

Reactions of tris(trimethylsilyl)silanecarboxylates with organolithium reagents

Joji Ohshita ^{a,*}, Eri Nekoda ^a, Shin Masaoka ^a, Mitsuo Ishikawa ^b

^a Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 739, Japan

^b Department of Chemical Technology, Kurashiki University of Science and the Arts, 2640 Nishinoura, Tsurushima, Kurashiki, Okayama 712, Japan

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Abstract

Chemical behavior of tris(trimethylsilyl)silanecarboxylates toward organolithium reagents was investigated. Treatment of triethylsilyl, triphenylsilyl, and methyl tris(trimethylsilyl)silanecarboxylate (**1a–c**) with organolithium reagents gave products which can be explained in terms of three types of reactions, the formation of lithium tris(trimethylsilyl)silanecarboxylate, abstraction of a trimethylsilyl group by the organolithium reagents, and addition of the organolithium reagents across the carbonyl bond. The formation of lithium tris(trimethylsilyl)silanecarboxylate was observed in the reactions of silyl carboxylates **1a** and **1b**, while addition of the organolithium to the carbonyl bond occurred in the reactions of **1b** and **1c**. Abstraction of a trimethylsilyl group was observed when tris(trimethylsilyl)silyllithium was used as the organolithium reagent. The reaction of **1b** with dimethylphenylsilyllithium afforded dimethylphenylsilyl tris(trimethylsilyl)silyl ketone in good yield, but the bis(silyl) ketone thus formed readily underwent evolution of carbon monoxide even at -80°C , yielding (dimethylphenylsilyl)tris(trimethylsilyl)silane. © 1997 Elsevier Science S.A.

Keywords: Polysilanecarboxylate; Organolithium reagent; Bis(silyl) ketone

1. Introduction

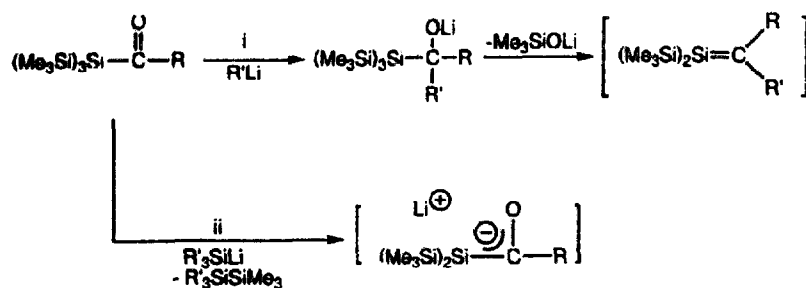
Acylpolysilanes are useful compounds as the precursors of silenes. It has been demonstrated that the photolysis [1,2] and thermolysis [3–6] of acyltris(trimethylsilyl)silanes afford the corresponding 2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)silenes via a 1,3-trimethylsilyl shift from the tris(trimethylsilyl)silyl group to the carbonyl oxygen. Recently, we have found that reactions of acyltris(trimethylsilyl)silanes with alkyl [7] and aryllithium reagents [8] produce the corresponding silenes by addition of the organolithium reagents across the carbonyl bond of the acylpolysilanes, followed by Peterson-type elimination of lithium trimethylsiloxy-

from the resulting anion (Scheme 1, path i) ¹. More recently, we have also demonstrated that treatment of acyltris(trimethylsilyl)silanes with silyllithium reagents gives lithium silenolates by replacement of a trimethylsilyl group with lithium (Scheme 1, path ii) [13,14]. These lithium silenolates are the first examples of silicon analogs of lithium enolates which are wholly characterized by NMR spectrometry. They react readily with several reagents, such as water [13,14], alkyl halides [14], and chlorosilanes [13,14] leading to substitution products. With dienes [15] and carbonyl compounds [16], they give the respective adducts. Oxidative coupling of lithium silenolates affords the first example of bis(acyl)-substituted polysilanes [17].

