Unexpected Reaction of Benzoates with Chlorovinylsilanes in the Presence of Magnesium: A Facile Synthesis of (3-Oxo-3-phenyl)propylvinylsilanes and Further Transformations

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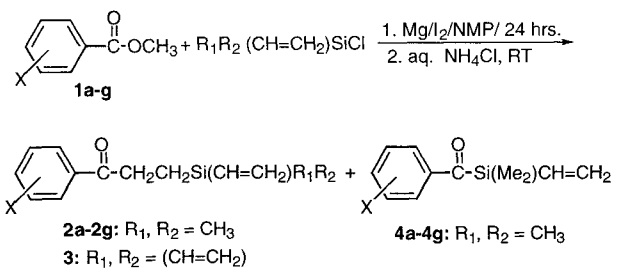
Received 1 November 1996; revised 14 March 1997

(3-Oxo-3-phenyl)propylvinylsilanes, new functionalized monomers, have been synthesized in modest to good yields, by the reaction of methyl benzoates with chlorodimethylvinylsilane in the presence of magnesium. The synthetic potential of these new compounds was investigated in siloxane synthesis and hydroxy transformation.

In connection with our ongoing projects exploring the utility of silyl aryl ketones,[1] we were seeking the methodology for the synthesis of functionalized and polymerizable silyl ketones. Recently we attempted to synthesize benzoylvinyldimethylsilane by reductive silylation of methyl benzoate using chlorodimethylvinylsilane,[1] and found that (3-oxo-3-phenyl)propylvinyldimethylsilane was formed as the major product. While a number of 3-oxo-organosilanes have been synthesized[2] and their potentials in organic syntheses have been shown,[3] no (3-oxo-3-phenyl)propylvinylsilane has been reported in the literature. Similar compounds were investigated recently in the synthesis of hyperbranched polycarbosilanes,[4] and can also be utilized for hydroxy transformation and siloxane synthesis.

In general, the reaction of a substituted or unsubstituted benzoate with excess chlorodimethylvinylsilane in the presence of magnesium, followed by hydrolysis under weak acidic conditions, gave the corresponding (3-oxo-3-phenyl)propylvinylsilanes **2a–g, 3** as the major products besides a small amount of corresponding acylvinylsilanes **4a–g**. The product mixture was separated by column chromatography and/or distillation, or by washing in acetonitrile with a weak base such as dilute sodium hydroxide, which destroys the acylvinylsilane impurities. The reactions can be carried out in different polar solvents, i.e. NMP, HMPT, DMF, and the workup is convenient.[5] A small amount of iodine initiated the reaction. Excess chlorodimethylvinylsilane is necessary, otherwise the products become complex.[6] Furthermore, (3-oxo-3-phenyl)propyltrivinylsilane **(3)** was also obtained by this method when trivinylchlorosilane was used as the chlorosilane (Scheme 1). The yields of the obtained (3-oxo-3-phenyl)propylvinylsilanes are summarized in Table 1.



Scheme 1

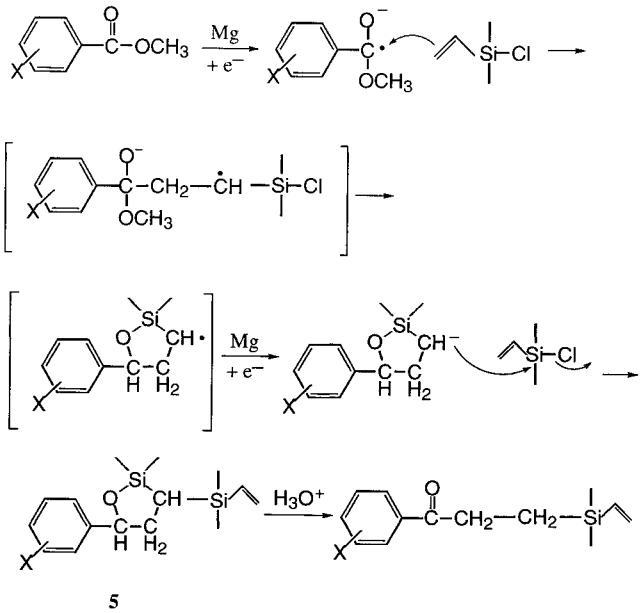
Although the reaction mechanism is not fully understood, the following mechanism can be tentatively proposed involving initial electron transfer to the carbonyl resulting in a ketyl radical intermediate (Scheme 2).[7] However, all our attempts to isolate and characterize the intermediate **5** were unsuccessful.

