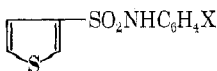


Table III  
Physical Constants and Absorption Spectra of Substituted 3-Thiophenesulfonanilides<sup>a,b</sup>



Registry no.	No.	X	Mp, °C	Formula	Ultraviolet spectra, nm		Infrared spectra, cm <sup>-1</sup>		
					$\lambda_{\max}$	Log $\epsilon$	NH stretch	SO <sub>2</sub> stretch asym	SO <sub>2</sub> stretch sym
51175-66-7	1	H	111-112	C <sub>10</sub> H <sub>9</sub> NO <sub>2</sub> S <sub>2</sub>	227	4.08	3240	1335	1145
					240 <sup>c</sup>	3.94			
51175-67-8	2	<i>m</i> -CH <sub>3</sub>	71	C <sub>11</sub> H <sub>11</sub> NO <sub>2</sub> S <sub>2</sub>	229	4.05	3235	1330	1145
51202-24-5	3	<i>p</i> -CH <sub>3</sub>	114-115	C <sub>11</sub> H <sub>11</sub> NO <sub>2</sub> S <sub>2</sub>	229	4.12	3240	1330	1145
51175-68-9	4	<i>p</i> -OCH <sub>3</sub>	128	C <sub>11</sub> H <sub>11</sub> NO <sub>3</sub> S <sub>2</sub>	232	4.19	3230	1335	1155
					280 <sup>c</sup>	3.24			
51175-69-0	5	<i>m</i> -Cl	83	C <sub>10</sub> H <sub>8</sub> ClNO <sub>2</sub> S <sub>2</sub>	234	4.08	3240	1330	1150
51202-25-6	6	<i>p</i> -Cl	108	C <sub>10</sub> H <sub>8</sub> ClNO <sub>2</sub> S <sub>2</sub>	235	4.20	3235	1320	1150
51175-70-3	7	<i>m</i> -NO <sub>2</sub>	166-167	C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub>	225 <sup>c</sup>	4.12	3240	1330	1145
					237	4.14			
					270 <sup>c</sup>	3.68			

<sup>a</sup> All the compounds were crystallized from aqueous ethanol. <sup>b</sup> Satisfactory combustion analytical data for C, H, N ( $\pm 0.35\%$ ) were reported for these compounds: Ed. <sup>c</sup> Inflection.

In a typical kinetic run a solution containing *ca.*  $3 \times 10^{-4}$  mol of 3-thiophenesulfonyl chloride in methanol (10 ml) was added to a methanol solution (90 ml) containing *ca.*  $1 \times 10^{-2}$  mol of aniline.

The pseudo-first-order rate constants were calculated from conventional plots of  $\log(a-x)$  against time from the slope obtained using the least-squares method.

The second-order rate constant was calculated from the slope of the line obtained by plotting the pseudo-first-order rate constants against aniline concentrations. At least three kinetic runs, at different aniline concentrations, were carried out at the established temperature.

The activation energies and  $\log A$  values were calculated from the Arrhenius equation, while the activation entropies were computed for 25° using the suitable equation.<sup>14</sup>

**Spectroscopy.** The uv spectra were recorded on a Hitachi Perkin-Elmer Model EPS 3T spectrometer in ethanol solutions ( $1 \times 10^{-5}$  mol l<sup>-1</sup>). The ir spectra were recorded in KBr disks on a Perkin-Elmer Model 237 spectrometer. The nmr spectra were obtained with a Varian A-60 spectrometer in carbon tetrachloride, using TMS as internal standard.

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**Registry No.**—3-Thiophenesulfonyl chloride, 51175-71-4; sodium 3-thiophenesulfonate, 51175-72-5.

