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A New Solvent-Free Reaction for the Preparation of Alkoxysilane from Cyclic Ethers, Alcohols, or Carbonyl Compounds

Leyla Pehlivan,[a] Estelle Métay,[a] Olivier Boyron,[b] Patrice Demonchaux,[c] Gérard Mignani,[d] and Marc Lemaire*[a]

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The 1,1,3,3-tetramethyldisiloxane/Pd/C system is reported here as a new method to accomplish the ring-opening of ethers and epoxides to give protected alcohols. The approach can also be used for the protection of primary or secondary alcohols and for the reduction of aldehydes and ketones to obtain alkoxysilanes.

Introduction

The Si–O bond is widely found in organic and inorganic chemistry in a large variety of applications. Alkoxysilanes can be used, for example, for the preparation of rubber and varnish. Renewable materials for organic synthesis are often polyoxygenated products. Unlike classical chemistry, valorization of vegetal raw material requires selective deoxygenation. Silanes are known to be suitable for this type of transformation. Corriu et al. described the alcoholysis of dihydro- and trihydrosilanes[1] with potassium carbonate, and Yamamoto et al. reported the reduction of carbonyl groups to a methyl group by using triethylsilane and $B(C_6F_5)_3$.[2] Although silane derivatives give rise to harmless silica as the ultimate by-product, trichlorosilane, trialkylsilane, methoxysilane are expensive, toxic, and difficult to use. The use of polymethylhydrosiloxane (PMHS) and 1,1,3,3-tetramethyldisiloxane (TMDS), which are relatively nontoxic hydride donors, appears to be a good alternative for the reduction of several functions. Moreover TMDS offers the advantage of being easier to handle and of giving a linear polymer as a by-product. In terms of biomass valorization, the modification of tetrahydrofuran derivatives to protected alcohols is interesting.

[a] Laboratoire de Catalyse et Synthèse Organique, Institut de Chimie et Biochimie Moléculaires et Supramoléculaires (ICBMS), CNRS, UMR 5246, Université Lyon 1, 43 boulevard du 11 novembre 1918, bat. CPE, 69622 Villeurbanne, France
Fax: +33-4-72431408
E-mail: marc.lemaire@univ-lyon1.fr
[b] Laboratoire de Chimie, Catalyse, Polymères et Procédés C2P2, CNRS, UMR 5265, Bât. F308, B. P. 2077, 43 Bd du 11 Nov. 1918, 69616 Villeurbanne cedex, France
[c] Minakem SAS, 145 Chemin des Lilas, 59310 Beuvry la Foret, France
[d] Rhodia, Lyon Research center, 85 Avenue des Frères Perret, B. P. 62, 69192 Saint-Fons Cedex, France

In the family of cyclic ethers, epoxides are easily prepared from alkenes, which are present in a large variety of natural products. The ring-opening of epoxides can be realized by the use of boron and aluminum hydrides (KBH_4, $NaBH_4$, $ZnBH_4$, chloroalanes, etc.) either with or without the assistance of a metal.[3–10] However, drawbacks associated with their use are well-documented, particularly in respect to their high reactivity with water, the use of hydrosoluble solvent, and the toxicity of the formed salts. The regioselectivity of the reaction depends on the nature of the reducing agent or the substrate.[3] Hydrogenation with Pd catalysts can also be used for the same application with good selectivities, indeed, only one product was obtained in several cases.[11–13] When siloxanes such as PMHS and palladium complexes were employed in the presence of allylic ether, the corresponding alcohol was formed.[14] Based on a literature survey, reductions performed with PMHS and Pd on charcoal in ethanol can be compared to a low-pressure hydrogenation.[15] These conditions allowed the reduction of nitro to amines,[16] dehalogenation of aromatic compounds,[17] reduction of aromatic acid chlorides to aldehydes,[18] isoxazolines, and indoles,[19] and reduction of aldehydes and double bonds to alkanes.[15]

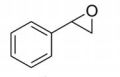
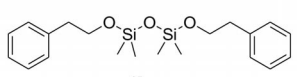
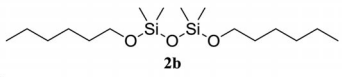
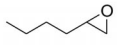
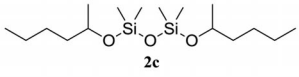
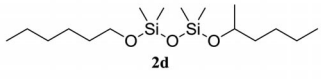
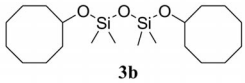
In our laboratory, we demonstrated that TMDS can be used to efficiently reduce a range of functions, such as phosphane oxides,[20] nitriles,[21] amides,[22] and nitro[23] groups, depending on the metal catalyst. Recently, Martin et al.[24] described a useful application of TMDS in the presence of nickel complexes that allowed the cleavage of anisole derivatives.

