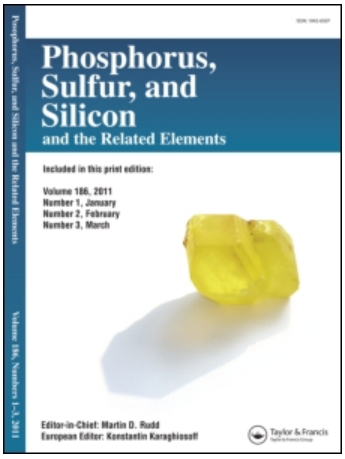

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REACTIONS OF DICHLOROMETHANE WITH THIOANIONS. 3. PREPARATION AND AMINOLYSIS OF BIS(ALKOXYTHIOCARBONYLTHIO)METHANES

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Bis(alkoxythiocarbonylthio)methanes are prepared by reaction of sodium O-alkyldithiocarbonates in water with dichloromethane catalyzed by polyethylenglycol 1,500. The aminolysis of these products with monoalkylamines, in 1:7 molar proportion, in the presence of CH_2Cl_2 and the polymer above, affords 5-alkyl-1,3,5-dithiazinane, and dialkylcarbamothioate, in 1:2 molar proportion.

Keywords: Dichloromethane double substitution; bis(alkoxythiocarbonylthio) methanes; 5-alkyl-1,3,5-dithiazinanes; polyethyleneglycol as catalyst

In previous papers we have reported that dichloromethane experiences a double substitution by thioanions, such as *N,N*-dialkyldithiocarbamates and sulfide, catalyzed by polyethylenglycol (PEG) 1,500. In the first case, bis(*N,N*-dialkylthiocarbamoylthio)methanes **1** are obtained[1] and in the second case polymethylene sulfide is formed. However, if a monoalkylamine is also present, 5-alkyl-13,5-dithiazinanes **2** and 3,5-dialkyl-1,3,5-thiadiazinanes **3** are produced along with polymethylene sulfide.[2] The formation of methylenic heterocycles **2** and **3** means that dichloromethane can be substituted by either the same (SCH_2S moiety in **2** or NCH_2N in **3**) or different nucleophiles.

In this paper we report the reactions of some sodium O-alkyldithiocarbonates **4** with dichloromethane, catalyzed by PEG-1500, forming bis(alkoxythiocarbonylthio) methanes **5** and the aminolysis of these identically substituted methyl-

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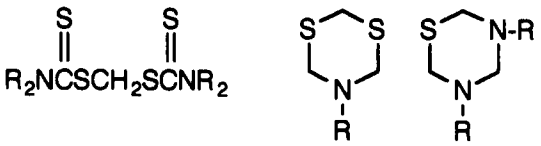
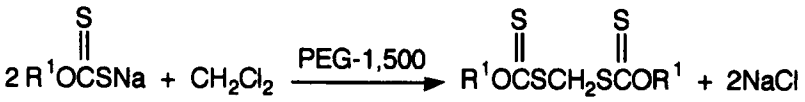


1 **2** **3**

enic products. These products have been patented as collectors in flotation of sulfide minerals.[3]



4 **5**

We found that the best conditions to prepare the bis(alkoxythiocarbonylthio)methanes **5** was to stir a solution of 50 mmol of **4** in 15 mL of water with 25 or 40 mL of CH_2Cl_2 in the presence of 2.5 mmol of PEG-1,500 for 6 h at room temperature. In this way products **5** were produced ranging in yield from 54 to 84%. Table I shows the compounds obtained and some of their physical properties.

The products **5b–e** are viscous liquids which decompose on heating. The use of proportions of water and CH_2Cl_2 different from those described above resulted in impure products.

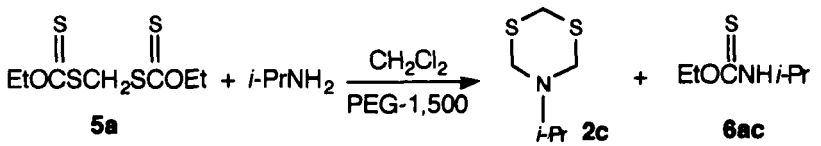
We also studied the chemistry of the bis(alkoxythiocarbonylthio)methanes **5** which have the functional groups thionoester and dithioacetal. We selected isopropylamine as the nucleophile because it is simple and easy to handle. When this amine was added to bis(ethoxythiocarbonylthio)methane (**5a**) in CH_2Cl_2 at room temperature ethyl *N*-isopropylcarbamothioate (**6ac**) was rapidly formed. However, if the solution of **5a** in CH_2Cl_2 was stirred with isopropylamine in

