Anal. Calcd for $C_8H_{12}O_4$: C, 55.80; H, 7.02. Found: C, 56.05; H, 7.08.

In one run it was possible to get some *cis* acid by fractional crystallization (for use as a standard) but the procedure of Skita and Rossler[9] gave far better separation. From 20 g of the mixture of isomers, shown by glpc to be 60% *cis* and 40% *trans*, 9.9 g of *cis* acid, mp 164–167° (lit.[9] mp 167.5°), and 7.0 g of *trans* acid, mp 147–150° (lit.[9] mp 150.5°), were obtained. Each was shown by glpc to be a single component.

Cyclohexane-1,4-dicarboxylic Acid.—Hydrogenation of terephthalic acid gave essentially *cis* acid. In one reduction the solution was filtered hot and the catalyst cake was washed with 50 ml of hot water. The well-cooled mixture yielded less than 0.5 g of material, mp 280–295° (impure *trans* acid). The filtrate was concentrated to dryness. The residue (6.8 g) was extracted with 1000 ml of analytical grade chloroform. The extract on concentration under reduced pressure yielded 6.5 g (75.7% of *cis* acid), mp 170–171° (lit.[10] mp 166–167°). Glpc showed it to be of high purity (99.6–99.8%). The portion, insoluble in chloroform, after recrystallization from water melted at 310° (lit.[10] mp 312–313°, *trans* acid.)

In other runs, after reduction was complete the mixture was filtered hot, the catalyst cake was washed thoroughly with hot water, and the combined filtrates were concentrated to dryness. Yields were over 90% and the products after isolation melted in the range of 160–172°.[11] None showed any aromatic bands in their infrared spectra. One lot melting at 158–164° was found by glpc to be a mixture of 80% *cis* and 20% *trans* isomers.

[9] A. Skita and R. Rossler, *Ber.*, **72**, 265 (1939).

[10] R. Malachowski and J. Jankiewiczowna, *ibid.*, **67**, 1783 (1934).

[11] One of the referees called Japanese Patent 27245 (1964) to our attention. It described the hydrogenation of aromatic dicarboxylic acids with rhodium oxide at 60–70° (100 atm). *cis*-1,4-Cyclohexanedicarboxylic acid was obtained in 88% yield.

Thionoacyloxysilanes

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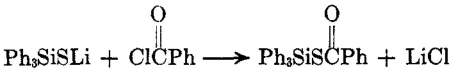
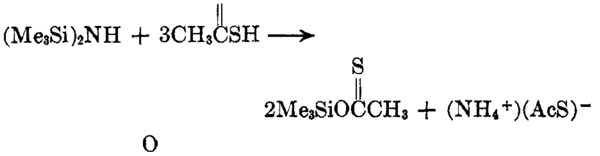
The preparation of only one thiolacyloxysilane has appeared in the literature.[1] Apparently no thionoacyloxysilanes have been reported. This Note describes the preparation and some properties of this new type of compound.

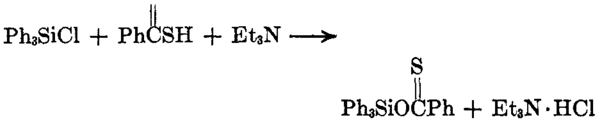


$$\mathrm{Ph_3SiSLi + Cl\overset{O}{\overset{\|}{C}}Ph \longrightarrow Ph_3SiS\overset{O}{\overset{\|}{C}}Ph + LiCl}$$

Two methods were used to prepare thionoacyloxysilanes (eq 1 and 2).



$$\mathrm{(Me_3Si)_2NH + 3CH_3\overset{O}{\overset{\|}{C}}SH \longrightarrow 2Me_3SiO\overset{S}{\overset{\|}{C}}CH_3 + (NH_4^+)(AcS)^-} \quad (1)$$

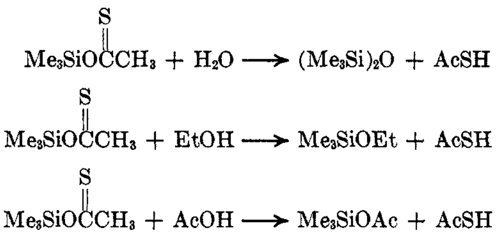


$$\mathrm{Ph_3SiCl + Ph\overset{O}{\overset{\|}{C}}SH + Et_3N \longrightarrow Ph_3SiO\overset{S}{\overset{\|}{C}}Ph + Et_3N\cdot HCl} \quad (2)$$

Thionoacyloxysilanes prepared in these ways have a bright yellow color. These new compounds possess infrared spectra showing no normal carbonyl absorptions as reported by Gilman and Lichtenwalter[1] for thiolbenzoxytriphenylsilane. In agreement with West's theory,[2] the ultraviolet spectra of thionoacetoxysilanes are similar to the spectra of O-alkyl thioacetates. The ultraviolet spectra of thionoacetoxytrimethylsilane and dithionoacetoxydimethylsilane showed absorption peaks at 245 mμ (ε 4570) and 243 mμ (ε 4400), respectively. Janssen[3] reported an absorption peak at 241 mμ (ε 9600) for O-ethyl thioacetate.

