21.5 g (66%). The infrared spectrum showed absorption for SH at 2551 cm^{-1} (w) and for -NC(=S)- at 1481 cm^{-1} (s).[11]

The crude thiol (19.3 g) in 300 ml of ethyl ether was oxidized to **3** with 80 ml of 1 *N* aqueous iodine–potassium iodide solution to an iodine-color end point. Yellow precipitate was collected and washed with ether and then with *n*-hexane. A solution of the crude **3** in hot acetone (500 ml) was decolorized with charcoal, diluted with 300 ml of *n*-hexane, and chilled, giving a yield of **3** as fine needles of 18.0 g (94%): mp 112–113°; lit. mp 111° (at first believed to be thiol **2**—*cf.* discussion),[4,5] 104–105°,[6] and 112–114°.[7b]

Anal. Calcd for $C_{16}H_{28}N_2S_6$: C, 43.59; H, 6.40; S, 43.65; mol wt, 441. Found: C, 43.55; H, 6.41; S, 43.44; mol wt, 450.

Strong infrared bands were found at 2940, 1470, 1430, 1278, 1240, 1230, 1120, 1110, 1000, 970, 890, and 850 cm^{-1}. The nmr spectrum (CS_2) showed an unresolved multiplet centered at τ 8.3 (12H, β,γ ring), one multiplet in each of the regions of τ 6.8–7.2 and 6.2–6.7 in the integral ratio 4:4 (two different CH_2- units), and a broad singlet centered at τ 6.0 (8H, α ring).

(2-Acetamidoethyl)dithioethyl 1-Piperidinocarbodithioate (4).—Freshly prepared **2** (44.3 g) in 200 ml of ethanol was added to a stirred solution of 2-acetamidoethyl 2-acetamidoethanethiolsulfonate (50.0 g)[12] in 200 ml of ethanol, and stirring was continued for 2 hr. After evaporation of solvent, the viscous residue was thoroughly washed by rubbing and shaking with water (1 l.) and then was kept at 0° for 2 days. After trituration with *n*-hexane (500 ml) containing ether (50 ml) until all yellow color was discharged, 80 g of wet product resulted (mp 49–51°). Recrystallization to constant melting point of still-wet **4** from ethyl acetate by addition of *n*-hexane (1:1) gave 62.0 g (98%) of **4**, mp 67–69°.

Anal. Calcd for $C_{12}H_{22}N_2OS_4$: C, 42.57; H, 6.55; N, 8.28; S, 37.88. Found: C, 42.44; H, 6.28; N, 8.41; S, 37.62.

The infrared spectrum (KBr pellet) showed complete absence of -SH and new absorption bands at 3340 (m, -NHC(O)CH_3), 1650 (s, amide I), and 1530 (s, amide II) cm^{-1}. The nmr spectrum (CS_2) showed an unresolved multiplet centered at τ 8.3 (6H, β,γ ring), a sharp N-acetyl singlet at τ 8.12 (3H), one multiplet in each of the regions τ 6.9–7.4 and 6.3–6.8 in the integral ratio 4:4, a broad singlet at τ 6.0 (4H, α ring), and an extremely broad NH singlet at τ 2.9 (1H).

S-Benzyl 2-Aminoethyldithiocarbamate Hydrochloride (8).—Carbon disulfide (7.61 g, redistilled, bp 46°) in 12.5 ml of dimethylformamide (DMF) was added slowly with chilling to 6.01 g of ethylenediamine (redistilled, bp 116–117°) in 12.5 ml of DMF, the temperature being kept below 25°. Stirring was continued at room temperature for 1 hr. Without isolation of the salt **5**, 6.33 g of benzyl chloride was added slowly so that the temperature did not rise above 40°. A creamy white suspension resulted immediately. The reaction mixture then was heated at 65–70° until the odor of benzyl chloride had disappeared (2 hr). As much as possible of the DMF was removed below 50° under reduced pressure, and the viscous residue thus obtained was triturated with absolute alcohol–ether (60 ml, 1:5). Filtration gave 8.50 g (65%) of **8**, mp 177–185°. Recrystallization from ethanol–water (3:1) gave 6.0 g (46%) of **8** as a fine white solid having mp 201–203° dec.

Anal. Calcd for $C_{10}H_{15}ClN_2S_2$: C, 45.69; H, 5.75; Cl, 13.49; N, 10.67; S, 24.40. Found: C, 45.62; H, 5.77; Cl, 13.57; N, 10.80; S, 24.28.

