An unexpected product of the reaction of organophosphorus betaines containing a P^+–C–Si–S^- fragment with acetyl chloride

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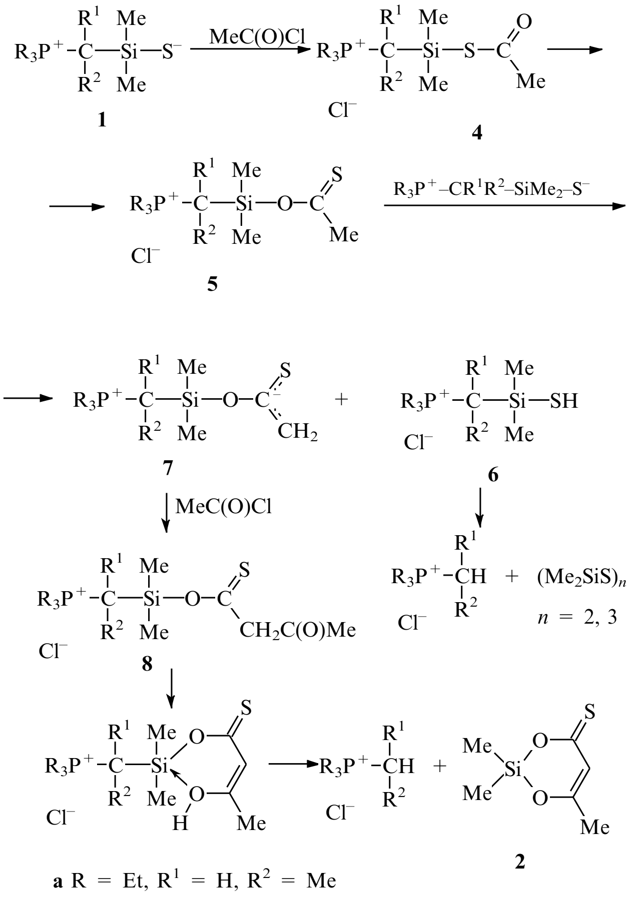
The reaction of MeC(O)Cl with R_3P^+–CR^1Me–$SiMe_2$–S^- 1 affords the heterocycle $\mathrm{Me_2\underline{Si{-}O{-}C({=}S){-}CH{=}CMe{-}O}}$ 2.

We have recently shown[1,2] that organocyclosilathianes react with alkylidenephosphoranes to give the betaines **1**.

$$n\,R_3P{=}CR^1R^2 + (R^3R^4SiS)_n \longrightarrow \underset{\mathbf{1}}{n\,R_3P^+{-}CR^1R^2{-}SiR^3R^4{-}S^-}$$

Alkylation of these compounds in THF gave the expected phosphonium salts.[2] However, the reactions of betaines **1** with acetyl chloride proceed in an unusual way and the results depend on the molar ratio of reagents. Thus treatment of the THF suspension of betaine Et_3P^+–CHMe–$SiMe_2$–S^- **1a** with 1 equivalent of acetyl chloride (~ 5 °C, 5 days) gave the cyclic compound $\mathrm{Me_2\underline{Si{-}O{-}C({=}S){-}CH{=}CMe{-}O}}$ **2** as yellow crystals in 98% yield.

In our opinion the formation of **2** proceeds through a number of consecutive steps. Primarily the *S*-acetyl derivative **4** is formed which easily undergoes rearrangement with migration of the organosilicon moiety to the oxygen atom. This process is thermodynamically favourable. The second molecule of betaine **1**, acting as a base, deprotonates the thioacetate **5**. This deprotonation of thiocarbonyl compounds is well known.[3] Acetylation of the thioenolate ion **7** leads to the β-thiocarbonyl compound **8**. After the enolization the formation of the 'macroergical' Si–O bond completes the cyclization and the formation of **2**. The phosphonium salt **6** decomposes by breaking the Si–C bond as expected.[4]



a R = Et, R^1 = H, R^2 = Me
b R = Ph, R^1 = R^2 = Me

Scheme 1

The structure of **2** was confirmed by X-ray analysis† and by multinuclear NMR.‡ The bond lengths and angles are shown in Table 1 and the molecular structure is shown in Figure 1.

