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An Efficient Catalytic Approach for the Synthesis of Unsymmetrical Siloxanes

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The potential for expanding the variety of catalytic methods for siloxane bond formation is explored. Alkoxysilanes react with methylallylsilanes in the presence of scandium(III) trifluoromethanesulfonate to yield disiloxanes and isobutene. The reaction proceeds through one-pot hydrolysis/*O*-sil-

ylation of alkoxysilanes with allylsilanes (via silanol intermediates) under mild conditions. Unsaturated siloxane products are used as substrates for further functionalization through the catalytic hydrosilylation reaction.

Introduction

Functionalized, unsymmetrical disiloxanes have a broad range of potential applications including healthcare products, functional materials as liquid-crystalline polymers, or resins for the fabrication of high-refractive-index and low-dielectric-constant materials and components of biocompatible oils.^[1] Conventional approaches to unsymmetrical siloxanes involve condensation of silanols with chloro-, amino-, acyloxy-, or alkoxysilanes, and cohydrolysis of two chloro- or alkoxysilanes.^[2] In recent years, not only stoichiometric reactions, but also catalytic methods such as rhodium(I)-catalyzed dehydrocoupling of silanols with hydrosilanes,^[3] reduction of amides by hydrodisilanes in the presence of [(Me₃N)Mo(CO)₅] catalyst,^[4] or dealkylative coupling of hydrosilanes with alkoxysilanes^[5] have been reported for disiloxane bond formation. Unsymmetrical siloxanes were also obtained from silanols and hydrosilanes by using a phase-transfer catalytic system.^[6] Recently, we have developed a new catalytic route for efficient *O*-silylation of silanols with vinylsilanes catalyzed by [RuHCl(CO)(PCy₃)₂] (Cy = cyclohexyl),^[7] whereby vinylsilane acts as a metalating agent and hydrogen acceptor to form a SiO–Si bond, respectively, with evolution of ethylene. This mode of reactivity has been successfully extended to catalytic activation of O–H bonds in silanols by other alkenyl-substituted silanes.^[8]

In the course of our recent studies on the catalytic activation of SiO–H bonds, we have found that metalation of silanols by 2-methylallylsilanes or 2-methylallylgermanes in the presence of scandium(III) trifluoromethanesulfonate [Sc(OTf)₃] with the formation of isobutylene as a neutral and harmless byproduct proceeded under mild conditions

to give unsymmetrical disiloxanes and germasiloxanes in high yields (Scheme 1).^[8] This study has been prompted by earlier reports on the effectiveness of allylsilanes in the silylation of alcohols^[9] and the silylation of SiO–H groups of the silica surface with 2-methylallylsilanes in the presence of Lewis acids.^[10]



Scheme 1. Synthesis of disiloxanes or germasiloxanes.

Results

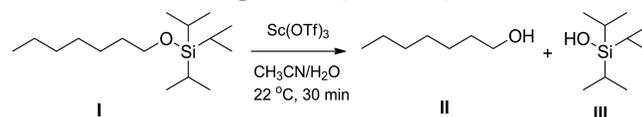
Recently we have focused our research on the use of alkoxysilanes as a reactant for the synthesis of siloxanes. The hydrolysis reaction of these compounds generally leads to symmetrical siloxanes,^[11] but depending on the reaction conditions and the nature of the substrates, synthesis of the corresponding silanol is also possible.^[12] In view of our recent reports on the successful use of 2-methylallylsilanes as new hydrogen acceptors for the *O*-silylation of silanols, the aim of this work was to check the possibility of replacing silanols by more accessible and stable alkoxysilanes as reagents in the selective synthesis of the disiloxane bond by means of one-pot hydrolysis of alkoxysilane followed by *O*-silylation of newly formed silanol by allylsilane in the presence of Sc(OTf)₃.

