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Synthesis, Molecular Structure, and Some Reactions of Bis(dimethylphenylsilyl) Ketone

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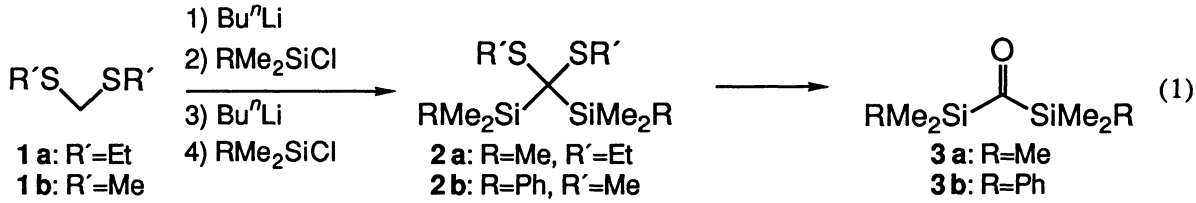
The title compound was prepared from bis(methylthio)methane as a crystalline compound. The molecular structure was determined by X-ray crystallographic analysis, and reactions with alkyl metals and a Wittig reagent were examined.

Acyl groups frequently exhibit characteristic properties when they are attached with hetero atoms. For example, acylsilanes are used in organic synthesis as acyl anion equivalents.[1] In view of the character of acylsilanes, it appeared of interest to synthesize disilyl ketones in order to gain further insight into the effect of adjacent silyl groups on the structural and chemical properties.

As for the syntheses of disilyl ketones, the first unsuccessful attempt was performed by Brook et al.[2] by the dithiane route which is the common synthetic procedure of acylsilanes.[1] Then Brook [2] and Ricci [3] synthesized bis(triphenylsilyl) ketone and bis(trimethylsilyl) ketone respectively by the different oxidative routes. Disilyl ketone is known to be labile to oxidation; oxygen, for instance, reacts with bis(trimethylsilyl) ketone to generate trimethylsilyl carboxylic acid trimethylsilyl ester.[3a] It was, therefore, desirable to devise a practical synthetic route which does not involve such a final oxidative step.

The failure by the above dithiane route is presumably due to the fact that the hydrolysis of trimethylene dithioacetal is rather troublesome. So we examined the synthesis from a bis(alkylthio)methane **1** instead of 1,3-dithiane, because dialkyl dithioacetal is more easily hydrolyzed.

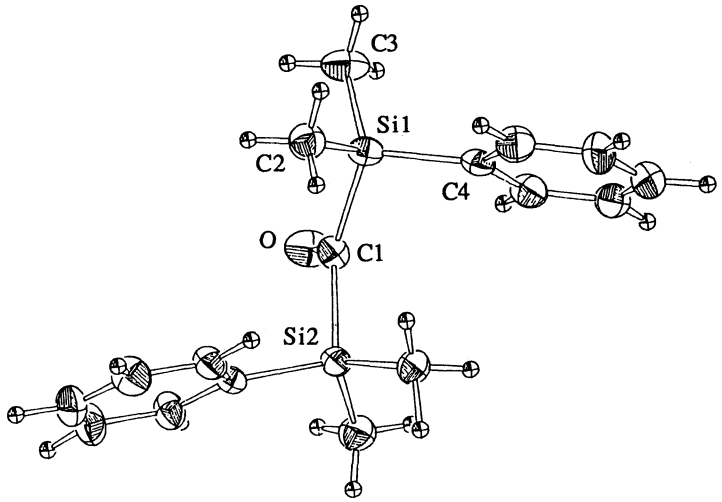
Bis(ethylthio)bis(trimethylsilyl)methane (**2a**) was prepared in the usual way,[4] and the hydrolysis of the dithioacetal group was examined by various methods. When **2a** was treated with HgO-BF_3•Et_2O,[5] bis(trimethylsilyl) ketone (**3a**) was detected as a pink colored oil,[6] but it could not be purified owing to its lability. To stabilize the disilyl ketone sterically, bulkier groups were introduced on the silyl groups. Though the preparations of bis(*t*-butyldimethylsilyl)- and bis(triphenylsilyl)bis(alkylthio)methanes were unsuccessful, the dithioacetal having two dimethylphenylsilyl groups **2b** was obtained in 60 % yield in one pot from bis(methylthio)methane by the following sequence: Lithiation of **1b** by Bu^{n}Li, addition of dimethylphenylsilyl chloride, then lithiation and the second addition of dimethylphenylsilyl chloride. The dithioacetal **2b** was smoothly hydrolyzed with HgO-BF_3•Et_2O,[5] and the purification by column chromatography on florisil gel[3b] (pentane-dichloromethane) under an argon atmosphere at 0 °C afforded bis(dimethylphenylsilyl) ketone (**3b**) in 56% yield as a fairly stable pink colored solid.[7]