The ring in molecule **2** is planar. The tetrahedral geometry of the silicon atom in the ring is distorted. The bond angles O–Si–O 103.7(1)° and C–Si–C 115.1(1)° differ significantly from the ideal tetrahedral value of 109.5° and the Si–O bond lengths 1.668(2) and 1.675(2) A are considerably larger than the average bond length (1.645 A).[5] These distortions probably result in the strain which is responsible for the high reactivity of **2**, which is in particular very sensitive to oxygen and moisture.

Heating of betaine **1a** with a large excess of acetyl chloride in ether gives the salt **3a** in near quantitative yield. In the absence of **1** the enolization of **5** does not proceed and typical

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† *Crystal data for* **2**: $C_6H_{10}O_2SSi$, $M = 174.29$, orthorhombic, space group *Pnma*, −90 °C, $a = 8.834(2)$, $b = 7.361(2)$, $c = 13.454(2)$ A, $U = 874.9(3)$ A^3, $Z = 4$ (molecule occupies a special position on the mirror plane), $D_c = 1.323$ g cm^{-3}. Unit cell parameters and 994 reflections intensities were measured with automated 4-circle Siemens P3/PC diffractometer (183 K, λMoKα, graphite monochromator, $\theta/2\theta$-scan, $\theta < 28°$). The structure was solved by direct method and refined by full-matrix least-squares technique in anisotropic approximation for non-hydrogen atoms. Hydrogen atoms, located objectively in the difference Fourier map, were refined in isotropic approximation. The final discrepancy factors are $R_1 = 0.033$ for 980 unique reflections with $I > 2\sigma(I)$ and $wR_2 = 0.107$ for all 994 unique reflections. All calculation were carried out using SHELXTL PLUS and SHELXL-93 programs.

‡ ^{1}H, ^{13}C, ^{29}Si and ^{31}P NMR spectra were recorded on a Bruker AM360 spectrometer ($SiMe_4$ was used as an internal standard for ^{1}H, ^{13}C and ^{29}Si NMR spectra and 85% H_3PO_4 in D_2O was used as an external standard for ^{31}P, δ/ppm, J/Hz in parentheses, C_5D_5N).

For **2**: ^{1}H NMR (360 MHz, C_6D_6): δ 0.07 (6 H, s, $^2J_{SiH}$ 7.5, Me_2Si), 1.45 (3 H, d, $^4J_{HH}$ 0.7, MeC), 6.13 (1 H, q, $^4J_{HH}$ 0.7, CH=C). ^{13}C NMR (90.6 MHz, C_6D_6): δ −2.01 ($^1J_{CH}$ 121.5, $^1J_{CSi}$ 73.6, Me_2Si), 21.73 ($^1J_{CH}$ 128.7, $^4J_{CH}$ 3.0, CH_3C), 112.54 ($^1J_{CH}$ 170.3, $^3J_{CH}$ 3.9, –CH=), 159.59 ($^2J_{C=CH} \approx {}^2J_{C-CH_3} \approx 6.5$, –CMe=), 203.20 ($^2J_{CH}$ 4.8, C=S). ^{29}Si NMR (71.5 MHz, C_6D_6): δ 10.40.

