PERKIN 1

Synthesis of trimethylgermyl trimethylsilyl ketone and bis(trimethylgermyl) ketone

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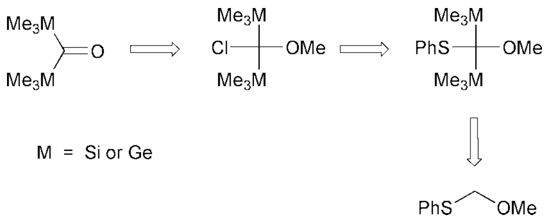
Trimethylgermyl trimethylsilyl ketone **7a** and bis(trimethylgermyl) ketone **7b** have been prepared by hydrolysis of α-chloro ethers **6** on silica gel. Spectroscopic data for the ketones **7** have been compared with data from di-*tert*-butyl ketone, *tert*-butyl trimethylsilyl ketone and bis(trimethylsilyl) ketone.

Introduction

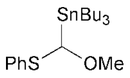
Bis(trimethylsilyl) ketone was first prepared in pure form in 1985.[1] One striking feature of this compound is its unusually large downfield ^{13}C absorption of the carbonyl carbon: δ 318.8.[1] An increasing value for the carbonyl carbon has been observed in going from di-*tert*-butyl ketone to *tert*-butyl trimethylsilyl ketone to bis(trimethylsilyl) ketone (see Table 1).[2] We have recently reported a new synthesis of bis(trimethylsilyl) ketone[3] and were interested to see what happened to the ^{13}C value for the carbonyl carbon when the series was extended to germanium. The UV spectra of triethylgermyl trimethylsilyl ketone and bis(triethylgermyl) ketone and the IR spectrum of bis(triphenylgermyl) ketone have been reported previously, but other properties were not investigated due to the instability of these compounds.[4]

Our strategy for the synthesis of bis(metalloidal) ketones is shown in Scheme 1.[3] A key point in this protocol is the preparation of the ketones in a non-oxidative environment, since these compounds are usually very sensitive to oxidative conditions.[2,4]



Scheme 1

A germyl–carbon bond can be cleaved by halogens.[5] Thus there might be competition between cleavage of the C–S bond and the C–Ge bond in compounds such as **3** (Scheme 2) when they are reacted with halogens. It should be noted that in the tin compound **1** the C–Sn is cleaved in preference to the C–S bond with sulfuryl dichloride.[6]



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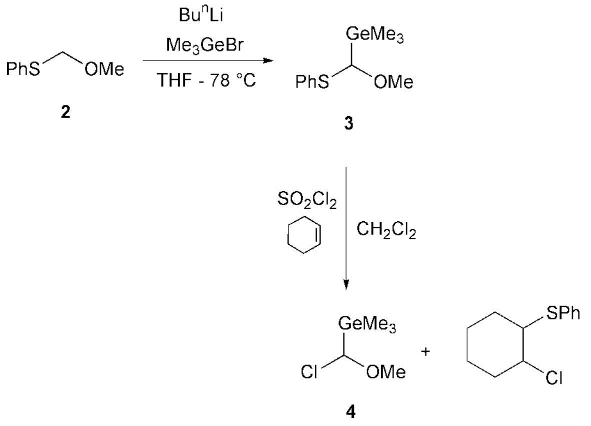
Results and discussion

To investigate the stability of the C–Ge bond towards halogens in *O*,*S*-acetals, compound **3** was prepared and reacted with sulfuryl dichloride (Scheme 2). Only cleavage of the *C*–*S* bond was observed and the α-chloro ether **4** was isolated in good yield (77%).



Scheme 2

With the information that a C–S bond can selectively be cleaved in the presence of a C–Ge bond in molecules like **3**, the synthesis of compounds **6** and **7** was attempted. Silylation and germylation of **3** proceeded well using *tert*-butyllithium in THF at low temperature and the *O*,*S*-acetals **5a** and **5b** were isolated in 90 and 92% yield respectively (Scheme 3).

