Cross Aldol Products from α-Haloalkoxysilanes and Silyl Enol Ethers

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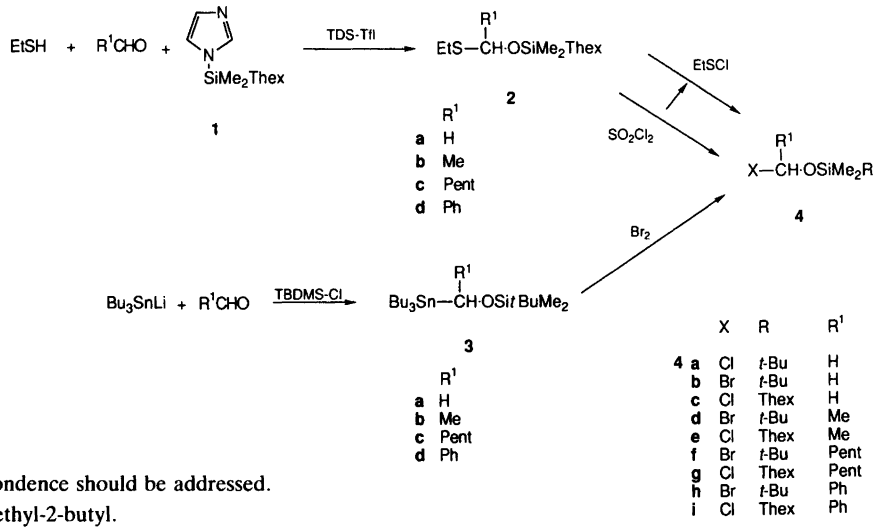
Antonsen, Ø., Benneche, T., Gundersen, L.-L. and Undheim, K., 1992. Cross Aldol Products from α-Haloalkoxysilanes and Silyl Enol Ethers. – Acta Chem. Scand. 46: 172–177.

α-Haloalkoxysilanes have been prepared by cleavage of the C–S bond in *O,S*-acetals with sulfuryl chloride, and by cleavage of C–Sn bond in α-silyloxystannanes by bromine. The α-haloalkoxysilanes, both after isolation or after preparation *in situ* react with silyl enol ethers to yield silyl-protected cross aldol products. The reaction is catalyzed by Lewis acids.

The aldol reaction is an efficient tool for the formation of C–C bonds.[1] Problems associated with this reaction, such as dehydration, self-condensation and polyaldol condensation[2] can be avoided by reaction of silyl enol ethers with aldehydes in the presence of fluoride ion as a catalyst.[3] Ketones will participate in the reaction when stoichiometric amounts of titanium tetrachloride are used.[4] Aldol products, where the alcoholic oxygen is protected with an alkyl substituent, are obtained by reacting silyl enol ethers with α-halo ethers.[5] Alkyl groups, however, have limited value in the protection of alcohols because of the conditions required for their removal.[6] In recent years silyl groups, e.g. *t*-butyldimethylsilyl (TBDMS), have gained wide popularity in alcohol protection, because of their stability and their ready removal under mild conditions.[7] We report herein the formation of aldol products where the alcoholic oxygen is protected with a *t*-butyldimethylsilyl or a dimethylthexylsilyl† group. The silyl protected aldol products were obtained by reaction of α-haloalkoxysilanes with silyl enol ethers.

The primary *O,S*-acetal **2a** (R^1 = H) was prepared from ethanethiol and paraformaldehyde followed by reaction with dimethylthexylsilyl chloride in the presence of an amine base.[8] The secondary hemithioacetals **2b** and **2d**, however, were not formed in the corresponding reaction between ethanethiol and acetaldehyde or benzaldehyde. Instead, these hemithioacetals and **2c** were prepared by an alternative method based on a recently published method for the synthesis of *O*-trimethylsilyl monothioacetals from thiols and carbonyl compounds.[9] The reaction was effected by addition of the aldehyde to a mixture of ethanethiol, 1-(dimethylthexylsilyl)imidazole and a catalytic amount of dimethylthexylsilyl triflate (TDS-Tfl), and the products were the corresponding *O*-dimethylthexylsilyl monothioacetals **2b–2d** (53–61 % yields) (Scheme 1).

The α-haloalkoxysilanes **4** were formed from the *O,S*-acetals **2** or stannanes **3** in sulfuryl chloride- or bromine-mediated cleavage reactions. The former reaction is an extension of our previous work on the cleavage of the C–S bond in *O,S*-acetals by sulfuryl chloride.[8,10] In the cleavage



Scheme 1.