(1)

The disilyl ketone **3b** was recrystallized from pentane. The pure ketone **3b** gradually decomposes with oxygen but can be stored at least one month under argon at 0 °C. The spectroscopic data (^{13}C-NMR, UV, IR) of the carbonyl group of **3b** are quite different from those of the alkyl ketones.[7,8]

X-Ray crystallographic analysis of **3b** was undertaken to confirm its exact structure.[9] The following figure shows ORTEP drawing of **3b** with some selected bond lengths and a bond angle. The characteristic feature of **3b** is the long bond length of Si1-C1. Compared with the bond length of Si1-C2, Si1-C3, and Si1-C4 (1.843(6)-1.855(6) Å), that of Si1-C1 is rather long (1.945(6) Å). This bond is also longer than the Si-carbonyl bond of acetyltriphenylsilane (1.926(14) Å).[10] On the other hand, C1-O bond (1.218(6) Å) is relatively shorter than the usual carbonyl bond (1.23(1) Å).[11] As can be seen in this figure, the carbonyl moiety is sterically surrounded by the bulky substituents on the silicons.



Si1-C1	1.945(6) Å
Si1-C2	1.843(6) Å
Si1-C3	1.844(6) Å
Si1-C4	1.855(6) Å
C1-O	1.218(6) Å
Si1-C1-Si2	125.4(3) °

Fig. 1. The ORTEP drawing of bis(dimethylphenylsilyl) ketone (**3b**).

Since the carbonyl group of **3b** exhibited unusual properties as shown in the above spectroscopic and structual analyses, the reactivity of **3b** was investigated. Results of the reactions of **3b** with alkyl metals are summarized in Table 1. MeLi, which has no ß-hydrogen, reacted immediately at -78 °C to produce the addition product **4** and allyllithium also afforded the addition product **5**. The ketone **3b** was, however, reduced by the alkyl metals having a ß-hydrogen, giving the disilylmethanol **7**. Even in the presence of a silyl enol ether, the reaction with $EtAlCl_2$ afforded the reduction product **7** without the formation of the aldol product. When **3b** was

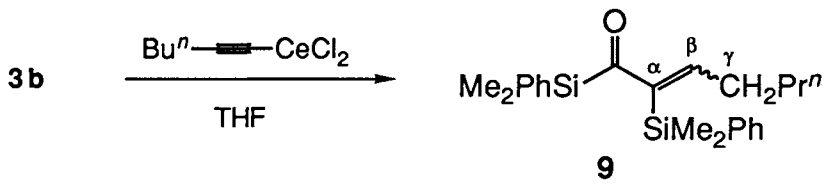
treated with zinc and ethyl bromoacetate in THF at r.t.,[12] Reformatosky reaction slowly progressed to give the ß-hydroxy ester **8**.

Table 1. Reactions of disilyl ketone **3b** with alkyl metals

R-M	Product	Yield / %
MeLi	$(Me_2PhSi)_2C(Me)OH$ (**4**)	79
$CH_2=CHCH_2Li$	$(Me_2PhSi)_2C(CH_2CH=CH_2)OH$ (**5**)	56
Bu^nLi	$(Me_2PhSi)_2C(Bu^n)OH$ (**6**)[a]	39
Bu^nMgBr	$(Me_2PhSi)_2CHOH$ (**7**)	69
$EtAlCl_2$	**7**	91
$LiAlH_4$	**7**	84
$Zn + BrCH_2CO_2Et$	$(Me_2PhSi)_2C(OH)CH_2CO_2Et$ (**8**)	74

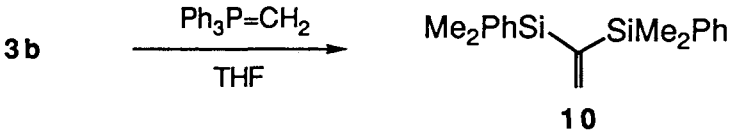
a) **7** was also obtained in 37% yield.

