Acta Chemica Scandinavica, 1998: 52: 1141–1143
Printed in UK – all rights reserved

ACTA
CHEMICA SCANDINAVICA
ISSN 0904-213X

Synthesis of Bis(trimethylsilyl) Ketone and Reactions with Organometallic Compounds

Ming Pan and Tore Benneche*

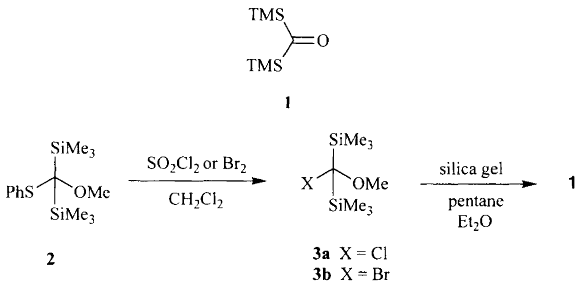
Department of Chemistry, University of Oslo, 0315 Oslo, Norway

Pan, M. and Benneche, T., 1998. Synthesis of Bis(trimethylsilyl) Ketone and Reactions with Organometallic Compounds. – Acta Chem. Scand. 52: 1141–1143. © Acta Chemica Scandinavica 1998.

Bis(trimethylsilyl) ketone (1) has been prepared by hydrolysis of the α-chloro ether **3a** on silica gel. Reaction of ketone **1** with organoaluminium, organomagnesium and organolithium compounds gave addition products and/or bis(trimethylsilyl)methanol (**5**).

Bis(trimethylsilyl) ketone (**1**) was reported in 1968 as a hydrolysis product of 1,1-bis(trimethylsilyl)-1,3-dithiane.[1] The compound could, however, not be purified because of its lability. Hydrolysis of bis(trimethylsilyl)bis(methylthio)methane met with the same problems.[2] The pure ketone **1** has been isolated from the ozonolysis [bis(trimethylsilyl)methylene]triphenylphosphorane[3] and by oxidation of tris(trimethylsilyl)methylthiomethane with *m*-chloroperbenzoic acid followed by a sila-Pummerer rearrangement.[4]

We have recently reported that bis(trimethylsilyl) ketone (**1**) can be readily prepared in good yield (75%) from the α-bromo ether **3b** by hydrolysis on a silica gel coloumn.[5] It turns out that the corresponding α-chloro ether **3a** can be used equally well (Scheme 1).



Scheme 1.

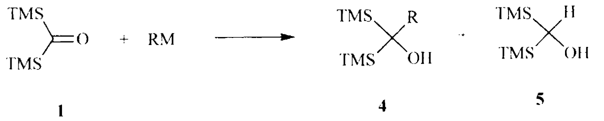
The α-chloro ether **3a** was prepared by cleavage of the *O,S*-acetal **2**[6] by sulfuryl chloride. The benzenesulfenyl chloride generated was trapped with cyclohexene. This adduct has a much higher boiling point[7] than the α-chloro ether **3a**, which could then be separated from the adduct by distillation. Addition of the α-chloro ether **3a** to a silica gel column and elution under N_2 with a mixture of pentane and diethyl ether gave the ketone **1** in 78% yield.

It has been shown that bis(trimethylsilyl) ketone (**1**) can be regarded as a CO^{2-} equivalent.[3a] Thus treatment of ketone **1** with fluoride ion in the presence of 2-cyclohexenone afforded, after hydrolysis, 3-formylcyclohexenone.[3a] In this paper we show that bis(trimethylsilyl) ketone (**1**) also reacts like a 'normal' ketone by addition of different organometallic compounds giving 1,1-bis(trimethylsilyl) substituted alcohols. Such compounds have previously been prepared by reductive silylation of carboxylic esters.[8] The reactivity of **1** towards organometallic compounds has, as far as we know, not been reported.

The reaction of bis(trimethylsilyl) ketone (**1**) with excess methyl organometallic reagents gave 1,1-bis(trimethylsilyl)ethanol in 44–59% yield (Scheme 2, entries 1–3). Lower yields were obtained when the organometallic compound was not used in excess.

