Studies of Thio Acids. I. The Synthesis of Thiostearic Acid[*1]

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Many studies have been made of lower aliphatic thio acids, such as thioacetic acid and simple aromatic thio acids, and the knowledge recognized hitherto of the properties of thio acids has been mainly based on the properties of thioacetic acid or on those of thiobenzoic acid.[1,2] On the other hand, the studies of higher aliphatic thio acids have been very scanty, except for some short reports of the synthesis[3],[*3] of thiomyristic acid and thiopalmitic acid, and their properties have scarcely been studied at all.[4]

The authors made a series of studies for the purpose of obtaining extensive knowledge of higher aliphatic thio acids and examining the general properties of thio acids.

In this first paper of the present series, the synthesis of thiostearic acid from stearoyl chloride and sodium hydrogen sulfide will be described.

Stearoyl chloride prepared from stearic acid and thionyl chloride was added drop by drop into the ethanol solution of sodium hydrogen sulfide with heating. By the fractional crystallization of the crude product (Table I), thiostearic acid was obtained in the form of colorless crystals (m. p. 39.8∼40.3°C), together with small amounts of distearoyl disulfide (m. p. 81.8∼82.3°C), stearic acid, and ethyl stearate.

The separation of thiostearic acid from these by-products was achieved by fractional crystallization from petroleum ether or hexane; it was difficult to achieve by fractional distillation under reduced pressure or by fractional crystallization from other solvents.

The quantities of by-products depend upon the condition of the reaction. The yield of thiostearic acid was higher when the liquid temperature at dropping was higher, the time of dropping was shorter, the stirring was more vigorous, and the molar ratio of sodium hydrogen sulfide to chloride was larger. For example, the yields of thiostearic acid at the reaction temperatures of 40°C and 65°C were 25.2% and 53.3%[*4] respectively, other conditions being the same. The formation of ethyl

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[*1] Most of this study was presented at the 9th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1956.

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1) H. Gilman, "Organic Chemistry, An Advanced Treatise," Vol. I, John Wiley and Sons, Inc., New York (1949), p. 929.

2) D. S. Tarbell and D. P. Harrish, *Chem, Revs.*, **49**, 1 (1951).

3) V. Auger and M. Billy, *Compt. rend.*, **136**, 555 (1903).

[*3] After the authors presented this study at the 9th Annual Meeting of the Chemical Society of Japan (1956), a report on thiostearic acid was found (F. J. Ritter, *Rubber Stickting, Delft, Commun.*, **No. 324**, 100 (1956); *Chem. Abstr.*, **50**, 16168 (1956)). The synthetic method in the report corresponds well with the authors' method in this paper, but the melting point of the thiostearic acid obtained was reported to be 29∼51°C, indicating the presence of an impurity.

4) K. S. Markley, "Fatty Acids," Intersience Publishers, Inc., New York (1947), p. 520.

[*4] The yields were calculated for pure thiostearic acid separated from the crude product by recrystallization. If the sulfur contents (iodine method) in the crude product were attributed solely to thiostearic acid, the quantities of thiostearic acid in the crude product should be 72.2% and 90.9% respectively.

stearate made the separation of thiostearic acid difficult in fractional crystallization and gave a lower yield of thiostearic acid.

Distearoyl disulfide was obtained from the fraction with the higher melting point. Ethyl stearate was isolated from the mother liquor of the recrystallization of thiostearic acid by applying a method similar to the lead salt-alcohol method for the separation of solid fatty acids from liquid ones.

It is assumed that thiostearic acid and ethyl stearate were produced according to Eqs. 1—4 below and that distearoyl disulfide was produced as follows: in the preparation of a sodium hydrogen sulfide-ethanol solution, some sodium disulfide was produced, and then this reacted with stearoyl chloride to produce distearoyl disulfide.

$$\mathrm{RCOCl+C_2H_5OH \longrightarrow RCOOC_2H_5+HCl} \qquad (1)$$

$$\left.\begin{array}{l}\mathrm{RCOCl+NaSH \longrightarrow RCOSH+NaCl}\\ \mathrm{RCOSH+NaSH \rightleftarrows RCOSNa+H_2S}\\ \mathrm{RCOSNa+RCOCl \longrightarrow RCOSOCR+NaCl}\end{array}\right\} \qquad (2)$$

$$\left.\begin{array}{l}\mathrm{2\,NaSH \rightleftarrows Na_2S+H_2S}\\ \mathrm{2\,RCOCl+Na_2S \longrightarrow RCOSOCR+2NaCl}\end{array}\right\} \qquad (3)$$