The thiolacetate anion exists in both the thiol [$CH_3C(O)S^-$] and thiono [$CH_3C(O^-){=}S$] forms.[4] Therefore, either thiono- or thiolacetoxysilanes might have been expected. However, bond energies[5,6] indicate that a thionoacetoxysilane should be more stable than a thiolacetoxysilane by approximately 15 kcal.

Thionoacetoxytrimethylsilane reacts with compounds containing an hydroxyl group as summarized.



$$\mathrm{Me_3SiO\overset{S}{\overset{\|}{C}}CH_3 + H_2O \longrightarrow (Me_3Si)_2O + AcSH}$$
$$\mathrm{Me_3SiO\overset{S}{\overset{\|}{C}}CH_3 + EtOH \longrightarrow Me_3SiOEt + AcSH}$$
$$\mathrm{Me_3SiO\overset{S}{\overset{\|}{C}}CH_3 + AcOH \longrightarrow Me_3SiOAc + AcSH}$$

The products were identified by gas–liquid partition chromatography (glpc), by comparison of retention times with authentic standards, and by infrared analyses of the reaction mixtures. Reaction with water or ethanol is rapid at room temperature. The reaction with acetic acid is slow unless it is catalyzed with sodium acetate. These reactions are accompanied by a loss of the yellow color.

Experimental Section

Thiolacetic acid was prepared as described in the literature.[7] Thiolbenzoic acid was obtained from Evans Chemitics, Inc., and was freshly distilled. Triphenylchlorosilane (neut equiv 300, calcd 295), hexamethyldisilazane, and dimethyldichlorosilane were obtained from Dow Corning Corp.

Thionoacetoxytrimethylsilane was prepared by adding thiolacetic acid (20 ml, 0.279 mole) dropwise to a solution of hexamethyldisilazane (19.7 ml, 0.093 mole) in hexane (50 ml). After the mixture was cooled to room temperature, it was filtered free of ammonium thioacetate. After the salt was washed with five 10-ml portions of hexane and dried, it weighed 8.0 g (92% of theory). Distillation of the filtrate and washings gave 23.3 g (85% yield) of yellow liquid: bp 84–85° (160 mm); n^{25}_D 1.4513; d^{25}_4 0.929; λ_{max}^{hexane} 207 mμ (ε 2730), 245 (4570), and 389 (11.5); $\lambda_{max}^{CCl_4}$ 3.35 (m), 3.44 (w), 5.82 (w), 5.92 (w), 7.36 (s), 16.7 (w), 20.7 (m), 28.6 (w), and 35 (m) μ; $\lambda_{max}^{CS_2}$ 7.84 (s), 8.00 (s), 8.20 (s), 9.90 (s), 11.8 (s), 14.3 (w), and 15.4 (m) μ. The nmr spectrum showed two absorptions in the ratio 3:1 at τ 9.62 (Si—Me) and 7.49 (C═SMe), respectively. τ values are relative to tetramethylsilane (τ 10).

Anal. Calcd for $C_5H_{12}OSSi$: Si, 18.9; S, 21.6; mol wt, 148. Found Si, 18.5; S, 21.1; mol wt, 163 (cryoscopically in benzene).

Di(thionoacetoxy)dimethylsilane was prepared by adding triethylamine (38.5 ml, 0.275 mole) to a solution of dimethyl-

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[1] H. Gilman and G. D. Lichtenwalter, *J. Org. Chem.*, **25**, 1064 (1960).

[2] R. West, *J. Organometal. Chem.*, **3**, 314 (1965).

[3] M. J. Janssen, *Rec. Trav. Chim.*, **79**, 454 (1960).

[4] E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. 4, Chemical Publishing Co., Inc., New York, N. Y., 1965, p 18.

[5] C. Eaborn, "Organosilicon Compounds," Butterworth and Co. (Publishers) Ltd., London, 1960, p 90.

[6] L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, p 1157.

