

oxygenated compounds, whereas no such increase occurs by treatment with alumina (3). We have confirmed this finding with oils refined by the two processes, but do not believe that the small amounts of triene present in the bleached oils can account for their inferior quality. An investigation has been made of the nature of the materials removed from the alumina columns after treatment of an oil in an effort

to determine the mechanism of the improvement in quality. This work will be published at a later date.

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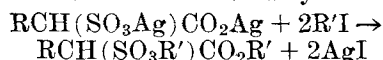
[Received April 21, 1961]

## Diesters and Diamides of $\alpha$ -Sulfopalmitic and $\alpha$ -Sulfostearic Acids<sup>1</sup>

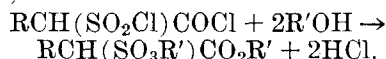
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$\alpha$ -Methylsulfopalmitic acid and dimethyl, diethyl, dibutyl, and isomeric methyl butyl esters of  $\alpha$ -sulfopalmitic and stearic acids were prepared and characterized. Reaction of a silver salt with an alkyl iodide was preferred to the acid chloride method found to involve competing side reactions. Diamides of  $\alpha$ -sulfopalmitic and stearic acids were prepared from ammonia, ethanolamine, and isopropanolamine by an acid chloride method. Infrared spectra of representative compounds are discussed.

THE DIESTERS of short chain  $\alpha$ -sulfo fatty acids have been made in the past either by reaction of an appropriate silver salt with an alkyl iodide,



or by reaction of the acid chloride with an alcohol or alkoxide,

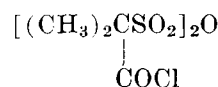


Diethyl sulfoacetate has been prepared from the silver salt and ethyl iodide by Franchimont (1) and Manzelius (3) who found this diester to resemble diethyl malonate in alkylation reactions. Dimethyl sulfoisobutyrate (4) has also been prepared from the silver salt; and dimethyl, diethyl, and dipropyl sulfoacetates from the acid chloride (6). Both methods should be versatile in the synthesis of either simple or mixed diesters.

We have found the silver salt method for diesters to be easier to carry out without complicating side reactions. Diesters of a single alcohol were conveniently prepared by the reaction shown above. Esters of the sulfonic acid group only can be prepared from the mono-silver salt  $\text{RCH}(\text{SO}_3\text{Ag})\text{CO}_2\text{H}$  and an alkyl iodide. Mixed diesters of  $\alpha$ -sulfostearic acid,  $\text{C}_{16}\text{H}_{33}\text{CH}(\text{SO}_3\text{R}'')\text{CO}_2\text{R}'$ , were formed from an alkyl iodide  $\text{R}'\text{I}$  and the silver salt of the monoester  $\text{C}_{16}\text{H}_{33}\text{CH}(\text{SO}_3\text{Ag})\text{CO}_2\text{R}'$ , prepared by direct esterification of  $\alpha$ -sulfostearic acid and conversion to the silver salt.

The acid chloride method for diesters or diamides is less easily adapted to higher fatty acids. Vieillefosse (6) succeeded in the preparation of  $\text{CH}_2(\text{SO}_2\text{Cl})\text{COCl}$  as a colorless liquid bp 90C/8 mm by heating sulfoacetic acid with excess of thionyl chloride in a sealed tube at 120C; and found the sulfonyl chloride group

to be less reactive than the carboxylic acid chloride. Moll van Charante (4) has reported that when one attempts to prepare the diacid chloride of  $\alpha$ -sulfoisobutyric acid at lower temperatures the anhydride



is the principal product. The sulfonic acid anhydride is considered to be more reactive than the sulfonyl chloride.

