TABLE III

ANALYSES OF ESTERS STUDIED

Compound		Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N	Dec., °C.	Rep. dec., °C.
Methylphthalamate	$C_9H_9NO_3$	60.33	5.06	7.82	60.20	5.12	7.90	98-102	98-102[a]
Methyl N-methylphthalamate	$C_{10}H_{11}NO_3$	62.17	5.74	7.25	62.17	5.90	7.50	112-114	
Methyl N-phenylphthalamate	$C_{15}H_{13}NO_3$	70.58	5.13	5.49	70.81	5.28	5.67	111-112	
Methyl N-(*p*-methylphenyl)-phthalamate	$C_{16}H_{15}NO_3$	71.36	5.61	5.20	71.09	5.63	5.22	145-146	
Methyl N-(*p*-nitrophenyl)-phthalamate	$C_{15}H_{12}N_2O_5$	60.00	4.03	9.33	60.06	4.14	9.24	158-159	
Methyl N-(*p*-cyanophenyl)-phthalamate	$C_{16}H_{12}N_2O_3$	68.56	4.32	10.00	68.81	4.48	9.87	157-158	

[a] See ref. 9.

from chloroform–hexane at room temperature, and gave acceptable elemental analyses (Table III).

Substituted N-phenylphthalimides were prepared by heating the corresponding substituted anilines in refluxing glacial acetic acid for half an hour with phthalic anhydride.[11] These imides have been reported previously and their melting points checked with those reported in the literature.

Ammonium phthalamate and ammonium N-methylphthalamate were prepared by adding phthalic anhydride to concentrated ammonia or 25% aqueous methylamine according to a method described by Chapman and Stephen.[12] The corresponding silver salts were prepared by dissolving the ammonium salts in water and adding an equivalent of concentrated silver nitrate solution.

Methyl N-methylphthalamate and methylphthalamate were prepared from their silver salts by methods described earlier.

All materials whose origin is not specified were obtained commercially in the highest purity available and purified when necessary, until their melting points corresponded to those previously reported.

Solutions.—Dioxane-water buffer was 40/60 v./v. The solution formally contained 0.0112 *M* Na_2HPO_4, 0.0128 *M* NaH_2PO_4, and enough sodium chloride to make the ionic strength 0.12. The apparent pH was 7.8. In all other buffers water was the only solvent and the ionic strength was 0.10 with the concentration of ionized acid less than 0.02 *M*.

Measurements of pH were made with a Cambridge Research Model pH meter.

Kinetics.—The rate of disappearance of reactant or the appearance of product was followed with a Beckman DU spectrophotometer by observing the change in optical density (D) with time in a thermostated cell. The following wave lengths were employed to study the various decompositions: phthalimide, N-methylphthalimide, N,N'-dimethylphthalamide, phthalamide, methyl phthalamate, and methyl N-methylphthalamate, 299 mμ; methyl N-phenylphthalamate, 275 mμ; methyl N-(*p*-methylphenyl)phthalamate, 281 mμ; methyl N-(*p*-nitrophenyl)phthalamate, 320 mμ; methyl N-(*p*-cyanophenyl)phthalamate, 294 mμ. For the esters plots of $-\ln(D - D_\infty)$ or $-\ln(D_\infty - D)$ were linear in time, and their slopes gave the pseudo first-order rate constants. In the case of the decomposition of phthalamide and N,N'-dimethylphthalamide, consecutive first-order reaction theory was used to obtain the rate of imide formation and decomposition. The formation of the imide intermediates was verified by the similarity between the rate constants assigned to the hydrolysis of the imides from the decomposition of the amides and to the rate constants observed from the separate hydrolyses of the imides.

Where the products were stable, they were identified by the similarity between their ultraviolet spectra and those of the expected products.