Results and Discussion

The ring-opening of a range of epoxides was tested at room temperature with 1.2% Pd/C as catalyst and TMDS as the hydride source (Table 1). The ring-opening of styrene oxide under these conditions was selective because only iso-

mer **1b** was observed, with complete conversion and a good yield after 20 h of reaction (Table 1, Entry 1). This isomer was also obtained as the major product when a mixture of sodium borohydride, moist alumina, and $PdCl_2$ was used for the ring-opening of the styrene oxide,[8] or by hydrogenation using $Pd(OAc)_2$,[13] whereas 1-phenylethanol was obtained as the major product when sodium aluminum hydride[25] or lithium aluminum hydride *N*-methylpyrrolidine[26] are used. Because these methods require the use of hydrides, which react violently with air and water, the use of Pd/C and TMDS is a good alternative. With 1,2-epoxyhexane, the reaction was complete and the yield quantitative, however, no particular selectivity was observed. NMR and GC–MS analyses revealed that a mixture of three products was obtained with a ratio of 20:20:60 for **2b**, **2c**, and **2d**, respectively. The observed ratio was close to the expected statistical ratio. In the literature, the hydrogenation of an alkyl epoxide with Pd was describe to give the branched alcohol as the major product,[11] and the same results were observed through the association of $NaBH_4$ and $PdCl_2$,[8] whereas the use of $ZnBH_4$ associated with zeolite gave the linear product.[9]

Table 1. Ring-opening of epoxides.[a]

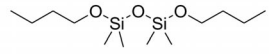
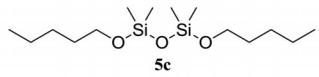
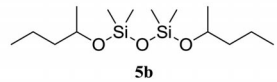
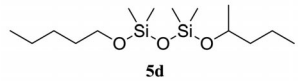
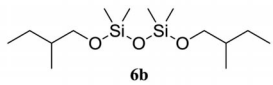
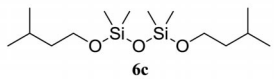
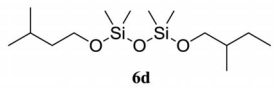
Entry	Substrate	Product	Conv.[b] [%]	Mass yield [%]
1	 **1a**	 **1b**	>99	92
		 **2b**		
2	 **2a**	 **2c**	>99	>99
		 **2d**		
3	 **3a**	 **3b**	75	65[c]

[a] Reagents and conditions: substrate (17 mmol), Pd/C (1.2%), TMDS (8.5 mmol), r.t. [b] Conversions were determined by ^1H NMR spectroscopy and GC–MS analysis. [c] Yield of cyclooctanol after deprotection by TBAF followed by flash chromatography (**3b′**).

The ring-opening of the cyclooctene oxide gave the desired product with 75% conversion. To test whether the product could be deprotected, compound **3b** was treated with 1 M tetrabutylammonium fluoride (TBAF) in tetrahydrofuran (THF) overnight. Under these conditions, cyclooctanol was isolated with good yield after flash chromatography (Table 1, Entry 3).

Tetrahydrofuran (**4a**) was converted into **4b** with 70% conversion and 56% yield (Table 2, Entry 1). With 2-methyltetrahydrofuran (**5a**), the conversion was lower and a mixture of three products was obtained (Table 2, Entry 2). The reaction was not selective because a 31:20:49 ratio was observed corresponding to compounds **5b**, **5c** and **5d**, respectively.

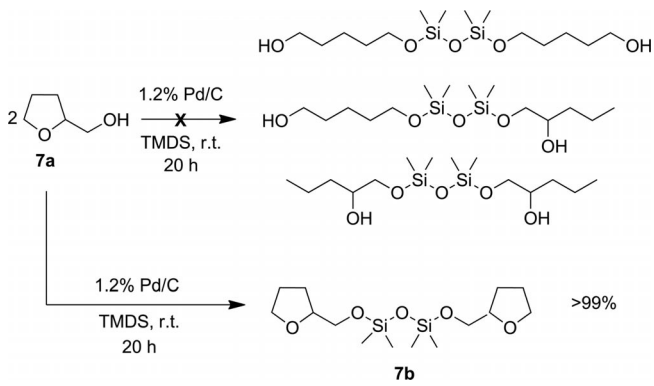
Table 2. Ring-opening of tetrahydrofuran derivatives.[a]