The infrared spectrum showed strong bands (KBr pellet) at 3200, 3020–2450 (br), 1515, 1453, 1400, 1370, 1310, 1170, 1065, 1025, 970, 922, 775, 710, and 690 cm^{-1}.

Cyclication of 8 with Formation of α-Toluenethiol.—A solution of 6.57 g of **8** prepared in 150 ml of hot water was cooled, and a solution of 1.40 g of potassium hydroxide in 15 ml of water was added (pH 7–8). A creamy appearance resulted immediately, but after a stirring period of 5 min more, clear solution resulted with an oil floating. Stirring was continued at room temperature for 1 hr. Then the mixture was extracted three times with 50 ml of ether, which was dried over anhydrous magnesium sulfate. An aliquot of one-fourth of the extract consumed 27.78 ml of 0.1 *N* iodine–potassium iodide solution (corresponding to a yield of 44% of α-toluenethiol); benzyl disulfide, isolated after the titration and recrystallized, amounted to 0.50 g (corresponding to 65% yield of α-toluenethiol over-all).

When 2 equiv of potassium hydroxide were used, benzyl disulfide was directly obtained in 78% yield without iodine oxidation.

Evaporation of the aqueous layer from both experiments almost to dryness and recrystallization of the precipitate from ethanol–water (6:1) gave in each instance 2.55 g (100%) of 2-imidazolidinethione (**7**), mp and mmp 195–197° (infrared spectrum identical with that of authentic sample).[6]

S-2-Aminoethyl 2-Aminoethyldithiocarbamate Dihydrobromide (9).—2-Bromoethylamine hydrobromide (10.3 g) in 12.5 ml of DMF was slowly added (10 min) to the salt **5** prepared exactly as described above, the temperature meanwhile being kept below 25°. A creamy white suspension resulted. Stirring was continued overnight and the DMF was then removed under reduced pressure below 50°. The oily residue was triturated with 25 ml of absolute alcohol and kept at *ca.* 0° overnight. Filtration gave 15.0 g (88%) of **9** as white solid, mp 199–202° dec. The **9** was recrystallized from ethanol–water (2:1): yield, 10.4 g (61%); mp 215–217° dec.

Anal. Calcd for $C_5H_{15}Br_2N_3S_2$: C, 17.60; H, 4.43; Br, 46.85; N, 12.32; S, 18.80. Found: C, 17.80; H, 4.53; Br, 46.70; N, 12.35; S, 18.86.

The infrared spectrum showed strong bands (KBr pellet) at 3435 (br), 2900–2000 (br), 1550, 1510, 1480, 1460, 1385, 1330, 1310, 1265, 1155, 1050, 1025, 935, 880, 845, and 820 cm^{-1}.

When the reaction of 2-bromoethylamine hydrobromide with **5** was carried out at 75°, the only product which could be isolated was an ethylenediamine salt, obtained finally as its picrate in *ca.* 62% yield.

Cyclization of 9.—A solution of **9** (6.8 g) in 50 ml of warm water was prepared and then was cooled. Upon addition of sodium hydroxide (1.60 g) in water (16 ml), the pH rose to 10 and turbidity increased as addition of base proceeded. Stirring was continued for 1 hr and the mixture then was acidified with concentrated hydrochloric acid (pH 2), after which 3 ml of 8.34 *M* hydrogen peroxide was added until a positive starch–iodide test resulted. After 1 hr of stirring, 0.6 g of precipitate (sulfur?) which had deposited was removed by filtration. The aqueous solution was evaporated to a viscous residue, which was extracted with water by centrifugation. The combined extracts were evaporated, and the resulting oil was triturated with absolute ethanol–ether; the mixed ethylenediamine salts (**10**, plus the hydrochloride) weighed 3.5 g: mp above 300°; picrate mp and mmp 230–235° dec (lit.[13] picrate mp 233–235° dec). No cystamine salt could be isolated despite considerable effort.

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[11] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 357.

[12] L. Field, T. C. Owen, R. R. Crenshaw, and A. W. Bryan, *J. Am. Chem. Soc.*, **83**, 4414 (1961).

[13] S. Gabriel and J. Weiner, *Ber.*, **21**, 2670 (1888).