In order to learn more about the chemical behavior of polysilyl-substituted carbonyl compounds toward

* Corresponding author. Fax: +81 824 22 7191.

¹ For related works, see Refs. [9–12].



Scheme 1.

organolithium reagents, we investigated the reactions of triethylsilyl-, triphenylsilyl-, and methyl tris(trimethylsilyl)silanecarboxylate with tris(trimethylsilyl)silyl-, dimethylphenylsilyl-, phenyl-, and methyl lithium.

2. Results and discussion

2.1. Reactions of triethylsilyl tris(trimethylsilyl)silanecarboxylate (1a)

When we carried out the reaction of **1a** with tris(trimethylsilyl)silyllithium (**2a**) in THF at -80°C and the resulting mixture was treated with tert-butylchlorodimethylsilane, three products, tert-butyltrimethylsilyl tris(trimethylsilyl)silanecarboxylate (**1d**), tris(trimethylsilyl)(triethylsilyl)silane (**3a**), and tetrakis(trimethylsilyl)silane (**4**) were obtained in 53%, 49%, and 14% yields, respectively, as shown in Scheme 2. The formation of **1d** and **3a** clearly indicates that triethylsilyl=Li exchange, leading to the formation of lithium tris(trimethylsilyl)silanecarboxylate (**1e**) takes place in this reaction. For product **4**, it seems likely that abstraction of a trimethylsilyl group by **2a** is involved.

Similar treatment of **1a** with dimethylphenylsilyllithium (**2b**) and then tert-butylchlorodimethylsilane gave **1d** and 2,2,2-triethyltrimethylphenyldisilane (**3b**) in 69% and 55% yields, respectively, again indicating the formation of lithium carboxylate **1e** (Scheme 2). In this reaction, however, no pentamethylphenyldisilane analogous to **4** was detected by GLC analysis of the

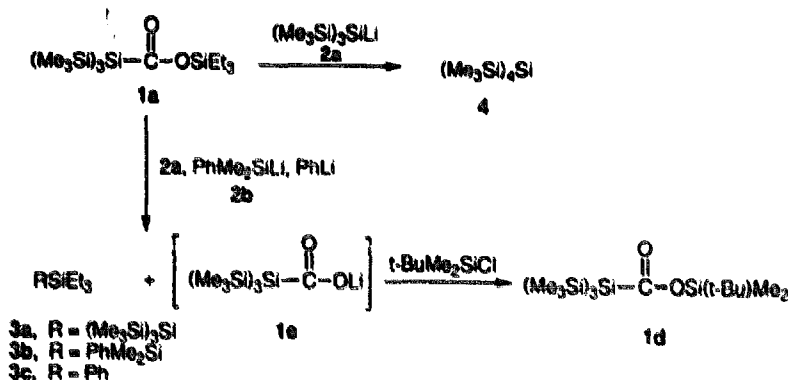
reaction mixture. The lower yields of **3a** and **3b** than those of **1d** suggest that the other reactions leading to the formation of **1e** are involved in these reactions.

The reaction of **1a** with phenyllithium, followed by treatment of the resulting mixture with tert-butylchlorodimethylsilane gave **1d** and triethylphenylsilane (**3c**) in 94% and 93% yields, respectively. The reaction of **1a** with methyl lithium under the same conditions gave many products in less than 10% yields and a large amount of nonvolatile substances. All attempts to improve the reaction by changing the reaction conditions and the quenching reagent from the chlorosilane to water and methyl iodide were unsuccessful.

