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The Addition of (Thioacyloxy)silanes to Carbonyl Compounds

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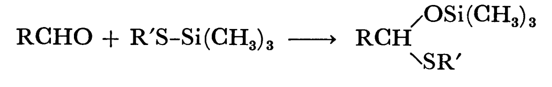
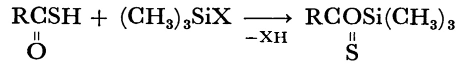
The reactions of (thioacyloxy)silane (*O*-trimethylsilyl thioacetate and thiobenzoate) with some aldehydes (propionaldehyde, butylaldehyde, and benzaldehyde) gave *S*-(1-substituted alkyl) thioacetates (*S*-[1-(trimethylsilyloxy)propyl, and -butyl] thioacetates, and *S*-[α-(trimethylsilyloxy)benzyl] thioacetate), and the three corresponding thiobenzoates respectively. The reactions were catalyzed by 1,8-diazabicyclo[5.4.0]undec-7-ene(DBU), and also by its salt with thiobenzoic acid.

Trimethylsilylated thiols were recently disclosed to undergo a carbonyl-insertion reaction at their Si–S bonds under mild conditions and to be useful as protecting reagents of the carbonyl group.[1] Although the products formed by the trimethylsilylation of thiocarboxylic acids have been reported to be (thioacyloxy)silanes[2,3] with a Si–O bond, there have been only a few reports[2,4] concerning the reactions of these compounds. It is interesting to examine whether or not carbonyl insertion at the Si–O bond of the (thioacyloxy)silane occurs.



$$\mathrm{RCHO} + \mathrm{R'S{-}Si(CH_3)_3} \longrightarrow \mathrm{RCH}\genfrac{}{}{0pt}{}{\diagup \mathrm{OSi(CH_3)_3}}{\diagdown \mathrm{SR'}}$$

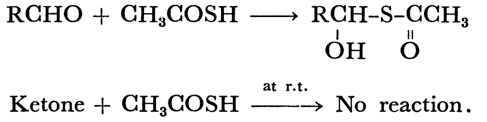


$$\underset{\substack{\parallel\\ \mathrm{O}}}{\mathrm{RCSH}} + \mathrm{(CH_3)_3SiX} \xrightarrow[-\mathrm{XH}]{} \underset{\substack{\parallel\\ \mathrm{S}}}{\mathrm{RCOSi(CH_3)_3}}$$

In this paper, we wish to describe the reaction of (thioacyloxy)silanes(**1** and **2**) with aldehydes(**3a**—**c**), and the isolations, identification, and physical properties of the resulting adducts (**4a**—**c** and **5a**—**c**).

Results and Discussion

Thiocarboxylic acids are known[5] to react with aldehydes to produce the corresponding adducts, which are so stable as to be isolated even at room temperature. On the other hand, thioacetic acid–ketone adducts have been reported[6] to be present only at low temperatures, while over *ca.* −60 °C they are in fast equilibrium with the reactants:

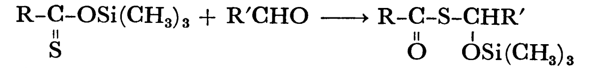


$$\mathrm{RCHO} + \mathrm{CH_3COSH} \longrightarrow \mathrm{RCH{-}S{-}CCH_3}\ \ (\mathrm{OH\ on\ CH},\ \mathrm{=O\ on\ C})$$

$$\mathrm{Ketone} + \mathrm{CH_3COSH} \xrightarrow{\text{at r.t.}} \text{No reaction.}$$

Trimethylsilylated compounds of these adducts are expected to be produced by the reaction of (thioacyloxy)silanes with carbonyl compounds.