In the case of the methyl esters of the substituted phthalamic acids, the fact that the ultraviolet spectra of the esters approached that of the corresponding imide was taken as verification of the postulated reaction path. However, here the true infinity reading had to be calculated from the extinction coefficients of the imide and the concentration of the reactant, since in a time corresponding to ten half-lives of imide formation, the imide hydrolysis could not be neglected. Imide hydrolysis could be neglected during the first half-life of imide formation.

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[11] A. I. Vogel, "A Textbook of Practical Organic Chemistry," 3rd Ed., Longmans, London, 1959, p. 423.

[12] E. Chapman and H. Stephen, *J. Chem. Soc.*, **127**, 1791 (1925).

Derivatives of Sulfenic Acids. XLII. 3-Chloroformylpropanesulfenyl Chloride and 1,2-Thiazan-3-one[1]

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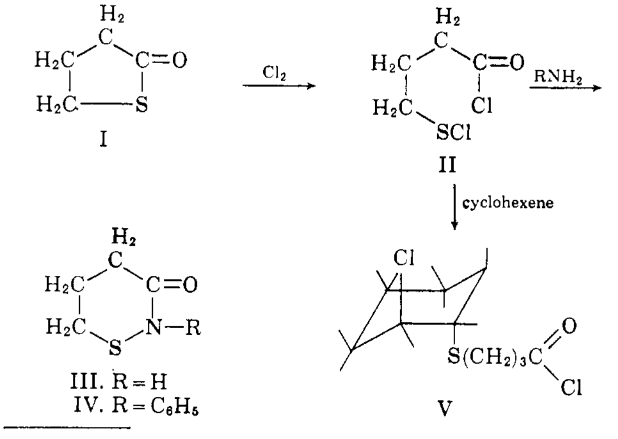
While aromatic sulfenyl chlorides have been studied in considerable detail,[2] less attention has been given to aliphatic examples, although the works of Douglass and co-workers, and of Brintzinger and others are notable.[3] Aliphatic polyfunctional sulfenyl chlorides have been mentioned in only a few cases, and even those recorded are very little known.[4]

We now report the synthesis of 3-chloroformylpropanesulfenyl chloride (II), by chlorinolysis of γ-thiobutyrolactone (I), and describe the properties of the former compound. For laboratory scale, the preparation of I is carried out conveniently by pyrolysis of γ-mercaptobutyric acid,[5] which is obtained, in turn, from γ-butyrolactone *via* the isothiuronium bromide.[6] Treatment of I with chlorine, or with sulfuryl chloride, in anhydrous chlorinated solvents at −20° leads



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[1] This study was supported by a grant from the Stauffer Chemical Co., and contract DA-04-495-Ord 901 with the Army Research Office (Durham).

[2] Earlier papers in this series; *cf.* also N. Kharasch, Chap. 32, "Organic Sulfur Compounds," Vol. 1, Pergamon Press, 1961, pp. 375–396.

[3] I. B. Douglass, *ibid.*, pp. 350–360.

[4] H. Brintzinger, M. Langheck, and H. Ellwanger, *Ber.*, **87**, 320 (1954); H. Brintzinger, H. Schmahl, and H. Witte, *ibid.*, **85**, 338 (1952); *cf.* also ref. 3.

[5] B. Holmberg and E. Schjanberg, *Arkiv Kemi, Mineral. Geol.*, **14A**, No. 7 (1940); *Chem. Abstr.*, **35**, 2113 (1941).

[6] L. Schotte, *Arkiv Kemi*, **8**, 457 (1955).

smoothly to high yields of 3-chloroformylpropanesulfenyl chloride (II), a fuming, orange liquid.

Compound II was characterized by its ready reaction with cyclohexene to form 2-chlorocyclohexyl 3-chloroformylpropyl sulfide (V), assumed to be the *trans* adduct. By reaction of anhydrous ammonia and II, a first example of a new type of heterocyclic system, 1,2-thiazan-3-one (III), was obtained as the principal product. The substitution of aniline for ammonia in this reaction leads to 2-phenyl-1,2-thiazane-3-one (IV). The course of reactions of II, followed by disappearance of the color associated with the –SCl function, with cyclohexene, ammonia, and aniline clearly show the greater reactivity of the sulfenyl chloride function in comparison with the acyl chloride group.

