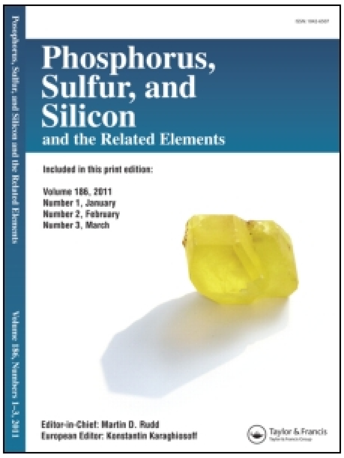


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

PYROTHIOCARBONATES V. SYNTHESIS AND SOME REACTIONS OF S-TRIMETHYLSILYL O-ALKYLDITHIOCARBONATES

Mario A. Palominos[a]; Juan C. Vega[a]
[a] Facultad de Química, Pontificia Universidad Católica de Chile, Santiago, Chile

To cite this Article Palominos, Mario A. and Vega, Juan C.(1991) 'PYROTHIOCARBONATES V. SYNTHESIS AND SOME REACTIONS OF S-TRIMETHYLSILYL O-ALKYLDITHIOCARBONATES', Phosphorus, Sulfur, and Silicon and the Related Elements, 61: 3, 319 — 324

To link to this Article: DOI: 10.1080/10426509108036812

URL: http://dx.doi.org/10.1080/10426509108036812

Phosphorus, Sulfur, and Silicon, 1991, Vol. 61, pp. 319–324
Reprints available directly from the publisher
Photocopying permitted by license only

PYROTHIOCARBONATES V. SYNTHESIS AND SOME REACTIONS OF S-TRIMETHYLSILYL O-ALKYLDITHIOCARBONATES

MARIO A. PALOMINOS and JUAN C. VEGA*
Facultad de Química. Pontificia Universidad Católica de Chile. Casilla 6177. Santiago, Chile

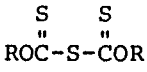
(Received September 10, 1990; in final form January 28, 1991)

Non-reported S-trimethylsilyl O-alkyldithiocarbonates (**2**) are prepared by reaction of O,O-dialkyltrithiodicarbonates with N-methyl N-trimethylsilylaniline in 87–96% yield. These are air-sensitive liquids which are separated from the accompanying phenyl methyl alkylcarbamothioates by fractional distillation. The reaction of **2** with acetyl chloride gives the unsymmetrical dithioanhydrides S-acetyl O-alkyldithiocarbonates in 93–97% yield. With the less powerful electrophilic reagent, iodomethane, S-trimethylsilyl O-ethyldithiocarbonate (**2a**) forms S-methyl O-ethyldithiocarbonate in 30% yield. When a chloroform solution of **2a** is stirred with water the unstable compound O-ethyldithiocarbonic acid is obtained.

Key words: Masked O-alkyldithiocarbonic acids; O,O-dialkyltrithiodicarbonates; S-acetyl O-alkyldithiocarbonates.

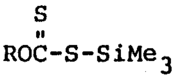
Although O,O-dialkyl pyrotrithiocarbonates or O,O-dialkyltrithiodicarbonates (**1**) were described at the beginning of the century,[2] little is known about the chemistry of these thioanhydrides. Some reactions of O,O-diethyltrithiodicarbonate (**1a**) with amines[3] and enolates[4] have been published. In this paper we report the use of **1** to prepare S-trimethylsilyl O-alkyldithiocarbonates (**2**) which are silyl derivatives of xanthates. Because xanthates **2** are unknown compounds some of their reactions were also studied.