[7] E. K. Ellingboe, "Organic Syntheses," Coll. Vol. IV, N. Rabjohn, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, p 928.

dichlorosilane (30.0 ml, 0.25 mole) and thiolacetic acid (20 ml, 0.27 mole) in hexane (175 ml). After 1 day at room temperature, the mixture was filtered. The solid was washed with benzene and hexane. The washes and filtrate were combined and distilled to give 20 g (39% yield) of yellow liquid: bp 55° (3 mm); $n^{25}\text{D}$ 1.5034; d_4^{25} 1.102; λ_{max}^{hexane} 222 mμ (ε 3940), 243 (4400), and 389 (22.1); $\lambda_{max}^{CCl_4}$ 3.38 (m), 3.44 (w), 5.82 (w), 7.00 (m), 7.36 (w), 19.6 (m), 20.0 (m), 21.3 (w), 27.8 (m), 28.6 (m), 31.3 (m), and 34.5 (w) μ; $\lambda_{max}^{CS_2}$ 8.00 (s), 8.20 (s), 8.93 (w), 9.90 (s), 11.8 (s), 12.3 (m), 14.5 (w), and 15.9 (w) μ. The nmr spectrum showed two absorptions of equal intensity at τ 9.28 (Si—Me) and 7.44 (C=SMe).

Anal. Calcd for $C_6H_{12}O_2S_2Si$: C, 34.6; H, 5.8; Si, 13.5; S, 30.7; mol wt, 208.4. Found: C, 34.8; H, 5.5; Si, 13.8; S, 31.1; mol wt, 191 (cryoscopically in benzene).

Thionobenzoxytriphenylsilane was prepared by adding triethylamine (8.0 ml, 0.06 mole) to a solution of triphenylchlorosilane (14.75 g, 0.05 mole) and thiolbenzoic acid (6.9 g, 0.05 mole) in benzene (50 ml). After about 30 min, the mixture was filtered free of solids which were washed with benzene (25 ml), then with hexane until colorless, and dried to give 6.2 g of triethylamine hydrochloride (theory is 6.8 g). The benzene wash and filtrate were combined and concentrated. The residue was crystallized from heptane (50 ml) to give 15.7 g (80% yield) of yellow crystals, mp 40–50° (Fisher-Johns melting point apparatus). A portion of the crystals slowly recrystallized from cyclohexane at room temperature had the following properties: mp 96–98°; $\lambda_{max}^{CCl_4}$ 3.26 (w), 3.29 (w), 6.33 (w), 6.76 (w), 6.93 (m), 7.01 (m), 7.63 (s), 19.6 (s), and 20.8 (s) μ; $\lambda_{max}^{CS_2}$ 7.93 (s), 8.20 (s), 8.47 (w), 8.55 (m), 8.85 (s), 9.10 (sh), 9.34 (m), 9.70 (w), 12.6 (s), 13.0 (m), 13.5 (m), 14.1 (s), 14.4 (s), 14.6 (s), 15.4 (w), and 15.6 (w) μ.

Anal. Calcd for $C_{25}H_{20}OSSi$: S, 8.1; Si, 7.1. Found: S, 8.2, 8.5; Si, 6.8, 7.1.

Reactions of Thionoacetoxytrimethylsilane.—Thionoacetoxytrimethylsilane (1.48 g, 0.01 mole) and water (0.18 ml, 0.01 mole) were put in a vial and shaken vigorously. After a few minutes an exothermic reaction was observed. A small amount of water remained. The clear solution above the water was analyzed by glpc, which showed only two products, hexamethyldisiloxane and thiolacetic acid. The elution times were checked with authentic standards. The infrared spectrum of the reaction mixture showed a strong carbonyl absorption at 5.72 μ (neat).

In a similar manner thionoacetoxytrimethylsilane reacted with ethanol and acetic acid. The products with ethanol were shown by glpc to be ethoxytrimethylsilane and thiolacetic acid. The infrared spectrum showed a strong carbonyl absorption at 1750 cm⁻¹. The reaction with acetic acid was slower but was accelerated by a small amount of sodium acetate. The products, acetoxytrimethylsilane and thiolacetic acid, were identified by glpc also.

The Reactions of Carbamoyl Azides with Sulfur Nucleophiles

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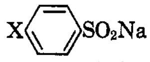
A topic of current interest is the behavior of organic azides under thermal and photolytic conditions, a field stimulated greatly by the elegant work of Lwowski and co-workers[1] on the formation and reactivity of carbethoxynitrene. These results have encouraged us to investigate the decompositions of carbamoyl azides in the presence of sulfur nucleophiles. In particular, we have considered reactions which could provide compounds of pharmaceutical interest.