Thus it would seem that conversion to the diacid chloride requires higher temperatures than are usual for conversion of carboxylic acids, yet excessive heat must be avoided to prevent the type of decomposition reported by Hemilian (2):

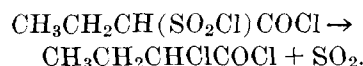


TABLE I  
Diesters of  $\alpha$ -Sulfo Acids

	Melting point	$n_D^{20}$	Saponification equivalent <sup>a</sup>		% S	
			Found	Theo.	Found	Theo.
Palmitic acid						
$\text{C}_{16}\text{H}_{33}\text{CH}(\text{SO}_2\text{CH}_3)\text{CO}_2\text{H}^b$	69.5°	1.4450	179	175	9.76	9.15
$\text{C}_{16}\text{H}_{33}\text{CH}(\text{SO}_2\text{CH}_3)\text{CO}_2\text{CH}_3$	60°	1.4376	183	182	8.77	8.80
$\text{C}_{16}\text{H}_{33}\text{CH}(\text{SO}_2\text{C}_2\text{H}_5)\text{CO}_2\text{C}_2\text{H}_5$	14°	1.4340	199	196	8.07	8.17
Stearic acid						
$\text{C}_{18}\text{H}_{35}\text{CH}(\text{SO}_2\text{CH}_3)\text{CO}_2\text{CH}_3$	65°	1.4389	201	196	8.05	8.17
$\text{C}_{18}\text{H}_{35}\text{CH}(\text{SO}_2\text{C}_2\text{H}_5)\text{CO}_2\text{C}_2\text{H}_5$	31°	1.4353	211	210	7.64	7.62
$\text{C}_{18}\text{H}_{35}\text{CH}(\text{SO}_2\text{C}_4\text{H}_9)\text{CO}_2\text{C}_4\text{H}_9^c$	27°	1.4372	249	238	6.97	6.73
$\text{C}_{18}\text{H}_{35}\text{CH}(\text{SO}_2\text{C}_4\text{H}_9)\text{CO}_2\text{CH}_3^d$	30.5°	1.4379	216	217	7.16	7.38
$\text{C}_{18}\text{H}_{35}\text{CH}(\text{SO}_2\text{C}_4\text{H}_9)\text{CO}_2\text{C}_4\text{H}_9^e$	29°	1.4380	217	217	7.54	7.38

<sup>a</sup> The reflux time was increased in order to approach complete hydrolysis of the carboxylic ester (5). A 0.3 g sample was refluxed 3 hr with excess of 0.2 N alcoholic KOH.

<sup>b,c,d,e</sup> Systematic names are as follows: 2-sulfohexadecanoic acid, 2-methyl ester; dibutyl 2-sulfooctadecanoate; methyl 2-sulfooctadecanoate, 2-butyl ester; butyl 2-sulfooctadecanoate, 2-methyl ester.

<sup>1</sup> Presented at the fall meeting, American Oil Chemists' Society, Chicago, October 30-November 1, 1961.

<sup>2</sup> Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

### Mono and Diesters

**Silver Salts.** Because of the low solubility of both mono- and disilver salts of  $\alpha$ -sulfo-palmitic and stearic acids, purified ammonium salts (7) were used as the starting material to prepare the silver salts without need for subsequent crystallization. The monosilver salt  $\text{RCH}(\text{SO}_3\text{Ag})\text{CO}_2\text{H}$  was prepared by adding one mole of silver nitrate to one mole of monoammonium salt in aqueous solution. To prepare the disilver salt the monoammonium salt was dissolved in water, converted to the diammonium salt with aqueous ammonia, and treated with the theoretical amount of silver nitrate. Silver  $\alpha$ -sulfo-palmitic acid, silver  $\alpha$ -sulfo-stearic acid, disilver  $\alpha$ -sulfo-palmitic, and disilver  $\alpha$ -sulfo-stearate were obtained as white solids, with no melting point below 200C.

Silver salts of carboxylic acid esters  $\text{RCH}(\text{SO}_3\text{Ag})\text{-CO}_2\text{R}'$  were obtained by esterification of the diacid (5) and treatment with alcoholic silver nitrate. Silver ethyl  $\alpha$ -sulfo-palmitate mp 59C, silver methyl  $\alpha$ -sulfo-stearate mp 95C, and silver butyl  $\alpha$ -sulfo-stearate mp 57C were obtained as white solids soluble in alcohol and easily soluble in water to give surface active solutions.

The following example illustrates the method for conversion of the appropriate silver salt to monoesters, simple diesters, and mixed diesters.

