Kutscher-Steudel* extractor. The Et_2O solution was washed with 3 × 200 ml of H_2O (elimination of tetra(ethylene glycol)), dried over Na_2SO_4, and the solvent was evaporated. Distillation of the residue through a *Vigreux*-column gave, at 164°/10^{-2} Torr, 205.5 g (50%) of 13-phenyl-3,6,9,12-tetraoxatridecan-1-ol as viscous colorless oil (purity (GC) 98.9%), n_D^{20} = 1.4964, d^{20} = 1.087 g·cm^{-3} ([24]: n_D^{20} = 1.4974, d^{20} = 1.091 g·cm^{-3}). Anal. calc. for $C_{15}H_{24}O_5$ (284.35): C 63.36, H 8.51; found: C 63.45, H 8.61.

5.5.2. *1-Phenyl-2,5,8,11,14-pentaoxapentadecane.* Under Ar, 14.7 g (0.64 mol) of Na was added to a solution of 181 g (0.64 mol) of 13-phenyl-3,6,9,12-tetraoxatridecan-1-ol in 650 ml of toluene. The mixture was heated to 60°, and after the dissolution of the Na (8 h), 182 g (1.28 mol) of CH_3I was added dropwise (precipitation of NaI). The mixture was heated at 60° overnight, cooled, extracted with 200 ml and 2 × 100 ml of H_2O, then part of the solvent was evaporated at 12 Torr to give a final volume of 300 ml. To this residue, 29.0 g (0.20 mol) of phthalic anhydride was added, heated to reflux for 2 h, cooled, extracted with 3 × 100 ml of sat. $NaHCO_3$ (elimination of the hydrogen phthalate of the starting product) and washed with 3 × 100 ml of H_2O. After evaporation of the solvent, distillation of the residue gave, at 148–150°/10^{-2} Torr, 153 g (80%) of 1-phenyl-2,5,8,11,14-pentaoxapentadecane, colorless oil (purity (GC) 99.8%) n_D^{20} = 1.4880, d^{20} = 1.048 g·cm^{-3} ([24]: n_D^{20} = 1.4882, d^{20} = 1.052 g·cm^{-3}). Anal. calc. for $C_{16}H_{26}O_5$ (298.38): C 64.40, H 8.78; found: C 64.50, H 8.73.

5.5.3. *3,6,9,12-Tetraoxatridecan-1-ol.* In an autoclave (1 l), 153 g (0.51 mol) of 1-phenyl-2,5,8,11,14-pentaoxapentadecane was hydrogenated in 600 ml of 2,5,8-trioxanonane at r.t. and 4.5 atm H_2 during 30 h in the presence of 29.0 g of Pd/C 1:9 (g/g). The catalyst was filtered on a short silica-gel column (60 g), and the solvent was evaporated. Distillation of the residue gave, at 115–117°/10^{-2} Torr, 91.8 g (86%) of 3,6,9,12-tetraoxatridecan-1-ol, viscous colorless oil (purity (GC) 99.0%), n_D^{20} = 1.4432, d^{20} = 1.051 g·cm^{-3} ([24]: n_D^{20} = 1.4440, d^{20} = 1.054 g·cm^{-3}; see also [25]). Anal. calc. for $C_9H_{20}O_5$ (208.25): C 51.91, H 9.68; found: C 51.95, H 9.58.

5.5.4. *4,7,10,13,16-Pentaoxa-1-heptadecene* (**1o′**). Under Ar, 10.2 g (0.44 mol) of Na was dissolved at 60° (6 h) in a mixture of 91.8 g (0.44 mol) of 3,6,9,12-tetraoxatridecan-1-ol and 350 ml of toluene. At 60°, 54.2 g (0.45 mol) of allyl bromide was added dropwise (*ca.* 2 h). The mixture was then heated to 70° overnight, cooled, and extracted with 2 × 50 ml of H_2O. After evaporation of the toluene, distillation of the residue gave, at 96°/10^{-2} Torr, 82.7 g (75%) of **1o′**, colorless liquid (purity (GC) 99.1%) n_D^{20} = 1.4438, d^{20} = 0.881 g·cm^{-3}. Anal. calc. for $C_{12}H_{24}O_5$ (248.32): C 58.04, H 9.74; found: C 58.05, H 9.84.

6. Alkylchlorodimethylsilanes. – 6.1. *General.* The substances decompose with humidity, therefore, elemental analysis was omitted. For the analysis of *active chlorine*, about 1.5 mmol of chlorosilane was weighed in a sealed ampoule which was then crushed in a solution of 20 ml of 0.1M NaOH. The excess was titrated with HCl 0.1M. Chlorosilanes with oxaalkyl substituents were not isolated (*cf.* [17] [18]). The *catalyst solution* for hydrosilylation was prepared by dissolving $H_2PtCl_6 \cdot H_2O$ in i-PrOH to give a concentration of Pt of 5.0 mg·ml^{-1}.

6.2. *Chlorotrimethylsilane* (**1a″**) (research-grade) from *Fluka* was distilled before use.

