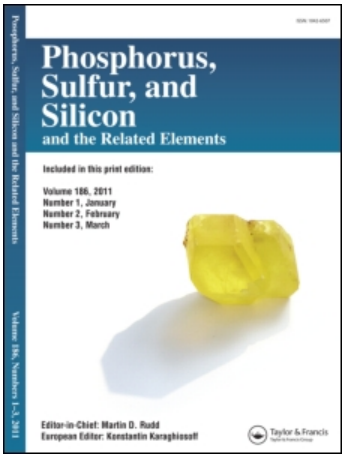

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PYROTHIOCARBONATES III. SYNTHESIS OF *S*-(ALKOXYCARBONYL) *O*-ALKYLDITHIOCARBONATES

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PYROTHIOCARBONATES III. SYNTHESIS OF *S*-(ALKOXYCARBONYL) *O*-ALKYLDITHIOCARBONATES

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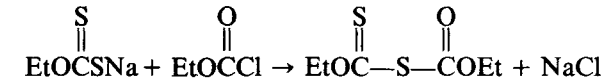
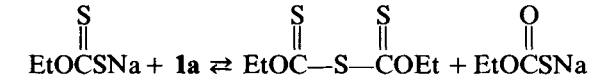
An efficient and general preparation of *S*-(alkoxycarbonyl)-*O*-alkyldithiocarbonates is described. The method is based on the reaction of potassium *O*-alkylmonothiocarbonates with *O*-alkylchlorothiocarbonates in acetone–water (9 : 1) at 0°C. The yields are 91–100%.

INTRODUCTION

S-(ethoxycarbonyl) *O*-ethyldithiocarbonate (**1a**), which is utilized as collector in flotation of copper sulfides, was obtained by the Holmberg's method[1] which consists in the reaction of sodium *O*-ethyldithiocarbonate with ethyl chlorocarbonate using ethanol or acetone as solvents. Variable amounts of bis(ethoxythiocarbonyl) sulfide (**2**) and bis(ethoxycarbonyl) sulfide (**3**) are also found in this reaction. Formation of reaction products **1a**, **2** and **3** may be explained on the basis of the following sequence of reactions:



1a



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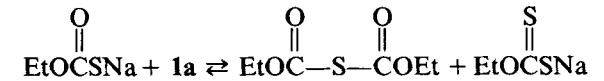
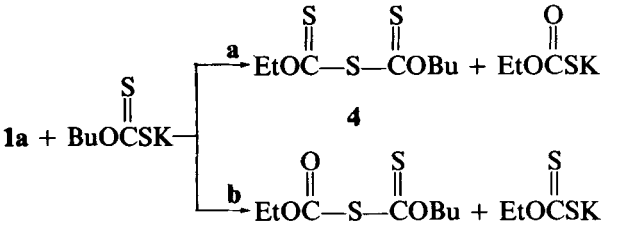


3

Further study of these reactions pointed out that the relative amounts of products **1a**, **2** and **3** depended on the addition order of reactants and the molar proportion of these reactants.[2] It was found that **1a** was obtained with 89% purity when sodium *O*-ethyldithiocarbonate was added over an excess (1 : 5) of ethyl chlorocarbonate. The other products were mainly **2** and **3**.

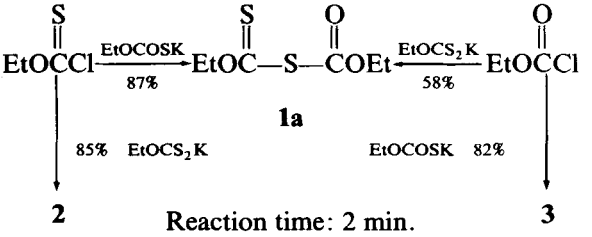
In recent work, the thiolysis reaction of **1a** was studied utilizing potassium *O*-butyldithiocarbonate in ethanol at 0°C to shed more light on the relative reactivities of their carbonyl and thiocarbonyl groups.[3]



Product **4** was formed before **5**; this fact implies a greater reactivity of the C=S group (path "**a**"). In the course of the reaction, **2** and **3** were also formed by means of transesterification reactions of the leaving groups with **1a** and $(BuOCS)_2S$, formed by the reaction of $BuOCS_2K$ with **4** and **5**.

RESULTS AND DISCUSSION

With the purpose of preparing the *S*-(alkoxycarbonyl) *O*-alkyldithiocarbonates for the systematic study of their mineralurgical activities, a general and efficient method of synthesis was developed to get pure products, since compounds **1** are thermally unstable liquids. An alternative method to that described by Holmberg may be the reaction of *O*-alkylchlorothiocarbonate (ROCSCl) with potassium *O*-alkylmonothiocarbonate (ROCOSK); therefore, a previous assay was made to determine the relative reactivities of potassium salts of *O*-ethyldithiocarbonate and *O*-ethylmonothiocarbonate relative to *O*-ethylchlorocarbonate and chlorothiocarbonate in acetone : water (9 : 1) at 0°C for 2 min. The results are summarized in Scheme 1.