Entry	Substrate	Product	Conv.[b] [%]	Mass yield[c] [%]
1	 **4a**	 **4b**	70	56
		 **5c**		
2	 **5a**	 **5b**	50	48
		 **5d**		
3	 **6a**	 **6b**	>99	>99
		 **6c**		
		 **6d**		

[a] Reagents and conditions: substrate (17 mmol), Pd/C (1.2 mol-%), TMDS (8.5 mmol), r.t. [b] Conversions were determined by ^1H NMR spectroscopy and GC–MS analysis. [c] Yield obtained after evaporation of the starting material.

The ring-opening was then tested on 3-methyltetrahydrofuran (**6a**). Surprisingly, in this case, both the conversion and the yield were excellent (Table 2, Entry 3). NMR analysis showed that three products were obtained, however, because they are branched, they were not resolved by GC–MS analysis.

Tetrahydrofurfuryl alcohol (**7a**) was then studied, but the ring-opening did not occur in this case. Instead, the formation of the protected alcohol was observed (Scheme 1).



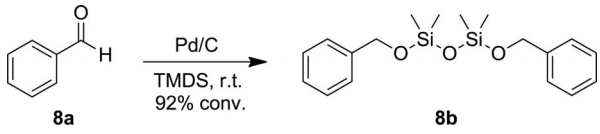
Scheme 1. Attempted ring-opening of **7a**.

Use of an excess amount of TMDS did not allow the ring-opening of the tetrahydrofurfuryl moiety from either **7a** or **7b**. To confirm that the ring-opening did not proceed due to degradation of the catalyst, compound **7b** was prepared and added to 1.2 mol-% palladium in the presence of TMDS. NMR analysis of the crude reaction mixture revealed that conversion was very low after 20 h, however, deprotection with TBAF was undertaken to determine a possible selectivity. Unfortunately, no selectivity was observed toward either 1,5- or 1,2-pentanediol.

These conditions were applied to other cyclic and linear ethers, such as tetrahydropyrane, 1,3-benzodioxole, phenyl benzyl ether, and glyme, but no reaction occurred.

To verify whether the TMDS/Pd/C system could be used for the reduction of other functional groups, such as aldehydes or ketones, benzaldehyde was used as the test reagent. In the literature, the use of Pd for the hydrogenation of benzaldehyde in $scCO_2$ under pressure and heat has already been reported,[27] but different products, including the alcohol, were obtained. Moreover, this system was inefficient for aliphatic substrates. Another method using Pd/C and potassium formate[28] gave alcohols, but low conversions were observed with aliphatic aldehydes and aromatic ketones. Sodium hypophosphite was also used with potassium carbonate and Pd/C, and similar observations were noticed.[29] Associated with silanes, other metals have been tested. Indeed, the $PdCl_2/Et_3SiH$ system was used to reduce benzaldehyde to toluene and a small amount of alcohol was observed,[30] whereas Et_3SiH and trifluoroacetic acid[31] or $B(C_6F_5)_3$[32] systems were found to be efficient ways to obtain alcohols. Oxorhenium salen[33] catalyst and fluoride salts[34] were also described as having a moderate to good efficiency for the transformation of benzaldehyde.

In our case, after 20 h of reaction at room temperature, NMR analysis showed that benzaldehyde was reduced to benzyl alcohol with 92% conversion, and GC–MS revealed that the protected benzyl alcohol **8b** was formed (Scheme 2).



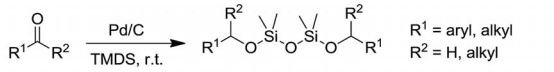
Scheme 2. Formation of protected benzyl alcohol **8b**.

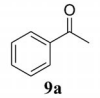
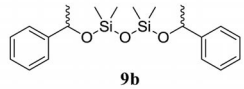
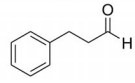
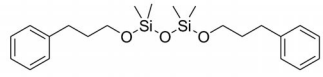
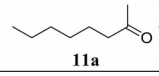
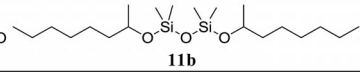
This result led us to try other aromatic and aliphatic substrates under the reaction conditions. The reaction with acetophenone gave the expected mixture of diastereoisomers **9b** with 80% conversion (Table 3, Entry 1); no side product, such as phenylethane, was observed.