Our preliminary studies indicated that (thioacyloxy)silanes (**1** and **2**) react slowly at room temperature with several aldehydes to afford the corresponding adducts. In order to search for more appropriate conditions, *O*-trimethylsilyl thioacetate(**1**) and benzaldehyde(**3c**) were chosen as representative substances and were allowed to react in an NMR tube under several conditions; the progress was observed by monitoring the decrease in the ^{1}H NMR trimethylsilyl signal of the starting material(**1**) and the increase in that of the product(**4c**). The heating of equimolar amounts of **1** and **3c** at 115 °C for 6.5 h in an NMR tube resulted in the formation of the adduct(**4c**) (see Table 1). However, the reaction in the presence of a small amount (0.03 equiv) of DBU was completed within 15 min at room temperature. Also, by the addition of triethylamine, the reaction was accelarated to afford the adduct in an 82% yield after 4 h. These results show that catalytic amounts of the amines accelerate the present reaction.



$$\underset{\substack{\parallel\\ \mathrm{S}}}{\mathrm{R{-}C}}\mathrm{{-}OSi(CH_3)_3} + \mathrm{R'CHO} \longrightarrow \underset{\substack{\parallel\\ \mathrm{O}}}{\mathrm{R{-}C}}\mathrm{{-}S{-}}\underset{\substack{|\\ \mathrm{OSi(CH_3)_3}}}{\mathrm{CHR'}}$$

1: $\mathrm{R=CH_3}$ **3a**—**c** **4a**—**c**: $\mathrm{R=CH_3}$
2: $\mathrm{R=C_6H_5}$ **5a**—**c**: $\mathrm{R=C_6H_5}$
a: $\mathrm{R'=CH_3CH_2}$
b: $\mathrm{R'=CH_3CH_2CH_2}$
c: $\mathrm{R'=C_6H_5}$

Thus, a series of thiocarboxylates(**4a**—**c** and **5a**—**c**) were synthesized by the addition of a small amount (*ca.* 0.03 equiv) of DBU to an equimolar mixture of **1** or **2** and **3** at room temperature without a solvent. The yields and the properties of the products are

Table 1. Monitoring of the production of **4c** and **5b** in an NMR tube

Compd	Solvent	Catalyst	Temp °C	Time h	Yield[a)] %
4c	No	No	r.t.	20	58
4c	No	No	115	6.5	46
4c	No	$\mathrm{Et_3N}$[b)]	r.t.	1	59
4c	No	$\mathrm{Et_3N}$[b)]	r.t.	4	82
4c	No	DBU[c)]	r.t.	15 min	100[f)]
5b	$\mathrm{CDCl_3}$[d)]	No	r.t.	20	No
5b	$\mathrm{CDCl_3}$[d)]	DBU·PhCOSH[e)]	r.t.	1	100[g)]

a) Indicating 100[**4c**/(**4c**+**1**)]% or 100[**5b**/(**5b**+**2**)]%, based on the peak heights[7)] of the trimethylsilyl signals. b) 0.09 equiv. c) 0.03 equiv. d) Containing 0.5 mmol of **2** and 0.6 mmol of **3b** in 0.935 g of $\mathrm{CDCl_3}$. e) 0.09 equiv. f), g) Disappearance of the **1** or **2** reactant respectively.

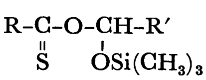
Table 2. Yields and physical and analytical data of **4a**—**c** and **5a**—**b**