TABLE I Bis(alkoxythiocarbonylthio)methanes **5**

5	R^1	Yield %	n_D(20°C) [M.P. (°C)]	NMR[a](δ, ppm) OCH				
				^1H	^{13}C	SCH_2S ^1H	SCH_2S ^{13}C	$C{=}S$ ^{13}C
a	Et	84	[38]	4.64	70.66	4.78	42.09	212.74
b	*n*-Pr	72	1.5891	4.56	76.14	4.80	41.86	212.71
c	*i*-Pr	57	1.5844	5.74	78.51	4.77	41.38	211.74
d	*n*-Bu	55	1.5685	4.60	74.62	4.80	41.96	212.98
e	*sec*-Bu	54	1.5681	5.62	76.45	4.70	41.38	212.16

[a]$CDCl_3$; 35°C

water in the presence of 5% molar PEG-1,500 with respect to **5a**, not only **6ac** was formed but also 5-ethyl-1,3,5-dithiazinane (**2c**). In the absence of PEG-1,500, the main product was **6ac**, and no dithiazinane **2c** was produced.



This result suggests that the solvent reacts with the aminolysis products giving the heterocyclic **2c** and producing HCl. Since no 1,3-diethyl-1,3,5-thiadiazinane (**3**, R = ethyl) was found, it appears that heterocyclic **2c** was not produced from the reaction of sulfide anion, dichloromethane, and the amine as described above. Although the amine was a nucleophile and an acid acceptor, we assayed different molar ratios of isopropylamine to **5a** in an effort to determine the best conditions to produce **2c** whose parent compounds were of interest of us.[4] These assays appear in Table II.

According to assays 3 and 4, the molar proportion between **2c** and **6ac** is 33:67 or 1:2, obtained by ^{1}H-NMR analysis. The formation of molecule **2c** consumes two molecules of CH_2Cl_2 and liberates four molecules of HCl; therefore the reaction between substrate **5** and monoalkylamines could be represented by the following general equation:

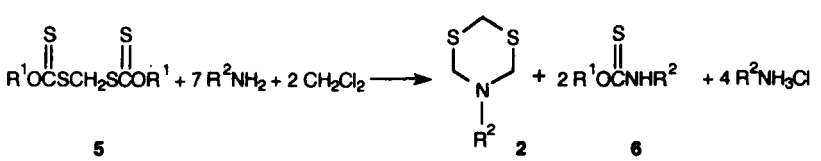


TABLE II Assays of reaction of bis(ethoxythiocarbonylthio)methane (**5a**) with isopropylamine and CH_2Cl_2

Assay Nr[a]	*Molar ratio i-PrNH$_2$/5a*	*Crude*[b] *weight (g)*	*Rel.proportion*[c] *(%)*		*Yield(%)*
			6ac	*2c*	*2c*
1	3:1	1.12	57	43	38
2	4:1	1.37	50	50	54
3	7:1	3.15	67	33	82
4	10:1	1.99	67	33	52

[a]Room temp. Time: 30 min.
[b]Weight of **2c** + **6ac**;
[c]^{1}H-NMR analysis.

This equation implies that the amine consumption is seven times that of substrate **5** without taking into account the basicity of **2**. The data of assays 1–3 support this because when the amount of amine is insufficient (assays 1,2), the yield of **2c** is 38 and 54%, calculated on the basis that one mol of **5a** gives one mol of **2c**. In contrast, when such amount is adequate (assay 3), the yield is 82%, and the crude weight of **2c** + **6ac** is the largest. The use of an amine excess (assay 4) produces a deleterious effect. If in assay 1, water is replaced by an equal volume of 10% NaOH or 10% Na_2CO_3 solution a deleterious effect in crude weight and **2c** yield is also realized.

On the basis of these results, we selected the conditions used in assay 3 to apply them to the reactions of several monoalkylamines with bis(ethoxythiocarbonylthio)methane (**5a**) and bis(isopropoxythiocarbonylthio)methane (**5c**). These reactions and the results therefrom are shown in Table III.

After the elimination of PEG-1,500 by selective extraction from the crude product, the mixture of **2** and **6** products could only be separated by preparative layer chromatography using silica gel, with partial decomposition of products **2**. These compounds have low stability because of their acetal nature. Separation attempts using silica gel column chromatography produced total decomposition of products **2**.