6.3. *Chloro(ethyl)dimethylsilane* (**1b″**). At 6 atm and r.t., ethylene was introduced into an autoclave (1 l, mechanical stirrer) containing 59.5 g (0.628 mol) of chlorodimethylsilane, 350 ml of Et_2O, and 3.0 ml of catalyst solution. After 2 h, the autoclave was heated to 45° for 10 h. Distillation of the crude mixture gave, at 85–89°/720 Torr, 62.2 g (80% based on silane) of **1b″**, colorless oil, n_D^{20} = 1.4057, d^{20} = 0.883 g·cm^{-3} ([23]: n_D^{20} = 1.4050, d^{20} = 0.876 g·cm^{-3}). Anal. calc. for $C_4H_{11}ClSi$ (122.67): Cl 28.90; found: Cl 28.55.

6.4. *Chlorodimethyl(propyl)silane* (**1c''**) (see *6.3*). At 6 atm, 42.5 g (0.449 mol) of chlorodimethylsilane in 300 ml of Et_2O and 2.4 ml of catalyst solution was reacted with propene. Distillation gave, at 105–112°/720 Torr, 55.0 g (89% based on silane) **1c''**, colorless oil, $n_D^{20} = 1.4123$, $d^{20} = 0.876$ g·cm^{-3} ([23]: $n_D^{20} = 1.4145$, $d^{20} = 0.868$ g·cm^{-3}). Anal. calc. for $C_5H_{13}ClSi$ (136.70): Cl 25.93; found: 25.67.

6.5. *Chloro(hexyl)dimethylsilane* (**1d''**). Under Ar, 33.7 g (0.356 mol) of chlorodimethylsilane was added dropwise to a mixture of 30.0 g (0.356 mol) of 1-hexene, 100 ml of Et_2O and 0.60 ml of catalyst solution. Then, the mixture was heated to reflux for 15 h. After evaporation of the solvent and non-reacted chlorodimethylsilane, distillation of the residue gave, at 77–78°/15 Torr, 51.2 g (80% based on 1-hexene) of **1d''**, colorless oil, $n_D^{20} = 1.4307$, $d^{20} = 0.873$ g·cm^{-3}. Anal. calc. for $C_8H_{19}ClSi$ (178.78): Cl 19.83; found: Cl 19.61.

6.6. *Chloro(decyl)dimethylsilane* (**1e''**; see *6.5*). From 33.7 g (0.356 mol) of chlorodimethylsilane, 50.0 g (0.356 mol) of 1-decene, 700 ml of Et_2O, and 0.60 ml of catalyst solution. Distillation gave, at 98–101°/1 Torr, 68.8 g (82%) **1e''**, colorless oil, $n_D^{20} = 1.4433$, $d^{20} = 0.912$ g·cm^{-3}. Anal. calc. for $C_{12}H_{27}ClSi$ (234.88): Cl 15.09; found: Cl 14.91.

6.7. *Chlorodimethyl(tetradecyl)silane* (**1f''**; see *6.5*). From 33.7 g (0.356 mol) of chlorodimethylsilane, 70.0 g (0.356 mol) of 1-tetradecene, 700 ml of Et_2O, and 0.60 ml of catalyst solution. Distillation gave, at 131–134°/10^{-1} Torr, 88.9 g (86%) **1f''**, colorless oil, $n_D^{20} = 1.4482$, $d^{20} = 0.890$ g·cm^{-3}. Anal. calc. for $C_{16}H_{35}ClSi$ (290.99): Cl 12.18; found Cl 12.11.

6.8. *Chlorodimethyl(octadecyl)silane* (**1g''**; see *6.5*). From 44.4 g (0.469 mol) of chlorodimethylsilane, 118.4 g (0.469 mol) of 1-octadecene, 1200 ml of Et_2O, and 0.80 ml of catalyst solution. Distillation gave, at 155–160°/$5 \cdot 10^{-3}$ Torr, 139.2 g (85%) of **1g''**, colorless oil that solidified on standing, m.p. 28–31°. Anal. calc. for $C_{20}H_{43}ClSi$ (347.10): Cl 10.21; found: Cl 10.08.

6.9. *Chloro(docosyl)dimethylsilane* (**1h''**) was prepared according to [23].

6.10. *Chloro(3,3-dimethylbutyl)dimethylsilane* (**1i''**; see *6.5*). From 22.4 g (0.237 mol) of chlorodimethylsilane, 20.0 g (0.237 mol) of 3,3-dimethyl-1-butene, 400 ml of Et_2O, and 0.40 ml of catalyst solution. Distillation gave, at 158–159°/720 Torr, 34.4 g (81%) **1i''**, colorless oil, $n_D^{20} = 1.4278$, $d^{20} = 0.870$ g·cm^{-3}. Anal. calc. for $C_8H_{19}ClSi$ (178.78): Cl 19.83; found: Cl 19.59.

6.11. *Chloro(2-cyclohexylethyl)dimethylsilane* (**1j''**; see *6.5*). From 7.9 g (84 mmol) of chlorodimethylsilane, 8.0 g (72 mmol) of vinylcyclohexane, 80 ml of Et_2O, and 0.30 ml of catalyst solution. Distillation gave, at 84.5–85°/5 Torr, 12.33 g (83%) of **1j''**, colorless oil, $n_D^{20} = 1.4597$, $d^{20} = 0.988$ g·cm^{-3}. Anal. calc. for $C_{10}H_{21}ClSi$ (204.81): Cl 17.31; found: Cl 17.19.