**Dimethyl  $\alpha$ -Sulfo-palmitate.** Disilver  $\alpha$ -sulfo-palmitate 22 g (0.04 mole), methyl iodide 14 g (0.10 mole) and 100 ml benzene were stirred 1.5 hr at reflux temperature. Yellow silver iodide was filtered from the benzene solution and washed with petroleum ether. Combined filtrate and washings were chilled to -20C to crystallize the product in 68% yield. Properties of the esters are recorded in Table I.

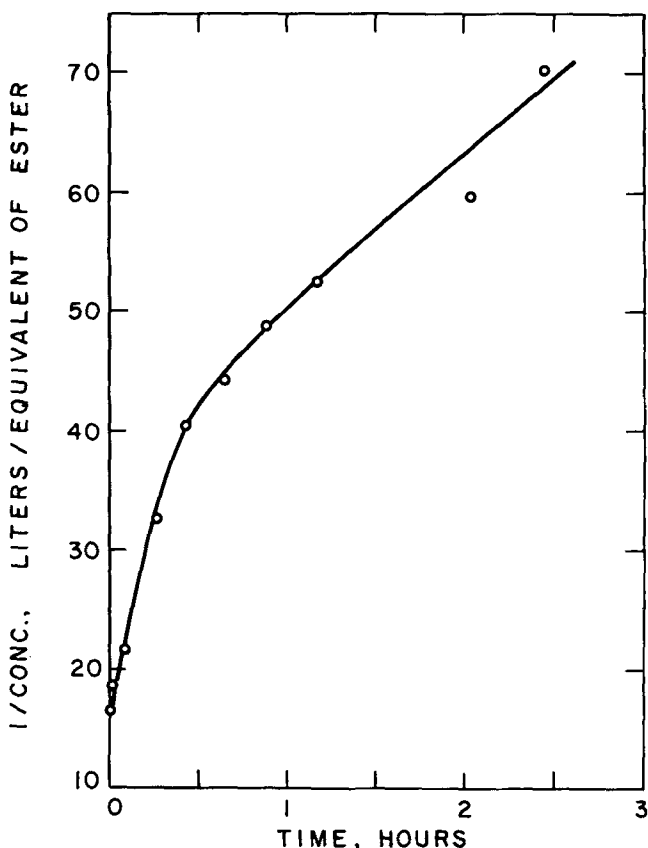


Fig. 1. Alkaline hydrolysis of diethyl  $\alpha$ -sulfo-stearate at 100C.

**Stability to Hydrolysis.** Figure 1 shows a plot of the reciprocal of ester concentration against time for the hydrolysis of 0.005 moles of diethyl  $\alpha$ -sulfo-stearate with 0.01 mole of sodium hydroxide in 150 ml of 30% ethanol at 100C. From the curve it appears two hydrolyses are proceeding at different rates, but because of the effect of one upon the other the second order constant could not be accurately determined. Toward the end of the hydrolysis the rate is about 0.3 liters per mole per min, the same order of reactivity as that reported for the carboxylic ester, sodium methyl  $\alpha$ -sulfo-palmitate [0.14 liters per mole per min (5)]. The rate in the early stage, evidently due to the sulfonic ester, is about 4 times as fast. Rate of hydrolysis of the sulfonic acid monoester,  $\alpha$ -methylsulfo-palmitic acid, was too rapid to be measured under the same conditions.

Dimethyl  $\alpha$ -sulfo-stearate stirred in boiling water without acid or alkaline catalyst hydrolyzed to the extent of one equivalent ester group in less than 1 hr.  $\alpha$ -Methylsulfo-palmitic acid showed about 50% hydrolysis as it went into solution when quickly heated to 75C; hydrolysis at 100C was too rapid for precise measurement.

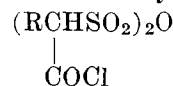
**Mixed Esters.** As shown in Table I methyl  $\alpha$ -butylsulfo-stearate and butyl  $\alpha$ -methylsulfo-stearate were found to have nearly the same melting point and refractive index. A mixture of the two isomers gave a melting point depression of about 5C. Nonidentity was further shown by hydrolysis. On heating with one equivalent of sodium hydroxide in 80% ethanol at 80C for 1 hr methyl  $\alpha$ -butylsulfo-stearate produced sodium methyl  $\alpha$ -sulfo-stearate, and butyl  $\alpha$ -methylsulfo-stearate produced sodium butyl  $\alpha$ -sulfo-stearate, identified by melting point and elemental analysis.