Organic Disulfides and Related Substances. XVI. Synthesis of Bisthiolsulfonates[1a-d]

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Synthesis of a number of bisthiolsulfonates has been reported, but essentially the same general reac-

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[1] (a) For paper XV in the series, see L. Field and H. K. Kim, *J. Org. Chem.*, **31**, 597 (1966). (b) This investigation was supported in part by the U. S. Army Medical Research and Development Command, Department of the Army, under Research Contract No. DA-49-193-MD-2030. (c) We thank Drs. D. P. Jacobus, T. R. Sweeney, and P. Coad for evaluation of antiradiation-drug activity; this was done at the Walter Reed Army Institute of Research, Washington, D. C., by procedures described by Field, *et al.*[2] Tests for antitumor activity were kindly provided by the Cancer Chemotherapy National Service Center, Bethesda, Md. (d) Abstracted from part of the Ph.D. Dissertation of W. B. L., Vanderbilt University, Aug. 1965. (e) W. B. L. is indebted to the U. S. Department of Health, Education, and Welfare for an National Defense Education Act Fellowship, 1961–1964.

[2] L. Field, A. Ferretti, R. R. Crenshaw, and T. C. Owen, *J. Med. Chem.*, **7**, 39 (1964).

tion was used in all instances.[3] A typical synthesis is exemplified by reaction of the salt of a bisthiolsulfonic acid with an alkyl halide, as shown in eq. 1.[3c] This

$$2\mathrm{AlkBr} + \mathrm{KS{-}O_2S(CH_2)_2SO_2{-}SK} \longrightarrow \mathrm{AlkS{-}O_2S(CH_2)_2SO_2{-}SAlk} + 2\mathrm{KBr} \quad (1)$$

paper reports an investigation of new methods potentially useful in the synthesis of bisthiolsulfonates. Such an investigation was of particular interest because certain thiolsulfonates, in which the sulfonyl moiety is a protecting group for aminothiols, are protective against the lethal effects of ionizing radiation.[2]

Two methods, useful in the synthesis of unsymmetrical monothiolsulfonates, were chosen for study. As a model compound for the study, bis(2-acetamidoethyl) 1,4-butanebisthiolsulfonate (1), a novel compound, was selected.

$$\underset{\mathbf{2}}{\mathrm{2AcNH(CH_2)_2SO_2S(CH_2)_2NHAc}} + \mathrm{NaO_2S(CH_2)_4SO_2Na} \quad (2)$$

$$\Big\downarrow \; -2\mathrm{AcNH(CH_2)_2SO_2Na}$$

$$\underset{\mathbf{1}}{\mathrm{AcNH(CH_2)_2S{-}O_2S(CH_2)_4SO_2{-}S(CH_2)_2NHAc}}$$

$$\Big\uparrow \; -4n\text{-}\mathrm{C_4H_9OH},\ 4\mathrm{NO}$$

$$2\mathrm{AcNH(CH_2)_2SH} + 4n\text{-}\mathrm{C_4H_9ONO} + \mathrm{HO_2S(CH_2)_4SO_2H} \quad (3)$$

The first route, and in this instance perhaps the more effective, involves thioalkylation of a sulfinate salt by a thiolsulfonate (eq. 2). The interchange equilibrium on which it is based (eq. 4) has been studied

$$\mathrm{RSO_2^-} + \mathrm{R'SO_2SR'} \rightleftharpoons \mathrm{RSO_2SR'} + \mathrm{R'SO_2^-} \quad (4)$$

in some detail, but without report of yields of products, perhaps because of the difficulty of separating the desired thiolsulfonate from the reaction mixture.[4] This method has been shown to be synthetically quite useful in instances where advantage can be taken of a difference in physical properties of product and starting material to force the reaction to completion.[5]

In application of the interchange reaction to a bifunctional system (eq. 2), reaction of 2-acetamidoethyl 2-acetamidoethanethiolsulfonate (2)[6] with disodium 1,4-butanedisulfinate[7] in water afforded the desired bisthiolsulfonate (1) in 80% yield. The equilibrium was shifted toward formation of the desired compound (1) because **1** precipitated from the solvent. The structure of the thiolsulfonate **1** was confirmed by using it to thioalkylate *p*-toluenethiol, in a clearly defined reaction,[8] to give 2-(*p*-tolyldithio)-1-acetamidoethane[6] and 1,4-butanedisulfinic acid.[7]

This method should be applicable to synthesis of analogs and homologs of the model compound **1**. Limitations would be availability of starting materials and a method for selectively removing the product from the reaction mixture as it is formed. When applicable, we feel this to be the method of choice because of its simplicity and the high yield of quite pure product.