6.12. *[2-(1-Adamantyl)-ethyl]chlorodimethylsilane* (**1k''**; see *6.5*). From 26.5 g (0.280 mol) of chlorodimethylsilane, 39.5 g (0.243 mol) of **1k'**, 200 ml of Et_2O, and 1.00 ml of catalyst solution. After elimination of the solvent and the non-reacted chlorodimethylsilane under reduced pressure in an Ar stream (18 Torr/50°/5 h), the residue crystallized: 54.8 g (87%) of **1k''**, crystalline mass, m.p. 37–38°. The product (containing the catalyst) was used in the next step without further purification. Anal. calc. for $C_{14}H_{25}ClSi$ (256.89): Cl 13.80; found: Cl 13.68.

6.13. *Chlorodimethyl(phenyl)silane* (**1l''**) (research-grade, *Fluka*) was distilled before use.

6.14. *Chlorodimethyl(4-oxapentyl)silane* (**1m''**) and *chloro(4,7-dioxaoctyl)dimethylsilane* (**1n''**) were prepared according to [23]; the crude product was used immediately after preparation.

6.15. *Chlorodimethyl(4,7,10,13,16-pentaoxaheptadecyl)silane* (**1o''**). Under Ar, 11,4 g (0.120 mol) of chlorodimethylsilane was added dropwise to a boiling mixture of 30.0 g (0.120 mol) of **1o'**, 100 ml of Et_2O, and 200 ml of catalyst solution. After 15 h, volatiles were eliminated at r.t. under reduced pressure (12 Torr) in an Ar stream. The crude product was dissolved in 350 ml of hexane and used immediately for the preparation of the (dimethylamino)silane.

6.16. *Chlorotriphenylsilane* (**4''**) (research-grade, *Fluka*) was used without further purification.

7. **Dialkyl(bromo)methylsilanes.** 7.1. *Bromo(methyl)bis(3,3,3-trifluoropropyl)silane* (**2''**). 7.1.1. *1,1,1,3-Tetrachloropropane* was prepared according to [26].

7.1.2. *3-Chloro-1,1,1-trifluoropropane* was prepared by a modified procedure of [26]: Under Ar, a solution of 296 g (1.66 mol) of anh. SbF_3 in 106 ml (248 g; 0.830 mol) of $SbCl_5$ was heated to 165° for 2.5 h. After cooling, 240 ml of 1,2-dichloropropane was added at 50° while vigorously agitating the mixture to give a light-brown fine suspension (without agitation a compact mass was obtained). After further cooling, 99.0 g (0.544 mol) of 1,1,1,3-tetrachloroethane was added at 0° dropwise (*ca.* 3 h), then the red mixture was stirred at r.t. overnight. Volatiles were distilled off at 40–50°/20 Torr into a trap cooled at −70°, the distillate was washed with 2 × 50 ml of 5M HCl/2.5M H_2SO_4 1:1, then with 2 × 50 ml of sat. $NaHCO_3$ and 2 × 50 ml of H_2O, then dried over $CaSO_4$. Distillation in a 'Spaltrohr'-column gave, at 46°/720 Torr, 41.0 g (57%) of 3-chloro-1,1,1-trifluoropropane, colorless liquid (purity (GC) > 99.9%), $n_D^{20} = 1.3275$, $d^{20} = 1.207$ g·cm^{-3} ([26]: $n_D^{20} = 1.3280$). Anal. calc. for $C_3H_4ClF_3$ (132.51): C 27.19, H 3.04; found: C 26.98, H 3.01.

7.1.3. *Methylbis(3,3,3-trifluoropropyl)silane.* Under Ar, 2.92 g (120 mmol) of Mg covered by 10 ml of Et_2O was heated to reflux. First, a few mg of I_2, then dropwise 13.3 g (100 mmol) of 3-chloro-1,1,1-trifluoropropane (100 mmol) was added (*ca.* 2 h), and the mixture was refluxed for further 4 h. After cooling to 20° and addition of 20 ml of Et_2O, a mixture of 5.23 g (45 mmol) of dichloro(methyl)silane and 5 ml of Et_2O was introduced dropwise (after 10 min, a white precipitate appeared), 10 ml of THF was added to the resulting suspension, then it was heated to reflux for 15 h. The mixture was hydrolyzed with 50 ml of sat. NH_4Cl, the aq. phase extracted with 2 × 50 ml of pentane, the org. phase was washed with 2 × 50 ml of H_2O, dried over Na_2SO_4, and the solvent evaporated. Distillation of the residue through a 'Spaltrohr'-column gave, at 65°/40 Torr, 10.2 g (95% based on dichloro(methyl)silane) of methylbis(3,3,3-trifluoropropyl)silane, colorless oil (purity (GC) 99.5%), $n_D^{20} = 1.3535$, $d^{20} = 1.176$ g·cm^{-3} ([27]: $n_D^{20} = 1.3525$, $d^{20} = 1.164$ g·cm^{-3}). Anal. calc. for $C_7H_{12}F_6Si$ (238.25): C 35.29, H 5.08; found: C 35.04, H 5.04.

