Studies of Thio Acids. V.[1] The Reaction of Distearoyl Sulfide with Alcohol and Alkali[*1]

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In the course of an investigation of the mechanism of the formation of stearic esters from thiostearic acid and alcohols by heating, the formation of distearoyl sulfide as an intermediate in the reaction was confirmed.[*3] However, detailed knowledge of the properties of diacyl sulfide was still lacking. Therefore, the present authors synthesized distearoyl sulfide and clarified its properties by investigating the products obtained by heating it in alcohol or by neutralizing it in organic solvents with ethanolic or aqueous potassium hydroxide, thus determining each reaction mechanism. The above mechanisms will be discussed in this paper.

Distearoyl sulfide (m. p. 79.5—80.5°C) was synthesized from potassium thiostearate and stearoyl chloride. Its ultraviolet absorption curve in cyclohexane (Fig. 1) exhibits an absorption maximum at 240 mμ ($\varepsilon=4030$) and an inflection in the 280—320 mμ region; the former is undoubtedly associated with conjugation between the π electrons of the carbonyl group and the unshared valency electrons of the sulfur atom, while the latter is probably an R-band due to the carbonyl group. The neutralization value (N. V.) of distearoyl sulfide as determined by neutralization with ethanolic potassium hydroxide in benzene-ether using phenolphthalein as an indicator[*4] was 100.4, a value which shows that the reaction between distearoyl sulfide and potassium hydroxide occurs at an equimolar ratio under the above conditions. The sulfur content (in the SH form) of distearoyl sulfide as determined by titration with an iodine solution in ethanol-ether or ethanol-benzene was naught, but that determined by titration with an iodine solution after neutralization with ethanolic potassium hydroxide in the above solvent was 5.70%, in good accord with the sulfur content as determined by Kitamura's method. (The sulfur contents determined by the above methods will be described below as S(J), $S(J)_{NV}$, and S(K) respectively.)

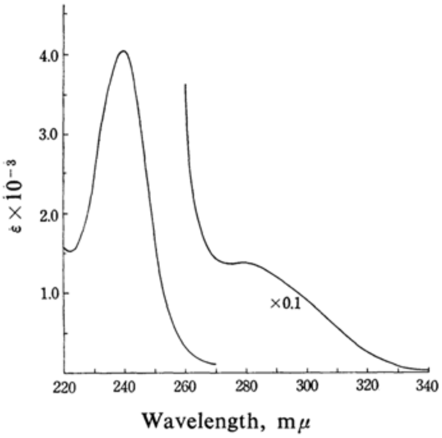

Fig. 1. Ultraviolet absorption spectrum of distearoyl sulfide in cyclohexane.

When distearoyl sulfide (3 g.) had been refluxed with absolute methanol (300 ml.) for 30 hr., the reaction product obtained was found to be composed of distearoyl sulfide (5%), thiostearic acid (35%) and methyl stearate (60%), but methyl thiostearate could not be isolated. This result suggests the following mechanism: When distearoyl sulfide is heated with methanol, methanolysis occurs as shown in Eq. 1, and methyl stearate and thiostearic acid are formed. Starting from the thiostearic acid, distearoyl sulfide is reformed by the elimination of hydrogen sulfide, as is shown in Eq. 2, and then the reaction of Eq. 1 is repeated.[*5] It is still unknown whether the reaction of Eq. 3 occurs or not, but the reaction of Eq. 1 is firmly supported by the formation of a large amount of thiostearic acid.

When distearoyl sulfide in benzene or benzene-ether was neutralized with ethanolic potassium hydroxide, it was confirmed that

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[1] Part IV of this series: Y. Hirabayashi, This Bulletin, 38, 175 (1965).

[*1] Most of this study was presented at the 11th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1958.

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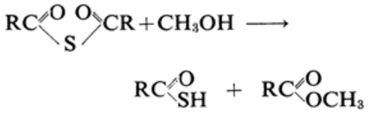
[*3] When thiostearic acid is heated with alcohol, first hydrogen sulfide is evolved and distearoyl sulfide is formed as an intermediate, and then the stearic ester and thiostearic acid are formed by the reaction of the intermediate and alcohol. This reaction mechanism will be discussed in the following paper of this series.

