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Synthesis of organofunctional silanes with sterically hindered substituents at silicon atoms

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Organofunctional silanes with more sterically hindered substituents at the silicon atom than the typical methoxy (ethoxy) group have lately been frequently used as silane coupling agents, in polymer coupling systems, sol-gel processes and also as interpenetrating polymer network substrates. New and very efficient synthetic ways leading to organofunctional silanes of the above type with methacryl, amine, chloro and isocyanato functional groups are proposed here. Catalytic transesterification and/or alcoholysis of chloropropyltrialkoxysilanes followed by nucleophilic substitution has been employed. Copyright © 2001 John Wiley & Sons, Ltd.

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INTRODUCTION

Organofunctional silanes of the general formula $X_3Si(CH_2)_mY$ (**I**) where $m = 0,2,3$, $Y = Cl$, NH_2, NHR, NCO, $CH{=}CH_2$, SH, S_n, $OCH_2\overbrace{CHCH_2O}$ and $CH_2{=}C(CH_3)C(O)O$ $X = RO$, Cl or $CH_3C(O)O$ and $R = CH_3$, C_2H_5 have been known for many years as a family of silanes of great practical importance.[1] They have been mainly applied as silane coupling agents—for coupling of inorganic fillers with organic polymers—but recently they have appeared to be suitable substrates for polymer coupling systems and the sol–gel process and have frequently been used as (co)monomers of functional siloxanes.[2]

Organofunctional silane producers have started to improve typical synthetic routes to the silanes mentioned above, or have found new, more effective, synthetic ways to produce them, but only a few new products have been introduced to the market since 1990. Interest has now focused on organofunctional silanes of the general formula $X_2(CH_3)Si(CH_2)_mY$ and $X_3Si(CH_2)_mY$ with $X = RO$, but with R being of a more developed steric hindrance than the typical methoxy (or ethoxy) substituent. For example vinyltris(2-methoxyethoxy)silane (Z-6082 of Dow Corning, A-172 of OSi (Witco), KBC 1003 of Shin-Etsu or VTMOEO of Hüls), 3-aminopropyltris(2-methoxyethoxy)silane (1302 of Hüls), 3-methacryloxypropyl-tris(2-methoxyethoxy)silane (Gelest Inc.) are found on the market; however, the information on their synthesis is limited.

Silanes of this particular structure react significantly slower with water to create intermediate hydroxy groups at the silicon atom and can be used successfully in systems of high water content. It is generally known that the rate of hydrolysis depends on the pH of the silane solution, silane concentration, reaction temperature and steric and electronic effects of the R and Y groups. The hydrolysis rate depends on the R structure according to the following order:[2] $CH_3COO > CH_3O > C_2H_5O > CH_3OCH_2CH_2O > C_3H_7O > C_4H_9O$. Introduction of only one sterically demanding group at the silicon atom significantly changes the rate of hydrolysis. Silanes with ethoxy substituents have become commercial products; for example ethoxy substitutes of 3-methacryloxypropyltriethoxysilane (Y 11878) and 2-(3,4-epoxycyclohexyl)ethyltriethoxysilane (Y 11870) have been introduced, for

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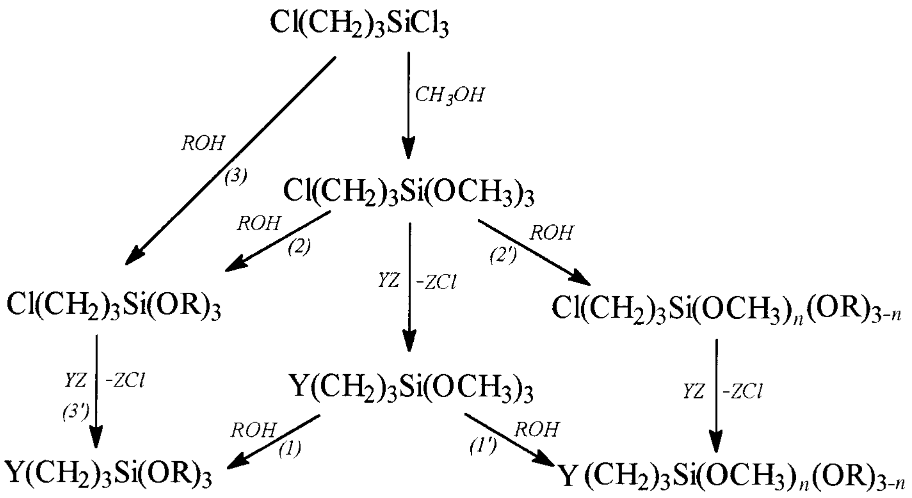

Scheme 1 Silanes synthesis routes.

example, by Witco Co. (OSi Specialties). Contrary to ethoxysilanes, the formation of toxic CH_3OH from the condensation process of methoxy derivatives may be harmful both for silane producers and their end-users.