For **3a**: ^{1}H NMR (C_5D_5N): δ 0.91 (6 H, s, Me_2Si), 1.32 (9 H, dt, $^3J_{PH}$ 18.00, $^3J_{HH}$ 7.6, CH_3CHP^+), 1.49 (3 H, dd, $^3J_{PH}$ 17.4, $^3J_{HH}$ 7.3, CH_3CHP^+), 2.64–2.94 (6 H, m, AB-part of $ABMX_3$ spectrum: complex multiplet, CH_2P^+), 4.14 (1 H, dq, $^2J_{PH}$ 20.1, $^3J_{HH}$ 7.3, CHP^+). ^{13}C NMR (C_5D_5N): δ 3.29 (br. s, $^1J_{SiC}$ 59.9, Me_2Si), 6.77 (d, $^2J_{PC}$ 5.3, CH_3CH_2–P^+), 9.23 (d, $^2J_{PC}$ 4.6, CH_3CHP^+), 13.16 (d, $^1J_{PC}$ 47.9, CH_2P^+), 13.36 (d, $^1J_{PC}$ 38.6, CHP^+). ^{31}P NMR (145.8 MHz, C_5D_5N): δ 44.41. ^{29}Si NMR (C_5D_5N): δ 30.91 (d, $^2J_{PSi}$ 3.2).

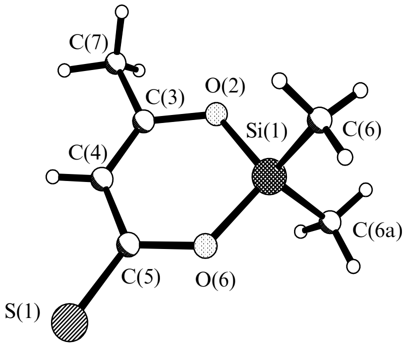
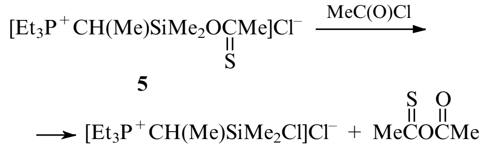


Figure 1 General view of molecule **2**.

breaking of the Si–O bond by MeC(O)Cl with the formation of salt **3a** takes place.

Other betaines, *e.g.* $Ph_3P^+–CMe_2–SiMe_2–S^-$ **1b**, react with MeC(O)Cl in a similar manner. The cyclic product **2** or the silylated phosphonium salt are formed depending on the ratio of reagents.



$$[Et_3P^+CH(Me)SiMe_2O\underset{\underset{S}{\|}}{C}Me]Cl^- \xrightarrow{MeC(O)Cl}$$

5

$$\longrightarrow [Et_3P^+CH(Me)SiMe_2Cl]Cl^- + Me\overset{\overset{S}{\|}}{C}O\overset{\overset{O}{\|}}{C}Me$$

3a

Scheme 2

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Table 1 Bond lengths (*d*) and bond angles (*Ψ*) of **2**.

Bond	*d*/A	Angle	*Ψ*/°
Si(1)–C(5)	1.645(2)	O(2)–Si(1)–O(6)	103.7(1)
Si(1)–O(6)	1.675(2)	O(6)–Si(1)–C(6)	110.1(1)
O(6)–C(5)	1.347(3)	C(3)–O(2)–Si(1)	123.2(1)
C(3)–C(7)	1.486(3)	C(4)–C(3)–O(2)	123.2(2)
Si(1)–O(2)	1.668(2)	O(2)–C(3)–C(7)	112.7(2)
Si(1)–C(6)	1.820(2)	O(6)–C(5)–C(4)	117.6(2)
O(2)–C(3)	1.350(2)	C(4)–C(5)–S(1)	123.1(2)
C(3)–C(4)	1.350(3)	O(2)–Si(1)–C(6)	108.7(1)
C(4)–C(5)	1.435(3)	C(6)–Si(1)–C(6)[a]	115.1(1)
		C(5)–O(6)–Si(1)	126.7(2)
		C(4)–C(3)–C(7)	124.1(2)
		C(3)–C(4)–C(5)	125.6(2)
		O(6)–C(5)–S(1)	119.3(2)

[a] Transformations of symmetry, used for the generation of equivalent atoms: $x,-y + 1/2, z$.

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