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SYNTHESIS OF SILICON - FUNCTIONALIZED DIMETHYLSILYL ENOL ETHERS FROM KETONES

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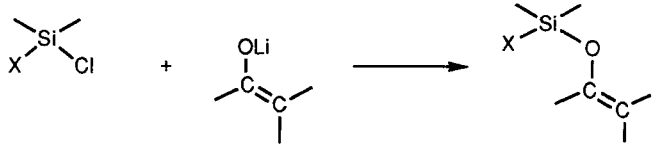
Symmetrical dimethylsilyl bis-enol ethers are obtained in good yield by reaction of ketones with dichlorodimethylsilane in the presence of triethylamine and sodium iodide. Reaction of ketones with N, N - diethylaminodimethylchlorosilane in the presence of triethylamine and sodium iodide followed by subsequent conversions provides a useful synthesis of silicon-functionalized dimethylsilyl enol ethers including unsymmetrical dimethylsilyl bis-enol ethers

Silicon-functionalized dimethylsilyl enol ethers (**1**, X=Cl[1], OR[2-5]) have been prepared by reaction of pre-formed alkali metal enolates with a variety of silyl chlorides (equation 1). A direct silylation of ketones

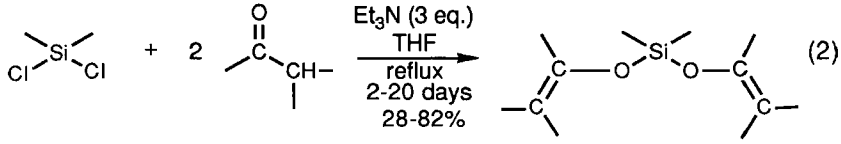


(1)

1

using a functionalized silyl chloride and triethlyamine would appear to offer an economical alternative to this route. However, Fataftah[3] has

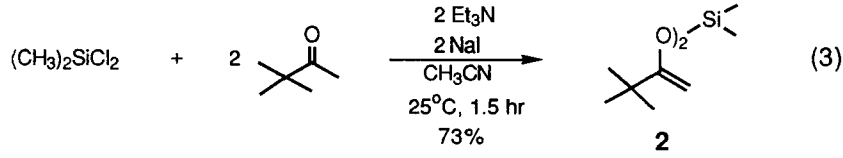
reported that the silylation of ketones with dichlorodimethylsilane requires extended reaction times and gives variable yields (equation 2).



(2)

Sodium iodide greatly accelerates the reactions of chlorotrimethylsilane with ketones. With this in mind, we examined the use of sodium iodide to promote the reaction of dichlorodimethylsilane with ketones.

The reaction of dichlorodimethylsilane with two equivalents of sodium iodide, two equivalents of triethylamine, and two equivalents of 3,3-dimethyl-2-butanone is complete in less than 2 hours at room temperature and gives a 73% yield of the bis-enol ether, **2**, (equation 3).

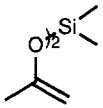
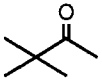
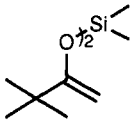
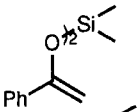
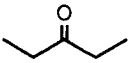
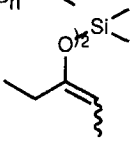
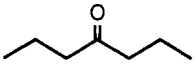
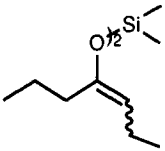
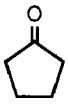
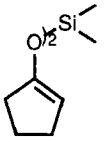
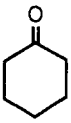
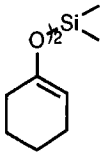
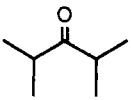
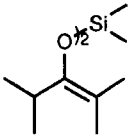


2 (3)

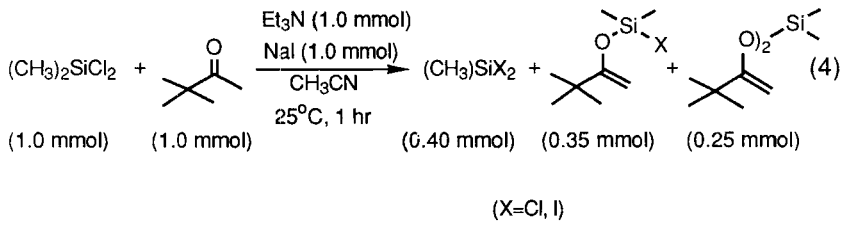
Under the same conditions, in the absence of sodium iodide, the yield of **2** was less than 5%. Using this sodium iodide procedure, a variety of ketones was converted to the corresponding bis-enol ethers in good yields (Table 1).