Silylation of alcohols by allylsilanes can be catalyzed by strong proton acids. The reaction with *p*-toluenesulfonic acid requires heating to 70–80 °C for 1.5–3.0 h.^[9] Triflic acid can be used as a catalyst in the silylation of alcohols by allyltrimethylsilane under anhydrous conditions; however, this process is limited only for trimethylsilyl substitu-

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ents and bulky substituted alcohols.^[13] For these reasons we decided to use scandium triflate in our studies. It is also important that $\text{Sc}(\text{OTf})_3$ is stable and acts like a Lewis acid in aqueous solution. Moreover, $\text{Sc}(\text{OTf})_3$ can be recovered and reused. As we reported previously, the scandium(III) trifluoromethanesulfonate catalyzed the silylation reactions of silanols and silanediols with methylallylsilanes under similar conditions (1.5–2 mol-% catalyst loading, CH_3CN or $\text{CH}_3\text{CN}/\text{THF}$ as a solvent, 1 h, room temperature). To comfortably control the progress of the tested reaction, particularly the hydrolysis of alkoxysilane, we decided to synthesize bulky *n*-heptoxytriisopropylsilane (**I**), the hydrolysis products of which can be easily monitored by means of GC–MS analysis. Then we studied the *O*-silylation reaction of *n*-heptoxytriisopropylsilane (**I**) with 2-methylallyldimethylvinylsilane catalyzed by scandium(III) trifluoromethanesulfonate in acetonitrile. In the first step we found that the addition of an equimolar amount of water into a solution of *n*-heptoxytriisopropylsilane (**I**) in acetonitrile does

not cause hydrolysis of alkoxysilane, but addition of $\text{Sc}(\text{OTf})_3$ (2 mol-%) to the mixture of reactants and solvent afforded exclusively the corresponding alcohol [heptan-1-ol (**II**)] and silanol [triisopropylsilanol (**III**)] in quantitative yield [GC–MS analysis of the reaction mixture confirmed the absence of condensation products (Figure 1)] after half an hour at room temperature (Scheme 2).



Scheme 2. Catalytic hydrolysis of heptoxytriisopropylsilane (**I**).

Addition of 2-methylallyldimethylvinylsilane (1 equiv.) to the reaction mixture afforded the respective siloxane (**1**) with trace amount of the product of *O*-silylation of the corresponding alcohol (**IV**) (less than 3% measured by GC–MS) and a moderate amount of tetramethyldivinylsiloxane (**V**) (less than 19%) after half an hour (Scheme 3).

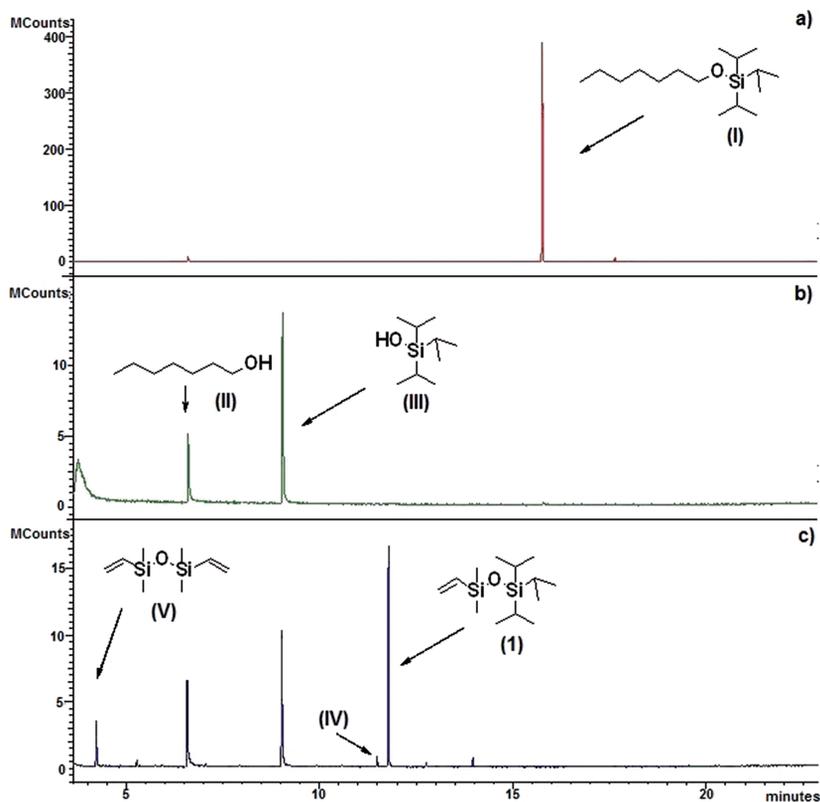
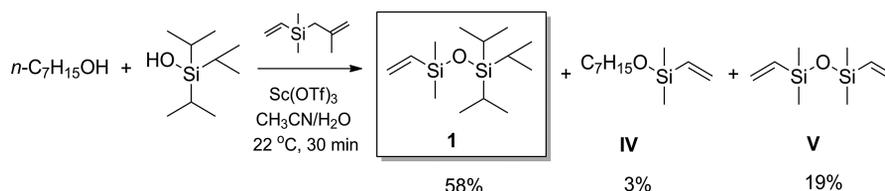