Products **2** and **6** were characterized mainly on the basis of their ^{1}H-NMR spectra. The ring methylene proton signals of heterocycles **2** are rather broad due to a slow interconversion between the two chair forms[5] and the remaining signals are the same as that shown by the same dithiazinanes already characterized by us.[2] The HCO and NH proton signals of thiocarbamates **6** appear as duplicated signals due to the existence of two conformers because of the hindered rotation about the N-C bond.[6]

TABLE III Reactions of bis(alkoxythiocarbonylthio)methanes **5** with monoalkylamines and CH_2Cl_2

5 R^1	*Amine* R^2	*Products*	*2 + 6 weight(g)*	*2:6 proportion (%)*	*Yield 2(%)*
a Et	a Et	**6aa, 2a**	2.38	77 23	37
	b *n*-Pr	**6ab, 2b**	6.03	80 20	74
	c *i*-Pr	**6ac, 2c**	3.15	67 33	82
	d *n*-Bu	**6ad, 2d**	3.92	74 26	56
	f Bz	**6af, 2e**	3.40	74 26	42
c *i*-Pr	a Et	**6ca, 2a**	2.68	86 14	25
	b *n*-Pr	**6cb, 2b**	4.40	78 22	59
	c *i*-Pr	**6cc, 2c**	4.24	67 33	86
	d *n*-Bu	**6cd, 2d**	4.29	71 29	70
	f Bz	**6cf, 2e**	4.27	71 29	66

EXPERIMENTAL

IR spectra were obtained on a Perkin Elmer model 1310 spectrophotometer, and ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AC-200 apparatus. Compounds **4** were prepared according to a literature procedure.[7] Many of products **2** and **6** have previously been characterized by us.[2,8]

Preparation of Bis(alkoxythiocarbonylthio)methanes 5

General Procedure

Freshly prepared sodium O-alkyldithiocarbonate **4** (50 mmol) in water (15 mL) was stirred with polyethylene glycol, average Mn 1,500, (2.5 mmol) in dichloromethane (25 mL, in case of **4a**, 40 mL was used) for 6 h at room temperature. The separated organic layer was dried over $MgSO_4$ and evaporated at 30°C under reduced pressure. To the resulting viscous product, hexane (100 mL) was added, and the solution was washed with water three times (100 mL each) to extract PEG. The dried hexane solution was evaporated at 50°C under reduced pressure. **5b–e** are viscous liquids which decompose on heating. Analytical samples were purified by preparative layer chromatography using silica gel (Merck, art. 7747) and hexane as eluent. **5a** is a solid which was crystallized from ethanol.

Physical Properties and Microanalyses of 5

Bis(ethoxythiocarbonylthio)methane (**5a**): colorless crystals; m.p. 38°C, ^{1}H-NMR ($CDCl_3$) δ 4.78 (s, 2 H, SCH_2S); 4.64 (q, 2 H, CH_2); 1.43 (t, 3H, CH_3). ^{13}C-NMR ($CDCl_3$) δ 212.74, 70.66, 42.09, 13.88; IR(KBr), 2980, 2930, 1445, 1365, 1245, 1110, 1040, 805, 758 cm^{-1}.

Anal. Calcd for $C_7H_{12}O_2S_4$: C, 32.78, H, 4.71, S, 50.0. Found: C, 32.98, H, 4.52, S, 50.46.

Bis(propoxythiocarbonylthio)methane (**5b**): yellow liquid n_D^{20} 1.5891; ^{1}H-NMR ($CDCl_3$) δ 4.80 (s, 2 H, SCH_2S); 4.56 (t, 2 H, OCH_2); 1.83 (m, 2 H, CH_2); 1.00 (t, 3 H, CH_3); ^{13}C-NMR ($CDCl_3$) δ 212.71, 76.14, 41.86, 21.66, 10.43; IR (neat) 2968, 2878, 1468, 1378, 1258, 1228, 1048, 848, 758 cm^{-1}.

Anal. Calcd. for $C_9H_{16}O_2S_4$: C, 37.99, H, 5.67. S, 45.07. Found: C, 38.10, H, 5.89, S, 45.20

Bis(*iso*-propoxythiocarbonylthio)methane (**5c**): yellow liquid; n_D^{20} 1.5844; ^{1}H-NMR ($CDCl_3$) δ 5.74 (m, 1 H, OCH); 4.77 (s, 2 H,SCH_2S); 1.39 (d, 6 H, CH_3); ^{13}C-NMR ($CDCl_3$) δ 211.74, 78.51, 41.38, 21.17; IR (neat) 2965, 2950, 1465, 1375, 1250, 1095, 1035, 815, 750 cm^{-1}.

Anal. Calcd. for $C_9H_{16}O_2S_4$: C, 37.99, H, 5.67, S, 45.07. Found: C, 37.62, H, 5.89, S, 44.95.