Unfortunately, the sodium iodide promoted reaction of dichlorodimethylsilane with one equivalent of ketone does not give a useful synthesis of chlorodimethylsilyl enol ethers. Under a variety of conditions, with one or two equivalents of sodium iodide, a mixture of mono- and bis-enol ethers is produced. The result shown in equation 4,

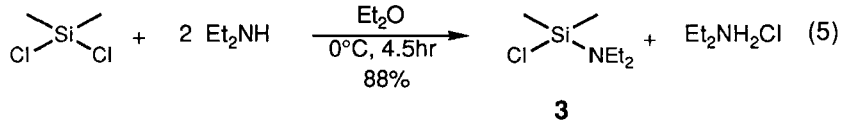
Table 1 - Preparation of Dimethylsilyl Bis-Enol Ethers

Entry	Ketone	Product	Time (hr)	Yield (%)
1			2	73
2			1.5	73
3			1.75	83
4			1.5	76
5			5	76
6			1.5	76
7			2	72
8			20	72

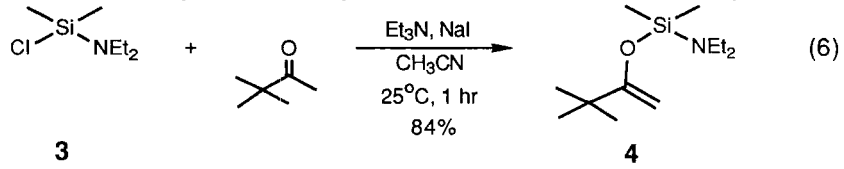
obtained with 3,3-dimethyl-2-butanone and based on the integration of ^1H NMR signals, is representative.



Because N,N-diethylaminodimethylchlorosilane, **3**, is readily prepared[6], equation 5, and because the silicon-nitrogen bond is readily converted to a variety of silicon-heteroatom bonds, we examined the silylation reactions of ketones with compound **3**.



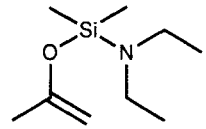
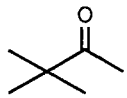
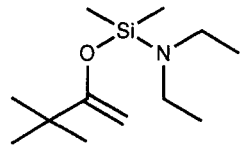
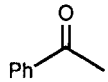
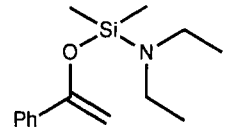
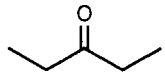
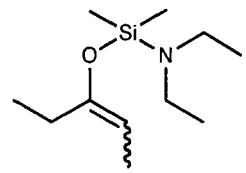
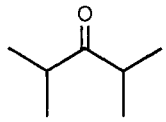
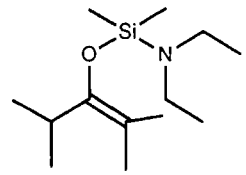
Reaction of 3,3-dimethyl-2-butanone with **3** in the presence of sodium iodide gave an 84% yield of the mono-enol ether **4**, equation 6.



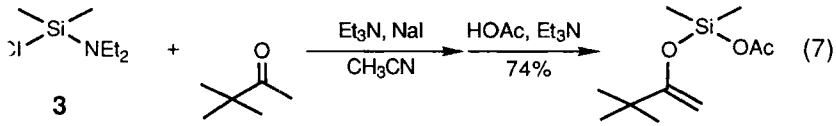
A similar reaction conducted in the absence of sodium iodide gave less than 1% of **4**. Using the sodium iodide procedure, a series of ketones was converted to the corresponding mono-enol ethers in generally good yields as shown in Table 2.

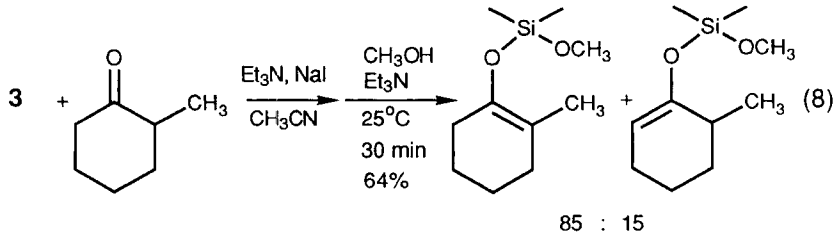
Quenching the silylation reaction mixtures with acetic acid or with methanol gives a simple synthesis of the corresponding acetoxy (equation 7) or methoxy (equation 8) substituted enol ethers. Equation 8

Table 2 - Preparation of N,N-diethylaminodimethylsilyl Enol Ethers

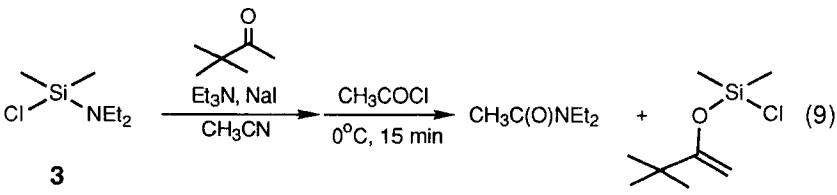
Entry	Ketone	Product	Yield (%)
1			79
2			84
3			66
4			87
5			63

illustrates the regioselectivity of the silylation step which appears to be quite similar to that observed for chlorotrimethylsilane in the presence of sodium iodide and triethylamine.