Some organometallic derivatives of O-ethyldithiocarbonates (**3**) have been prepared by reaction of potassium O-ethyldithiocarbonate with triaryl (or alkyl) metal (IVb) chlorides. Thus, compounds **3** have been synthesized by reaction of triphenylgermanium, -tin, and -lead chloride with potassium O-ethyldithiocarbonate.[5]



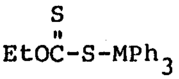
$RO\overset{S}{\overset{\|}{C}}-S-\overset{S}{\overset{\|}{C}}OR$

1



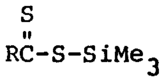
$RO\overset{S}{\overset{\|}{C}}-S-SiMe_3$

2



$EtO\overset{S}{\overset{\|}{C}}-S-MPh_3$

3



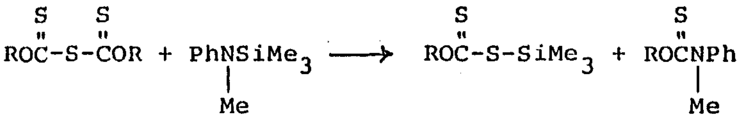
$R\overset{S}{\overset{\|}{C}}-S-SiMe_3$

4

M= Ge, Sn, Pb

When we attempted to prepare S-trimethylsilyl O-ethyldithiocarbonate by direct reaction of potassium O-ethyldithiocarbonate dissolved with chlorotrimethylsilane in acetone, only decomposition of the reaction mixture was observed. This was also noticed by Schmidt *et al.*[5] However, the related compounds, S-trimethylsilyl esters of dithiocarboxylic acids, (**4**), have been obtained.[6]

Compounds **2** were prepared by reaction of **1** with N-methyl N-trimethylsilylaniline, (**5**), in hexane at room temperature under nitrogen atmosphere. In this reaction the corresponding phenyl methyl O-alkylcarbamothioates (**6**) were also formed. Products **2** and **6** were liquids in most cases and could be separated by fractional distillation. Thiocarbamates **6**, which have not been described, show spectral data which are consistent with their structures. Table I shows the yields of the obtained compounds **2** and some of their physical properties.



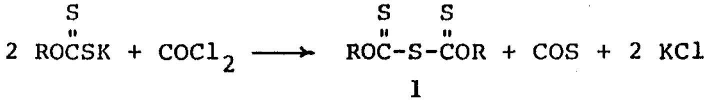
$$\mathrm{RO\overset{S}{\overset{\|}{C}}-S-\overset{S}{\overset{\|}{C}}OR + Ph\underset{\underset{Me}{|}}{N}SiMe_3 \longrightarrow RO\overset{S}{\overset{\|}{C}}-S-SiMe_3 + RO\overset{S}{\overset{\|}{C}}\underset{\underset{Me}{|}}{N}Ph}$$

1 **5** **2** **6**

When N-trimethylsilylmorpholine was used instead of **5**, only reaction mixture formed by reaction with **1a** could be separated. The other mixtures could not be separated by fractional distillation.

Because thiosilanes **2** are sensitive to humidity, no direct elemental analysis could be made. Conversion of these compounds into derivatives S-(4-nitrobenzoyl)-O-alkyldithiocarbonates (**7**) was performed by reaction with freshly prepared 4-nitrobenzoyl chloride in hexane for 4 h at room temperature. The work up left solids which could be easily crystallized from hexane and gave satisfactory microanalyses.

With the exception of **1a**, thioanhydrides **1** were prepared by the method of Zhuravlev and Galchenko[7] which was modified by adding a 20% solution of phosgene in toluene to an acetone solution of potassium O-alkyldithiocarbonate



$$\mathrm{2\ RO\overset{S}{\overset{\|}{C}}SK + COCl_2 \longrightarrow RO\overset{S}{\overset{\|}{C}}-S-\overset{S}{\overset{\|}{C}}OR + COS + 2\ KCl}$$

1

TABLE I

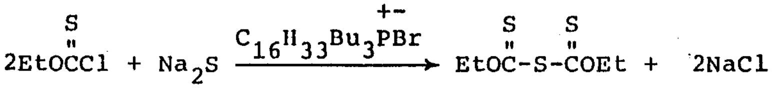
S-Trimethylsilyl O-alkyldithiocarbonates (**2**) prepared

2^a	R	Yield^b (%)	b.p. (°C)/torr	IR ν(cm^{-1}) S=C-O	(neat) C-Si	^{1}H-NMR($CDCl_3$/TMS) $(CH_3)_3Si$	HCOCS
						δ, Hz (ppm)	
a	Et	90	42/0.1	1210,1055	845	0,46	4.56(q, 2H)
b	n-Pr	92	50/0.1	1210,1060	845	0,46	4.51(t, 2H)
c	i-Pr	90	48/0.1	1220,1060	845	0,45	5.73(m, 1H)
d	Bu	95	59/0.1	1210,1060	850	0.46	4.54(t, 2H)
e	i-Bu	96	54/0.1	1215,1060	845	0.47	4.33(d, 2H)
f	sec-Bu	87	56/0.1	1215,1050	845	0.45	5.61(m, 1H)

[a] Characterized through their derivatives S-(4-nitrobenzoyl)-O-alkyldithiocarbonates (**7**). See Experimental.