The second route involved extension of a unique synthesis of unsymmetrical aromatic monothiolsulfonates introduced by Kresze and Kort in 1961.[9] This reaction involves simultaneous oxidation of a sulfinic acid and a thiol with an alkyl nitrite (eq. 5). Kresze

$$\mathrm{RSO_2H} + \mathrm{R'SH} + 2\mathrm{R''ONO} \longrightarrow \mathrm{RSO_2SR'} + 2\mathrm{R''OH} + 2\mathrm{NO} \quad (5)$$

and Kort demonstrated the utility of the method for the preparation of aryl arenethiolsulfonates but did not apply it to alkyl systems. Kresze and Kort indicate that thionitrites (3), disulfides (4), nitrososulfones (5), and disulfonylhydroxylamines (6) are formed when thiols and sulfinic acids react with alkyl nitrites (eq. 6 and 7). Apparently, however, they consider only

$$2\mathrm{RSH} + 2\mathrm{R'ONO} \longrightarrow \underset{\mathbf{3}}{2\mathrm{RSNO}} \longrightarrow \underset{\mathbf{4}}{\mathrm{RSSR}} + 2\mathrm{NO} \quad (6)$$

$$\mathrm{RSO_2H} + \mathrm{R'ONO} \longrightarrow \underset{\mathbf{5}}{[\mathrm{RSO_2NO}]} \xrightarrow{\mathrm{RSO_2H}} \underset{\mathbf{6}}{(\mathrm{RSO_2})_2\mathrm{NOH}} \quad (7)$$

the disulfides to be by-products, rather than possible intermediates, in the formation of the thiolsulfonates. Evidently formation of the red-violet thionitrite (3) is the first step in the reaction,[9] but there remained the question of whether the sulfinic acid, the nitrososulfone (5), or the hydroxylamine (6) was the species which reacted with the thionitrite to yield the thiolsulfonate.

After exploratory reactions, which afforded information on the nature of the process, we finally were able to prepare the model thiolsulfonate (1) in 64% yield (eq. 3) by reaction of equivalent quantities of 2-acetamidoethanethiol and 1,4-butanedisulfinic acid with excess *n*-butyl nitrite in refluxing ethanol for 2–3 hr. That the thionitrite **3** is a reactant[9] is confirmed by our finding that for best results its characteristic red color should be developed to the maximum extent before the sulfinic acid is added. It is particularly interesting that the reaction proceeds so well with a bifunctional sulfinic acid, since cyclization to a disulfonylhydroxylamine or polymerization might well have predominated.

In the exploratory reactions an excess of thiol proved undesirable, probably because it is thioalkylated by the product **1**. An excess of the sulfinic acid proved undesirable, probably because reaction is favored at only one of the sulfinic acid sites, rather than at both.

In further experiments, the disulfonylhydroxylamine (6) resulting from the reaction of *p*-toluenesulfinic acid and *n*-butyl nitrite was treated with an aromatic thiol and *n*-butyl nitrite under the conditions of the Kresze–Kort synthesis. No thiolsulfonate resulted, and the disulfonylhydroxylamine was recovered unchanged, although the thiol was oxidized to the corresponding disulfide; a similar reaction with omission of *n*-butyl nitrite also resulted in recovery of the disulfonylhydroxylamine **6**. The thionitrite resulting from reaction of 2-acetamidoethanethiol

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[3] (a) R. Otto and A. Rössing, *Ber.*, **20**, 2079 (1887); (b) J. C. A. Chivers and S. Smiles, *J. Chem. Soc.*, 697 (1928); (c) B. G. Boldyrev, L. E. Kolmakova, and T. K. Bilozor, *J. Gen. Chem. USSR*, **33**, 1926 (1963); (d) T. P. Johnston and A. Gallagher, *J. Org. Chem.*, **29**, 2442 (1964); (e) S. Hayashi, H. Ueki, S. Harano, J. Komiya, S. Iyama, K. Harano, K. Miyata, J. Niigata, and Y. Yonemura, *Chem. Pharm. Bull.* (Tokyo), **12**, 1271 (1964); *Chem. Abstr.*, **62**, 6421 (1965).

