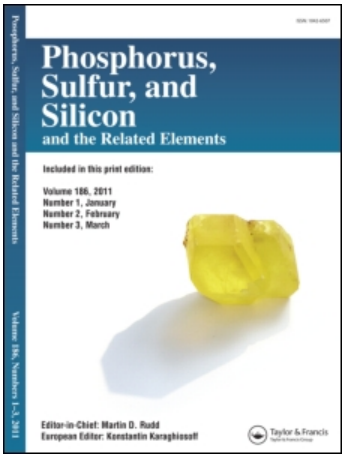

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NOVEL SYNTHESIS OF DISUBSTITUTED THIOLCARBAMATES VIA A SULFUR TRANSFER AGENT—POTASSIUM ALKYL OR BENZYL DITHIOCARBONATES

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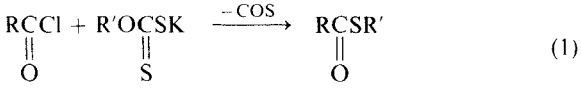
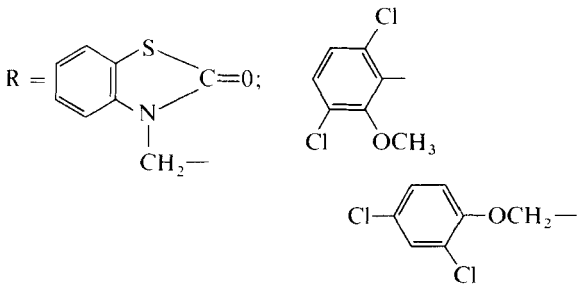
The reaction of N,N-disubstituted carbamoyl chlorides with potassium alkyl or benzyl dithiocarbonates afforded a novel synthesis of disubstituted thiolcarbamates.

The synthesis and the use of disubstituted thiolcarbamates as herbicides has been well documented in the literature.[1] We recently reported a novel synthesis of thiol esters by the reaction of certain acid chlorides with potassium alkyl or benzyl dithiocarbonates.[2]

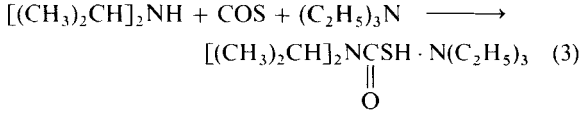


(1)



$R' = -CH_3; -C_2H_5; -CH_2C_6H_5$

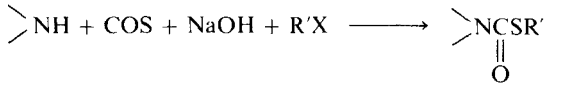
We now wish to report that replacing the above acid chlorides with disubstituted carbamoyl chlorides in Reaction 1 afforded a novel synthesis of disubstituted thiolcarbamates (Method I). In all probability the mixed anhydride A was formed but immediately decomposed to give carbonyl sulfide and the disubstituded thiolcarbamate (Reaction 2). Evidence for the liberation of carbonyl sulfide in Reaction 2 was obtained by the formation of the triethylamine salt of diisopropylthiolcarbamic acid when the liberated gas was allowed to bubble through a solution containing diisopropylamine and triethylamine at 0–10°C.



(3)

Based on elemental analysis and molecular weight, the alternative disubstituted thionocarbamate structure had to be considered. However, proof of structure for the thiolcarbamates was established by the following known methods:

Method II



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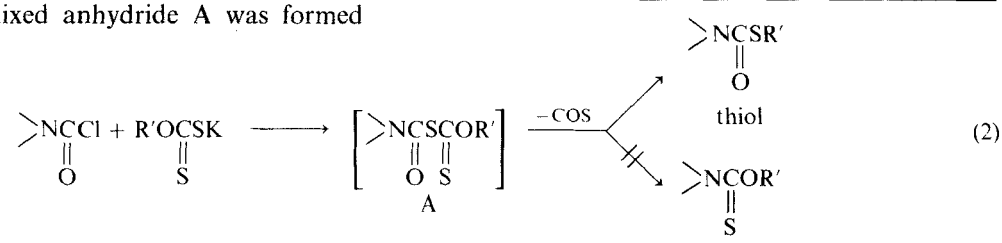
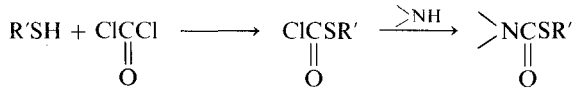


(2)

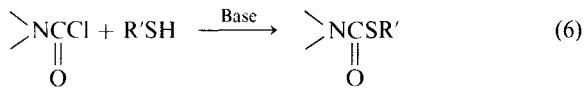
$R' = -CH_3; -C_2H_5; -CH_2C_6H_5$

Method III



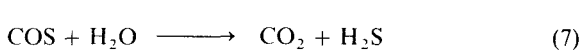
(5)

Method IV



(6)

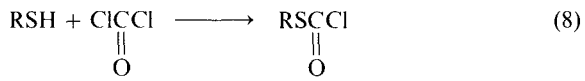
Even though there are numerous methods for preparing disubstituted thiolcarbamates, each suffers from various inherent drawbacks. Method II requires that the reaction be carried out at low temperature (0–10°C) and an excess (30–40%) of a secondary amine must be employed in order to minimize the hydrolysis of carbonyl sulfide to carbon dioxide and hydrogen sulfide which is toxic.



