A new method for generating organosilanones

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A new method for the generation of organosilanones by the reaction of betaines, $R_3P^+—CR^1R^2—SiR^3R^4—S^-$, with $(Et_3Sn)_2O$ was suggested.

Key words: organosilicon-phosphorus betaines, organosilanones, hexaethyldistannoxane.

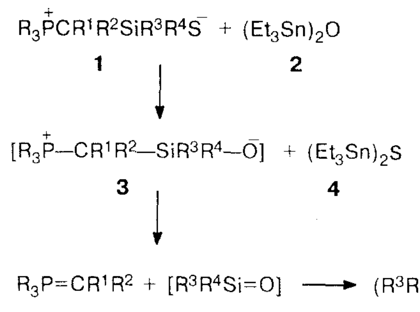
An extensive literature has been devoted to the chemistry of silanones.[1,2] In the present work, we suggest a convenient preparative method for generating these intermediates by the reaction of betaines, $R_3P^+—CR^1R^2—SiR^3R^4—S^-$ (**1**),[3] with $(Et_3Sn)_2O$ (**2**). Probably, the process involves a step of the formation of betaines (**3**), which readily undergo transformation of the retro Wittig reaction type[4] (Scheme 1).

The formation of silanones **5** has been definitely proven by performing the reaction in the presence of Me_3SiOMe, which readily "traps" silanones.[1]

$$\mathbf{5} + Me_3SiOMe \longrightarrow \underset{\mathbf{6}}{Me_3SiOSiR^3R^4OMe}$$

a: $R^3 = R^4 = Me$
b: $R^3 = Me$; $R^4 = Ph$

Scheme 1



$$\underset{\mathbf{1}}{R_3\overset{+}{P}CR^1R^2SiR^3R^4\bar{S}} + \underset{\mathbf{2}}{(Et_3Sn)_2O} \longrightarrow \underset{\mathbf{3}}{[R_3\overset{+}{P}—CR^1R^2—SiR^3R^4—\bar{O}]} + \underset{\mathbf{4}}{(Et_3Sn)_2S}$$

$$\mathbf{3} \longrightarrow R_3P{=}CR^1R^2 + \underset{\mathbf{5}}{[R^3R^4Si{=}O]} \longrightarrow (R^3R^4SiO)_n$$

a: R = Ph; $R^1 = R^2 = R^3 = R^4 = Me$
b: $R = R^3 = Ph$; $R^1 = R^2 = R^4 = Me$

Experimental

All reactions were carried out in a 10^{-3} Torr vacuum in seamless sealed vessels, using a technique with breaking diaphragms and ampoules.

Siloxanes **6a** and **6b** used for identifying the products were obtained by the reaction of Me_3SiOLi with (chloro)methoxydimethyl- or -methylphenylsilane, respectively, in ether. The physicochemical constants of compound **6a** agree with the literature data. For **6b**: 67 %, b.p. 71—72 °C (0.1 Torr), n_D^{20} 1.4592. ^1H, ^{13}C, ^{29}Si, and ^{31}P NMR spectra were recorded on a Bruker AM-360 spectrometer in degassed solutions of samples in pyridine-d_5 relative to Me_4Si (^1H, ^{13}C, and ^{29}Si) or relative to 85% H_3PO_4 in D_2O (^{31}P). GLC analyses were carried out on an LKhM-80 chromatograph (2 m × 0.3 mm column, 5 % SE-30 on silanized Chromosorb G, 80/100 mesh).

