sulted from the oxidation of a secondary alcohol. The bicarbonate washings were acidified with dilute sulfuric acid and extracted with ether. The ether extracts were washed with water, dried, and evaporated leaving a residue of 0.4 g. of solid. Recrystallization from hexane gave a mixture which melted from 116 to 137°. The mixture was separated into two components by adsorption on a column of aluminum oxide "nach Brockmann." A hexane solution of the mixture was put through the column. Examination with ultraviolet light showed two bands near top of the column. These were developed by successively putting the following solutions through the column: 50:50 hexane–ethyl ether and 50:50 hexane–acetone. The chromatogram developed into two areas which were cut apart and each extracted with 10% sodium carbonate solution. The extracts were acidified, taken up in ether, washed, etc. After recrystallizing from hexane, the acid extracted from the upper layer had a m.p. of 117.2–118°. Its analysis corresponded to 2-carboxycoumaran (VIII).

Anal. Calcd. for $C_9H_8O_3$: C, 65.85; H, 4.88; neut. equiv. wt., 164.15. Found: C, 66.05; H, 5.07; neut. equiv. wt., 172.

The recrystallized acid from the lower band, m.p. 157–159° proved to be salicylic acid.

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Organic Disulfides and Related Substances. VII. Reaction of Lead Tetraacetate with Alkyl Disulfides[1,2]

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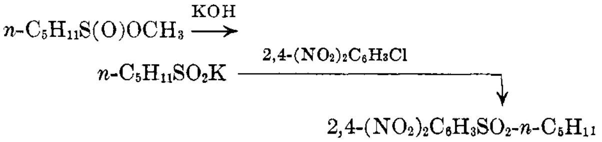
A preliminary report showed that reaction of various disulfides and thiols with lead tetraacetate in a mixture of chloroform and an alcohol afforded a promising synthesis of sulfinic esters, probably according to the equation[4]

$$\mathrm{RSSR + 3Pb(OAc)_4 + 4R'OH \longrightarrow 2RS(O)OR' + 3Pb(OAc)_2 + 4AcOH + 2AcOR'}$$

Preparation of methyl 1-pentanesulfinate was reported, with the reservation that the utility of the reaction for preparing alkanesulfinates from alkyl disulfides would be clear only after further work.[4] A subsequent report elaborated on the reaction for certain systems other than aliphatic ones.[2] This paper describes results with some alkyl disulfides.

Reaction of *n*-pentyl disulfide with lead tetraacetate in chloroform–methanol gave methyl 1-pentanesulfinate (I) in 35% yield. Evidence for the structure of I is afforded by: (1) elemental analysis; (2) molar refraction; (3) infrared absorption in the regions characteristic of sulfinates[2]; (3) saponification, followed by preparation of a known sulfone, according to the equation



$$n\text{-}\mathrm{C_5H_{11}S(O)OCH_3} \xrightarrow{\mathrm{KOH}} n\text{-}\mathrm{C_5H_{11}SO_2K} \xrightarrow{\mathrm{2,4\text{-}(NO_2)_2C_6H_3Cl}} \mathrm{2,4\text{-}(NO_2)_2C_6H_3SO_2}\text{-}n\text{-}\mathrm{C_5H_{11}}$$

and (4) consumption of potassium permanganate in accord with expectation and isolation of methyl 1-pentanesulfonate (53%).

Modification of the usual addition time (two hours) of lead tetraacetate from one to eleven hours gave virtually the same yield. In instances in which these latter products were analyzed however, results were unsatisfactory, thus strongly indicating that the reaction is not a smooth reliable means of preparing alkanesulfinates. Evidently, rapid concurrent reactions lead to by-products which cannot be separated practicably, even with an efficient fractionating column. Even so, close similarity of the infrared spectra and the refractive index showed that the principal component of the product was always I. The nature of some of the contaminants is suggested by early work in which but little methanol was used; acetoxylated species appeared to be present. When methanol was omitted altogether, reaction of some kind ensued but no pure product could be obtained; here again, a proper study of products was prevented by an inability to effect purification. Similar results were encountered with ethyl disulfide when it was used in the hope of obviating decomposition during distillation, which seemed a possible cause of the difficulty in obtaining a rigorously pure sulfinic ester. Methyl ethanesulfinate (II) was isolated in 31% yield. Analysis indicated presence of a small amount of impurity, but the identity of the bulk of the product was demonstrated by items (1)–(3) which were mentioned for I.