Compounds **2a–g** are valuable intermediates and can be converted to the corresponding alcohols and siloxanes. Various methods for the conversion of carbon–silicon bonds to carbon–oxygen bonds have been reported to date.[8] Fleming, et al., have utilized the phenyldimethylsilyl functionality,[9] while Tamao and Ishida use the allyldimethylsilyl group as a latent hydroxyl group.[10] The general procedure for hydroxy and siloxane transformation first involves the conversion of the vinylsilyl group to the silyl fluoride. Potassium hydrogen fluoride (KHF_2) in excess of trifluoroacetic acid was found to be a con-

Table 1. Compounds **2a–g**, **3** Prepared

Substrate	Product	Yield[a] (%)	pb (°C)/Torr[b]
$PhCO_2Me$ **(1a)**	$PhCOCH_2CH_2SiMe_2CH=CH_2$ **(2a)**	57	110/0.5
4-$MeOC_6H_4CO_2Me$ **(1b)**	4-$MeOC_6H_4COCH_2CH_2SiMe_2CH=CH_2$ **(2b)**	67	132/0.4
2-$MeC_6H_4CO_2Me$ **(1c)**	2-$MeC_6H_4COCH_2CH_2SiMe_2CH=CH_2$ **(2c)**	57	112/0.75
4-$MeC_6H_4CO_2Me$ **(1d)**	4-$MeC_6H_4COCH_2CH_2SiMe_2CH=CH_2$ **(2d)**	52	115/0.75
4-$ClC_6H_4CO_2Me$ **(1e)**	4-$ClC_6H_4COCH_2CH_2SiMe_2CH=CH_2$ **(2e)**	38	138/3
4-$(MeO)_2HCC_6H_4CO_2Me$ **(1f)**	4-$H(O)CC_6H_4COCH_2CH_2SiMe_2CH=CH_2$ **(2f)**	33	145/2
4-$BrC_6H_4CO_2Me$ **(1g)**	4-$BrC_6H_4COCH_2CH_2SiMe_2CH=CH_2$ **(2g)**	33[c]	–
$PhCO_2Me$ **(1a)**	$PhCOCH_2CH_2Si(CH=CH_2)_3$ **(3)**	33	83/1.75

[a] Yield of isolated product.
[b] Boiling points are uncorrected.
[c] Isolated as a 3:2 mixture with **4g**, yield based on GC/MS.



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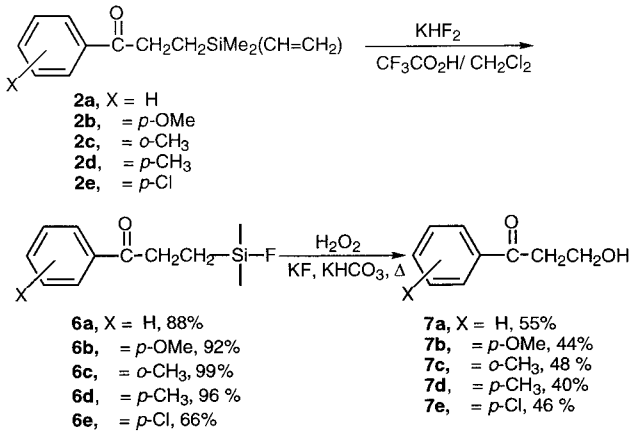
Scheme 2

venient reagent for this conversion. When only a threefold excess of KHF_2 was used,[10] a mixture of the silyl fluoride and starting material was obtained. Subsequent oxidation of the corresponding silyl fluorides **6a–e** in 30% H_2O_2 following Tamao's procedures[8] gave the alcohols **7a–e** (Scheme 3).