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## Effect of a Neighboring Trimethylsilyl Group on the Photochemical and Mass Spectral Fragmentation Pathways of S-Alkyl Thioacetates

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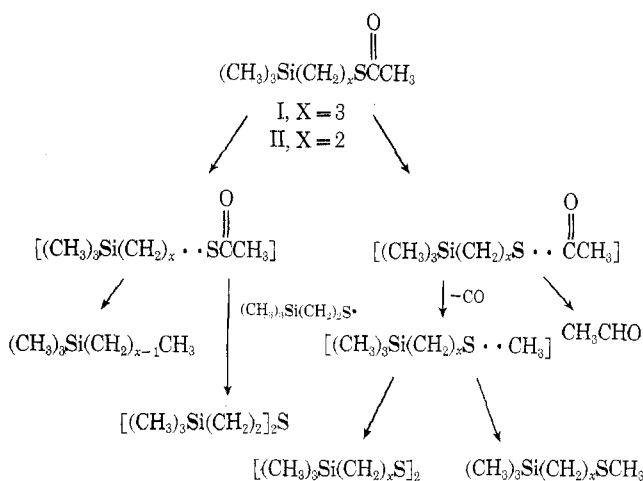
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The photolyses of 3-(trimethylsilyl)propyl thioacetate (I) and 2-(trimethylsilyl)ethyl thioacetate (II) have been studied. Products arising from both sulfur-acyl and sulfur-alkyl bond cleavage have been observed. Sulfur-alkyl bond cleavage is more important in II. The mass spectrum of II, on the other hand, is dominated by ions arising from interaction of the silyl center with the oxygen and sulfur atoms of the thioacetate group.

The photochemistry of S-alkyl thiocarboxylates has been shown to be dominated by products arising from cleavage of the sulfur-acyl bond to the exclusion of products arising from the Norrish type II process.<sup>1,2</sup> This "normal behavior" dominates the photolysis of 3-(trimethylsilyl)propyl thioacetate (I) in dilute benzene solution. Thus the major products of photolysis of I were found to be acetaldehyde (22.7%), 3-(trimethylsilyl)propyl methyl sul-

fide (41.2%), and bis-3-(trimethylsilyl)propyl disulfide (3.9%). In addition, however, trimethylpropylsilane (6.3%) was isolated and shown to be a primary photolysis product since it was present in reactions carried to less than 5% conversion.<sup>3,4</sup> Formation of trimethylpropylsilane may be economically explained as arising from initial sulfur-alkyl bond scission followed by abstraction of a hydrogen atom by the initially formed carbon radical. Sulfur-alkyl bond

Scheme I  
Photolysis of  $\omega$ -(Trimethylsilyl)alkyl Thioacetates



scission has not been previously observed in the photolysis of *S*-alkyl thioacrylates.<sup>1,2</sup> Several higher molecular weight components were also detected by glpc but were not identified. The product yields reported are corrected for recovered starting material (approximately 50%). The formation of these products is outlined in Scheme I.

Products arising from sulfur-alkyl bond cleavage are even more important in the photolysis of 2-(trimethylsilyl)ethyl thioacetate (II) in both dilute benzene and *n*-nonane solutions. Initial sulfur-acyl bond scission leads to 2-(trimethylsilyl)ethyl methyl sulfide (24.6%), bis-2-(trimethylsilyl)ethyl disulfide (14.4%), and acetaldehyde (31.5%). Whereas primary sulfur-alkyl bond scission leads to trimethylsilyl ethane (16%) and bis-2-(trimethylsilyl)ethyl sulfide (7%), both of which were shown to be primary photolysis products. The formation of these products is outlined in Scheme I.