Methyl sulfite was obtained in 9% yield, along with the sulfinate II. Like II, the methyl sulfite could not be purified completely, but comparison of its infrared spectrum with that of authentic material (and saponification equivalent) left no doubt of its identity. That both methyl groups originated from methanol is suggested by isolation of *n*-butyl sulfite (in low yield) when *n*-butyl alcohol was substituted for methanol.

Efforts were made to improve the yield and purity of II. Since both the sulfinate and sulfite are

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[1] Research supported by the U. S. Army Research Office, Durham, North Carolina. Abstracted from portions of Ph.D. dissertations, Vanderbilt University, of J.M.L. (January, 1962), C.B.H. (January, 1960), and J.E.L. (August, 1957). Presented in part at Southeastern Regional Meetings of the American Chemical Society at Durham, North Carolina (November 14–16, 1957), and Birmingham, Alabama (November 3–5, 1960).

[2] Paper VI, L. Field, C. B. Hoelzel, and J. M. Locke, *J. Am. Chem. Soc.*, **84**, 847 (1962).

[3] DuPont Postgraduate Teaching Fellow, 1955–1957.

[4] L. Field, C. B. Hoelzel, J. M. Locke, and J. E. Lawson, *J. Am. Chem. Soc.*, **83**, 1256 (1961).

fairly soluble in water, the low yield could have been associated with the water wash conventionally used; omission of the wash necessitated a tedious removal of lead salts, however, and effected no improvement. In the hope of minimizing undesirable cleavages, the amounts of lead tetraacetate and of methanol were reduced, and lower temperatures were used, all to no avail. Indeed, use of only one half of the methanol required by the equation led to formation of about a dozen different substances, according to indications of vapor phase chromatography.

Benzyl disulfide, with lead tetraacetate in chloroform–methanol, gave methyl sulfite, benzaldehyde, and benzaldehyde dimethyl acetal. The disulfide was recovered in 24% yield, and no sulfinic ester was isolated. Evidently carbon-sulfur cleavage, once started, proceeded rapidly until the oxidant was consumed, thus leaving some of the original disulfide unattacked.

t-Butyl disulfide was used to determine whether poor results also would ensue with an alkyl disulfide which lacked methylenic hydrogen atoms on the carbon which adjoined the sulfur atoms. Results were unpromising.

It seems clear that oxidation of alkyl disulfides with lead tetraacetate is not promising as a reliable and general synthesis of *pure* alkyl alkanesulfinates. Important side reactions, such as carbon-sulfur cleavage, formation of alkyl sulfites, of aldehydes, or their derivatives, or of acetoxylated species, produce impurities which are difficult to separate from the desired alkanesulfinates by any means which would be practicable on a preparative scale.

Experimental[5]

Reactions of *n*-Pentyl Disulfide.—In the procedure which seems best, a solution of *n*-pentyl disulfide (15.48 g., 0.075 mole) in chloroform (140 ml.) and methanol (140 ml.) was heated to the reflux temperature and lead tetraacetate (0.3 mole) in chloroform (600 ml.) was added during 2 hr. The mixture then was heated under reflux for 12 hr. and cooled. Water (100 ml.) was added to decompose excess lead tetraacetate and the mixture was filtered through paper coated with Celite filter aid. The chloroform layer was washed with water until the washings gave a negative test for lead ions (no precipitate with aqueous sodium sulfide), dried (anhydrous magnesium sulfate), and concentrated to an oil using a rotating-flask evaporator. Distillation through a 47-cm. spinning-band column (Nester and Faust, Wilmington, Delaware) with potassium carbonate (5 g.)[7] in the pot gave 7.95 g. (35%) of methyl 1-pentanesulfinate (I) which had n^{25}_{D} 1.4450–1.4452; pure I had b.p. 39–40° (0.1 mm.), n^{25}_{D} 1.4450, d^{25}_{D} 0.9972, *M*D calcd. 40.44,[8] found 40.10; strong infrared absorption at *ca.* 982–1009 cm.$^{-1}$ and at *ca.* 1136 cm.$^{-1}$.