Compd	Yield[a)] %	Molecular distillation °C (mmHg)	Formula	Analysis (%)			NMR in CCl_4 δ/ppm	IR in CCl_4 ν/cm^{-1}
					Calcd	Found		
4a	60	40 (0.05)	$C_8H_{18}O_2SSi$	C, H, S,	46.56 8.79 15.54	46.26 8.97 15.32	0.12(s, $(CH_3)_3Si$, 9H) 0.97(t, J=7 Hz, CH_3, 3H), 1.77(qd, J=7 and 6 Hz, CH_2, 2H), 2.27(s, CH_3CO, 3H), 5.49(t, J=6 Hz, CH, 1H)	1665 1245
4b	65	40 (0.04)	$C_9H_{20}O_2SSi$	C, H, S,	49.05 9.15 14.55	48.83 9.33 14.10	0.11(s, $(CH_3)_3Si$, 9H), 0.95(t, J=6 Hz, CH_3, 3H), 1.1—1.8(m, CH_2CH_2, 4H), 2.25(s, CH_3, 3H), 5.54(t, J=6 Hz, CH, 1H)	1690 1252 847 740
4c	78	90 (0.1)	$C_{12}H_{18}O_2SSi$	C, H, S,	56.65 7.13 12.60	56.30 7.17 12.52	0.14(s, $(CH_3)_3Si$, 9H), 2.28(s, CH_3CO, 3H), 6.58(s, CH, 1H), 7.12—7.44(m, aromatic, 5H)	1685 1245
5a	70	120 (0.1)	$C_{13}H_{20}O_2SSi$	C, H, S,	58.16 7.51 11.94	57.80 7.58 11.76	0.15(s, $(CH_3)_3Si$, 9H), 1.03(t, J=7 Hz, CH_3, 3H), 1.89(qd, J=7 and 6 Hz, CH_2, 2H), 5.71(t, J=6 Hz, CH, 1H), 7.28—8.00(m, aromatic, 5H)	1655 1245
5b	79	120 (0.04)	$C_{14}H_{22}O_2SSi$	C, H, S,	59.53 7.85 11.35	59.71 7.99 11.06	0.14(s, $(CH_3)_3Si$, 9H), 0.97(t, J=7 Hz, CH_3, 3H), 1.3—2.0(m, CH_2CH_2, 4H), 5.78(t, J=6 Hz, CH, 1H), 7.28—8.00(m, aromatic, 5H)	1663 1253 848 740
5c	74	150 (0.04)	$C_{17}H_{20}O_2SSi$	C, H, S,	64.52 6.37 10.13	64.80 6.44 10.17	0.19(s, $(CH_3)_3Si$, 9H), 6.83(s, CH, 1H), 7.16—8.04(m, aromatic, 10H)	1665 1245

a) The values are isolated yields based on the aldehydes (**3a**—**c**) used.

summarized in Table 2.

The IR spectra of the products (**4a**—**c** and **5a**—**c**) showed strong absorption bands in the region of 1655—1690 cm^{-1} which were considered to be a characteristic of the carbonyl stretching mode. The results indicate that these products were not the thiocarboxylic *O*-ester (**9**), but the *S*-esters (**4** and **5**).



$\mathrm{R\text{-}\underset{\underset{S}{\|}}{C}\text{-}O\text{-}\underset{\underset{OSi(CH_3)_3}{|}}{CH}\text{-}R'}$

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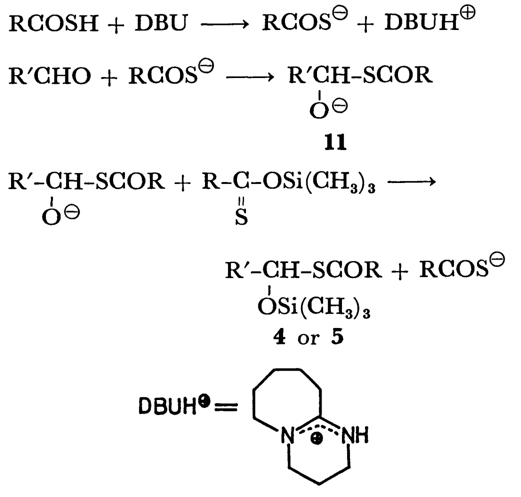
The present reaction was found to be catalyzed also by the salt (**10**). For example, the reaction of **2** with **3b** in chloroform-*d*, which did not proceed at room temperature even after 20 h in the absence of the catalyst, was completed within 1 h by the addition of traces of **10** prepared separately (see Table 1). Consequently, in the acceleration by DBU, the first step seems to involve the formation of the salt of DBU with thiocarboxylic acid, which may be present in traces as a hydrolysis-product of (thioacyloxy)silane (**1** or **2**). As is shown in Scheme 1, the possible reaction mechanism of the catalytic behavior of DBU or the salt (**10**) involves the carbonyl addition of RCOS$^-$, affording the resulting **11** in equilibrium concentrations; **11** is converted to the adduct (**4** or **5**) by the subsequent bimolecular silicon transfer. Similar schemes have been presented by Evans *et al.*[1)] concerning the anion-catalyzed addition reactions of a variety of silicon derivatives to aldehydes and ketones, in which cases the catalysts were the potassium cyanide–crown ether complex, tetrabutylammonium cyanide, and tetrabutylammonium fluoride.