7.1.4. *Bromo(methyl)bis(3,3,3-trifluoropropyl)silane* (**2″**). Under Ar, a solution of 6.40 g (40.0 mmol) of Br_2 in 40 ml of CCl_4 was added slowly and dropwise at r.t. to a stirred solution of 9.53 g (40.0 mmol) of methylbis(3,3,3-trifluoropropyl)silane in 20 ml of CCl_4 (3.5 h). After evaporation of the solvent, distillation of the residue gave, at 64°/12 Torr, 12.3 g (97%) of **2″**, colorless oil, $n_D^{20} = 1.3910$, $d^{20} = 1.510$ g·cm^{-3} ([28]: $n_D^{20} = 1.3890$, $d^{20} = 1.455$ g·cm^{-3}). Anal. calc. for $C_7H_{11}BrF_6Si$ (317.14): Br 25.19; found: Br 24.87.

7.2. *Bromo(didocosyl)methylsilane* (**3″**). 7.2.1. *1-Bromodocosane* was prepared from distilled, pure 1-docosanol according to method B of [29].

7.2.2. *Didocosyl(methyl)silane.* Mg (4.16 g, 171 mmol) was covered with a 50-ml portion of a solution of 62.0 g (159 mmol) of 1-bromodocosane in 200 ml of Et_2O. First, 2.20 g (11.7 mmol) of 1,2-dibromoethane was added (evolution of ethylene), then dropwise at slight reflux, the rest of the 1-bromodocosane solution. The mixture was heated to reflux for further 8 h. To this solution of the *Grignard* reagent, 5.50 g (48.7 mmol) of dichloromethylsilane was added dropwise, and the mixture was heated to reflux overnight. After cooling, 200 ml of sat. NH_4Cl and 400 ml of cyclohexane were added, the org. phase was separated and washed with 3 × 100 ml of H_2O, dried over Na_2SO_4, filtered through a column with 300 g of silica gel, and eluted with additional 300 ml of cyclohexane. After evaporation of the solvent, 46.0 g of a crystalline residue remained; after 3 recrystallizations from Et_2O/EtOH 45:55, 28.6 g (89% based on dichloro(methyl)silane) of didocosyl(methyl)silane, colorless crystals, m.p. 62–66°. Anal. calc. for $C_{45}H_{94}Si$ (663.32): C 81.48, H 14.28; found: C 81.46, H 14.23.

7.2.3. *Bromo(didocosyl)methylsilane* (**3″**). Under Ar, a solution of 5.08 g (31.8 mmol) of Br_2 in 40 ml of CCl_4 was added dropwise at r.t. to a stirred solution of 21.1 g (31.8 mmol) of didocosyl(methyl)silane in 400 ml of CCl_4. The solvent was evaporated and the residue dried in an Ar stream at 50° for 5 h: 23.5 g (100%) of **3″** as a crystalline wax, m.p. 61–65°. The product was not further purified. Anal. calc. for $C_{45}H_{93}BrSi$ (742.22): Br 10.77; found: Br 10.74; elem. anal. calc.: C 72.82, H 12.63; found: C 73.00, H 12.62, Br 10.72.

8. Trialkyl(dimethylamino)silanes. 8.1. *General.* (Dimethylamino)silanes are stable up to *ca.* 200° and even higher. They are extremely sensitive to humidity, therefore, elemental analysis was omitted. *Determination of active N_2:* Some 1.5 mmol of (dimethylamino)silane was weighed and sealed in an ampoule, then the ampoule was crashed in a solution containing 20.0 ml of 0.1M HCl, and the excess of acid was titrated with 0.1M NaOH in the presence of methyl-red. The result is given as N%. *Purity* (see [11]): Some 10 mg of (dimethylamino)silane was dissolved in 100 µl of abs. EtOH and heated to 60° for 45 min to give the ethoxysilane in quantitative yield. The solution was analyzed by GC, the result is listed in *Table 3* as 'purity GC' (% surface in the chromatogram). All (dimethylamino)silanes were prepared following the same procedure. Reaction is quantitative, lower yields were due to losses during manipulations.

8.2. *A typical procedure.* The gas phase of a flask equipped with a condenser at −10° and containing a solution of 49.6 g (0.277 mol) of **1d″** in 300 ml of hexane under Ar was connected to that of a second, smaller flask containing 27.5 g (0.610 mol) of anh. liq. Me_2NH. At r.t., the Me_2NH distilled slowly (3.0 h) and reacted with the chlorosilane to give a white precipitate of Me_2NH_2Cl. The mixture was stirred overnight, then the cooling of the condenser was stopped in order to eliminate excess Me_2NH. The solution was filtered in a glass-sintered funnel with Ar pressure and the hexane evaporated. Distillation of the residue gave, at 89–91°/15 Torr, 45.7 g (88%) of *(dimethylamino)hexyldimethylsilane* (**1d″**), colorless oil. Physical properties, see *Table 3.* Anal. calc. for $C_{10}H_{25}NSi$ (187.40): N 7.47; found: N 7.43.

Remarks. Preferred *solvent* was hexane; isopentane was used for the preparation of low-boiling (dimethylamino)silanes; benzene or toluene was used if the solubility was too low in hexane. The *concentration* of the chlorosilane was 1M, but not higher than 200 g·l^{-1}. Lower concentrations were also used for reasons of solubility. Chlorosilanes with oxaalkyl substituents were used as crude products.