Anal. Calcd. for $C_6H_{14}O_2S$: C, 47.97; H, 9.39; S, 21.34. Found: C, 48.21; H, 9.51; S, 21.62.

The sapon. equiv. of I was 142, 158 (calcd. 150). A typical saponification product after neutralization and removal of solvent was heated with 2,4-dinitrochlorobenzene in ethanol for 1.5 hr. and gave, after three recrystallizations from ethanol, *n*-pentyl 2,4-dinitrophenyl sulfone in 99% yield, m.p. 85–85.5° (m.p. reported, 83°).[9] The ester I (1.5206 g.) in acetone consumed 1.0999 g. of potassium permanganate, which was added in water (5.5 g. in 250 ml.) containing magnesium sulfate heptahydrate (17.2 g.) until a pink color persisted; the consumption was 103% of expectation based upon the stoichiometry of the equation: $3RS(O)OCH_3 + 2KMnO_4 + H_2O \rightarrow 3RS(O)_2OCH_3 + 2KOH + 2MnO_2$. Precipitate was removed by filtration and both it and the filtrate were washed with chloroform. Distillation of the dried extract gave 0.89 g. (53%) of methyl 1-pentanesulfonate, n^{25}_{D} 1.4314–1.4316, which was identical in infrared spectrum with similarly obtained material (n^{25}_{D} 1.4320) which was analyzed.

Anal. Calcd. for $C_6H_{14}O_3S$: C, 43.35; H, 8.49. Found: C, 43.87; H, 8.38.

A number of variations in the general procedure were made in an effort to improve the yield. Variations in the time of addition of the lead tetraacetate from 1 to 11 hr. still gave yields only of about 25–38%; moreover, analyses of two products were unsatisfactory although the n^{25}_{D} was 1.4445–1.4451 and the infrared spectra were essentially identical with that of the I reported above.

In early work, before the function of methanol was recognized, products of several reactions obtained using only 4 *M* proportions of methanol or less were combined (3.1 g., n^{25}_{D} 1.4425) and oxidized with potassium permanganate. Salts obtained after neutralization, filtration, and evaporation were heated with phosphorus pentachloride. Treatment of the volatile product with aniline gave 128 mg. of acetanilide after extensive purification, m.p. and mixture m.p. 113.5–114.5°, showing that acetyl groups were present in such products (probably in the form of acetoxylated sulfur compounds). Strong infrared absorption at 1775 cm.$^{-1}$ and a positive hydroxamic acid test confirmed the probability of acetoxylated impurities in such products.

When methanol was omitted altogether, low conversion occurred to a product which it was thought might be a sulfenyl acetate (R—S—OAc) until such compounds where R is aryl were reported to be quite unstable.[10] Such material could not be obtained pure and, since the conversion was poor, was not studied extensively. It had an apple-like odor, n^{25}_{D} *ca.* 1.4349–1.4881, sapon. equiv. 162, and a positive hydroxamic acid test for esters. Material with b.p. 57° (1 mm.), n^{25}_{D} 1.4349, had C% 52.27, H% 9.51.

Reactions of Ethyl Disulfide (a).—A solution of lead tetraacetate (0.68 mole) in chloroform (1200 ml.) was added during 2 hr. to ethyl disulfide (18.34 g., 0.150 mole) in chloroform (280 ml.)–methanol (152 ml.) under reflux with stirring. After 10 hr. under reflux, the mixture was cooled and water added (200 ml.). After the usual filtration, washing, and drying, chloroform was removed using a Vigreux column (instead of an evaporator), and distillation then was continued using a 106-cm. spinning band column to give 17.59 g. of material, b.p. 38–63° (27 mm.). Redistillation (29 mm.) gave thirty-seven fractions in four groups: A (0.09 g.), b.p. 40–41°; B (3.05 g.), b.p. 41–44°, n^{25}_{D} 1.4135–1.4226; C (0.72 g.), b.p. 44–54°, n^{25}_{D} 1.4137–1.4200; D (9.95 g.), b.p. 57–62°, n^{25}_{D} 1.4261–1.4385.

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[5] Melting points are corrected and boiling points are uncorrected. Analyses were by Galbraith Microanalytical Laboratories, Knoxville, Tennessee, or by L. Haynes, Nashville, Tennessee. Infrared spectra were determined using neat liquids with a Model 137 Perkin-Elmer Infracord spectrophotometer. Lead tetraacetate was stored, assayed, etc., as described previously.[6]

[6] L. Field and J. E. Lawson, *J. Am. Chem. Soc.*, **80**, 838 (1958).