There are three possible ways to synthesize the silanes under study (Scheme 1). These can be described as follows:

- catalytic transesterification of the commercial methoxy-substituted silane coupling agents (1);
- catalytic transesterification of the commercially produced 3-chloropropyltrimethoxysilane with an appropriate alcohol, followed by a nucleophilic chlorine atom substitution step (2,2′);
- alcoholysis of 3-chloropropyltrichlorosilane with an appropriate alcohol, followed by nucleophilic substitution, mentioned above (3,3′).

One can say that some silanes can be obtained *via* all the routes described, but, of course, with different overall yields and selectivities.

Because of the scarce information on the synthesis of organofunctional silanes of formula **I** with R groups containing more than two carbon atoms[3] and, on the other hand, the increasing amounts of information on the practical application of such silane coupling agents,[4–7] the aim of this study was to describe the most efficient synthetic ways of leading to such silanes products as: $Y(CH_2)_3Si(OR)_3$ and $Y(CH_2)_3Si(OCH_3)_n(OR)_{3-n}$ where Y = Cl, $NH_2CH_2CH_2NH$, $CH_2{=}C(CH_3)C(O)O$, NCO and R = $CH_3OCH_2CH_2$, $i\text{-}C_3H_7$ and $t\text{-}C_4H_9$.

RESULTS AND DISCUSSION

Transesterification of commercial methoxy-substituted silanes

Catalytic transesterification of methoxy silanes seems to be the simplest way to achieve the silanes needed;[8] however, this route is limited by possible activity of the Y group of the silane coupling agent against alcohol (for example isocyanato substituents react with alcohols) and usually this process runs with very poor selectivity (Eqn [1]):

$$Y(CH_2)_3Si(OCH_3)_3 + ROH \xrightarrow{\text{catalyst}} Y(CH_2)_3Si(OCH_3)_{3-n}(OR)_n \quad [1]$$

$$\mathbf{1}, \mathbf{2}(\mathbf{a}\text{–}\mathbf{f})$$

$$Y = NH_2CH_2CH_2NH(\mathbf{1}), CH_2{=}C(CH_3)C(O)O(\mathbf{2})$$

$$R = CH_3OCH_2CH_2(\mathbf{a}\text{–}\mathbf{c}), i\text{-}C_3H_7(\mathbf{d}\text{–}\mathbf{f})$$

$$n = 1(\mathbf{a}, \mathbf{d}), 2(\mathbf{b}, \mathbf{e}), 3(\mathbf{c}, \mathbf{f})$$

Tin, titanium and vanadium compounds ($Ti(i\text{-}OPr)_4$, $VO(i\text{-}OPr)_3$, $Ti(OBu)_4$, $SnOBu_2$) are typical catalysts of this process.[9]

Transesterification of $NH_2CH_2CH_2NH(CH_2)_3Si(OCH_3)_3$ with 2-methoxyethanol in the presence of $Ti(OBu)_4$ led to 95% conversion of the starting material, but with a mixture of three possible products, viz. $NH_2CH_2CH_2NH(CH_2)_3Si(OCH_3)_2(OCH_2CH_2OCH_3)$ (**1a**), $NH_2CH_2CH_2NH(CH_2)_3Si(OCH_3)(OCH_2CH_2OCH_3)_2$ (**1b**) and $NH_2CH_2CH_2NH(CH_2)_3Si(OCH_2CH_2OCH_3)_3$ (**1c**) in amounts of 48%, 31% and 21% respectively. Their structures were confirmed by gas chromatography–mass spectrometry (GC–MS) techniques. Similar results were obtained in the presence of $SnOBu_2$ as a catalyst. Further attempts to shift the reaction pathway towards product **1c** failed; the resulting product consisted of all the silanes (**1a–c**); however, fully substituted **1c** was the major product.