The reduction of 3-phenylpropionaldehyde (**10a**) gave good conversion (89%) (Table 3, Entry 2), and 2-octanone (**11a**) was converted into the desired product **11b** with a conversion of 74% (Table 3, Entry 3).

The reduction was also tested on a substrate containing two aldehyde functions. Solid terephthalaldehyde (**12a**) was diluted in toluene and treated with Pd/C and TMDS at

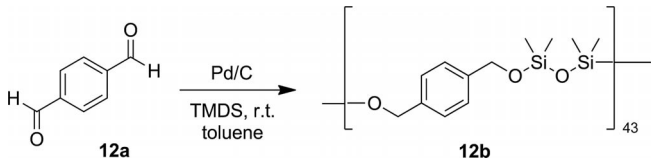
Table 3. Reduction of aldehydes and ketones.[a]



Entry	Substrate	Product	*t* [h]	Conv.[b] [%]
1	 **9a**	 **9b**	20	80
2	 **10a**	 **10b**	20	89
3	 **11a**	 **11b**	20	74

[a] Reagents and conditions: substrate (10 mmol), Pd/C (1.2 mol-%), TMDS (5 mmol), r.t. [b] Conversions were determined by ^1H NMR spectroscopy and GC–MS analysis.

room temperature. After one hour, the formation of a jelly-like product was observed; after treatment, analyses revealed that polymer **12b** was formed (Mn = 9476, Mw = 17400) (Scheme 3).



Scheme 3. Formation of polymer **12b** from **12a**.

Kiskan et al.[35] described the synthesis of poly(β-ala-tetramethyldisiloxane) from an allylic amine by Pt-catalyzed hydrosilylation in toluene at 90 °C with TMDS. Another method, described by Wang et al.,[36] consists of initial silylation of carboxylic acids, followed by polymerization with a platinum catalyst of the hydrosilyl ester and a terminal unsaturated carbon–carbon bond. To the best of our knowledge, Pd/C associated with TMDS has not been used for the reduction followed by polymerization of carbonyl groups.

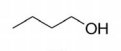
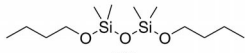
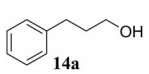
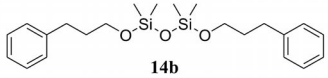
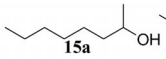
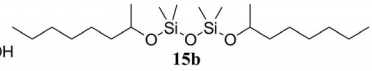
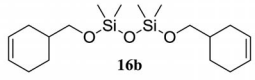
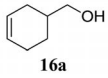
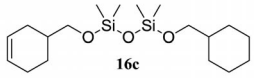
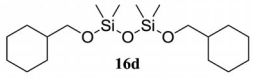
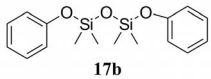
Following these results, the protection of alcohols under the same conditions was studied. Organosilicon chemistry has been widely used for the protection of alcohols with chlorosilanes[37] in the presence of HCl acceptor and, in the presence of silanes and Lewis acid, alcohols can be protected or reduced to alkanes. Under the same conditions, ethers have been cleaved to give the protected alcohols.[38–44]

As detailed in Scheme 1, use of the TMDS/Pd/C system allows the formation of alkoxysilanes. This observation was recently described in a patent[45] in which the reaction was shown to occur at 50 °C.

Several examples were realized for the protection of alcohols. The conditions described above were applied to butan-1-ol (**13a**) giving protected derivative **13b** with a complete conversion (Table 4, Entry 1). The protection of alcohol **14a** gave compound **14b** with 93% conversion

(Table 4, Entry 2). The protection could also be applied to secondary alcohols as shown by the protection of octan-2-ol, which was converted into compound **15b** in 89% yield (Table 4, Entry 3).

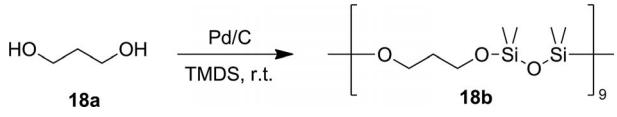
Table 4. Protection of alcohols.[a]

Entry	Substrate	Product	Conv.[b] [%]
1	 **13a**	 **13b**	>99
2	 **14a**	 **14b**	93
3	 **15a**	 **15b**	89
		 **16b**	
4	 **16a**	 **16c**	>99[c]
		 **16d**	
5	 **17a**	 **17b**	60

[a] Reagents and conditions: substrate (10 mmol), Pd/C (1.2 mol-%), TMDS (5 mmol), 20 h, r.t. [b] Conversions were determined by ^{1}H NMR spectroscopy and GC–MS analyses. [c] After 1 h reaction.