Figure 1. GC monitoring of the one-pot hydrolysis/*O*-silylation of **I** with 2-methylallyldimethylvinylsilane: (a) equimolar solution of water and **I** in acetonitrile, (b) 30 min after addition of $\text{Sc}(\text{OTf})_3$ (2 mol-%), and (c) 30 min after the addition of 2-methylallyldimethylvinylsilane (1 equiv.).

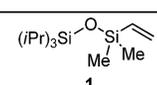
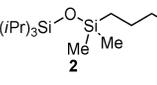
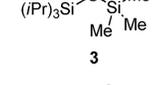
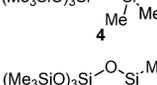
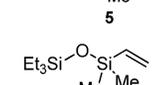
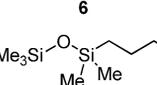
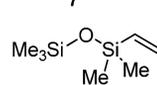
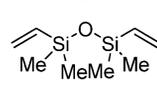
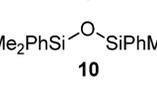
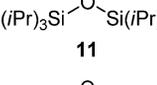
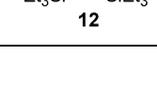


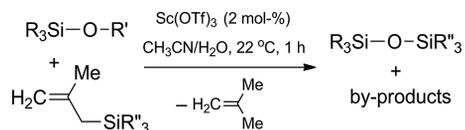
Scheme 3. *O*-Silylation reaction of a mixture of **II** and **III** with 2-methylallyldimethylvinylsilane catalyzed by $\text{Sc}(\text{OTf})_3$.

Since the reaction of equimolar amounts of *n*-heptoxytriisopropylsilane with 2-methylallyldimethylvinylsilane proceeded with a maximum of 60% conversion of the resulting silanol to yield a mixture of 1,1-dimethyl-3,3,3-triisopropyl-1-vinyl-disiloxane (**1**) as well as *n*-heptoxydimethylvinylsilane (**IV**) and tetramethyldivinyl-disiloxane (**V**) as a result of the competitive *O*-silylation reaction of heptan-1-ol (**II**) and obtained *n*-heptoxydimethylvinylsilane (**IV**) with 2-methylallyldimethylvinylsilane, a two-and-a-half excess amount of allylsilane was necessary to achieve complete conversion of the silanol. Although the excess amount of allylsilane in the presence of a scandium triflate enabled competitive formation of the siloxane and alkoxy-silane, its use permits quantitative conversion of the silanol to the silylation product after one hour at room temperature in the presence of 2 mol-% Sc(OTf)₃ in acetonitrile. Moreover, the accompanying

products can be easily separated by column chromatography or simple evaporation from the reaction mixture. Almost the same results have been observed when other alkoxy-silanes [e.g., ethoxytriisopropylsilane, ethoxytriethylsilane, and ethoxyltris(trimethylsiloxy)silane] have been used with different allylsilanes, and when the reactants and the catalyst were added simultaneously. When trimethylethoxy-silane or dimethylvinylethoxysilane (that is, a silane without steric hindrance) were used as a source of silanols in the *O*-silylation reaction with allylsilanes in the presence of Sc(OTf)₃, apart from the expected products, volatile disiloxanes from the homohydrolysis of alkoxy-silanes as byproducts were also observed (Scheme 4). Therefore, a fourfold excess amount of alkoxy-silanes was necessary to achieve complete conversion of allylsilane. In this case, the accompanying side products could be also easily separated.

Table 1. Reaction of alkoxy-silanes with 2-methylallylsilanes catalyzed by Sc(OTf)₃. The reaction conditions: acetonitrile, room temperature, 1 h.

