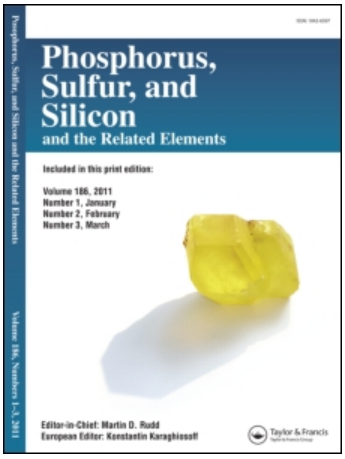

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REACTIONS OF DICHLOROMETHANE WITH THIOANIONS. 1. PREPARATION OF BIS(N,N-DIALKYLTHIOCARBAMOYLTHIO)METHANES

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The preparation of some bis(N,N-dialkylthiocarbamoylthio)methanes, mainly published in the patent literature, is described. The method is based on the reaction of sodium N,N-dialkyldithiocarbamates in water with dichloromethane catalyzed by poly(ethylene glycol) 1,500. The yields are 50–80%.

Key words: Thioanions; dichloromethane; phase transfer catalyst; IR spectra.

In our studies about the reactions of some thioorganic compounds using poly(ethylene glycol) (PEG) 1,500 as phase transfer catalyst and dichloromethane as solvent, we have found that the latter compound also acts as a reagent. The reactivity of dichloromethane in double substitution reactions is well documented. Some examples are the acetals formation from alkoxides and phenoxides,[1] the reaction of dichloromethane with thiols to afford dithioacetals,[2] and the generation of animals from amines.[3] The two first examples use quaternary ammonium salts as phase transfer catalysts.

In this paper we report the preparation of bis(N,N-dialkylthiocarbamoylthio)methanes (**2**) by reaction of sodium N,N-dialkyldithiocarbamates (**1**) in water with dichloromethane catalyzed by PEG-1,500. The preparation of some of these compounds has mainly been reported in the patent literature.[4,5] To our knowledge the use of PEG in reactions of CH_2Cl_2 as a phase transfer catalyst has only been applied by us,[6] in one case.

$$\underset{\mathbf{1}}{2R_2NCS^-Na^+} + CH_2Cl_2 \xrightarrow[H_2O]{PEG} \underset{\mathbf{2}}{R_2NCS{-}CH_2{-}SCNR_2} + 2NaCl$$

With the aim of knowing the best conditions to prepare compounds **2**, sodium 1-piperidinecarbonodithioate was taken as a representative dithiocarbamate which was dissolved in different water amounts and the solutions stirred with dichloromethane at room temperature in the presence of PEG-1,500. These assays appear in Table I.

As time increases and the water volume decreases the reaction yield increases. The results of the two last experiments show the catalytic activity of PEG-1,500. More prolonged reaction times or heating do not produce better yields.

The organic phase crude products, obtained one after two hours and the other after four hours, according to the conditions used for the first experiment of Table

TABLE I

Preparation[a] of bis(1-piperidinecarbonodithio)methane $[(C_5H_{10}NCS_2)_2CH_2$; **2f**]

Vol. H_2O (mL)	Time (h)	PEG-1,500 (mmol)	Yield (%)
15	4	2	68
15	8	2	70
15	12	2	76
25	12	2	75
50	8	2	50
50	8	0	7

[a]: Substrate: 20 mmol; CH_2Cl_2: 50 mL; temp.: 20°C.

TABLE II

Bis(N,N-dialkylthiocarbamoylthio)methanes (**2**)

2	R	Yield(%) PEG	Yield(%) No PEG	M.p.(°C) (n_D^{25})	IR(KBr), ν(cm^{-1}) N-(C=S)S	^{1}H-NMR($CDCl_3$/TMS), δ(ppm) NCH	^{1}H-NMR($CDCl_3$/TMS), δ(ppm) SCH_2S
a	CH_3CH_2-	53	0.6	71	1480, 1355, 1070	3.71(q) 4.03(q)	5.41
b	-$(CH_2)_2O(CH_2)_2$-	50	1.7	229-231	1425, 1275, 1005	3.89(s.br.) 4.33(s.br.)	5.44
c	-$(CH_2)_4$-	51	1.0	230	1445, 1335, 1015	3.62(t) 3.92(t)	5.37
d	$CH_3(CH_2)_2$-	71	1.0	57-58	1485, 1370, 1095	3.58(t) 3.89(t)	5.40
e	$CH_3(CH_2)_3$-	80	4.5	(1.5770)	1490, 1375, 1105	3.62(t) 3.94(t)	5.40
f	-$(CH_2)_5$-	75	7	166-167	1485, 1285, 1010	3.84(s.br.) 4.27(s.br.)	5.45

q: quartet; s.br.: broad singlet; t: triplet.

I, did not show the possible intermediate $C_5H_{10}NCS—SCH_2Cl$ according to their ^{1}H-NMR spectra. This means that this presumed intermediate is very reactive and could be the reason for the less-than-quantitative yield observed.

Next we studied the reaction of dichloromethane with other sodium N,N-dialkyldithiocarbamates dissolving 20 mmol of compound **1** in 15 mL of water and stirring with 50 mL of CH_2Cl_2 for 12 h at room temperature, in the presence (2 mmol) or the absence of PEG-1,500. These conditions are milder than those reported in the patent literature.[4] The results, together with some physical properties of products **2**, are shown in Table II.