As expected methylmagnesium bromide and methyllithium react more rapidly with **1** than does trimethylaluminium: ca. 30 min for completion for the magnesium and lithium reagents and 24 h for the aluminium reagent. (Trimethylsilyl)methylmagnesium chloride reacted to give the adduct **4b** in good yield (79%, entry 4). From the reaction of butylmagnesium bromide only the reduction product bis(trimethylsilyl)methanol (**5**) (entry 5) was isolated. In the crude product there was < 10% of compound **4c** according to ^1H NMR spectroscopy. The corresponding lithium compound, however, gave a 2:1 mixture of **4c** and **5** according to ^1H NMR spectroscopy (entry 6). Compound **5** was the only product in the reaction with triisobutylaluminium and diisobutylaluminium hydride (DIBAH) (entries 7 and 8). Vinylmagnesium bromide and phenylmagnesium bromide gave the addition products **4d** and **4e**, respectively, in low yield (entries 9 and 10). Compound **4e** could be identified only by ^1H NMR, due to rapid decomposition. In the

* To whom correspondence should be addressed.



1 4 5

Entry	RM	Product	Yield **4** (%)[a]	Yield **5** (%)[a]
1	MeMgBr	**4a**	59	—
2	MeLi	**4a**	58	—
3	Me_3Al	**4a**	44	—
4	Me_3SiCH_2MgCl	**4b**	79	—
5	*n*-BuMgBr	**4c**	—[b]	46
6	*n*-BuLi	**4c**	35	—[c]
7	$(i\text{-Bu})_3Al$	—	—[d]	54
8	$(i\text{-Bu})_2AlH$	—	—[d]	58
9	VinylMgBr	**4d**	32	—
10	PhMgBr	**4e**	25	—
11	PhC≡CLi	—	—	—

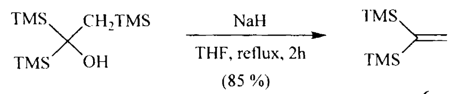
[a]Isolated. [b]<10% of the crude product (^{1}H NMR). [c]A 2:1 mixture of **4c** and **5** in the crude product (^{1}H NMR). [d]Not observed in the crude product (^{1}H NMR).

Scheme 2.

reaction of lithium phenylacetylide no addition product was observed (entry 11).

It seems that the stability of the 1,1-bis(trimethylsilyl) alcohols **4** may be dependent on the electronic properties of the R-group. When R is an electron-donating group, the compounds seem quite stable, but the more electron-withdrawing R is, the more easily the compounds decompose. From the literature only 1,1-bis(trimethylsilyl)-alkan-1-ols having electron-donating substituents on the alcohol carbon are known.[8]

The reactivity of 1,1-bis(trimethylsilyl)alkan-1-ols has been very little investigated. We can report that treatment of compound **4b** with sodium hydride in boiling THF for 2 h gave the Peterson elimination product **6** in good yield (Scheme 3). We are currently investigating the synthesis and reactivity of other bis(silyl) ketones.



4b 6

Scheme 3.

Experimental

The ^{1}H NMR spectra were recorded at 200 MHz with a Varian Gemini 200 or a Bruker DPX 200 instrument. The ^{13}C NMR spectra were recorded at 50 MHz with a Gemini 200 or a Bruker DPX 200. The NMR spectra were recorded in C_6D_6. The mass spectra, under electron impact conditions, were recorded at 70 eV ionizing energy. Isobutane was used for chemical ionization (CI); the spectra are presented as m/z (% rel. int.).

Bis(trimethylsilyl) ketone (**1**).[3–5] Bis(trimethylsilyl)-chloro(methoxy)methane (0.674 g, 3.0 mmol) in pentane (3.0 ml) was added to silica gel in degassed pentane. The elution was conducted essentially as described for the purification of ketone **1** in the literature:[3b] elution was first done with degassed pentane and then with a degassed mixture of pentane and diethyl ether (20:1). All the colourless fractions were discarded. Yield 0.410 g (78%). The analytical data were in accordance with the previously published values.[3–5]

Bis(trimethylsilyl) chloro(methoxy) methane (**3a**). Sulfuryl chloride (0.81 ml, 10 mmol) in dry dichloromethane (7 ml) was added dropwise with stirring to a solution of bis(trimethylsilyl)methoxy(phenylthio)methane[6] (2.98 g, 10 mmol) in dry dichloromethane (14 ml) under N_2 at 0 °C. Cyclohexene (1.22 ml, 12 mmol) in dry dichloromethane (7 ml) was then added dropwise and stirred for 30 min. The solvent was evaporated off and the residue was purified by Kugelrohr distillation (1.0 mmHg, oven temp. 45–55 °C). Yield 1.47 g (65%). ^{1}H NMR ($CDCl_3$): δ 0.18 (s, 2 × $SiMe_3$), 3.47 (s, OMe). ^{13}C NMR ($CDCl_3$): δ −1.1 ($SiMe_3$), 56.4 (OMe), 109.5 (CCl).