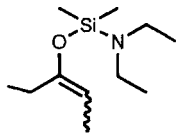
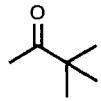
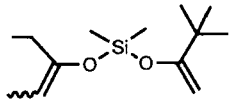
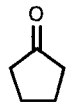
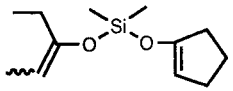
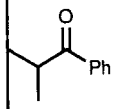
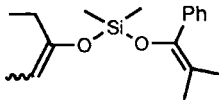
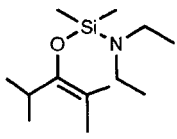
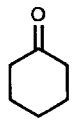
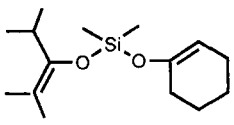
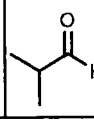
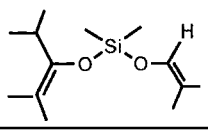


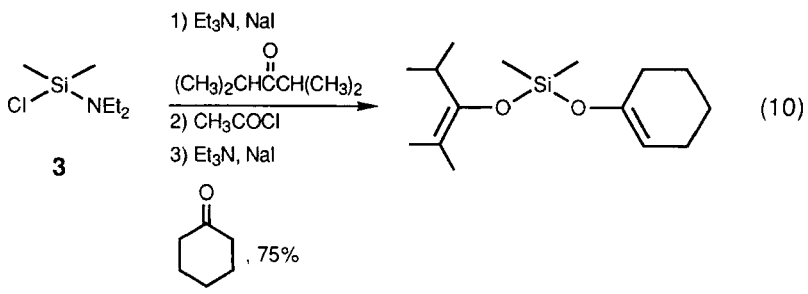
Quenching the silylation reaction mixtures with acetyl chloride results in acylation at nitrogen to produce N,N-diethylacetamide together with chlorodimethylsilyl enol ethers (equation 9). This simple synthesis



of chlorosilyl enol ethers should allow for substitution at silicon with a range of nucleophiles. In particular, sodium iodide promoted reaction with ketones furnishes a useful synthesis of unsymmetrical bis-enol ethers as shown in equation 10 and Table 3. These previously unknown compounds are of interest for application in the known coupling reactions of silyl enol ethers[7] and we shall report our results in this area shortly.

Table 3 - Preparation of Unsymmetrical Bis-Enol Ethers

Entry	Aminosilyl Enol Ether	Ketone	Product	Yield (%)
1				45
2				52
3				28
4				75
5				63



Experimental

General

Solvents, amines and ketones were dried by distillation from CaH_2. Dichlorodimethylsilane was distilled from CaH_2 and stored over polyvinylpyridine. Sodium iodide was dried in an abderhalden apparatus at 0.1 mmHg with refluxing toluene for 8 hours. ^1H and ^{13}C NMR spectra were recorded with a Varian VXR-300 (s) at 300 MHz and 75 MHz respectively. All glassware used in the following procedures was oven dried (120° C) and purged with argon. Typically, the reactions were conducted in round bottom flasks fitted with magnetic stirring, a gas takeoff valve (to Hg bubbler) and a septum inlet. Addition of reagents employed standard syringe or cannula transfer techniques. Concentration of organic extracts was accomplished at reduced pressure (aspirator) using a rotory evaporator.

Preparation of Symmetrical Dimethylsilyl Bis-enol Ethers

The following procedure is representative. The results apprear in Table 1.

1. Bis (1-propenyl-2-oxy)dimethylsilane

To a solution of NaI (45 g, 300 mmol) in CH_3CN (300 mL) dichlorodimethylsilane (18.2 mL, 150 mmol) was added and allowed to stir for 10 minutes at room temperature. Et_3N (42 mL, 300 mmol) followed by acetone (22 mL, 300 mmol) were added and allowed to stir for 1 hour and 50 minutes at room temperature. Workup in 400 mL 1:1 ice/saturated aqueous $NaHCO_3$ and 200 mL pentane. The aqueous layer was extracted 2 x 50 mL pentane and the combined organic layers dried over Na_2SO_4. Filtered, concentrated and distilled through a 15 cm Vigreux column gave 18.73 (73%) at 87° C (70 mm Hg).

IR (neat): 3115, 2990, 2968, 2957, 2922, 1642, 1443, 1260, 1051, 907.

^1H NMR (300 Mz, $CDCl_3$): δ 0.26 (s, 6H, $SiCH_3$) 1.79 (d, 6H, 1Hz, CH_3), 4.10 (bs, 2H, enol), 4.2 (s, 2H, enol)

^{13}C NMR (75 MHz, $CDCl_3$): δ -2.50, 22.30, 92.17, 154.77.

MS-EI (70 eV): 157 (M-15, 9), 144 (49), 115 (46), 77 (41), 75 (base).

2. Bis-(3,3-dimethyl-1-butenyl-2-oxy)dimethylsilane

Using the procedure described above on a 80 mmol scale gave 15.05 g (73%) at 115-118° C (3 mm Hg).

IR (neat): 3125, 1969, 2913, 2872, 1626, 1464, 1254, 1015, 885.

^1H NMR (300 MHz, $CDCl_3$): δ 0.24 (s, 6H, $SiCH_3$), 1.05 (s, 18H, t-Bu), 4.12 (s, 4H, enol)

^{13}C NMR (75 MHz, $CDCl_3$): δ -2.92, 27.99, 36.34, 87.04, 165.92.