Bis(butoxythiocarbonylthio)methane (**5d**): yellow liquid; n_D^{20} 1.5685; ^{1}H-NMR ($CDCl_3$) δ 4.80 (s, 2 H, SCH_2S) 4.60 (t, 2 H, OCH_2); 1.79 (m, 2 H, CH_2); 1.44 (m 2 H, CH_2) 0.99 (t, 3 H, CH_3); ^{13}C-NMR ($CDCl_3$) δ 212.98, 74.62, 41.96, 30.24, 19.17, 13.72; IR (neat) 2962, 2872, 1467, 1382, 1247, 1207, 1127, 1042, 807, 752 cm^{-1}.

Anal. Calcd. for $C_{11}H_{20}O_2S_4$: C, 42.27, H, 6.45, S, 41.02. Found: C, 42.20, H, 6.50, S, 40.89

Bis(*sec*-butoxythiocarbonylthio)methane (**5e**): yellow liquid; n_D^{20} 1.5681; ^{1}H-NMR ($CDCl_3$) δ 5.62 (m, 1 H, OCH); 4.70 (s, 2 H, SCH_2S); 1.75 (m, 2 H, CH_2); 1.36 (d, 3 H, CH_3); 0.95 (t, 3 H, CH_3); ^{13}C-NMR ($CDCl_3$) δ 212.16, 76.45, 41.38, 28.51, 18.70, 9.58; IR (neat) 2970, 2880. 1465, 1385, 1250, 1110, 1085, 1040, 880, 810, 750 cm^{-1}.

Anal. Calcd. for $C_{10}H_{20}O_2S_4$; C, 42.27, H, 6.45, S, 41.02. Found: C, 41.98, H, 6.58, S, 40.89.

Reaction of Bis(ethoxythiocarbonylthio)methane (5a) with Isopropylamine

To a solution of **5a** (10 mmol) and polyethyleneglycol, Mn ca. 1,500, (1 mmol) in CH_2Cl_2 (20 mL) cooled at 0°C, a solution of isopropylamine (30, 40, 70 or 100 mmol) in water (10 mL) was slowly added with magnetic stirring which was continued for 30 min after isopropylamine addition, at room temperature. A 5% water sodium hydroxide solution (10 mL) was added to the separated aqueous layer, and the resulting mixture was extracted three times with dichloromethane (10 mL each). The combined dichloromethane extracts were dried and evaporated under reduced pressure. The resulting semisolid residue was dissolved in hexane (100 mL), and this solution was washed with water three times (100 mL each), to extract PEG, then dried with $MgSO_4$, evaporated under reduced pressure and weighed. Part of this residue was separated by preparative thin layer chromatography using silica gel (Merck, art 7747) and chloroform as eluent.

The same procedure was used for the reaction of **5a** with isopropylamine without PEG. **5a** (10 mmol) in CH_2Cl_2 (20 mL), was treated with isopropylamine (30 mmol) in CH_2Cl_2 (10 mL). After the reaction, the dichloromethane solution was washed with water (50 mL), dried with $MgSO_4$, and evaporated. The ^{1}H-NMR spectrum of the residue did not show the **2c** product.

Reaction of Bis(Alkoxythiocarbonylthio)Methanes (5a,5c) with Monoalkylamines and CH_2Cl_2

The same conditions for the reaction of **5a** with isopropylamine in the presence of PEG, **5a** or **5c** (10 mmol) were used for the reactions with ethylamine, n-propylamine, i-propylamine, n-butylamine, and benzylamine using 70 mmol of these amines in each reaction. The same procedure for separation of products **2c** and **6ac** was performed to obtain isolated products **2** and **6** as colorless liquids. **2** and **6** decompose on heating.

^{1}H-NMR Spectra of 2 and 6 (δ, ppm, $CDCl_3$)

3-Ethyl-1,3,5-dithiazinane (**2a**): δ 4.45 (b.s., 4 H, SCH_2N); 4.10 (b.s., 2 H, SCH_2S), 3.07 (q, 2 H, CH_2); 1.08 (t, 3 H; CH_3).

3-Propyl-1,3,5-dithiazinane (**2b**): δ 4.44 (b.s., 4 H, SCH_2N); 4.11 (b.s., 2 H, SCH_2S); 2.97 (t, 2 H, CH_2); 1.47 (m, 2 H, CH_2); 0.93 (t, 2 H, CH_3).