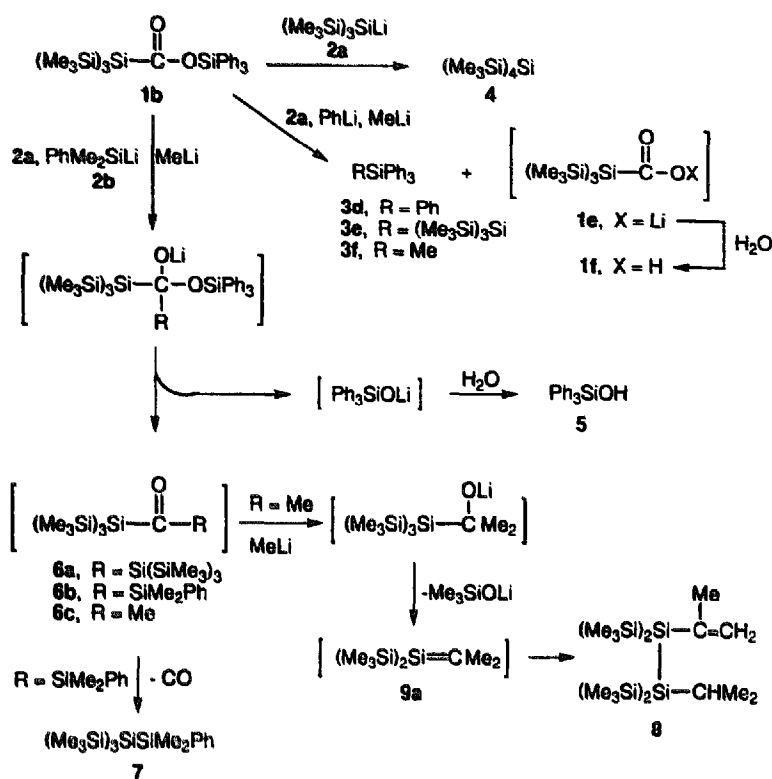
2.2. Reactions of triphenylsilyl tris(trimethylsilyl)silanecarboxylate (1b)

The reaction of **1b** with phenyllithium proceeded in a similar fashion to that of **1a** to produce lithium carboxylate **1e**, as shown by the formation of tris(trimethylsilyl)silanecarboxylic acid (**1f**) and tetraphenylsilane (**3d**) each in 63% yield, when the reaction mixture was hydrolyzed with water (Scheme 3).

Treatment of **1b** with **2a** in THF, followed by hydrolysis gave a rather complex mixture containing **1f**, tris(trimethylsilyl)(triphenylsilyl)silane (**3e**), **4**, and triphenylsilanol (**5**), in 58%, 46%, 19%, and 37% yields, respectively. The formation of products **1f** and **3e**, and **4** can be explained by triphenylsilyl-Li exchange and abstraction of a trimethylsilyl group by **2a**, respectively, as observed in the reaction of **1a** with **2a**. On the other



Scheme 2.



Scheme 3.

hand, for the formation of **5**, addition of **2a** across the carbonyl bond in **1b** producing lithium (triphenylsiloxy)bis[tris(trimethylsilyl)silyl]methoxide would be involved, as shown in Scheme 3. The lithium alkoxide would split into lithium triphenylsiloxy and bis[tris(trimethylsilyl)] ketone (**6a**). Although all attempts to detect **6a** by spectrometric analysis of the reaction mixture were unsuccessful, GC mass spectrometry of the reaction mixture shows the formation of products less than 5% yields, whose parent ions appeared at m/z 522, corresponding to the calculated molecular weight of **6a**. Presumably, bis(silyl) ketone **6a** underwent some isomerization reactions under the reaction conditions.

Similarly, the reaction of **1b** with **2b**, followed by hydrolysis gave **5** and 2,2-dimethyl-2-phenyltris(trimethylsilyl)disilane (**7**) in 61% and 64% yields, respectively, in addition to a 10% yield of **1f**, again suggesting the formation of bis(silyl) ketone **6b** (Scheme 3).