Table 3. *Physical Properties of (Dimethylamino)silanes*

	R^1	R^2	R^3	Purity		m.p.	d^{20}[c])	n_D^{20}[d])
				titr.[a]) [%]	GC[b]) [%]	[°C]	g cm^{-3}	
1a'''	Me	Me	Me	98.7	99.4		0.741	1.3950[e])
1b'''	Et	Me	Me	98.6	99.5		0.767	1.4111
1c'''	Pr	Me	Me	99.1	99.2		0.773	1.4164
1d'''	C_6H_{13}	Me	Me	99.5	99.4		0.792	1.4307
1e'''	$C_{10}H_{21}$	Me	Me	99.1	98.9		0.806	1.4411
1f'''	$C_{14}H_{29}$	Me	Me	99.4	99.3		0.815	1.4476
1g'''	$C_{18}H_{37}$	Me	Me	99.0	99.6		0.822	1.4518
1h'''	$C_{22}H_{45}$	Me	Me	98.2	98.9	41–43		
1c'''	$(CH_3)_3CCH_2CH_2$	Me	Me	99.9	99.4		0.787	1.4282
1j'''	cyclo-$C_6H_{11}CH_2CH_2$	Me	Me	99.7	99.1		0.870	1.4583
1k'''	adamantyl-CH_2CH_2	Me	Me	99.6	99.5		0.976	1.4960
1l'''	Ph	Me	Me	99.4	99.0		0.912	1.4975
1m'''	$CH_3O(CH_2)_3$	Me	Me	99.8	99.7		0.857	1.4241
1n'''	$CH_3(OCH_2CH_2)_2CH_2$	Me	Me	99.1	99.4		0.896	1.4363
1o'''	$CH_3(OCH_2CH_2)_5CH_2$	Me	Me	98.2	98.7		0.963	1.4485
2'''	$CF_3CH_2CH_2$	CF_3CH_2CH	Me	98.8	99.1		1.158	1.3729
3'''	$C_{22}H_{45}$	$C_{22}H_{45}$	Me	99.5	–	44–49		
4'''	Ph	Ph	Ph	98.7	98.4	68		

[a]) Purity calculated from the determination of active N as 100 (N% found/N% calc.).

[b]) Purity by GC of the ethoxy derivative (surface area percentage; flame ionisation detector).

[c]) Error of the density at 20.0 ± 0.1° estimated to $\Delta_{95} = 0.003$ g · cm^{-3}.

[d]) Error of the refraction index n_D^{20} estimated to $\Delta_{95} = 0.0005$.

[e]) [30]: $n_D^{20} = 1.3950$; [31]: $d^{20} = 0.741$ g · cm^{-3}.

8.3. *(Dimethylamino)trimethylsilane* (**1a'''**). From 47.9 g (0.441 mol) of chlorotrimethylsilane, 500 ml of isopentane, and 44.2 g (0.980 mol) of Me_2NH. Distillation gave, at 77–79°/720 Torr, 38.9 g (75%) of colorless oil. Anal. calc. for $C_5H_{15}NSi$ (117.27): N 11.94; found: N 11.78.

8.4 *(Dimethylamino)ethyldimethylsilane* (**1b'''**). From 55.0 g (0.448 mol) of **1b''**, 500 ml of isopentane, and 44.4 g (0.985 mol) of Me_2NH. Distillation gave, at 105–110°/720 Torr, 47.6 g (81%) of colorless oil. Anal. calc. for $C_6H_{17}NSi$ (131.29): N 10.67; found: N 10.52.

8.5. *(Dimethylamino)dimethyl(propyl)silane* (**1c'''**). From 55.0 g (0.402 mol) of **1c''**, 500 ml of isopentane, and 39.9 g (0.885 mol) of Me_2NH. Distillation gave, at 123–127°/720 Torr, 50.0 g (86%) of colorless oil. Anal. calc. for $C_7H_{19}NSi$ (145.32): N 9.64; found: N 9.55..

8.6. *Decyl(dimethylamino)dimethylsilane* (**1e'''**). From 67.7 g (0.288 mol) of **1e''**, 500 ml of hexane, and 28.5 g (0.632 mol) of Me_2NH. Distillation gave, at 103–105°/5 × 10^{-2} Torr, 58.5 g (83%) of colorless oil. Anal. calc. for $C_{14}H_{33}NSi$ (243.51): N 5.75; found: N 5.70.

8.7. *(Dimethylamino)dimethyl(tetradecyl)silane* (**1f'''**). From 77.7 g (0.267 mol) of **1f''**, 500 ml of hexane, and 26.5 g (0.588 mol) of Me_2NH. Distillation gave, at 115–118°/3 × 10^{-3} Torr, 67.6 g (84%) of colorless oil. Anal. calc. for $C_{18}H_{41}NSi$ (299.61): N 4.67; found: N 4.64.

8.8. *(Dimethylamino)dimethyl(octadecyl)silane* (**1g'''**). From 132 g (0.380 mol) of **1g''**, 800 ml of hexane, and 37.7 g (0.836 mol) of Me_2NH. Distillation gave, at 141–144°/3 × 10^{-3} Torr, 108.4 g (80%) of viscous, colorless oil. Anal. calc. for $C_{22}H_{49}NSi$ (355.72): N 3.94; found: N 3.90.

