

Grants AI16943. An S.E.R.C. Fellowship to A.B.J. is gratefully acknowledged, as is an American Cancer Society Fellowship to A.P. S.L.S. is pleased to acknowledge discussions with Professor Gary Keck (University of Utah) regarding the preparation and properties of the stannane reagent employed in this investigation.

**Supplementary Material Available:**  $^1\text{H}$  NMR spectra for 8, 10-16, 20, and 21 (19 pages). Ordering information is given on any current masthead page.

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Received October 18, 1988

## Cobalt(II) Chloride Promoted Thionation of Carbonyl Compounds: A Simple Access to Silyl Thioketones and Thioaldehydes

**Summary:** The  $\text{CoCl}_2$ -catalyzed reaction of  $\text{Me}_3\text{SiSSiMe}_3$  with acylsilanes and simple aldehydes affords a direct and easy entry to their sulfur analogues.

**Sir:** Thiocarbonyl containing molecules are versatile synthetic intermediates, which find many applications in the synthesis of complex natural products.<sup>1</sup> Several methods have so far been reported for the formation of such molecules, based on direct conversion of carbonyl derivatives<sup>2</sup> or on pyrolytic<sup>3</sup> and photochemical techniques.<sup>4</sup>

Our long-standing interest in the chemistry of acylsilanes 1 as nucleophilic acylating agents<sup>5</sup> prompted us to focus attention on thioacylsilanes, a closely related but only recently explored<sup>6</sup> class of exotic molecules. We report here that a wide range of acylsilanes reacts with bis(trimethylsilyl) sulfide under mild conditions in the presence of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  as catalyst, affording in high yields the corresponding thiocarbonyl derivatives 2 (Scheme I).

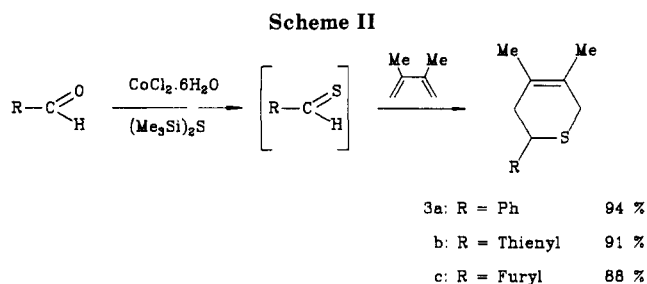
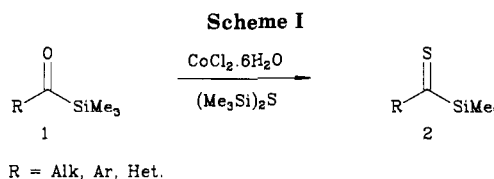
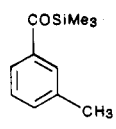
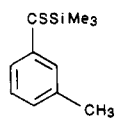
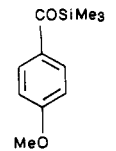
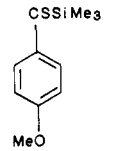
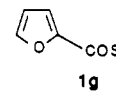
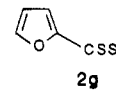
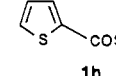
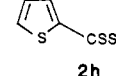


Table I. Synthesis of Thioacylsilanes

entry	acylsilane	product	yield, <sup>a</sup> %
1	$\text{CH}_3\text{COSiMe}_3$ 1a	$\text{CH}_3\text{CSSiMe}_3$ 2a	30 <sup>b</sup>
2	$\text{CH}_3(\text{CH}_2)_5\text{COSiMe}_3$ 1b	$\text{CH}_3(\text{CH}_2)_5\text{CSSiMe}_3$ 2b	64
3	$\text{PhCOSiMe}_3$ 1c	$\text{PhCSSiMe}_3$ 2c	92
4	$\text{PhCOSiPh}_3$ 1d	-	
5	 1e	 2e	74
6	 1f	 2f	66
7	 1g	 2g	68
8	 1h	 2h	59

<sup>a</sup> Yields refer to isolated material. <sup>b</sup> Dimers and trimers were isolated together with the wanted compound.