Transesterification of *N*-2-aminoethyl-3-aminopropyltrimethoxysilane with *iso*-propanol, irrespective of the catalyst used, led to a mixture of products (**1d–f**), with substrate conversion close to 96%. In this case, $NH_2(CH_2)_2NH(CH_2)_3Si(OCH_3)(i\text{-}OC_3H_7)_2$ (**1e**) was the main reaction product with a selectivity of 91%. *tert*-Butanol was found to be inactive in the transesterification route under the conditions studied.

3-Methacryloxypropyltrimethoxysilane treated with 2-methoxyethanol, both in the presence of $Ti(OBu)_4$ or $SnOBu_2$, did not result in the expected **2c** derivative. Low conversion of the substrate was observed (up to 50% in the presence of the tin catalyst) and several undefined by-products accompanied the main product $CH_2{=}C(CH_3)C(O)O(CH_2)_3Si(OCH_2CH_2OCH_3)_3$ (**2c**). In the case of *iso*-propanol practically all the substrate was consumed, but only several low boiling point by-products were detected. Transesterification of 3-chloropropyltrimethoxysilane followed by a nucleophilic substitution step is another pathway to synthesize the silanes of interest (Eqn [2]):

$$Cl(CH_2)_3Si(OCH_3)_3 + nROH \xrightarrow{\text{catalyst}} Cl(CH_2)_3Si(OCH_3)_{3-n}(OR)_n + nCH_3OH \quad [2]$$

$$\mathbf{3(a\text{–}f)}$$

$R = CH_3OCH_2CH_2(\mathbf{a\text{–}c})$

$i\text{-}C_3H_7(\mathbf{d\text{–}f})$

$n = 1(\mathbf{a},\mathbf{d}), 2(\mathbf{b},\mathbf{e}), 3(\mathbf{c},\mathbf{f})$

The process of transesterification in the presence of 2-methoxyethanol under normal conditions led to a mixture of silanes (**3a–c**) with selectivities of 20%, 35% and 95% respectively. Addition of further portions of alcohol and a catalyst led, after 12 h of heating, almost selectively to $Cl(CH_2)_3Si(OCH_2CH_2OCH_3)_3$ (**3c**). Spectroscopic data for the isolated product fully confirmed its nature. In the case of transesterification with *iso*-propanol, a mixture of silanes (**3d–f**) was found, but the selectivities were 38%, 60% and 2% respectively. Continuation of the transesterification process did not lead to product **3f**, and di-substituted silane **3e** was the major product. All attempts to replace methoxy substituents at the silicon atom by *tert*-butoxy groups failed.

Alcoholysis of 3-chloropropyltrichlorosilane

Esterification of 3-chloropropyltrichlorosilane with chosen alcohols is another way to obtain 3-chloropropyltrialkoxysilanes. In the presence of *iso*-propanol, 95% conversion of the substrate led to only one product—trisubstituted **3f** with high selectivity and a resonable isolation yield of over 80%.

The silane $Cl(CH_2)_3Si(OCH_2CH_2OCH_3)_3$ (**3c**) was synthesized with high selectivity (97%) and yield (77%), using 2-methoxyethanol as the starting alcohol. Chromatographic and spectroscopic data of the products fully confirmed their identity. The use of *tert*-butanol was not so effective: some gaseous products were observed and fast gelation of the reaction mixture terminated the process.

Nucleophilic substitution of alkoxy-substituted chlorosilanes 3c and 3f

Catalytic nucleophilic substitution of the C—Cl bond in 3-chloropropyltrialkoxysilanes was the last step to form the expected organofunctional silanes with alkoxy substituents with three carbon atoms.[10] The reaction with potassium methacrylate (Eqn [3])

$$Cl(CH_2)_3Si(OR)_3CH_2{=}C(CH_3)C(O)OK \xrightarrow{\text{catalyst}} CH_2{=}C(CH_3)C(O)O(CH_2)_3Si(OR)_3 + KCl \quad [3]$$

$$\mathbf{2c}, \mathbf{2f}$$

should lead to the expected products **2c** and **2f**: The reaction occurred in the presence of KI, in DMF as a solvent and 4-dimethylaminopyridine (DMAP) as a catalyst. In the case of triisopropoxysilane **3c**, after 4.5 h a 93% conversion was observed and product **2f** was isolated at a yield of 87%. Tris(2-

methoxyethoxy)-substituted silane **3f** was transformed to product **2c**; despite the high conversion (95%) the isolation yield was only 71%. Both products, **2c** and **2f**, were characterized and identified (see Experimental section).

