108–109°. Acetonitrile was Eastman White Label, redistilled, b.p. 79.5–81.5°.

Analytical Precedures.—The composition of the reaction mixtures was determined by vapor chromatography at 100° using a 4-ft. commercial Narcoil column with helium at 10 p.s.i. as the carrier. Components of the mixture were identified by comparison of retention times with those of authentic samples. Quantitative information, especially for the disappearance of chloroformate, was obtained by comparison of peak areas.

Reaction of *n*-Propyl Chloroformate and Silver Nitrate at 40°.—Into a 200-ml. three-necked flask which, in addition to a stirrer, was fitted with a gas addition tube and water-cooled reflux condenser connected to a gas train consisting of a Dry Ice trap, Ascarite tube, and mineral oil bubbler vented to atmosphere, were placed 22.60 g. (0.133 mole) of silver nitrate and 75 ml. of acetonitrile. The stirrer was started, and argon was passed through the system overnight. The bath was then brought to 40.0 ± 0.3°, and 15.0 ml. (0.133 mole) of *n*-propyl chloroformate was pipetted into the flask. Silver chloride began to precipitate almost at once.

Disappearance of the chloroformate and appearance of *n*-propyl nitrate paralleled the evolution of carbon dioxide. Two small by-product bands appeared in the vapor chromatogram; their intensities were unchanged by flash distillation of the total liquids. One by-product was identified as 1-propanol.

The reaction was stopped at 28 hr. Carbon dioxide evolution amounted to 4.91 g. (84%). The silver chloride weighed 16.94 g. (89%). Residual chloroformate amounted to about 9%.

Reaction of *n*-Propyl Chloroformate and Silver Nitrate at −10°.—This experiment was carried out in exactly the same manner as the previous experiment except that the reaction temperature was maintained at −10° ± 7° by a cooling bath. The reaction was terminated at 48.5 hr. by suction filtration in the cold and flash distillation of the filtrate in the cold at reduced pressure. Chromatography indicated *ca.* 10% *n*-propyl chloroformate consumed although only 5.3% carbon dioxide was evolved. Silver chloride amounted to 2.07 g. (10.9%). The same two by-products as observed at 40° were present in both the crude reaction mixture and the flash distillate. *n*-Propyl nitrate was the major product.

Catalyzed Reaction of *n*-Propyl Chloroformate and Silver Nitrate at 25°.—The apparatus and reactants were as in the previous two runs except that no temperature-controlling bath was used. Two milliliters of pyridine was added with stirring. Before the addition could be completed, an extremely vigorous evolution of gas commenced and a copious precipitation took place. The reaction mixture became quite warm and turned yellow. No measure of the rate of carbon dioxide evolution was possible. Although the reaction appeared to be over within 5 min., the mixture was stirred for 1 hr. before an aliquot was chromatographed. The chromatogram showed the complete absence of starting chloroformate, over 90% *n*-propyl nitrate, less than 10% 1-propanol, and none of the second by-product.

Catalyzed Reaction of *n*-Propyl Chloroformate and Silver Nitrate at −17°.—In the 200-ml. flask were placed 22.60 g. (0.133 mole) of silver nitrate, 50 ml. of acetonitrile, and 2.0 ml. of pyridine. The mixture was stirred to solution, cooled to −17°, and maintained at −17 ± 2° while 15.0 ml. (0.133 mole) of *n*-propyl chloroformate in 30 ml. of acetonitrile was added dropwise over a period of 1 hr. Two hr. after the addition had been completed, the Ascarite tube showed no weight gain. Vapor chromatography indicated that 60% of the starting chloroformate had disappeared. Strong *n*-propyl nitrate and carbon dioxide bands were also present in the chromatogram.

The reaction mixture was allowed to warm to room temperature overnight. The vapor chromatogram then showed (other than an acetonitrile band) a single peak corresponding to *n*-propyl nitrate. No other peaks were observable, even at high detector sensitivity.

Notes

Synthesis of Fatty Acid Diesters of the Sulfur Analogs of Batyl and Chimyl Alcohols

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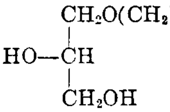
The α-glyceryl ethers are widely distributed materials in animal lipid systems with chimyl alcohol (I) and batyl alcohol (II) being the most important saturated members of the α-glyceryl ethers. In all natural sources the α-glyceryl ethers are found to be esterified with fatty acids.[2] Therefore we have prepared the sulfur analogs of these two important saturated alkoxy diglycerides, which correspond to the triglycerides tristearin and tripalmitin. These sulfur analogs of α-glyceryl ether esters are being used as part of our search of potential tuberculostatic agents and also in connection with their associated hemopoietic effects.[3,4] The results of this study will be reported elsewhere.