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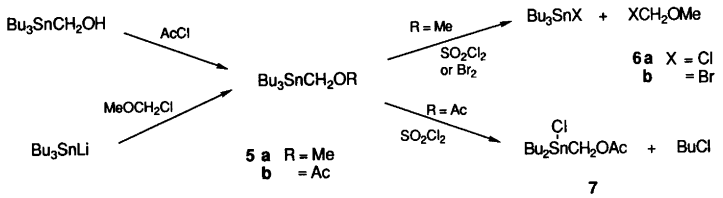
† Thexyl = 2,3-dimethyl-2-butyl.

of the *O,S*-acetals with sulfuryl chloride, ethanesulfenyl chloride is formed together with the α-halo ether. The former is a powerful electrophile itself which reacts with silyl enol ethers,[11] but which can, however, be removed together with the solvent on evaporation. Alternatively, ethanesulfenyl chloride can be used for the cleavage of the *O,S*-acetals to α-chloro ethers in which case diethyl disulfide is the coproduct. Thus in the reaction with sulfuryl chloride 0.5 mol equivs. of sulfuryl chloride were used to cleave half of the *O,S*-acetal. The remaining half was cleaved by the ethanesulfenyl chloride generated in the first reaction.[10e]

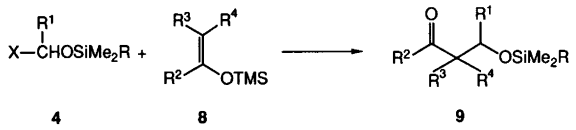


Scheme 2.

It is well known that C–Sn bonds are cleaved by bromine or iodine,[12] and in Bu_3SnCH_2SR it is the alkylthiomethyl group which is selectively split off by halogens.[13] This work confirms the selective formation of α-halo ethers **4** from α-silyloxyalkylstannanes in reactions with sulfuryl chloride, or preferably bromine.

The C–S bond in the *O,S*-acetals **2** is cleaved faster than the C–Sn bond in the stannanes **3** by sulfuryl chloride. The reaction with the acetals is run at −78 °C whereas only **3a** of the stannanes reacts at ambient temperature. The stannanes, however, can be cleaved by bromine at −78 °C.

The preferential cleavage of the ether substitutent in the stannanes **3** can be rationalized in terms of the ability of tin



4 **8** **9**

	R	R^1	R^2	R^3	R^4
9 a	*t*-Bu	H	Me	H	H
b	Thex	H	Me	H	H
c	Thex	H	-(CH2)3-		H
d	Thex	H	-(CH2)4-		H
e	Thex	H	Ph	H	H
f	Thex	H	MeO	Me	Me
g	*t*-Bu	Me	Me	H	H
h	Thex	Me	Ph	H	H
i	*t*-Bu	Pent	Me	H	H
j	Thex	Pent	Ph	H	H
k	*t*-Bu	Ph	Me	H	H
l	Thex	Ph	Ph	H	H

Scheme 3.

to stabilize an adjacent carbocation. Support for this postulate was sought in a separate study where the electronic nature of the oxygen substituent was changed from a methyl to an acyl group in compound **5** (Scheme 2). The methoxymethyl derivative **5a** was cleaved by sulfuryl chloride to give the α-chloromethyl ether **6a** whereas in the acetoxymethyl derivative **5b**, the cleavage using sulfuryl chloride was between the metal and a butyl group to give butyl chloride and the stannyl chloride **7**. The same type of change in regioselectivity has been observed in the sulfur series.[14]

The reactions between the α-haloalkoxysilanes and the silyl enol ethers were run at −78 °C because of low thermal stability of the former, except in the case of the chloromethyl silyl ether **4c** where the reaction could be run at 0 °C. The reactions are slow in the absence of a Lewis acid catalyst. We have found that the presence of zinc bromide in up to ca. 10 mol % is effective. This is demonstrated by the reactions between the silyl enol ether **8** (R^2 = Ph, R^3 = R^4 = H) with the chloromethyl ether **4a** at 0 °C when the yield of the aldol product increased from <5 % (after 48 h) to 74 % (after 3 h) on addition of catalyst; with the α-chloroethyl ether **4e** at −78 °C, the figures were 20 % (after 20 h) and 69 % (after 3 h); with **4g** <10 % (after 20 h) and 72 % (after 20 h); with **4i** 44 % (after 20 h) and 67 % (after 3 h).

For the reactions of the α-bromo ethers **4b**, **4d**, **4f** and **4h** addition of zinc bromide was not required. The bromo ethers were formed from the corresponding stannanes at −78 °C and could not be isolated because of instability (*vide supra*). They react further *in situ* with the silyl enol ethers **8** in the presence of the tributylstannyl bromide formed in the bromination of the stannanes **3**. Presumably the tributylstannyl bromide is responsible for the catalysis. This assumption is supported by the finding that addition of tributylstannyl bromide to a mixture of pure α-bromo ether **4b** and 2-trimethylsilyloxypropene (**8**, R^2 = Me, R^3 = R^4 = H) leads to the formation of the aldol **9b**. In the absence of tributylstannyl bromide, **9b** was not formed.

Experimental

The mass spectra were recorded at 70 eV ionizing current and ammonia was used for chemical ionization (CI); the spectra are presented as *m/z* (% rel. int.). The ^1H NMR spectra were recorded at 200 or 300 MHz; the ^{13}C NMR spectra at 50 or 75 MHz. The solvent was $CDCl_3$.