It has been observed[2] that the decomposition of carbamoyl azides in the presence of hydroxylic solvents is accompanied by Curtius-type rearrangement. To avoid this complication, we have carried out our reactions by heating equimolar amounts of a carbamoyl azide and a sulfur compound without solvent at 125° until gas evolution ceased.

Sulfinate salts react as nucleophiles at the sulfur atom; reactions with alkyl halides, for instance, produce sulfones.[3] It was expected, therefore, that a sulfinate salt would react with a carbamoyl azide to form a sulfonylurea. When the arylsulfinate salts **1** and **2** were heated with the carbamoyl azides **3** and **4**,[4] respectively, vigorous reactions occurred, and the sulfonylureas **5** and **6** (the antidiabetic drugs tolbutamide and chlorpropamide)[5] were obtained in low yields.



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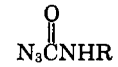
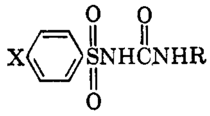
2, X = Cl

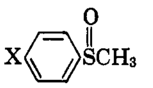


$N_3C(=O)NHR$

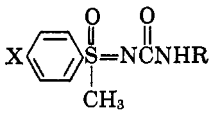
3, R = n-C_4H_9
4, R = n-C_3H_7



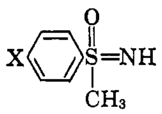
5, X = CH_3; R = n-C_4H_9
6, X = Cl; R = n-C_3H_7



7, X = CH_3
8, X = Cl



9, X = CH_3; R = n-C_4H_9
10, X = Cl; R = n-C_3H_7



11, X = CH_3
12, X = Cl

Horner and Christmann[6] have shown that the reaction of *p*-toluenesulfonyl azide with dimethyl sulfoxide leads to a sulfoximine derivative. Similarly, the carbamoyl azides **3** and **4** underwent gentle reactions with the sulfoxides **7** and **8**[7] to provide, in low yields, the N-carbamoylsulfoximines **9** (mp 63–64°) and **10** (mp 109–111°). The structures of the novel sulfonylurea analogs **9** and **10** were confirmed by independent synthesis from the sulfoximines **11** and **12**[8] and butyl and propyl isocyanate.

Whether these reactions proceed through nitrene intermediates or are best explained as the bimolecular additions of azides to sulfur compounds followed by loss of nitrogen has not been established.

Experimental Section[9]

1-Butyl-3-*p*-tolylsulfonylurea (**5**).—A mixture of 0.71 g (5.0 mmoles) of butylcarbamoyl azide[4] and 0.89 g (5.0 mmoles) of sodium *p*-toluenesulfinate was heated for 0.5 hr in a 125° oil bath. A vigorous reaction occurred. The mixture was diluted with water, made strongly basic with 1 *N* sodium hydroxide, and filtered. The filtrate was acidified with 6 *N* hydrochloric acid, and an oily solid separated. Recrystallization from ethanol provided 0.11 g (8% yield) of colorless crystals, mp 123–124° (lit.[10] mp 128–129°). The infrared spectrum was identical with that of an authentic sample.

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[1] W. Lwowski and T. W. Mattingly, Jr., *Tetrahedron Letters*, 277 (1962), and subsequent papers.

[2] F. L. Scott, *Chem. Ind.* (London), 959 (1954); W. Lwowski, *et al.*, *Tetrahedron Letters*, 3285 (1964).

[3] A. Schöberl and A. Wagner, "Houben-Weyl-Methoden der Organischen Chemie," Vol. 9, Georg Thieme Verlag, Stuttgart, 1955, p 231.

[4] E. Oliveri-Mandala and F. Noto, *Gazz. Chim. Ital.*, **43**, 514 (1913).

[5] W. C. Cutting, "Handbook of Pharmacology," Appleton-Century-Crofts, Inc., New York, N. Y., 1964, p 374.

[6] L. Horner and A. Christmann, *Chem. Ber.*, **96**, 388 (1963).

[7] A. Cerniani and G. Modena, *Gazz. Chim. Ital.*, **89**, 843 (1959).

[8] F. Misani, T. W. Fair, and L. Reiner, *J. Am. Chem. Soc.*, **73**, 459 (1951).

[9] Melting points were determined in a Hershberg apparatus and are uncorrected. Microanalyses were performed by Mr. L. M. Brancone and staff. Nmr spectra were determined by Mr. W. Fulmor and staff on a Varian A-60 spectrometer with tetramethylsilane as an internal standard.

[10] G. Ehrhart, *Naturwissenschaften*, **43**, 93 (1956).