The relatively high yield of **2e** obtained without PEG-1,500 can be attributed to the lipophilic character of sodium N,N-dibutyldithiocarbamate since this compound is soluble in dichloromethane. The ^{1}H-NMR signals of protons α to the nitrogen atom of products **2** are duplicated due to the existence of rotational isomerism because of the restricted rotation about the $S_2C—NR_2$ bond.[7]

When sodium N-butyl- and N-cyclohexyldithiocarbamates were treated with di-

chloromethane under the same conditions as the sodium N,N-dialkyldithiocarbamates complex mixtures of reaction products were obtained. In the case of sodium N-cyclohexyldithiocarbamate (**3**) cyclohexyl isothiocyanate (**4**) could be separated from the reaction mixture by preparative thin layer chromatography. This points out the acidic character of the NH hydrogen.

$$c\text{—}C_6H_{11}NHCS_2Na \rightarrow c\text{—}C_6H_{11}N{=}C{=}S$$

3 4

In conclusion, bis(N,N-dialkylthiocarbamoylthio)methanes can be prepared from the common solvent dichloromethane under mild conditions.

EXPERIMENTAL

IR spectra were obtained on a Perkin Elmer model 1310 spectrophotometer and ^{1}H-NMR spectra were recorded on a Bruker AC-200 apparatus. Compounds **1** were formed by reaction of CS_2, amine and NaOH[8] but using ground alkali suspended in hexane.

Preparation of bis(N,N-dialkylthiocarbamoylthio)methanes (**2**): *General Procedure.* Freshly prepared sodium N,N-dialkyldithiocarbamate (**1**) (20 mmol) in water (15 mL) was stirred with poly(ethylene glycol) 1500 (2 mmol) in dichloromethane (50 mL) by 12 h at room temperature. The evaporated organic layer was treated with hot water to remove the PEG and the solid residues (**2a–d, 2f**) were crystallyzed from hexane-isopropanol (4:1). **2e** is a viscous liquid which decomposes on heating.

Physical properties and microanalyses of **2**.

Bis(N,N-diethylthiocarbamoylthio)methane (**2a**): colorless crystals; m.p. 71°C; IR (KBr) 2970, 2930, 1480, 1355, 1070 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.28 (t, 3H, CH_3), 3.71, 4.03 (q, 2H, CH_2); 5.41 (s, 2H, SCH_2S).

Anal. Calcd. for $C_{11}H_{22}N_2S_4$: C, 42.58, H, 7.14. Found: C, 42.86, H, 7.53.

Bis(4-morpholinecarbonodithio)methane (**2b**): colorless crystal; m.p. 229–231°C; IR (KBr) 2950, 2890, 2870, 1425, 1275, 1130, 1005 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 3.76 (s, br, 4H, CH_2OCH_2), 3.89, 4.33 (s, br, 4H, CH_2), 5.44 (s, 2H, SCH_2S).

Anal. Calcd. for $C_{11}H_{18}N_2O_2S_4$: C, 39.03; H, 5.36. Found: C, 38.97; H, 5.35.

Bis(1-pyrrolidinecarbonodithio)methane (**2c**): colorless crystals; m.p. 230°C; IR (KBr) 2970, 2950, 1445, 1335, 1015 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2,00 (m, 4H, CH_2CH_2), 3,62, 3.92 (t, 4H, CH_2NCH_2), 5.37 (s, 2H, SCH_2S).

Anal. Calcd. for $C_{11}H_{18}N_2S_4$: C, 43.10; H, 5.92. Found: C, 43.32; H, 6.01.

Bis(N,N-dipropylthiocarbamoylthio)methane (**2d**): pale green crystals; m.p. 57–58°C; IR (KBr) 2960, 2930, 2870, 1485, 1370, 1095 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.93 (t, 3H, CH_3), 1.74 (m, 2H, CH_2), 3.58, 3.89 (t, 2H, CH_2), 5.40 (s, 2H, SCH_2S).

Anal. Calcd. for $C_{15}H_{30}N_2S_4$: C, 49,13; H, 8.25. Found: C, 49.36; H, 7.80.

Bis(N,N-dibutylthiocarbamoylthio)methane (**2e**): pale green liquid; n_D^{25}: 1.5770; IR (neat) 2950, 2930, 2870, 1490, 1375, 1105 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.94 (t, 3H, CH_3), 1.35 (m, 2H, CH_2), 1.67 (m, 2H, CH_2), 3.62, 3.94 (t, 2H, CH_2), 5.40 (s, 2H, SCH_2S).

Anal. Calcd. for $C_{19}H_{38}N_2S_4$: C, 53.98; H, 9.06. Found: C, 53.77; H, 8.94.

Bis(1-piperidinecarbonodithio)methane (**2f**): white crystals; m.p. 166–167; IR (KBr) 2990, 2930, 2850, 1485, 1285, 1010 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.69 (s, br, 6H, 3 × CH_2) 3.84, 4.27 (s, br, 4H, 2 × CH_2), 5.45 (s, 2H, SCH_2S).

Anal. Calcd. for $C_{13}H_{22}N_2S_4$: C, 46.67; H, 6.63. Found: C, 46.32; H, 6.72.

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