[b] Isolated product.

Compound **1a** was formed in 97% yield by the reaction of O-ethylcarbonochloridothioate (**8**) with sodium sulfide in CH_2Cl_2 with hexadecyltributylphosphonium bromide as phase transfer catalyst.[8]

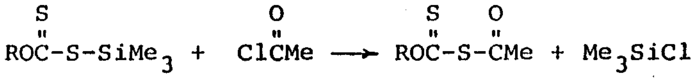


$$2\,EtO\overset{S}{\overset{\|}{C}}Cl + Na_2S \xrightarrow{C_{16}H_{33}Bu_3\overset{+-}{P}Br} EtO\overset{S}{\overset{\|}{C}}{-}S{-}\overset{S}{\overset{\|}{C}}OEt + 2NaCl$$

8 **1a**

An alternative route to **1** via desulfuration of bis(alkoxythiocarbonyl) disulfide $[(ROCS)_2S_2]$ could not be realized for the higher homologues of **1a** due to decomposition.[9] The trithiodicarbonates **1b–f** obtained, along with their yields and selected physical properties, are shown in Table II. Products **1** are thermally unstable yellow liquids which can not be distilled but they were pure enough according to ^{1}H-NMR analysis. No relevant physical data were reported for these compounds.

We also studied the reactions of **2** with acetyl chloride, a powerful electrophile. The reaction of this with potassium O-ethyldithiocarbonate in ether has been described and it was found that the reaction product S-acetyl O-ethyldithiocarbonate (**9a**) decomposes giving ethyl acetate and CS_2 as the main products.[10] When the same reaction was conducted in CCl_4, product **9a** was reported in high yield.[11] When acetyl chloride was reacted with **2a** in hexane at room temperature for 3 h **9a** was obtained in 95% yield. In the same way S-acetyl derivatives of **2** were prepared in high yield (93–97%). In these reactions chlorotrimethylsilane was also formed. Dithioanhydrides **9** are yellow liquids which can be distilled without decomposition. Their yields and physical properties appear in Table III.



$$RO\overset{S}{\overset{\|}{C}}{-}S{-}SiMe_3 + Cl\overset{O}{\overset{\|}{C}}Me \longrightarrow RO\overset{S}{\overset{\|}{C}}{-}S{-}\overset{O}{\overset{\|}{C}}Me + Me_3SiCl$$

9

TABLE II

O,O-Dialkyltrithiodicarbonates (**1**) prepared by the phosgene method

1	R	Yield (%)	IR (neat) ν(cm^{-1}) S=C-O	^{1}H-NMR ($CDCl_3$/TMS) δ,Hz (ppm) HCO
b	Pr	93	1270,1005	4.62(t, 2H)
c	i-Pr	93	1270,980	5.78(m, 1H)
d	Bu	95	1280,1005	4,68(t, 2H)
e	i-Bu	97	1275,1005	4,45(d, 2H)
f	sec-Bu	90	1280,990	5,68(m, 1H)

TABLE III

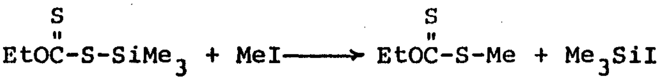
S-Acetyl O-alkyldithiocarbonates (**9**) prepared in this work