Starting materials available by literature methods: (Dimethylthexylsilyloxy)methyl ethyl sulfide (**2a**),[8] (*t*-butyldimethylsilyloxymethyl)tributylstannane (**3a**),[15] chloromethoxy(*t*-butyl)dimethylsilane (**4a**),[10d] chloromethoxy(di-

methyl)thexylsilane (**4c**),[8] and (methoxymethyl)tributylstannane (**5a**).[16]

1-(Dimethylthexylsilyl)imidazole **1**.[17] Dimethylthexylsilyl chloride (9.6 ml, 50 mmol) and imidazole (3.4 g, 50 mmol) in triethylamine (150 ml) under N_2 were heated together under reflux for 5 h, after which the mixture was filtered and the filtrate evaporated. The product was purified by distillation. Yield 7.48 g (72 %); colourless liquid, b.p. 140–143 °C / 0.40 mmHg. ^{1}H NMR: δ 0.40 (SiMe), 0.72 (d, *J* 6.7 Hz, Me in thexyl), 0.75 (Me in thexyl), 1.50 (m, *J* 6.7 Hz, CH in thexyl), 6.86 (NCHN), 7.02 and 7.47 (d, *J* 14.2 Hz, NCHC). ^{13}C NMR: δ −2.9 (SiMe), 18.5 and 20.5 (Me in thexyl), 25.0 (C in thexyl), 34.1 (CH in thexyl), 121.5, 130.6 and 141.2 (CH in imidazole). MS (CI): 211 (36, *M*+1), 160 (9), 126 (3), 114 (3), 110 (2), 94 (5), 91 (3), 84 (8), 69 (100), 58 (11).

General procedure for the preparation of the O,S-*acetals* **2b–d**. A mixture of ethanethiol (1.48 ml, 20 mmol), 1-(dimethylthexylsilyl)imidazole (2.10 g, 10 mmol) and dimethylthexylsilyl triflate (0.09 ml, 0.5 mmol) under N_2 was stirred at ambient temperature for 3 h. The aldehyde (13 mmol) was added dropwise. After 120 h of stirring, diethyl ether was added and the solution washed with 1 M sodium hydroxide (×2) and brine (×2). The dried ($MgSO_4$) solution was evaporated and the crude product purified by flash chromatography on silica gel using EtOAc–hexane (1:40) for elution.

1-(Dimethylthexylsilyloxy)ethyl ethyl sulfide **2b**. Yield 1.52 g (61 %); colourless liquid. Anal. $C_{12}H_{28}OSSi$: C,H. ^{1}H NMR: δ 0.12 (SiMe), 0.81 (Me in thexyl), 0.85 (d, *J* 6.8 Hz, Me in thexyl), 1.22 (t, *J* 7.5 Hz, Me), 1.47 (d, *J* 6.2 Hz, Me), 1.60 (m, *J* 6.8 Hz, CH in thexyl), 2.56 (1 H, dq, *J* 12.3 and 7.5 Hz, H_A, CH_2), 2.63 (1 H, dq, *J* 12.3 and 7.5 Hz, H_B, CH_2), 5.02 (q, *J* 6.2 Hz, CH). ^{13}C NMR: δ −2.7 and −2.3 (SiMe), 15.2 (Me) 18.7 and 20.3 (Me in thexyl), 22.5 (CH_2), 25.0 (C in thexyl), 25.7 (Me), 34.3 (CH in thexyl), 74.3 (CH). MS (CI): 249 (15, *M*+1), 187 (78), 163 (15), 136 (22), 120 (100), 91 (29), 90 (31), 89 (74), 74 (31), 73 (23).

1-(Dimethylthexylsilyloxy)hexyl ethyl sulfide **2c**. Yield 1.76 g (58 %); colourless liquid. Anal. $C_{16}H_{36}OSSi$: C,H. ^{1}H NMR: δ 0.11 and 0.15 (SiMe), 0.81 (Me in thexyl), 0.85 (d, *J* 6.9 Hz, Me in thexyl), 0.8–0.9 and 1.1–1.8 (m, pentyl and CH in thexyl), 1.21 (t, *J* 7.4 Hz, Me), 2.57 (q, *J* 7.4 Hz, CH_2), 4.76 (t, *J* 6.3 Hz, CH). ^{13}C NMR: δ −2.9 and −2.1 (SiMe), 14.2 and 15.2 (Me) 18.7, 18.8, 20.3 and 20.4 (Me in thexyl), 21.8, 22.8, 26.0, 31.7 and 39.1 (CH_2), 25.1 (C in thexyl), 34.3 (CH in thexyl), 78.8 (CH). MS (CI): 305 (1, *M*+1), 243 (30), 222 (4), 219 (3), 176 (100), 159 (5), 145 (5), 136 (7), 91 (6), 90 (11).

α-*(Dimethylthexylsilyloxy)benzyl ethyl sulfide* **2d**. Yield 1.64 g (53 %). Anal. $C_{17}H_{30}OSSi$: C,H. ^{1}H NMR: δ 0.04 and 0.23 (SiMe), 0.88 and 0.89 (Me in thexyl), 0.92 (d, *J* 7.0 Hz, Me in thexyl), 1.15 (t, *J* 7.4 Hz, Me) 1.68 (m, *J* 7.0 Hz, CH in thexyl), 2.36 (1 H, dq, *J* 12.4 and 7.4 Hz, H_A, CH_2), 2.56 (1 H, dq, *J* 12.4 and 7.4 Hz, H_B, CH_2), 5.99 (CH), 7.2–7.5 (m, Ph). ^{13}C NMR: δ −1.9 and −1.4 (SiMe), 15.8 (Me) 19.8, 19.9, 21.3 and 21.5 (Me in thexyl), 22.0 (CH_2), 23.7 (C in thexyl), 35.3 (CH in thexyl), 80.3 (SCHO), 127.5, 128.9 and 129.5 (CH in Ph), 144.1 (C in Ph). MS (CI): 311 (1,*M*+1), 249 (100), 234 (3), 225 (3), 182 (23), 165 (9), 151 (13), 91 (27), 90 (23), 73 (18).