MS-EI (70 eV): 241 (M-15, 1.5), 199 (16), 157 (7), 155 (10), 75 (base), 57 (14).

3. Bis (α-styryloxy)dimethylsilane

Using the procedure described above on 43 mmol scale gave 10.63 g (83%) at 112-113° C (0.008 mm Hg).

IR (neat): 3119, 3108, 3085, 3059, 3036, 3029, 2967, 2907, 1688,, 1624, 1576, 1445, 1262, 1015, 853.

^{1}H NMR (300 MHz, CD_3CN): δ 0.40 (s, 6H, $SiCH_3$), 4.65 (d, 2H, 2 Hz, enol), 5.06 (d, 2H, 2 Hz, enol), 7.3-7.4 (m, 6H, Ar), 7.65-7.8 (m, 4H, Ar).
^{13}C NMR (75 MHz, CD_3CN): δ -3.04, 92.59, 125.54, 128.73, 129.02, 137.16, 155.04.
MS-EI (70 eV): 297 (M+1, 9), 296 (35), 281 (17), 268 (base), 219 (3), 205 (57),, 176 (25), 103 (9), 75 (49).

4. Bis-(2-pentenyl-3-oxy)dimethylsilane

Using the procedure described above on a 90 mmol scale gave 15.55 g (76%) at 117-120° C (10 mm Hg) as a mixture of isomers: 66 ZZ : 30ZE : 4EE.
IR (neat): 3046, 2971, 2940, 2921, 2882, 1682, 1464, 1260, 1040, 909.
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.21 (minor) 0.23 (major) (s, 6H, $SiCH_3$), 1.01 (t, 6H, 7.5 Hz, $\underline{CH_2}CH_3$), 1.51 (dt, 6H, 6.6 Hz, 1.5 Hz, $=CHCH_3$), 2.08 (m, 4H, $CH_2\underline{CH_3}$), 4.52 (qt, 1.4H, 6.6 Hz, 1.2 Hz, enol (major)), 4.73 (q, 0.7H, 6.6 Hz, enol (minor)).
^{13}C NMR (75 MHz, $CDCl_3$): δ -1.95 (minor), -1.56 (major), 10.59, 11.56, 11.66, 11.68, 23.94 (EE), 29.28 (ZE), 29.35 (ZZ), 101.02 (major), 101.07 (minor), 152.12.
MS-EI (70 eV): 229 (M+1, 1.3), 228 (1), 159 (25), 147 (41), 133 (19), 75 (base), 73 (72), 69 (3).

5. Bis(3-heptenyl-4-oxy)dimethylsilane

Using the procedure described above on a 50 mmol scale gave 10.85 g (76%) at 88-93° C (1.2 mm Hg) as a mixture of isomers: ZZ/ZE 53:47.
IR (neat): 3048, 2956, 2934, 2874, 1676, 1458, 1260, 1046, 970.
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.20 (minor) 0.21 (major) (s, 6H, $SiCH_3$), 0.84-0.96 (m, 12H, CH_3), 1.47 (sextet, 4H, 7.5 Hz, $CH_3\underline{CH_2}CH_2$), 1.87-2.07 (m, 8H, CH_2), 4.43 (t, H, 67.5 Hz, enol (major)), 4.74 (t, 7.5H, enol (minor)).
^{13}C NMR (75 MHz, $CDCl_3$): δ -1.96 (minor), -1.59 (major), 13.63, 13.65, 13.71, 14.42, 15.26, 18.58, 18.63, 20.20, 20.21, 20.27, 32.98 (EE), 38.45 (ZE), 38.51 (ZZ), 110.15 (minor) 110.31 (major), 110.37 (minor), 148.89.
MS-EI (70 eV): 285 (M+1, 3), 284 (12), 241 (4), 171 (36), 170 (base), 113 (3), 75 (64).

6. Bis(cyclopentenyl-1-oxy)dimethylsilane

Using the procedure described above on a 100 mmol scale gave 16.95 g (76%) at 74° C (0.55 mm Hg).
IR (neat): 3071, 2959, 2903, 2853, 1649, 1441, 1264, 1032, 938.
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.26 (s, 6H, $SiCH_3$), 1.84 (quintet, 4H, 7.5H, CH_2 C-4), 2.20-2.32 (m, 8H, CH_2), 4.74 (quintet, 2H, 1.8 Hz, enol).
^{13}C NMR (75 MHz, $CDCl_3$): δ -2.46, 21.32, 28.64, 33.11, 103.58, 153.71.
MS-EI (70 eV): 225 (M+1, 8), 224 (33), 195 (19), 75 (base), 67 (75).

7. Bis(cyclohexenyl-1-oxy)dimethylsilane

Using the procedure described above on a 100 mmol scale gave 16.95 g (76%) at 74° C (0.55 mm Hg).
IR (neat): 3071, 2959, 2903, 2853, 1649, 1441, 1264, 1032, 938.