9	R	Yield[a] (%)	B.P. °C/torr	n_D(20°C)	Molecular Formula[b]	IR(neat) ν(cm^{-1}) C=O	^{1}H-NMR δ(CDCl$_3$/TMS) C(=O)CH$_3$	HCO δ,Hz(ppm)
a	Et	95	40/0.1	1.5503	$C_5H_8O_2S_2$ 164,2	1740,1710	2.43	4.73(q, 2H)
b	Pr	96	49/0.1	1.5425	$C_6H_{10}O_2S_2$ 178,3	1740,1710	2.44	4.63(t, 2H)
c	i-Pr	93	44/0.1	1.5370	$C_6H_{10}O_2S_2$ 178,3	1740,1710	2.44	5.78(m, 1H)
d	Bu	95	58/0.1	1.5335	$C_7H_{12}O_2S_2$ 192,3	1740,1710	2.43	4.66(t, 2H)
e	i-Bu	97	52/0.1	1.5302	$C_7H_{12}O_2S_2$ 192,3	1740,1710	2.44	4.43(d, 2H)
f	sec-Bu	95	53/0.1	1.5332	$C_7H_{12}O_2S_2$ 192,3	1740,1710	2.43	5.67(m, 1H)

[a] Isolated product.

[b] Satisfactory microanalyses obtained: C ± 0.29; H ± 0.28.

A less powerful electrophilic reagent tested was iodomethane. This compound was reacted with **2a** in chloroform. After 24 h S-methyl O-ethyl dithiocarbonate (**10**) and iodotrimethylsilane were formed. The yield of **10** was only 30%. In a comparative experiment potassium O-ethyldithiocarbonate dissolved in acetone was reacted with iodomethane giving immediately product **10** in 90% yield.



$$\mathrm{EtO\overset{\overset{S}{\|}}{C}{-}S{-}SiMe_3 + MeI \longrightarrow EtO\overset{\overset{S}{\|}}{C}{-}S{-}Me + Me_3SiI}$$

2a **10**

As a nucleophile we chose water because its reaction with **2a** would give O-ethyldithiocarbonic acid (**11**) which is a very unstable compound. This acid has been prepared by careful acidification of potassium O-ethyldithiocarbonate followed by extraction with chloroform.[12] In this medium its UV spectrum has been taken[12] but no NMR data has been reported to our knowledge. A chloroform solution of **2a** was stirred with water. The UV spectrum of the organic layer presented a maximum at 240 nm which is the same as that published for O-ethyldithiocarbonic acid.[12]

$$\mathbf{2a} + \mathrm{H_2O \longrightarrow EtOCS_2H + Me_3SiOH}$$

11

In order to verify the nature of **11** a ^{1}H-NMR spectrum of the reaction of **2a** in $CDCl_3$ with D_2O was run. A triplet at 1.41 and a quartet at 4.56 δ were observed corresponding to the ethyl group of **11** and a singlet at 0.16 δ due to hexamethyldisiloxane formed by dehydration of deuterated trimethylsilanol. A new spectrum of this reaction mixture taken 20 h later showed signals at 1.26 and 3.66 δ of EtOD, the decomposition product of $EtOCS_2D$.

In conclusion, S-trimethylsilyl O-alkyldithiocarbonates can be prepared in high yields and these compounds act as masked O-alkyldithiocarbonic acids.

EXPERIMENTAL

IR spectra were obtained on a Perkin Elmer Model 1310 spectrophotometer and ^{1}H-NMR spectra were recorded on a Varian XL-100 apparatus. Compounds **2, 7, 9** were formed under nitrogen using anhydrous solvents. Compounds **1a**,[9] **5**,[13] **8**,[14] and N-trimethylsilylmorpholine[15] were prepared according to literature procedures. For the preparation of **5**, an ultrasonic cleaner was used instead of stirring.

Preparation of O,O-dialkyltrithiodicarbonates (**1b–f**); *General Procedure.* The preparation of these compounds must be performed in a well ventilated hood because of highly poisonous phosgene. A 20% phosgene (50 mmol) toluene solution in acetone (75 mL) was added to a solution of potassium O-alkyldithiocarbonate (105 mmol) in acetone (400 mL) with stirring at 0°C. The mixture was left at room temperature for 0.5 h, then the acetone was removed on a rotary evaporator (bath temp. <20°C). Water (100 mL) was added and the mixture extracted with dichloromethane (3 × 100 mL). The pooled extracts were dried with $MgSO_4$ and the dichloromethane and toluene were distilled off around 5 torr. (bath temp. <20°C). The trithiodicarbonates were viscous liquids which decomposed when distilled in vacuo.