General procedure for the preparation of (silyloxyalkyl)-tributylstannane compounds **3**. Butyllithium in hexane (31.3 ml, 50 mmol) was added to a solution of dry isopropylamine (5.57 g, 55 mmol) in dry THF (100 ml) under nitrogen at 0 °C. After 15 min tributylstannane (13.0 ml, 50 mmol) was added dropwise, and the solution was stirred at 0 °C for 30 min and cooled to −78 °C before the aldehyde was added over 1 min. The solution was stirred for 10 min before 1 M NH_4Cl (aq.) was added, and the mixture extracted with diethyl ether. The washed and dried ($MgSO_4$) ether solution was evaporated and the residue dissolved in dichloromethane (100 ml). *tert*-Butyldimethylsilyl chloride (8.31 g, 55 mmol), triethylamine (6.07 g, 60 mmol), and 4-*N*,*N*-dimethylaminopyridine (0.24 g, 2 mmol) were added, and the resultant solution was stirred at ambient temperature overnight. The solution was then washed with 1 M NH_4Cl (aq.) (50 ml), dried ($MgSO_4$), evaporated and the product purified by flash chromatography on silica gel using pentane for elution.

*[1-(*t*-Butyldimethylsilyloxy)ethyl]tributylstannane* **3b**. Yield 79 %; colourless liquid. Anal. $C_{20}H_{46}OSiSn$: C,H. ^{1}H NMR: δ 0.02 and 0.04 (SiMe), 0.8–1.6 (m, Bu, *t*-Bu and Me), 4.17 (q, *J* 7.3 Hz, CH). ^{13}C NMR: δ −4.9 and −4.4 (SiMe), 8.6, 13.7, 27.6, 29.3 (Bu), 18.1 (C in *t*-Bu), 24.5 (Me), 25.9 (Me in *t*-Bu), 63.8 (CH). MS (CI): 452/451/450/449/448/447/446 (1/1/2/1/2/1/1, *M*), 414 (11), 412 (11), 411 (15), 410 (59), 409 (24), 408 (48), 407 (19), 406 (25), 308 (25), 306 (18), 304 (12), 159 (100).

*[1-(*t*-Butyldimethylsilyloxy)hexyl]tributylstannane* **3c**. Yield 63 %; colourless liquid. Anal. $C_{24}H_{54}OSiSn$: C,H. ^{1}H NMR: δ 0.01 and 0.04 (SiMe), 0.8–1.0 and 1.2–1.8 (m, Bu, *t*-Bu and pentyl), 4.1–4.2 (m, CH). ^{13}C NMR: δ −5.1 and −4.8 (SiMe), 8.9, 13.6, 27.5, 29.2 (Bu), 13.9, 22.6, 26.9, 32.0, 38.5 (pentyl), 15.4 (C in *t*-Bu), 25.8 (Me in *t*-Bu), 69.3 (CH). MS(CI): 508/507/506/505/504/503/502 (1/1/1/1/1/1/1, *M*), 466 (13), 464 (11), 449 (3), 382 (4), 380 (4), 308 (7), 215 (100).

*[α-(*t*-Butyldimethylsilyloxy)benzyl]tributylstannane* **3d**. Yield 59 %; colourless liquid. Anal. $C_{25}H_{48}OSiSn$: C,H. ^{1}H NMR: δ −0.19 and 0.03 (SiMe), 0.7–1.5 (m, Bu and *t*-Bu), 5.17 (CH), 7.0–7.5 (m, Ph). ^{13}C NMR: δ −5.2 and −4.7 (SiMe), 9.3, 13.6, 27.5, 29.0 (Bu), 18.2 (C in *t*-Bu), 26.0 (Me in *t*-Bu), 71.4 (CH), 123.0, 124.0, 128.0, (CH in Ph) 147.9

(C in Ph). MS (CI): 512/510 (1/1, *M*), 315 (16), 313 (26), 311 (19), 291 (17), 289 (12), 257 (11), 235 (20), 233 (16), 221 (52), 179 (80), 73 (100).

Bromomethoxy(t-butyl)dimethylsilane **4b**. Bromine in tetrachloromethane (1.0 M, 2.0 ml) was added dropwise to a solution of (*t*-butyldimethylsilyloxymethyl)tributylstannane **3a** (2.0 mmol) in dichloromethane (2 ml) under nitrogen at −78 °C. The resultant solution was stirred for 10 min and the α-bromo ether **4b** trapped with 2-trimethylsilyloxypropene at −78 °C (*vide infra,* **9a**).

1-Bromoethoxy(t-butyl)dimethylsilane **4d**. Compound **4d** was prepared as **4b** above and trapped with 2-trimethylsilyloxypropene (*vide infra,* **9g**).

