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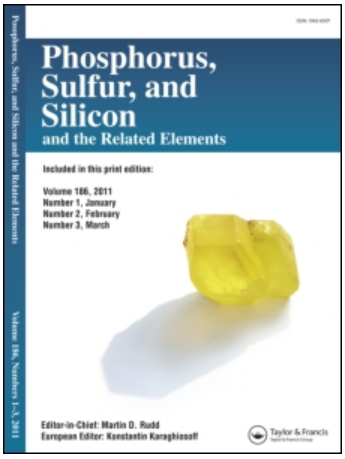

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
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ALKOXYTHIOAMINES

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To cite this Article Díaz, C. , Copaja, S. and González, G.(1985) 'ALKOXYTHIOAMINES', Phosphorus, Sulfur, and Silicon and the Related Elements, 22: 3, 317 — 321
To link to this Article: DOI: 10.1080/03086648508073370
URL: http://dx.doi.org/10.1080/03086648508073370

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Phosphorus and Sulfur, 1985, Vol. 22, pp. 317–321
0308-664X/85/2203-0317/$10.00/0

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ALKOXYTHIOAMINES

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(*Received September 18, 1984; in final form December 13, 1984*)

A series of alkoxythioamines, R_2NSOR' (NR_2 = morpholino, piperidino and diethylamino; R' = Me, Et, *i*-Pr), has been prepared by the alcoholysis of *N,N'*-thiobisamines induced by the presence of $CuCl_2$ and HCl. The products were characterized by their IR, ^{1}H-NMR spectra and elemental analyses.

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INTRODUCTION

Although alkoxythioamines have been known for a long time,[1] and the preparation of some compounds has been reported, no systematic study of their synthesis has been carried out. Until now, the derivatives 1-chloro-ethoxy-thiodimethylamine,[1] ethoxy-thiopiperidine[2] and isopropoxy-thio-*N*-methylaniline[3] were synthesized from the corresponding aminesulfenyl chloride, R_2NSCl, and ethylene oxide, ethanol, and sodium isopropoxide respectively.

In a previous work we have reported the formation of ethoxy-thiomorpholine in the reaction of thiobismorpholine with ethanol in the presence of copper(II)-ions.[4] In this work we report the synthesis of a number of alkoxythioamines *via* the alcoholysis of *N,N'*-thiobisamines.

RESULTS AND DISCUSSION

Although *N,N'*-thiobisamines are normally crystallized from alcohols, alcoholysis can be induced by adding $CuCl_2$ to the solutions giving rise to alkoxythioamines as principal products. Qualitative similar results are obtained by replacing the copper(II) salts by hydrogen chloride; but the procedure using HCl affords (two to seven times) the yields as cupric chloride. Thus, by carrying out the following reactions (1) and (2) with equimolar quantities of the alcohols in inert media, the alkoxythioamines 1a–1c, 2a–2c and 3a–3c were synthesized.

Compared with the traditional synthesis of sulfur(II) compounds *via* the amino-sulfenyl chloride[5,6]—obtained from the same precursor as the thiobisamines, SCl_2—this method starting from the thiobisamine has some advantages. The relatively high inertness of the *N,N'*-thiobisamines permits easy preparation of pure starting materials as well as relatively simple separation and purification of the

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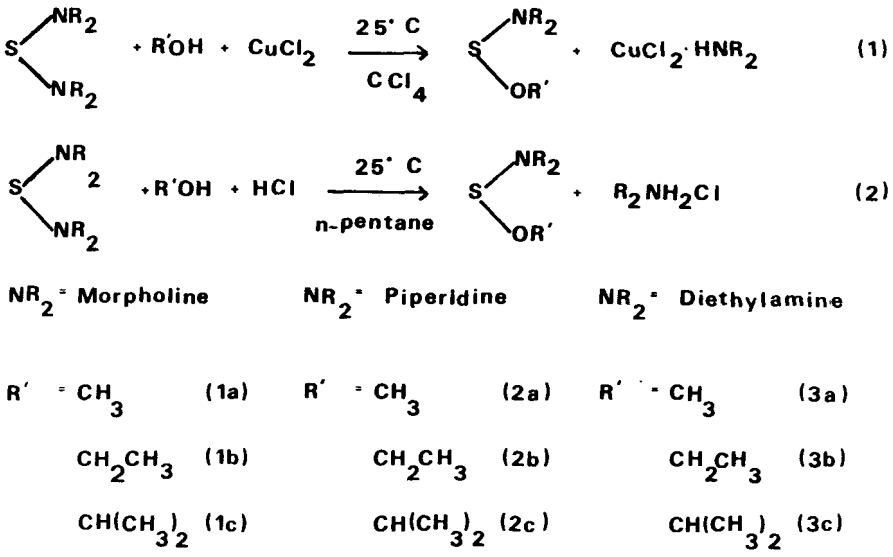

products. Moreover, the lower exothermicity associated with the formation of HNR_2 compared with that of HCl make it easier to control the reaction permitting the reaction to be carried out at room temperature.