$$\mathrm{RCOSOCR+C_2H_5OH \longrightarrow RCOOC_2H_5+RCOSH} \qquad (4)$$

$$\mathrm{R=C_{17}H_{35}-}$$

The ultraviolet absorption spectrum of the obtained thiostearic acid in a cyclohexane solution is shown in Fig. 1, in which $\lambda_{max}=221$ mμ and $\varepsilon_{max}=1800$. An inflection is indicated at 260～280 mμ in the 0.1% solution,[*5] but it is not observed in the 0.01% solution. In the infrared absorption spectra measured by the Nujol-mull method and by the potassium bromide-disk method (Fig. 2), an absorption band for the S–H group evidently appears at 2548 cm^{-1} as well as an absorption band for the C=O group at 1662 cm^{-1}, indicating that the synthesized thiostearic acid assumes the thiolic acid form; this is in accordance with the view of Sheppard[5] and Crouch[6] that thioacetic acid has the thiolic acid form.

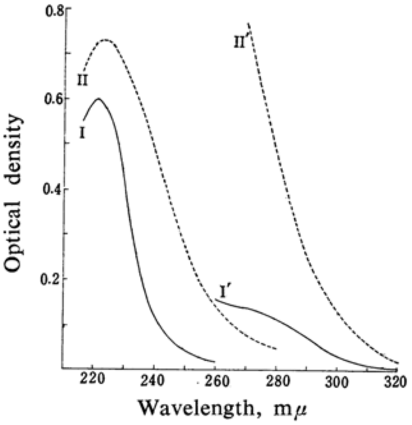

Fig 1. Ultraviolet absorption spectra of thiostearic acid (I, I') and distearoyl disulfide (II, II') in cyclohexane.
I, II, 0.01; I', II', 0.1% solution

Experimental

The Synthesis of Stearoyl Chloride.—Stearic acid (a product of the Nippon Yushi Co.) was recrystallized several times from methanol (neutralization value, 197.3; m. p. 70.0～70.5°C). When stearoyl chloride was synthesized by Ralston's process[7] from freshly-distilled thionyl chloride (85 g.) and stearic acid (105 g.), 100 g. of the fraction with the b. p. of 180～183°C/2.5 mmHg was retained.

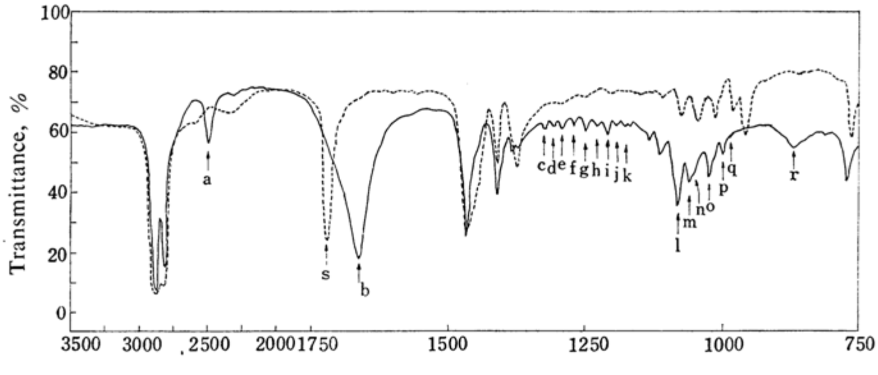

Fig. 2. Infrared absorption spectra of thiostearic acid (T) (——) in potassium bromide disk and distearoyl disulfide (J) (- - -) in Nujol mull.

[*5] Ultraviolet absorption spectrum will be discussed later.

[5] N. Sheppared, *Trans. Faraday Soc.*, **45**, 693 (1949).

[6] W. W. Crouch, *J. Am. Chem. Soc.*, **74**, 2926 (1952).

[7] A. W. Ralston and W. M. Selby, ibid., **61**, 1019 (1939).

The Preparation of a Sodium Hydrogen Sulfide-Ethanol Solution. — Metallic sodium (10 g.) was dissolved in 150 ml. of absolute ethanol (previously distilled with the addition of metallic sodium), and then purified and dried hydrogen sulfide[8] was rapidly introduced into the solution until an excess of hydrogen sulfide was produced. The solution was colored a light yellow and was somewhat turbid.

The Synthesis of Thiostearic Acid.—Stearoyl chloride (31 g.) was vigorously stirred, drop by drop, into the above sodium hydrogen sulfide-ethanol solution at 40°C in 10 min. Then the mixture was refluxed on a water bath for 1 hr., followed by the separation of ethanol under a vacuum to obtain a white jelly residue. The residue was dissolved in 3 l. of water, acidified with dilute hydrochloric acid, and extracted with ether, and the ether layer was washed with water. An insoluble white matter suspended between the ether and the water was filtered off: 0.4 g. (A′). The ether layer was dried over anhydrous sodium sulfate, and the ether was expelled to obtain 27 g. of a crude product (light yellow colored; m. p. 32∼34 °C; neutralization value 138.3; and sulfur content 7.7% (by the iodine method)). The crude product (23.0 g.) was recrystallized from hexane. The yields and melting points of several crystallization fractions are shown in Table I. These fractions were identified as follows:

TABLE I. YIELDS AND MELTING POINTS OF FRACTIONS OBTAINED BY RECRYSTALLIZATION OF CRUDE PRODUCT (23.0 g.)