(7)

The recovery of the expensive excess amine from an aqueous medium is tedious and difficult.

Method III requires another step, that is, the synthesis of alkyl chlorothiolformates which are prepared from two toxic intermediates, mercaptans and phosgene.



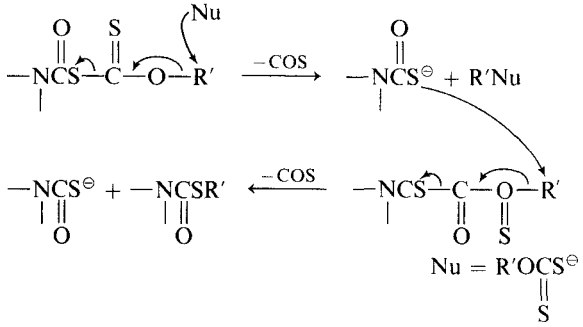
(8)

Method IV requires the use of mercaptans which are toxic, easily oxidized and odoriferous. With the exception of 5 the yields obtained by this novel Method I were equal and in two cases superior to the yields obtained by Methods II, III or IV.

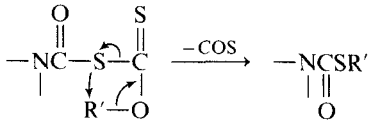
The proposed mechanisms for Reaction 2 are depicted in Scheme I and we favor the nucleophilic displacement mechanism. However, the alternative mechanisms such as the concerted or ion-pair processes are also conceivable but less likely.

In summary, our novel Method I provides a synthesis of disubstituted thiolcarbamates that is fast, efficient, economical and uncomplicated by side reactions. It has been shown that mercaptans, phosgene and alkyl chlorothiolformates which are toxic can be replaced by potassium alkyl or benzyl dithiocarbamates to give disubstituted thiolcarbamates in good yields. Moreover, these potassium

(*1*) *Nucleophilic displacement*

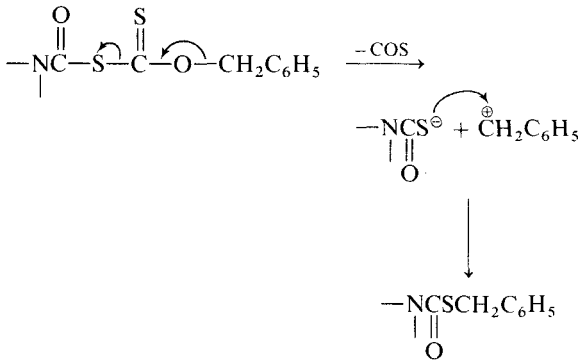


(*2*) *Concerted mechanism*



(*3*) Ion-pair mechanism

Carbonium ion (R′ = $-CH_2C_6H_5$)



Scheme 1

salts can be prepared in excellent yields from alcohols, potassium hydroxide and carbon disulfide, which are readily available, inexpensive and nontoxic.[3] Finally, this novel method illustrates the use of these potassium salts as effective sulfur transfer agents.

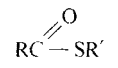
EXPERIMENTAL

NMR spectra were obtained with a Varian T-60 NMR spectrometer. The chemical shifts are reported in δ, using tetramethylsilane as reference. All melting points were taken upon a Fisher-Johns block and are uncorrected.

Disubstituted thiolcarbamates, Method I—(1 to 6)

To a stirred slurry containing 0.33 mol of potassium methyl, ethyl or benzyl dithiocarbonate dihydrate in 200 mL of acetone,