The application of an alkene-containing substrate was then studied. 1,2,3,6-Tetrahydrobenzyl alcohol (**16a**; Table 4, Entry 4) was engaged in the reaction at room temperature and at 50 °C. After one hour of reaction, three products were observed: At room temperature a 29:52:19 ratio of **16b**, **16c** and **16d** was observed, whereas at 50 °C, the ratio was 16:21:63. After 18 h of reaction, the ratio changed at room temperature to 18:55:27 and at 50 °C only product **16d** was observed. Thus, the double bond was completely reduced when heating, whereas, at room temperature, compound **16c** was obtained as the major product. Conducting the reaction with phenol afforded the desired product **17b** with moderate conversion (Table 4, Entry 5). Because phenol is solid, palladium then TMDS were introduced at 50 °C.

To polymerize 1,3-propanediol, the substrate was treated with Pd/C and TMDS to afford polymer **18b** (Scheme 4) with complete conversion. GC analysis allowed the number molecular weight (Mn) and the weight-average molecular weight (Mw) to be determined (1348 and 1825, respectively).



18a **18b**

Scheme 4. Polymerization of diol **18a**.

Conclusions

We have demonstrated an effective use of the versatile TMDS/Pd/C system to access alkoxysilanes. Besides the ring-opening of epoxides and cyclic ethers, this system allows the protection of alcohols and the formation of new polymers from diols or dialdehydes, with low ecological impact. Depending on the substrates, this methodology can also be selective for the ring-opening of styrene oxide.

Experimental Section

General Information: All reagents were obtained from commercial sources. Tetramethyldisiloxane (TMDS, 97%) was purchased from Acros, and Pd/C (5%) from Strem Chemicals. All reagents and reactants were used without further purification. All reactions were performed under an inert atmosphere (argon) in a round-bottomed flask. All compounds were characterized by their spectroscopic data. NMR spectra were recorded with a Bruker ALS or DRX 300 spectrometer (^{1}H: 300 MHz, ^{13}C: 75 MHz), chemical shifts are expressed in ppm, J values are given in Hz. $CDCl_3$ was used as solvent. GC–MS were measured with focus DSQ electronic ionization with a DBS phase. Column dimension: 30 m, 0.25 mm. Initial temperature: 70 °C (except for **4a** and **5a** for which 40 °C was used), initial time: 2 min, rate: 15 deg/min. Average molecular weights for compound **17b** were determined with a size exclusion chromatography (SEC) system (Waters) equipped with an isocratic pump (Waters 515) operated at a flow rate of 1 mL/min with THF (Aldrich), an autosampler (Waters 717 Plus), a column oven, and a refractive index detector (Waters 410) with integrated temperature controller maintained at 30 °C. Data collection and processing were performed with the software Empower Pro version 5.0 from Waters Corporation. For molecular mass separation, a guard column (PL gel 5 μm), three polymer Laboratory columns [2 × PLgel 5 μm Mixed C (300 × 7.5 mm), and 1× PLgel 5 μm 500 A (300 × 7.5 mm)] (Shropshire, UK) were used in series at 30 °C. Calibration was carried out using narrow-distributed polystyrene standards. The mobile phase was THF (HPLC grade) from Acros Organics. Polymer samples were dissolved in THF to form a homogeneous solution. Chromatography was carried out after sample filtration through a 0.45 μm cellulose membrane filter. Absolute molecular weights of copolymer **11b** were determined with a Waters Size Exclusion Chromatography system coupled to an RI detector (Waters 410) with integrated temperature controller maintained at 30 °C, and a triple-angle light scattering (LS) detector (MiniDAWN Tristar; Wyatt Technology, Santa Barbara, CA, USA). The two signals were measured simultaneously because of the online multiangle laser light scattering/refractive index (SEC-MALLS/RI) arrangement; so the absolute molecular weight of the copolymers could be deduced. Data collection and processing were performed using two software packages; ASTRA (version 4.5) from Wyatt Technology and Empower Pro (version 5.0) from Waters Corporation.