1,1-Bis(trimethylsilyl)ethanol (**4a**). To a solution of bis(trimethylsilyl) ketone (0.205 g, 1.18 mmol) in THF (6 ml) at −78 °C under N_2 was added methylmagnesium bromide (2.0 ml, 1.4 M in toluene–THF 3:1, 2.8 mmol). After the pink colour of the solution had disappeared (30 min), the mixture was allowed to warm to 0 °C, before 10% NH_4Cl (10 ml) and diethyl ether (20 ml) were added. The mixture was stirred for another 30 min before the organic layer was separated and washed with saturated aqueous $NaHCO_3$ (2 × 10 ml) and saturated aqueous NaCl (2 × 10 ml), successively. The dried ($MgSO_4$) solution was evaporated and the crude product purified by flash chromatography on silica gel using hexane–ethyl acetate (8:1) for elution. Yield: 0.132 g (59%). Oil. ^{1}H NMR (C_6D_6): δ 0.026 (s, 2 × $SiMe_3$), 1.14 (s, Me). ^{13}C NMR (C_6D_6): δ −2.7 ($SiMe_3$), 21.9 (Me), 58.6 (C–OH). MS (CI): 190 (M^+, 24), 189 (34), 175 (31), 164 (123), 159 (7), 148 (14), 117 (8), 102 (22), 90 (100), 73 (20).

1,1,2-Tris(trimethylsilyl)ethanol (**4b**). Procedure as for **4a**. Compound **4b** was prepared from bis(trimethylsilyl) ketone (0.07 g, 0.4 mmol) and (trimethylsilyl)methylmagnesium bromide (1 M in THF, 1.5 ml, 1.5 mmol). The crude product was purified by flash chromatography on silica gel using hexane–ethyl acetate (20:1) for elution Yield 0.082 g (79%). ^{1}H NMR (C_6D_6): δ 0.024 (s, 2 × $SiMe_3$), 0.19 (s, $SiMe_3$), 1.24 (s, CH_2). ^{13}C NMR (C_6D_6): δ −1.92 (C–Si$\underline{C}H_3$), 2.19 ($CH_2Si\underline{C}H_3$), 23.69 (CH_2), 60.94 (COH). MS (CI): 259 (0.3), 247 (1), 231 (27), 172 (28), 159 (28), 158 (16), 157 (77), 147 (26), 143 (35), 79 (16), 75 (20), 73 (100).

1,1-Bis(trimethylsilyl)pentan-1-ol (**4c**). Procedure as for **4a**. Compound **4c** was prepared from bis(trimethylsilyl) ketone (0.125 g, 0.72 mmol) and *n*-butyllithium (1.6 M in hexane, 1.0 ml, 1.6 mmol). The crude product was a mixture of **4c** and **5** (2 : 1, ^{1}H NMR), which was separated by flash chromatography on silica gel using hexane–ethyl acetate (10 : 1) for elution. Yield **4c** 0.056 g (35%). ^{1}H NMR (C_6D_6): δ 0.095 (s, 2 × $SiMe_3$), 0.88 (t, Me, *J* 7 Hz), 1.17–1.38 (m, 4 H), 1.60–1.72 (m, 2 H). ^{13}C NMR (C_6D_6): δ 1.4 ($SiCH_3$), 14.3 (CH_3), 24.2 (CH_2), 28.2 (CH_2), 37.7 (C–$\underline{C}H_2$), 62.7 (COH). MS (CI): 232 (M^+,1.4), 217 (5), 201 (15), 185 (4), 173 (8), 159 (11), 149 (10), 148 (28), 147 (100), 127 (77), 99 (22), 73 (94).

1,1-Bis(trimethylsilyl)prop-2-en-1-ol (**4d**). Procedure as for **4a**. Compound **4d** was prepared from bis(trimethylsilyl) ketone (0.44 g, 2.5 mmol) and vinylmagnesium bromide (1 M in THF, 5.0 ml, 5.0 mmol). The crude product was purified by flash chromatography on silica gel using hexane–ethyl acetate (6 : 1) for elution. Yield 0.164 g (32%). ^{1}H NMR (C_6D_6): δ 0.042 (s, 2 × $SiMe_3$), 4.76 (d, 1 H, *J* 16.9 Hz), 4.87 (d, 1 H, *J* 11.0 Hz), 5.96 (dd, 1 H, *J* 11.0, 16.9 Hz). ^{13}C NMR (C_6D_6): δ −1.3 ($SiMe_3$), 70.7 (COH), 104.8 (=CH_2), 141.3 (=CH). MS (EI): 202 (M^+, 5), 171 (7), 148 (9), 147 (53), 133 (9), 97 (12), 75 (29), 74 (9), 73 (100), 45 (16).