Fraction	Yield, g.	M. p., °C
A	0.3	81.8∼82.3
B	0.1	
C	1.1	69.5∼70.0
D	1.6	51 ∼55
E	5.8	39.8∼40.3
F	4.5	31 ∼35
G	8.4	30 ∼31

(A): Obtained by the recrystallization of A′ from benzene; colorless crystals.

Found: S, 0 (iodine method), 10.70 (Kitamura's method[9]). Calcd. for $C_{36}H_{70}O_2S_2$: S, 10.60%

This product did not show any depression in melting point when mixed with authentic distearoyl disulfide. Furthermore, the ultraviolet and infrared spectra of the two products were quite identical.

(C): Neutralization value 197.2. No depression in melting point was observed by mixing it with stearic acid.

(E): Colorless. Found: neutralization value 185.9; C, 72.03; H, 12.16; S, 10.57 (iodine method), 10.60 (Kitamura's method), 10.61 (Carius method). Calcd. for $C_{18}H_{36}OS$: neutralization value 186.7; C, 71.94; H, 12.07; S, 10.67%.

This fraction was thus identified as thiostearic acid $C_{17}H_{35}COSH$.

G): The neutralization value of 88.7, the sulfur content of 5.00% (iodine method) or 5.20% (Kitamura's method), and the melting point did not vary when recrystallization was repeated from hexane. A solution of this product (6 g.) in ethanol (20 ml.) was neutralized with a 0.1 N potassium hydroxide-ethanol solution. A soluton of lead acetate (0.4 g.) in ethanol (20 ml.) was added to the above solution, and the mixture settled for 3 hr. at room temperature. The solution was filtered, and then the filtrate was decomposed with dilute hydrochloric acid and extracted with ether; ethyl stearate (0.3 g.) was obtained: m. p. 33∼34°C, saponification value 184.4. The precipitate was decomposed with dilute hydrochloric acid and extracted with ether to obtain a mixture of thiostearic acid and a small amount of stearic acid: m. p. 37.5∼39°C, neutralization value 175.1, sulfur content (iodine method) 9.5%.

The Synthesis of Distearoyl Disulfide.—An iodine solution (0.1N) was added drop by drop into a mixture of thiostearic acid (3 g.) and ethanol (100 ml.) until coloring was observed; the reaction mixture was diluted by water, and the product (3 g.) was recrystallized from benzene to give 2.8 g. of the crystals with a m. p. of 81.8∼82.3°C.

Found: C, 72.22; H, 11.83; S, 0 (iodine method), 10.70% (Kitamura's method). Calcd. for $C_{36}H_{70}O_2S_2$: C, 72.18; H, 11.78; S. 10.69%.

Infrared Absorption Spectra.—The infrared absorption spectra of thiostearic acid (T) and distearoyl disulfide (J) are shown in Fig. 2. A Hilger H-800 infrared spectrophotometer was used for measuring.

In T, the S–H stretching band is evidently indicated at 2548 cm^{-1} (a). The C=O stretching bands are indicated at 1662 (b) in T and at 1713 cm^{-1}(s) in J. In the spectrum of T measured by the potassium bromide disk method, absorption bands corresponding to the progression bands reported by Jones[10] appear at 1327(c), 1307(d), 1288(e), 1268(f), 1248(i), 1228(h), 1208(i), 1188(j) and 1172 cm^{-1} (k), but they are not evident in the spectrum measured by the Nujol mull method. Absorption bands appear at 1081(l), 1060(m), 1045(n), 1025(o), 996(p), and 977 cm^{-1} (q) in T, but their assignments are not evident. A low-intensity absorption band is indicated at 868 cm^{-1} (r) in T; this is probably due to the S–H group.

Ultraviolet Absorption Spectra. — They were measured by using a Shimadzu Quartz spectrophotometer, model QB-50, and silica cells (1 cm.).

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[8] G. Brauer, "Handbuch der Präparativen Anorganischen Chemie," Verdinand Enke, Stuttgart (1954), p. 270.

[9] R. Kitamura, *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), **57**, 31 (1937).

[10] R. N. Jones, A. F. Mckay and R. G. Sinclair, *J. Am. Chem. Soc.*, **74**, 2575 (1952).