Preparation of S-trimethylsilyl O-alkyldithiocarbonates (**2**); *General Procedure.* A mixture of **1** (7 mmol), N-methyl N-trimethylsilyl aniline (7 mmol) and hexane (30 mL) was stirred at room temperature until a change of color occurred (40–60 min). The solvent was evaporated and the residue was distilled off at 0.1 torr. The first fraction consisted of compounds **2**; these products are easily decomposed by humidity.

Physical properties and microanalyses of **6**. N-Ethoxythiocarbonyl-N-methyl aniline (**6a**): colorless liquid; bp 70°C/0.07 torr; η_D^{20} 1.5762; ^{1}H-NMR ($CDCl_3$) δ 1.22 (*t*, 3H, CH_3), 3.60 (*s*, 3H, CH_3), 4.52 (*q*, 2H, CH_2), 7.08–7.60 (*m*, 5H, H arom); IR (neat) 2980, 1590, 1490, 1445, 1370, 1290, 1205, 1145, 770 cm^{-1}. Anal. Calcd. for $C_{10}H_{13}NOS$: C, 61.51; H, 6.71. Found: C, 61.42; H, 6.88.

N-Propoxythiocarbonyl-N-methyl aniline (**6b**): colorless liquid; bp 84°C/0.1 torr; η_D^{20} 1.5655; ^{1}H-NMR ($CDCl_3$) δ 0.84 (*t*, 3H, CH_3), 1.65 (*m*, 2H, CH_2), 3.61 (*s*, 3H, CH_3); 4.41 (*t*, 2H, CH_2), 7.00–7.60 (*m*, 5H, H arom.); IR (neat) 2970, 1595, 1490, 1450, 1370, 1290, 1205, 1140, 770, 700 cm^{-1}. Anal. Calcd. for $C_{11}H_{15}NOS$: C, 63.12; H, 7.22. Found: C, 63.20; H, 7.32.

N-Isopropoxythiocarbonyl-N-methyl aniline (**6c**): colorless crystals; mp 72°C; ^{1}H-NMR ($CDCl_3$) δ 1.23 (*d*, 6H, CH_3), 3.60 (*s*, 3H, CH_3), 5.60 (*m*, H, CH), 7.10–7.60 (*m*, 5H, H arom.); IR (KBr) 2980, 1595, 1485, 1460, 1375, 1290, 1215, 1145, 1135, 1085, 795, 710 cm^{-1}. Anal. Calcd. for $C_{11}H_{15}NOS$: C, 63.12, H, 7.22. Found: C, 63.15; H, 7.38.

N-Butoxythiocarbonyl-N-methyl aniline (**6d**): colorless liquid; bp 90°C/0.07 torr, $^{20}_{D}$ 1.5575; ^{1}H-NMR ($CDCl_3$) δ 0.84 (*t*, 3H, CH_3), 1.00–1.80 (*m*, 4H, CH_2CH_2), 3.60 (*s*, 3H, CH_3), 4.45 (*t*, 2H, CH_2), 7.15–7.55 (*m*, 5H, H arom.), IR (neat) 2970, 1595, 1495, 1445, 1370, 1290, 1205, 1145, 770, 700 cm^{-1}. Anal. Calcd. for $C_{12}H_{17}NOS$: C, 64.54; H, 7.67. Found: C, 64.70, H, 7.67.

N-Isobutoxythiocarbonyl-N-methyl aniline (**6e**): colorless liquid; bp 82°C/0.07 torr; η_D^{20} 1.5560; ^{1}H-NMR ($CDCl_3$) δ 0.77 (*d*, 6H, CH_3), 1.65–2.20 (*m*, H, CH), 3.63 (*s*, 3H, CH_3), 4.22 (*d*, 2H, CH_2), 7.10–7.62 (*m*, 5H, H arom.); IR (neat) 2960, 1595, 1490, 1460, 1375, 1290, 1210, 1140, 770, 700 cm^{-1}. Anal. Calcd. for $C_{12}H_{17}NOS$: C, 64.54, H, 7.67. Found: C, 64.50; H, 7.55.