The reaction of 3-chloropropyltrialkoxysilanes in excess of ethylenediamine resulted in the following amino derivatives (Eqn [4]):

$$\underset{\mathbf{3(c,f)}}{Cl(CH_2)_3Si(OR)_3} + NH_2CH_2CH_2NH_2 \rightarrow \underset{\mathbf{1(c,f)}}{NH_2CH_2CH_2NH(CH_2)_3Si(OR)_3} \quad [4]$$

leading to **1f** (R = i-C_3H_7) at a yield of 76% and to **1c** (R = $CH_2CH_2OCH_3$) at a yield of 46%.

Nucleophilic substitution of the C—Cl bond in chloropropylsilanes with potassium cyanate, in the presence of KI and in DMF as solvent, gave derivatives with the NCO group (Eqn [5]):

$$\underset{\mathbf{3c,3f}}{Cl(CH_2)_3Si(OR)_3} + KOCN \xrightarrow[KCl]{} \underset{\mathbf{4c,4f}}{(RO)_3Si(CH_2)_3NCO} \quad [5]$$

$$R = CH_2CH_2OCH_3 \quad (\mathbf{c})$$

$$R = i - C_3H_7 \quad (\mathbf{f})$$

Conversion of **3c** was equal to 80% and product **4f** was isolated at a yield of only 70%. Product **4c** was obtained at a similar yield; however, it was accompanied by an unidentified high boiling point by-product of a very similar structure.

CONCLUSIONS

Catalytic transesterification of the commercially available methoxy-substituted silanes was found as a possible synthetic pathway but is limited to some substrates and with low selectivity; usually, the mixture of all possible three products was observed. The reaction time, the nature of the catalyst and its concentration influence the reaction progress. All the results are collected in Table 1.

Alcoholysis of 3-chloropropyltrichlorosilane with the use of *iso*-propanol and 2-methoxy-ethanol was far more effective and selective (see Table 2).

The resulting 3-chloropropyltrialkoxysilanes underwent a nucleophilic substitution; however, this process was not so smooth as that observed for trimethoxy derivatives. Additionally, some problems with isolation of the reaction products limited the isolation yield. However, six products with methacrylate, amine and isocyanate groups were successfully isolated at yields of up to 87% (see Table 3).

All the compounds isolated were fully characterized spectroscopically.

A comparison of the selectivity and yield of different pathways led to us to the conclusion that there is no general optimum way to synthesize the expected products. Aminofunctional tri(isopropoxy)silanes and 3-chloropropyltris(2-methoxyethoxy)silane were produced most efficiently *via* transesterification of functional methoxy-substituted silanes (with over 90% yield). For 3-chloropropyltri(isopropoxy)silane the alcoholysis of 3-chloropropyltrichlorosilane is the method of choice (with a yield close to 80%); for methacryloxyfunctional silanes with isopropoxy substituents at the silicon atom the nucleophilic substitution of the C—Cl bond in 3-chloropropylsilane seems to be the only route for synthesis (with 87% of isolation yield).

Further studies on the scale-up of the silane manufacturing process, as well as on the application of this class of silane coupling agents, are in progress (first tests on butadiene–acrylonitrile rubber filled with silica showed the successful use of some of the silanes prepared[7]).

EXPERIMENTAL

Materials

The chemicals were obtained from the following sources: *N*-2-aminoethyl-3-aminopropyltrinethoxysilane, 3-chloropropyltrichlorosilane, 3-chloropropyltrimethoxysilane and 3-methacryloxypropyltrimethoxysilane from UniSil (Poland); alcohols: t-C_4H_9OH (Acros), i-C_3H_7OH (POCh) and $CH_3OCH_2CH_2OH$ (Fluka) were freshly distilled and dried prior to use; catalysts: $Ti(OC_4H_9)_4$ (ABCR), $SnO(C_4H_9)_2$ (Aldrich), 4-hydroxyanisole (Aldrich), DMAP (Fluka) and potassium iodide (POCh) were used without any purification; additional reagents; ethylenediamine (POCh), KNCO (Fluka) and $CH_2{=}C(CH_3)C(O)OK$ were dried by standard methods prior to use.