Entry	Alkoxy-silane ROSiR' ₃	Allylsilane CH ₂ =C(CH ₃)CH ₂ SiR ₃	Molar ratio [ROSiR' ₃]:[H ₂ O] [CH ₂ =C(CH ₃)CH ₂ SiR ₃]:[Sc(OTf) ₃]	Product	Isolated yield (%)
1	EtOSi(<i>i</i> Pr) ₃	SiMe ₂ CH=CH ₂	1:1:2.5:0.02		89
2	EtOSi(<i>i</i> Pr) ₃	SiMe ₂ (<i>n</i> Bu)	1:1:2.5:0.02		91
3	EtOSi(<i>i</i> Pr) ₃	SiMe ₃	1:1:2.5:0.02		88
4	EtOSi(OSiMe ₃) ₃	SiMe ₂ CH=CH ₂	1:1:2.5:0.02		92
5	EtOSi(OSiMe ₃) ₃	SiMe ₃	1:1:2.5:0.02		86
6	EtOSiEt ₃	SiMe ₂ CH=CH ₂	1:1:2.5:0.02		83
7	EtOSiMe ₃	SiMe ₂ (<i>n</i> Bu)	4:4:1:0.02		88
8	EtOSiMe ₃	SiMe ₂ CH=CH ₂	4:4:1:0.02		85
9	EtOSiMe ₂ CH=CH ₂	SiMe ₂ CH=CH ₂	1:1:1:0.02		94
10	EtOSiMe ₂ Ph	SiMe ₂ Ph	1:1:1:0.02		98
11	EtOSi(<i>i</i> Pr) ₃	Si(<i>i</i> Pr) ₃	1:1:1:0.02		95
12	EtOSiEt ₃	SiEt ₃	1:1:1:0.02		94



Scheme 4. Synthesis of siloxanes by $\text{Sc}(\text{OTf})_3$ -catalyzed coupling reaction.

It is worth noting that the process described led to the exclusive formation of siloxanes (without byproducts) when allylsilane and alkoxy silane with the same substituents were used (Table 1, entries 9–12).

All siloxane products were isolated and characterized spectroscopically. This consecutive hydrolysis of alkoxy silane followed by *O*-silylation of silanols by allylsilanes is attractive since it allows the synthesis of functional compounds with vinyl groups that may be used as reagents for further transformations.^[14] As an extension to the present study we investigated the hydrosilylation reaction^[15] of 1,1-dimethyl-3,3,3-triisopropyl-1-vinyl disiloxane with different silanes in the presence of platinum Karstedt catalyst (Scheme 5). Interesting results were obtained when 1,2-bis(dimethylsilyl)ethane and 1,1-dimethyl-3,3,3-triisopropyl-1-vinyl disiloxane (**1**) were used as substrates in the hydrosilylation reaction. GC-MS and NMR spectroscopic analyses of the reaction mixtures and isolated products have shown that hydrosilylation reaction allows the selective synthesis of product **14** or **15** when the molar ratio was 1:2 or 1:1. It is worth noting that **15** can be used for further hydrosilylation for, for example, the synthesis of

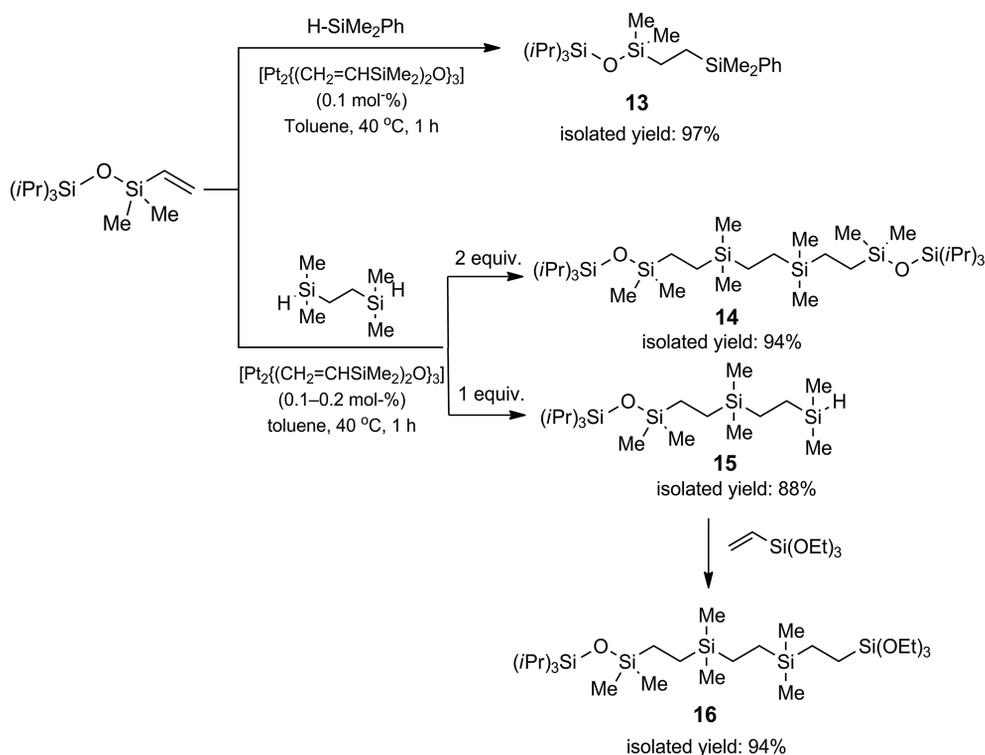
ethoxy-substituted monomer **16**, which can be used for the modification of silica or glass surfaces.

