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NOVEL SYNTHESIS OF THIOL ESTERS VIA A SULFUR TRANSFER AGENT-POTASSIUM ALKYL OR BENZYL DITHIOCARBONATES¹

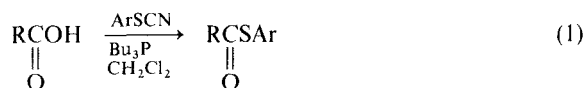
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(Received March 26, 1979)

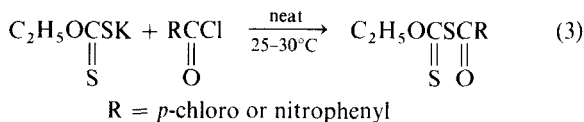
The reaction of certain acid chlorides with potassium alkyl or benzyl dithiocarbonates afforded a novel synthesis of thiol esters.

Considerable attention has been focused on the synthesis of thiol esters.² A recent communication by R. A. Grieco and co-workers³ describing a novel synthesis of thiol esters (Reaction 1) prompts us to report our work in this area of chemistry.



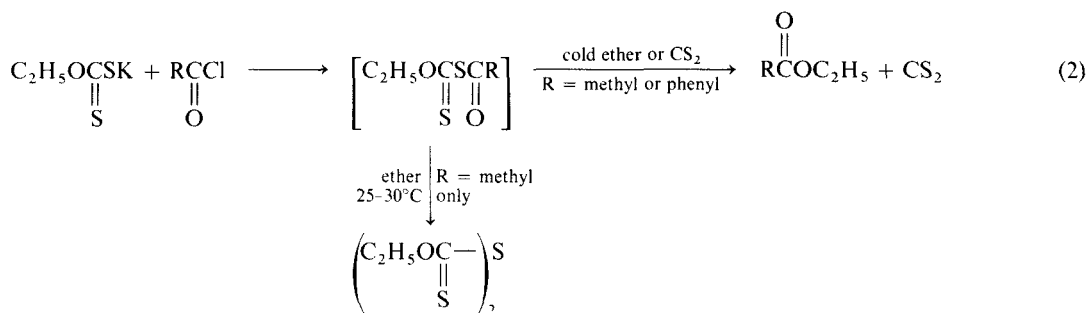
O. W. Willcox⁴ reported that the reaction of potassium ethyl dithiocarbonate with acetyl chloride dissolved in cold ethyl ether furnished the O-ethyl-S-acetyl dithiocarbonate, which readily decomposed to ethyl acetate and carbon disulfide. However, when the acetyl chloride was dissolved in only a small quantity of ethyl ether at room temperature, the main product was diethylsulphur dithiocarbonate. M. M. Richter⁵ using cold carbon disulfide as a solvent similarly obtained the decomposed products, ethyl acetate and carbon disulfide. He also reported that replacing acetyl chloride with benzoyl chloride gave O-ethyl-S-benzoyl dithiocarbonate which readily decomposed to ethyl benzoate and carbon disulfide.

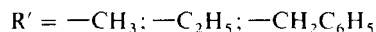
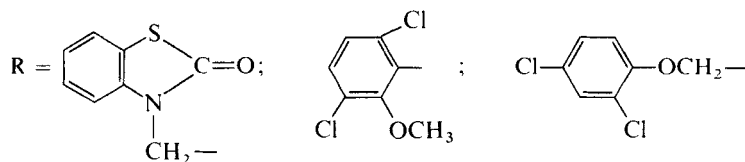
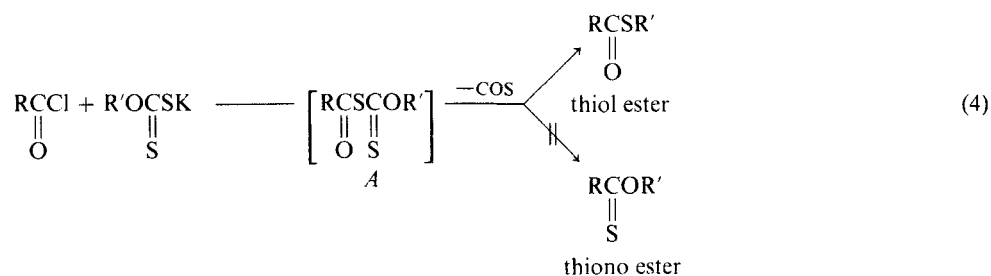
G. Bulmer and F. G. Mann⁶ reported that the reaction of potassium ethyl dithiocarbonate with *p*-chloro or nitrobenzoyl chloride without solvent furnished the stable mixed anhydride, O-ethyl-S-*p*-chloro or nitrobenzoyl dithiocarbonate.