8.9. *(Dimethylamino)docosyldimethylsilane* (**1h'''**). From 53.0 g (0.131 mol) of **1h''**, 300 ml of hexane, and 13.0 g (0.288 mol) of Me_2NH. Distillation gave, at 185–186°/3 × 10^{-3} Torr, 43.1 g (82%) of colorless, viscous oil which crystallized on standing, m.p. 34–36°. Anal. calc. for $C_{26}H_{57}NSi$ (411.83): N 3.40; found: N 3.34.

8.10. *(Dimethylamino)(3,3-dimethylbutyl)dimethylsilane* (**1i'''**). From 31.8 g (0.178 mol) of **1i''**, 350 ml of hexane, and 17.6 g (0.390 mol) of Me_2NH. Distillation gave, at 156–160°/720 Torr, 27.8 g (83%) of colorless oil. Anal. calc. for $C_{10}H_{15}NSi$ (187.40): N 7.47; found: N 7.46.

8.11. *(2-Cyclohexylethyl)(dimethylamino)dimethylsilane* (**1j'''**). From 12.1 g (59.1 mmol) of **1j''**, 250 ml of hexane, and 6.4 g (142 mmol) of Me_2NH. Distillation gave, at 69°/0.4 Torr, 10.8 g (86%) of colorless oil. Anal. calc. for $C_{12}H_{27}NSi$ (213.44): N 6.56; found: N 6.54.

8.12. *[2-(1-Adamantyl)ethyl](dimethylamino)dimethylsilane* (**1k‴**). From 54.0 g (0.210 mol) of **1k″**, 900 ml of hexane/toluene 1:2, and 24.0 g (0.532 mol) of Me_2NH. Distillation gave, at 95°/10^{-3} Torr, 51.4 g (93%) of colorless oil. Anal. calc. for $C_{16}H_{31}NSi$ (265.51): N 5.28; found: N 5.26.

8.13. *(Dimethylamino)dimethyl(phenyl)silane* (**1l‴**). From 100.0 g (0.586 mol) of **1l″**, 100 ml of hexane, and 58.0 g (1.287 mol) of Me_2NH. Distillation gave, at 82–83°/15 Torr, 100.0 g (95%) of colorless oil. Anal. calc. for $C_{10}H_{17}NSi$ (179.34): N 7.81; found: N 7.76.

8.14. *(Dimethylamino)dimethyl(4-oxapentyl)silane* (**1m‴**). From 98 g (*ca.* 0.60 mol) of crude **1m″**, 500 ml of isopentane, and 52.9 g (1.170 mol) of Me_2NH. Distillation gave, at 160–167°/720 Torr, 51.7 g (*ca.* 50%) of colorless oil. Anal. calc. for $C_8H_{21}ONSi$ (175.35): N 7.99; found: N 7.97.

8.15. *(Dimethylamino)dimethyl(4,7-dioxaoctyl)silane* (**1n‴**). From 38 g (*ca.* 0.18 mol) of crude **1n″**, 500 ml of hexane, and 18.7 g (0.410 mol) of Me_2NH. Distillation gave, at 48°/10^{-2} Torr: 30.9 g (47%) of colorless oil. Anal. calc. for $C_{10}H_{25}O_2NSi$ (219.40): N 6.38; found: N 6.32.

8.16. *(Dimethylamino)dimethyl(4,7,10,13,16-pentaoxaheptadecyl)silane* (**1o‴**). From 41 g (*ca.* 0.11 mol) of crude **1o″**, 350 ml of hexane, and 10.9 g (0.240 mol) of Me_2NH. Distillation gave, at 125–129°/10^{-2} Torr, 21.7 g (*ca.* 51%) of colorless oil. Anal. calc. for $C_{16}H_{37}O_5NSi$ (351.56): N 3.98; found: 3.91.

8.17. *(Dimethylamino)methylbis(3,3,3-trifluoropropyl)silane* (**2‴**). From 13.0 g (41.0 mmol) of **2″**, 150 ml of isopentane, and 45.0 g (100 mmol) of Me_2NH. Distillation gave, at 70°/12 Torr, 10.4 g (86%) of colorless oil. Anal. calc. for $C_9H_{17}F_6NSi$ (281.32): N 4.98; found: N 4.92.

8.18. *Didocosyl(dimethylamino)methylsilane* (**3‴**). From 23.5 g (32.0 mmol) of **3″**, 600 ml of hexane, and 3.10 g (68.8 mmol) of Me_2NH. After evaporation of the solvent, the residue was dried in a dry Ar stream at 40° for 10 h: 20.8 g (91%) of crystalline mass, m.p. 44–49°. Anal. calc. for $C_{47}H_{99}NSi$ (706.39): N 1.98; found titr.: N 1.97; elem. anal. calc.: C 79.92, H 14.13, N 1.98; found: C 79.69, H 14.23, N 1.75.

8.19. *(Dimethylamino)triphenylsilane* (**4‴**) was prepared as in [11].

