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.

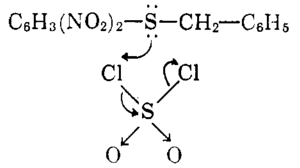
Other methods for preparing 2,4-dinitrobenzenesulfenyl chloride include the chlorinolysis of 2,4-dinitrophenyl thiolbenzoate,[4] 2,4-dinitrophenyl thiolacetate,[5] and the reaction of 2,4-dinitrobenzenethiol with chlorine.[6] The preparation of sulfenyl chlorides by chlorinolysis of benzyl aryl sulfides 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.

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

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

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).

zenesulfenyl chloride is consistent with the results reported for other methods of preparing this compound.[11] A good preparation for this compound is still required.

The synthesis of 2,4,6-trinitrobenzenesulfenyl chloride by the chlorinolysis of 2,4,6-trinitrophenyl benzyl sulfide was also attempted, but the sulfide was recovered unchanged after long heating with sulfuryl chloride. Ultraviolet irradiation of solutions of 2,4,6-trinitrophenyl benzyl sulfide also failed to initiate its cleavage by chlorine.

1-Anthraquinonesulfenyl chloride (II) was also prepared conveniently by the cleavage of 1-anthraquinonyl benzyl sulfide with sulfuryl chloride. This sulfenyl chloride was first reported by Fries,[12] who treated bis(1-anthraquinonyl) disulfide with chlorine.

The intermediate 1-anthraquinonyl benzyl sulfide was obtained in good yield by the reaction of sodium benzyl mercaptide with 1-chloroanthraquinone.[13] 1-Anthraquinonyl benzyl sulfide has been reported by Gatterman,[14] who prepared it from 1-mercaptoanthraquinone and a benzyl halide, and by Hoffman and Reid[15] who used 1-anthraquinonesulfonic acid and benzyl mercaptan.

The synthesis of aromatic sulfenyl chlorides by chlorinolysis of aryl benzyl sulfides is undoubtedly capable of considerable extension. However, substituent effects, steric factors, and the stability of the product under the reaction conditions will have to be taken into account in each case.

Experimental

2,4-Dinitrophenyl Benzyl Sulfide (IV).—A mixture of 202 g. (1.0 mole) of 2,4-dinitrochlorobenzene (m.p. 50–52°), 400 ml. of methanol, 124 g. (1.0 mole) of benzyl mercaptan, and 87 g. (1.1 moles) of pyridine was stirred and heated at reflux for 16 hr., cooled to 0°, washed with cooled methanol, and dried at 60–80°. Yield: 250 g. or 86%, m.p. 128–129° (lit. m.p. 128°).[16]

2,4-Dinitrobenzenesulfenyl Chloride (I).—To a suspension of 232 g. (0.8 mole) of dry IV (material prepared previously gave good results without further purification) in 400 ml. of dry ethylene chloride was added, at room temperature, 119 g. (0.88 mole) of sulfuryl chloride. A mildly exothermic reaction raised the temperature 10–15°, and the solid dissolved within 1–2 min. The clear yellow solution which resulted was concentrated to an oil by heating on a steam bath under aspirator vacuum. After cooling to room temperature, four volumes of dry petroleum ether were added, with vigorous hand stirring. The oil quickly crystallized and the yellow, crystalline solid was collected, washed well with petroleum ether, and dried at 60–80°. The yield was 160 g. or 86% of a product melting at 95–96° (lit.[2] m.p. 96°). This material gave no melting point depression with samples of I which were prepared by the chlorinolysis of bis(2,4-dinitrophenyl) disulfide. Infrared spectra of the two materials were also identical. Derivatives with methanol, m.p. 125–126° (lit.[3b] m.p. 125°), and with cyclohexene, m.p. 118–120° (lit.[3b] m.p. 117–118°), were prepared.

By concentrating the petroleum ether solution from the previous preparation, a lachrymatory colorless liquid was obtained, b.p. 80–82° (25 mm.). Infrared spectra of this liquid and a known sample of benzyl chloride (J. T. Baker, purified grade) were identical. Yield: 85 g. or 95.5%.