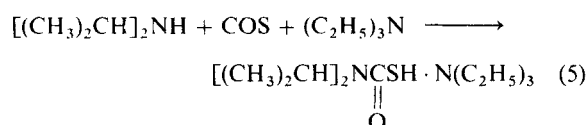
We repeated their experiment and also used ethyl ether or carbon disulfide as a solvent and similarly obtained the mixed stable anhydrides.

Based on the above technology, it was anticipated that replacing the above acid chlorides with the ones shown in Reaction 4 would have afforded either the mixed anhydrides A or its decomposition products, the ester and carbon disulfide. However this was not realized and in all probability the mixed anhydride A did form but immediately decomposed to give carbonyl sulfide and the thiol esters (Reaction 4) in good yields. Evidence for the liberation of carbonyl sulfide in Reaction 4 was obtained by the formation of the triethylamine



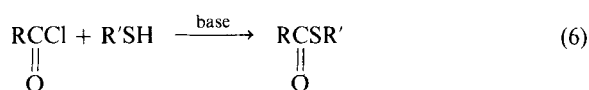


salt of diisopropylthiolcarbamic acid when the liberated gas was allowed to bubble through a solution containing diisopropylamine and triethylamine at 0–10°C.



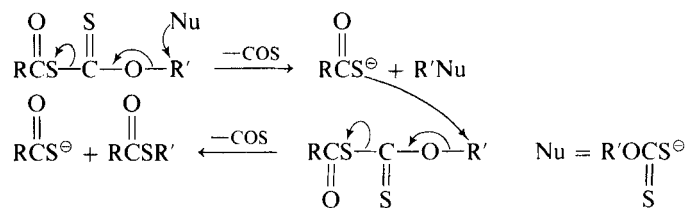
Based on elemental analysis and molecular weight, the alternative thiono ester structure had to be considered. However proof of structure for the

thiol esters was established by the following conventional reaction:

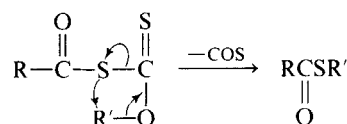


The yields of thiol esters obtained by this novel method I were equal and in one case superior to the yields obtained by the conventional method II (Reaction 6). The proposed possible mechanisms for reaction 4 are depicted in Scheme 1 and we favor the nucleophilic displacement mechanism.

(1) *Nucleophilic displacement*

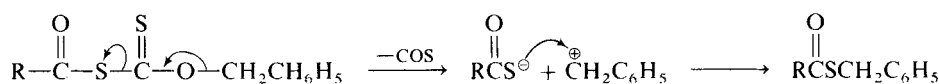


(2) *Concerted mechanism*



(3) *Ion pair mechanism*

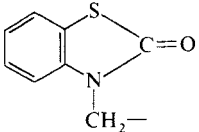
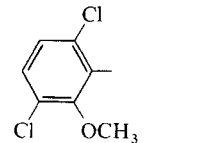
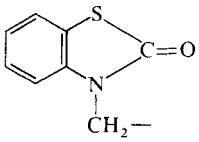
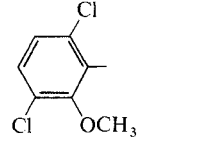
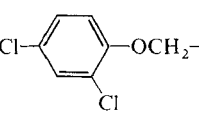
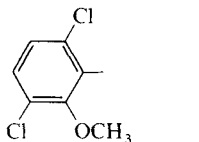
carbonium ion ($\text{R}' = -\text{CH}_2\text{C}_6\text{H}_5$)