The bis(trimethylgermyl) compound **5b** can be prepared in one step from the *O*,*S*-acetal **2** using 2.4 equivalents of *tert*-butyllithium and 2.4 equivalents trimethylgermyl bromide. The two-step procedure, with isolation of compound **3**, gave, however, a higher total yield of compound **5b** (46 and 85% respectively). As in the *O*,*S*-acetal **3** only the C–S bond in compounds **5** was cleaved by sulfuryl dichloride. The α-chloro ethers **6** were not separated from the adduct formed between benzenesulfenyl chloride and cyclohexene, but directly run through a silica gel column to give the ketones **7a** and **7b** in 53 and 65% yield, respectively (Scheme 3).†

The compound **7a** has a red colour while **7b** is orange. Both compounds are extremely sensitive to air and their synthesis is preferentially performed in a glove box under an inert atmosphere.

Table 1 shows a comparison of spectroscopic data for

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† The ^{1}H NMR spectrum of the crude product from reaction of **5** with sulfuryl dichloride indicated formation of the α-chloro ethers **6** [**6a** δ_H(CDCl$_3$) 0.16 (9H, s. SiMe$_3$), 0.33 (9H, s, GeMe$_3$), 3.45 (3H, s, OMe); **6b** δ_H(CDCl$_3$) 0.28 (18H, s, GeMe$_3$), 3.43 (3H, s, OMe)].

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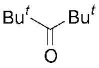
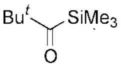
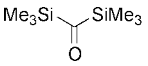
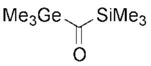
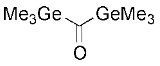
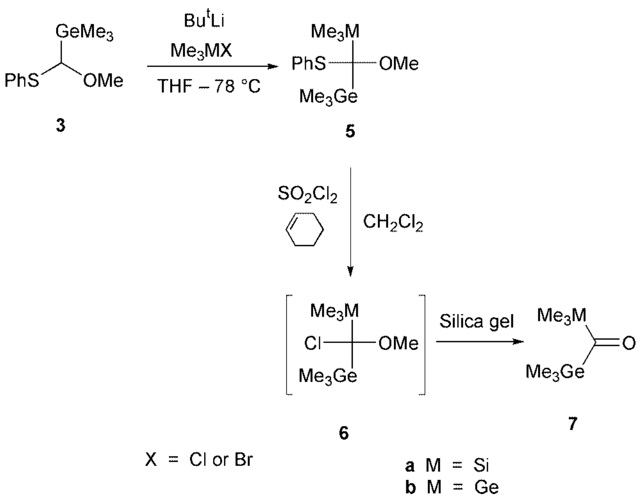
Table 1 $\delta_{C=O}$ ^{13}C, λ_{max} (nm) and $\nu_{C=O}$ (cm^{-1}) data for di-*tert*-butyl ketone, trimethylsilyl *tert*-butyl ketone, bis(trimethylsilyl) ketone, trimethylsilyl trimethylgermyl ketone **7a** and bis(trimethylgermyl) ketone **7b**

				 **7a**	 **7b**
$\delta_{C=O}$ ^{13}C	$218^{2,a}$	$249^{2,a}$	$318.8^{2,b}$	309.1^{b}	300.6^{b}
λ_{max}/nm	$298^{2,c}$	367^{2}	$533^{2,d}$	521^{d}	509^{d}
$\nu_{C=O}$/cm^{-1}	$1689^{2,e}$	$1640^{2,e}$	$1570^{2,e}$	1565^{f}	1585^{f}

[a] $CDCl_3$. [b] C_6D_6. [c] Cyclohexane. [d] CH_2Cl_2. [e] Film. [f] In CCl_4.

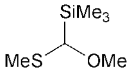


Scheme 3

di-*tert*-butyl ketone,[2] trimethylsilyl *tert*-butyl ketone,[2] bis(trimethylsilyl) ketone,[2] trimethylsilyl trimethylgermyl ketone **7a** and bis(trimethylgermyl) ketone **7b**.