[4] (a) J. D. Loudon and A. Livingston, *J. Chem. Soc.*, 896 (1935); (b) D. T. Gibson and J. D. Loudon, *ibid.*, 487 (1937).

[5] L. Field, T. F. Parsons, and R. R. Crenshaw, *J. Org. Chem.*, **29**, 918 (1964).

[6] L. Field, T. C. Owen, R. R. Crenshaw, and A. W. Bryan, *J. Am. Chem. Soc.*, **83**, 4414 (1961).

[7] M. T. Beachem, J. T. Shaw, G. D. Sargent, R. B. Fortenbaugh, and J. M. Salsbury, *ibid.*, **81**, 5430 (1959).

[8] T. F. Parsons, J. D. Buckman, D. E. Pearson, and L. Field, *J. Org. Chem.*, **30**, 1923 (1965).

[9] G. Kresze and W. Kort, *Chem. Ber.*, **94**, 2624 (1961).

and *n*-butyl nitrite upon treatment with 1,4-butanedisulfinic acid under the conditions of the synthesis of bisthiolsulfonate **1**, but without additional *n*-butyl nitrite, likewise gave none of the thiolsulfonate **1**. Thus we conclude that neither reaction of the thiol or thionitrite (**3**) with the disulfonylhydroxylamine (**6**) nor of the sulfinic acid with the thionitrite (**3**) can be significant steps in the formation of the thiolsulfonate **1**. The most attractive explanation for the reaction of eq. 3 is that the thionitrite (**3**) and the nitrososulfone (**5**) are the reactive species directly involved in formation of the thiolsulfonate, as shown by eq. 8.

$$\mathrm{RSO_2NO + R'SNO \longrightarrow RSO_2SR' + 2NO} \qquad (8)$$

This method should be useful in the synthesis of other bisthiolsulfonates using 1,4-butanedisulfinic acid with both aliphatic and aromatic thiols and hopefully also in the preparation of thiolsulfonates using aromatic sulfinic acids and alkylene dithiols. A limitation of the method may be that 1,4-butanedisulfinic acid is perhaps the only alkylene disulfinic acid which is quite stable as the free acid.[7] However, many disulfinic acids may be prepared as salts,[7] suggesting that acidification of these salts in the presence of an alkyl nitrite and a thionitrite might permit their use *in situ*. The presence of alkyl nitrites in the medium would not, of course, be compatible with certain functional groups such as amines or amine salts.

Since the model bisthiolsulfonate **1** was inactive as an antiradiation drug[1c] and also in antitumor activity,[1c] work with this class was discontinued.

Experimental Section[10]

Bis(2-acetamidoethyl) 1,4-Butanebisthiolsulfonate (1). A. From the Bissulfinate Salt.—A solution of 2-acetamidoethyl 2-acetamidoethanethiolsulfonate (28.85 g.)[6] in 100 ml. of water was added to a stirred mixture of 1.0 *N* aqueous sodium hydroxide (108 ml.) and 1,4-butanedisulfinic acid (10.00 g.) in 100 ml. of water. A voluminous white precipitate of the bisthiosulfonate 1 resulted immediately upon mixing. The solution was stirred at room temperature for 15 min., and the product was collected by filtration and recrystallized from 500 ml. of water to give 18.0 g. (80%) of 1 as off-white leaflets, m.p. 135–137°. Recrystallizations from water gave 13.3 g. (59%) of 1 having a constant melting point of 137–138°; the infrared spectrum contained strong bands (KBr pellet) at 3300, 1635, 1545, 1310, 1290, 1275, 1120, 640, and 505 cm.$^{-1}$. The dihydrobromide salt corresponding to 1 has been reported.[3d]

Anal. Calcd. for $C_{12}H_{24}N_2O_6S_4$: C, 34.27; H, 5.75; N, 6.66; S, 30.49. Found: C, 34.29; H, 5.83; N, 6.66; S, 30.34.

To confirm the structure of 1, a solution of 0.59 g. of *p*-toluenethiol in absolute ethanol (10 ml.) was added, in one portion, to a solution of 1.00 g. of 1 in absolute ethanol (10 ml.). The mixture was warmed to 35–38° and stirred for 48 hr. Solvent was removed below 40° to minimize disproportionation of the expected unsymmetrical disulfide. The residue was triturated under dry ether and the suspended solid (0.45 g., m.p. 105–115°) was collected by filtration. This solid was triturated with cold chloroform, collected by filtration, and dried. The yield of colorless 1,4-butanedisulfinic acid was 0.35 g. (79%), m.p. 114–118°, identical (mixture melting point, infrared spectrum) with an authentic sample.[7] The ether was removed from the filtrate and the residue was recrystallized from 1:1 benzene–pentane to yield 0.65 g. (57%) of 2-(*p*-tolyldithio)-1-acetamidoethane, m.p. and m.m.p. 62–64°, identical in infrared spectrum with authentic[6] material.