The reaction of $Ph_3P^+—CMe_2—SiMe_2—S^-$ (1a) with 2. *A.* A mixture of compound **2** (0.41 g, 0.96 mmol) and Me_3SiOMe (1 g, 9.6 mmol) was added to a suspension of compound **1a** (0.38 g, 0.96 mmol) in pyridine-d_5 (1.5 mL). The mixture was kept for 12 h at –20 °C, which resulted in a dark claret solution. According to GLC data and ^1H, ^{13}C, ^{29}Si, and ^{31}P NMR spectroscopy, the reaction proceeded quantitatively to give $Ph_3P{=}CMe_2$, $(Et_3Sn)_2S$, **6a** (yield 83 %), and $D_4—D_5$ oligomers (17 %). ^1H NMR, δ: $Ph_3P{=}CMe_2$: 2.00 (d, Me_2C, $J_{P,H}$ = 16.5 Hz); 7.38—7.80 (m, Ph_3P); $(Et_3Sn)_2S$: 1.07—1.28 (m, CH_2Sn); 1.33—1.54 (t, $C\underline{H}_3CH_2Sn$); **6a**: 0.20 (s, Me_3Si); 0.17 (s, Me_2Si); 3.54 (s, SiOMe). ^{13}C NMR, δ: $Ph_3P{=}CMe_2$: 8.72 (d, P=C, $J_{P,C}$ = 123.9 Hz); 20.69 (d, Me_2CP, $J_{P,C}$ = 13.7 Hz); 128.41 (d, C_m, $J_{P,C}$ = 11.0 Hz); 130.78 (d, C_p, $J_{P,C}$ = 2.6 Hz); 133.88 (d, C_o, $J_{P,C}$ = 8.9 Hz); 133.31 (d, C_i, $J_{P,C}$ = 81.3 Hz); $(Et_3Sn)_2S$: 7.22 (s, CH_2Sn, $J_{^{117}Sn,^{13}C}$ = 323.9 Hz, $J_{^{119}Sn,^{13}C}$ = 338.9 Hz); 10.77 (s, CH_3CH_2Sn, $J_{^{117/119}Sn,^{13}C}$ = 24.0 Hz); **6a**: 1.32 (s, Me_2Si); 1.89 (s, Me_3Si); 49.76 (s, SiOMe). ^{29}Si NMR, δ: **6a**: –11.19 (s, Me_2Si); 7.81 (s, Me_3Si). ^{31}P NMR: $Ph_3P{=}CMe_2$: 10.69.

B. Compound **2** (0.432 g, 1.02 mmol) was added to a suspension of compound **1a** (0.4 g, 1.02 mmol) in pyridine-d_5 (2 mL). After 5—10 min the solution turned pink. After 2—3 h the coloring turned to dark claret simultaneously with dissolu-

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tion of betaine **1a**. According to GLC data and ^{1}H, ^{13}C, ^{29}Si, and ^{31}P NMR spectroscopy, the reaction almost ceased after 5 days. The main products included $Ph_3P{=}CMe_2$, $(Et_3Sn)_2S$, and a mixture of D_4—D_5 oligomers in an almost quantitative yield. ^{29}Si NMR, δ: −18.90; −21.28.

The reaction of Ph_3P^+—CMe_2—SiMePh—S^- (1b) with 2. ***A.*** Compound **1b** (0.53 g, 1.16 mmol) was mixed with compound **2** (0.49 g, 1.16 mmol) and Me_3SiOMe (1 g, 9.6 mmol) in pyridine-d_5 (1.5 mL). According to GLC data and ^{1}H, ^{13}C, ^{29}Si, and ^{31}P NMR spectroscopy, after ~12 h the reaction mixture contained $Ph_3P{=}CMe_2$, $(Et_3Sn)_2S$, and **6b** (yield 95 %) along with a small amount of oligomers derived from methylphenylsilanone. For compound **6b**: ^{1}H NMR, δ: 0.28 (s, Me_3Si); 0.44 (s, MeSi); 3.57 (s, SiOMe); 7.39—7.84 (m, PhSi). ^{13}C NMR, δ: −2.17 (s, MeSi); 1.93 (s, Me_3Si); 50.16 (s, SiOMe); 128.24 (s, PhSi-*m*); 130.26 (s, PhSi-*p*); 134.10 (s, PhSi-*o*); 136.65 (s, PhSi-*i*). ^{29}Si NMR, δ: −24.08 (s, MeSi); +9.11 (s, Me_3Si).

B. Compound **1b** (0.56 g, 1.23 mmol) was mixed with compound **2** (0.52 g, 1.23 mmol) in pyridine-d_5 (2 mL). According to GLC data and ^{1}H, ^{13}C, ^{29}Si, and ^{31}P NMR spectroscopy, after 7 days the solution contained the original compounds (~65 %), $Ph_3P{=}CMe_2$, $(Et_3Sn)_2S$, and methylphenylsilanone oligomers.

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