The compounds prepared are listed in Table I with the exception of the methyl, ethyl and propyl derivatives.[3]

Experimental

Preparation of N,N′-Dialkyloxamides.—The N,N′-dialkyloxamides were in general readily prepared by the reaction of ethyl oxalate with two moles of the desired primary amine in ethanol or aqueous ethanol. The reaction was exothermic. The flask was then allowed to stand until it cooled and the contents generally formed a solid cake due to precipitation of the oxamide. With the lower amines it was necessary to stopper the flask during the initial reaction to prevent loss of the amine. The reaction mixture was then warmed gently just to the boiling point and diluted with an equal volume of boiling alcohol. On cooling to room temperature, the oxamides were isolated in average yields of 80% or better and in a relatively high state of purity. Without the dilution nearly quantitative yields of somewhat less pure materials were obtained.

In the case of the higher amines, beginning approximately at decyl, it was found that repeating the warming procedure twice or more before dilution was advisable in order to complete the reaction. All of the dialkyloxamides readily recrystallized from 95% ethanol in which they were only sparingly soluble at room temperature but in which they were readily soluble at the boiling point.

Preparation of N,N′-Dipentadecyloxamide.—Into 25 cc. of 95% ethanol were placed 1.46 g. (0.01 mole) of ethyl oxalate and 4.55 g. (0.02 mole) of *n*-pentadecylamine. The reaction mixture was warmed to the boiling point and permitted to cool to room temperature twice and, on the third warming, it was diluted with an equal volume of boiling ethanol. After standing at room temperature for one hour, the crystalline oxamide was filtered, sucked dry on the funnel, and finally dried at 100° in an air oven. 4.2 g. or 82% of the oxamide was obtained, m.p. 116–117°. Two recrystallizations from 95% ethanol gave the compound with m.p. 119.5–119.8°.

Anal. Calcd. for $C_{32}H_{64}N_2O_2$: N, 5.51. Found: N, 5.42.

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[3] Dermer and Hutcheson, *Proc. Okla. Acad. Sci.*, **23**, 60 (1943).

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Reactions of Trimethylene Sulfide with Chlorine and Bromine

BY JOHN M. STEWART AND CHARLES H. BURNSIDE

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A previous report[1] from this Laboratory has dealt with the cleavage of the three-membered sulfide ring in propylene sulfide by chlorine and bromine. Varying the amount of halogen used or the manner of addition of the reactants, or changing from anhydrous solutions to aqueous solutions led to the formation of a number of different types of products. It was of interest to see whether these reactions could be extended to the four-membered sulfide ring compound, trimethylene sulfide. The four-membered sulfide ring has been shown to be more stable to cleavage than the three-membered sulfide ring. For example, trimethylene sulfide formed a stable sulfone when treated with 30% hydrogen peroxide or potassium permanganate,[2,3] while propylene sulfide was cleaved by 30% hydrogen peroxide to yield 2-hydroxy-1-propanesulfonic acid and sulfuric acid.[1] Cleavage of the trimethylene sulfide ring has been reported to take place on treatment with methyl iodide[4] and ammonia.[2,5] Nitric and hydrochloric acids have been reported to cause polymerization.[3,5] Bost and Conn[3] found that trimethylene sulfide formed an addition compound with bromine which decomposes even at −15°. They did not identify the decomposition products.

Discussion

When chlorine was added to trimethylene sulfide in a chloroform solution in a ratio of one mole of chlorine to two moles of the sulfide, bis-(3-chloropropyl) disulfide (I) was formed as the principal product. Reaction of this compound with excess piperidine gave bis-(3-piperidinopropyl) disulfide (II) isolated as the dihydrochloride salt. Similarly, addition of bromine to a chloroform solution of trimethylene sulfide resulted in the formation of an addition compound which was, however, unstable to heat and could not be purified by distillation. Sulfur analysis on the crude product showed a rough agreement with that calculated for bis-(3-bromopropyl) disulfide, and reaction of this crude product with piperidine gave the same compound II previously obtained from I.

When the manner of addition of the reactants was reversed and trimethylene sulfide in a chloroform solution was added to a solution of chlorine in chloroform at temperatures of −40 to −60° with a one-to-one molecular ratio of reactants, one of the principal products was 3-chloro-1-propanesulfenyl chloride (III). This compound was stable enough to be purified by vacuum distillation and had the characteristic odor and deep color of the sulfenyl halides. It was necessary to add a small amount of hydroquinone as chlorination inhibitor in order to obtain even fair yields of III. Reaction of III with a molecular equivalent of trimethylene sulfide gave I. It appears likely, then, that III is an intermediate when chlorine is added to trimethylene sulfide in a one-to-two molecular ratio and that III then reacts further with the sulfide to form I. These results parallel those obtained in the study of the reactions of propylene sulfide with the same halogens[1] and a similar mechanism to that proposed in the discussion of that work may operate in this case.