In an effort to learn more about the formation of **6b**, we carried out the reaction of **1b** with **2b** in a mixed solvent of THF and THF- d_8 at -80°C and the reaction progress was followed by ^1H and ^{13}C NMR spectrometry at this temperature. The ^{13}C NMR spectrum showed that the signal due to carbonyl carbon in **1b** at 188.3 ppm disappeared and a new signal at 238.0 ppm which is attributable to the carbonyl carbon of **6b** appeared, immediately after addition of **2b** to a THF solution of

1b. ^1H and ^{13}C NMR spectra of the mixture showed no signals due to the starting compounds **1b** and **2b**, and the yields of **6b** and lithium triphenylsiloxy were calculated to be approximately 70% on the basis of the integral ratios of the signals in the ^1H NMR spectrum. In these spectra, several unidentified signals with low intensities which may include those of lithium carboxylate **1e** were also observed. As expected, when the mixture was allowed to stand at -80°C for 20 h, **6b** was converted to **7** quantitatively. The IR spectrum of the reaction mixture revealed an absorption band due to carbon monoxide at 2083 cm^{-1} . GLC analysis of the mixture on a molecular sieves (13X-S) column also showed the presence of carbon monoxide.

Treatment of **1b** with 2 equiv of methyllithium, followed by hydrolysis gave products **1f**, **5**, methyltriphenylsilane (**3f**), and 1-(2-propenyl)-2-(2-propyl)-tetraakis(trimethylsilyl)disilane (**8**) in 38%, 17%, 20%, and 18% yields, respectively. The formation of **5** and **8** can be explained by a series of reactions including addition of methyllithium across the carbonyl bond of **1b** as the initial step, followed by elimination of lithium triphenylsiloxy producing acetyltris(trimethylsilyl)silane (**6c**). Acylpolysilane **6c**, thus formed would react with methyllithium to give silene **9a** which dimerizes to afford **8**. The reaction of **6c** with methyllithium, yielding **8** has been previously reported [7]. The different chemical behavior of **6c** from that of bis(silyl) ketones

6a and **6b** may be ascribed to the fact that bis(silyl) ketone are thermally less stable than acylpolysilanes [18,19].

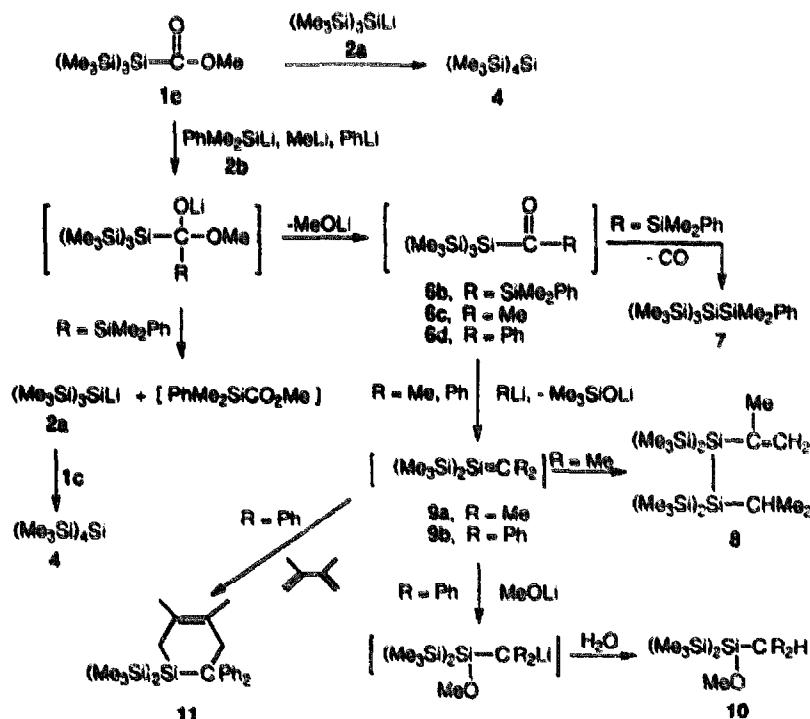
2.3. Reactions of methyl tris(trimethylsilyl)silane-carboxylate (**1c**)

