Sulfur Dichloride Diadducts of Unsaturated Fatty Derivatives.
II. Reactions with Nucleophiles

ROBERT A. GRIMM, T. L. Daniels Research Center,
Archer Daniels Midland Company, Bloomington, Minnesota

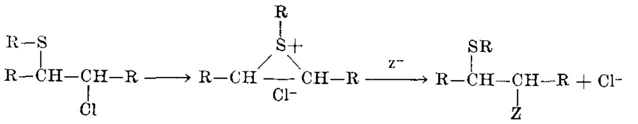
Abstract

The chloro groups in the bis-9(10)-[alkyl-10(9)-chlorooctadecanoate]-sulfides described previously (9) underwent reaction with water, alcohols, ammonia, amines, cyanides, cyanates, thiocyanates, and azides. The rates of these reactions were such that the chloro groups were completely replaced before significant attack on the ester group occurred. Without exception, the products of these reactions were the open-chain disubstituted-sulfide diesters, e.g. bis-9(10)-[ethyl-10(9)-aminooctadecanoate]-sulfide, and no evidence was found for cyclic, *e.g.* thiomorpholine, structures. The sulfur dichloride diadducts from *cis*-2-butene and *trans*-2-butene were also subjected to hydrolysis and ammonolysis and again, only the open-chain sulfides, e.g. bis-2-[3-aminobutyl]-sulfide, were formed. The diol-sulfides from *cis*-olefins differed from the diol-sulfides of *trans*-olefins in both physical and special properties. A similar difference was noted in the diamino-sulfides. Several of the fatty products were oxidized to the corresponding disubstituted sulfone diesters.

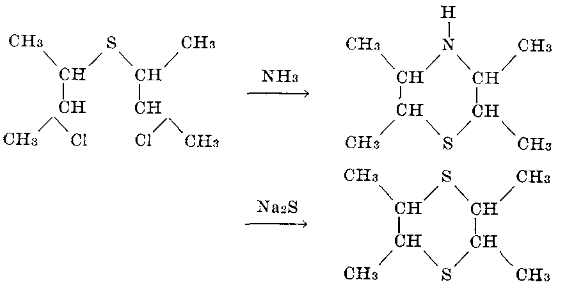
Introduction

THIS PAPER REPORTS the results of our studies on the reaction of sulfur dichloride-oleate diadducts with some nucleophiles. Intermolecular replacement reactions on fatty halides are usually rather sluggish reactions. Primary chlorides undergo replacement by nucleophiles but the primary bromides are the preferred reactants because of their greater reactivity (14). As chloro groups are moved more toward the center of a hydrocarbon chain, their replacement is known to become even more difficult because of steric effects (5,7). With fatty acids, substitution reactions still occur in the α (11), γ and δ positions of the chain (10) but when the chlorine atoms are located in the 9 or 10 positions (or both) substitution reactions are extremely slow. In a control experiment (19) dissolution of a sample of ethyl 9,10-dichlorostearate in ethanolic ammonia for 24 hr gives only slight amidolysis and the chloro groups remain essentially intact. More vigorous treatment with stronger bases usually results in extensive and complex dehydrohalogenation (12) and this treatment can be used as a means of increasing the unsaturation of certain fatty materials. We wanted to find an efficient and economical way to introduce reactive groups into the chain of a fatty molecule and thought that the sulfur dichloride-oleate diadducts (β,β′-dichlorosulfide diesters) might be suitable for this purpose.

The β,β′-dichlorosulfides or the sulfur mustards undergo replacement of the chlorine atoms more rapidly than the corresponding systems in which the sulfur atom has been replaced by a methylene group (2,8). The extent of the rate increase is governed by electronic and steric factors and is sensitive to other reaction variables such as solvent (1,17). Apparently



the electrons on the sulfur atom facilitate the removal of the β-chlorine atoms by forming an intermediate sulfonium chloride (8), a powerful alkylating agent. The sulfonium chloride then reacts with a nucleophile to give the β-substituted sulfide. On the basis of previous studies of β,β′-dichlorosulfides such as those from ethylene or 2-butene we anticipated cyclic products from the replacement of the chlorines with groups like hydroxyl or amino (3). Idson and Spoerri (13) reported, for example, that ammonolysis of bis-2-(3-chlorobutyl)-sulfide gives 2,3,5,6-tetramethylthiomorpholine and in earlier work Pope and Smith (18) apparently found that the same β,β′-dichlorosulfide, upon treatment with sodium sulfide, gives the 2,3,5,6-tetramethyl-1,4-dithiane. We studied the hydrolysis and ammonolysis of the sulfur dichloride diadducts



of *cis* and *trans*-2-butene because we expected that these compounds would be models of oleate and elaidate but would be easier to purify and work with.