Earlier examples of the chlorinolyses of thiol esters include the first preparation of 2,4-dinitrobenzenesulfenyl chloride from 2,4-dinitrophenyl thiolbenzoate[7] and the studies of Douglass and Osborne,[8] leading to alkyl sulfur trichlorides from methyl and ethyl thiolesters. The formation of II from I is thus in agreement with the earlier examples.

The observed infrared absorption spectra of the compounds described are in agreement with the proposed structures. In particular, the absorption peak attributed to the acidic carbonyl group shifted to the anticipated frequency for the derivative in every case. Although it was not possible to obtain analytical results of highest accuracy for II, due to its instability, the values obtained are not far off and are in line with decompositions involving loss of chlorine.

Experimental

γ-Mercaptobutyric Acid.—A mixture of 430 g. of γ-butyrolactone (5.0 moles), 380 g. of thiourea (5.0 moles), and 1000 g. of hydrobromic acid (48%) was refluxed with stirring, for 6 hr. After cooling, 625 g. of sodium hydroxide in 625 ml. of water was added gradually with good stirring. (Caution! As the neutral point was approached, the mixture began to foam quite suddenly. Considerable care was required to prevent overflow.) After all the base had been added, the mixture was heated to reflux for 2 hr. with stirring, cooled, and extracted with ether. The ether was discarded and the aqueous layer was acidified to pH 1 with concentrated hydrochloric acid. After cooling again it was extracted several times with ether. The combined ether extracts were dried over calcium chloride. After removal of the ether on a water bath, under aspirator vacuum, the residual oil was distilled under reduced pressure. To avoid pyrolysis, care was taken to keep the pot temperature below 100°. B.p. 85–90° (2 mm.). Yield: 437 g. or 73%. The infrared spectrum shows a strong peak at *ca.* 1710 cm.^{-1}, typical of carboxylic acids, and a weak mercapto peak at *ca.* 2600 cm.^{-1}

3-Carboxypropyl 2,4-dinitrophenyl sulfide, a derivative, was prepared from γ-mercaptobutyric acid by reaction with an equivalent of 2,4-dinitrobenzenesulfenyl chloride; m.p. 128–129°, after recrystallizing from aqueous methanol.

Anal. Calcd. for $C_{10}H_9O_6N_2S_2$: S, 20.0. Found: S, 20.15.

Pyrolysis of γ-Mercaptobutyric Acid to γ-Thiobutyrolactone.—A 240-g. sample of γ-mercaptobutyric acid was heated slowly in a distilling apparatus, at atmospheric pressure. Removal of water was complete at 105°. The temperature then rose to 185°, at which point a second colorless liquid began to distil. The temperature stabilized at 197°, with no sign of any more water separating. At this point the residue was allowed to cool, and the distillate was separated from the water, dried over sodium sulfate, and returned to the pot. After drying the apparatus, distillation was continued under reduced pressure. B.p. 40–45° (1–2 mm.). Yield: 160 g. or 78%. The infrared spectrum showed a strong peak at *ca.* 1670 cm.^{-1}, indicative of the carbonyl group, but the peak at 2600 cm.^{-1} found in the mercapto acid had disappeared.

4-Mercaptobutyranilide, prepared as a derivative, was obtained by heating a sample of the thiolactone with aniline, giving a white solid, m.p. 88–89°, after recrystallization from benzene-ligroin mixture.

Anal. Calcd. for $C_{10}H_{13}NOS$: N, 7.17. Found: N, 7.32.