N-sec-Butoxythiocarbonyl-N-methyl aniline (**6f**): colorless liquid; bp 90°C/0.1 torr; η_D^{20} 1.5530; ^{1}H-NMR ($CDCl_3$) δ 0.82 (*t*, 3H, CH_3), 1.23 (*d*, 3H, CH_3), 2.58 (*m*, 2H, CH_2), 3.63 (*s*, 3H, CH_3), 5.47 (*m*, H, CH), 7.10–7.60 (*m*, 5H, H arom.); IR (neat) 2970, 1595, 1490, 1440, 1370, 1290, 1210, 1135, 770, 700 cm^{-1}. Anal. Calcd. for $C_{12}H_{17}NOS$: C, 64.54; H, 7.57. Found: C, 64.60; H, 7.47.

Formation of derivatives **7**. Derivatives **7** were formed by mixing **2** (5 mmol) with a hexane (30 mL) solution of freshly prepared 4-nitrobenzoyl chloride (5 mmol) crystallized from hexane at room temperature for 4 h. After work-up products **7** were crystallized from hexane.

S-(4-Nitrobenzoyl)-O-ethyldithiocarbonate (**7a**): yellow crystals; mp 61°C; ^{1}H-NMR ($CDCl_3$) δ 1.52 (*t*, 3H, CH_3), 4.79 (*q*, 2H, CH_2), 8.12 (*d*, 2H, H arom.), 8.40 (*d*, 2H, H arom.); IR (KBr) 2990, 1695, 1670, 1600, 1520, 1350, 1280, 1190, 1100, 1040, 845 cm^{-1}. Anal. Calcd. for $C_{10}H_9NO_4S_2$: C, 44.27; H, 3.35. Found: C, 44.36; H, 3.44.

S-(4-Nitrobenzoyl)-O-propyldithiocarbonate (**7b**): yellow crystals, mp 48°C; ^{1}H-NMR ($CDCl_3$) δ 1.10 (*t*, 3H, CH_3), 1.92 (*m*, 2H, CH_2), 4.68 (*t*, 2H, CH_2), 8.11 (*d*, 2H, H arom.), 8.39 (*d*, 2H, H arom.). IR (KBr) 2970, 1685, 1600, 1520, 1345, 1260, 1190, 1025, 840. Anal. Calcd. for $C_{11}H_{11}NO_4S_2$: C, 46.30; H, 3.89. Found: C, 46.45; H, 3.29.

S-(4-Nitrobenzoyl)-O-isopropyldithiocarbonate (**7c**): yellow crystals; mp 47°C; ^{1}H-NMR ($CDCl_3$) δ 1.26 (*d*, 6H, CH_3), 5.80 (*m*, H, CH), 8.10 (*d*, 2H, H arom.), 8.39 (*d*, 2H, H arom.). IR (KBr) 2980, 1680, 1600, 1520, 1345, 1270, 1190, 1035, 1015, 845 cm^{-1}. Calcd. for $C_{11}H_{11}NO_4S_2$: C, 46.30, H, 3.89. Found: C, 46.26; H, 3.93.

S-(4-Nitrobenzoyl)-O-butyldithiocarbonate (**7d**): yellow crystals; mp 42°C; ^{1}H-NMR ($CDCl_3$) δ 1.00 (*t*, 3H, CH_3), 1.34–2.08 (*m*, 4H, CH_2CH_2), 4.72 (*t*, 2H, CH_2), 8.13 (*d*, 2H, H arom.), 8.40 (*d*, 2H, H arom.); IR (KBr) 2960, 1685, 1600, 1520, 1345, 1265, 1190, 1030, 845 cm^{-1}. Anal. Calcd. for $C_{12}H_{13}NO_4S_2$: C, 48.15, H, 4.38. Found: C, 48.18; H, 4.46.

S-(4-Nitrobenzoyl)-O-isobutyldithiocarbonate (**7e**): yellow crystals; mp 56°C; ^{1}H-NMR ($CDCl_3$) δ 1.10 (*d*, 6H, CH_3), 2.23 (*m*, H, CH), 4.50 (*d*, 2H, CH_2), 8.12 (*d*, 2H, H arom.), 8.40 (*d*, 2H, H arom.). Ir (KBr) 2960, 1690, 1600, 1520, 1345, 1270, 1195, 1040, 845. Anal. Calcd. for $C_{12}H_{13}NO_4S_2$: C, 48.15; H, 4.38. Found: C, 48.39; H, 4.47.