Conclusion

In conclusion, we have reported an efficient one-pot methodology for the synthesis of unsymmetrical disiloxanes based on consecutive catalytic hydrolysis of easily accessible and stable alkoxy silanes and *O*-silylation of silanols with 2-methylallylsilanes. The 2-methylallylsilanes act as metalating agents and hydrogen acceptors for in situ generated silanol to form an Si–Si bond with evolution of isobutylene. Mild conditions, good functional group compatibility, and the simplicity of the experimental technique of this new catalytic approach to functionalized siloxanes are attractive features of the reaction. We have also demonstrated a synthetic approach to the synthesis of ethoxy-substituted siloxanes that involves the hydrosilylation reaction of dihydro-substituted silane in the presence of a platinum Karstedt catalyst.

Experimental Section

General: The reagents and $\text{Sc}(\text{OTf})_3$ as well as Karstedt catalyst used for experiments were purchased from Sigma–Aldrich Co. and Gelest Inc. and used without further purification. ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded with a Varian XL 300 spectrometer using C_6D_6 as a solvent. GC analyses were performed with a Varian 3400 with a Megabore column (30 m) and thermal conductivity detector (TCD). Mass spectra of the products



Scheme 5. Synthesis of modified siloxanes by the hydrosilylation reaction.

were determined by GC–MS analysis with a Varian Saturn 2100 T equipped with a BD-5 capillary column (30 m) and a Finigan Mat 800 ion-trap detector.

Synthesis of Siloxanes: A mixture that consisted of alkoxy silane (1.0–4.0 mmol), 2-methylallylsilanes (1.0–2.5 mmol; according to the conditions indicated in Table 1), Sc(OTf)₃ (0.02 mmol), water (1.0–4.0 mmol), and acetonitrile (15 mL) were placed in a 50 mL one-necked round-bottomed flask and stirred at room temperature for 1 h. After this time, the solvent was evaporated and the product was purified by column chromatography on silica gel by eluting with *n*-hexane to give the corresponding compounds (**1–12**) as colorless liquids. The synthesis of 1,1-dimethyl-3,3,3-triisopropyl-1-vinylidisiloxane (**1**) was also performed on a larger scale under the same reaction conditions. A mixture that consisted of ethoxytriisopropylsilane (10 mmol, 2.02 g), 2-methylallyldimethylvinylsilane (25 mmol, 3.5 g), Sc(OTf)₃ (0.2 mmol, 0.25 g), water (10 mmol, 0.18 g), and acetonitrile (50 mL) were placed in a 100 mL one-necked round-bottomed flask and stirred at room temperature for 1 h. After this time, the solvent was evaporated and the product was isolated by “bulb-to-bulb” distillation to give 2.27 g (88%) of **1** as a colorless liquid.

1,1-Dimethyl-3,3,3-triisopropyl-1-vinylidisiloxane (1): ¹H NMR (300 MHz, C₆D₆): δ = 0.22 (s, 6 H, SiCH₃), 0.88–1.02 (m, 3 H, SiCH), 1.03–1.12 [m, 18 H, SiCH(CH₃)₂], 5.70–5.78 (dd, *J* = 3.9, 20.4 Hz, 1 H, CH=CH₂), 5.86–5.93 (dd, *J* = 3.9, 14.9 Hz, 1 H, CH=CH₂), 6.15–6.27 (dd, *J* = 14.9, 20.4 Hz, 1 H, CH=CH₂) ppm. ¹³C NMR (75 MHz, C₆D₆): δ = 0.3 (SiCH₃), 12.7 (SiCH), 17.7 [SiCH(CH₃)₂], 131.3 (CH=CH₂), 139.6 (CH=CH₂) ppm. C₁₃H₃₀O₂Si₂ (258.6): calcd. C 60.39, H 11.70; found C 60.55, H 11.63.

