A Simple Thiol Synthesis

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The reaction of organic halides with sodium trithiocarbonate has been widely used for the preparation of disubstituted trithiocarbonates.[1] During a recent investigation of the chemistry of dialkyl trithiocarbonates, we found alkyl mono- and dihalides, upon treatment with sodium trithiocarbonate, could easily be converted into the corresponding mono- or dimercaptan.[2] The reaction is rapid, simple to conduct, and affords the thiol in good yield.

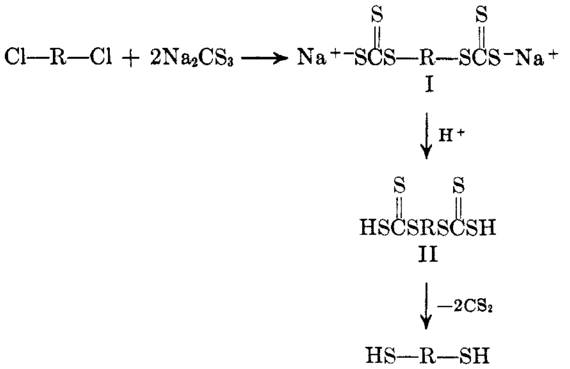
Thus, addition of 1.0 mol of dichlorodiethyl ether (I, R = $CH_2CH_2OCH_2CH_2$) to 2.0 mol of aqueous sodium trithiocarbonate at 40° resulted in a slightly exothermic reaction. The reaction mixture was heated to 60° for 2 hr; however, we have found the reaction to be quite rapid and essentially completed after 15–30 min. Similarly, reaction temperatures of 40–70° had no noticeable effect on the yield. Extraction of the basic reaction mixture permitted the removal of the nonacidic by-product, namely, thioxane (10–15%). Acidification was understandably exothermic liberating carbon disulfide and β,β'-dimercaptodiethyl ether.

The results of this simple one-step thiol synthesis are summarized in Table I. Yields are based on product isolation; the products were identified by physical constants and infrared and pmr spectroscopy.

We postulate the reaction proceeding through the sodium salt of the monoalkyl trithiocarbonic acid (I) which, upon acidification, yields the monoalkyltrithiocarbonate (II). The monoalkyltrithiocarbonate, being unstable,[3] decomposes spontaneously to liberate the mercaptan and carbon disulfide.

An alternate mechanism, such as the acid hydrolysis of either the cyclic or polymeric dialkyl trithiocarbonate,[1] may be excluded since the trithiocarbonate should be extractable from the basic reaction mixture. Similarly, the lack of carbon disulfide generation during the reaction permits the exclusion of mercaptide formation. Additional evidence for our mechanism was obtained by pmr spectroscopy. The pmr spectra of the aqueous basic reaction mixture (after solvent extraction) and an authentic sample of I, prepared from the dimercaptan, sodium hydroxide, and carbon disulfide, exhibited an identical complex multiplet.[4] This information along with Hantzsch's observation that II is less stable than I has prompted us to favor the sequence outlined in Scheme I.

SCHEME I



Experimental Section

All boiling points are uncorrected. All infrared spectra were recorded with a Perkin-Elmer Infracord spectrophotometer. Pmr spectra were determined at 27° (probe temperature) with a Varian Associates Model A-60A spectrometer using tetramethylsilane (TMS) as an internal standard. Chemical shifts are given on the τ scale in parts per million (ppm) relative to TMS (τ 10.00). For each compound, chemical shifts cited are the centers of the multiplets. Numbers in parentheses refer to the multiplicity of the observed resonance. An F & M Scientific Corporation Model 810 and an Aerograph Model 350 chromatograph were used for glpc analyses.

Reagents.—The reagents were all obtained from commercial sources and used without further purification.

Preparation of Aqueous Sodium Trithiocarbonate.—Sodium sulfide (1030 g, 4.3 mol) was dissolved in 500 ml of water at 30°. To this solution was added 356 g (4.7 mol) of carbon disulfide. The reaction mixture was warmed to 40° and allowed to stir for 6 hr. The excess carbon disulfide was removed by evaporation at reduced pressure; the resulting deep red liquid was diluted to 2 l. to afford an ~33% solution.

General Procedure.—The halide was added dropwise to the aqueous sodium trithiocarbonate at 25°. The reaction mixture was heated at 60° for 1–5 hr. During the reaction essentially no carbon disulfide formation was observed. The basic reaction mixture was extracted with ether to remove any unreacted starting material or other nonacidic products. Acidification of the aqueous layer with sulfuric acid resulted in carbon disulfide generation and recovery (90%). The acidic aqueous medium was extracted three times with ether; the combined ether extract was washed with water, dried over anhydrous magnesium sulfate, and evaporated at reduced pressure to yield the dimercaptan.