2,4-Dinitrobenzenesulfenyl Bromide (III).—To a suspension of 2,4-dinitrophenyl benzyl sulfide in 150 ml. of carbon tetrachloride was added, in portions, 16 g. of bromine. As there was no apparent reaction the mixture was heated, at first gently and then at reflux, on a steam bath. After about 15 min. the solid had disappeared and the bromine color had become much less intense. On standing overnight at room temperature a crystalline precipitate had formed. This was collected by filtration, washed with carbon tetrachloride and then petroleum ether, and dried in an 80° oven to constant weight (only a few minutes were required). The orange colored crystals melted at 103° (uncor.) (lit.[17] m.p. 104.5–105.5°). Yield: 15.5 g. On heating further the color faded to pale yellow and the melt resolidified at about 140°. This solid decomposed at 270–280°. (Note: bis(2,4-dinitrophenyl) disulfide decomposed at 280°.) The adduct of III to cyclohexene corresponded to the known product.[17]

Concentration of the mother liquor on a 40° water bath under aspirator vacuum gave a residual oil which, on stirring with four volumes of petroleum ether, gave a second crop of III. Yield: 8.5 g. Combined yield: 24 g. or 86%.

On concentrating and distilling the wash liquids under reduced pressure a colorless, lachrymatory liquid was obtained, b.p. 45–50° (2–4 mm.). Its infrared spectrum was identical with that recorded[18] for benzyl bromide. Yield: 13.5 g. or 79%.

Identity of III was verified by preparation of its derivatives with cyclohexene, m.p. 120° (uncor.) (lit.[19] m.p. 123°). A comparison of the infrared spectra of I and II showed them to be nearly identical. No peaks which could be attributed to a benzyl group were present.

2-Nitrophenyl Benzyl Sulfide.—To a sodium methoxide solution prepared from 7.7 g. of sodium and 200 ml. of absolute methanol was added 41.3 g. of benzyl mercaptan in 100 ml. of methanol. To this was added, portionwise with swirling, a solution of 52.5 g. of 2-nitrochlorobenzene. There was no exothermic or apparent reaction. After heating for 1 hr. the mixture was allowed to stand at room temperature overnight. Beautiful large yellow crystals formed, m.p. 81–82°, on recrystallization from methanol, m.p. 83.5–84.5° (uncor.) (lit.[20] m.p. 82–83°). Yield: 64 g. or 78%. A second crop was obtained by chilling the mother liquor to −20°. Yield: 6.2 g.

2-Nitrobenzenesulfenyl Chloride.—To a suspension of 12.2 g. of 2-nitrophenyl benzyl sulfide in 80 ml. of carbon tetrachloride was added a solution of 6.8 g. of sulfuryl chloride in 25 ml. of carbon tetrachloride. The temperature rose about 5° and all but a few crystals of the sulfide had dissolved within a minute. These also disappeared on warming to 45°. After concentrating an oil, by heating on a steam bath under aspirator vacuum, 25 ml. of carbon tetrachloride was added. To the resulting solution was added, with good stirring, 100 ml. of petroleum ether. The product precipitated as yellow needles. After chilling to −20° the precipitate was collected, petroleum ether washed, and dried. Yield: 7.8 g. or 82%. M.p. 73–74° (lit.[21] m.p. 73–74.5°). From the mother liquor and washing benzyl chloride was isolated and identified as before. Yield: 3.2 g. or 51%.

2,4,6-Trinitrophenyl Benzyl Sulfide.—To 24.7 g. of picryl chloride in 100 ml. of methanol was added 12.4 g. of benzyl mercaptan and 8.7 g. of pyridine. The mixture turned red when the pyridine was added, the temperature rose to 52°, and color faded to orange within 5 min. (Note: in one run the reaction did not begin on addition of the pyridine, but on warming to about 50° on steam bath it was initiated. From that point on the reaction, and yield, appeared to be normal.) A yellow precipitate began to form within 5–10 min. After standing 30 min. the mixture was chilled and the precipitate collected and washed with cold methanol. The product was dried at 80°. Yield: 30.5 g. or 90%; m.p. 109–110°; 112–113° after recrystallization from methanol.

Anal. Calcd. for $C_{13}H_9O_6S$: C, 46.56; H, 2.71; S, 9.55. Found: C, 46.71; H, 2.90; S, 9.22.