Experimental

Bis-9(10)-[isopropyl-10(9)-hydroxyoctadecanoate]-sulfide

Into a 3-liter flask was placed saturated sodium bicarbonate solution (1000 ml) and bis-9(10)-[isopropyl-10(9)-chlorooctadecanoate]-sulfide (100 g, 0.133 mole) and the resulting mixture was stirred vigorously and heated to reflux for 16 hr. The mixture was allowed to cool and the oil layer was extracted into ether. The ether solution was then washed several times with water, dried over sodium sulfate and was concentrated under vacuum to give a pale yellow oil which was filtered through a medium porosity fritted funnel and stored in a bottle whereupon it began to crystallize after several hours. The yield was essentially quantitative.

Anal. Calc. for $C_{42}H_{82}O_6S$: C, 70.5; H, 11.5; S, 4.5; M.W. 715; Hydroxyl Value 157 mg/g; saponification value 157 mg/g; Acid Value 0.0.

Found: C, 70.6; H, 11.3; S, 4.8, M.W. 700; Hydroxyl Value 162 mg/g; saponification value 160 mg/g; Acid Value 0.0.

Subsequent preparations of this material usually resulted in crude products with hydroxyl values in the range 120–140 mg/g. Methyl esters, *n*-propyl esters and *n*-butyl esters of the β,β'-dichlorosulfide-diacid were used in these reactions and even for the methyl esters the acid value rarely rose above 0.2 mg/g. Also, for oleates containing less than about 8% *trans* double bond the related diol-sulfides were solids or crystalline slushes at room temperature. As the amount of *trans* double bond in the oleate increased the diol-sulfide tended to become more liquid. For example, Emery 233LL (8.3% *trans*) esters gave half-liquid, half-solid diols and Emery 3528R (12.2% *trans*) esters, ADM Monoenoic acid (35% *trans*) esters and elaidate esters gave diols that were liquid at room temperature. The solid diols could be recrystallized from hexane or acetone (−78C) to give white powders, mp (methyl ester) 40C–41C.

The physical state of these fatty materials was reflected by the diols from the *cis*-2-butene and *trans*-2-butene-sulfur dichloride adducts. The diol-sulfide from the *cis*-2-butene diadduct was a solid, mp 46C, while the diol-sulfide from the *trans*-2-butene diadduct was a liquid at room temperature.

The diol-sulfide-diesters produced by this route were oxidized by hydrogen peroxide in glacial acetic acid to give nearly colorless oils, the infrared spectra of which were compatible with diol-sulfone-diesters. Excess peracetic acid at 50C for 4–5 hr was usually sufficient to complete the oxidation.

Glycerol Derivative

A mixture of *bis*-9(10)-[isopropyl-10(9)-chlorooctadanoate]-sulfide (20 g, 0.027 mole) glycerol (88 g, 0.96 mole) *t*-butyl alcohol (200 ml) and sodium bicarbonate (4 g, 0.05 mole) was stirred magnetically and heated to 50C. After 48 hr the reaction mixture was filtered to remove sodium chloride and the *t*-butyl alcohol was removed under vacuum. As the *t*-butyl alcohol was removed an emulsion formed that separated into two layers, the upper layer contained the fatty derivative and the lower layer glycerol. The fatty layer was removed, suspended in ether and the ether extract was washed three times with water, dried over sodium sulfate and concentrated to give a nearly quantitative yield of a yellow oil. We were unable to purify this product further.

Anal. Calc. for $C_{48}H_{94}O_{10}S$: Hydroxyl Value 260 mg/g.
Found: Hydroxyl Value 210 mg/g.