General Procedure for the Ring-Opening of Epoxides and Ethers and Protection of Alcohols: To a round-bottomed flask, under inert atmosphere, containing the substrate (17 mmol) were added with caution Pd/C (1.2%, 217 mg) and TMDS (8.5 mmol, 1.5 mL) at

room temperature (the reaction is exothermic). After 20 h the reaction mixture was diluted with ethyl ether and filtered through a plug of Celite by flushing with ethyl ether. The filtrate was concentrated to afford the desired product as a colorless oil. The products were identified by NMR and GC–MS analyses.

Reduction of Aldehydes/Ketones: To a round-bottomed flask, under inert atmosphere, containing the substrate (10 mmol) were added with caution Pd/C (1.2%, 127 mg) and TMDS (5 mmol, 0.88 mL) at room temperature. The reaction is exothermic. After 20 h, the reaction mixture was diluted in ethyl ether and filtered through a plug of Celite by flushing with ethyl ether. The filtrate was concentrated to afford the desired product as a colorless oil. The products were identified by NMR and GC–MS analyses.

Preparation of Polymers: To a round-bottomed flask, under inert atmosphere, containing the substrate (10 mmol) were added with caution Pd/C (1.2%, 127 mg) and TMDS (5 mmol, 0.88 mL) at room temperature (the reaction is exothermic). After 1 h, the reaction mixture was diluted with either diethyl ether (for **16b**) or dichloromethane (for **11b**). The products were then filtered through a plug of Celite and filtrates were evaporated under vacuum. Polymers were obtained as a viscous colorless oil. The products were identified by NMR and GPC analyses.

1,1,3,3-Tetramethyl-1,3-diphenethoxydisiloxane (1b): Pale-yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.07–0.17 [m, 12 H, 2× $Si(CH_3)_2$], 2.91 (t, J = 7.2 Hz, 2 H, CH_2), 3.91 (t, J = 7.2 Hz, 2 H, CH_2), 7.23–7.33 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.8, 39.6, 67.3, 126.5, 128.5, 129.3 ppm. GC–MS: t_R = 14.14 min.

1,5-Dihexyl-2,2,4,4-tetramethyldisiloxane [564453–35–6] (2b), 1,3-Bis(hexan-2-yloxy)-1,1,3,3-tetramethyldisiloxane (2c), and 1-Hexan-2-yloxy-3-(hexyloxy)-1,1,3,3-tetramethyldisiloxane (2d): Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.07–0.17 [m, 12 H, 2× $Si(CH_3)_2$], 0.88–0.90 (t, J = 6.8 Hz, 18 H, CH_3), 1.16 (d, J = 6.2 Hz, 9 H, CH_3), 1.25–1.39 (m, 28 H, CH_2), 1.53–1.58 (m, 10 H, CH, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.8, 0.0, 1.3, 14.4, 23.0, 24.0, 25.8, 28.4, 32.0, 32.9, 39.6, 62.7, 68.7 ppm. GC–MS: t_R = 8.2 (**2c**), 8.59 (**2d**), 9.04 min (**2b**).

Cyclooctanol [696–71–9] (3b′): Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.39–1.57 (m, 9 H, CH_2), 1.62–1.79 (m, 4 H, CH_2), 1.81–1.83 (m, 2 H, CH_2), 3.82–3.89 (m, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.9, 25.4, 27.6, 34.8, 72.2 ppm. GC–MS: t_R = 6.26 min.

1,3-Dibutoxy-1,1,3,3-tetramethyldisiloxane [18043–98–6] (4b): Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.1 [m, 12 H, 2× $Si(CH_3)_2$], 0.90 (t, J = 7.3 Hz, 6 H, CH_3), 1.30–1.38 (sext, J = 7.1 Hz, 4 H, CH_2), 1.47–1.56 (quint, J = 6.7 Hz, 4 H, CH_2), 3.65 (t, J = 6.6 Hz, 4 H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.8, 1.93, 14.1, 19.3, 35.0, 62.3 ppm. GC–MS: t_R = 9.54 min.