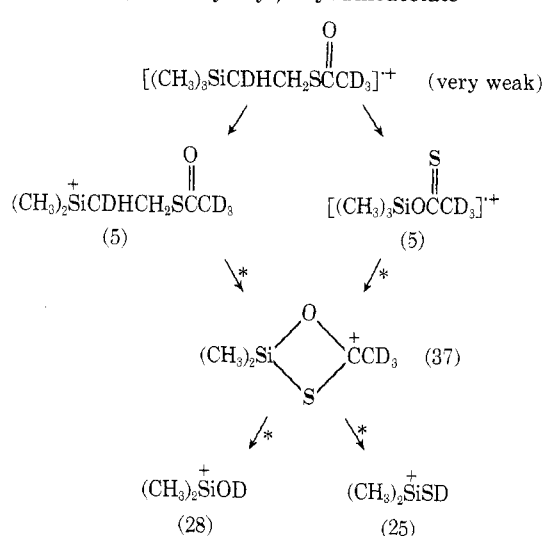
No products arising from the Norrish type II process were detected, *i.e.*, trimethylvinylsilane and thiolacetic acid, even in reactions run in cyclohexene to trap any thiolacetic acid produced.

Apparently a radical center  $\beta$  to a trimethylsilyl group is more favorable than one  $\gamma$ . This could be explained if the radical pair formed by sulfur-alkyl bond breaking has some polar character in which the thioacetate radical has some negative character, while the carbon radical has some positive character, since silicon is well known to stabilize a carbonium ion center  $\beta$  to it.<sup>5-8</sup>

The following observations provide additional evidence that a radical center  $\beta$  to silicon is stabilized. The only product detected by glpc in the photochemically initiated addition of thiolacetic acid to trimethylallylsilane was 3-(trimethylsilyl)propyl thioacetate. On the other hand, addition of thiolacetic acid to trimethylvinylsilane leads to two isomeric products: 2-(trimethylsilyl)ethyl thioacetate (90%) and 1-(trimethylsilyl)ethyl thioacetate (10%).<sup>9</sup> The addition of thiolacetic acid to an alkene is thought to proceed by addition of the thiyl radical to the carbon-carbon double bond to yield a carbon radical which abstracts a hydrogen from thiolacetic acid to regenerate the thiyl radical.<sup>10,11</sup> Clearly in the case of trimethylvinylsilane a primary carbon radical center  $\beta$  to the trimethylsilyl group is able to compete with a secondary carbon radical center  $\alpha$  to the silyl center.

The mass spectrum of 2-(trimethylsilyl)ethyl thioacetate is quite interesting. However, most of the fragmentation processes observed are not related to those observed in the photolysis. This lack of correlation between photo-

Scheme II  
Mass Spectral Fragmentation Pattern of  
2-(Trimethylsilyl)ethyl Thioacetate<sup>a</sup>



<sup>a</sup> An asterisk indicates that a metastable peak was observed. Figures in parentheses are relative intensities.