TABLE I



No.	R	R′	Mp °C or (bp °C/mm)	% Yield	NMR, δ(ppm) $CDCl_3$—Me_4Si	Empirical formula[a]
1	$(C_2H_5)_2N$—	$-CH_2C_6H_5$	(132–3/1) N_D^{25} = 1.5568	67	1.03(t,6,$CH_2\underline{CH_3}$) 3.21(q,4,$\underline{CH_2}CH_3$) 4.02(s,2,$\underline{CH_2}C_6H_5$) 7.00–7.43(m,5,ArH)	$C_{12}H_{17}NOS$
2		$-C_2H_5$	(92–3/1) N_D^{25} = 1.5172	63	1.3(t,3,$CH_2\underline{CH_3}$) 1.68–2.18(m,4,CH_2CH_2) 2.94(q,2,$\underline{CH_2}CH_3$) 3.15–3.70(br m,4,CH_2NCH_2)	$C_7H_{13}NOS$
3	$(CH_3)_2N$—	$-C_2H_5$	(30–1/0.3) N_D^{25} = 1.4910	85	1.33(t,3,$CH_2\underline{CH_3}$) 2.90(q,2,$\underline{CH_2}CH_3$) 2.97(s,6,$N(CH_3)_2$)	$C_5H_{11}NOS$
4	$C_6H_5N(CH_3)$—	$-CH_3$	47–8	91	2.20(s,3,SCH_3) 3.22(s,3,NCH_3) 7.27(s,5,ArH)	$C_9H_{11}NOS$
5	$C_6H_{11}N(CH_2CCl{=}CH_2)$—	$-C_2H_5$	(140–2/1.0) N_D^{25} = 1.5260	50	1.27(t,3,$CH_2\underline{CH_3}$) 0.8–2.0(br envel.,11,C_6H_{11}) 2.83(q,2,$\underline{CH_2}CH_3$) 3.97(s,2,NCH_2) 5.22(s,2,$CCl{=}CH_2$)	$C_{12}H_{20}ClNOS$
6	$C_6H_{11}N(CH_2CCl{=}CH_2)$—	$-CH_2C_6H_5$	Stripped at max. temp. of 195°C at 1–2 mm. N_D^{20} = 1.5707	96	0.7–2.1(br envel.,11,C_6H_{11}) 4.03(s,2,NCH_2) 4.17(s,2,$\underline{CH_2}C_6H_5$) 5.32(s,2,$CCl{=}CH_2$) 7.30(m,5,ArH)	$C_{17}H_{22}ClNOS$

[a] Satisfactory analytical data (±0.4% for C, H, N, and S) were reported.

0.3 mol of dimethylcarbamoyl chloride, diethylcarbamoyl chloride, N-methyl-N-phenylcarbamoyl chloride, 1-pyrrolidinecarbamoyl chloride, or N-(2-chloroallyl)-N-cyclohexylcarbamoyl chloride was added in one portion. The stirred reaction mixture was heated at reflux for 6 hr and then at 25–30°C for 18 hr. During this heating period carbonyl sulfide was liberated. To the stirred reaction mixture, 600 mL of water and 600 mL of ethyl ether were added and stirring contained at 25–30°C for 15 min. The separated ether layer was washed with water until neutral to litmus and dried over sodium sulfate. The ether was removed *in vacuo* at a maximum temperature of 80°C for **1** to **5** and 195°C for **6** at 1–2 mm, respectively. The data are summarized in Table I.

Method II—1 and 2

To a stirred mixture at 0°C containing 0.56 mol of diethylamine or pyrrolidine, 32 g (0.4 mol) of 50% aqueous sodium hydroxide and 100 mL of water, 26.4 g (0.44 mol) of carbonyl sulfide was passed in at 0–10°C over a 20 to 30 min period. To this stirred solution 0.4 mol of benzyl chloride or ethyl bromide was added in one portion. The stirred reaction mixture was maintained from 0°C to 20°C for the first 4 hr and then at 25–30°C for 18 hr. To the stirred reaction mixture 200 mL of water and 500 mL of ethyl ether were added and stirring continued at 25–30°C for 15 min. The remainder of the procedure was identical as described in Method I. The boiling point and index of refraction for **1** and **2** were the same as obtained by Method I and their NMR spectra were identical. The yields of **1** and **2** were 68 and 55%, respectively.

Method III—3 and 4

To a stirred mixture containing 0.2 mol of dimethylamine or N-methylaniline, 400 mL of ethyl ether and 28 g (0.2 mol) of potassium carbonate, 0.22 mol of ethyl chlorothioformate or methyl chlorothioformate was added dropwise at 0–10°C. After stirring at 25–30°C for 24 hr, 200 mL of water was added and stirring continued for 15 min. The remainder of the procedure was identical as described in Method I. The boiling point and index of refraction for **3** and the melting point for **4** were the same as obtained by Method I and their NMR spectra were identical. The yields of **3** and **4** were 63 and 91%, respectively.

Method IV—1, 2, 5, and 6

To a stirred solution containing 0.2 mol of benzyl or ethyl mercaptan and 13.2 g (0.2 mol) of 85% potassium hydroxide in 200 mL of acetone, 0.2 mol of diethylcarbamoyl chloride, 1-pyrrolidinecarbamoyl chloride or N-(2-chloroallyl)-N-cyclohexylcarbamoyl chloride was added in one portion. An exothermic reaction set in causing a temperature rise from 22°C to

about 50°C. After stirring at 25–30°C for 24 hr, 600 mL of water and 600 mL of ethyl ether were added. The remainder of the procedure was identical as described in Method I except for **6** the ether was removed *in vacuo* at a maximum temperature of 195°C at 1–2 mm. The boiling point and index of refraction for **1**, **2** and **5** were the same as obtained by Methods I or II and their NMR spectra were identical. The index of refraction for **6** was the same as obtained by Method I and their NMR spectra were identical. The yields of **1**, **2**, **5** and **6** were 55, 63, 85 and 96%, respectively.

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3. A. I. Vogel, *Practical Organic Chemistry*, Longmans, Green and Co., 1956, Chapter 3, p 499. C_2H_5OCSSK can be purchased from Eastman.