Table 1 Transesterification of methoxy-substituted organofunctional silanes[a]

Substrates		Silane conversion (%)	Product	Selectivity (%)
Silane	Alcohol			
$NH_2(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$	$CH_3OCH_2CH_2OH$	95	$NH_2(CH_2)_2NH(CH_2)_3Si(OCH_3)_2(OCH_2CH_2OCH_3)$ **1a**	48
			$NH_2(CH_2)_2NH(CH_2)_3Si(OCH_3)(OCH_2CH_2OCH_3)_2$ **1b**	31
			$NH_2(CH_2)_2NH(CH_2)_3Si(OCH_2CH_2OCH_3)_3$ **1c**	21
$NH_2(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$	i-C_3H_7OH	96	$NH_2(CH_2)_2NH(CH_2)_3Si(OCH_3)_2$(O-i-$C_3H_7$) **1d**	4
			$NH_2(CH_2)_2NH(CH_2)_3Si(OCH_3)$(O-i-$C_3H_7)_2$ **1e**	91
			$NH_2(CH_2)_2NH(CH_2)_3Si$(O-i-$C_3H_7)_3$ **1f**	5
$CH_2{=}C(CH_3)C(O)O(CH_2)_3Si(OCH_3)_3$	$CH_3OCH_2CH_2OH$	50[b]	$CH_2{=}C(CH_3)C(O)O(CH_2)_3Si(OCH_2CH_2OCH_3)_3$ **2c**	4
$Cl(CH_2)_3Si(OCH_3)_3$	$CH_3OCH_2CH_2OH$	98	$Cl(CH_2)_3Si(OCH_3)(OCH_2CH_2OCH_3)_2$ **3b**	6
			$Cl(CH_2)_3Si(OCH_2CH_2OCH_3)_3$ **3c**	94
$Cl(CH_2)_3Si(OCH_3)_3$	i-C_3H_7OH	98	$Cl(CH_2)_3Si(OCH_3)_2$(O-i-C_3H_7) **3d**	38
			$Cl(CH_2)_3Si(OCH_3)$(O-i-$C_3H_7)_2$ **3e**	60
			$Cl(CH_2)_3Si)$(O-i-$C_3H_7)_3$ **3f**	2

[a] For details, see Experimental Section.
[b] Conversion toward transesterification ~15%.

Table 2 Alcoholysis of 3-chloropropyltrichlorosilane[a]

Alcohol	Silane conversion (%)	Product	Yield (%)	Yield of isolated product (%)
i-C_3H_7OH	95	$Cl(CH_2)_3Si(O\text{-}i\text{-}C_3H_7)_3$ **3f**	92	82
$CH_3OCH_2CH_2OH$	88	$Cl(CH_2)_3Si(OCH_2CH_2OCH_3)_3$ **3c**	85	77
t-C_4H_9OH	7	$Cl(CH_2)_3Si(O\text{-}t\text{-}C_4H_9)_3$	Traces	0

[a] For details, see Experimental section.

Equipment and analytical measurements

The NMR spectra (^1H, ^{13}C) were recorded on a Varian XL 300 spectrometer. In all cases C_6D_6 was used as a solvent. An FT-IR Brucker IFS 113v was used for recording of IR spectra. GC–MS analyses were carried out with a Varian 3300 chromatograph (equipped with a DB-1, 30 m, capillary column) connected to a Finnigan Mat 700 mass detector. GC analyses were performed on a Varian 3800 chromatograph equipped with a Megabore column (DB-1, 30 m).

Synthetic procedures and analysis of products

Transesterification (general procedure)

The process of transesterification was performed in a typical glassware set. The starting silane in excess of alcohol and with catalyst ($Ti(OC_4H_9)_4$ or $SnO(C_4H_9)_2$—1 ml/100 ml of alcohol) was stirred and heated. Methanol was collected and the reaction mixture composition was controlled using GC.

(a) Transesterification of *N*-2-aminoethyl-3-aminopropyltrimethoxysilane by 2-methoxyethanol: 19.5 ml (0.09 mol) of *N*-2-aminoethyl-3-aminopropyltrimethoxysilane was treated with 22 ml (0.28 mol) of 2-methoxyethanol in the presence of 0.22 ml $Ti(OC_4H_9)_4$. A mixture of three products, **1a, 1b** and **1c**, was obtained (see Table 1), which was confirmed by GC–MS analysis.