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.26 (s, 6H, $SiCH_3$), 1.84 (quintet, 4H, 7.5Hz, CH_2 C-4), 2.20-2.32 (m, 8H, CH_2), 4.74 (quintet, 2H, 1.8 Hz, enol).
^{13}C NMR (75 MHz, $CDCl_3$): δ -2.46, 21.32, 28.64, 33.11, 103.58, 153.71.
MS-EI (70 eV): 225 (M+1, 8), 224 (33), 195 (19), 75 (base), 67 (75).
Spectral data is in agreement with reference 5.

e. Bis(2,4-dimethyl-2-pentenyl-3-oxy)dimethylsilane

Using the procedure described above on a 57.5 mmol scale gave 12.34 g (75%) at 85-88° C (0.85 mm Hg).
IR (neat): 2967, 2930, 2903, 2870, 1749, 1470, 1560, 1252, 1074, 959.
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.19 (s, 6H, $SiCH_3$), 0.99 (d, 12H, 6.9 Hz, $CH(\underline{CH_3})_2$), 1.61 (s, 12H, $=C(CH_3)_2$), 2.82 (septet, 2H, 6.9 Hz, $\underline{CH}(CH_3)_2$).
^{13}C NMR (75 MHz, $CDCl_3$): δ -1.86, 18.52, 1870, 20.00, 29.18, 107.14, 149.80.
MS-EI (70 eV): 285 (M+1, 0.2), 284 (0.4), 269 (0.3), 170 (85), 155 (27), 75 (base).

Preparation of Dialkylaminodimethylsilyl Enol Ethers

The following procedure is representative. The results appear in Table 2.

1. 2-(N,N-diethylaminodimethylsiloxy)propene

To a solution of NaI (30 g, 200 mmol) in CH_3CN (200 mL) N,N-diethylaminodimethylchlorosilane (29.8 g, 196 mmol) was added and allowed to stir for 10 minutes at room temperature. Et_3N (28 mL, 200 mmol) followed by acetone (14.7 mL, 200 mmol) were added and allowed to stir for 2 hours at room temperature. The mixture was extracted 4 x 50 mL with pentane via syringe. Concentration and distillation at reduced pressure through a 7 cm Vigreux column gave 29.2 g (79%) at 82-84° C (10 mm Hg).
IR (neat): 3115, 2967, 2932, 2869, 1636, 1449, 1373, 1279, 1256, 1173, 1044, 934.
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.16 (s, 6H, $SiCH_3$), 0.99 (t, 6H, 7 Hz, NCH_2CH_3), 1.75 (d, 3H, 0.6 Hz), 2.85 (q, 4H, 7 Hz, NCH_2CH_3), 4.03 (d, 1H, 0.6 Hz, enol), 4.05 (s, 1H, enol).
^{13}C NMR (75 MHz, $CDCl_3$): δ -2.13, 15.64, 22.77, 39.59, 91.45, 155.82.
MS-EI (70 eV): 172 (M-15, 26), 130 (4), 115 (59), 75 (16), 58 (88), 40 (base).

2. 2-(N,N-diethylaminodimethylsiloxy)-3,3-dimethyl-1-butene

Using the procedure described above on a 200 mmol scale gave 38.38 g (84%) at 55° C (0.65 mm Hg). (literature[1]) bp. 101-105° C, 25 mm Hg).
IR (neat): 3127, 2967, 2932, 2913, 2890, 1617, 1483, 1375, 1298, 1258, 1186, 1032, 934, 791, 693.
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.16 (s,6H, $SiCH_3$), 0.99 (t, 6H, 7 Hz, $NCH_2\underline{CH_3}$) 1.02 (s, 9H, $(CH_3)_3$, 2.86 (q, 4H, 7 Hz, $N\underline{CH_2}CH_3$), 3.92 (d, 1H, 1Hz, enol) 4.02 (d, 1H, 1 Hz, enol).

^{13}C NMR (75 MHZ, $CDCl_3$): δ -1.85, 15.64, 28.15, 36.55, 39.65, 85.25, 167.05.
MS-EI (70 eV): 229 (M+, 3), 214 (30), 172 (7), 157 (26), 130 (26), 75 (base).

3. α-(N,N-diethylaminodimethylsiloxy)styrene

Using the procedure described above on a 200 mmol scale gave 33.02 g (66%) at 89-91° C (0.45 mm Hg).
IR (neat): 3059, 3027, 2968, 2930, 2869, 1617, 1574, 1493, 1466, 1447, 1318, 1304, 1288, 1258, 1173, 1030, 936, 831.

^1H NMR (300 MHz, CD_3CN): δ 0.22 (s, 6H, $SiCH_3$), 0.98 (t, 6H, 7 Hz, NCH_2CH_3), 2.89 (q, 4H, 7 Hz, NCH_2CH_3), d 4.46 (d, 1H, 1.5 Hz, enol) 4.94 (d, 1H, 1.5 Hz, enol), 7.4-7.2 (m, 3H, Ar), 7.65-7.55 (m, 2H, Ar).

^{13}C NMR (75 MHz, $CDCl_3$): δ -2.27, 15.65, 39.64, 91.14, 125.22, 127.96, 127.99, 137.88, 155.52.
MS-EI (70 eV): 249 (M+, 12), 234 (25), 177 (base), 101 (22), 77 (12), 75 (84), 58 (20).

4. 3-(N,N-diethylaminodimethylsiloxy)-2-pentene.