S-(4-Nitrobenzoyl)-O-sec-butoxydithiocarbonate (**7f**): yellow crystals; mp 40°C; ^{1}H-NMR ($CDCl_3$) δ 1.03 (*t*, 3H, CH_3), 1.44 (*d*, 3H, CH_3), 1.66–2.04 (*m*, 2H, CH_2), 5.69 (*m*, H, CH), 8.11 (*d*, 2H, H arom.), 8.39 (*d*, 2H, H arom.); IR (KBr), 2970, 1685, 1600, 1520, 1345, 1270, 1190, 1100, 1015, 845 cm^{-1}. Anal. Calcd. for $C_{12}H_{13}NO_4S_2$: C, 48.15; H, 4.38. Found: C, 48.20; H, 4.47.

Preparation of S-acetyl O-alkyldithiocarbonates (**9**); *General Procedure.* Freshly distilled acetyl chloride (5.5 mmol) in hexane (10 mL) was added to a solution of S-trimethylsilyl O-alkyldithiocarbonate (5 mmol) in hexane (20 mL) at room temperature. The mixture was stirred for 3 h and the solvent evaporated. The residue was a pure liquid according to ^{1}H-NMR. Small scale and heating not over 20°C above the b.p. is important when distilling compounds **9**.

Reactions of **2a** *with CH_3I and D_2O.* **2a** (0.5 mmol) was introduced into an NMR tube and mixed with iodomethane (0.7 mmol) in $CDCl_3$ (1 mL). ^{1}H-NMR spectra were recorded at different times. After 24 h, the amount of product **10** formed reached a constant value and its yield was 30% according to GC analysis. The iodotrimethylsilane presented its typical ^{1}H-NMR value at 0.80 δ.

The reaction of **2a** with water carried out by adding a few drops of D_2O to a solution of **2a** (0.5 mmol) in $CDCl_3$ (1 mL) in an NMR tube and recording the ^{1}H-NMR spectra of the reaction mixture.

REFERENCES

1. Part of this work was presented at the 12th International Symposium of Organic Chemistry of Sulfur held at Nijmegen, The Netherlands, 1986.
2. E. E. Reid, "Organic Chemistry of Bivalent Sulfur" (Chemical Publishing Co., New York, 1962), Vol. IV. Chap. 2.
3. M. Herrera, V. M. Ruiz, R. Tapia, J. Valderrama and J. C. Vega, *An Quim.*, **76C,** 183 (1980).
4. M. A. Palominos, R. Rodríguez and J. C. Vega, *Chem. Lett.*, 1251 (1986).
5. M. Schmidt, H. Schumann, F. Gliniecki and J. E. Jaggard, *J. Organometal. Chem.*, **17,** 277 (1966).
6. S. Kato and H. Mazuta, *J. Organometal. Chem.*, **55,** 121 (1973).
7. S. V. Zhuravlev and M. I. Galchenko, *Zhur. Priklad. Khimm.*, **20,** 1038 (1947); *Chem. Abstr.*, **43,** 143i (1949).
8. S. Julia and J. C. Vega, *Synth. Commun.*, **12,** 897 (1982).
9. M. A. Palominos, J. G. Santos, J. Valderrama and J. C. Vega, *J. Chem. Soc. Perkin I* 2641 (1983).
10. O. W. Willcox, *J. Am. Chem. Soc.*, **28,** 1031 (1906).
11. H. Bohme, M. Brinkmann and H. P. Steudel, *Liebigs Ann. Chem.*, 1244 (1981).
12. A. Pomianowski and J. Leja, *Canad. J. Chem.*, **41,** 2219 (1963).
13. G. Rauchschwalde and H. Ahlbrecht, *Synthesis*, 663 (1974).
14. M. A. Martínez and J. C. Vega, *Synthesis* 760 (1986).
15. R. A. Pike and R. L. Schank, *J. Org. Chem.*, **27,** 2190 (1962).