(b) Transesterification of *N*-2-aminoethyl-3-aminopropyltrimethoxysilane by *iso*-propanol: 19.5 ml (0.09 mol) of *N*-2-aminoethyl-3-aminopropyltrimethoxysilane was treated with 21 ml (0.28 mol) of *iso*-propanol in the presence of 0.2 ml $Ti(OC_4H_9)_4$. The conversion of starting silane was 96% and a mixture of three products, **1d, 1e** and **1f**, was obtained (mainly **1e**) (see Table 1).

(c) Transesterification of 3-methacryloxypropyltrimethoxysilane by 2-methoxyethanol: 19 ml (0.08 mol) of starting silane was treated with 19 ml (0.25 mol) of 2-methoxyethanol in the presence of $Ti(OC_4H_9)_4$ (0.2 ml), but only traces of the products were obtained. The reaction was repeated in the presence of $SnO(C_4H_9)_2$ as a catalyst. In this case the conversion of the starting silane was 50%, but only 4% of the main product **2c** was obtained, together with a mixture of low boiling point co-products.

(d) Transesterification of 3-chloropropyltrimethoxysilane by 2-methoxyethanol: 20 ml (0.08 mol) of starting silane was treated with 20.4 ml (0.26 mol) of 2-methoxyethanol in the presence of $Ti(OC_4H_9)_4$ (0.2 ml). A mixture of products **3a, 3b** and **3c** was obtained. A further portion of 2-methoxyethanol was added and finally, after 12 h, the main product **3c** was obtained, accompanied by a small amount of **3b**. Product **3c** was isolated by distillation (b.p. = 145 °C/1 mmHg) and fully characterized.

Anal. Found: C, 42.9; H, 7.9. Calc. for $C_{12}H_{27}ClO_6Si$: C, 43.5; H, 8.2%.

Spectroscopic data for **3c**: ^1H NMR (δ, ppm) (C_6D_6) 0.78–0.83 (m, 2H), 1.85–1.95 (m, 2H), 3.36 (s, 9H), 3.88–3.93 (t, 6H), 3.40–3.54 (m, 8H). ^{13}C NMR (δ, ppm) (C_6D_6): 7.69 ($SiCH_2$), 26.06 (CH_2), 47.22 ($ClCH_2$), 58.0 (OCH_2), 73.42 (OCH_2CH_2), 61.92 (OCH_3). MS-EI: (*m/z*) 255 (100%, $[M]-OCH_2CH_2OCH_3$)

(e) Transesterification of 3-chloropropyltrimethoxysilane by *iso*-propanol: 20 ml (0.08 mol) of starting silane was treated with 20 ml (0.26 mol) of *iso*-propanol in the presence of $Ti(OC_4H_9)_4$ (0.2 ml). A mixture of three

Table 3 Nucleophilic substitution of C—Cl bond in 3-chloropropyltrialkoxysilanes[a]

Substrates		Silane conversion (%)	Product	Yield of isolated product (%)
Silane	Other			
$Cl(CH_2)_3Si(O\text{-}i\text{-}C_3H_7)_3$	$CH_2{=}C(CH_3)C(O)OK$	93	$CH_2{=}C(CH_3)C(O)O(CH_2)_3Si(O\text{-}i\text{-}C_3H_7)_3$ **2f**	87
$Cl(CH_2)_3Si(O\text{-}i\text{-}C_3H_7)_3$	$NH_2CH_2CH_2NH_2$	99	$NH_2CH_2CH_2NH(CH_2)_3Si(O\text{-}i\text{-}C_3H_7)_3$ **1f**	76
$Cl(CH_2)_3Si(O\text{-}i\text{-}C_3H_7)_3$	KNCO	80	$OCN(CH_2)_3Si(O\text{-}i\text{-}C_3H_7)_3$ **4f**	70
$Cl(CH_2)_3Si(OCH_2CH_2OCH_3)_3$	$CH_2{=}C(CH_3)C(O)OK$	95	$CH_2{=}C(CH_3)C(O)O(CH_2)_3Si(OCH_2CH_2OCH_3)_3$ **2c**	71
$Cl(CH_2)_3Si(OCH_2CH_2OCH_3)_3$	$NH_2CH_2CH_2NH_2$	67	$NH_2CH_2CH_2NH(CH_2)_3Si(OCH_2CH_2OCH_3)_3$ **1c**	46
$Cl(CH_2)_3Si(OCH_2CH_2OCH_3)_3$	KNCO	78	$OCN(CH_2)_3Si(OCH_2CH_2OCH_3)_3$ **4c**	67

[a] For details, see Experimental section.

products, **3d, 3e** and **3f**, was obtained (mainly **3e**), which was confirmed by GC–MS analysis.