The reaction of **1c** with **2a** gave **4** in 63% yield as the sole volatile product (Scheme 4). Compound **4** indicates that abstraction of a trimethylsilyl group from **1c** by **2a** occurred, as in the reactions of **1a** and **1b** with **2a**. However, all attempts to trap the anionic species which must be produced simultaneously with **4**, by chlorosilanes, water, and methyl iodide, were unsuccessful. We also attempted to detect the anionic species by direct NMR spectrometry of the reaction mixture at low temperature. ^1H and ^{13}C NMR spectra of the mixture, however, showed no signals due to the anionic species, although almost all starting materials **1c** and **2a** were found to be consumed. Many broad and multiple signals were always observed in these spectra. We have recently demonstrated that similar treatment of acyltris(trimethylsilyl)silanes with **2a** affords the respective lithium silenolates and **4** by abstraction of a trimethylsilyl group [13,14]. Lithium silenolates are thermally stable if they have a sterically large substituent, like mesityl, tert-butyl, and adamantyl on the carbonyl carbon atom. With a less bulky phenyl group, however, the silenolate readily oligomerizes to non-volatile substances even at -80°C . Introduction of a bolder alkoxy group onto the carbonyl carbon seems to

be necessary to stabilize the anionic species arising from the reactions of tris(trimethylsilyl)silane-carboxylates with **2a**.

Reaction of **1c** with **2b** gave products **4** and **7** in 18% and 12% yields, respectively. Product **7** can be explained by CO extrusion from **6b**, while compound **4** seems to indicate the formation of **2a** and methyl dimethylphenylsilane-carboxylate by addition-elimination process involving cleavage of an Si-C bond. Silyllithium **2a** would react with **1c** to give **4**. Similar formation of **2a** from the reaction of pivaloyltris(trimethylsilyl)silane with methyllithium has been reported, previously [7]. Methyl dimethylphenylsilane-carboxylate would decompose under the conditions used.

The reactions of **1c** with methyl- and phenyllithium produced the corresponding acylsilanes by addition-elimination process, as shown in Scheme 4. Thus, treatment of **1c** with methyllithium at -80°C gave **8** in 58% yield, indicating the formation of silene **9a** as observed for the reaction of **1b** with methyllithium. With phenyllithium, **1c** gave (diphenylmethyl)methoxybis(trimethylsilyl)silane (**10**) in 29% yield, as the sole volatile product. Product **10** can be understood by the formation of benzoyltris(trimethylsilyl)silane (**6d**). Acylpolysilane **6d** reacts with phenyllithium to produce silene **9b**. The reaction of **9b** with methoxylithium followed by hydrolysis gives product **10**. In fact, when we carried out the reaction of **1c** with phenyllithium in the presence of an excess of 2,3-dimethylbutadiene, a [2 + 4] cycloadduct (**11**) arising from the reaction of silene **9b** with the butadiene was obtained in 49% yield.



Scheme 4.

3. Conclusion

It has been demonstrated that the reactions of tris(trimethylsilyl)silanecarboxylates with organolithium reagents proceeded with three types of reactions, (a) the formation of lithium tris(trimethylsilyl)silanecarboxylate, (b) abstraction of a trimethylsilyl group by the organolithium reagent, and (c) addition of the organolithium reagent across the carbonyl bond in the carboxylates. Path a was involved only in the reactions of **1a** and **1b**, while path c was observed in the reactions of carboxylate **1b** and **1c**. Path b occurred when **2a** was used as the organolithium reagent.

Lithium tris(trimethylsilyl)silyl(alkoxy)methoxides arising from path c did not undergo Peterson-type olefination, in contrast to the lithium adducts produced from the reactions of acylpolysilanes with methyl- and phenyllithium [7,8]. The present adduct underwent cleavage of the O–C or Si–C bond reproducing a carbonyl bond.