### Diacid Chlorides and Diamides

In a previous report (8) the formation was noted of diamide by-products when salts of carboxylic acid amides were prepared from acid chlorides of  $\alpha$ -sulfo-palmitic and stearic acids. Diacid chlorides would be attractive intermediates for diesters, diamides, and other derivatives and different methods for their formation were explored. Phosphorus pentachloride, phosphorus trichloride, phosphorus oxychloride, thionyl chloride, and oxalyl chloride were caused to react with diacids, monosodium and disodium salts, with and without a solvent in the presence or absence of an amine catalyst. Acid chloride reaction products were converted to the amide for ease of isolation and identification.

The best results were obtained by the reaction of thionyl chloride or phosphorus pentachloride with the diacid or disodium salt in chlorinated solvents, or with phosphorus oxychloride as a solvent at 80C. At a higher reaction temperature, 120C, the product contained chlorine instead of sulfur, probably having the structure  $\text{RCHClCONH}_2$  (2).

In each case the yield of diamide never exceeded 50%. This and the fact that amides cannot be formed in aqueous ammonia, showing a much greater reactivity than has been reported for sulfonyl chlorides, indicates that sulfonic acid anhydrides



rather than sulfonyl chlorides have been formed.

Dialkanolamides were produced in lower yields as

TABLE II  
 Diamides of  $\alpha$ -Sulfo Acids

	Melting point	% N		% S	
		Found	Theo.	Found	Theo.
Palmitic Acid $C_{14}H_{26}CHCONH_2$ SO <sub>2</sub> NH <sub>2</sub>	166.8– 167.5°	9.39	9.59	8.17	8.38
Stearic acid $C_{18}H_{34}CHCONH_2^a$ SO <sub>2</sub> NH <sub>2</sub>	166.4– 166.9°	8.81	8.85	7.59	7.73
$C_{18}H_{34}CHCONHC_2H_4OH^b$ SO <sub>2</sub> NHC <sub>2</sub> H <sub>4</sub> OH	160– 165°	6.94	7.12	6.29	6.22
$C_{18}H_{34}CHCONHC_2H_4OHCH_2CHOHCH_3^c$ SO <sub>2</sub> NHC <sub>2</sub> H <sub>4</sub> OHCH <sub>2</sub> CHOHCH <sub>3</sub>	84– 85.6°	6.59	6.70	5.57	5.85

<sup>a, b, c</sup> Systematic names are as follows: 2-sulfamoyloctadecanamide; N-2-hydroxyethyl-2-(2-hydroxyethylsulfamoyl)octadecanamide; N-2-hydroxypropyl-2-(2-hydroxypropyl)sulfamoyl]octadecanamide.

by-products in the production of monoamides using thionyl chloride (8). An example illustrates the method for simple amides.

*$\alpha$ -Amidosulfostearamide.* Disodium  $\alpha$ -sulfostearate 20 g (0.05 mole), phosphorus pentachloride 24 g (0.115 mole) and 58 ml of phosphorus oxychloride were stirred 3 hr on the steam bath. Phosphorus oxychloride was removed under vacuum and the residue was dissolved in chloroform. The vessel was surrounded by an ice bath and a slow stream of ammonia was introduced keeping the reaction temperature below 15°C. Chloroform was replaced by ethanol. The crude product crystallized therefrom at 0°C in a yield of 72% was found to consist of 58% monoamide and 42% diamide, based on neutral equivalent and sodium analysis.

Diamide was separated from the monoamide by extraction of a 50% aqueous alcohol solution with toluene. The toluene solution was re-extracted with aqueous alcohol and the diamide was crystallized therefrom in 35% yield. Melting points and analyses of the diamides are shown in Table II.

### Solubility

The diesters of Table I are soluble in alcohol, petroleum ether, and benzene but insoluble in water.  $\alpha$ -Methylsulfopalmitic acid became water soluble only after the ester group had been hydrolyzed.