(1-Chloroethoxy)dimethylthexylsilane **4e**. Sulfuryl chloride (0.04 ml, 0.5 mmol) in dry dichloromethane (1 ml) was added with stirring to a solution of the *O,S*-acetal **3b** (1.0 mmol) in dichloromethane (1 ml) under N_2 at −78 °C. The mixture was stirred for 20 min and the title compound **4e** trapped with 1-phenyl-1-trimethylsilyloxyethene at −78 °C (*vide infra,* **9h**).

1-Bromohexyloxy(t-butyl)dimethylsilane **4f**. Compound **4f** was prepared as for **4b** above and trapped with 2-trimethylsilyloxypropene (*vide infra,* **9i**).

(1-Chlorohexyloxy)dimethylthexylsilane **4g**. Compound **4g** was prepared as **4e** above and trapped with 1-phenyl-1-trimethylsilyloxyethene (*vide infra,* **9j**).

α-Bromobenzyloxy(t-butyl)dimethylsilane **4h**. Compound **4h** was prepared as **4b** above and trapped with 2-trimethylsilyloxypropene (*vide infra,* **9k**).

(α-Chlorobenzyloxy)dimethylthexylsilane **4i**. Compound **4i** was prepared as for **4e** above and trapped with 1-phenyl-1-trimethylsilyloxyethene (*vide infra,* **9l**).

(Acetoxymethyl)tributylstannane **5b**. Acetyl chloride (3.4 ml, 48.3 mmol) was added at 0 °C to a mixture of hydroxymethyltributylstannane[18] (14.1 g, 43.9 mmol), triethylamine (6.8 ml, 48.3 mmol) and 4-*N,N*-dimethylaminopyridine (244 mg, 2 mmol) in dichloromethane (100 ml). The mixture was stirred for 24 h while reaching ambient temperature and the solution was washed successively with water, 1 M HCl, sodium hydrogen carbonate and brine. Yield 14.6 g (92 %). 2.0 g of the crude product were distilled under reduced pressure to give the product; 1.65 g, b.p. 96–100 °C/0.1 mmHg. ^{1}H NMR: δ 0.8–1.0 (Bu), 1.2–1.5 (Bu), 1.4–1.6 (Bu), 2.00 (MeCO), 4.11 (CH_2O). ^{13}C NMR: δ 9.7 and 13.7 (Bu), 20.6 (MeCO), 27.7 and 29.0 (Bu), 55.7 ($SnCH_2O$), 171.6 (CO).

Chloromethyl methyl ether **6a**. Sulfuryl chloride (0.39 ml, 4.8 mmol) was added dropwise to (methoxymethyl)tributylstannane (1.54 g, 4.5 mmol) at 0 °C. The mixture was stirred at 0 °C for 3 h and chloromethyl methyl ether distilled off at atmospheric pressure. Yield 120 mg (33 %), b.p. 54–58 °C[19] [a substantial amount of product was lost during distillation]. ^{1}H NMR: δ 3.44 (Me), 5.38 (CH_2).

Bromomethyl methyl ether **6b**. Bromine (0.21 ml, 4.1 mmol) in tetrachloromethane (4 ml) was added dropwise at 0 °C to a solution of (methoxymethyl)tributylstannane (1.38 g, 4.1 mmol) in tetrachloromethane (4 ml). The mixture was stirred at 0 °C for 30 min before bromomethyl methyl ether was distilled off together with the solvent. [^{1}H NMR: δ 3.35 (Me), 5.88 (CH_2)] To the distillate was added a solution of thiophenol (0.40 ml, 3.9 mmol) and triethylamine (0.55 ml, 3.9 mmol) in dichloromethane. The mixture was stirred at ambient temperature for 18 h, diethyl ether added, and the solution washed with sodium carbonate, dried ($MgSO_4$) and evaporated. The crude product was distilled under reduced pressure to give (methoxy)methylthiobenzene.[20] Yield 0.55 g (87 %), b.p. 58–60 °C/0.1 mmHg. ^{1}H NMR: δ 3.35 (Me), 4.86 (CH_2), 7.1–7.6 (m, Ph).

(Acetoxymethyl)dibutylchlorostannane **7**. Sulfuryl chloride (0.45 ml, 7 mmol) was added at 0 °C to a solution of acetoxymethyltributylstannane (1.90 g, 5.2 mmol) in chloroform (10 ml). The mixture was stirred at 0 °C for 3 h and at ambient temperature for 1 h, before butyl chloride and chloroform were distilled off at atmospheric pressure [^{1}H NMR: δ 0.7–2.0 (7 H, m), 3.55 (2 H, t, *J* 7 Hz), BuCl[21]]. The residue **7** was dried at 0.1 mmHg. Yield 1.60 g (90 %). ^{1}H NMR: δ 0.8–1.0 (6 H, Bu), 1.3–1.5 (8 H, Bu), 1.6–1.7 (4 H, Bu), 2.15 (MeCO), 3.90 (CH_2Sn).