Using the procedure described above on a 150 mmol scale gave 26.37 g (92%) at 45-46° C (0.4 mm Hg) as a mixture of isomers, Z/E 88:12.
IR (neat): 3042, 2969, 2934, 2867, 1678, 1466, 1375, 1256, 1208, 1194, 1175, 1030, 934.

^1H NMR (300 MHz, $CDCl_3$): δ 0.16 (s, 6H, $SiCH_3$), 0.99 (t, 6H, 6.9 Hz, NCH_2CH_3), 1.00 (t, 3H, 7.5 Hz, CH_3CH_2-), 1.50 (dt, 3H, 6.6, 1.5 Hz, $=CHCH_3$), 2.02 (qt, 2H, 7.5, 1.5 Hz, CH_3CH_2-), 2.86 (q, 4H, 6.9 Hz, NCH_2CH_3), 4.45 (q, 0.9 H, 6.6 Hz, enol (Z)), 4.60 (q, 0.1 H, 6.6 Hz, enol (E)).

^{13}C NMR (75 MHz, $CDCl_3$): δ -1.71, 10.63, 11.77, 15.68, 24.00 (E), 29.34 (Z), 39.56, 100.35, 152.74.
MS-EI (70 eV): 216 (M+1, base), 200 (6), 130 (11), 86 (9), 75 (37), 73 (69), 69 (27).

5. 3-(N,N-diethylaminodimethylsiloxy)-2,4-dimethyl-2-pentene

Using the procedure described above on a 60 mmol scale gave 9.15 g (63%) at 54-56° C (0.4 mm Hg).
IR (neat): 2967, 2930, 2867, 1672, 1468, 1375, 1264, 1204, 1169, 1073, 1030, 932.

^1H NMR (300 MHz, $CDCl_3$): δ 0.15 (s, 6H, $SiCH_3$), 0.96 (d, 6H, 6.6 Hz, $(CH_3)_2CH$), 0.99 (t, 6H, 6.9 Hz, $N(CH_2CH_3)_2$) 1.57 (s, 3H, $=C(CH_3)_2$), 1.58 (s, 3H, $=C(CH_3)_2$), 2.77 (septet, 1H, 6.6 Hz, $(CH_3)_2CH$), 2.88 (q, 4H, 6.9 Hz, $N(CH_2CH_3)_2$).

^{13}C NMR (75 MHz, $CDCl_3$): δ -1.50, 15.54, 1855, 18.81, 20.06, 29.38, 39.67, 106.59, 149.15.
MS-EI: (70 eV): 244 (M+1, base), 229 (12), 201 (10), 149 (31), 133 (25), 97 (30), 75 (4), 73 (5).

Preparation of 2-(acetoxydimethylsiloxy)-3,-dimethyl-1-butene

To a solution of NaI (7.5 g, 50 mmol) in CH_3CN (50 mL) N,N-dimethylaminodimethylchlorosilane (6.89 g, 50 mmol) was added and allowed to stir for 15 minutes at room temperature, Et_3N (7.0 mL, 50 mmol) followed by pinacolone (6.3 mL, 50 mmol) were added and allowed to stir for 1 hour at room temperature. Et_3N (7.0 mL, 50 mmol) followed by acetic acid (2.9 mL, 50 mmol) were added and allowed to stir for 0.5 hour at room temperature. The reaction mixture was extracted 5 x 50 mL pentane via syringe. The combined pentane extracts were concentrated to give 14.64 g crude yellow liquid. Distillation at reduced pressure gave 8.01 g (74%) at 86-92° C (32 mm Hg).
IR (neat): 3127, 2969, 2915, 2872, 1728, 1630, 1483, 1464, 1267, 1042, 1019, 885.
^1H NMR (300 MHz, $CDCl_3$): δ 0.39 (s, 6H, $SiCH_3$), 1.06 (s, 9H, $(CH_3)_3$), 2.09 (s, 3H, $COCH_3$), 4.13 (d, 1H, 1.5Hz, enol), 4.18 (d, 1H, 1.5Hz, enol)
^{13}C NMR (75 MHz, $CDCl_3$): δ -2.10, 22.75, 27.92, 36.30, 87.98, 132.15 165.76.
MS-EI (70 eV): 216 (M+, 2), 201 (0.6), 157 (0.3), 117 (base), 75 (70), 43 (16).

Preparation of 1-(methoxydimethylsiloxy)-2-methylcyclohexene and 1-(methoxydimethylsiloxy)-6-methylcyclohexene.