2,2,4,4-Tetramethyl-1,5-dipentyldisiloxane [191108–98–2] (5b), 1,1,3,3-tetramethyl-1,3-bis(pentan-2-yloxy)disiloxane (5c), and 1,1,3,3-Tetramethyl-1-(pentan-2-yloxy)-3-(pentyloxy)disiloxane (5d): Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.1 [m, 36 H, $Si(CH_3)_2$], 0.90 (t, J = 6.8 Hz, 18 H, CH_3), 1.16 (d, J = 6.2 Hz, 9 H, CH_3), 1.28–1.38 (m, 24 H, CH_2), 1.53–1.58 (m, 8 H, CH_2), 3.66 (t, J = 6.8 Hz, 6 H, CH_2), 3.89–3.93 (m, 3 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.8, 14.3, 23.0, 24.0, 25.8, 28.3, 32.0, 32.9, 39.6, 62.6, 68.7 ppm. GC–MS: t_R = 8.12 (**5c**), 8.59 (**5d**), 9.04 min (**5b**).

1-(Isopentyloxy)-1,1,3,3-tetramethyl-3-(2-methylbutoxy)disiloxane (6b), 2,2,4,4-Tetramethyl-1,5-bis(3-methylbutyl)disiloxane [131357–84–1] (6c), and 1,3-Bis(isopentyloxy)-1,1,3,3-tetramethyldisiloxane (6d): Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.07- 0.1 [m, 36 H, $Si(CH_3)_2$], 0.86–0.91 (t, J = 7.2, 9 H, CH_3 and d, J = 7.2 Hz, 27 H, CH_3), 1.10–1.18 (quint, J = 6.2 Hz, 6 H, CH_2), 1.39–1.50 (q, J = 7.7 Hz, 6 H, CH_2), 1.53–1.60 (m, 3 H, CH), 1.65–1.75 (m, 3 H, CH), 3.41 and 3.51 (2× dd, J = 6.5 and 9.8 Hz, J = 6.0 and 10.0 Hz, 6 H, CH_2), 3.7 (t, J = 7.2, 6 H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.8, 11.7, 16.5, 22.9, 25.0, 26.2, 37.5, 41.9, 61.0, 67.6, 68.2 ppm. GC–MS: t_R = 8.36 min.

1,1,3,3-Tetramethyl-1,3-bis[(tetrahydrofuran-2-yl)methoxy]disiloxane (7b): Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.10–0.12 [m, 12 H, 2× $Si(CH_3)_2$], 1.61–1.70 (m, 2 H, CH_2), 1.82–1.97 (m, 6 H, CH_2), 3.63 (d, J = 6.0 Hz, 4 H, CH_2), 3.74–3.79 (m, 2 H, CH_2), 3.82–3.89 (m, 2 H, CH_2), 3.96–4.00 (m, 2 H, 2 CH) ppm. GC–MS: t_R = 11.61 min.

1,3-Bis(benzyloxy)-1,1,3,3-tetramethyldisiloxane (8b): Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.07–0.12 [m, 12 H, 2× $Si(CH_3)_2$], 4.72 (s, 2 H, CH_2), 7.19–7.32 (m, 10 H, C_6H_5) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.7, 64.4, 126.7, 126.8, 128.5, 140.8 ppm. GC–MS: t_R = 13.10 min.

1,1,3,3-Tetramethyl-1,3-bis(1-phenylethoxy)disiloxane (9b): Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.05–0.17 [m, 12 H, 2× $Si(CH_3)_2$], 1.43–1.45 (d, J = 5.3 Hz, 6 H, CH_3), 4.94 (q, J = 6.2 Hz, 2 H, CH), 7.19–7.35 (m, 10 H, C_6H_5) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.4, 27.1, 70.5, 125.6, 127.1, 128.4, 146.5 ppm. GC–MS: t_R = 12.89 min.

1,1,3,3-Tetramethyl-1,3-bis(3-phenylpropoxy)disiloxane (10b): Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.05–0.15 [m, 12 H, 2× $Si(CH_3)_2$], 1.84–1.90 (m, 4 H, CH_2), 2.67 (t, J = 6.6 Hz, 6 H, CH_2), 3.69 (t, J = 6.6 Hz, 6 H, CH_2), 7.17–7.27 (m, 10 H, C_6H_5) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.8, 0.6, 1.3, 32.3, 34.3, 62.2, 65.2, 126.1, 128.7 ppm. GC–MS: t_R = 15.34 min.

1,1,3,3-Tetramethyl-1,3-bis(octan-2-yloxy)disiloxane (11b): Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.07–0.17 [m, 12 H, 2× $Si(CH_3)_2$], 0.88 (m, 6 H, CH_3), 1.16 (d, J = 6.0 Hz, 6 H, CH_3), 1.22–1.37 (m, 2 H, CH_2=CH), 1.45–1.67 (m, 2 H, CH_2), 3.85–3.95 (m, 1 H, CH) ppm.