SCHEME 1

Under these conditions, it may be inferred that EtOCSCl is more reactive that EtOCOCl and that EtOCOSK is more reactive than $EtOCS_2K$; therefore, pyrothiocarbonate **1a** can be prepared more efficiently by reaction of EtOCSCl with EtOCOSK. On the other hand, since in thiolysis reactions the thiocarbonyl group of **1a** is more reactive than the carbonyl one, EtOCOSK originates an indistinguishable reaction, while the reaction:

$$\mathbf{1a} + EtOCOSK \rightarrow \mathbf{3} + EtOCS_2K$$

is less favored, and in consequence the formation of **2** by reaction of **1a** with the leaving group of the above reaction is also less favored.

The method found to prepare *S*-(ethoxycarbonyl) *O*-ethyldithiocarbonate (**1a**) can be applied to other pyrodithiocarbonates **1** according to the following equation:

$$R^1OCCl + R^2OCSK \xrightarrow[0°C]{Me_2CO/H_2O} R^1OC(=S)-S-COR^2 + KCl$$

1

Table I shows the obtained yields of **1**, it can be appreciated that yields for all studied compounds are excellent. By means of GLC, the corresponding pyromonothio and pyrotrithiocarbonates are not detected.

TABLE I

S-(alcoxycarbonyl) *O*-alkyldithiocarbonates

1	R^1	R^2	YIELD (%)
a	Et	Et	99
b	*n*-Bu	Et	94
c	*i*-Bu	Et	96
d	Et	*i*-Pr	93
e	*n*-Bu	*i*-Pr	91
f	*i*-Bu	*i*-Pr	93
g	Et	*n*-Bu	95
h	*n*-Bu	*n*-Bu	98
i	*i*-Bu	*n*-Bu	100
j	Et	*i*-Bu	95
k	*n*-Bu	*i*-Bu	99
l	*i*-Bu	*i*-Bu	93

EXPERIMENTAL

^{1}H-NMR spectra at 100 MHz were run on a Varian XL-12 WG instrument. Solutions were in $CDCl_3$ ($SiMe_4$ as internal reference). IR spectra were run using KBr plates on a Perkin-Elmer 1310 instrument. The GLC analyses were performed with a Perkin-Elmer 900 chromatograph equipped with a flame-ionization detector a 1 m × 1/8 in stainless-steel column filled with 3% SE-30 on Chromosorb W.

Preparation of potassium *O*-ethyldithiocarbonate,[4] potassium *O*-ethylmonothiocarbonate,[5] *O*-alkylchlorothiocarbonates,[6] bis(ethoxythiocarbonyl) sulfide,[7] and bis(ethoxycarbonyl)[7] sulfide has been previously described.

The microanalyses were performed by "Departamento de Anàlisis y Técnicas instrumentales" of "Instituto de Química Orgánica General". Madrid, Spain.

Thiolysis of O-ethylchlorothiocarbonate and chlorocarbonate. To a stirred solution of *O*-alkylchlorothiocarbonate (10 mmol) in acetone (20 mL) at 0°C a solution was added of potassium *O*-ethyldithiocarbonate or *O*-ethylmonothiocarbonate (10 mmol) in 30 mL of acetone: water (5 : 1). After 2 min., 5% HCl (25 mL), was added, acetone was evaporated, the resulting mixture was extracted with CH_2Cl_2 and the organic layer was dried with $MgSO_4$ and the solvent was eliminated. The residue was diluted to 10 mL with CCl_4 and analyzed by GLC.

Synthesis of S-(alkoxycarbonyl) O-alkyldithiocarbonates. To a solution of *O*-alkylchlorothiocarbonate (10 mmol) in 20 mL of acetone a solution of potassium *O*-alkylmonothiocarbonate (10 mmol) in 30 mL of acetone : water (5 : 1) was slowly added with stirring over an ice-water bath for 15 min. Later, acetone was evaporated, the mixture was extracted with CH_2Cl_2, the organic layer was dried with $MgSO_4$, the solvent was eliminated and the residue was weighed. This corresponded, in all the studied cases, to pure products according to GLC analyses.

S-(ethoxycarbonyl) *O*-ethyldithiocarbonate (**1a**): yellow oil; η_D^{20} 1.5202. ^{1}H-NMR ($CDCl_3$): δ, 1.33 (t, 3 H, CH_3CH_2OCO), 1.48 (t, 3 H, CH_3CH_2OCS), 4.33 (q, 2 H, CH_2OCO), 4.72 (q, 2 H, CH_2OCS). IR (KBr): ν, 1750, 1715 (C=O) 1270, 1135, 1025, 840 (O(C=S)S).