B. By the Method of Kresze and Kort.[9]—A solution of 2-acetamidoethanethiol (2.38 g.)[11] and *n*-butyl nitrite (3.15 g., Eastman White Label, used as received) in 50 ml. of absolute ethanol was heated at reflux for 15 min. During this time the red color due to the intermediate thionitrite (**3**) reached a maximum. *n*-Butyl nitrite (3.15 g.) was added in one portion, followed by dropwise addition of a solution of 1,4-butanedisulfinic acid (1.86 g.)[7] in 50 ml. of absolute ethanol during 15 min. Reflux was continued until the red color disappeared and the evolution of nitric oxide had ceased (2.5 hr.). The reaction mixture was cooled and the ethanol was removed. The residue was suspended in 25 ml. of ether, and the crude product was separated by filtration, washed with three 10-ml. portions of water, and dried: yield of bisthiolsulfonate 1, 2.70 g. (64%), m.p. 135–137°. The material was identical (mixture melting point, infrared spectrum) with the 1 described under A.

C. Exploratory Experiments with the Kresze–Kort Synthesis.—Lower yields resulted from addition of the sulfinic acid in one portion (50%), addition of the sulfinic acid to the thionitrite without additional nitrite (0%), use of excess sulfinic acid with excess nitrite (26%), use of excess thiol with excess nitrite (45%), and elimination of the reflux period necessary for the formation of thionitrite (33%).

When a solution of *n*-butyl nitrite (2.12 g.) in anhydrous ether (10 ml.) was added to a stirred solution at 0° of N,N-di(*p*-tolylsulfonyl)hydroxylamine (2.30 g.)[9] and *p*-chlorothiophenol (1.95 g.) in 40 ml. of anhydrous ether, color developed as before but did not disappear after 3.5 hr. at 0°. The mixture was warmed to 25° and stirred for 1 hr., during which time the color disappeared with evolution of nitric oxide. Addition of pentane and filtration separated 1.80 g. (78%) of the unchanged disulfonylhydroxylamine, m.p. and m.m.p. 121–126° (infrared spectrum identical with that of starting material). The filtrate contained 1.70 g. (88%) of *p*-chlorophenyl disulfide (identical by infrared spectrum), m.p. and m.m.p. 70–72°. The same reaction without added nitrite resulted in the recovery of unchanged disulfonylhydroxylamine (93%) and *p*-chlorothiophenol (94%).

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[10] Melting points are corrected. Elemental analyses were by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Infrared spectra were obtained using a Perkin-Elmer Model 137B or a Beckman IR-10 spectrophotometer with the sample in Nujol mulls or potassium bromide pellets. Evaporation of solvents usually was done under reduced pressure using a rotary evaporator.

[11] R. Kuhn and G. Quadbeck, *Chem. Ber.*, **84**, 844 (1951).

Mercaptan–Sulfur Reaction. Alkyl Trisulfides

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Trisulfides (I) can be obtained in good yields from the amine-catalyzed reaction of most mercaptans with sulfur at room temperature. Although the oxidation

$$\underset{}{\mathrm{2RSH + 2S \longrightarrow}} \underset{\mathrm{I}}{\mathrm{RS_3R}} \mathrm{+ H_2S}$$

of mercaptans with sulfur is well known, the reaction has been of little preparative value, since a mixture of polysulfides is usually formed.[1]

The course of the reaction is strongly influenced by the steric requirements of the mercaptan. From the sterically hindered *t*-butyl mercaptan, very little trisulfide is formed. Instead, the tetrasulfide is obtained in 85–90% yield. All the other mercaptans investigated (isopropyl, *sec*-butyl, isobutyl, and *n*-butyl) formed trisulfides as the predominant product in 70–95% yields.

If the sulfur is not used in excess of the stoichiometric amount for trisulfide formation, the charge

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[1] For a review of polysulfide chemistry, see E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. III, Chemical Publishing Co., New York, N. Y., 1960, p 387.