1-*n*-Butyl-1,1-dimethyl-3,3,3-triisopropylidisiloxane (2): ¹H NMR (300 MHz, C₆D₆): δ = 0.16 (s, 6 H, SiCH₃), 0.57–0.68 (m, 2 H, SiCH₂), 0.87–1.02 (m, 6 H, SiCH and CH₃), 1.03–1.14 [m, 18 H, SiCH(CH₃)₂], 1.31–1.45 (m, 4 H, CH₂CH₂) ppm. ¹³C NMR (75 MHz, C₆D₆): δ = 0.3 (SiCH₃), 12.8 (SiCH), 13.7 (SiCH₃), 17.8 [SiCH(CH₃)₂], 18.4 (SiCH₂), 25.7 (CH₂), 26.5 (CH₂) ppm. C₁₅H₃₆O₂Si₂ (288.6): calcd. C 62.42, H 12.57; found C 62.50, H 12.69.

1,1,1,5,5-Pentamethyl-5-vinyl-3,3-bis(trimethylsiloxy)trisiloxane (4): ¹H NMR (300 MHz, C₆D₆): δ = 0.23 (s, 27 H, OSiCH₃), 0.29 (s, 6 H, SiCH₃), 5.81–5.90 (dd, *J* = 4.0, 20.2 Hz, 1 H, CH=CH₂), 5.93–6.00 (dd, *J* = 4.0, 14.9 Hz, 1 H, CH=CH₂), 6.21–6.33 (dd, *J* = 14.9, 20.2 Hz, 1 H, CH=CH₂) ppm. ¹³C NMR (75 MHz, C₆D₆): δ = 0.3 (SiCH₃), 1.8 (OSiCH₃), 132.2 (CH=CH₂), 139.2 (CH=CH₂) ppm. C₁₃H₃₆O₄Si₅ (396.9): calcd. C 39.34, H 9.14; found C 39.44, H 9.08.

1-*n*-Butyl-1,1,3,3,3-pentamethylidisiloxane (7): ¹H NMR (300 MHz, C₆D₆): δ = 0.06–0.19 (m, 15 H, SiCH₃), 0.53–0.63 (m, 2 H, SiCH₂), 0.86–0.96 (m, 3 H, CH₃), 1.30–1.42 (m, 4 H, CH₂CH₂) ppm. ¹³C NMR (75 MHz, C₆D₆): δ = 0.16 (SiCH₃), 1.75 (SiCH₃), 13.7 (SiCH₃), 18.1 (SiCH₂), 25.6 (CH₂), 26.4 (CH₂) ppm. C₉H₂₄O₂Si₂ (204.5): calcd. C 52.87, H 11.83; found C 52.96, H 11.92.

Experimental Procedure for the Hydrosilylation Reaction of 1,1-Dimethyl-3,3,3-triisopropyl-1-vinylidisiloxane with Dimethylphenylsilane: A mixture that consisted of 1,1-dimethyl-3,3,3-triisopropyl-1-vinylidisiloxane (0.13 g, 0.5 mmol), dimethylphenylsilane (0.075 g, 0.55 mmol), platinum(0)-1,3-divinyl-1,1,3,3-tetramethylidisiloxane complex (5 × 10^{−4} mmol), and toluene (5 mL) was placed in 20 mL Schlenk bomb flask fitted with a plug valve and heated at 60 °C for 1 h. Next, after cooling the reaction to room temperature, the solvent was evaporated, and the product was purified by column chromatography on silica gel by eluting with *n*-hexane to give the product (**13**) as a colorless liquid in 97% yield.