2a, X = H
2b, = *p*-OMe
2c, = *o*-CH_3
2d, = *p*-CH_3
2e, = *p*-Cl

6a, X = H, 88%
6b, = *p*-OMe, 92%
6c, = *o*-CH_3, 99%
6d, = *p*-CH_3, 96 %
6e, = *p*-Cl, 66%

7a, X = H, 55%
7b, = *p*-OMe, 44%
7c, = *o*-CH_3, 48 %
7d, = *p*-CH_3, 40%
7e, = *p*-Cl, 46 %

Scheme 3

Furthermore, hydrolysis of the silyl fluorides **6a,b** with 40% tetrabutylammonium hydroxide gave siloxanes **8a,b** after aqueous workup. These siloxanes can be polymerized with octamethylcyclosiloxane under acidic conditions[11] to give new functionalized siloxane polymers **9a,b** (Scheme 4).

The new functionalized siloxanes are characterized in Table 2. Molecular weights of the polymers are the GPC molecular weights calibrated against polystyrene standards, and can be used only as rough estimates.

Table 2. Polymer Characterization

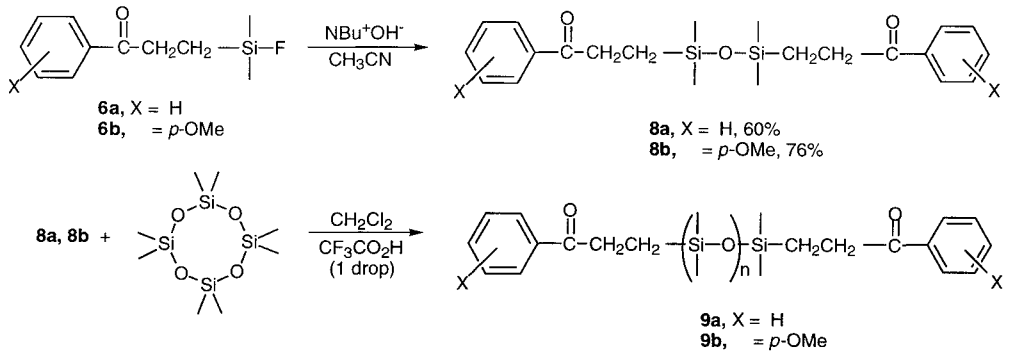
Product	X	Conversion %	$Mw^a \times 10^{-3}$	Mw/Mn
9a	H	96	4.6	1.5
9b	4-Me	98	8.6	1.6

[a] Measured by SEC in THF using linear polystyrene standard.

In summary, we have described a convenient disproportionation method for the synthesis of a series of new (3-oxo-3-phenyl)propylvinylsilane compounds using benzoates and dimethylvinylchlorosilane. As both starting materials are inexpensive and readily available, these new compounds are potentially useful in developing new functionalized polymer materials.

^1H and ^{13}C NMR spectra were taken in $CDCl_3$ solutions and internal TMS as standard on a Varian Unity 300 (300 MHz) instrument. GC/MS data were obtained from a Hewlett Packard 5890 series mass spectrometer. HRMS data were taken by the Southern California Mass Spectrometry Facility at University of California Riverside. NMP was purchased from Aldrich in Sure-Seal bottles, and used without further purification. Dimethylvinylchlorosilane was purchased from Aldrich and distilled prior to use. All benzoates except for **1f**[12] are commercially available.

(3-Oxo-3-phenyl)propylvinylsilanes 2a–g, 3; General Procedure:
Mg powder (0.05 mol, 1.2 g), I_2 (0.8 mmol, 0.2 g), NMP (60 mL) and excess dimethylvinylchlorosilane (0.2 mol, 27 mL) (trivinylchlorosilane for **3**) were mixed and stirred for a few minutes before the appropriate methyl benzoate **1** (0.025 mol, 3.1 mL) was added dropwise. In some cases, the reaction mixture was heated for 3–4 h to increase the ratio of (3-oxo-3-phenyl)propylvinylsilanes to vinylacylsilane. The mixture was left stirring overnight at r.t., quenched with aq NH_4Cl, and extracted with pentane (3 × 100 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated to give the crude product, which was purified by distillation and/or column chromatography.