In going from di-*tert*-butyl ketone to bis(trimethylsilyl) ketone the ^{13}C NMR absorption for the carbonyl carbon shifts to a lower field, from δ 218 to 318.8 (Table 1). When a trimethylsilyl group in bis(trimethylsilyl) ketone is substituted with a trimethylgermyl group, this absorption moves to a higher field again (δ 309.1), and moves even higher (δ 300.6) when both trimethylsilyl groups are exchanged with trimethylgermyl groups. An explanation of the effect of the silyl groups on the ^{13}C chemical shift of carbonyl carbons in acylsilanes has been given.[7] A shift to lower values is also seen for the λ_{max} value (Table 1). The ν_{CO} value shifts to a higher value on going from the trimethylsilyl germyl ketone **7a** to the bis(trimethylgermyl) ketone **7b** (Table 1).

In the synthesis of the α-chloro ether **4** benzenesulfenyl chloride is formed. The sulfenyl chloride is trapped with cyclohexene and the α-chloro ether is separated from the adduct by distillation. In the preparation of the ketones **7**, we did not manage to achieve a good separation of the α-chloro ethers **6** from the adduct by distillation. The mixture was therefore run through a silica gel column and the formation of the ketones **7** and the separation from the adduct were done in one operation.‡ In this procedure care has to be taken to avoid product contamination by the adduct. To improve the procedure we wanted to use a methylsulfanyl group in the *O*,*S*-acetal **5** instead of a phenylsulfanyl group. This would yield methanesulfenyl choride instead of benzenesulfenyl chloride and methanesulfenyl chloride could be removed together with the solvent.[8] The crude α-chloro ether could then hopefully be used directly without being distilled prior to hydrolysis. To test this procedure the hemithioacetal **8**[9] was reacted with *tert*-butyllithium followed by trimethylgermyl bromide. We were, however, not able to purify the crude product properly.



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By running the germylation of **8**, the C–S bond cleavage reaction and the hydrolysis without any purification of the intermediates, the ketone **7a** was isolated in 15% yield. In comparison the procedure from the phenylsulfanyl hemiacetal **3** gave the ketone **7a** in 60% overall yield.

Experimental

All reactions were conducted under an inert amosphere of either Ar or N_2. THF was distilled from sodium and benzophenone, and dichloromethane from CaH_2. NMR spectra were recorded at 300 MHz (^1H) and at 75 MHz (^{13}C) on a Bruker Avance DPX 300 instrument. Mass spectra, under electron impact conditions, were recorded at 70 eV ionizing energy on a Fision ProSpec instrument. The spectra are presented as *m*/*z* (% rel. int.). IR spectra were recorded on a Nicolet Magna FT-IR 550 instrument using attenuated total reflection. UV spectra were recorded on a Shimadzu Recording Spectrophotometer UV-260.

Methoxy(phenylsulfanyl)(trimethylgermyl)methane 3

tert-Butyllithium (1.6 M, 1.00 cm^3, 1.60 mmol) was added dropwise to a solution of methoxy(phenylsulfanyl)methane[10] (205 mg, 1.33 mmol) in dry THF (2 cm^3) under N_2 at −78 °C. The mixture was stirred at −40 °C for 30 min, recooled to −78 °C before a solution of trimethylgermyl bromide (316 mg, 1.60 mmol) in dry THF (1 cm^3) was added dropwise. The mixture was stirred at −78 °C for 2 h before water was added and the product extracted into benzene, washed with water, dried ($MgSO_4$) and evaporated to give the title compound (335 mg, 93%) as a colourless oil. The crude product could be used in the next step without further purification. An analytical sample was prepared by flash chromatography using silica gel (eluent hexane–$CHCl_3$ 3:1) (Found: M$^+$, 272.0285. $C_{11}H_{18}GeOS$: requires 272.0290); δ_H($CDCl_3$) 0.23 (9H, s, $GeMe_3$), 3.36 (3H, s, OCH_3), 4.82 (1H, s, CH), 7.22–7.25 (3H, m, Ph), 7.46–7.49 (2H, m, Ph); δ_C($CDCl_3$) −2.6 ($GeCH_3$), 56.6 (OCH_3), 84.9 (C), 126.7, 128.7, 131.0, 138.0 (Ph); *m*/*z* (EI) 272 (M$^+$, 9), 257 (21), 153 (100), 135 (23), 119 (35), 105 (16), 91 (17), 77 (15).

