consisted of β-propionylglutarobislactone and some sodium propionate. The bislactone was extracted with chloroform, and on addition of ice-cold low boiling Skellysolve, the bislactone crystallized.

A total of 45.0 g. (0.27 mole) of bislactone was obtained, 80%. It was easily purified by dissolving it in a minimum of anhydrous acetone and adding a few drops of anhydrous ether. It crystallized as colorless needles, m.p. 62.0–62.5°.

Anal. Calcd. for $C_8H_{10}O_4$: C, 56.46; H, 5.92. Found: C, 56.78, 56.82; H, 6.18, 6.24.

The infrared absorption spectrum showed a single absorption maximum in the carbonyl region, at 5.60 μ, in nujol mull.

β-Propionylglutaric Acid.—To 150 cc. of water was added 19.3 g. of β-propionylglutarobislactone, and the solution was refluxed for 18 hours. Water was distilled *in vacuo*. The residual sirup solidified on trituration with low boiling Skellysolve, 19.0 g., m.p. 82–87°. Colorless crystals were obtained from anhydrous toluene, m.p. 87–88°.

Anal. Calcd. for $C_8H_{12}O_5$: C, 51.06; H, 6.43. Found: C, 51.20, 51.51; H, 6.37, 6.23.

Ethyl β-Propionylglutarate.—A mixture of 40.0 g. (0.21 mole) of β-propionylglutaric acid, 200 cc. of absolute ethanol, 100 cc. of benzene and 20 cc. of concentrated sulfuric acid was distilled through an 18″ electrically heated Vigreux column to which was attached an azeotropic distillation head. When only one liquid phase appeared in the condensed distillate and the temperature of the overhead vapor reached 68°, the distillation was stopped. Most of the remaining benzene and alcohol was distilled *in vacuo* and the residue neutralized with sodium bicarbonate. The mixture was extracted with ether and dried over anhydrous sodium sulfate. The ether was distilled and the crude ester fractionated. After a slight forerun there was obtained 41.0 g. (79%) of ethyl β-propionylglutarate, b.p. 121–122° (0.2 mm.).

Anal. Calcd. for $C_{12}H_{20}O_5$: C, 59.00; H, 8.25. Found: C, 59.61; H, 8.27.

The infrared spectrum of the liquid showed a somewhat broad absorption band at 5.81 μ. There was a small shoulder at 5.60 μ, probably indicating the presence of a trace of β-propionylglutarobislactone as impurity.

A higher boiling fraction in the above distillation consisted of 1.5 g. of β-propionylglutarobislactone, b.p. 137° (0.2 mm.), m.p. 62.0–62.5°.

Reduction of β-Propionylglutarobislactone with Sodium Borohydride.—To a solution of 53.0 g. (0.312 mole) of the bislactone in 250 cc. of water containing 11 g. of potassium hydroxide was added 12.0 g. of sodium borohydride in small portions during three hours. The reaction was carried out in an erlenmeyer flask with stirring by a magnetic stirrer. The mixture was stirred for an additional six hours, then allowed to stand 12 hours more. The mixture was acidified with 6 *N* hydrochloric acid, then extracted with ether in a continuous extraction apparatus for 48 hours. γ-Caprolactone-β-acetic acid crystallized in the ether flask, 50.0 g. (93%). Colorless crystals were obtained from toluene, m.p. 98.0–98.4°.

Anal. Calcd. for $C_8H_{12}O_4$: C, 55.80; H, 7.03. Found: C, 56.03, 55.78; H, 7.15, 7.15.

Reduction of Ethyl β-Propionylglutarate with Sodium Borohydride.—To a solution of 55.0 g. (0.23 mole) of ethyl β-propionylglutarate in 180 cc. of ethanol was slowly added a solution of 5.4 g. of sodium borohydride in 180 cc. of ethanol and 37 cc. of 2 *N* sodium hydroxide solution. The reaction mixture was mechanically stirred during the addition of the sodium borohydride solution and for 15 minutes thereafter. A white complex which had formed was dissolved by addition of 55 cc. of water, and the solution was stirred for three hours, with occasional warming on the steam-bath. The solution was filtered and the alcohol distilled *in vacuo*. The aqueous alkaline solution was acidified and thoroughly extracted with ether. The ether solution was dried over anhydrous sodium sulfate.