4-t-Butyldimethylsilyloxy-2-butanone **9a**. 2-Trimethylsilyloxypropene (0.52 g, 4.0 mmol) was added at −78 °C to a mixture of bromomethoxy(*t*-butyl)dimethylsilane (2.0 mmol, *vide supra*) and the mixture was allowed to reach ambient temperature overnight. The solvent was evaporated the residual material dissolved in diethyl ether and the ether solution washed with saturated aquous potassium fluoride, dried ($MgSO_4$) and evaporated to leave the crude product which was purified by flash chromatography on silica gel using EtOAc–hexane (1:10) for elution. Yield 89 mg (22 %); colourless liquid. Anal $C_{10}H_{22}O_2Si$: C,H. ^{1}H NMR: δ −0.05 (SiMe), 0.84 (*t*-Bu), 2.13 (Me), 2.57 (t, *J* 6.3 Hz, CH_2CO), 3.84 (t, *J* 6.3 Hz, CH_2O). ^{13}C NMR: δ −5.4 (SiMe), 18.3 (C in *t*-Bu), 25.9 (Me in *t*-Bu), 30.7 (Me), 46.7 (CH_2CO), 59.0 (CH_2O).

4-Dimethylthexylsilyloxy-2-butanone **9b**. (Chloromethoxy)-dimethylthexylsilane (1.05 g, 5.0 mmol) in dry dichloromethane (5 ml) was added dropwise under N_2 at 0 °C to a stirred mixture of 2-trimethylsilyloxypropene (1.31 g, 10.0 mmol) and zinc bromide (113 mg, 0.5 mmol) in dry di-

chloromethane (10 ml). The mixture was stirred for 3 h, during which time it reached ambient temperature, diluted with diethyl ether and washed with saturated aqueous sodium hydrogen carbonate (× 2) and brine (× 2). The dried ($MgSO_4$) solution was evaporated and the crude product purified by flash chromatography using EtOAc–hexane (1:20). Yield 810 mg (70%); colourless liquid. Anal. $C_{12}H_{26}O_2Si$: C,H. ^1H NMR: δ 0.09 (SiMe), 0.82 (Me in thexyl), 0.86 (d, *J* 6.9 Hz, Me in thexyl), 1.58 (m, *J* 6.9 Hz, CH in thexyl), 2.18 (Me), 2.61 (t, *J* 6.3 Hz, CH_2CO), 3.87 (t, *J* 6.3 Hz, CH_2O). ^{13}C NMR: δ −3.7 (SiMe), 18.4 and 20.2 (Me in thexyl), 24.9 (C in thexyl), 30.6 (Me), 34.1 (CH in thexyl), 46.4 (CH_2CO), 58.5 (CH_2O), 208.0 (CO). MS (CI): 231 (27, *M*+1), 215 (3), 159 (1), 145 (100), 129 (1), 115 (5), 106 (4), 89 (2), 75 (1).

2-(Dimethylthexylsilyloxymethyl)cyclopentanone **9c**. Compound **9c** was prepared as for **9b** above. Yield 820 mg (64%); colourless liquid. Anal. $C_{14}H_{28}O_2Si$: C,H. ^1H NMR: δ 0.06 and 0.07 (SiMe), 0.81 (Me in thexyl), 0.86 (d, *J* 6.9 Hz, Me in thexyl), 1.59 (m, *J* 6.9 Hz, CH in thexyl), 1.8–2.3 (m, CH_2 and CH), 3.71 (1 H, dd, *J* 9.9 and 3.2, H_A, CH_2), 3.86 (1 H, dd, *J* 9.9 and 4.6, H_B, CH_2). ^{13}C NMR: δ −3.9 and −3.8 (SiMe), 18.3 and 20.1 (Me in thexyl), 20.8, 26.2 and 39.0 (CH_2), 24.9 (C in thexyl), 34.1 (CH in thexyl), 50.8 (CH), 61.6 (CH_2), 219.9 (CO). MS (CI): 257 (100, *M*+1), 173 (7), 171 (95), 157 (11), 141 (13), 97 (33), 92 (29), 89 (18), 84 (5), 75 (10).

2-(Dimethylthexylsilyloxymethyl)cyclohexanone **9d**. Compound **9d** was prepared as for **9b** above. Yield 970 mg (72%); colourless liquid. Anal. $C_{15}H_{30}O_2Si$: C,H. ^1H NMR: δ 0.08 and 0.09 (SiMe), 0.83 (Me in thexyl), 0.87 (d, *J* 6.9 Hz, Me in thexyl), 1.4–2.3 (m, CH_2 and CH), 3.56 (1 H, dd, *J* 10.3 and 8.0, H_A, CH_2), 3.95 (1 H, dd, *J* 10.3 and 4.6, H_B, CH_2). ^{13}C NMR: δ −3.6 (SiMe), 18.4 and 20.4 (Me in thexyl), 24.6 (C in thexyl), 25.1, 27.6, 31.0 and 42.1 (CH_2), 34.2 (CH in thexyl), 52.8 (CH), 62.0 (CH_2), 212.2 (CO). MS (CI): 271 (65, *M*+1), 255 (3), 243 (2), 185 (100), 171 (13), 155 (3), 143 (1), 106 (4), 89 (2), 75 (3).