6a, X = H
6b, = *p*-OMe

8a, X = H, 60%
8b, = *p*-OMe, 76%

8a, 8b +

9a, X = H
9b, = *p*-OMe

Scheme 4

3-Oxo-(3-phenylpropyl)dimethylvinylsilane (**2a**):

^{1}H NMR: δ = 0.10 (6 H, s), 0.93–0.99 (2 H, m), 2.89–2.95 (2 H, m), 5.69 (1 H, dd, J_{trans} = 20 Hz, J_{gem} = 4 Hz), 5.97 (1 H, dd, J_{cis} = 15 Hz, J_{gem} = 4 Hz), 6.12 (1 H, dd, J_{trans} = 20 Hz, J_{cis} = 14 Hz), 7.42 (2 H, br t), 7.51 (1 H, br t), 7.92 (2 H, d, J = 8 Hz).

^{13}C NMR: δ = −3.5 [Si(CH_3)$_2$], 9.5, 32.9 (CH_2CH_2), 127.9, 128.5, 132.7, 136.7 (C_6H_5), 132.2 (=CH_2), 138.2 (=CH), 201.0 (CO).

^{29}Si NMR: δ = −2.64.

MS: m/z = 218 (M^+, 6), 203 (100), 191 (81), 175 (35), 105 (52), 85 (86).

HRMS: m/z Calc. 217.1048 $(M-H)^+$, Found 217.1036 $(M-H)^+$.

3-Oxo-3-(4-methoxyphenylpropyl)dimethylvinylsilane (**2b**):

^{1}H NMR: δ = 0.10 (6 H, s), 0.92–0.97 (2 H, m), 2.84–2.90 (2 H, m), 3.85 (3 H, s), 5.69 (1 H, dd, J_{trans} = 20 Hz, J_{gem} = 4 Hz), 5.97 (1 H, dd, J_{cis} = 15 Hz, J_{gem} = 4 Hz), 6.14 (1 H, dd, J_{trans} = 20 Hz, J_{cis} = 15 Hz), 6.91 (2 H, d, J = 9 Hz), 7.91 (2 H, d, J = 9 Hz).

^{13}C NMR: δ = −3.6 [Si(CH_3)$_2$], 9.6, 32.5 (CH_2CH_2), 55.2 (OCH_3), 113.5, 129.6, 130.1, 163.1 (C_6H_4), 132.1 (=CH_2), 138.1 (=CH), 199.4 (CO).

^{29}Si NMR: δ = −4.87.

MS: m/z = 248 (M^+, 6), 233 (60), 221 (47), 147 (17), 135 (100), 85 (18).

HRMS: m/z Calc. 249.1311 $(MH)^+$, Found 249.1316 $(MH)^+$.

3-Oxo-3-(2-methylphenylpropyl)dimethylvinylsilane (**2c**):

^{1}H NMR: δ = 0.09 (6 H, s), 0.89–0.95 (2 H, m), 2.45 (3 H, s), 2.80–2.86 (2 H, m), 5.69 (1 H, dd, J_{trans} = 20 Hz, J_{gem} = 4 Hz), 5.96 (1 H, dd, J_{cis} = 15 Hz, J_{gem} = 4 Hz), 6.10 (1 H, dd, J_{trans} = 20 Hz, J_{cis} = 15 Hz), 7.23 (2 H, m), 7.34 (1 H, br t), 7.56 (1 H, d, J = 7 Hz).

^{13}C NMR: δ = −3.5 [Si(CH_3)$_2$], 9.5, 36.1 (CH_2CH_2), 21.2 (ArCH_3), 125.6, 128.1, 130.9, 131.8, 137.7 (C_6H_4), 132.3 (=CH_2), 138.2 (=CH), 205.4 (CO).

^{29}Si NMR: δ = −6.24.

MS: m/z = 232 (M^+, 0.6), 217 (45), 205 (22), 131 (31), 119 (100), 91 (39).

HRMS: m/z Calc. 233.1362 $(MH)^+$, Found 233.1367 $(MH)^+$.