1,4-Butanedithiol.—To 350 ml (0.75 mol) of aqueous sodium trithiocarbonate at 25° was added 31.8 g (0.25 mol) of 1,4-dichlorobutane in 25 min. The reaction mixture was heated to 60° and allowed to stir at 60° for 5 hr. Isolation of the product by the general procedure described above afforded 18.7 g (61%) of 1,4-butanedithiol: bp 65–68° (13 mm) (lit.[5] bp 75–76° (11 mm)); infrared spectrum, 2548 cm^{-1}; pmr spectrum (CS_2 solution), τ 8.67 (S–H, 3), 8.28 (CH_2–C, 2 × 3), 7.43 (CH_2–S,C).

Anal. Calcd for $C_4H_{10}S_2$: S, 52.5; SH, 54.0; mol wt, 122. Found: S, 52.3; SH, 53.4; mol wt, 120 (osmometer).

β,β'-Dimercaptodiethyl Ether.—To 350 ml (0.75 mol) of aqueous sodium trithiocarbonate at 40° was added 36 g (0.25 mol) of dichlorodiethyl ether in 30 min. The reaction mixture was heated to 60° and allowed to stir at 60° for 2 hr. Isolation of the product by the general procedure described above followed by distillation afforded 23.0 g (66%) of β,β'-dimercaptodiethyl ether: bp 83–85° (9 mm) (lit.[6] bp 90° (10 mm)); infrared spectrum, 2550 cm^{-1}; pmr spectrum (CS_2 solution), τ 8.48 (S–H, 3), 7.40 (CH_2–S, 2 × 3), 6.47 (CH_2–O, 3). The infrared spectrum and glpc retention time were identical with an authentic sample.

Triglycol Dimercaptan.—To 400 ml (0.86 mol) of aqueous sodium trithiocarbonate at 25° was added 56 g (0.3 mol) of triglycol dichloride in 15 min. The reaction mixture was heated to 60° and allowed to stir at 60° for 5 hr. The product was isolated as described above to afford 42.0 g (77%) of triglycol di-

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[1] E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. IV, Chemical Publishing Co., Inc., New York, N. Y., 1958.

[2] After the completion of our work a patent appeared describing similar results: Belgium Patent 668,364 (Dec 16, 1965) to Dr. Speiss G.m.b.H.; *Chem. Abstr.* **65**, 5418 (1966).

[3] A. Hantzsch and W. Bucerius, *Ber.*, **59**, 793 (1926). Hantzsch observed that ethyl trithiocarbonate decomposed easily whereas its salt, $C_2H_5SCS_2{}^-M^+$, was quite stable.

[4] A multiplet at τ 8.5–9.0 relative to acetone (internal standard) was observed for I (R = $CH_2CH_2OCH_2CH_2$–).

[5] G. Schwarzenback and A. Epprecht, *Helv. Chim. Acta*, **19**, 169 (1934); *Chem. Abstr.*, **30**, 4074 (1936).

[6] H. Rheinboldt, E. Giesbrecht, and S. Mathias, *Univ. Sao Paulo, Fac. Filosof., Cienc. Letras, Botan.*, Bol. No. 129, 133 (1951); *Chem. Abstr.*, **46**, 7554 (1952).

TABLE I

REACTION OF HALIDES WITH SODIUM TRITHIOCARBONATE

Halide	Reaction conditions	Product	Yield,[a] %
$ClCH_2CH_2CH_2CH_2Cl$	5 hr at 60°	$HSCH_2CH_2CH_2CH_2SH$	61
$ClCH_2CH_2OCH_2CH_2Cl$	2 hr at 60°	$HSCH_2CH_2OCH_2CH_2SH$	66
$ClCH_2CH_2OCH_2CH_2OCH_2CH_2Cl$	5 hr at 60°	$HSCH_2CH_2OCH_2CH_2OCH_2CH_2SH$	77
$C_6H_5CH_2Cl$	1 hr at 60°	$C_6H_5CH_2SH$	25

[a] No attempt was made to optimize yields.

mercaptan: bp 86° (0.4 mm) (lit.[7] bp 125–131° (5 mm)); infrared spectrum, 2557 cm^{-1}; pmr spectrum (neat), τ 8.08 (S-H, 3), 7.33 (CH_2-S, 2 × 3), 6.43 (CH_2-O, 3). The infrared spectrum was identical with an authentic sample.