The reaction of trimethylene sulfide and excess chlorine in a 75% acetic acid solution was found to give a good yield of a liquid product whose physical constants were in close agreement to those reported for 3-chloro-1-propanesulfonyl chloride by Helberger, *et al.*[6] The sulfonamide derivative of this material had a melting point identical to that reported for 3-chloro-1-propanesulfonamide by Kharasch, *et al.*[7]

The behavior of trimethylene sulfide and of propylene sulfide with chlorine and bromine under the same conditions is identical as to the types of products formed. The only differences appear to be a slower rate of reaction of the four-membered

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[1] J. M. Stewart and H. P. Cordts, THIS JOURNAL, **74**, 588 (1952).

[2] E. Griskevich-Trokhimovskii, *J. Russ. Phys. Chem. Soc.*, **48**, 880 (1916).

[3] R. W. Bost and M. W. Conn, *Ind. Eng. Chem.*, **25**, 526 (1933).

[4] G. M. Bennet and A. L. Hock, *J. Chem. Soc.*, 2496 (1927).

[5] D. S. Tarbell and D. P. Harnish, *Chem. Revs.*, **49**, 22 (1951).

[6] J. H. Helberger, G. Manecke and H. M. Fischer, *Ann.*, **562**, 23 (1949).

[7] M. S. Kharasch, E. M. May and F. R. Mayo, *J. Org. Chem.*, **3**, 187 (1938).

sulfide ring compound accompanied by a somewhat lower yield of the final products.

Experimental

Trimethylene sulfide was prepared by a modification of the procedure of Bennet and Hock[4] in an average yield of 45%, b.p. 90–93° (680–685 mm.), n^{20}D 1.5070.

Bis-(3-chloropropyl) Disulfide (I).—A solution of 5 g. (0.0676 mole) of trimethylene sulfide in 25 ml. of chloroform was stirred and externally cooled by a cold water-bath while 2.4 g. (0.0338 mole) of chlorine was passed in as a vapor beneath the surface of the solution. Argon was then bubbled through the mixture for a short time and the solvent was stripped. On distillation and redistillation there was obtained 3.6 g. (48.7%) of a colorless oil, b.p. 113–115° (1 mm.), n^{20}D 1.5450.

Anal.[8] Calcd. for $C_6H_{12}Cl_2S_2$: C, 32.87; H, 5.52; S, 29.25. Found: C, 33.03; H, 5.22; S, 29.57.

A solid derivative was prepared by refluxing the above product with excess piperidine in ethanol, followed by water-washing to remove unreacted piperidine and ethanol, drying the product, and then dissolving it in absolute ethanol and bubbling dry hydrogen chloride through the solution. Ether was added to precipitate the dihydrochloride of II. Recrystallization from an ethanol–ether mixture gave white crystals, melting with decomposition at 210–212°.

Anal. Calcd. for $C_{16}H_{34}Cl_2N_2S_2$: Cl, 18.21; S, 16.46. Found: Cl, 18.03; S, 16.30.

Bis-(3-bromopropyl) Disulfide.—The reaction between trimethylene sulfide and bromine was carried out as in the preparation of I described above except that a solution of bromine in chloroform was added dropwise. Attempts to distil the crude product resulted in decomposition. A sulfur analysis was made on the *crude* product.

Anal. Calcd. for $C_6H_{12}Br_2S_2$: S, 20.81. Found: S, 22.03.

Reaction of the crude product with piperidine followed by dry hydrogen chloride as described for I gave a dihydrochloride identical with that prepared from I, m.p. 210–212° with decomposition. A mixed melting point of the two dihydrochlorides showed no depression.

3-Chloro-1-propanesulfenyl Chloride (III).—A solution of 3.83 g. (0.054 mole) of chlorine in 10 ml. of chloroform to which a few crystals of hydroquinone had been added was chilled in a Dry Ice–acetone-bath. To this a solution of 4 g. (0.054 mole) of trimethylene sulfide in 40 ml. of chloroform, also precooled in a Dry Ice–acetone-bath, was added dropwise over a period of 10 minutes. The reaction mixture was allowed to warm to room temperature, argon was bubbled through it for a short time, and the solvent was stripped. Distillation gave about 3 ml. of orange liquid of extremely strong and irritating odor, b.p. 48–55° (3.5 mm.), and a mixture of higher-boiling lighter-colored liquids of no definite boiling range. The orange liquid was redistilled and yielded 2.3 g. (30%) of product, b.p. 51–53° (4 mm.), n^{20}D 1.5190. This compound III was not analyzed directly, but was immediately combined with trimethylene sulfide (1.2 g.) in chloroform to form the previously prepared bis-(3-chloropropyl) disulfide in a yield of 1.9 g. (54%), b.p. 112–115° (1 mm.), n^{20}D 1.5456. Reaction of this compound with piperidine followed by dry hydrogen chloride gave the same derivative, bis-(3-piperidinopropyl) disulfide dihydrochloride, previously prepared from I.