3-Oxo-3-(4-methylphenylpropyl)dimethylvinylsilane (**2d**):

^{1}H NMR: δ = 0.10 (6 H, s), 0.92–0.98 (2 H, m), 2.38 (3 H, s), 2.87–2.92 (2 H, m), 5.70 (1 H, dd, J_{trans} = 20 Hz, J_{gem} = 4 Hz), 5.97 (1 H, dd, J_{cis} = 15 Hz, J_{gem} = 4 Hz), 6.17 (1 H, dd, J_{trans} = 20 Hz, J_{cis} = 15 Hz), 7.23 (2 H, d, J = 7 Hz), 7.83 (2 H, d, J = 8 Hz).

^{13}C NMR: δ = −3.4 [Si(CH_3)$_2$], 9.7, 32.9 (CH_2CH_2), 21.6 (ArCH_3), 128.2, 128.6, 129.3, 143.5 (C_6H_4), 132.3 (=CH_2), 138.3 (=CH), 200.8 (CO).

^{29}Si NMR: δ = −2.32.

MS: m/z = 232 (M^+, 2), 217 (100), 205 (54), 131 (41), 119 (56), 91 (40).

HRMS: m/z Calc. 233.1362 $(MH)^+$, Found 233.1352 $(MH)^+$.

3-Oxo-3-(4-chlorophenylpropyl)dimethylvinylsilane (**2e**):

^{1}H NMR: δ = 0.10 (6 H, s), 0.92–0.97 (2 H, m), 2.86–2.92 (2 H, m), 5.69 (1 H, dd, J_{trans} = 20 Hz, J_{gem} = 4 Hz), 5.98 (1 H, dd, J_{cis} = 15 Hz, J_{gem} = 4 Hz), 6.13 (1 H, dd, J_{trans} = 20 Hz, J_{cis} = 15 Hz), 7.41 (2 H, d, J = 8 Hz), 7.86 (2 H, d, J = 8 Hz).

^{13}C NMR: δ = −3.4 [Si(CH_3)$_2$], 9.5, 33.1 (CH_2CH_2), 128.8, 129.4, 135.0, 139.2 (C_6H_4), 132.4 (=CH_2), 138.1 (=CH), 199.8 (CO).

^{29}Si NMR: δ = −2.32.

MS: m/z = 254 (M+2, 1), 252 (M^+, 4), 237 (96), 225 (87), 151 (68), 139 (40), 85 (100).

HRMS: m/z Calc. 253.0815 $(MH)^+$, Found 253.0813 $(MH)^+$.

3-Oxo-3-(4-formylphenylpropyl)dimethylvinylsilane (**2f**):

^{1}H NMR: δ = 0.11 (6 H, s), 0.94–0.99 (2 H, m), 2.94–2.99 (2 H, m), 5.70 (1 H, dd, J_{trans} = 20 Hz, J_{gem} = 4 Hz), 5.98 (1 H, dd, J_{cis} = 14 Hz, J_{gem} = 4 Hz), 6.14 (1 H, dd, J_{trans} = 19 Hz, J_{cis} = 14 Hz), 7.95 (2 H, d, J = 8 Hz), 8.06 (2 H, d, J = 8 Hz), 10.08 (1 H, s).

^{13}C NMR: δ = −3.5 [Si(CH_3)$_2$], 9.3, 33.5 (CH_2CH_2), 128.5, 129.7, 138.8, 141.0 (C_6H_4), 132.4 (=CH_2), 137.9 (=CH), 191.4 (CHO), 200.2 (CO).

^{29}Si NMR: δ = −2.86.

MS: m/z = 246 (M^+, 10), 231 (100), 203 (29), 133 (29), 105 (20), 91 (21).

HRMS: m/z Calc. 247.1154 $(MH)^+$, Found 247.1147 $(MH)^+$.

3-Oxo-3-(4-bromophenylpropyl)dimethylvinylsilane (**2g**):
Could not be characterized due to difficulties in separation from **4g**.

3-Oxo-(3-phenylpropyl)trivinylsilane (**3**):

^{1}H NMR: δ = 1.11–1.17 (2 H, m), 2.95–3.01 (2 H, m), 5.81 (3 H, dd, J_{trans} = 17 Hz, J_{cis} = 8 Hz), 6.08–6.22 (6 H, m), 7.40–7.55 (3 H, m), 7.92 (2 H, d, J = 7 Hz).