The products are oily volatile liquids with strong lachrymose properties and are characterized by means of elemental analysis and spectral characteristics.

TABLE I

Proton magnetic resonance spectra of alkoxythioamines

	A. Resonance of alkoxy-group protons[a]				
	Methoxy	Ethoxy		Isopropoxy	
	(CH_3)	$(CH_3)^b$	$(CH_2)^c$	$(CH_3)^d$	$(CH)^e$
Morpholine	3.75	1.21	3.90	1.20	3.70
Piperidine	3.70	1.18	3.85	1.18	3.80
Diethyl amine	3.66	1.23	3.83	1.20	3.87

	B. Resonance of amino-group protons[a]					
	Diethylamine		Morpholine		Piperidine	
	$(CH_3)^b$	$(CH_2)^c$	$(N(CH_2)_2)^f$	$((CH_2)_2O)^f$	$((CH_2)_3)^f$	$(N(CH_2)_2)^f$
Methoxy	1.16	3.33	3.46	3.58	1.58	3.41
Ethoxy	1.23	3.30	3.36	3.60	1.58	3.38
Isopropoxy	1.20	3.30	3.33	3.56	1.58	3.36
Amine	0.96	2.85	3.20	3.55	1.53	3.23

[a] ppm from TMS, in CCl_4 solutions.
[b] Triplet.
[c] Quartet.
[d] Doublet.
[e] Septet.
[f] Multiplet.

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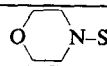
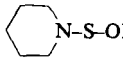
TABLE II

IR spectra of alkoxythioamines (in cm^{-1})[a]

Compound	ν(S—N)	ν(S—O)	ν(C—O)
			
R′: CH_3	952 (st)	920 (w)	990 (st)
CH_3CH_2	952 (st)	875 (st)	1080 (st)
$CH(CH_3)_2$	956 (st)	825 (st)	910 (st)
			
R′: CH_3	948 (st)	920 (w)	992 (st)
CH_3CH_2	943 (st)	870 (st)	1012 (st)
$CH(CH_3)_2$	951 (st)	826 (st)	915 (st)
(CH_3CH_2)N–S–OR′			
R′: CH_3	930 (st)	920 (m, sh)	990 (vst)
CH_3CH_2	930 (m)	827 (st)	1015 (st)
$CH(CH_3)_2$	925 (m, sh)	820 (st)	910 (st)

[a] Thin films. st = strong, vst = very strong, m = medium, w = weak, sh = shoulder.

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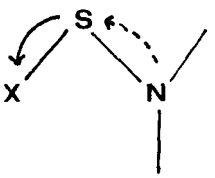
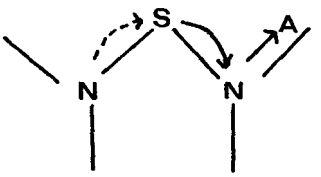
The ^{1}H-NMR data of the products are shown in Table I. The amino group protons in the alkoxythioamines are more deshielded than in the corresponding thiobisamines showing also a slight dependence on the nature of the alkoxy group. The chemical shifts of the alkoxy group protons, being in a range characteristic for S–OR compounds,[7–9] also show some dependence on the nature of the amine group.

Selected frequencies from the IR spectra of the alkoxythioamines are reproduced in Table II. The assignment of the frequencies was made according to a previous vibrational study of the thiobisamines[10] and other available literature data.[9,11–13] The comparison of the S—N frequencies in the thiobisamines with those for the alkoxy derivatives shows, as expected for the substitution of an amine group by a more electronegative substituent, a reinforcement of the S—N linkage with, probably, an increase of the sp^2 character of the nitrogen orbitals.