Poly(4-{[(1,1,3,3-Tetramethyldisiloxanyl)oxy]methyl}phenyl)-methanol (12b): Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.20–0.28 [m, 12 H, 2× $Si(CH_3)_2$], 4.88 (s, 4 H, CH_2), 7.39–7.41 (s, 4 H, C_6H_4) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.6, 1.3, 64.3, 126.8, 139.9 ppm. GPC (SEC-multiangle laser light scattering/refractive index): Mn = 9476, Mw = 17400, IP = 1.83.

1,1,3,3-Tetramethyl-1,3-bis(octan-2-yloxy)disiloxane (15b): Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.07–0.16 [m, 12 H, 2× $Si(CH_3)_2$], 0.88 (t, J = 7.0 Hz, 6 H, CH_3), 1.16 (d, J = 6.2 Hz, 6 H, CH_3), 1.22–1.35 (m, 20 H, CH_2), 1.83–1.97 (sext., J = 6.0 Hz, 2 H, CH), 1.95–2.00 (m, 4 H, CH_2), 3.70 (t, J = 7.4 Hz, 4 H, CH_2), 5.08 (t, J = 7.4 Hz, 2 H, CH_2=CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.1, 0.03, 1.0, 1.3, 14.3, 22.9, 23.7, 26.2, 29.7, 32.2, 39.8, 68.7 ppm. GC–MS: t_R = 12.14 min.

1,3-Bis(cyclohex-3-en-1-ylmethoxy)-1,1,3,3-tetramethyldisiloxane (16b), 1-(Cyclohex-3-en-1-ylmethoxy)-3-(cyclohexylmethoxy)-1,1,3,3-tetramethyldisiloxane (16c), and 1,3-Bis(cyclohexylmethoxy)-1,1,3,3-tetramethyldisiloxane (16d): Reaction performed at room temperature for 1 h. Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.09–0.16 [m, 36 H, $Si(CH_3)_2$], 1.19–1.28, 1.65–1.82, 2.01–2.15 (m, 36 H, CH_2 and CH), 3.44 and 3.52–3.55 (d and m, J = 6.6 Hz, 12 H, CH_2) ppm. GC–MS: t_R = 12.54 (**16d**), 12.65 (**16c**), 12.75 min (**16b**).

1,3-Bis(cyclohexylmethoxy)-1,1,3,3-tetramethyldisiloxane (16d): Reaction performed at 50 °C for 18 h. Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.09–0.15 [m, 12 H, $Si(CH_3)_2$], 1.16–1.25, 1.46–1.48, 1.68–1.73 (m, 11 H, CH_2 and CH), 3.44 (d, J = 6.6 Hz, 4 H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.8, 1.3, 26.2, 27.0, 29.9, 40.5, 68.3 ppm. GC–MS: t_R = 12.75 min (**16b**).

1,3-Bis(cyclohexylmethoxy)-1,1,3,3-tetramethyldisiloxane (16d): Reaction performed at 50 °C for 18 h. Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.09–0.15 [m, 12 H, $Si(CH_3)_2$], 1.16–1.25, 1.60–1.73 (m, 4 H, CH_2 and CH), 3.44 (d, J = 6.6 Hz, 4 H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.8, 0.6, 1.3, 26.2, 27.0, 30.0, 68.3 ppm. GC–MS: t_R = 12.54 min (**16d**).

1,1,3,3-Tetramethyl-1,3-diphenoxydisiloxane [116401–29–7] (17b): Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.07–0.38 [m, 12 H, 2× $Si(CH_3)_2$], 6.83 (d, J = 6.4 Hz, 4 H, CH), 6.91 (t, J = 7.3 Hz, 2 H, CH), 7.20–7.27 (m, 4 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.3, 1.2, 115.7, 120.9, 129.9, 155.8 ppm. GC–MS: t_R = 11.67 min.

3-[(1,1,3,3-Tetramethyldisiloxanyl)oxy]propan-1-ol (18b): Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.08–0.13 [m, 12 H, 2× $Si(CH_3)_2$], 1.77 (quint, J = 6.2 Hz, 2 H, CH_2), 3.79 (t, J = 6.2 Hz, 4 H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.9, 1.0, 34.4, 61.2 ppm. GPC (polystyrene equivalent): Mn = 1348, Mw = 1825, IP = 1.35.

Acknowledgments

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