In the case of metal acetylide, **3b** reacted in a different way. Using a lithium salt of 1-hexyne, the pink color disappeared immediately at -78 °C, but the reaction was complicated to give a mixture of many unidentified products. The reaction with 2 equiv. of cerium salt [13] of 1-hexyne at -78 °C gave the rearrangement product **9**[14] in 52% yield (Eq. 2). Also a complicated reaction mixture was resulted from the reaction using more than 2 equiv. of cerium salt.



9 (2)

When **3b** was allowed to react with phosphorus ylide at 0 °C, the Wittig reaction occurred immediately to afford 1,1-disilylethylene **10** in 47% yield (Eq. 3). Reaction with trimethylsilylmethylmagnesium chloride gave the addition product **11** in 67% yield, which was converted to the Peterson product **10** in 87% yield by treatment with KH in THF[15] (Eq. 4). These methods provide useful and alternative procedures for the preparation of 1,1-disilylethylene **10**.[16]



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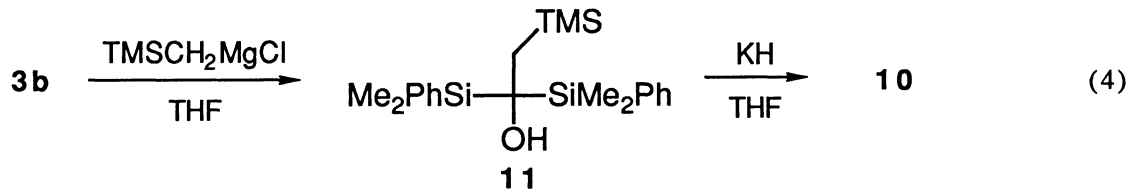

(4)

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3) a) A. Ricci, M. Fiorenza, A. Degl'Innocenti, G. Seconi, P. Dembech, K. Witzgall, and H. J. Bestmann, *Angew. Chem., Int. Ed. Engl.*, **24**, 1068 (1985); b) A. Ricci, A. Degl'Innocenti, and M. Ancilloti, *Tetrahedron Lett.*, **27**, 5985 (1986).
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6) **3a** was identified by ^{13}C NMR (125 MHz, $CDCl_3$): δ = 320.8 (CO) (Ref. 3a).
7) Compound **3b**: mp 62-63 °C; ^1H NMR (500 MHz, $CDCl_3$) δ = 0.24 (s, 12H), 7.26-7.38 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = -5.20, 127.94, 129.62, 134.30, 135.53, 316.53; IR (CH_2Cl_2) 1690, 1557, 1112, 835, 798, 642, 466 cm^{-1}; UV (hexane) λ (ε) 546.0 nm (22); High resolution MS: Found: m/z 298.1195. Calcd for $C_{17}H_{22}OSi_2$: M, 298.1210.
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9) Crystallograghic data: M. F. = $C_{17}H_{22}OSi_2$, M. W. = 298.53, monoclinic, a = 31.99(1), b = 6.483(4), c = 17.075(4) (Å), V = 3507(3) ($Å^3$), ß = 97.99(4)°, space group C2/c, Z = 8, Dc = 1.131 g/cm^3, $\mu(MoK_\alpha)$ = 1.90 cm^{-1}. Data collection: crystal size = 0.3 x 0.1 x 1.0 mm, Tc = 21 °C, MoK_α radiation (graphite monochrometer), 4420 independent reflections ($2\theta < 55.1$ °). The structure was finally refined anisotropically for Si, C, and O, and isotropically for H to give an R factor of 0.051 for 1212 reflections with $Fo > 3\sigma$ (Fo).
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14) The structure of **9** was determined by HMBC [A. Bax and M. F. Summers, *J. Am. Chem. Soc.*, **108**, 2093 (1986).]. Correlation peaks $\delta_{C\alpha}$ = 152 - $\delta_{H\gamma}$ = 1.80 and $\delta_{C\alpha}$ = 143 - $\delta_{H\gamma}$ = 1.80 were observed.
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