9. Reaction of Silica Samples with (Dimethylamino)silanes. – 9.1. *Typical Experiment.* In the dry-box, 100 mg surface-hydrated silica was weighed in an ampoule. (Dimethylamino)silanes higher boiling than **1d‴** (10 $\mu mol \cdot ml^{-2}$ if not otherwise stated) were dissolved in 200 mg of isopentane. This solution was added into the ampoule outside the dry-box, the isopentane was evaporated in an Ar stream by heating at 60° and dried at 10^{-2} Torr/40° for 20 min. Lower boiling (dimethylamino)silanes were added without solvent. The ampoule was cooled in liquid N_2, evacuated to 10^{-2} Torr and sealed. The ampoule was heated in an oven at the desired temp. for the desired period, cooled, opened, and the product was washed 5 times by suspending in 10 ml of Et_2O, sedimenting by centrifugation (25000 g) for 10 min, and decanting the supernatant. The air-dry powder was then heated at 110°/10^{-2} Torr for 12 h.

9.2. *Surface Concentration.* The C-content was determined on a sample of 5 mg by burning in He/O_2 (with every series of elemental analyses, the C-content of a trimethylsiloxy-covered standard was also determined as a control). Surface concentration, Γ_{sox}, was calculated from the carbon percent, P_C, following *Eqn. 6* [21] [32].

$$\Gamma_{sox} = \frac{10^6}{s^{(BET)}} \cdot (1201.1 \cdot a_C / P_C - M(R) + \delta)^{-1} \ \mu mol \cdot m^{-2} \qquad (6)$$

where $s^{(BET)}$ [m^2g^{-1}] is the specific surface area of the silica determined by the BET-method [5], a_C is the stoichiometric ratio of C-atoms in the substituent (for trimethylsiloxy, C_3H_9Si, $a_C = 3$), $M(R)$ the molecular weight of the substituent, R, and δ is a correction for H_2O desorbed during treatment and the proton substituted ($\delta \approx 5$ for our carefully stored samples).

9.3. *Surface Concentration after Successive Treatments.* In a first series of experiments, standard silica was treated with triorganyl(dimethylamino)silanes, with R^1,R^2, and R^3 as shown in *Table 4*, 3 times consecutively at 180°C. In the first treatment, 10 $\mu mol \cdot m^{-2}$ of silane was applied for 170 h. After workup, as described in *9.1*, the product was treated with 5 $\mu mol \cdot m^{-2}$ of silane at the same temperature for 120 h, then the third time under the same conditions as in the second treatment. Surface concentrations are shown in *Table 4*. The analysis of variance of the results is shown in *Table 5*.

9.4. *Surface Concentrations at Different Temperatures.* In a second series of experiments, standard silica was treated with triorganyl(dimethylamino)silanes as in *9.1* between T = 100 and 400° at every 25° for 120 and 170 h. Surface concentrations are listed in *Table 6*, the analysis of variance of the results is shown in *Table 7*.

9.5. *Surface Concentrations of Different Triorganylsiloxy Groups.* In a third series of experiments, standard silica was treated with triorganyl(dimethylamino)silanes in *9.1* at 180° for 120 and 170 h and at 200° for 170 h. Surface concentrations are listed in *Table 8*.

Table 4. *Surface Concentration Γ_{sox} [µmol m^{-2}] on Standard Silica after Successive Treatments with Triorganyl(dimethylamino)silanes at 180°*

	R^1	R^2	R^3	Γ_{sox} [µmol m^{-2}][a]) after		
				1st treatment	2nd treatment	3rd treatment
1a	Me	Me	Me	4.78	4.80	4.85
1g	$C_{18}H_{37}$	Me	Me	4.17	4.19	4.23
1i	$(CH_3)_3CCH_2CH_2$	Me	Me	4.02	4.05	4.06
1l	Ph	Me	Me	4.19	4.22	4.20
1o	$CH_3(OCH_2CH_2)_5CH_2$	Me	Me	4.09	4.18	4.36
2	$CF_3CH_2CH_2$	$CF_3CH_2CH_2$	Me	3.12	3.36	3.62
	average			4.06	4.13	4.22

[a]) In the 1st treatment, 10 µmol · m^{-2} of (dimethylamino)silane was applied for 170 h; for the 2nd and 3rd: 5 µmol · m^{-2}/120 h.

Table 5. *Analysis of Variance of the Results Listed in Table 4*

Source of variance	SQ[a])	Φ[b])	V[c]) [µmol m^{-2}]^2	F[d])	Significance [%]
Silane	3.20518	5	0.64103	68.8	0.1
Treatment	0.07543	2	0.03772	4.05	5
Second-order effect[e])	0.09323	10	0.00932		

[a]) SQ = sum of squares. [b]) Φ = degree of freedom. [c]) V = variance. [d]) F = *Fisher's F*. [e]) The second-order effect is taken as the residual variance.