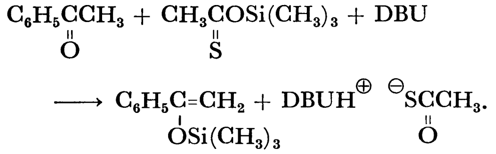
$\mathrm{RCOSH + DBU \longrightarrow RCOS^{\ominus} + DBUH^{\oplus}}$

$\mathrm{R'CHO + RCOS^{\ominus} \longrightarrow R'\underset{\underset{O^{\ominus}}{|}}{CH}\text{-}SCOR}$ **11**

$\mathrm{R'\text{-}\underset{\underset{O^{\ominus}}{|}}{CH}\text{-}SCOR + R\text{-}\underset{\underset{S}{\|}}{C}\text{-}OSi(CH_3)_3 \longrightarrow R'\text{-}\underset{\underset{OSi(CH_3)_3}{|}}{CH}\text{-}SCOR + RCOS^{\ominus}}$ **4** or **5**

Scheme 1.

The additions of **1** or **2** to ketones, *i.e.*, acetophenone, acetone, or cyclohexanone, did not occur at high temperatures (70—115 °C) nor in the presence of a catalytic amount of DBU. However, in the presence of an equimolar amount of DBU, acetophenone reacted with **1** in benzene at room temperature to produce the corresponding *O*-silylated enolate in a 38% yield:



$$C_6H_5\underset{\substack{\| \\ O}}{C}CH_3 + CH_3\underset{\substack{\| \\ S}}{C}OSi(CH_3)_3 + DBU \longrightarrow C_6H_5\underset{\substack{| \\ OSi(CH_3)_3}}{C}{=}CH_2 + DBUH^{\oplus}\ {}^{\ominus}S\underset{\substack{\| \\ O}}{C}CH_3.$$

The lack of any production of the adducts of ketones seems to reflect the character of the adducts of thiocarboxylic acids to ketones.

Experimental

The NMR spectra were taken on a JEOL MH-100 spectrometer, using carbon tetrachloride as the solvent and tetramethylsilane as the internal standard, unless otherwise stated. The abbreviations in the NMR spectra are as follows: s, singlet; d, doublet; qd, quartet of doublets; m, multiplet. The infrared spectra were recorded on a JASCO IR-S or JASCO 701G spectrometer. The mass spectra were measured on a Shimadzu-LKB 9000 spectrometer. Alumina (M. Woelm, activity I) was used for the column chromatography.

Materials. The *O*-trimethylsilyl thioacetate (**1**) and thiobenzoate (**2**) were prepared by the method in the literature.[2] The DBU and aldehydes (**3a—c**) were commercially available, and the latter were used after distillation.

*General Procedure for the Preparations of **4a—c** and **5a—c**.* To a stirred mixture of 4.2 mmol of (thioacyloxy)silane (**1** or **2**) and 4 mmol of aldehyde (**3a—c**) we added one drop (0.1—0.15 mmol) of DBU. After about 15 min at room temperature, the mixture was dissolved in hexane and filtered through a short alumina column to remove any minor impurities. The subsequent removal of the solvent under a vacuum gave a colorless liquid, which was found to be pure **4a—c** or **5a—c** by NMR analyses. The samples obtained by molecular distillation were subjected to elemental analyses and spectral measurements (see Table 2).

*Preparation of DBU·PhCOSH Salt (**10**).* DBU (3.0 g, 20 mmol) was added dropwise to stirred solution of thiobenzoic acid (2.76 g, 20 mmol) in ether at room temperature. Stirring was then continued for an additional 1 h. The precipitate was collected by filtration and recrystallized from chloroform-ether to give the title compound (4.5 g) in a 75.5% yield; mp 116.5—117.5 °C; MS *m/e* 152 (DBU$^+$), 137 (PhCOS$^+$). Found: C, 66.26; H, 7.77; N, 9.55; S, 10.98%. Calcd for $C_{16}H_{22}N_2OS$: C, 66.17; H, 7.64; N, 9.65; S, 11.04%.

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7) The intensities of sharp spectra which lie close together can be obtained more accurately by the measurement of the peak heights than by integration; "Jikken-kagaku Koza Zoku," ed by the Chemical Society of Japan, Tokyo (1967), Vol. 12, p. 552.