Thin-layer chromatography (ethanol: ammonium hydroxide, 16:1 v/v) of this product showed that neither starting material nor glycerol remained in the product. This product as well as the oxidized material below had a very slippery feel.

Glycerol Derivative Oxidation

A sample of the glycerol derivative was oxidized by peracetic acid at 50C for 4 hr. The oxidized material was a pale yellow sirup at room temperature. Hydroxyl value, Calc. 251 mg/g; Found: 202 mg/g.

Cis-2-butene-1,4-diol Derivative

A mixture of bis-9(10)-[isopropyl-10(9)-chlorooctadecanoate]-sulfide (17 g, 0.023 mole), *cis*-2-butene-1,4-diol (53 g, 0.6 mole), dimethyl formamide (50 g) and sodium bicarbonate (2 g, 0.024 mole) was stirred magnetically and heated to 50C for 48 hr. The mixture was allowed to cool whereupon two phases formed. The upper phase was separated, dissolved in ether and the ether extracts were washed with water, dried over sodium sulfate and concentrated to yield a yellow oil. This oil could not be purified further. Hydroxyl Value, Calc.: 131 mg/g; Found: 112 mg/g. Absorption in the infrared at 3010 cm^{-1} indicated the presence of a double bond. This supposition was confirmed by the NMR spectrum which showed new absorptions at δ 4.07–4.15 ppm, 5.67 ppm and 3.3 ppm. *Cis*-2-butene-1,4-diol by comparison has absorptions at δ 4.10–4.25 ppm, 5.71 ppm and 4.69 ppm (hydroxyl).

Thin-layer chromatography showed this oil to be free of starting materials.

Bis-9(10)-[ethyl-10(9)-aminooctadecanoate]-sulfide

Bis-9(10)-[ethyl-10(9)-chlorooctadecanoate]-sufide (50 g, 0.069 mole) was added to ethanol (1000 ml) saturated with ammonia. The reaction vessel was tightly stoppered and the reaction mixture was stirred magnetically and kept at room temperature for 16 hr. The reaction mixture was then mixed with water (3000 ml) and the resulting oil was extracted into ether. The ether extract was washed once with 10% sodium hydroxide (50 ml) and then with water until the wash was neutral. The extract was then dried over sodium sulfate and concentrated to give a yellow oil (41.6 g, 88%).

Anal. Calc. for $C_{40}H_{80}N_2O_4S$: Total amine nitrogen 4.1; MW, 685
Found: Total amine nitrogen 3.5; MW, 644.

The product from the above reaction was dissolved in hexane (100 ml) and the solution was saturated with hydrogen chloride. The resulting oil was cooled, triturated with hexane and shaken next with 10% sodium hydroxide and ether. The ether extracts were washed with water until neutral, dried over sodium sulfate and concentrated to a yellow oil.

Anal. Calc. for $C_{40}H_{80}N_2O_4S$: C, 70.1; H, 11.7; N, 4.1; S, 4.7; MW, 685
Found: C, 69.9; H, 11.1; N, 4.1; S, 5.0; MW, 710.

Bis-9(10)-[ethyl-10(9)-cyanooctadecanoate]-sulfide

A mixture of acetonitrile (1500 ml), potassium cyanide (20 g, 0.31 mole) and bis-9(10)-[ethyl-10(9)-chlorooctadecanoate]-sulfide (92.5 g, 0.128 mole) was stirred magnetically and heated to 35C for 20 hours. The mixture was then filtered through a Buchner funnel and the filtrate concentrated under vacuum to give an orange oil (87.5 g, 97%). The crude product was dissolved in ether and washed several times with water to insure complete removal of cyanide ion. The ether solution was then dried and concentrated under vacuum to give an oil.

Anal. Calc. for $C_{42}H_{76}N_2O_4S$: N, 4.0; S, 4.6
Found: N, 3.4; S, 4.8

The corresponding isothiocyanate derivative was prepared by a similar route except that the solution was stirred for 30 hr. The product was a mixed thiocyanate-isothiocyanate but the thiocyanate was converted to the more stable isothiocyanate by heating the product at 80C for 2 hr.

Anal. Calc. for $C_{42}H_{76}N_2O_4S_3$: C, 65.6; H, 10.0; N, 3.7; S, 12.5
Found: C, 66.1; H, 10.1; N, 3.6; S, 10.8.