Alcoholysis of 3-chloropropyltrichlorosilane (general procedure)

The process of alcoholysis was performed in a typical glassware set. To 3-chloropropyltrichlorosilane the, alcohol was slowly added at room temperature, and then the product was isolated by distillation and thoroughly purified to eliminate traces of HCl, using standard procedures.

(a) Alcoholysis of 3-chloropropyltrichlorosilane by *iso*-propanol: to a reactor with 235 ml of 3-chloropropyltrichlorosilane, 516 ml of *iso*-propanol was added dropwise over 2 h. The crude product was degassed to remove HCl and then distilled under vacuum and the main product was collected at 110 °C/13 mmHg.

Anal. Found: C, 51.6; H, 10.1. Calc for $C_{12}H_{27}ClO_3Si$: C, 50.9; H, 9.6%.

Spectroscopic data for **3f**: ^1H NMR (δ, ppm) (C_6D_6) 0.33–0.38 (m, 2H), 1.35–1.41 (m, 2H), 2.47–2.58 (m, 2H), 0.94(d, 18H); 4.01(h, 3H). ^{13}C NMR (δ, ppm) (C_6D_6) 47.55 ($ClCH_2$), 76.57 (OCH), 26.76 (CH_2), 9.61 ($SiCH_2$), 25.71 (CH_3). MS, EI: (*m/z*) 77 (30%, $[(CH_2)_3Cl]$); 99 (28%, $[(CH_2)_3SiOCH]$); 121 (30%, $[Cl(CH_2)_3SiO]$); 164 (31%, $[Cl(CH_2)_3SiOC_3H_7]$); 205 (100%, $[M]-Cl(CH_2)_3$); 223 (98%, $[M]-OC_3H_7$); 240 (20%, $[M]-C_3H_7$).

(b) Alcoholysis of 3-chloropropyltrichlorosilane by 2-methoxyethanol: to a reactor with 233 ml of 3-chloropropyltrichlorosilane, 534 ml of 2-methoxyethanol was added dropwise over 45 min. The crude product was degassed to remove HCl and then distilled under vacuum; the main product was collected at 140–145 °C/1 mmHg. Spectroscopic data for **3c** were presented previously.

Nucleophilic substitution of chlorine in 3-chloropropyltrialkoxysilane (general procedure)

This process was performed in a typical glassware set. To a mixture of 3-chloropropyltrichlorosilane, KI and DMAP as a catalyst, $CH_2{=}C(CH_3)C(O)OK$, $NH_2CH_2CH_2NH_2$ or KNCO were added. The reaction mixture was heated to 120 °C (4–5 h). The course of the reaction was controlled by GC analysis. After the reaction, precipitated KCl was removed from the reaction mixture and the crude product was distilled under vacuum.

(a) Reaction of 3-chloropropyltri(isopropoxy) silane with $CH_2{=}C(CH)_3C(O)OK$: to a mixture of 40 g (0.14 mol) 3-chloropropyltri-(isopropoxy)silane, 0.21 g 4-dimethylaminopyridine and 2 g KI, a solution of 21.9 g (0.14 mol) $CH_2{=}C(CH_3)C(O)OK$ in DMF (12 g) was added. Additionally, 0.2 g of 4-hydroxyanisole was added as an inhibitor of polymerization. The reaction proceeded for 4.5 h at 120 °C. The KCl precipitate was removed from the reaction mixture by filtration. The main product was isolated *via* distillation (b.p. = 125 °C/1 mmHg) with yield 87%.

Anal. Found: C, 56.9; H, 10.0. Calc. for $C_{16}H_{32}O_5Si$: C, 57.8; H, 9.7%.

Spectroscopic characterization for **2f**: ^1H NMR (δ, ppm) (C_6D_6): 0.44–0.54 (m, 2H), 0.97 (d, 18H), 1.57–1.71 (m, 5H), 1.81 (s, 3H), 3.81–3.98 (m, 2H), 4.02–4.15 (m, 3H), 5.42 (s, 1H), 5.97 (s, 1H). ^{13}C NMR (δ, ppm) (C_6D_6): 9.27 (CH_3), 19.11 (CH_3), 23.76 (CH_2), 26.43 ($SiCH_2$), 65.76 (OCH_2), 67.50 (OCH), 125.17 (=C), 137.59 ($=CH_2$), 167.33 (C=O). IR: 1721 cm^{-1} (C=C), 1040 cm^{-1} (Si—O—C), 1640 cm^{-1} (C=O).