This effect, that agrees with the shifts observed in the ^{1}H-NMR spectra, has also been detected by analysing the dependence of the barrier for rotation around the S—N bond; in the parent compounds $C_6H_5CH_2(CH(CH_3)_2)$N—S—X, the barrier increase with increasing electronegativity of the ligands at sulfur atom.[14]

The relatively low reactivity of thiobisamines to protic reagents as water and alcohols is normally attributed to the stabilization of the S—N bond by π interactions.[15–17] The enhanced reactivity observed in the presence of a Lewis or a Bronsted acid (A) permitting the synthesis described in this work should be then related to a greater sp^3 character of the nitrogen orbitals induced by the coordination of A making the amine a better leaving group.



Thus, the higher efficiency for activating the alcoholysis of the thiobisamines exhibited by the HCl than the $CuCl_2$ can be attributed to a greater activity of the protons than the Cu(II)-ions in the interactions with the amine groups of the thiobisamine as well as to a thermodynamic effect provining from the higher stability of the tetraalquilammonium chlorides R_2NH_2Cl respect to that of the Cu(II)-amine complexes.

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EXPERIMENTAL

N,N'-thiobisamines were prepared and purified according to literature procedures.[18,19] Alcohols and other solvents were dried with molecular sieves. Anhydrous cupric chloride was obtained from the dihydrate by warming at 100°C under vacuum. All reactions were performed under nitrogen atmosphere. ^{1}H-NMR spectra were obtained on a Varian T-60 spectrometer. The chemical shifts were determined using tetramethylsilane (TMS) as internal standard. IR spectra were recorded on a Perkin-Elmer Model 621 grating spectrometer using thin liquid samples.

General procedures for the synthesis of the alkoxythioamines:

(A) A solution of 25 mmol of the thiobisamine in an inert solvent (CCl_4 for 1a–c and 3a–c, and diethyl ether for 2a–c) is added to a suspension of the equivalent (25 mmol) of $CuCl_2$ and the alcohol in the same solvent. The mixture is then stirred for 24 h at room temperature. After filtering the $CuCl_4$-amine complex, the solution is transferred to a column of basic alumina which is then eluted with CCl_4. The solvent is removed under vacuum and the crude products fractionated at reduced pressure.

(B) To a solution of equimolar quantities (ca. 25 mmol) of the thiobisamine and the alcohol in *n*-pentane is added the equivalent quantity of dry hydrogen chloride. The solution is stirred for about 15 min. After filtering the amine hydrochloride, the solvent is removed under vacuum. The products can be purified by fractional distillation under reduced pressure.

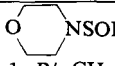
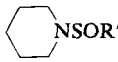
Analytical data, the yields and some physical properties of the products are shown in Table III.

ACKNOWLEDGMENT

The authors wish to thank Prof. Dr. E. Fluck, Gmelin Institut Frankfurt-Main for facilities on writing this work.

TABLE III

Analytical data and physical properties of alkoxythioamines

Compound	Yield (%)[a] A	B	B.P. (°C) (mm Hg)	n_D (25°C)	Elemental Analysis Found/(calc.) C	H	N	S
								
1a R′: CH_3	27	50	25 (0.2)	1.486	39.05 (40.24)	7.20 (7.42)	9.33 (9.38)	20.72 (21.48)
1b CH_2CH_3	23	56	42 (0.2)	1.481	43.93 (44.14)	7.50 (8.02)	8.42 (8.58)	19.72 (19.64)
1c $CH(CH_3)_2$	40	60	90 (0.2)	1.475	46.50 (47.43)	7.75 (8.52)	7.36 (7.90)	17.43 (18.08)
								
2a R′: CH_3	32	66	35 (0.1)	1.489	48.61 (48.97)	8.81 (8.84)	9.67 (9.52)	22.57 (21.76)
2b CH_2CH_3	40	74	40 (0.08)	1.480	51.51 (52.13)	9.62 (9.37)	8.76 (8.68)	
2c $CH(CH_3)_2$	30	40	45 (0.09)	1.473	54.90 (54.85)	10.04 (9.71)	7.82 (8.00)	18.88 (18.28)
$(CH_3CH_2)_2NSOR'$								
3a R′: CH_3	10	67	21 (0.05)	1.451	42.80 (44.42)	10.09 (10.36)	9.61 (9.62)	22.38 (23.69)
3b CH_2CH_3	38	69	27 (0.05)	1.449	47.89 (48.30)	10.33 (10.06)	9.47 (9.39)	21.30 (21.46)
3c $CH(CH_3)_2$	25	66	25 (0.05)	1.449	51.45 (51.51)	10.84 (10.42)	10.52 (8.58)	19.07 (19.62)

[a]Yields by using $CuCl_2$ (A) and HCl (B).

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