Chloro(methoxy)(trimethylgermyl)methane 4

Sulfuryl dichloride (84 mg, 0.62 mmol) in dry dichloromethane (1 cm^3) was added dropwise to a solution of compound **3** (141 mg, 0.52 mmol) in dry dichloromethane (1 cm^3) under N_2 at 0 °C. The mixture was stirred at 0 °C for 30 min before a solution of cyclohexene (51 mg, 0.62 mmol) in dry dichloromethane (1 cm^3) was added dropwise. The mixture was stirred

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‡ Not trapping the benzenesulfenyl chloride reduces the yield of the ketones **7**.

at 0 °C for 30 min before the solvent was removed and the crude product distilled in a Kugelrohr apparatus (oven temp. 60–70 °C, 1 mmHg) to give the title compound (79 mg, 77%) as a colourless oil; δ_H(CDCl$_3$) 0.03 (9H, s, GeMe$_3$), 3.51 (3H, s, OMe), 5.49 (1H, s, CH); δ_C(CDCl$_3$) −4.1 (GeMe$_3$), 60.0 (OMe), 99.7 (CH).

Methoxy(phenylsulfanyl)(trimethylgermyl)(trimethylsilyl)methane 5a

tert-Butyllithium (1.6 M, 0.46 cm^3, 0.74 mmol) was added dropwise to a solution of compound **3** (167 mg, 0.62 mmol) in dry THF (2 cm^3) under N$_2$ at −78 °C. The mixture was stirred for 30 min at −78 °C before a solution of trimethylsilyl chloride (80 mg, 0.74 mmol) in dry THF (0.5 cm^3) was added dropwise. The mixture was stirred at ambient temperature for 2 h before an aqueous solution of NH$_4$Cl (10%) was added and the product extracted into benzene, washed with water, dried (MgSO$_4$) and evaporated to give the title compound (192 mg, 90%) as a colourless oil. The crude product could be used in the next step without further purification. An analytical sample was prepared by flash chromatography using silica gel (eluent hexane–CHCl$_3$ 3:1) (Found: M$^+$, 344.0697. C$_{14}$H$_{26}$GeOSSi: requires 344.0685); δ_H(CDCl$_3$) 0.07 (9H, s, SiMe$_3$), 0.25 (9H, s, GeMe$_3$), 3.58 (3H, s, OMe), 7.21–7.25 (3H, m, Ph), 7.42–7.46 (2H, m, Ph); δ_C (CDCl$_3$) −0.4 (SiMe$_3$), 0.6 (GeMe$_3$), 53.0 (OMe), 85.0 (C), 127.7, 128.3, 135.2, 135.8 (Ph); *m*/*z* (EI) 344 (M$^+$, 2), 301 (10), 225 (61), 213 (8), 119 (33), 89 (24), 73 (100).