We are unable to explain the low sulfur analysis.

Bis-9(10)-[ethyl-10(9)-isocyanatooctadecanoate]-

sulfide was prepared as was the cyanide derivative except that the reaction was run for 10 days. The product was a yellow oil with a very faint odor.

Anal. Calc. for $C_{42}H_{76}N_2O_6S$: N, 3.8; S, 4.3; % NCO, 11.4
Found: N, 3.7; S, 4.5; % NCO, 10.3.

The reaction of sodium azide in ethanol with the dichlorosulfide-diester gave an adduct that appears to be bis-9(10)-[ethyl-10(9)-azidooctadecanoate]-sulfide. This stable yellow oil has very strong infrared absorptions at 2080 cm^{-1} due to azide.

Anal. Calc. for $C_{40}H_{76}N_6O_4S$: C, 65.3; H, 10.3; S, 4.4; N, 11.4
Found: C, 65.7; H, 10.3; S, 4.7; N, 10.5.

Thermal gravimetric analysis indicates that the molecule begins to decompose around 225C. At 250C a rather sudden weight loss occurs amounting to 7.4% (7.6% theoretical) of the sample weight.

Bis-2-(3-hydroxybutyl)-sulfide

A mixture of water (100 ml), sodium bicarbonate (20 g, 0.24 mole) and bis-2-(3-chlorobutyl)-sulfide (from *trans*-2-butene, 21.8 g, 0.10 mole) was stirred magnetically and heated under reflux for 24 hr. The reaction mixture was allowed to cool and the oil layer was separated from the aqueous phase. The aqueous phase was extracted with ether and this extract was mixed with the oily material. The combined solution was dried over sodium sulfate and was concentrated under vacuum to give an off-white oil (17.2 g, 95%). This material was distilled on a 24-plate spinning band column to give a water-white oil (14.9 g, 83%), bp 88C–90C at 0.25 mm. The product appears to be homogeneous by TLC (benzene-ether, 1:1, v/v) and was found to have a hydroxyl value of 622 (calculated: 630). The NMR spectrum showed absorptions at δ 2.2–2.7 ppm (two doublets, relative intensity 6.05), 5.5–6.5 ppm (8 peaks, relative intensity 1.00) and 7.0–8.3 ppm (8 peaks superimposed on broad absorptions, relative intensity 1.97).

Bis-2-(3-chlorobutyl)-sulfide from *cis*-2-butene was hydrolyzed by a similar procedure to give a white oil (10.9 g), bp 78–80C at 0.05 mm and a pale yellow oil (4.0 g), bp 130C at 0.05 mm. The overall yield of distilled products was 88%. The lower boiling white oil crystallized, mp 46C–48C, and had a hydroxyl value of 626 (calculated: 630). The NMR spectrum of this solid had absorptions at δ 2.3–2.9 ppm (two doublets, relative intensity 6.07), 5.1–6.1 ppm (5 peaks, relative intensity 0.96) and 7.0–8.3 ppm (broad singlet, 8.13 ppm relative intensity 1.0 and 4 or 5 peaks, relative intensity 1.0).