3-(Dimethylthexylsilyloxy)propiophenone **9e**. Compound **9e** was prepared as for **9b** above. Yield 1.08 g (74%); colourless liquid. Anal. $C_{17}H_{28}O_2Si$: C,H. ^1H NMR: δ 0.05 (SiMe), 0.72 (Me in thexyl), 0.78 (d, *J* 6.9 Hz, Me in thexyl), 1.50 (m, *J* 6.9 Hz, CH in thexyl), 3.10 and 3.96 (t, *J* 6.6 Hz, CH_2), 7.4–8.0 (m, Ph). ^{13}C NMR: δ −3.7 (SiMe), 18.3 and 20.1 (Me in thexyl), 24.9 (C in thexyl), 34.0 (CH in thexyl), 41.5 and 59.0 (CH_2), 128.1, 128.3 and 132.8 (CH in Ph), 137.2 (C in Ph), 201.8 (CO). MS (CI): 310 (3, *M*+18), 293 (100, *M*+1), 253 (14), 248 (2), 240 (20), 223 (16), 207 (31), 177 (1), 120 (1), 105 (7), 91 (5).

Methyl 2,2-dimethyl-3-dimethylthexylsilyloxypropionate **9f**. Compound **9f** was prepared as for **9b** above. Yield 1.17 g (85%); colourless liquid. Anal. $C_{14}H_{30}O_3Si$: C,H. ^1H NMR: δ 0.00 (SiMe), 0.77 (Me in thexyl), 0.81 (d, *J* 6.8 Hz, Me in thexyl), 1.10 (Me), 1.54 (m, *J* 6.8 Hz, CH in thexyl), 3.50 (CH_2), 3.60 (MeO). ^{13}C NMR: δ −3.7 (SiMe), 18.6 and 20.4 (Me in thexyl), 22.1 (Me), 25.2 (C in thexyl), 34.5 (CH in thexyl), 45.1 (C), 51.8 (MeO), 70.3 (CH_2), 177.8 (CO). MS (CI): 275 (100, *M*+1), 259 (1), 243 (2), 205 (12), 203 (14), 189 (46), 106 (22), 105 (11), 91 (13), 74 (18).

4-(t-Butyldimethylsilyloxy)-2-pentanone **9g**. Compound **9g** was prepared as for **9a** above. Yield 270 mg, (62%), colourless liquid. Anal $C_{11}H_{24}O_2Si$: C,H. ^1H NMR: δ 0.04 and 0.06 (SiMe), 0.86 (*t*-Bu), 1.17 (d, *J* 6.1 Hz, Me), 2.16 (MeCO), 2.42 (1 H, dd, *J* 15.0 and 5.3 Hz, H_A, CH_2), 2.64 (1 H, dd, *J* 15.0 and 7.2 Hz, H_B, CH_2), 4.29 (m, *J* 7.2, 6.3 and 5.1 Hz, CH). ^{13}C NMR: δ −4.9 and −4.6 (SiMe), 18.0 (C in *t*-Bu), 24.0 (Me), 25.8 (Me in *t*-Bu), 31.5 (MeCO), 53.3 (CH_2), 65.7 (CH), 207.6 (CO). MS (CI): 219 (16, *M*+1), 218 (16, *M*), 217 (100), 203 (10), 159 (83), 115 (13), 92 (23), 91 (20), 74 (40).

3-(Dimethylthexylsilyloxy)butyrophenone **9h**. 1-Phenyl-1-trimethylsilyloxyethene (384 mg, 2.0 mmol) in dry dichloromethane (1 ml) and zinc bromide (23 mg, 0.1 mmol) was added with stirring to a solution of (1-chloroethoxy)-dimethylthexylsilane (1.0 mmol, *vide supra*) in dichloromethane (2 ml) at −78 °C under N_2. After being stirred at −78 °C for 3 h, the reaction was worked up and purified as for **9b**. Yield 210 mg (69%); colourless liquid. Anal. $C_{18}H_{30}O_2Si$: C,H. ^1H NMR: δ −0.05 and 0.07 (SiMe), 0.71 and 0.73 (Me in thexyl), 0.79 (d, *J* 6.7 Hz, Me in thexyl), 1.23 (d, *J* 6.0 Hz, Me), 1.52 (m, *J* 6.7 Hz, CH in thexyl), 2.84 (1 H, dq, *J* 15.2 and 5.7 Hz, H_A, CH_2), 3.25 (1 H, dq, *J* 15.2 and 6.9 Hz, H_B, CH_2), 4.44 (m, *J* 6.9, 6.7 and 5.7 Hz, CH), 7.4–7.6 (3 H, m, Ph), 7.9–8.0 (2 H, m, Ph). ^{13}C NMR: δ −2.9 and −2.4 (SiMe), 18.7, 20.3 and 20.4 (Me in thexyl), 24.6 (Me), 24.9 (C in thexyl), 34.3 (CH in thexyl), 48.5 (CH_2), 66.4 (CH), 128.9, 129.0 and 133.5 (CH in Ph), 138.1 (C in Ph), 200.0 (CO). MS (CI): 307 (100, *M*+1), 291 (3), 221 (93), 194 (11), 187 (14), 177 (13), 147 (2), 120 (39), 105 (8), 75 (4).