Preparation of 1-Anthraquinonyl Benzyl Sulfide.—To a solution of sodium methoxide, made by dissolving 2.74 g. of sodium in 300 ml. of absolute methanol was added 14.75 g. of benzyl mercaptan. After refluxing this mixture 1 hr., 28.6 g. of 1-chloroanthraquinone[13] was added. Heating was continued for

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[11] T. Zincke and S. Lenhart, *Ann.*, **400**, 1 (1913).

[12] K. Fries, *Ber.*, **45**, 2968 (1912).

[13] W. J. Scott and C. H. F. Allen, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 128.

[14] L. Gatterman, *Ann.*, **393**, 113 (1912).

[15] W. S. Hoffman and E. E. Reid, *J. Am. Chem. Soc.*, **45**, 1833 (1923).

[16] C. Willgerodt, *Ber.*, **18**, 331 (1885).

[17] N. Kharasch, C. M. Buess, and S. I. Strashun, *J. Am. Chem. Soc.*, **74**, 3422 (1952).

[18] Sadtler Standard Spectra, no. 2504, Sadtler Research Laboratories, Philadelphia, 1959.

[19] N. Kharasch, D. P. McQuarrie, and C. M. Buess, *J. Am. Chem. Soc.* **75**, 2658 (1953).

[20] A. Sieglitz and H. Koch, *Ber.*, **58**, 82 (1925).

[21] M. H. Hubacher, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 455.

15 hr. On cooling to room temperature the precipitate was collected and washed with three 100-ml. portions of hot methanol. The solid was then boiled with 500 ml. of methanol and filtered hot. Yield: 32 g. or 91%. M.p. 241–242°. Recrystallization from 6 l. of glacial acetic acid gave 31 g. of a product which had a melting point of 242°, in agreement with the literature value.

1-Anthraquinonesulfenyl Chloride.—To 21.75 g. of 1-anthraquinonyl benzyl sulfide in 800 ml. of dry benzene was added 8.9 g. of sulfuryl chloride. The mixture was warmed and shaken until a reaction occurred and a clear solution resulted. After filtering, the solution was allowed to cool to room temperature. The resulting crystalline precipitate was collected and the mother liquor was concentrated to obtain a second and a third crop. Yield: 17.9 g. or 99%. M.p. 220–223° (first crop), m.p. 216–220° (later crops) (lit. m.p. 224°). Recrystallization did not improve the melting point of the lower melting product.

Symmetrical Anhydrides of Hydroxy Acids[1]

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The symmetrical anhydrides of carboxylic acids containing unprotected hydroxyl functions apparently have not been prepared or described. This paper reports the synthesis and characterization of a series of these derivatives and establishes the symmetrical anhydrides of hydroxy acids as a known class of compounds.

In the course of amide syntheses using mixed carboxylic–carbonic anhydrides of the hydroxy fatty acids obtainable from castor oil,[2a,b] a series of experiments was performed to determine the reactivity of the secondary alcohol functions under the reaction conditions employed. The hydroxyl groups in these compounds were found to be unreactive at 0° toward ethyl chloroformate or toward the mixed carboxylic–carbonic anhydrides[3] formed from ethyl chloroformate and the triethylammonium salts of the carboxylic acids. Neither carbethoxylation nor esterification could be discounted *a priori* since both types of reaction are known to take place with secondary alcohols[4,5] under conditions suitable for the mixed anhydride reaction.

Since the alcohol functions in question were quite inert it seemed worth while to determine if the mixed anhydride method could be utilized for symmetrical anhydride formation with these hydroxy acids, as has been done in a few cases involving other carboxylic acids,[6,7] and if the products could be isolated despite the presence of both hydroxyl and anhydride functions in the same molecule.