To a solution of NaI (5.25 g, 35 mmol) in CH_3CN (70 mL) $(CH_3)_2Si(Cl)N(CH_3)_2$ (4.82 g, 35 mmol) was added and allowed to stir for 15 minutes at room temperature. Et_3N (4.9 mL, 25 mmol) followed by 2-methylcyclohexanone (4.2 mL, 35 mmol) were added and allowed to stir for 30 minutes at room temperature. The mixture was cooled to 0° C with an ice bath and Et_3N (4.9 mL, 35 mmol) followed by CH_3OH (1.4 mL, 35 mmol) were added and allowed to stir for 30 minutes. Workup with 150 mL 1:1 ice/$NaHCO_3$ and 150 mL pentane. The aqueous layer was extracted 2 x 50 mL pentane and the combined organic layers dried over Na_2SO_4. Filtered and concentrated to give 7.33 g crude material. Distilled at reduced pressure to give 4.47 g (64%) at 52-56° C (0.3 mm Hg), as a mixture of isomers 85 : 15 (more substituted / less substituted).
IR (neat): 2963, 2932, 2859, 2838, 1692, 1447, 1258, 1184, 1094, 947, 831.
^1H NMR (300 MHz, $CDCl_3$): δ 0.14 (s, 6H, $SiCH_3$), 1.03 (d, 0.45H, 6.9 Hz, 6-Me (minor)), 1.68-1.46 (m, 6.4 H), 1.96-1.88 (m, 2H), 2.09-2.01 (m, 2H), 3.50 (s, 3H, OCH_3), 4.89 (td, 0.15H, 4.0, 1.2 Hz, enol (minor)).
^{13}C NMR (75 MHz, $CDCl_3$): δ -2.90, 2.89, 16.13, 18.62, 20.13, 22.94, 23.76, 30.00, 30.11, 30.12, 31.56, 33.41, 50.13, 103.98, 111.96, 142.35.
MS-EI (70 eV): 200 (M^+, 2.3), 185 (29), 112 (28), 75 (10), 73 (base)

Preparation of Unsymmetrical Dimethylsilyl Bis-Enol Ethers
The results appear in Table 3.

1. 3-(3',3'-dimethyl-1'-butenyl-2'-oxydimethylsiloxy)-2-pentene

To a solution of 3-(N,N-diethylaminodimethylsiloxy)-2-pentene (6.7 g, 35 mmol) in CH_3CN (70 mL) cooled to 0° C, acetyl chloride (2.49, 35 mmol) was added and allowed to stir for 15 minutes at 0° C. Pinacolone (4.4 mL, 35 mmol), Et_3N (4.9 mL, 35 mmol), NaI (5.25 g, 35 mmol) and pentane (70 mL) were added in that order and allowed to stir for 30 minutes at 0° C. The cooling bath was removed and the reaction mixture was allowed to stir for 3.5 hours at room temperature. The supernatent pentane layer was removed via syringe and the reaction mixture extracted 4 x 20 mL with pentane via syringe. The combined pentane layers were concentrated and distilled at reduced pressure to give 3.81 g (45%) at 50-53 ° C (0.2 mmHg), as a mixture of isomers 88:12 Z/E.

IR (neat): 3125, 3046, 2969, 2940, 2917, 2870, 1682, 1626, 1464, 1296, 1260, 1036, 839.

^1H NMR (300 MHz, $CDCl_3$): δ 0.23 (minor), 0.26 (major) (s, 6H, $SiCH_3$), 1.03 (t, 3H, 7.5 Hz, $CH_2\underline{CH_3}$), 1.05 (s, 9H, $(\underline{CH_3})_3C$), 1.53 (dt, 3H, 6.6 Hz, 1.2 Hz, $=CH\underline{CH_3}$), 2.09 (m, 2H, $\underline{CH_2}CH_3$), 4.11 (d, 1H, 1.2 Hz, enol), 4.14 (d, 1H, 1.2 Hz, enol), 4.54 (major), 4.75 (minor) (q, 1H, 6.6 Hz, enol)).

^{13}C NMR (75 MHz, $CDCl_3$): δ -2.59 (minor), -2.27 (major), 10.52, 11.57, 11.71, 23.90 (minor), 28.02, 29.23 (major), 36.35, 87.03, 101.12, 152.21, 166.00.

MS-EI (70 eV): 243 (M+1, 7), 242 (2), 227 (5), 185 (38), 157 (20), 142 (base), 113 (25), 75 (25).

2. 3-(cyclopentenyl-1'-oxydimethylsiloxy)-2-pentene

Using the procedure described above on a 35 mmol scale gave 4.11 g (52%) at 68-71° C (0.75 mmHg), as a mixture of isomers 88:12 Z/E.

IR (neat): 3069, 3046, 2969, 2940, 2921, 2853, 1682, 1648, 1456, 1262, 1040, 909.

^1H NMR (300 MHz, $CDCl_3$): δ 0.22 (minor), 0.24 (major) (s, 6H, $SiCH_3$), 0.95-1.10 (m, 3H, 7.5 Hz, $CH_2\underline{CH_3}$), 1.49 (dt, 3H, 6.6 Hz, 1.2 Hz, $=CH\underline{CH_3}$), 1.80-2.40 (m, 8H, CH_2), 4.52 (qt, 0.9H, 6.6 Hz, 1.2 Hz, enol, major), 4.73 (quintet, 1.1H, 1.8 Hz, enol), 4.54 (major), 4.75 (minor) (q, 1H, 6.6 Hz, enol)).

^{13}C NMR (75 MHz, $CDCl_3$): δ -2.02 (major), 7.90, 10.48, 11.65, 21.35, 23.21 (minor), 28.64, 29.22 (major), 33.24, 35.43, 101.15, 103.44, 152, 154.