Fractionation of the organic layer gave 14.5 g. (31%) of ethyl γ-caprolactone-β-acetate, b.p. 133–136° (0.08 mm.), $n^{30}D$ 1.4525.

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 59.88; H, 8.06. Found: C, 59.77, 59.75; H, 8.33, 8.53.

The infrared spectrum of ethyl γ-caprolactone-β-acetate showed carbonyl absorption bands at 5.63 and 5.80 μ.

A second major fraction from the distillation consisted of 15.0 g. (38%) of γ-caprolactone-β-acetic acid, b.p. 175–180° (0.03–0.05 mm.), m.p. 98.0–98.4°.

Ethyl γ-Caprolactone-β-acetate. A. *Via* **the Acid Chloride.**—To 20.0 g. of γ-caprolactone-β-acetic acid in a flask fitted with a stirrer and reflux condenser was added dropwise 14.0 g. of thionyl chloride. The mixture was refluxed on the steam-bath for an additional hour. The unreacted thionyl chloride was removed by distillation, then 25 cc. of absolute ethanol was added and the mixture refluxed on the steam-bath for one hour. Ethanol was distilled *in vacuo*, and the residue was fractionated. There was obtained 22.0 g. (94%) of ethyl γ-caprolactone-β-acetate, b.p. 135° (0.09 mm.).

B. **Azeotropic Esterification.**—The reaction was carried out in the same manner as that described for ethyl β-propionylglutarate. From 50.0 g. of γ-caprolactone-β-acetic acid there was obtained 48.0 g. (83%) of the ester.

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N,N′-Dialkyloxamides[1]

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In the course of another investigation we have prepared the series of symmetrical N,N′-dialkyloxamides through octadecyl, with the exception of heptadecyl. The oxamides were obtained in excellent yields by the reaction of 2 moles of a primary amine with one mole of ethyl oxalate. In all cases the compounds formed readily at room temperature and separated in a high state of purity. Several members of the series had been previously prepared in isolated cases.

The derivatives may be formed in an aqueous alcohol medium in contrast to acid chlorides and aryl isocyanates which are not water stable. Ethyl oxalate, besides being readily available, is not readily affected by water. In addition, this reagent may be used to separate mixtures of primary, secondary and tertiary amines, as the last two are unreactive with ethyl oxalate under the conditions employed.

TABLE I

N,N′-DIALKYLOXAMIDES, R—NHC(=O)—C(=O)—NH—R

R	Formula	M.p., °C.	Nitrogen, % Calcd.	Found
Butyl	$C_{10}H_{20}N_2O_2$	153–154	13.99	14.08
Amyl	$C_{12}H_{24}N_2O_2$	141–142	12.27	11.82
Hexyl	$C_{14}H_{28}N_2O_2$	134–135	10.93	10.71
Heptyl	$C_{16}H_{32}N_2O_2$	132–132.5	9.85	9.45
Octyl	$C_{18}H_{36}N_2O_2$	124–125	8.97	8.93
Nonyl	$C_{20}H_{40}N_2O_2$	128–129	8.23	8.33
Decyl	$C_{22}H_{44}N_2O_2$	122–123	7.60	7.97
Hendecyl	$C_{24}H_{48}N_2O_2$	124–125	7.06	7.33
Dodecyl[a]	$C_{26}H_{52}N_2O_2$	123–124	6.59	6.67
Tridecyl	$C_{28}H_{56}N_2O_2$	120–121	6.19	6.29
Tetradecyl[b]	$C_{30}H_{60}N_2O_2$	117.5–119	5.82	5.98
Pentadecyl	$C_{32}H_{64}N_2O_2$	120	5.51	5.42
Hexadecyl[b]	$C_{34}H_{68}N_2O_2$	117–118	5.22	5.02
Octadecyl	$C_{38}H_{76}N_2O_2$	118–120	4.72	4.54

[a] Grunfeld, *Compt. rend.*, **194**, 893 (1932). [b] S. P. Massie, *Iowa State Coll. J. Sci.*, **21**, 41 (1946).

(1) Supported in part by a grant from the Geschickter Fund for Medical Research, Inc.

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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.

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

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Reactions of Trimethylene Sulfide with Chlorine and Bromine

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

(6) J. H. Helberger, G. Manecke and H. M. Fischer, *Ann.*, **561**, 23 (1949).

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