4. Experimental section

4.1. General

All reactions were carried out in dark under an atmosphere of purified argon. NMR spectra were recorded on a JEOL EX-270 spectrometer using tetramethylsilane as an internal standard. IR spectra were measured on a Perkin-Elmer FT1600 spectrophotometer. Mass spectra were measured on a Shimadzu QP-1000 spectrometer. Exact mass spectra were measured on a Hitachi M-80B spectrometer.

4.2. Materials

THF was dried over sodium–potassium alloy and distilled just before use. Tris(trimethylsilyl)silane-carboxylates **1b** and **1c** [20] and silyllithium reagents **2a** [21] and **2b** [22] were prepared as reported in the literature.

4.3. Preparation of **1a**

Compound **1a** was prepared in a similar fashion to that of **1b** [20]. To a solution of 3.2 g (10.6 mmol) of **1f** in 100 mL of benzene was added a mixture of 2.0 mL (11.9 mmol) of chlorotriethylsilane and 1.4 mL (17.5 mmol) of pyridine at room temperature. The mixture was heated at 40°C overnight and the resulting precipitates were filtered off. The solvent was evaporated under reduced pressure to give 4.3 g (99% yield) of **1a** as colorless viscous oil; MS m/z 406 (M^+); 1H NMR δ (C_6D_6) 0.33 (s, 27H, Me_3Si), 0.78 (q, 6H, $J = 7.9$ Hz, CH_3CH_2Si), 1.02 (t, 9H, $J = 7.9$ Hz, CH_3CH_2Si);

^{13}C NMR δ (C_6D_6) 0.9 (Me_3Si), 5.3 (CH_3CH_2Si), 7.0 (CH_3CH_2Si), 188.3 (C=O); IR $\nu_{C=O}$ 1648 cm^{-1} . Anal. Found: C, 47.26; H, 10.44. $C_{16}H_{42}O_2Si_5$. Calc.: C, 47.23; H, 10.40%.

4.4. Reaction of **1a** with **2a**

To a solution of 0.626 g (1.539 mmol) of **1a** in 15 mL of THF was added 1.539 mmol of **2a** in 15 mL of THF at $-80^\circ C$. The mixture was allowed to warm to room temperature over a period of 24 h, and then 0.344 g (2.285 mmol) of tert-butylchlorodimethylsilane was added to the resulting mixture. After evaporation of the solvent, the residue was analyzed by GLC using 0.020 g (0.102 mmol) of teradecane as an internal standard as being **1d** (53% yield), **3a** (49% yield), and **4** (14% yield). Compounds **1d**, **3a**, and **4** were isolated by treating the mixture with preparative GPC eluting with benzene. All spectral data obtained for **3a** are identical with those reported in the literature [14]. All spectral data obtained for **4** are identical with those of the authentic sample prepared as reported in the literature [23]. For **1d**: colorless oil; MS m/z 406 (M^+); 1H NMR δ (C_6D_6) 0.34 (s, 6H, Me_2Si), 0.36 (s, 27H, Me_3Si), 1.03 (s, 9H, t-Bu); ^{13}C NMR δ (C_6D_6) -3.9 (Me_2Si), 0.9 (Me_3Si), 17.9, 26.1 (t-Bu), 188.0 (C=O); IR $\nu_{C=O}$ 1648 cm^{-1} ; Exact MS: $C_{13}H_{33}O_2Si_4$ ($M^+ - SiMe_3$) calc.: 333.1556. Found: 333.1586.

All other reactions of tris(trimethylsilyl)silanecarboxylates **1a–c** with organolithium reagents were carried out as above. Yields were determined by GLC using a hydrocarbon as an internal standard. Products were isolated by preparative GPC or silica gel column chromatography. All spectral data obtained for products **1f** [20], **8** [7], and **11** [8] were identical with those prepared as reported in the literature. Mass spectra and GLC retention times for products **3c**, **3f**, and **5** are identical with those of the authentic samples purchased from Shin-Etsu Chemical Co. Ltd.