Compound 13: ¹H NMR (300 MHz, C₆D₆): δ = 0.14 (s, 6 H, SiCH₃), 0.27 (s, 6 H, SiCH₃), 0.53–0.64 (m, 2 H, SiCH₂), 0.75–0.85 (m, 2 H, SiCH₂), 0.87–1.01 (m, 3 H, SiCH), 1.03–1.15 [m, 18 H, SiCH(CH₃)₂], 7.17–7.27 (m, 3 H, Ph), 7.44–7.55 (m, 2 H, Ph) ppm. ¹³C NMR (75 MHz, C₆D₆): δ = −3.8 (SiCH₃), −0.3 (SiCH₃), 7.5, 10.6 (CH₂), 12.8, (SiCH), 17.8 [SiCH(CH₃)₂], 127.8, 128.8, 133.6, 139.0 (Ph) ppm. C₂₁H₄₂O₂Si₃ (394.8): calcd. C 63.88, H 10.72; found C 63.95, H 10.68.

Hydrosilylation of 1,1-Dimethyl-3,3,3-triisopropyl-1-vinylidisiloxane with 1,2-Bis(dimethylsilyl)ethane: A mixture that consisted of 1,1-dimethyl-3,3,3-triisopropyl-1-vinylidisiloxane (0.13 g, 0.5 mmol), 1,2-bis(dimethylsilyl)ethane (0.5 or 1.0 mmol), platinum(0)-1,3-divinyl-1,1,3,3-tetramethylidisiloxane complex (5 × 10^{−4} or 1 × 10^{−3} mmol), and toluene (5 mL) was placed in a 20 mL Schlenk bomb flask fitted with a plug valve and heated at 40 °C for 1 h. Next, after cooling the reaction mixture to room temperature, the solvent was evaporated and the product was purified by column chromatography on silica gel by eluting with *n*-hexane to give the expected product (**14** or **15**) as colorless liquids in 88–94% yields.

Compound 14: ¹H NMR (300 MHz, C₆D₆): δ = 0.08 (s, 12 H, SiCH₃), 0.21 (s, 12 H, SiCH₃), 0.46–0.68 (m, 12 H, SiCH₂), 0.89–1.22 [m, 42 H, SiCH, SiCH(CH₃)₂] ppm. ¹³C NMR (75 MHz, C₆D₆): δ = −4.6 (SiCH₃), −0.3 (SiCH₃), 6.3, 6.8, 10.7 (CH₂), 12.8 (SiCH), 17.8 [SiCH(CH₃)₂] ppm. C₃₂H₇₈O₂Si₆ (663.5): calcd. C 57.93, H 11.85; found C 57.88, H 11.70.

Compound 15: ¹H NMR (300 MHz, C₆D₆): δ = 0.10–0.34 (m, 18 H, SiCH₃), 0.40–0.74 (m, 8 H, SiCH₂), 0.80–1.44 [m, 21 H, SiCH and SiCH(CH₃)₂] ppm. ¹³C NMR (75 MHz, C₆D₆): δ = −4.6, −1.1, −0.3 (SiCH₃), 6.0, 6.4, 9.8, 10.6 (CH₂), 12.8 (SiCH), 17.8 [SiCH(CH₃)₂] ppm. C₁₉H₄₈O₂Si₄ (404.9): calcd. C 56.36, H 11.95; found C 56.41, H 11.84.

Hydrosilylation of Vinyltriethoxysilane with 15: A mixture that consisted of **15** (0.2 g, 0.5 mmol), vinyltriethoxysilane (0.11 g, 0.6 mmol), platinum(0)-1,3-divinyl-1,1,3,3-tetramethylidisiloxane complex (5 × 10^{−4} mmol), and toluene (5 mL) was placed in a 20 mL Schlenk bomb flask fitted with a plug valve and heated at 40 °C for 1 h. Next, after cooling the reaction mixture to room temperature, the solvent was evaporated and 0.28 g of the product (**16**) was afforded as a colorless liquid in 94% yield.

Compound 16: ¹H NMR (300 MHz, C₆D₆): δ = 0.02–0.12 (m, 12 H, SiCH₃), 0.15–0.28 (m, 6 H, SiCH₃), 0.48–0.87 (m, 12 H, SiCH₂), 0.92–1.02 (m, 3 H, SiCH), 1.03–1.15 [m, 18 H, SiCH(CH₃)₂], 1.16–1.27 (t, 9 H, CH₃CH₂O), 3.77–3.91 (q, 6 H, CH₃CH₂O) ppm. ¹³C NMR (75 MHz, C₆D₆): δ = −4.7, −4.6, −0.3 (SiCH₃), 3.0, 5.9, 6.2, 6.7, 6.8, 10.6 (CH₂), 12.8 (SiCH), 17.8 [SiCH(CH₃)₂], 18.3 (CH₃CH₂O), 58.2 (CH₃CH₂O) ppm. C₂₇H₆₆O₄Si₅ (595.3): calcd. C 54.48, H 11.18; found C 54.39, H 11.04.