Chlorinolysis of γ-Thiobutyrolactone to 3-Chloroformylpropanesulfenyl Chloride.—To a solution of 20.4 g. (0.2 mole) of γ-thiobutyrolactone in 100 ml. of dry carbon tetrachloride, kept at −20° to −30°, was added, in small portions with good stirring, a solution of 14 g. (0.2 mole) of chlorine in 100 ml. of dry carbon tetrachloride, at the same temperature. The addition rate was regulated to prevent the exothermic reaction from causing the temperature to rise above −20°. A transient white precipitate, possibly the alkyl sulfur trichloride, formed with each addition of chlorine, but dissolved within several seconds into the stirred reaction mixture. An orange solution formed, becoming more colored as chlorine addition progressed. After chlorine addition was complete the reaction mixture was removed from the cooling bath and allowed to stand for a few minutes. The solvent was then removed under aspirator vacuum on a 40° water bath. A viscous orange liquid remained; crude yield: 35 g., theoretical, 34.4 g.

The crude material was immediately distilled under reduced pressure. B.p. 64–69° (1 mm.). Yield: 23.5 g. or 67%. This distillate was redistilled, b.p. 66–68° (1 mm.). Yield: 14.5 g. or 61% of the first distillate.

The product was an orange colored, oily liquid which fumed in air, and had a sharp odor like the aliphatic carboxyl chlorides. When stored at room temperature in a sealed bottle, considerable pressure (HCl) formed within a day. An analytical sample which stood 3 days at room temperature showed a loss of about 12% of its chlorine. To obtain a satisfactory elemental analysis, a freshly prepared and twice distilled sample was stored in Dry Ice and analyzed within 16 hr.

Anal. Calcd. for $C_4H_6Cl_2OS$: C, 27.76; H, 3.49; Cl, 40.98. Found: C, 28.39; H, 3.49; Cl, 40.06.

The infrared spectrum had a strong peak at 1790 cm.^{-1}, typical of acid chlorides; $n^{20}\text{D}$ 1.6174.

2-Chlorocyclohexyl 3-Chloroformylpropyl Sulfide.—To a solution of 6 g. of freshly prepared 3-chloroformylpropanesulfenyl chloride in 25 ml. of dry carbon tetrachloride at −10° was added a solution of 3 g. of cyclohexene in 25 ml. of dry carbon tetrachloride. This was added portionwise, with stirring, at a rate which did not let the exothermic reaction cause the temperature to rise above 0°. Almost all of the orange color of the sulfenyl chloride had disappeared within 1 min. after addition of the cyclohexene was complete. Removal of the solvent under reduced pressure left a yellow colored liquid; crude yield: 9 g. The product was distilled under reduced pressure. B.p. 136–137° (1 mm.). Yield: 6.5 g. or 78%. When redistilled, b.p. was 128–129° (1 mm.). The product had a trace of yellow color, which was probably due to impurities.

Anal. Calcd. for $C_{10}H_{16}Cl_2OS$: C, 46.63; H, 6.28; Cl, 27.39. Found: C, 47.24; H, 6.71; Cl, 27.92.

The infrared spectrum shows a sharp peak at 1790 cm.^{-1}, typical of acid chlorides; $n^{20}\text{D}$ 1.5276.

1,2-Thiazan-3-one.—To 20 g. of anhydrous ammonia in 300 ml. of dry carbon tetrachloride at −20° was added, in small portions with good stirring, a solution of 17 g. of 3-chloroformylpropanesulfenyl chloride[9] in 100 ml. of dry carbon tetrachloride, also at −20°. There was a strong exothermic reaction and a large amount of white solid formed. The mixture was allowed to stand overnight, then warmed to room temperature, and filtered. After drying, the solid weighed 19 g. This material was stirred with 200 ml. of water at room temperature to remove ammonium chloride, collected, and dried. Yield: 12 g., theoretical, 11.7 g. A sample was recrystallized from water four times to obtain a constant melting point; m.p. 160° (uncor.).

Anal. Calcd. for C_4H_7NOS: C, 41.00; H, 6.02; N, 11.96; S, 27.36. Found: C, 41.35; H, 6.08; N, 12.06; S, 27.15.