^{13}C NMR: δ = 6.5, 32.6 (CH_2CH_2), 127.9, 128.4, 133.9, 136.7 (C_6H_5), 132.8 (=CH_2), 135.0 (=CH), 200.3 (CO).

^{29}Si NMR: δ = −16.74.

MS: m/z = 242 (M^+, 1), 215 (100), 200 (15), 117 (54), 109 (66), 105 (39).

HRMS: m/z Calc. 243.1205 $(MH)^+$, Found 243.1200 $(MH)^+$.

1-Aryl-3-(fluorodimethylsilyl)propan-1-ones 6; General Procedure:
To a solution of **2** (4 mmol) in CH_2Cl_2 (5 mL) was added KHF_2 (8 mmol) and CF_3CO_2H (5 mL, 65 mmol), and the mixture set to reflux for 3 h. The mixture was quenched with some ice water, followed by extraction of the organic layer with CH_2Cl_2 or Et_2O. The collected organic layers were washed with aq dil $NaHCO_3$, and dried ($MgSO_4$). Removal of the solvent gave the silyl fluoride **6**, which was used without further purification.

3-(Fluorodimethylsilyl)-1-phenylpropan-1-one (**6a**):

^{1}H NMR: δ = 0.04 (6 H, d, J = 7 Hz), 0.79–0.87 (2 H, m), 2.85 (2 H, t, J = 8 Hz), 7.19–7.25 (3 H, m), 7.71 (2 H, d, J = 8 Hz).

^{13}C NMR: δ = −1.4 [Si(CH_3)$_2$, d, J = 60 Hz], 10.1 (CH_2, d, J = 60 Hz), 31.8 (CH_2), 127.8, 128.4, 132.8, 136.4 (C_6H_5), 199.9 (CO).

^{19}F NMR: δ = −160.6.

^{29}Si NMR: δ = 30.8 (d, J = 1400 Hz).

MS: m/z = 210 (M^+, 10), 209 (M^+ −1, 49), 195 (27), 107 (100), 77 (66).

3-(Fluorodimethylsilyl)-1-(4-methoxyphenyl)propan-1-one (**6b**):

^{1}H NMR: δ = 0.26 (6 H, d, J = 7 Hz), 1.01–1.08 (2 H, m), 3.04 (2 H, t, J = 8 Hz), 3.85 (3 H, s), 6.92 (2 H, d, J = 9 Hz), 7.93 (2 H, d, J = 9 Hz).

^{13}C NMR: δ = −1.4 [Si(CH_3)$_2$, d, J = 60 Hz], 10.3 (CH_2, d, J = 60 Hz), 31.5 (CH_2), 55.3 (OCH_3), 113.6, 130.2, 163.3 (C_6H_4), 198.7 (CO).

^{19}F NMR: δ = −160.5.

^{29}Si NMR: δ = 31.5 (d, J = 1400 Hz).

MS: m/z = 240 (M^+, 5), 255 (30), 209 (8), 135 (100), 92 (26), 77 (52).

3-(Fluorodimethylsilyl)-1-(2-methylphenyl)propan-1-one (**6c**):

^{1}H NMR: δ = 0.26 (6 H, d, J = 7 Hz), 0.99–1.07 (2 H, m), 2.47 (3 H, s), 2.99 (2 H, t, J = 8 Hz), 7.21–7.35 (3 H, m), 7.61 (2 H, d, J = 7 Hz).

^{13}C NMR: δ = −1.4 [Si(CH_3)$_2$, d, J = 60 Hz], 10.3 (CH_2, d, J = 60 Hz), 21.1 (Ar-CH_3), 34.8 (CH_2), 125.6, 128.1, 131.1, 131.8, 137.8 (C_6H_4), 204.1 (CO).

^{19}F NMR: δ = −160.8.

^{29}Si NMR: δ = 30.7 (d, J = 1400 Hz).

MS: m/z = 224 (M^+, 14), 209 (29), 119 (100), 91 (82), 77 (62).