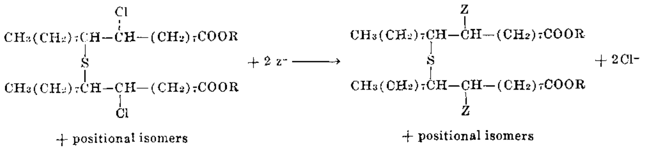
Bis-2-(3-aminobutyl)-sulfide

To a solution of ammonia (25.5 g, 1.5 moles) in ethanol (500 ml) was added bis-2-(3-chlorobutyl)-sulfide (from *cis*-2-butene, 21.8 g, 0.1 mole) and the vessel was stoppered and allowed to stand for 60 hr. The solution was then decanted from the ammonium chloride that had precipitated. The solution was partially concentrated on a rotary evaporator (200 ml) and a solution of ethanolic potassium hydroxide was added until further addition caused no precipitate formation. The precipitate was filtered and the filtrate concentrated under vacuum and distilled to give one fraction boiling at 63C–65C at 0.05 mm (11.6 g) and another boiling at 160C at 0.05 mm (2.5 g). The overall yield of distilled product was 79%. The low-boiling product appeared to be homogeneous by TLC (ethanol-ammonium hydroxide, 26:1, v/v) and contained 14.9% (calculated: 15.9%) of amine nitrogen. The NMR spectrum of the lower boiling product had absorptions at δ 1.0–1.4 ppm (5 peaks, apparently a singlet and two doublets, relative intensity 4.05) and 2.3–3.1 ppm (8 peaks, relative intensity 1.0). The higher-boiling (160C) product contained 12.2% (calculated for triamine: 12.5%) of amine nitrogen.

Bis-2-(3-chlorobutyl)-sulfide from *trans*-2-butene was treated similarly to give a 77% yield of an oil all of which distilled from 75–85C at 0.1 mm. TLC of the product (ethanol-ammonium hydroxide, 26:1, v/v) showed that two components were present. The product was distilled on a 24-plate spinning band column to give a water-white oil, bp 58C–59C at 0.05 mm, containing 14.9% (calculated 15.9%) of amine nitrogen. TLC of this material still showed the two spots in about the same relative proportions as before the distillation. The NMR spectrum of this material showed absorptions from δ 0.9–1.4 ppm (apparently three doublets and a singlet, relative intensity 4.0) and from 2.5–3.2 ppm (about 12–15 peaks, relative intensity 1.0).

Discussion

The experimental results show that we can replace the two chloro groups of the β,β′-dichlorosulfide diester without significantly disturbing the two ester groups. The hydrolysis reaction of the β,β′-dichlorosulfide dinitrile from oleylnitrile has been studied and a similar result, i.e., the chloro groups react before the nitrile groups, appears to hold.

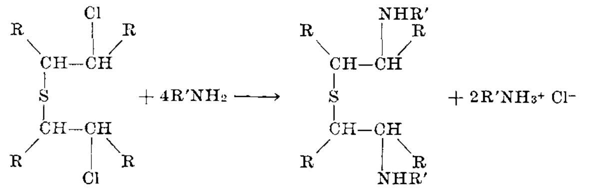


The hydrolysis products of these β,β′-dichlorosulfide diesters are *diol*-sulfide diesters. From the analytical data, neither saponification nor transesterification nor intramolecular cyclization occurs to any noticeable extent during the hydrolysis reaction. The conversion of the 2-butene sulfur dichloride diadducts to *diol*-sulfides also supports the view that intramolecular cyclization reactions are negligible in this system. The observation that the *diol*-sulfides from *cis*-2-butene and from oleates are higher melting than the corresponding diol-sulfides from *trans*-2-butene and elaidates suggests that the 2-butenes are suitable model compounds for 9-octadecenoates. The NMR spectra of the 2-butene based diol-sulfides are consistent with the stated structures. However, the fine structure of the tertiary proton absorptions is different from the *cis* versus the *trans*-2-butene based diols. This suggests that the different melting point behavior of the two diol-sulfides is probably due to different configurational isomers. We were unable to observe much fine structure in the NMR spectra of the fatty diol-sulfides.

The hydrolysis reaction is a two-phase reaction and vigorous stirring is required in order to minimize intermolecular condensation reactions, i.e. ether formation. The *cis*-2-butene diadduct undergoes hydrolysis to give mainly the dihydroxy-sulfide but 27% of a high boiling material, probably a dimer, is also formed. The *trans*-2-butene diadduct undergoes hydrolysis to give a diol-sulfide and no high-boiling product. Co-solvents were tried in an attempt to improve the solubility of the diadducts in the aqueous phase, but the desirability of co-solvents is questionable. When *t*-butyl alcohol was used it illustrated a difference between the butene diadducts and the fatty diadducts. The butent diadduct resulted in two low-boiling products and no high-boiling products. The hydroxyl value of these two (inseparable) products was only about 80% of the theoretical suggesting ether formation. With the fatty diadduct, the use of a co-solvent boosted the hydroxyl value in a typical run by about 10%. Thus the *t*-butyl alcohol appears to combine with the butene diadduct but not with the fatty diadduct probably because the steric requirements are greater. The glycerol and *cis*-2-butene-1,4-diol derivatives of the fatty ester-sulfur dichloride diadducts were prepared with co-solvents. In these systems co-solvents are desirable in order to form a more mobile mixture and to make filtration of the acid acceptor, sodium bicarbonate, faster.