The infrared spectrum shows a sharp peak at 1650 cm.^{-1}, typical of amides. In the ultraviolet, a maximum was noted at 2510 Å.

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[7] K. Fries and W. Buchler, *Ann.*, **454**, 258 (1927).

[8] I. B. Douglass and C. E. Osborne, *J. Am. Chem. Soc.*, **75**, 4582 (1953).

[9] Crude 3-chloroformylpropanesulfenyl chloride appears to be as satisfactory as redistilled material for synthetic purposes. Comparison of the infrared spectra of the crude and redistilled material also indicated that the product was of high purity before distillation. Because of its rapid decomposition, however, II was prepared only as required for immediate use.

2-Phenyl-1,2-thiazan-3-one.—To a solution of 17.3 g. (0.1 mole) of 3-chloroformylpropanesulfenyl chloride in 100 ml. of dry carbon tetrachloride was added, dropwise with good stirring, at −20°, a solution of 9.1 g. (0.1 mole) of aniline and 16 g. (0.2 mole) of pyridine, in 100 ml. of dry carbon tetrachloride. A white precipitate formed during the addition, but when the mixture was allowed to warm to room temperature over about 2 hr., the precipitate became nearly black and tarlike. The solvent was decanted and the residue was dissolved in 200 ml. of hot methanol. After repeated treatment with decolorizing carbon a light brown solution was obtained. Addition of 75 ml. of water to the boiling solution induced crystallization. On chilling a tan precipitate was obtained; m.p. 158–161°. Yield: 11 g. After recrystallizing three times from 95% ethanol the product was obtained as white needles; m.p. 169–170°.

Anal. Calcd. for $C_{10}H_{11}OHS$: C, 62.15; H, 5.74; N, 7.26. Found: C, 62.43; H, 5.93; N, 7.02.

The infrared spectrum showed a peak at *ca.* 1650 cm.$^{-1}$, typical of the carbonyl group in amides.[10]

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(10) The infrared spectra of all liquids were made on the neat liquids pressed between sodium chloride plates. Solids were pressed in potassium bromide pellets.

Derivatives of Sulfenic Acids. XLIII. The Chlorinolysis of Certain Aryl Benzyl Sulfides as a Route to Sulfenyl Chlorides[1]

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The synthesis of 2,4-dinitrobenzenesulfenyl chloride (I) by catalytic chlorinolysis of bis(2,4-dinitrophenyl) disulfide has until now been the recommended method[2] for preparing this generally useful reagent.[3a,b] This procedure, however, has certain disadvantages which occasionally cause the synthesis to fail even in the hands of investigators who are thoroughly familiar with the preparation. The major difficulty has been in assuring the rigorously dry conditions or reagent purities needed for the effective action of the catalyst. The long reflux periods required at elevated temperatures and the very low solubility of bis(2,4-dinitrophenyl) disulfide in the solvents usually used, carbon tetrachloride or ethylene chloride, also present difficulties which led us to seek a more satisfactory synthesis of 2,4-dinitrobenzenesulfenyl chloride.

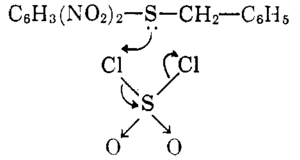
Other methods for preparing 2,4-dinitrobenzenesulfenyl chloride include the chlorinolysis of 2,4-dinitrophenyl thiolbenzoate,[4] 2,4-dinitrophenyl thiolacetate,[5] and the reaction of 2,4-dinitrobenzenethiol with chlorine.[6] The preparation of sulfenyl chlorides by chlorinolysis of benzyl aryl sulfides has been reported by Zincke,[7] and the formation, but not isolation of I by the cleavage of 2,4-dinitrophenyl benzyl sulfide (IV) was recorded.[8] In connection with a study of the scission of carbon–sulfur bonds, we have now developed the latter method into a convenient and fully reliable procedure for the preparation of 2,4-dinitrobenzenesulfenyl chloride.