Benzyl Mercaptan.—To 135 ml (0.3 mol) of aqueous sodium trithiocarbonate at 25° was added 25.2 g (0.2 mol) of benzyl chloride in 21 min. The reaction mixture was warmed to 60° and allowed to stir at 60° for 1 hr. Isolation of the product as described in the general procedure afforded 6.2 g (25%) of benzyl mercaptan: bp 88–89° (11 mm) (lit.[8] bp 100° (22 mm)); infrared spectrum, 2560 cm^{-1}; pmr spectrum (CS_2 solution), τ 8.43 (S-H, 3), 6.48 (CH_2-S, 2), 2.88 (C_6H_5, 1). This material was identical in all respects with an authentic sample.

Registry No.—1,4-Butanedithiol, 1191-08-8; β,β'-dimercaptodiethyl ether, 2150-02-9; triglycol dimercaptan, 14970-87-7; benzyl mercaptan, 100-53-8.

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(7) J. R. Dann, P. P. Chiesa, and J. W. Gates, Jr., *J. Org. Chem.*, **26**, 1991 (1961).

(8) J. H. Chapman and L. N. Owen, *J. Chem. Soc.*, 579 (1950); *Chem. Abstr.* **44**, 6810 (1950).

The Reaction of Lead Tetraacetate with Malonic Acid

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Since the effect of malonic acid on lead tetraacetate (LTA) decomposition was first reported,[3] it has generally been assumed that the source of this effect is due to the methylene hydrogens of malonic acid. This assumption, which was not tested, received support from the success of methylmalonic acid and ethyl acetoacetate and the failure of dimethylmalonic acid in effecting methylation of aromatic compounds.[3]

We have found, however, that malonic acid is not attacked by LTA except by carboxylate exchange to yield an insoluble mixed salt which decomposes much more readily than does LTA itself.

Our interest in this interaction arose because of the possibility that malonic acid might give rise to a methylenelike species through oxidative bisdecarboxylation similar to that observed with 1,2-dicarboxylic acids.[4] Since the fate of the malonic acid in Fieser's work was not determined, such a process could have occurred to an appreciable extent without being detected.

Whereas LTA and malonic acid separately do not evolve gas in pyridine at room temperature, a mixture of the two yields 0.6 ± 0.2 mol of CO_2 per mole of LTA in less than 2 hr. The amount of CO_2 remains essentially constant over a range of LTA–malonic acid mole ratios of 0.2 to 1.0. Before gas evolution begins, a precipitate forms. A similar result is obtained in benzene except that decomposition occurs at an appreciable rate only at reflux. The precipitate can be collected; heating it produces the same results, with insoluble material remining after gas evolution is complete. Both precipitates have been analyzed (Table I); clearly, the percentage of malonate increases during decomposition. The data in Table I are not intended to correspond to molecular formulas; the precipitates are probably polymeric.[5] Heating the filtrate produces no gas evolution, thus ruling out formation of acetyl peroxide in the exchange process.[6] From 80 to 90% of the original malonic acid routinely has been accounted for in the final precipitate, and the acid has been recovered and positively identified.

TABLE I

PRECIPITATES FORMED FROM LTA AND VARIOUS ACIDS

Acid	% Pb	Acetate/ acid	Moles of CO_2/ mole of Pb	Half-life, hr[a]
Malonic[b]	45.4	3.5	0.5	1.4
Malonic[c]	57.2	1.2		
Succinic[b]	37.5	1.6	1.25	1.6
Dimethylmalonic[b]	37.4	2.2	0.6	1.0

[a] Time required for half of the total CO_2 to be evolved in refluxing benzene. [b] Precipitate before heating. [c] Precipitate obtained after CO_2 evolution was complete.

Attempts were made to detect methylene formation by inclusion of cyclohexene under a variety of reaction conditions. Both cyclohexene and norcarane react with LTA, but at a rate slower than does malonic acid.[7] No materials could be detected which implied formation and further reaction of norcarane.

In pyridine, a 15% yield of picolines, based on CO_2 evolution, is obtained. The ratio of 2- to 3- and 4-picolines is approximately 2:1, which corresponds to the ratio reported for free-radical attack.[8] Electrophilic substitution proceeds almost entirely in the 3

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(2) NDEA Fellow, 1963–1966.

(3) L. F. Fieser and F. C. Chang, *J. Amer. Chem. Soc.*, **64**, 2043 (1942).

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