3-Isopropyl-1,3,5-dithiazinane (**2c**): δ 4.52 (b.s., 4 H, SCH_2N); 4.14 (b.s., 2 H, SCH_2S); 3.77 (m, 1 H, CH); 1.15 (d, 6 H, CH_3).

3-Butyl-1,3,5-dithiazinane (**2d**): δ 4.44 (b.s., 4 H, SCH_2N); 4.11 (b.s., 2 H, SCH_2S); 3.01 (t, 2 H, CH_2); 1.49 – 1.27 (m, 4 H, CH_2CH_2); 0.93 (t, 3 H, CH_3).

3-Benzyl-1,3,5-dithiazinane (**2f**): δ 4.55 (b.s., 4 H, SCH_2N); 4.22 (b.s., 2 H, CH_2); 4.14 (b.s., 2 H, SCH_2S); 7.2–7.5 (m, 5 H, arom.).

Ethyl *N*-ethylcarbamothioate (**6aa**): δ 6.2–6.8 (b.s., 1 H, NH); 4.58, 4.48 (2q, 2 H, OCH_2); 3.57, 3.29 (2q, 2 H, NCH_2); 1.34, 1.28 (2t, 3 H, CH_3); 1.20, 1.14 (2t, 3 H, CH_3).

Ethyl *N*-propylcarbamothioate (**6ab**): δ 6.7 – 6.3 (b.s., 1 H, NH); 4.55, 4.47 (2q, 2 H, OCH_2); 3.32, 3.55 (2t, 2 H, NCH_2); 1.61 (m, 2 H, CH_2); 1.35 (t, 3 H, CH_3); 0.93 (t, 3 H, CH_3).

Ethyl *N*-isopropylcarbamothioate (**6ac**): δ 6.6 – 6.1 (b.s., 1 H, NH); 4.56, 4.46 (2q, 2 H, CH_2); 4.1–4.2 (m, 1 H, CH); 1.38 (t, 3 H, CH_3), 1.20 (d, 6 H, CH_3).

Ethyl *N*-butylcarbamothioate (**6ad**): δ 6.9 – 6.2 (b.s., 1 H, NH); 4.55, 4.47 (2q, 2 H, CH_2); 3.54, 3.27 (2t, 2 H, CH_2); 1.8 – 1.6 (m, 4 H, CH_2); 1.39 (t, 3 H, CH_3); 0.93 (t, 3 H, CH_3).

Ethyl *N*-benzylcarbamothioate (**6af**): δ 7.25–7.35 (m, 5 H, arom); 6.5–6.9 (b.s., 1 H, NH); 4.76, 4.71 (b.s., 2 H, CH_2); 4.72, 4.32 (2q, 2 H, CH_2); 1.33 (t, 3 H, CH_3).

Isopropyl *N*-ethylcarbamothioate (**6ca**): δ 6.6 – 6.1 (b.s., 1 H, NH); 5.7 – 5.4 (m, 1 H, CH); 3.56, 3.28 (2q, 2 H, CH_2); 1.33, 1.28 (2d, 6 H, CH_3); 1.16 (t, 3 H, CH_3).

Isopropyl *N*-propylcarbamothioate (**6cb**): δ 6.2–6.7 (b.s., 1 H, NH); 5.7 – 5.4 (m, 1 H, CH); 3.54, 3.33 (2t, 2 H, CH_2); 1.55 (m, 2 H, CH_2); 1.34, 1.28 (2d, 6 H, CH_3); 0.91 (t, 3 H, CH_3).

Isopropyl *N*-isopropylcarbamothioate (**6cc**): δ 6.6 – 6.1 (b.s., 1 H, NH); 5.7 – 5.4 (m, 1 H, CH); 4.2 – 4.1 (m, 1 H, CH); 1.33, 1.20 (2d, 6 H, CH_3); 1.20 (d, 6 H, CH_3).

Isopropyl *N*-butylcarbamothioate (**6cd**): δ 6.9 – 6.2 (b.s., 1 H, NH); 5.66 – 5.56 (m, 1 H, CH); 3.62, 3.30 (2t, 2 H, CH_2); 1.8 – 1.6 (m, 4 H, CH_2CH_2); 1.4 – 1.2 (d, 6 H, CH_3); 0.96 (t, 3 H, CH_3).

O-isopropyl *N*-benzylcarbamothioate (**6cf**): δ 7.36 – 7.24 (m, 5 H, arom.); 7.1 – 6.2 (b.s., 1 H, NH); 5.67 – 5.58 (m, 1 H, CH); 4.72, 4.34 (2b.s., 2 H, CH_2); 1.4 – 1.2 (d, 6 H, CH_3).

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