$$\begin{array}{l} \quad\;\; CH_2O(CH_2)_nCH_3 \\ \quad\;\; | \\ HO{-}CH \\ \quad\;\; | \\ \quad\;\; CH_2OH \end{array}$$

I. $n = 15$
II. $n = 17$

The diesters are synthesized by interaction of

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TABLE I

2,3-DIHYDROXYPROPYL ALKYL SULFIDE AND SULFONE DIESTERS

Compound	Yield, %	M.P.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
(2,3-Distearoylpropyl octadecane sulfide)	82	62–63	$C_{57}H_{112}SO_4$	76.61	76.59	12.63	12.67	3.59	3.61
(2,3-Distearoylpropyl octadecane sulfone)	85	82–83	$C_{57}H_{112}SO_6$	73.96	73.81	12.20	12.24	3.46	3.55
(2,3-Dipalmitoylpropyl hexadecane sulfide)	72	53–54	$C_{51}H_{100}SO_4$	75.68	75.60	12.45	12.63	3.96	4.04
(2,3-Dipalmitoylpropyl hexadecane sulfone)	75	75–76	$C_{51}H_{100}SO_6$	72.79	73.00	11.98	11.84	3.81	3.90

the fatty acid chlorides and the calculated quantity of the corresponding alcohol.[5]

EXPERIMENTAL

Starting materials. The palmitoyl and stearoyl chlorides were obtained from Matheson, Coleman and Bell, East Rutherford, N. J., and were used without any further purification. The thiochimyl alcohol (2,3-dihydroxypropylhexadecane sulfide) and thiobatyl alcohol (2,3-dihydroxypropyloctadecane sulfide) were prepared from alkyl halide and 3-mercapto-1,2-propanediol under basic conditions. The sulfones were obtained by oxidation of the sulfides with 30% hydrogen peroxide, using acetic acid as a solvent.[6] All melting points were obtained on a Fisher-Johns melting point apparatus and all compounds reported are racemic.

General procedures for preparation of 2,3-dihydroxypropyl alkyl sulfide and sulfone diesters. A mixture of 0.05 mole of appropriate alcohol and 0.11 mole of the fatty acid chloride was heated to 100° (hydrogen chloride being evolved) for 15 min. The hot oily reaction mixture was then flushed with dry nitrogen to remove the dissolved hydrogen chloride and 200 ml. of acetone was carefully added to the hot reaction mixture. The reaction mixture was immediately filtered and allowed to crystallize. The diester was then recrystallized two more times from acetone to yield material which was homogeneous when examined by the silicic acid thin layer chromatoplates method of Stahl.[7] The solvent system employed consisted of 90 parts by volume of petroleum ether (b.p. 30–60°), 10 parts anhydrous diethyl ether, and 1 part acetic acid. The plates were developed by spraying with 25% sulfuric acid and heating at 105° for 10 min. The infrared spectra of these sulfones showed a characteristic absorption band at 1300–1350 cm.$^{-1}$.

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Reaction of Triphenylsilyllithium with Anthracene

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The selective nucleophilicity of triphenylsilyllithium has been demonstrated by 1,4-addition of the silylmetallic compound to pyridine[1] and quinoline,[2] whereas alkyl- and aryllithium derivatives undergo predominantly 1,2-addition with these compounds.[3] However, triphenylsilyllithium underwent 9,10-addition to acridine,[4] as in the case of alkyl- and aryllithium reagents.[5] The silyllithium reagent has also been found to add to the olefinic linkage of 1,1-diphenylethylene and of triphenylethylene, but not to tetraphenylethylene and some other aliphatic and alicyclic olefins.[6] Since dimethylphenylmethylpotassium was found to add to anthracene and triphenylmethylpotassium showed little tendency to add,[7] it was of interest to extend our studies of the reaction of triphenylsilyllithium with polynuclear compounds[8] to anthracene.

Subsequently, it was found that triphenylsilyllithium added smoothly to anthracene to give 9,10-dihydro-10-lithio-9-(triphenylsilyl)anthracene (I), which upon hydrolysis gave 9,10-dihydro-9-(triphenylsilyl)anthracene (II).

The structure of II was confirmed by an independent synthesis involving monometalation of 9,10-dihydroanthracene and treatment of the organolithium compound with chlorotriphenylsilane. This reaction also gave a small amount of hexaphenyldisilane resulting from a halogen-metal interconversion reaction. The NMR spectrum of II showed a one proton peak at 5.56 τ, representing the proton at position 9 (benzhydryltriphenylsilane showed a single proton peak at 5.6 τ), and a quartet centered at 6.92 τ, typical of an AB system, for the two protons at position 10. The coupling constant for these two protons was 17 c.p.s. The non-equivalence of the two protons at the

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