Ammonolysis of the β,β′-dichlorosulfides from fatty esters and 2-butenes gives similar results in that the open-chain structures, e.g., bis-2-(3-aminobutyl)-sulfide, are the only products observed under our conditions. The *cis*-2-butene diadduct upon ammonolysis results mainly in a diamino-sulfide but 18% of a higher-boiling product, apparently a dimeric material, also forms. The *trans*-2-butene diadduct upon ammonolysis gives two products distilling at nearly the same temperature but the amine nitrogen determinations show that these materials are both the open-chain diamino-sulfides. In neither of these reactions is the thiomorpholine observed as a product. The results observed with the fatty ester-sulfur dichloride diadducts follow the results observed on the butene systems with the exception that, generally, the dimeric products do not seem to form. Solutions of ammonia in ethanol were used for most of the ammonolysis reactions, but in early ammonolysis work we used ammonium hydroxide as the ammonia source and the results were comparable if the two-phase system were vigorously mixed. Ammonia is more reactive than the water in these reactions since, for about the same reaction time, hydrolysis requires reflux temperatures (100C) while the ammonolysis occurs at room temperature. Most ammonolyses were run at room temperature. In one experiment the reaction mixture was heated to 70C in a stoppered flask and the reaction appeared complete in about one-half hour.

By following the procedure outlined for the ammonia derivative, we prepared a series of amino derivatives from the sulfur dichloride-oleate diadducts. They are listed in Table I. At least four moles of the amine are required for reaction with one mole of the diadduct according to the following stoichiometry. For the reactions of amines with the diadduct, we ordinarily used from 6–8 moles of amine per mole of the diadduct. All of the amines shown in the table are primary. The diadduct also reacts with secondary amines such as diethylamine but the reaction product contains only about half the theoretical amount of amine and we are unable to purify this sample farther. Diisopropylamine, a highly hindered secondary amine, does not react with the oleate-sulfur dichloride diadduct.

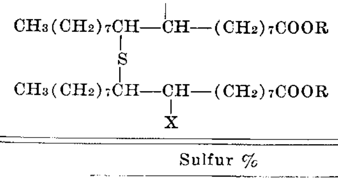


Fernelius and co-workers (6) have prepared and studied complexes formed between metal ions and low-molecular weight β,β′-diamino-sulfides such as bis-(2-aminoethyl)-sulfide. Some of our β,β′-diamino-sulfide systems also formed complexes with metal ions. Bis-2-(3-aminobutyl)-sulfide, upon admixture with aqueous copper nitrate, results in a homogeneous, intensely blue solution. The fatty β,β′-diamino-sulfide diester derivatives when shaken with aqueous solutions of copper salts form an intensely blue oil that is insoluble in water but soluble in hydrocarbon solvents. This complex can be quantitatively destroyed in a hydrocarbon solution of the complex by bubbling ammonia gas through it. A purple tetramine copper salt precipitates and the β,β′-diamino-sulfide diester is regenerated. Cobalt nitrate and uranyl acetate are also extracted from aqueous solutions by the β,β′-diamino-sulfide diesters. The ethylene-diamine derivative in a more polar solvent like ethyl acetate quantitatively extracts silver nitrate from aqueous solution. Again the complex is destroyed and the ligand regenerated by treatment with ammonia but we used aqueous ammonia here to prevent formation of the crystalline diamine silver nitrate which is explosive.