Table 6. *Surface Concentration Γ_{sox} [µmol m^{-2}] of $R^1R^2R^3SiO$ Groups on Standard Hydrated Silica after Treatment with the Corresponding (Dimethylamino)silane at Different Temperatures*

T		**1a**		**1a**		**1i**		**1l**		**2**		**1o**	
[°C]	R^1	Me		$C_{18}H_{37}$		$(CH_3)_3CCH_2CH_2$		Ph		$CF_3CH_2CH_2$		$CH_3(OCH_2CH_2)_5CH_2$	
	R^2	Me		Me		Me		Me		$CF_3CH_2CH_2$		Me	
	R^3	Me		Me		Me		Me		Me		Me	
		120 h	170 h[a])	120 h[a])	170 h[a])	120 h[a])	170 h[a])	120 h[a])	170 h[a])	120 h[a])	170 h[a])	120 h[a])	170 h[a])
100		4.55	4.67	4.02	4.08	3.86	3.89	4.03	4.01	3.03	3.00	3.93	3.90
125		4.74	4.80	4.19	4.14	3.96	3.96	4.11	4.08	3.12	3.17	2.14	4.08
150		4.73	4.69	4.17	4.16	4.02	3.99	4.18	4.19	3.20	3.13	2.90	4.08
175		4.78	4.78	4.17	4.19	4.00	4.03	4.18	4.19	3.06	3.11	4.05	4.10
200		4.73	4.76	4.16	4.20	3.98	4.01	4.19	4.18	3.09	3.16	4.09	4.09
225		4.76	4.78	4.17	4.18	4.04	4.07	4.21	4.20	3.15	3.15	4.17	4.10
250		4.78	4.85	4.17	4.18	4.02	4.00	4.15	4.12	2.96	3.02	3.87	4.17
275		4.78	4.81	4.19	4.19	4.06	4.01	4.15	4.20	3.07	3.01	4.00	4.09
300		4.69	4.76	4.13	4.17	4.02	4.02	4.07	4.09	3.07	2.93[b])	2.96[b])	2.98[b])
325		4.85	4.81	4.13	4.10	3.97	4.02	4.13	4.03	3.02[b])	2.97[b])	[c])	[c])
350		4.76	4.88	3.90	3.98	3.86	3.88	3.30	3.26	2.34[b])	2.67[b])	[c])	[c])
400		4.60[b])	4.47[b])	2.56[b])	2.50[b])	2.26[b])	2.20[b])	2.81	2.89	[c])	[c])	[c])	[c])

[a]) Silylation time.

[b]) Slightly carbonized sample.

[c]) Completely carbonized sample.

Table 7. *Analysis of Variance of the Results Listed in Table 6 within the Frame*

Source of variance	SQ[a])	Φ[b])	V[c]) [μmol m^{-2}]^2	F[d])	Significance[f])[g]) [%]
Silane	20.30868	4	5.07717	7161.0	0.1
Silylation time	0.00104	1	0.00104	1.47	–
Silylation temperature	0.01420	6	0.00237	3.34	1
Second-order effect[e])	0.07950	24	0.00331	4.66	0.1
Rest	0.02411	34	0.000709		

[a])[b])[c])[d])[e]) See *Table 5.*

[f]) Only significant effects are listed.

[g]) Error of a single determination at the 95% significance level calculated from the residual variance: $\Delta_{95} = 0.054$ μmol · m^{-2}. Error by considering effects of silylation time and temperature and second-order effect as non-significant: $\Delta_{95} = 0.087$ μmol · m^{-2}.

Table 8. *Surface Concentration Γ_{sox} [μmol · m^{-2}] of Different $R^1R^2R^3SiO$ Groups, after Treatment with the Corresponding (Dimethylamino)silane at 180° for 120 and 170 h and at 200° for 170 h*[a])

	R^1	R^2	R^3	Treatment at		
				180°/120 h [μmol · m^{-2}]	180°/170 h [μmol · m^{-2}]	200°/170 h [μmol · m^{-2}]
1a	Me	Me	Me	4.78	4.78	4.76
1b	Et	Me	Me	4.55	4.56	4.44
1c	Pr	Me	Me	4.33	4.31	4.29
1d	C_6H_{13}	Me	Me	4.34	4.37	4.34
1e	$C_{10}H_{21}$	Me	Me	4.30	4.30	4.31
1f	$C_{14}H_{29}$	Me	Me	4.19	4.23	4.24
1g	$C_{18}H_{37}$	Me	Me	4.17	4.19	4.20
1h	$C_{22}H_{45}$	Me	Me	4.10	4.17	4.15
1i	$(CH_3)_3CCH_2CH_2$	Me	Me	4.00	4.03	4.02
1j	cyclo-$C_6H_{11}CH_2CH_2$	Me	Me	4.25	4.26	4.23
1k	adamantyl-CH_2CH_2	Me	Me	3.85	3.82	3.82
1l	Ph	Me	Me	4.18	4.19	4.18
1m	$CH_3O(CH_2)_3$	Me	Me	3.28	3.37	3.44
1n	$CH_3(OCH_2CH_2)_2CH_2$	Me	Me	3.66	3.67	3.70
1o	$CH_3(OCH_2CH_2)_5CH_2$	Me	Me	4.05	4.10	4.09
2	$CF_3CH_2CH_2$	$CF_3CH_2CH_2$	Me	3.06	3.11	3.16
3	$C_{22}H_{45}$	$C_{22}H_{45}$	Me	2.77	2.81	2.84
4	Ph	Ph	Ph	2.38	2.46	2.41
Mean ($\Delta_{95} = 0.02$ μmol · m^{-2})				3.90	3.93	3.92

[a]) Mean surface concentration for individual substituents, see *Table 1.*

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