S-(ethoxycarbonyl) *O*-butyldithiocarbonate (**1b**): yellow oil; η_D^{20} 1.5148. ^{1}H-NMR: ($CDCl_3$) δ, 1.00 (t, 3 H, $CH_3CH_2CH_2CH_2O$), 1.36 (t, 3 H, CH_3CH_2O), 1.20–1.60 (m, 2 H, $CH_3C\underline{H}_2CH_2CH_2O$), 1.64–1.92 (m, 2 H, $CH_3CH_2C\underline{H}_2CH_2O$), 4.33 (q, 2 H, CH_3CH_2O), 4.66 (t, 2 H, $CH_3CH_2CH_2C\underline{H}_2O$). IR (KBr): ν, 1750, 1715 (C=O) 1270, 1135, 1030, 840 (O(C=S)S).

S-(ethoxycarbonyl) *O*-isobutyldithiocarbonate (**1c**): yellow oil; η_D^{20} 1.5155. ^{1}H-NMR ($CDCl_3$): δ, 1.08 (d, 6 H, $(C\underline{H}_3)_2CHCH_2O$), 1.36 (t, 3 H, CH_3CH_2O), 2.01 (m, H, CH), 4.35 (q, 2 H, CH_3CH_2O), 4.45 (d, 2 H, $(CH_3)_2CHCH_2O$). IR (KBr): ν, 1750, 1715 (C=O) 1270, 1135, 1035, 850 (O(C=S)S). Anal. Calcd. for $C_8H_{14}O_3S_2$: C, 43.22; H, 6.35; S, 28.84. Found: C, 42.80; H, 6.50; S, 28.36.

S-(isopropoxycarbonyl) *O*-ethyldithiocarbonate (**1d**): yellow oil; η_D^{20} 1.5170. ^{1}H-NMR ($CDCl_3$): δ, 1.36 (d, 6 H, $(CH_3)_2CHO$), 1.48 (t, 3 H, CH_3CH_2O), 4.73 (q, 2 H, CH_2O), 5.18 (m, H, CHO). IR (KBr): ν, 1745, 1710 (C=O) 1265, 1150, 1025, 840 (O(C=S)S). Anal. Calcd. for $C_7H_{12}O_3S_2$: C, 40.36; H, 5.81; S, 30.79. Found: C, 40.65; H, 6.00; S, 30.85.

S-(isopropoxycarbonyl) *O*-butyldithiocarbonate (**1e**): yellow oil; η_D^{20} 1.5103. ^{1}H-NMR ($CDCl_3$): δ, 0.98 (t, 3 H, $CH_3CH_2CH_2CH_2O$), 1.24–2.02 (m, 4 H, $CH_3C\underline{H}_2C\underline{H}_2CH_2O$), 1.36 (d, 6 H, $(CH_3)_2CHO$), 4.68 (t, 2 H, CH_2O), 5.18 (m, H, CHO). IR (KBr): ν, 1745, 1710 (C=O) 1265, 1155, 1030, 840 (O(C=S)S). Anal. Calcd. for $C_9H_{16}O_3S_2$: C, 45.74; H, 6.82; S, 27.13. Found: C, 45.65; H, 7.09; S, 27.20.

S-(isopropoxycarbonyl) *O*-isobutyldithiocarbonate (**1f**): yellow oil; η_D^{20} 1.5085. ^{1}H-NMR ($CDCl_3$): δ, 1.07 (d, 6 H, $(C\underline{H}_3)_2CHCH_2O$), 1.36 (d, 6 H, $(CH_3)_2CHO$), 2.21 (m, H, $(CH_3)_2CHCH_2O$), 4.45 (d, 2 H, CH_2O), 5.18 (m, H, CHO). IR (KBr): ν, 1745, 1715 (C=O) 1265, 1150, 1035, 840 (O(C=S)S). Anal. Calcd. for $C_9H_{16}O_3S_2$: C, 45.74; H, 6.82; S, 27.13. Found: C, 46.00; H, 7.02; S, 27.35.

S-(butoxycarbonyl) *O*-ethyldithiocarbonate (**1g**): yellow oil; η_D^{20} 1.5182. ^{1}H-NMR ($CDCl_3$): δ, 0.96 (t, 3 H, $CH_3CH_2CH_2CH_2O$), 1.20–1.86 (m, 4 H, $CH_3C\underline{H}_2C\underline{H}_2CH_2O$), 1.52 (t, 3 H, CH_3CH_2O), 4.30 (t, 2 H, $CH_3CH_2CH_2C\underline{H}_2O$), 4.74 (q, 2 H, CH_3CH_2O). IR (KBr): ν, 1750, 1710 (C=O) 1265, 1135, 1030, 830 (O(C=S)S). Anal. Calcd. for $C_8H_{14}O_3S_2$: C, 43.22; H, 6.35; S, 28.84. Found: C, 43.12; H, 6.58; S, 28.55.