SCHEME I

TABLE I



No.	R	R'	Mp °C or (bp °C/mm)	% Yield	NMR, δ (ppm), CDCl ₃ —Me ₄ Si	Empirical Formula ^d
1		—CH ₂ C ₆ H ₅	113–4 ^a	79	4.17 (s, 2, CH ₂ C ₆ H ₅) 4.83 (s, 2, NCH ₂) 6.78–7.55 (m, 9, ArH)	C ₁₆ H ₁₃ NO ₂ S ₂
2		—C ₂ H ₅	(138 – 9/0.2) (N _D ²⁵ = 1.5690)	91	1.38 (t, 3, CH ₂ CH ₃) 3.15 (q, 2, CH ₂ CH ₃) 3.89 (s, 3, OCH ₃) 7.06 and 7.34 (2d, 2, ArH)	C ₁₀ H ₁₀ Cl ₂ O ₂ S
3		—CH ₃	146–7 ^b	50	2.3 (s, 3, SCH ₃) 4.81 (s, 2, NCH ₂) 6.8–7.6 (m, 4, ArH)	C ₁₀ H ₉ NO ₂ S ₂
4		—CH ₂ C ₆ H ₅	38–9	95	3.75 (s, 3, OCH ₃) 4.30 (s, 2, CH ₂ C ₆ H ₅) 6.78–7.45 (m, 7, ArH)	C ₁₅ H ₁₂ Cl ₂ O ₂ S
5		—CH ₂ C ₆ H ₅	75–6 ^c	83	4.15 (s, 2, CH ₂ C ₆ H ₅) 4.62 (s, 2, OCH ₂) 6.5–7.4 (m, 8, ArH)	C ₁₅ H ₁₂ Cl ₂ O ₂ S
6		—CH ₃	43–4	76	2.60 (s, 3, SCH ₃) 3.94 (s, 3, OCH ₃) 7.05 and 7.33 (2d, 2, ArH)	C ₉ H ₈ Cl ₂ O ₂ S

^a Recrystallization from isopropyl alcohol.^b Recrystallization from methyl alcohol.^c Recrystallization from heptane.^d Satisfactory analytical data ($\pm 0.4\%$ for C, H, Cl, N and Cl were reported).

In summary, by the proper choice of the acid chloride the novel method I described above provides a synthesis of thiol esters that is fast, efficient, economical and uncomplicated by side reactions. It has been shown that the mercaptans which are toxic, easily oxidized and odoriferous can be replaced by potassium alkyl or benzyl dithiocarbonates to give thiol esters in good yields. Moreover these potassium salts can be prepared in excellent yields from alcohols, potassium hydroxide

and carbon disulfide, which are readily available, inexpensive and nontoxic.⁷ Finally, this novel method illustrates the use of these potassium salts as effective sulfur transferring 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.

Thiol Esters, Method I—(1 to 6) To a stirred slurry containing 0.12 mol of potassium methyl, ethyl or benzyl dithiocarbonate dihydrate in 200 mL of acetone, 0.1 mol of 2-oxo-3-benzothiazolineacetyl chloride⁸, 2-methoxy-3,6-dichlorobenzoyl chloride⁹, or (2,4-dichlorophenoxy) acetyl chloride¹⁰ was added in one portion. An exothermic reaction set in causing a temperature rise from 22°C to about 40°C. The reaction mixture was stirred at 25–30°C for 18 hr and during this period carbonyl sulfide was liberated. For **1**, **3** and **5**, 800 g of ice water was added and stirring continued at 0–10°C for 2 hr. The solid was collected by filtration, washed with water until the washings were neutral to litmus and air-dried at 25–30°C. For **2**, **4** and **6**, 500 mL of water and 600 mL of ethyl ether were added and stirring continued at 25–30°C for 15 minutes. 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 80–90°C at 1–2 mm. The data are summarized in Table I.

Method II (Conventional)—1, 2, 4 and 5 To a stirred solution containing 0.1 mol of ethyl or benzyl mercaptan, 200 mL of acetone and 6.6 g (0.1 mol) of 85% potassium hydroxide, 0.1 mol of the appropriate acid chloride was added in one portion. The remainder of the procedure was identical as described in Method I. The mixture melting point of **1**, **4** and **5** with the products derived by Method I was not depressed, the boiling point and index of refraction for **2** were the same and their NMR spectra were identical. The following yields were obtained:

No.	% Yield
1	79
2	91
3	43
5	83

ACKNOWLEDGMENT

We are indebted to Dr. Peter Beak, of the University of Illinois, for helpful suggestions concerning our proposed mechanisms.

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