3. 3-(β,β-dimethyl)-α-styryloxydimethylsiloxy)-2-pentene

To a solution of 3-(N,N-diethylaminodimethylsiloxy)-2-pentene (4.79 g, 25 mmol) in CH_3CN (25 mL), acetyl chloride (1.78 25 mmol) was added and allowed to stir for 10 minutes at room temperature. Isobutyrophenone (3.75 mL, 25 mmol), and Et_3N (3.5 mL, 25 mmol) were added and the mixture was heated to 40-50° C in an oil bath. NaI (4.5 g, 30 mmol) in CH_3CN (30 mL) was added dropwise via a pressure equalized addition funnel over 35 minutes. The mixture was maintained

at 40-50° C for an additional 55 minutes. Workup in 200 mL 1:1 ice/saturated aqueous $NaHCO_3$ and 100 mL pentane. The aqueous layer was extraced 2 x 50 mL pentane and the combined oragnic layers dried over Na_2SO_4. Concentration and distillation (bulb to bulb) at reduced pressure gave 2.04 g (28%) at 67-71° C (oven) (1.1 mm Hg) as a mixture of isomers Z/E 88:12.

IR (neat): 3058, 3025, 2968, 2919, 2880, 2863, 1682, 1653, 1260, 1154, 1047, 907, 866, 801.

^1H NMR (300 MHz, $CDCl_3$): δ 0.005 (minor), 0.01 (major) (s, 6H, $SiCH_3$), 0.92 (minor), 0.97 (major) (t, 3H, 7.5 Hz, $\underline{CH_3}CH_2$), 1.46 (dt, 3H, 6.6 Hz, 1.2 Hz, =CH$\underline{CH_3}$) 1.66 (s, 3H, CH_3), 1.81 (s, 3H, CH_3), 1.97 (m, 2H, $CH_3\underline{CH_2}$), 4.45 (major) (qt, 0.9H, 6.6 Hz, 1.2 Hz, enol), 4.62 (minor) (q, 0.1H, 6.6 Hz, enol), 7.18-7.38 (m, 5H, Ar).

^{13}C NMR (75 MHz, $CDCl_3$): δ -1.68 (minor), -1.34 (major), 10.52, 11.63, 18.19, 19.81, 23.85 (minor), 29.25 (major), 100.87, 113.40, 127.62, 127.70, 129.10, 138.55, 142.70, 152.09.

MS-EI (70 eV): 159 (2), 148 (2), 131 (1), 105 (base), 77 (79), 75 (11), 73 (8).

4. 3-(cyclohexenyl-1'-oxydimethylsiloxy)-2,4-dimethyl-2-pentene

Using the procedure described above on a 25 mmol scale gave 5.06 g (75%) at 81-84° C (0.50 mmHg), as a mixture of isomers Z/E 88:12.

IR (neat): 2965, 2932, 2886, 2863, 1672, 1458, 1368, 1258, 1190, 1074, 901.

^1H NMR (300 MHz, $CDCl_3$): δ 0.21 (s, 6H, $SiCH_3$), 0.98 (d, 6H, 6.9 Hz, iPr), 1.45-1.54 (m, 2H, CH_2), 1.58 (s, 3H, CH_3), 1.60 (s, 3H, CH_3), 1.61-1.69 (m, 2H, CH_2), 1.95-2.07 (m, 4H, CH_2), 2.80 (septet, 1H, 6.9 Hz, iPr), 4.98 (tt, 1H, 4 Hz, 1.2 Hz, enol).

^{13}C NMR (75 MHz, $CDCl_3$): δ -1.85, 18.48, 18.54, 19.92, 22.28, 23.12, 23.79, 29.04, 29.65, 104.64, 107.55, 148.58, 149.56.

MS-EI (70 eV): 269 (M+1, 2), 268 (6), 267 (1), 187 (10), 171 (25), 170 (base), 155 (18), 97 (1), 75 (3).

5. 3-(2'-methylpropenyl-1'-oxydimethylsiloxy)-2,4-dimethyl-2-pentene

Using the procedure described above on a 25 mmol scale gave 3.84 g (63%) at 63-65° C (0.8 mmHg).

IR (neat): 2967, 2926, 2872, 1686, 1676, 1456, 1260, 1163, 1076, 957, 884.

^1H NMR (300 MHz, $CDCl_3$): δ 0.20 (s, 6H, $SiCH_3$), 0.97 (d, 6H, 6.9 Hz, iPr), 1.53 (d, 3H, 1.5 Hz, CH_3), 1.57 (s, 3H, CH_3), 1.59 (d, 3H, 1.5 Hz, CH_3), 1.60 (s, 3H, CH_3), 2.80 (septet, 1H, 6.9 Hz, iPr), 6.12 (septet, 1H, 1.5 Hz, enol).

^{13}C NMR (75 MHz, $CDCl_3$): δ -2.46, 14.85, 18.45, 19.30, 19.86, 28.99, 107.69, 114.04, 132.18, 148.42.

MS-EI (70 eV): 243 (M+1, 2), 242 (1), 241(3), 227 (1), 187 (40), 129 (10), 113 (6), 75 (35), 73 (78), 71 (58), 59 (base), 55 (12).

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