Thus, treatment of a solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (26.2 mg, 0.112 mmol) and  $\text{PhCOSiMe}_3$  (50 mg, 0.28 mmol) in 0.5 mL of  $\text{CH}_3\text{CN}$  (RPE Carlo Erba) with a solution of

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$\text{Me}_3\text{SiSSiMe}_3$  (99.7 mg, 0.56 mmol) in 0.5 mL of  $\text{CH}_3\text{CN}$  led to an exothermic reaction, which was monitored by GC/MS analysis. Upon completion, the reaction mixture is directly poured onto a chromatographic column packed with Florisil, under inert atmosphere, and eluted with hexane. The blue fraction is collected, and the solvent is removed at room temperature under vacuum to afford a blue oily residue.<sup>7</sup>

Several representative examples are summarized in Table I. The above reaction could also be successfully applied to aldehydes: the mildness of our method, in this case, allows the in situ formation of the thioaldehydes<sup>8</sup> in the monomeric form, which can be trapped with dienes, leading for example to cycloadducts **3a-c** (Scheme II) in very high yields.<sup>9</sup>

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  proved in our hands to be the most effective and mild catalyst, with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  leading to a more extended degree of oligomerization in the case of aliphatic and aromatic compounds (**1a-f**) and to complete polymerization in the case of furoyl- and thenoyltrimethylsilane and of aldehydes.  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  proved, on the other hand, to be ineffective.

However ketones, such as acetophenone and benzophenone, when treated under the conditions of scheme I,

(7)  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.38 (s, 9 H), 6.82-8.20 (m, 5 H). MS: *m/e* (relative intensity) 194 ( $\text{M}^+$ , 30), 179 (57), 135 (45), 121 (31), 104 (61), 77 (22), 73 (100).  $\lambda_{\text{max}}$  ( $\text{Et}_2\text{O}$ ): 678 ( $\epsilon$  38).

(8) Reactions between aldehydes and organosilathianes have been reported: (a) Lebedev, E. P.; Mizhiritskii, M. D.; Baburina, V. A.; Zaripov, Sh. I. *Zh. Obshch. Khim.* 1979, 49, 1084; *Chem. Abstr.* 1979, 91, 39578y. (b) Segi, M.; Nakajima, T.; Suga, S.; Murai, S.; Ryu, I.; Ogawa, A.; Sonoda, N. *J. Am. Chem. Soc.* 1988, 110, 1976 and references cited therein.

(9) General experimental procedure: a solution of benzaldehyde (50 mg, 0.47 mmol), 2,3-dimethylbutadiene (57.4 mg, 0.70 mmol), and hexamethyldisilathiane (83.7 mg, 0.47 mmol) in 0.5 mL of  $\text{CH}_3\text{CN}$  (RPE Carlo Erba) was treated with a solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (22 mg, 0.094 mmol) in 1 mL of  $\text{CH}_3\text{CN}$ . The reaction mixture was stirred overnight, quenched with 5%  $\text{NaHCO}_3$ , extracted with ether, and eluted on silica gel to obtain 84.5 mg (88%) of compound **3c**.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.73 (s, 3 H), 1.75 (s, 3 H), 2.53 (broad d, 2 H,  $J = 6$  Hz), 2.93 (broad d, 1 H,  $J = 16.8$  Hz), 3.29 (broad d, 1 H,  $J = 16.8$  Hz), 4.11 (t, 1 H,  $J = 6.6$  Hz), 6.15 (m, 1 H), 6.32 (m, 1 H), 6.62 (m, 1 H) ppm. MS: *m/e* (relative intensity) 194 ( $\text{M}^+$ , 68), 126 (7), 113 (21), 112 (100), 67 (11).

failed to afford the desired thio derivatives, showing this reaction, at least in this first stage, to be limited to the much more reactive acylsilanes and aldehydes.