[7] Potassium carbonate appeared to retard autocatalytic decomposition to some extent. Thus a sample of methyl 1-pentanesulfinate (I) after 6.5 hr. at 140° in the presence of potassium carbonate changed in n^{25}_{D} from 1.4456 to 1.4476, but a control sample changed from n^{25}_{D} 1.4454 to 1.4493 in 4 hr.

[8] Calcd. using the value of 10.53 for the sulfinoxy group —S(O)O—.[2]

[9] R. W. Bost, J. O. Turner, and R. D. Norton, *J. Am. Chem. Soc.*, **54**, 1985 (1932).

[10] R. E. Putman and W. H. Sharkey, *ibid.*, **79**, 6526 (1957).

B was methyl sulfite (9%, assuming one mole of disulfide produces two of sulfite); sapon. equiv. 55 (calcd. 55), infrared spectrum identical with that of authentic material.[11] However, it contained considerable impurity (analysis, n^{25}_{D}, vile atypical odor) which could not be removed.

D was methyl ethanesulfinate (II, 31%). It had strong infrared absorption at 993–1000 cm.$^{-1}$ and 1139 cm.$^{-1}$. The sapon. equiv. after 1.5 hr. of heating was 117–119 (calcd. 108), and the sulfinate salt obtained after neutralization and evaporation gave, with 2,4-dinitrochlorobenzene, ethyl 2,4-dinitrophenyl sulfone in 80% yield, m.p. 156–157° (reported, 156°).[12] The sapon. equiv. cannot be relied upon; thus, heating for 0.8 hr. gave 198–200 and for 2.5 hr., 143–149. The best II afforded by distillation still was not pure; b.p. 62° (29 mm.), n^{25}_{D} 1.4383. Other material with n^{25}_{D} 1.4387 had d^{25}_{4} 1.093, M_D calcd. 26.58[8] found 26.00.

Anal. Calcd. for $C_3H_8O_2S$: C, 33.31; H, 7.46; S, 29.65. Found: C, 33.90; H, 7.71; S, 30.26.

(b) **Omission of Water Washing.**—The reaction was like that of (a), but after the 10 hr. of reflux, a slight excess of lead tetraacetate (starch-iodide test) was destroyed with a few drops of ethylene glycol. Chloroform was distilled and lead diacetate was removed occasionally by filtration after chilling. Since the yield was only 17%, this approach was unpromising.

(c) **With Reduction in Temperature and Proportion of Lead Tetraacetate.**—A solution of lead tetraacetate (0.25 mole) in chloroform (450 ml.) was added to ethyl disulfide (9.17 g., 0.075 mole) in chloroform (140 ml.)-methanol (76 ml.) during 4 hr. at 25–30°. After 6 hr., the solution was poured into water. The washed and dried chloroform layer upon distillation (47-cm. column) gave 1.13 g. (7%) of methyl sulfite, 9.35 g. of crude II (58%, n^{25}_{D} 1.4353–1.4479), and 1.2 g. of higher boiling material (infrared absorption at 1758 cm.$^{-1}$ suggested acetoxylated substances). Redistillation of II gave the usual yield, however: 4.99 g. (31%), b.p. 68° (39 mm.), n^{25}_{D} 1.4377–1.4397, infrared spectrum in agreement with that of II as reported above. After saponification (1 hr.; sapon. equiv. 113–116), ethyl 2,4-dinitrophenyl sulfone was obtained in 72% yield.

Essentially the same reaction at 0°, followed by 9 hr. of stirring at 25°, gave virtually the same result as at 25°.

(d) **With *n*-Butyl Alcohol.**—When the reaction of (c) at 25° was repeated with *n*-butyl alcohol instead of methanol, *n*-butyl sulfite resulted in 5% yield; infrared spectrum identical with that of commercial material. *n*-Butyl ethanesulfinate apparently resulted in *ca.* 9% yield (infrared spectrum) but could not be purified by distillation.