chemical and mass spectral behavior has been previously observed in the case of 5-trimethylsilyl-2-pentanone.<sup>12,13</sup> The parent ion at  $m/e$  176 is quite weak. Loss of a methyl radical from the quaternary silyl center leads to a  $P - 15$  ion at  $m/e$  161. The mass spectrum of 2-(trimethylsilyl)ethyl thioacetate-*d*<sub>3</sub>(II-*d*<sub>3</sub>), prepared by reaction of acetyl chloride-*d*<sub>3</sub> with 2-(trimethylsilyl)ethanethiol,<sup>14</sup> confirms that the methyl group is lost from the silyl center. The  $P - 15$  ion is thus a siliconium ion and not an acylium ion. The parent ion also fragments by loss of 28. A tempting possibility was that the  $P - 28$  ion was formed by loss of CO to form the 2-(trimethylsilyl)ethyl methyl sulfide cation radical in analogy to the major photochemical process. However, preparation of 2-(trimethylsilyl)ethyl-2-*d* thioacetate by addition of thiolacetic acid-*d*<sub>1</sub> to trimethylvinylsilane ruled this out conclusively, since C<sub>2</sub>H<sub>3</sub>D, *i.e.*, ethylene, is lost rather than CO. Thus, while the silyl Norrish type II process is not observed in the photolysis of II, the related silyl McLafferty rearrangement is favored (see Scheme II).<sup>15</sup> The  $P - 15$  ion also loses ethylene to form an ion of  $m/e$  133. The ion of  $m/e$  133 is also formed by loss of methyl radical from the  $P - C_2H_4$  cation radical. The mass spectrum of II-*d*<sub>3</sub> confirms that the methyl group lost in this process comes from the silyl center. Metastable peaks  $m^* = m_2^2/m_1$  in support of both of these processes are observed. The ion of  $m/e$  133 may have a structure in which the dimethylsilyl group is bonded to both sulfur and oxygen, since metastable peaks indicate that it decomposes by two pathways. The dimethylhydroxysiliconium ion of  $m/e$  75 is formed by loss of thioketene, while the (CH<sub>3</sub>)<sub>2</sub>SiSH<sup>+</sup> ion of  $m/e$  91 is formed by loss of ketene. The mass spectrum of II-*d*<sub>3</sub> indicates the existence of another pathway leading to the ion of  $m/e$  75. In addition to the expected ion at  $m/e$  76, an even more intense ion at  $m/e$  75 is observed. The trimethylsilyl siliconium ion of  $m/e$  73 is about of equal intensity to the base peak. This ion further fragments by loss of ethylene in what must be a most complicated process to yield the CH<sub>3</sub>SiH<sub>2</sub><sup>+</sup> ion of  $m/e$  45. The acylium ion CH<sub>3</sub>C=O<sup>+</sup> at  $m/e$  43 is the base peak. The acylium ion formed directly from the parent ion by sulfur-acyl bond cleavage may be related to the dominant initial photochemical process. See the microfilm edition for supporting data.<sup>16</sup>

### Experimental Section

Infrared spectra were obtained on a Perkin-Elmer 337 spectrometer and were calibrated against known bands in a polystyrene film. Ultraviolet spectra were obtained on a Cary 14 spectrophotometer in cyclohexane solvent. Nmr spectra ( $\delta$ ) were recorded on a Varian T-60 or on a Varian HA-100 spectrometer with benzene ( $\delta$  7.24) or  $\text{CH}_2\text{Cl}_2$  ( $\delta$  5.28) as internal standards. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E spectrometer or on an AEI-MS-902 spectrometer. Vapor phase chromatography was carried out on a Hewlett-Packard F & M 700. Microanalysis was performed by Elek Microanalytical Laboratories. Boiling points and melting points are uncorrected. All apparatus was flamed out prior to use and all reactions were performed under an inert atmosphere of purified nitrogen.

**2-(Trimethylsilyl)ethyl Thioacetate.** A mixture of trimethylvinylsilane<sup>17,18</sup> (25 g, 0.25 mol) and thioacetic acid (25 g, 0.32 mol) was placed in a 300-ml round-bottom flask equipped with a reflux condenser and a magnetic stirring bar. The reaction mixture was irradiated with a GE sun lamp for 2 hr. Distillation afforded a mixture of 2-(trimethylsilyl)ethyl thioacetate and 1-(trimethylsilyl)ethyl thioacetate (33.2 g, 75%), bp 91–93° (25 mm). Isomerically pure samples were obtained by preparative glpc on a 6 ft  $\times$  0.25 in. Apiezon L column at 125°: nmr ( $\text{CS}_2$ ) s (9 H) 0.13, m (2 H) 0.86, s (3 H) 1.97, m (2 H) 2.86; ir (film) 1690 (C=O), 1250, 845  $\text{cm}^{-1}$  ( $\text{SiCH}_3$ );  $\nu_{\text{max}}$  (cyclohexane) 2320  $\text{\AA}$  ( $\epsilon$  4400); mass spectrum  $m/e$  176 (parent). *Anal.* Calcd for  $\text{C}_7\text{H}_{16}\text{OSSi}$ : C, 47.67; H, 9.15. Found: C, 47.59; H, 9.10.