S-(butoxycarbonyl) *O*-butyldithiocarbonate (**1h**): yellow oil; η_D^{20} 1.5088. ^{1}H-NMR ($CDCl_3$): δ, 0.96 (t, 3 H, $CH_3CH_2CH_2CH_2OCO$), 1.00 (t, 3 H, $CH_3CH_2CH_2CH_2OCS$), 1.20–2.02 (m, 8 H, $CH_3C\underline{H}_2C\underline{H}_2CH_2O(C{=}S)S(C{=}O)OCH_2C\underline{H}_2C\underline{H}_2CH_3$), 4.30 (t, 2 H, CH_2OCO), 4.68 (t, 2 H, CH_2OCS). IR (KBr): ν, 1750, 1710 (C=O) 1265, 1135, 1030, 835 (O(C=S)S). Anal. Calcd. for $C_{10}H_{18}O_3S_2$: C, 47.97; H, 7.25; S, 25.61. Found: C, 47.93; H, 7.48; S, 25.68.

S-(butoxycarbonyl) *O*-isobutyldithiocarbonate (**1i**): yellow oil; η_D^{20} 1.5075. ^{1}H-NMR ($CDCl_3$): δ, 1.01 (t, 3 H, $CH_3CH_2CH_2CH_2O$), 1.08 (d, 6 H, $(C\underline{H}_3)_2CHCH_2O$), 1.24–1.78 (m, 4 H, $CH_3C\underline{H}_2C\underline{H}_2CH_2O$), 2.21 (m, H, CH), 4.30 (t, 2 H, $CH_3CH_2CH_2C\underline{H}_2O$), 4.45 (d, 2 H, $(CH_3)_2CHCH_2O$). IR (KBr): ν, 1750, 1715 (C=O) 1270, 1135, 1035, 840 (O(C=S)S). Anal. Calcd. for $C_{10}H_{18}O_3S_2$: C, 47.97; H, 7.25; S, 25.61. Found: C, 47.90; H, 7.49; S, 25.33.

S-(isobutoxycarbonyl) *O*-ethyldithiocarbonate (**1j**): yellow oil; η_D^{20} 1.5165. ^{1}H-NMR ($CDCl_3$): δ, 0.97 (d, 6 H, $C\underline{H}_3)_2CHCH_2O$), 1.49 (t, 3 H, CH_3CH_2O), 2.00 (m, H, CH), 4.09 (d, 2 H, $CHCH_2O$), 4.75 (q, 2 H, CH_3CH_2O). IR (KBr): ν, 1750, 1710 (C=O) 1265, 1135, 1030, 800 (O(C=S)S). Anal. Calcd. for $C_8H_{14}O_3S_2$: C, 43.22; H, 6.35. Found: C, 43.22; H, 6.54.

S-(isobutoxycarbonyl) *O*-butyldithiocarbonate (**1k**): yellow oil; η_D^{20} 1.5095. ^{1}H-NMR ($CDCl_3$): δ, 0.96 (d, 6 H, $C\underline{H}_3)_2CHCH_2O$), 0.99 (t, 3 H, $CH_3CH_2CH_2CH_2O$), 1.31–2.17 (m, 5 H, $CH_3C\underline{H}_2C\underline{H}_2CH_2O(C{=}S)S(C{=}O)OCH_2C\underline{H}(CH_3)_2$), 4.09 (d, 2 H, $CHCH_2O$), 4.69 (t, 2 H, $CH_3CH_2CH_2C\underline{H}_2O$). IR (KBr): ν, 1750, 1710 (C=O) 1265, 1130, 1030, 800 (O(C=S)S). Anal. Calcd. for $C_{10}H_{18}O_3S_2$: C, 47.97; H, 7.25. Found: C, 47.70; H, 7.50.

S-(isobutoxycarbonyl) *O*-isobutyldithiocarbonate (**1l**): yellow oil; η_D^{20} 1.5062. ^{1}H-NMR ($CDCl_3$): δ, 0.97 (d, 6 H, $(C\underline{H}_3)_2CHCH_2OCO$), 1.07 (d, 6 H, $(C\underline{H}_3)_2CHCH_2OCS$), 1.85–2.34 (m, 2 H, $C\underline{H}CH_2O(C{=}S)S(C{=}O)OCH_2C\underline{H}$), 4.07 (d, 2 H, CH_2OCO), 4.45 (d, 2 H, CH_2OCS). IR (KBr): ν,

1750, 1715 (C=O) 1270, 1130, 1030, 800 (O(C=S)S). Anal. Calcd. for $C_{10}H_{18}O_3S_2$: C, 47.97; H, 7.25. Found: C, 48.36; H, 7.49.

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