(e) **With Reduced Proportions of Methanol.**—A reaction like that of (c) at 25° but with only 13 ml. (0.32 mole) of methanol gave II in 23% yield, n^{25}_{D} 1.4370–1.4399, and nearly an equal weight of higher boiling material.

Reduction of the methanol to 0.15 mole, about one-half the theoretical amount, resulted after distillation in seventeen fractions which were combined into three groups. Vapor phase chromatography (162°, 10% Carbowax 400 on Fluoropak 80) indicated that one group consisted of II with at least five impurities, and another of two principal components with four impurities.

Reaction of Other Disulfides.—A solution of lead tetraacetate (0.25 mole) in chloroform (450 ml.) was added (2 hr.) to benzyl disulfide (18.91 g., 0.077 mole) in chloroform (140 ml.)-methanol (76 ml.) at 25°. After a stirring period of 22 hr. at 25°, isolation was effected as usual. Distillation of oil obtained (32.2 g.) gave four groups of fractions: (1) Methyl sulfite (identified by its infrared spectrum; 1.33 g., 8% conversion). (2) Benzaldehyde (1.96 g., 12% conversion assuming one mole of disulfide yields two of benzaldehyde); identity was established by the infrared spectrum and by conversion (66%) to the 2,4-dinitrophenylhydrazone, m.p. 241.5–243.5° (reported, 242–244.5°).[13] (3) Benzaldehyde dimethylacetal (n^{25}_{D} 1.4872–1.4915); infrared spectrum and n^{25}_{D} (1.4919), after purification, essentially identical with those of authentic material (n^{25}_{D} 1.4927); converted to benzoic acid and benzaldehyde 2,4-dinitrophenylhydrazone; yield 4.42 g., 19% conversion, assuming one mole of disulfide produces two of the acetal. (4) A mixture which could not be separated.

From undistilled residue, chromatography separated benzyl disulfide (24% recovery).

Essentially the procedure of (a) with *t*-butyl disulfide gave product which became black and evolved sulfur dioxide upon distillation. A distillate had strong infrared absorption at 1136 cm.$^{-1}$ and 990–1000 cm.$^{-1}$ but also had intense carbonyl absorption (1740 cm.$^{-1}$) and was not studied further.

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[11] H. H. Szmant and W. Emerson, *J. Am. Chem. Soc.*, **78**, 454 (1956).

[12] R. W. Bost, P. K. Starnes, and E. L. Wood, *ibid.*, **73**, 1968 (1951).

[13] D. Buckley, S. Dunstan, and H. B. Henbest, *J. Chem. Soc.*, 4901 (1957).

Reactions between Acids and Thiourea. II.[1] The Formation of Anilides from Acids and s-Diphenylthiourea[2]

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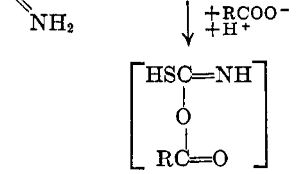
In a previous communication[1] the formation of amides by heating an equimolecular mixture of an acid and thiourea was described. A mechanism was suggested, based upon the intermediate formation of an addition product from the carboxylic acid and from the thiocyanic acid assumed to originate from the decomposition of thiourea (equation 1). This mechanism was proposed in analogy to that postulated by Rahman[1] for the formation of amides from acids and urea[3] in which the formation of an intermediate product from the carboxylic acid and from the isocyanic acid formed by thermal decomposition of urea was suggested. The difference between the two proposed mechanisms is that in the thermal decomposition of urea, isocyanic acid has been assumed to be the reactive tautomer, while in the decomposition of thiourea, thiocyanic acid is postulated to be the prevailing form in the equilibrium.



$$H_2NCSNH_2 \rightleftharpoons HSC(-NH_2)(=NH_2) \rightleftharpoons HSC{\equiv}N + NH_3 \xrightarrow{+RCOO^-,\ +H^+} \left[\begin{array}{c} HSC{=}NH \\ | \\ O \\ | \\ RC{=}O \end{array}\right] \quad (1)$$

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[1] Part I, A. Rahman, M. A. Medrano, and O. P. Mittal, *Rec. trav. chim.*, **79**, 188 (1960).

[2] Presented in the Latin-American Symposium on Synthetic Organic Chemistry, Bahía Blanca, September, 1961.

[3] A. Rahman, *Rec. trav. chim.*, **75**, 164 (1956).