**1-(Trimethylsilyl)ethyl thioacetate** had nmr ( $\text{CCl}_4$ ) s (9 H) 0.02, d (3 H) 1.20,  $J = 8$  Hz, s (3 H) 1.88, q (1 H) 2.63,  $J = 8$  Hz; ir (film) 1690 (C=O), 1250, 840  $\text{cm}^{-1}$  ( $\text{SiCH}_3$ );  $\nu_{\text{max}}$  (cyclohexane) 2350  $\text{\AA}$  ( $\epsilon$  3890); mass spectrum  $m/e$  176 (parent). *Anal.* Calcd for  $\text{C}_7\text{H}_{16}\text{OSSi}$ : C, 47.67; H, 9.15. Found: C, 47.88; H, 9.10.

**3-(Trimethylsilyl)propyl Thioacetate.** To a 500-ml, three-necked, round-bottomed flask equipped with a pressure-equalizing addition funnel, a reflux condenser, and a magnetic stirring bar was added 72.5 g (0.6 mol) of trimethylallylsilane.<sup>19</sup> Thioacetic acid (69.6 g, 0.9 mol) was placed in the addition funnel and the entire system was purged with nitrogen. While the stirred silane was irradiated with a GE sun lamp, the thioacetic acid was added dropwise. The reaction mixture was irradiated for a total of 12 hr. The progress of the reaction was monitored by nmr. Distillation led to isolation of 3-(trimethylsilyl)propyl thioacetate (40.6 g, 35.6%), bp 210–213°. Analytical samples were purified by preparative glpc on a 6 ft  $\times$  0.25 in. Apiezon L column at 110°: nmr ( $\text{CS}_2$ ) s (9 H) 0.15, m (2 H) 0.68, m (2 H) 1.62, s (3 H) 2.27, t (2 H) 2.85,  $J = 7$  Hz; ir (film) 1685 (C=O), 1245, 835, and 755  $\text{cm}^{-1}$  [ $\text{Si}(\text{CH}_3)_3$ ];  $\nu_{\text{max}}$  (cyclohexane) 2320  $\text{\AA}$  ( $\epsilon$  4190); mass spectrum  $m/e$  190 (parent). *Anal.* Calcd for  $\text{C}_8\text{H}_{18}\text{OSSi}$ : C, 50.47; H, 9.53. Found: C, 50.70; H, 9.48.

**Photolysis of 2-(Trimethylsilyl)ethyl Thioacetate.** A 30% benzene solution of 2-(trimethylsilyl)ethyl thioacetate (514.7 mg, 2.9 mmol) was deoxygenated with purified nitrogen and then photolyzed in a quartz nmr tube for 8 hr with a 450-W medium-pressure Hanovia Hg lamp. Similar results have been obtained on photolysis of 10% benzene and 10% *n*-nonane solutions. The product mixture was separated by preparative glpc on a 6 ft  $\times$  0.25 in. 10% Silar column. The analysis was begun at 50° and the temperature was increased at 2°/min. The following products were isolated and identified.

**Ethyltrimethylsilane (16.3%):** nmr ( $\text{CCl}_4$ ) s (9 H) 0.02, t (2 H) 0.58,  $J = 8$  Hz, m (3 H) 0.98.<sup>20</sup>

**Acetaldehyde (31.5%):** nmr identical with that of an authentic sample.

**2-(Trimethylsilyl)ethyl methyl sulfide (24.6%):** nmr ( $\text{CCl}_4$ ) s (9 H) 0.06, m (2 H) 0.88, s (3 H) 2.00, m (2 H) 2.48; ir (film) 1250 and 840  $\text{cm}^{-1}$  ( $\text{SiCH}_3$ ). *Anal.* Calcd for  $\text{C}_6\text{H}_{16}\text{SSi}$ : C, 48.59; H, 10.88. Found: C, 48.20; H, 10.34.

**Bis-2-(trimethylsilyl)ethyl sulfide (3.3%):** nmr ( $\text{CS}_2$ ) s (18 H) 0.07, m (4 H) 0.83, m (4 H) 2.52; ir (film) 1245 and 855  $\text{cm}^{-1}$  ( $\text{SiCH}_3$ ); mass spectrum (70 eV)  $m/e$  234 (parent).