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- [1] R. G. Jones, W. Ando, J. Chojnowski, *Silicon-Containing Polymers*, Kluwer, Dordrecht, The Netherlands, **2000**; D. E. Katsoulis, M. J. Loboda, E. Mc Quiston, L. Rodriguez, *WO* 2008097877; S. K. Lee, J. B. Seon, *EP* 1498443.
- [2] M. A. Brook, *Silicon, in: Organic, Organometallic and Polymer Chemistry*, Wiley, **2000**, p. 257–308 and 466–472.
- [3] Z. M. Michalska, *Transition Met. Chem.* **1980**, *5*, 125–129.

- [4] H. K. Sharma, R. Arias-Ugarte, D. Tomlinson, R. Gappa, A. J. Metta-Maganna, H. Ito, K. H. Pannell, *Organometallics* **2013**, *32*, 3788–3794.
- [5] J. Chojnowski, S. Rubinsztajn, J. A. Cella, W. Fortuniak, M. Cypriak, J. Kuriata, K. Kazmierski, *Organometallics* **2005**, *24*, 6077–6084.
- [6] R. Abele, E. Abele, M. Fleisher, S. Grinberga, E. Lukevics, *J. Organomet. Chem.* **2003**, *686*, 52–57.
- [7] B. Marciniec, P. Pawluć, G. Hreczycho, A. Macina, M. Madalska, *Tetrahedron Lett.* **2008**, *49*, 1310–1313.
- [8] G. Hreczycho, P. Pawluć, B. Marciniec, *New J. Chem.* **2011**, *35*, 2743–2746; G. Hreczycho, K. Kuciński, P. Pawluć, B. Marciniec, *Organometallics* **2013**, *32*, 5001–5004.
- [9] T. Morita, Y. Okamoto, H. Sakurai, *Tetrahedron Lett.* **1980**, *21*, 835–838; T. Veysoglu, L. A. Mitscher, *Tetrahedron Lett.* **1981**, *22*, 1299–1302.
- [10] Y. R. Yeon, Y. J. Park, J. S. Lee, J. W. Park, S. G. Kang, C. H. Jun, *Angew. Chem. Int. Ed.* **2008**, *47*, 109–112; *Angew. Chem.* **2008**, *120*, 115.
- [11] Y. R. Jorapur, T. Shimada, *Synlett* **2012**, *23*, 1633–1638.
- [12] S. E. Denmark, J. M. Kallemeyn, *Org. Lett.* **2003**, *5*, 3483–3486.
- [13] G. A. Olah, A. Husain, B. G. Balaram Gupta, G. F. Salem, S. C. Narang, *J. Org. Chem.* **1981**, *46*, 5212–5214; R. D. Howells, J. D. Mc Cown, *Chem. Rev.* **1977**, *77*, 69–92.
- [14] I. Fleming, A. Barbero, D. Walter, *Chem. Rev.* **1997**, *97*, 2063–2192.
- [15] B. Marciniec, H. Maciejewski, C. Pietraszuk, P. Pawluć, *Hydro-silylation: A Comprehensive Review on Recent Advances*, Springer, Dordrecht, The Netherlands, **2009**.

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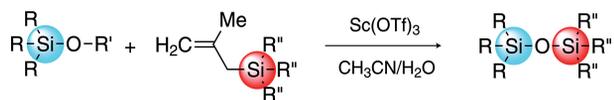
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Siloxanes

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An Efficient Catalytic Approach for the Synthesis of Unsymmetrical Siloxanes

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An efficient methodology for the synthesis of unsymmetrical disiloxanes by means of catalytic one-pot hydrolysis/*O*-silylation of alkoxy silanes with allylsilanes (via silanol intermediates) in the presence of scan-

dium(III) trifluoromethanesulfonate under mild conditions is described. Unsaturated siloxane products are used as substrates for further functionalization through the catalytic hydrosilylation reaction.