Bis(trimethylsilyl)phenylmethanol (**4e**). Procedure as for **4a**. Compound **4e** was prepared from bis(trimethylsilyl) ketone (0.087 g, 0.5 mmol) and phenylmagnesium bromide (1 M in THF, 1.5 ml, 1.5 mmol). The crude product was purified by flash chromatography on silica gel using hexane–ethyl acetate (10 : 1) for elution. Yield 0.032 g (25%). ^{1}H NMR (C_6D_6): δ 0.023 (s, 2 × $SiMe_3$), 6.95–7.03 (m, 2 H), 7.14–7.19 (m, 3 H).

Bis(trimethylsilyl)methanol (**5**). Diisobutylaluminium hydride solution (≈20% in hexane, 2 ml, 2 mmol) was added dropwise to a solution of bis(trimethylsilyl) ketone (0.157 g, 0.9 mmol) in THF (5 ml) under N_2 at −78 °C. The mixture was stirred for 30 min, quenched with water (10 ml), extracted with diethyl ether (20 ml), dried ($MgSO_4$) and evaporated. The crude product was purified by flash chromatography on silica gel using hexane–ethyl acetate (8 : 1) for elution. Yield 0.092 g, (58%). ^{1}H NMR (C_6D_6): δ 0.045 (s, 2 × $SiMe_3$), 2.77 (s, 1 H). ^{13}C NMR (C_6D_6): δ 0.0 ($SiCH_3$), 59.8 (COH). IR (neat, cm^{-1}). 3450 (br), 2950, 1725, 1250, 1045. MS (CI): 176 (M^+, 11), 175 (12), 161 (31), 160 (24), 143 (6), 130 (6), 102 (17), 90 (100), 73 (30).

1,1-Bis(trimethylsily)ethene (**6**).[9] Sodium hydride (0.06 g, 2.5 mmol) was added to a solution of 1,1,2-tris(trimethylsilyl)ethanol (0.113 g, 0.43 mmol) in THF (10 ml). The mixture was stirred under reflux for 3 h before the reaction was quenched with saturated NH_4Cl, washed with water, dried ($MgSO_4$) and evaporated. The crude product was purified by Kugelrohr distillation (oven temp. 50–60 °C, 95 mmHg,). Yield 0.063 g (85%). ^{1}H NMR (C_6D_6): δ −0.13 (s, 2 × $SiMe_3$), 6.31 (s, 2 H).

References

1. Brook, A. G., Jones, P. F. and Peddle, G. J. D. *Can. J. Chem. 46* (1968) 2119.
2. Narasaka, K., Saito, N., Hayashi, Y. and Ichida, H. *Chem. Lett.* (1990) 1411.
3. (a) Ricci, A., Fiorenza, M., Degl'Innocenti, A., Seconi, G., Dembech, P., Witzgall, K. and Bestmann, H. J. *Angew. Chem. 97* (1985) 1068; (b) Bestmann, H. J., Haas, W., Witzgall, K., Ricci, A., Lazzari, D., Degl'Innocenti, A., Seconi, G. and Dembech, P. *Liebigs Ann. Chem.* (1995) 415.
4. Ricci, A., Degl'Innocenti, A. and Ancillotti, M. *Tetrahedron Lett. 27* (1986) 5985.
5. Pan, M. and Benneche, T. *Synth. Commun. In press.*
6. Palomo, C., Aizpurua, J., Garcia, J. M., Ganboa, I., Cossio, F. P., Lecea, B. and Lopez, C. *J. Org. Chem. 55* (1990) 2498.
7. Benneche, T. and Undheim, K, *Acta Chem. Scand., Ser. B 37* (1983) 93.
8. (a) Picard, J. P., Ekkouya, A., Dunogues, J., Duffaut, N. and Calas, R. *J. Organomet. Chem. 93* (1975) 51; (b) Kuwajima, I., Sato, T., Minami, N. and Abe, T. *Tetrahedron Lett.* (1976) 1591.
9. Groebel, B. T. and Seebach, D. *Chem. Ber. 110* (1977) 852.

Received January 2, 1998.