**Bis-2-(trimethylsilyl)ethyl disulfide (14.4%):** nmr ( $\text{CS}_2$ ) s (18 H) 0.08, m (4 H) 0.92, m (4 H) 2.70; ir (film) 1240 and 855  $\text{cm}^{-1}$  ( $\text{SiCH}_3$ );  $\nu_{\text{max}}$  (cyclohexane) 2450  $\text{\AA}$  ( $\epsilon$  556); mass spectrum (70 eV)  $m/e$  266 (parent). *Anal.* Calcd for  $\text{C}_{10}\text{H}_{26}\text{Si}_2\text{S}_2$ : C, 45.05; H, 9.83. Found: C, 44.71; H, 9.33.

**Photolysis of 3-(Trimethylsilyl)propyl Thioacetate.** A benzene solution (10%) of 3-(trimethylsilyl)propyl thioacetate (492.2 mg, 2.5 mmol) was placed in a quartz nmr tube. The solution was deoxygenated with purified nitrogen and then photolyzed for 10

hr with a 450-W medium-pressure Hanovia Hg lamp. The product mixture was separated by preparative glpc on a 6 ft  $\times$  0.25 in. 10% Silar 5CP column. The analysis was begun at 50° and the temperature was increased 2°/min. The following compounds were isolated and identified.

**Trimethylpropylsilane (6.3%):** nmr ( $\text{CCl}_4$ ) s (9 H) 0.00, m (2 H) 0.50, m (2 H) 1.43, m (3 H) 1.97. Other properties were identical with those of an authentic sample.<sup>21</sup>

**Acetaldehyde (22.7%):** nmr spectrum identical with that of an authentic sample.

**3-(Trimethylsilyl)propyl methyl sulfide (41.2%):** nmr ( $\text{CCl}_4$ ) s (9 H) 0.03, m (2 H) 0.60, m (2 H) 1.52, s (3 H) 2.00, t (2 H) 2.45,  $J = 7$  Hz; ir (film) 1245 and 835  $\text{cm}^{-1}$  ( $\text{SiCH}_3$ ); mass spectrum  $m/e$  162 (parent). *Anal.* Calcd for  $\text{C}_7\text{H}_{18}\text{SSi}$ : C, 51.78; H, 11.17. Found: C, 51.69; H, 10.90.

**Bis-3-(trimethylsilyl)propyl disulfide (3.9%):** nmr ( $\text{CCl}_4$ ) s (18 H) 0.00, m (4 H) 0.52, m (4 H) 1.67, t (4 H) 2.55,  $J = 7$  Hz; ir (film) 1245 and 835  $\text{cm}^{-1}$  ( $\text{SiCH}_3$ ).

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**Registry No.**—2-(Trimethylsilyl)ethyl thioacetate, 18269-56-2; trimethylvinylsilane, 754-05-2; thioacetic acid, 507-09-5; 1-(trimethylsilyl)ethyl thioacetate, 16709-97-0; 3-(trimethylsilyl)propyl thioacetate, 17053-46-2; trimethylallylsilane, 762-72-1; ethyltrimethylsilane, 3439-38-1; 2-(trimethylsilyl)ethyl methyl sulfide, 28247-22-5; bis-2-(trimethylsilyl)ethyl sulfide, 18001-77-9; bis-2-(trimethylsilyl)ethyl disulfide, 51231-40-4; trimethylpropylsilane, 3510-70-1; 3-(trimethylsilyl)propyl methyl sulfide, 28247-28-1; bis-3-(trimethylsilyl)propyl disulfide, 51231-41-5.

**Supplementary Material Available.** Mass spectra of II, II-*d*<sub>3</sub>, and II-*d* will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105  $\times$  148 mm, 24 $\times$  reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JOC-74-1691.

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