The diamides of Table II are insoluble in petroleum ether and, except for the diethanolamide of  $\alpha$ -sulfostearic acid which forms a clear 1% gel in hot water, all the diamides are water insoluble.

The simple diamides have a solubility of less than 1% in 95% ethanol at room temperature, and less than 0.1% in hot chloroform or benzene.

Because of the acidic sulfonamide group the simple diamides are dispersible in hot aqueous sodium hydroxide. Both dialkanolamides are soluble in excess alkali at room temperature and soluble in equimolar amounts of hot NaOH.

Both dialkanolamides can form 1% solutions in cold chloroform, cold ethanol, and hot benzene. The diisopropanolamide of  $\alpha$ -sulfostearic acid forms a stable 1% solution in benzene at room temperature.

### Infrared Spectra

The infrared spectra of dimethyl  $\alpha$ -sulfopalmitate,  $\alpha$ -methylsulfopalmitic acid, and  $\alpha$ -amidosulfopalmitamide were obtained from 4000–650  $cm^{-1}$  with a Perkin-Elmer Model 21 instrument equipped with rock salt

optics. The spectrum of each compound was obtained by two different techniques: (a) as a Nujol mull and (b) as a thin film melted and resolidified between two rock salt plates.

*Dimethyl  $\alpha$ -Sulfopalmitate.* The Nujol spectrum showed strong bands close to 2900, 1740, 1340, 1165, 1000, 785, and 720  $cm^{-1}$ . Weak OH absorption close to 3200  $cm^{-1}$  was also observed. The spectrum was very similar to that of an authentic sample of dimethyl  $\omega$ -sulfoundecanoate, confirming the presence of  $-COOCH_3$  and  $-SO_3CH_3$  groups. When the sample was melted between NaCl windows and a spectrum of the resolidified melt obtained, significant changes had taken place: while most of the spectrum remained qualitatively similar to that of the Nujol specimen, new moderately strong bands appeared close to 3060, 3200, and 1040  $cm^{-1}$ . The bands in the 3000  $cm^{-1}$  region are most probably due to strongly hydrogen bonded OH groups, and the 1000  $cm^{-1}$  region band could also be associated with COH groups. In contrast the dimethyl  $\omega$ -sulfoundecanoate does not show this behavior. Accordingly it appears that melting and rapid cooling resulted in a rearrangement producing OH groups. If temperatures prevailing during the melting process result in a shift toward the enol form, which in turn does not revert to the keto form during relatively rapid cooling, these results could be explained. In any case attention is called to the fact that the two techniques do not produce identical spectra.

*$\alpha$ -Methylsulfopalmitic Acid.* The Nujol spectrum is qualitatively similar to that of dimethyl  $\alpha$ -sulfopalmitate, but the C = O absorption has shifted from about 1740 to 1725  $cm^{-1}$ , as expected by conversion of a  $-COOCH_3$  group to a  $-COOH$  group.

The spectrum of the resolidified melt again exhibited changes somewhat similar to those found in the molten and resolidified dimethyl ester. Thus, a new band appeared close to 1060  $cm^{-1}$ . Changes in the OH stretching region above 3000  $cm^{-1}$  are difficult to evaluate because of OH absorption due to the carboxyl group.

*$\alpha$ -Amidosulfopalmitamide.* The Nujol spectrum shows NH<sub>2</sub> bands between 3200 and 3450  $cm^{-1}$ , amide I and amide II bands at 1675 and 1620  $cm^{-1}$  and  $-SO_2-$  bands close to 1150 and 1350  $cm^{-1}$ . Again the spectrum of the resolidified melt is somewhat different, due probably to polymorphism in this case. Polymorphism may have contributed to the spectral behavior of dimethyl  $\alpha$ -sulfopalmitate and  $\alpha$ -methylsulfopalmitic acid, but the appearance of OH stretching bands in the dimethyl ester cannot be explained on this basis.

### Acknowledgment

We are especially indebted to Heino Susi for the section on infrared spectra and interpretation. Microanalyses were performed by Robert Maydole and Laverne Scroggins.

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[Received August 24, 1961]