Although group 14 organometallic sulfides have already been used for the formation of thiocarbonyl derivatives, our method offers several advantages and complements those previously reported. In fact, while Steliou's method<sup>10</sup> appears to be successful with ketones, it leads to lower yields for acylsilanes and affords isolation only of the trimers of thioaldehydes. On the other hand, the very recent procedure<sup>8b</sup> based on the *n*-BuLi-catalyzed addition of  $\text{Me}_3\text{SiSSiMe}_3$  to aldehydes does not appear to work at all when applied to acylsilanes.

Further synthetic applications of this new method are currently being investigated in our laboratory.

**Acknowledgment.** Financial support by the "Progetto Finalizzato Chimica Fine", CNR, Rome, is gratefully acknowledged.

**Registry No.** **1a**, 13411-48-8; **1b**, 82903-03-5; **1c**, 5908-41-8; **1e**, 68185-95-5; **1f**, 75748-09-3; **1g**, 80671-28-9; **1h**, 88372-95-6; **2a**, 117775-48-1; **2b**, 117775-49-2; **2c**, 79841-55-7; **2e**, 117775-50-5; **2f**, 117775-51-6; **2g**, 117775-52-7; **2h**, 117775-53-8; **3a**, 84040-18-6; **3b**, 117775-54-9; **3c**, 117775-55-0; PhCHO, 100-52-7;  $(\text{Me}_3\text{Si})_2\text{S}$ , 3385-94-2;  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , 7646-79-9;  $\text{H}_2\text{C}=\text{C}(\text{Me})\text{C}(\text{Me})=\text{CH}_2$ , 513-81-5; 2-thienylformaldehyde, 98-03-3; 2-furylformaldehyde, 98-01-1.

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Received June 15, 1988

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## Regiospecific Carbonylation and Ring Expansion of Thietanes and Oxetanes Catalyzed by Cobalt and/or Ruthenium Carbonyls

**Summary:** Dicobalt octacarbonyl and triruthenium dodecacarbonyl together catalyze the regiospecific insertion of carbon monoxide into the least substituted carbon-heteroatom bond of a thietane or oxetane, affording thiobutyrolactones or butyrolactones in fine yields.

**Sir:** Metal complex catalyzed carbonylation reactions have been widely utilized in synthetic organic chemistry.<sup>2,3</sup> An important class of carbonylation reactions are those that involve the direct incorporation of one or two molecules of carbon monoxide into a heterocyclic substrate resulting in ring expansion. This method has been particularly successful when applied to three-membered-ring heterocycles. Examples include the rhodium(I)-catalyzed monocarbonylation of 2-arylaziridines to 3-arylazetidines<sup>4</sup> and the double carbonylation of styrene oxides to  $\alpha$ -keto

lactones catalyzed by cobalt carbonyl under phase-transfer conditions.<sup>5</sup> The reaction is regiospecific in both cases, with carbon monoxide insertion occurring into the most substituted carbon-heteroatom bond.

Little is known concerning the direct conversion of four- to five-membered-ring heterocycles by carbonylation. A patent<sup>6</sup> describes the formation of  $\gamma$ -butyrolactone in 55% yield when oxetane is subjected to cobalt acetate catalyzed carbonylation at 250 atm and 200 °C. We now report that such a transformation actually proceeds at considerably lower pressure. Of greater significance are the results of a study using substituted oxetanes and thietanes, which demonstrates the regio- and stereospecificity of the reaction. An added feature, especially for thietanes, is the use of both ruthenium and cobalt carbonyls as catalysts in order to realize the formation of products in high yields.

Treatment of oxetane with carbon monoxide and a catalytic quantity of cobalt carbonyl [10:1 molar ratio of

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