(b) Reaction of 3-chloropropyltris(2-methoxyethoxy)silane with $CH_2{=}C(CH_3)C(O)OK$: to a mixture of 50 g (0.15 mol) 3-chloropropyltris(2-methoxyethoxy)silane, 0.18 g 4-dimethylaminopirydine and 2.5 g KI, a solution of 21.9 g (0.14 mol) $CH_2{=}C(CH_3)C(O)OK$ in DMF (15 g) was added. Additionally, 0.18 g of 4-hydroxyanisole was added as an inhibitor of polymerization. The reaction proceeded for 2 h at 120 °C. After filtration of KCl precipitate, the reaction mixture was distilled under vacuum and the main product was collected at 152 °C/0.5 mmHg. The yield of the main product **4f** was 71%.

Anal. Found: C, 51.2; H, 7.9. Calc. for $C_{16}H_{32}O_8Si$: C, 50.5; H, 8.5%.

Spectroscopic characterization for **2c**: ^1H NMR (δ, ppm) (C_6D_6): 0.58–0.69 (m, 2H), 1.68–1.78 (m, 2H), 1.84 (s, 3H), 3.30 (s, 9H), 3.42 (t, 6H), 3.85 (t, 6H), 4.04 (t, 2H), 5.47 (s, 1H), 6.02 (s, 1H). ^{13}C NMR (δ, ppm) (C_6D_6): 6.35 ($SiCH_2$), 18.22 (CH_2), 21.96 (CH_2), 58.80

(OCH_2), 73.58 (OCH_2CH_2), 61.95 (OCH_3), 125.01 (=C), 136.43 (=CH_2), 167.32 (C=O).

(c) Reaction of 3-chloropropyltri(isopropoxy) silane with $H_2NCH_2CH_2NH_2$: to 3-chloropropyltri(isopropoxy)silane (51 g, 0.18 mol), 43 ml (0.18 mol) of ethylenediamine was added slowly dropwise. The reaction mixture divided into two phases. After separation the crude product was distilled. The main product was collected at 105 °C/4 mmHg.

Anal. Found: C, 54.2; H, 10.1; N, 10.2. Calc. for $C_{14}H_{34}N_2O_3Si$: C, 54.8; H, 9.7; N, 9.5%.

Spectroscopic data for **1f**: ^{1}H NMR (δ, ppm) (C_6D_6): 0.58–0.62 (m, 2H), 1.18–1.24 (d, 2H), 1.60–1.66 (m, 2H), 2.6–2.8 (m, 6H), 4.2–4.3 (h, 3H). ^{13}C NMR (δ, ppm) (C_6D_6): 41.38 (CH_2), 64.32 (OCH), 23.79 (CH_2), 8.99 ($SiCH_2$), 25.02 (CH_3).

(d) Reaction of 3-chloropropyltri(2-methoxyethoxy)silane with $H_2NCH_2CH_2NH_2$: to 3-chloropropyltri(2-methoxyethoxy)silane (60 ml), 44 ml of ethylenediamine was added dropwise. Then the mixture was heated at 120 °C for 1 h. The reaction mixture divided into two phases. After separation the crude product was distilled. The main product **1c** was identified by GC–MS analysis.

(e) Reaction of 3-chloropropyltri(isopropoxy)-silane with KNCO: a mixture of 3-chloropropyltri(isopropoxy)silane (30 g), DMF (30 ml) and KI (2.2 g) was heated at 120 °C for 0.5 h, followed by addition of KNCO (13.2 g). The mixture was heated at 120 °C for 3.5 h. After filtration of KCl precipitate, the reaction mixture was distilled under vacuum. The main product **4f** was identified by GC–MS analysis.

(f) Reaction of 3-chloropropyltri(2-methoxyethoxy)silane with KNCO: the same methodology as above was used. A mixture of 3-chloropropyltri(2-methoxyethoxy)silane (40 g), DMF (40 ml) and KI (2 g) was activated for 0.5 h at 120 °C and then 9.7 g of KNCO was added. The mixture was heated at 120 °C for 9 h. After filtration of KCl, the crude product was distilled. The main product **4c** was identified by GC–MS analysis.

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