3-Chloro-1-propanesulfonyl Chloride.—To 80 ml. of a saturated, externally cooled solution of chlorine in 75% acetic acid was added dropwise with stirring 5.8 g. (0.0784 mole) of trimethylene sulfide, and chlorine was introduced below the surface at such a rate that an excess was always present. Addition of chlorine was continued for five minutes after all the sulfide had been added. Air was then blown through the reaction mixture to remove excess chlorine. The mixture was diluted with 400 ml. of water, extracted with ether and the combined extracts were dried over sodium sulfate. Distillation gave 10 g. (72%) of colorless liquid, b.p. 82–85° (1 mm.), n^{25}D 1.4890. The reported physical constants[6] for 3-chloro-1-propanesulfonyl chloride are b.p. 117–118° (15 mm.), n^{25}D 1.4900. The sulfonamide derivative was prepared and found to have a melting point of 62–63°. This is in agreement with the previously reported melting point of 63° for 3-chloro-1-propanesulfonamide.[7]

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[8] Microanalyses for carbon and hydrogen were performed by the Clark Microanalytical Laboratory, Urbana, Ill. Chlorine and sulfur analyses were performed by the authors.

Alkyl Esters of Isodehydroacetic Acid

BY RICHARD H. WILEY, NEWTON R. SMITH AND JOSEPH A. BAUER

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This note will serve to record the preparation and properties of some previously undescribed alkyl esters of isodehydroacetic acid. The esters were obtained by reaction of isodehydroacetic acid chloride with the alcohol. The acid chloride was prepared from the acid and thionyl chloride and the acid was obtained as previously described.[1] Since the acid chloride has not been previously characterized, details of its preparation and supporting analytical data are included. The methyl, *n*- and isopropyl, butyl, isoamyl and cetyl esters described in Table I have been obtained from the corresponding alcohols. The procedure used in their preparation is similar to that described for the *n*-propyl ester in the Experimental section. With redistilled, commercial 2-ethylhexyl alcohol a liquid product was obtained from which crystals separated on standing. This product did not give analytical values in accord with theory.

Since this procedure has not been previously used for the preparation of esters of isodehydroacetic acid, we have prepared the known methyl ester from the acid chloride and converted it to the known 3-bromo derivative. Both have melting points in agreement with those previously recorded for these compounds as prepared by other methods.

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Experimental[2]

Isodehydroacetic Acid Chloride.—Eighteen ml. (0.25 mole) of thionyl chloride was added to 25 g. (0.15 mole) of isodehydroacetic acid in a 125-ml. claisen flask. The mixture was heated under reflux for 10–20 minutes. The gaseous products and excess thionyl chloride were removed under vacuum. The residue was distilled to give 22–25.0 g. (79–90% of the theoretical amount) of isodehydroacetic acid chloride. b.p. 145–150° at 15 mm.; reported[3] b.p. 138–140° at 12 mm. The product solidifies on cooling, m.p. 52°.

Anal. Calcd. for $C_8H_7O_3Cl$: Cl, 19.00. Found: Cl, 18.88.

***n*-Propyl Isodehydroacetate.**—The acid chloride, prepared as above, was melted and portions (4.9–5.6 g.) were poured into 1 × 4 inch test-tubes. Such a sample of acid chloride (5.6 g., 0.03 mole) was melted under a reflux condenser on a water-bath and to it was added an excess (3.24 g., 0.054 mole) of dried *n*-propyl alcohol. The solution was refluxed 10–15 minutes and fractionated to give 5.0 g. (79% of the theoretical amount) of *n*-propyl isodehydroacetate, b.p. 166° at 8 mm.), $n^{23.5}$D 1.5093.

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[1] R. H. Wiley and N. R. Smith, THIS JOURNAL, 73, 3531 (1951).

[2] Analyses by Clark Microanalytical Laboratory and Micro-Tech Laboratory.

[3] H. M. Basel, *et al.*, U. S. Patent 2,364,304, December, 1944.