Data for **3b**: colorless oil; MS m/z 250 (M^+); 1H NMR δ ($CDCl_3$) 0.42 (s, 6H, $MeSi$), 0.66 (q, 6H, $J = 7.9$ Hz, CH_3CH_2Si), 0.95 (t, 9H, $J = 7.9$ Hz, CH_3CH_2Si), 7.34–7.36 (m, 5H, m - and p -Ph), 7.50 (br. dd, 6H, $J = 7.8$, 1.6 Hz, o -Ph); ^{13}C NMR δ ($CDCl_3$) -2.5 ($MeSi$), 3.2 (CH_3CH_2Si), 8.3 (CH_3CH_2Si), 127.7, 128.2, 133.7, 140.3 (Ph). Anal. Found: C, 67.26; H, 10.36. $C_{14}H_{26}Si_2$. Calc.: C, 67.12; H, 10.46%.

Data for **3e**: white solid; mp $138.5^\circ C$; MS m/z 506 (M^+); 1H NMR δ (C_6D_6) 0.29 (s, 27H, Me_3Si), 7.16–7.26 (m, 15H, Ph); ^{13}C NMR δ (C_6D_6) 3.2 (Me_3Si), 128.1, 129.5, 136.8, 136.9 (Ph). Anal. Found: C, 63.95; H, 8.24. $C_{27}H_{42}Si_5$. Calc.: C, 63.96; H, 8.35%.

Data for **7**: white solid; mp 73.0 – $73.8^\circ C$; MS m/z 382 (M^+); 1H NMR δ (C_6D_6) 0.28 (s, 27H, Me_3Si), 0.58 (s, 6H, Me_2Si), 7.21–7.27 (m, 3H, m - and p -Ph), 7.59–7.62 (m, 2H, o -Ph); ^{13}C NMR δ (C_6D_6) 1.34

(Me₂Si), 2.96 (Me₃Si), 128.0, 128.8, 134.4, 141.1 (Ph); ²⁹Si NMR δ (C₆D₆) -134.0 (SiSiMe₃), -12.9 (SiMe₃), -9.4 (SiMe₂Ph). Anal. Found: C, 53.12; H, 9.99. C₁₇H₃₈Si₅. Calc.: C, 53.32; H, 10.00%.

Data for **10**: colorless oil; MS m/z 372 (M⁺); ¹H NMR δ (CDCl₃) -0.0 (s, 18H, Me₃Si), 3.63 (s, 3H, MeO), 7.27–7.42 (m, 10H, Ph); ¹³C NMR δ (CDCl₃) -0.5 (Me₃Si), 45.5 (MeO), 54.0 (HCSi), 125.4, 127.3, 127.9, 128.4, 128.9, 143.5 (Ph); IR ν_{Si-O} 1067 cm⁻¹. Anal. Found: C, 64.41; H, 8.44. C₂₀H₃₂OSi₃. Calc.: C, 64.45; H, 8.65%.

Preparation of 6b: To a mixture of 0.224 g (0.406 mmol) of **1b**, 2.5 mL of THF, and 0.5 mL of THF-d₈ was added 0.440 mmol of **2b** in 0.35 mL of THF at -80°C and the resulting mixture was stirred at this temperature for 20 h. The 0.6 mL of the resulting mixture was placed in an NMR tube (5 mm φ) cooled at -80°C and analyzed by NMR spectrometry. For **6b**: ¹H NMR δ (THF + THF-d₈) 0.31 (s, 27H, Me₃Si), 0.67 (s, 6H, Me₂Si), 7.46–7.80 (m, 5H, Ph); ¹³C NMR δ (THF + THF-d₈) 3.1 (Me₃Si), 1.4 (Me₂Si), 128.0, 128.1, 136.3, 144.1 (Ph), 238.0 (C≡O).

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