Bis(trimethylgermyl)(methoxy)(phenylsulfanyl)methane 5b

Method 1. *tert*-Butyllithium (1.5 M, 0.84 cm^3, 1.26 mmol) was added dropwise to a solution of methoxy(phenylsulfanyl)methane[10] (81 mg, 0.53 mmol) in dry THF (1 cm^3) under N$_2$ at −78 °C. The mixture was stirred for 2 h at −78 °C before a solution of trimethylgermyl bromide (249 mg, 1.26 mmol) in dry THF (2 cm^3) was added dropwise. The mixture was stirred at ambient temperature for 1 h before an aqueous solution of NH$_4$Cl (10%) was added and the product extracted into benzene, washed with water, dried (MgSO$_4$) and evaporated. The crude product was purified by flash chromatography using silica gel (eluent hexane–CHCl$_3$ 5:1) to give the title compound (94 mg, 46%), as a colourless oil (Found: M$^+$, 390.0208. C$_{14}$H$_{26}$Ge$_2$OS: requires 390.0128); δ_H(CDCl$_3$) 0.15 (18H, s, GeMe$_3$), 3.55 (3H, s, OMe), 7.21–7.25 (3H, m, Ph), 7.41–7.43 (2H, m, Ph); δ_C(CDCl$_3$) 1.0 (GeMe$_3$), 53.2 (OMe), 86.9 (C), 127.7, 128.3, 135.0, 136.0 (Ph); *m*/*z* (EI) 390 (M$^+$, 2), 345 (4), 271 (69), 213 (38), 119 (100).

Method 2. *tert*-Butyllithium (1.5 M, 1.12 cm^3, 1.68 mmol) was added dropwise to a solution of compound **3** (380 mg, 1.40 mmol) in dry THF (4 cm^3) under N$_2$ at −78 °C. The mixture was stirred for 30 min at −78 °C before a solution of trimethylgermyl bromide (333 mg, 1.68 mmol) in dry THF (2 cm^3) was added dropwise. The mixture was stirred at ambient temperature for 1 h before an aqueous solution of NH$_4$Cl (10%) was added and the product extracted into benzene, washed with water, dried (MgSO$_4$) and evaporated to give the title compound (500 mg, 92%) as a colourless oil. The crude product could be used in the next step without further purification.

Trimethylsilyl trimethylgermyl ketone 7a

Sulfuryl dichloride (56 mg, 0.42 mmol) in dry dichloromethane (0.5 cm^3) was added dropwise to a solution of compound **5a** (119 mg, 0.35 mmol) in dry dichloromethane (1 cm^3) under N$_2$ at 0 °C. The mixture was stirred at 0 °C for 30 min before a solution of cyclohexene (34 mg, 0.42 mmol) in dry dichloromethane (0.5 cm^3) was added dropwise. The mixture was stirred at 0 °C for 30 min before the solvent was removed and the residue eluted through a silica gel column under Ar using first degassed pentane as eluent, then a degassed mixture of pentane–diethyl ether 20:1. The coloured fractions were collected to give the title compound (40 mg, 53%) as a red liquid; δ_H(C$_6$D$_6$) 0.03 (9H, s, SiMe$_3$), 0.22 (9H, s, GeMe$_3$); δ_C(C$_6$D$_6$) −3.84 (SiMe$_3$), −3.06 (GeMe$_3$), 309.1 (CO); ν_{max}(CCl$_4$)/cm^{-1} 1565 (CO); λ_{max}(CH$_2$Cl$_2$)/nm 522.

Bis(trimethylgermyl) ketone 7b

Sulfuryl dichloride (97 mg, 0.72 mmol) in dry dichloromethane (1.5 cm^3) was added dropwise to a solution of compound **5b** (231 mg, 0.60 mmol) in dry dichloromethane (3 cm^3) under N$_2$ at 0 °C. The mixture was stirred at 0 °C for 30 min before a solution of cyclohexene (59 mg, 0.72 mmol) in dry dichloromethane (1.5 cm^3) was added dropwise. The mixture was stirred at 0 °C for 30 min before the solvent was removed and the residue eluted through a silica gel column under Ar using first degassed pentane as eluent, then a degassed mixture of pentane–diethyl ether 20:1. The coloured fractions were collected to give the title compound (102 mg, 65%) as an orange liquid; δ_H(C$_6$D$_6$) 0.29 (18H, s, GeMe$_3$); δ_C(C$_6$D$_6$) −3.35 (GeMe$_3$), 300.6 (CO); ν_{max}(CCl$_4$)/cm^{-1} 1585 (CO); λ_{max}(CH$_2$Cl$_2$)/nm 509.

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