Other nucleophiles including cyanide, azide,

TABLE I

Structure of One of the Possible Isomers, with Assumption that the Sulfur Dichloride Can Add in Either Direction Across the Double Bond



$$\begin{array}{c} CH_3(CH_2)_7CH\text{—}\overset{X}{\overset{|}{C}}H\text{—}(CH_2)_7COOR \\ | \\ S \\ | \\ CH_3(CH_2)_7CH\text{—}\underset{X}{\underset{|}{C}}H\text{—}(CH_2)_7COOR \end{array}$$

Nucleophilic reagent	X	Sulfur %		Nitrogen %		Appearance
		Theory	Found	Theory	Found	
Ethylamine	CH_3CH_2NH-	4.20[b]	4.22	3.67	3.30	Yellow Oil
Aniline	—NH—	3.83	3.74	3.35	3.61	Orange Oil
2-Hydroxy-ethylamine	$HOCH_2CH_2NH$—	4.15	4.23	3.63	3.58	Yellow Oil
2-Amino-ethylamine	$H_2NCH_2CH_2NH$—	4.15	4.27	7.27	7.28	Yellow Oil[a]
Hydroxylamine	HONH—	4.31[b]	4.19	3.77	2.81	Yellow Oil

[a] Slowly polymerizes on standing. After several months at room temperature the sample is a dry crumbly solid.
[b] The isopropyl ester was used. Usually the derivatives were prepared from the corresponding ethyl esters.

cyanate, and thiocyanate are also found to react with the β,β′-dichlorosulfide diesters. The slower reaction rates are probably due to the low solubility of the salt in the solution containing the fatty material or vice versa. Otherwise, the preparation of these compounds was straightforward. The stability of the β,β′-diazido-sulfide diester compared to lower molecular weight azides (15) parallels stability relationships between fatty alkyl hydroperoxides and lower molecular weight hydroperoxides (4,16).

The toxicity of a few representative compounds were measured at the Wisconsin Alumni Research Foundation. The β,β′-diamino-sulfide diester, β,β′-dihydroxy-sulfide diester and the oxidized glycerol derivative are all found to be non-toxic and non-irritating according to the specifications of the Federal Hazardous Substances Labeling Act. In mice, the β,β′-diamino-sulfide diester causes a thickening of the skin at the site of application but the compound is not corrosive. The β,β′-dichlorosulfide diesters, etc., have not been tested but our routine handling of these chemicals in the laboratory resulted in no apparent health hazard. These fatty compounds, except for the β,β′-dichlorosulfide diester, appear to be stable indefinitely and have little or no odor. The sulfur atom in these fatty compounds does not contribute appreciably to the odor apparently because these materials have a relatively high molecular weight.

ACKNOWLEDGMENTS

Technical assistance by Arnold Bloomquist and David Horn; helpful discussions, R. Burrows and R. Slagel; elemental analyses, Huffman Labs, Denver, Colorado.

REFERENCES

1. Bohme, H., and K. Sell, Berichte *81*, 123 (1948).
2. Bordwell, F. G., and W. T. Branner, J. Am. Chem. Soc. *86*, 4645 (1964).
3. Burrows, L. A., and E. E. Reid, J. Am. Chem. Soc. *56*, 1720 (1934).
4. Coleman, J. F., H. B. Knight and D. Swern, JAOCS *32*, 135 (1955).
5. Eliel, E. E., in Newman, M. S., Steric Effects in Organic Chemistry, Wiley and Sons, New York, 1956, p. 73–79.
6. Gonick, E., W. C. Fernelius and B. E. Douglas, J. Am. Chem. Soc. *76*, 4671 (1954).
7. Gould, E. S., Mechanism and Structure in Organic Chemistry, Holt and Company, New York, 1959, p. 275, 323.
8. Ibid., p. 570–572.
9. Grimm, R. A., JAOCS, in press.
10. Guest, H. H., J. Am. Chem. Soc. *69*, 300 (1947).
11. Harwood, H. J., Chem. Rev. *62*, 104–106 (1962) and references therein.
12. Ibid., p. 132.
13. Idson, B., and P. E. Spoerri, J. Am. Chem. Soc. *76*, 2902 (1954).
14. Markley, K., "Fatty Acids," 2nd Ed., Vol. 2, Interscience Publishers, New York, 1961, p. 1119.
15. Noller, C. R., Chemistry of Organic Compounds, 3rd Ed., Saunders, Philadelphia, 1965, p. 291–292.
16. Ibid., p. 101.
17. Ogston, A. G., et al., Trans Faraday Soc. *44*, 45 (1948).
18. Pope, W. J. and J. L. B. Smith, J. Chem. Soc. 396–400 (1921).
19. Unpublished observation by author.

[Received May 18, 1967]