3-(Fluorodimethylsilyl)-1-(4-methylphenyl)propan-1-one (**6d**):

^{1}H NMR: δ = 0.26 (6 H, d, J = 7 Hz), 1.01–1.09 (2 H, m), 2.40 (3 H, s), 3.06 (2 H, t, J = 8 Hz), 7.24 (2 H, d, J = 8 Hz), 7.85 (2 H, d, J = 8 Hz).

^{13}C NMR: δ = −1.4 [Si(CH_3)$_2$, d, J = 60 Hz], 10.3 (CH_2, d, J = 60 Hz), 21.5 (ArCH_3), 31.8 (CH_2), 128.0, 129.2, 133.9, 143.7 (C_6H_4), 199.8 (CO).

^{19}F NMR: δ = −160.4.

^{29}Si NMR: $\delta = 30.8$ (d, $J = 1400$ Hz).

MS: $m/z = 224$ (M^+, 1), 209 (74), 119 (100), 91 (36), 77 (24).

3-(Fluorodimethylsilyl)-1-(4-chlorophenyl)propan-1-one (**6e**):
^{1}H NMR: $\delta = 0.26$ (6H, d, $J = 7$ Hz), 1.02–1.09 (2H, m), 3.05 (2H, t, $J = 8$ Hz), 7.42 (2H, d, $J = 8$ Hz), 7.89 (2H, d, $J = 8$ Hz).

^{13}C NMR: $\delta = -1.4$ [$Si(CH_3)_2$, d, $J = 60$ Hz], 10.1 (CH_2, d, $J = 60$ Hz), 31.9 (CH_2), 128.7, 129.4, 134.7, 139.3 (C_6H_4), 198.8 (CO).

^{19}F NMR: $\delta = -160.1$.

^{29}Si NMR: $\delta = 31.6$ (d, $J = 1400$ Hz).

MS: $m/z = 246$ ($M^+ + 2$, 2), 245 ($M^+ + 1$, 7), 244 (M^+, 4), 229 (41), 209 (55), 139 (100), 111 (38), 77 (39).

1-Aryl-3-hydroxypropan-1-ones 7; General Procedure:
To a solution of silyl fluoride **6** (1.5 mmol) in MeOH/THF (1:1, 10 mL) were added KF (3 mmol), $KHCO_3$ (1.6 mmol) and excess 30% H_2O_2 (0.29 mL, 4 mmol). After stirring at r.t. for 2–3 h, the reaction was quenched by careful addition of dilute $NaHSO_3$ at 0°C. The thick solution was filtered under vacuum, washing the filter cake with several portions of Et_2O. The filtrate was collected and washed with aq $NaHCO_3$, and dried ($MgSO_4$). Removal of solvent under rotary evaporator gave the crude product, which was purified through column chromatography (1:1 hexanes/EtOAc) to give the hydroxylated product.

3-Hydroxy-1-phenylpropan-1-one (**7a**):
^{1}H NMR: $\delta = 3.16$ (2H, t, $J = 5$ Hz), 3.60 (1H, br s), 3.98 (2H, t, $J = 5$ Hz), 7.39 (2H, t, $J = 8$ Hz), 7.48 (1H, t, $J = 8$ Hz), 7.89 (2H, d, $J = 8$ Hz).

^{13}C NMR: $\delta = 40.3$, 57.7 (CH_2CH_2), 127.8, 128.4, 133.2, 136.4 (C_6H_5), 199.9 (CO).

MS: $m/z = 132$ ($M^+ - 18$), 105 (58), 77 (100).

HRMS: m/z Calc. 151.0759 $(MH)^+$, Found 151.0762 $(MH)^+$.

3-Hydroxy-1-(4-methoxyphenyl)propan-1-one (**7b**):
^{1}H NMR: $\delta = 3.07$ (2H, t, $J = 5$ Hz), 3.16 (1H, br s), 3.76 (3H, s), 3.91 (2H, t, $J = 5$ Hz), 6.82 (2H, d, $J = 9$ Hz), 7.83 (2H, d, $J = 9$ Hz).