4-(t-Butyldimethylsilyloxy)-2-nonanone **9i**. Compound **9i** was prepared as for **9a** above. Yield (64%), colourless liquid. Anal $C_{15}H_{32}O_2Si$: C,H. ^1H NMR: δ 0.02 and 0.06 (SiMe), 0.87 (*t*-Bu), 1.2–1.5 (m, pentyl), 2.16 (Me), 2.47 (1 H, dd, *J* 15.0 and 5.1 Hz, H_A, CH_2), 2.60 (1 H, dd, *J* 15.0 and 6.9 Hz, H_B, CH_2), 4.1–4.2 (m, CH). ^{13}C NMR: δ −4.6 and −4.5 (SiMe), 14.0, 22.6, 24.8, 31.6, 32.0, 37.8 (pentyl and Me), 18.1 (C in *t*-Bu), 25.9 (Me in *t*-Bu), 51.2 (CH_2), 69.3 (CH), 207.7 (CO). MS(CI): 274 (24), 273 (100, *M*+1), 257 (3), 216 (16), 215 (97), 201 (3), 157 (5), 132 (8), 115 (15).

3-Dimethylthexylsilyloxy-1-phenyl-1-octanone **9j**. Compound **9j** was prepared as for **9h** above, except that the reaction mixture was stirred for 20 h, during which time it reached ambient temperature. Yield 524 mg (72%); colourless liquid. Anal. $C_{22}H_{38}O_2Si$: C,H. ^1H NMR: δ

−0.07 and 0.06 (SiMe), 0.71 and 0.74 (Me in thexyl), 0.79 (d, *J* 6.8 Hz, Me in thexyl), 0.8–0.9 and 1.2–1.6 (m, pentyl and CH in thexyl), 2.88 (1 H, dd, *J* 15.3 and 5.4 Hz, H_A, CH_2), 3.19 (1 H, dd, *J* 15.3 and 7.0 Hz, H_B, CH_2), 4.3–4.4 (m, CH), 7.3–7.6 (3 H, m, Ph), 7.9–8.0 (2 H, m, Ph). ^{13}C NMR: δ −2.7 and −2.4 (SiMe), 14.2 (Me), 18.7 and 20.4 (Me in thexyl), 22.8, 24.8, 32.2 and 38.2 (CH_2 in pentyl), 24.9 (C in thexyl), 34.3 (CH in thexyl), 46.1 (CH_2), 69.9 (CH), 128.9, 129.0 and 133.4 (CH in Ph), 138.2 (C in Ph), 200.2 (CO). MS (CI): 363 (100, *M*+1), 347 (2), 277 (84), 243 (16), 203 (34), 177 (22), 176 (30), 105 (18), 91 (11), 75 (16).

4-t-Butyldimethylsilyloxy-4-phenyl-2-butanone **9k**. Compound **9k** was prepared as for **9a** above. Yield 314 mg (56 %), colourless liquid. Anal $C_{16}H_{26}O_2Si$: C,H. ^1H NMR: δ 0.15 and 0.00 (SiMe), 0.85 (*t*-Bu), 2.15 (Me), 2.54 (1 H, dd, *J* 14.8 and 4.0 Hz, H_A, CH_2), 2.94 (1 H, dd, *J* 14.8 and 8.8 Hz, H_B, CH_2), 5.16 (dd, *J* 8.8 and 4.0 Hz, CH), 7.2–7.4 (m, Ph). ^{13}C NMR: δ −5.2 and −4.7 (SiMe), 18.1 (C in *t*-Bu), 25.8 (Me in *t*-Bu), 31.7 (Me), 54.5 (CH_2), 72.0 (CH). MS (CI): 280 (6, *M*), 279 (24), 263 (3), 223 (5), 222 (20), 221 (100), 164 (35), 147 (72).

3-(Dimethylthexylsilyloxy)-3-phenylpropiophenone **9l**. Compound **9l** was prepared as for **9h** above. Yield 247 mg (67 %); colourless liquid. Anal. $C_{23}H_{32}O_2Si$: C,H. ^1H NMR: δ −0.21 and 0.00 (SiMe), 0.69 (Me in thexyl), 0.76 (d, *J* 6.9 Hz, Me in thexyl), 1.50 (m, *J* 6.9 Hz, CH in thexyl), 2.93 (1 H, dd, *J* 15.3 and 4.0 Hz, H_A, CH_2), 3.57 (1 H, dd, *J* 15.3 and 8.6 Hz, H_B, CH_2), 5.35 (dd, *J* 8.6 and 4.0 Hz, CH), 7.2–7.6 (8 H, m, Ph), 7.9–8.0 (2 H, m, Ph). ^{13}C NMR: δ −3.2 and −2.4 (SiMe), 18.7, 20.3 and 20.4 (Me in thexyl), 25.0 (C in thexyl), 34.2 (CH in thexyl), 49.3 (CH_2), 72.6 (CH), 126.5, 127.9, 128.8, 129.0 and 133.5 (CH in Ph), 138.2 and 145.5 (C in Ph), 199.3 (CO). MS (CI): 369 (24, *M*+1), 353 (3), 338 (1), 283 (68), 265 (12), 249 (100), 226 (23), 209 (29), 105 (40), 75 (4).

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Received April 29, 1991.