2,4-Dinitrophenyl benzyl sulfide (IV) was prepared in 80–90% yields by reaction of 2,4-dinitrochlorobenzene with benzyl mercaptan, in the presence of pyridine. The resulting sulfide was readily cleaved to yield I, using either chlorine or sulfuryl chloride in chlorinated solvents. Because of the ease in handling, sulfuryl chloride was preferred for laboratory scale work. The reactions involved are shown.

$$2,4\text{-}(NO_2)_2C_6H_3Cl + C_6H_5CH_2SH + C_5H_5N \longrightarrow 2,4\text{-}(NO_2)_2C_6H_3SCH_2C_6H_5 + C_5H_5N{:}HCl$$

$$2,4\text{-}(NO_2)_2C_6H_3SCH_2C_6H_5 + SO_2Cl_2 \longrightarrow 2,4\text{-}(NO_2)_2C_6H_3SCl + C_6H_5CH_2Cl + SO_2$$

The rapid reaction of the sulfuryl chloride with the sulfide possibly involves a first step wherein positive chlorine, from sulfuryl chloride, transfers to the sulfur atom. The formation of benzyl chloride in near quantitative yield was observed, but the question of whether a cyclic mechanism, as inferred, actually occurs is not answered by the present work.



2,4-Dinitrobenzenesulfenyl bromide (III) was also obtained easily by the brominolysis of 2,4-dinitrophenyl benzyl sulfide. In the absence of catalysts, the reaction with bromine appears to be decidedly slower than that with chlorine, or sulfuryl chloride. However, in our experience with other methods for preparing this compound, the brominolysis of the benzyl sulfide is advantageous.

The reaction of bromine with 2,4-dinitrophenyl benzyl sulfide (IV), in cold chloroform, was reported by Fromm[9] to give an unidentified bromine-containing product, $C_{13}H_9BrN_2O_4S$. Our efforts to duplicate his work were unsuccessful, with no detectable amount of any such product being found. In all cases high yields of III were obtained. The sulfenyl bromide was identified by preparation of previously known derivatives and comparison of infrared spectra and melting points.

The synthesis of sulfenyl chlorides by chlorinolysis of aryl benzyl sulfides also succeeded in the case of 2-nitrobenzenesulfenyl chloride (V). This product was obtained in good quality and yield from 2-nitrophenyl benzyl sulfide. Although Zincke and Dahm[10] suggested this method for the synthesis of V they did not claim actually to have prepared the compound in this manner.

Efforts to obtain 4-nitrobenzenesulfenyl chloride by this method were not successful, however; in this case, bis(4-nitrophenyl) disulfide was obtained as the principal product. This difficulty in isolating 4-nitroben-

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(1) This study was supported by grants from the Stauffer Chemical Company and the Petroleum Research Fund of the American Chemical Society.

(2) D. D. Lawson and N. Kharasch, *J. Org. Chem.*, **24**, 858 (1958).

(3) (a) N. Kharasch, *J. Chem. Educ.*, **33**, 585 (1956); (b) R. B. Langford and D. D. Lawson, *ibid.*, **34**, 510 (1957).

(4) K. Fries and W. Buchler, *Ann.*, **454**, 258 (1927).

(5) N. Kharasch and R. B. Langford, unpublished work.

(6) G. W. Perold and H. L. F. Snyman, *J. Am. Chem. Soc.*, **73**, 2379 (1951).

(7) T. Zincke, *Ber.*, **44**, 769 (1911).

(8) R. H. Baker, R. M. Dodson, and B. Riegel, *J. Am. Chem. Soc.*, **68**, 2636 (1946).

(9) E. Fromm, *Ann.*, **396**, 89 (1913).

(10) T. Zincke and A. Dahm, *Ber.*, **45**, 3457 (1912).