^{13}C NMR: $\delta = 39.9$ (CH_2), 55.2 (OMe), 57.9 (CH_2), 113.5, 129.5, 130.1, 163.5 (C_6H_4), 198.6 (CO).

MS: $m/z = 162$ ($M^+ - 18$, 33), 135 (100), 92 (53), 77 (38).

HRMS: m/z Calc. 181.0865 $(MH)^+$, Found 181.0864 $(MH)^+$.

3-Hydroxy-1-(2-methylphenyl)propan-1-one (**7c**):
^{1}H NMR: $\delta = 2.46$ (3H, s), 3.08 (2H, t, $J = 5$ Hz), 3.40 (1H, br s), 3.94 (2H, t, $J = 5$ Hz), 7.18 (2H, t, $J = 7$ Hz), 7.31 (1H, t, $J = 7$ Hz), 7.62 (1H, d, $J = 8$ Hz).

^{13}C NMR: $\delta = 21.2$ ($ArCH_3$), 42.9, 57.8 (CH_2CH_2), 125.5, 128.6, 131.4, 131.7, 136.9, 138.1 (C_6H_4), 203.6 (CO).

MS: $m/z = 146$ ($M^+ - 18$, 99), 131 (63), 119 (58), 91 (100).

HRMS: m/z Calc. 165.0916 $(MH)^+$, Found 165.0915 $(MH)^+$.

3-Hydroxy-1-(4-methylphenyl)propan-1-one (**7d**):
^{1}H NMR: $\delta = 2.29$ (3H, s), 3.08 (2H, t, $J = 6$ Hz), 3.37 (1H, br s), 3.92 (2H, t, $J = 6$ Hz), 7.13 (2H, d, $J = 8$ Hz), 7.74 (2H, d, $J = 8$ Hz).

^{13}C NMR: $\delta = 21.3$ ($ArCH_3$), 40.2, 57.7 (CH_2CH_2), 127.9, 128.9, 133.9, 143.9 (C_6H_4), 199.5 (CO).

MS: $m/z = 146$ ($M - 18$, 35), 131 (7), 119 (100), 91 (85).

HRMS: m/z Calc. 165.0916 $(MH)^+$, Found 165.0912 $(MH)^+$.

3-Hydroxy-1-(4-chlorophenyl)propan-1-one (**7e**):
^{1}H NMR: $\delta = 2.00$ (1H, br s), 3.18 (2H, t, $J = 5$ Hz), 4.01 (2H, t, $J = 5$ Hz), 7.43 (2H, d, $J = 9$ Hz), 7.88 (2H, d, $J = 9$ Hz).

^{13}C NMR: $\delta = 40.4$, 57.8 (CH_2CH_2), 128.9, 129.3, 134.8, 139.8 (C_6H_4), 198.9 (CO).

MS: $m/z = 166$ ($M^+ - 18$, 30), 139 (100), 111 (43).

HRMS: m/z Calc. 185.0369 $(MH)^+$, Found 185.0371 $(MH)^+$.

Siloxane Synthesis and Siloxane Polymerization:
To a solution of silyl fluoride **6** (3.7 mmol) in MeCN (5 mL) was added 40% aq Bu_4NF (5 mmol) at r.t. over 2 h. MeCN was removed under vacuum, and the solvent replaced with CH_2Cl_2. The solution was worked up by first washing with dil AcOH, followed by washing with dil aq $NaHCO_3$. The organic layer was dried ($MgSO_4$), and the solvent removed to give the siloxane **8**. A small amount of the siloxane **8** (0.6 mmol) was dissolved in CH_2Cl_2 (0.50 mL), and the solution was cooled at 0°C, after which octamethylcyclosiloxane (3.7 mmol) and one drop of CF_3SO_3H were added successively. The reaction mixture was allowed to warm to r.t., and stirred overnight. The crude polymer was washed with excess MeOH, followed by extraction with pentane. Evaporation of pentane gave the siloxane polymer **9** (Table 2).

The support of our work by the Air Force Office of Scientific Research, MURI (Program Manager, Dr. Charles Lee), is gratefully acknowledged. Professor George Olah is thanked for his encouragement and support.

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