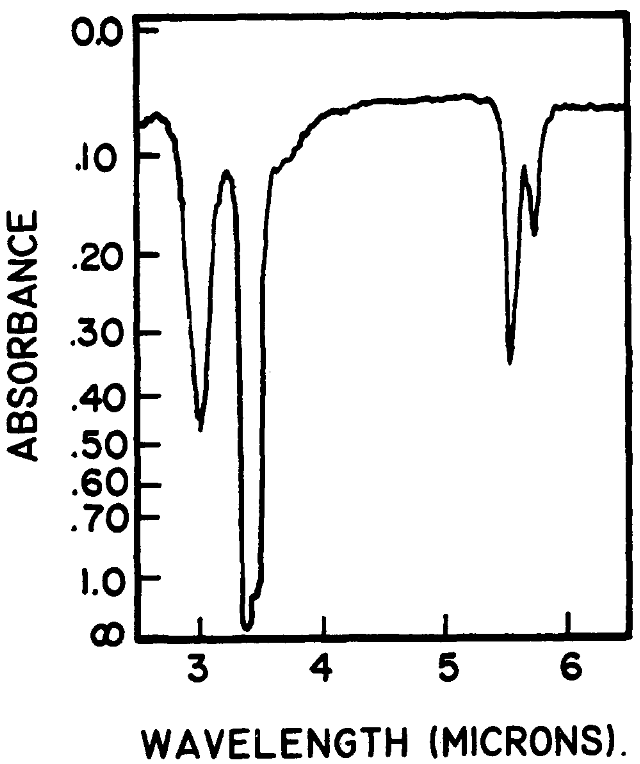
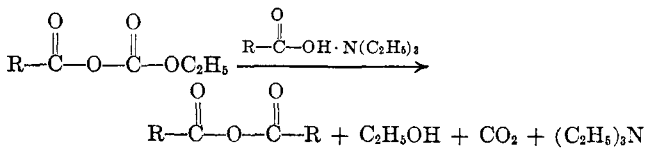


Fig. 1.—Infrared spectrum of 9,10-dihydroxyoctadecanoic anhydride: Nujol mull.

Reaction of the mixed carboxylic–carbonic anhydride of each hydroxy acid with one equivalent of the carboxylate anion of the same acid (present as the triethylammonium salt) in tetrahydrofuran at 0° gave a series of crystalline compounds, the symmetrical anhydrides, with melting points about 20° higher than those of the parent acids. These products (listed in Table I with yields and other pertinent data) have the expected infrared spectra for symmetrical hydroxy acid anhydrides. A typical example (Fig. 1) shows the hydroxyl band at 3.0 μ, and the paired carbonyl bands characteristic of carboxylic acid anhydrides.[8]

Though it has not been widely employed, this method of anhydride synthesis is a convenient, high yield procedure. Attack of the carboxylic acid anion on the carboxyl carbonyl of the mixed anhydride appears to be



$$R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow{R-\overset{O}{\overset{\|}{C}}-OH\cdot N(C_2H_5)_3} R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R + C_2H_5OH + CO_2 + (C_2H_5)_3N$$

rapid and straightforward. No detectable side reactions occurred in the cases reported here, and the yields were 95% or greater.

The hydroxy acid anhydrides are slowly decomposed at temperatures considerably above their melting points to give acidic material and polymeric esters. At ordinary temperatures, they apparently can be stored indefinitely. The 12-hydroxy-*cis*-9-octadecenoic symmetrical anhydride is best kept below 0°, but the other

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(1) Presented before the American Chemical Society Meeting in Miniature, Berkeley, Calif., December 17, 1962.

(2) (a) 12-Hydroxy-*cis*-9-octadecenoic, 12-hydroxy-*trans*-9-octadecenoic, 12-hydroxyoctadecanoic, 9,10-dihydroxyoctadecanoic, and 9,10,12-trihydroxyoctadecanoic acids; (b) T. H. Applewhite, Jane S. Nelson, and L. A. Goldblatt, *J. Am. Oil Chemists' Soc.*, **40**, 101 (1963).

(3) J. R. Vaughan, Jr., *J. Am. Chem. Soc.*, **73**, 3547 (1951); R. A. Boissonnas, *Helv. Chim. Acta*, **34**, 874 (1951); T. Wieland and H. Bernhard, *Ann. Chem.*, **572**, 190 (1951).

(4) N. F. Albertson, *Org. Reactions*, **12**, 157 (1962), has suggested such reactions as a possible cause of difficulties in mixed anhydride syntheses using hydroxy amino acids.

(5) L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., D. C. Heath and Co., Boston, Mass., 1955, p. 318, describes the carbethoxylation of alcohols with ethyl chloroformate.

(6) L. N. Akimova and N. I. Gavrilov, *Zh. Obshch. Khim.*, **23**, 417 (1953); *Chem. Abstr.*, **48**, 3904 (1954).

(7) E. Schipper and J. Nichols, *J. Am. Chem. Soc.* **80**, 5714 (1958).

(8) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., Methuen and Co. Ltd., London, 1958, p. 127.