[*4] In the following experiments, all neutralizations were carried out using phenolphthalein as an indicator.

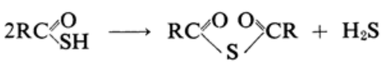
[*5] This will be discussed in the following paper of this series.

potassium thiostearate and ethyl stearate are formed in an equimolar ratio, as in Eq. 4. Therefore, it may be reasonably explained that the observed N. V. of distearoyl sulfide corresponds well with the value calculated by the equimolar ratio described above. It is also confirmed that the difference between the S(J) and the $S(J)_{NV}$ values is caused by the thiostearic acid formed by neutralization with ethanolic potassium hydroxide.

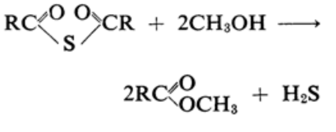
When a small amount (very different from the neutralization equivalent as a 1 : 1 mole ratio) of aqueous potassium hydroxide was added to a solution of distearoyl sulfide in benzene-ethanol, the reaction product was found to be composed of equimolar amounts of ethyl stearate and thiostearic acid (containing potassium thiostearate corresponding to the potassium hydroxide added); that is, alcoholysis occurs between a large amount of alcohol and distearoyl sulfide upon the addition of a small amount of alkali as a catalyzer, and then thiostearic acid and stearic acid ester are formed. This fact shows that when neutralization is carried out in benzene or benzene-ether with ethanolic potassium hydroxide, first alcoholysis occurs upon the addition of alcoholic potassium hydroxide, and then the acid thus formed is neutralized. However, a sufficient amount of alcohol in the solvent or in an alkali solution is needed for alcoholysis. The presence of a large amount of benzene and an equimole of alcohol to distearoyl sulfide does not accelerate the neutralization with aqueous potassium hydroxide. In a benzene - aqueous potassium hydroxide solution, distearoyl sulfide was not changed, even when vigorously stirred while being warmed and the hydrolysis shown in Eq. 5 did not occur. However, it still can not be known whether or not hydrolysis should occur by the regulation of the alkali concentration and the reaction temperature.



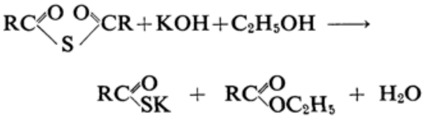
$$\mathrm{RC(=O)SC(=O)R + CH_3OH \longrightarrow RC(=O)SH + RC(=O)OCH_3} \qquad (1)$$



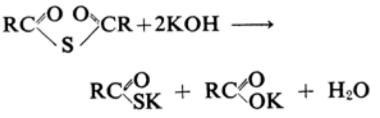
$$\mathrm{2RC(=O)SH \longrightarrow RC(=O)SC(=O)R + H_2S} \qquad (2)$$



$$\mathrm{RC(=O)SC(=O)R + 2CH_3OH \longrightarrow 2RC(=O)OCH_3 + H_2S} \qquad (3)$$



$$\mathrm{RC(=O)SC(=O)R + KOH + C_2H_5OH \longrightarrow RC(=O)SK + RC(=O)OC_2H_5 + H_2O} \qquad (4)$$



$$\mathrm{RC(=O)SC(=O)R + 2KOH \longrightarrow RC(=O)SK + RC(=O)OK + H_2O} \qquad (5)$$

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

Experimental*6

The Synthesis of Distearoyl Sulfide.—Potassium thiostearate was prepared by the neutralization of thiostearic acid with ethanolic potassium hydroxide in ethanol-ether (1 : 1) and by distilling off the solvent. Stearoyl chloride (9.2 g.) was added drop by drop to a suspension of the potassium thiostearate (10.4 g.) in anhydrous hexane (200 ml.), and then the mixture was refluxed for 7 hr. under a cooler with a calcium chloride tube. After the reaction mixture had been filtered while hot, hexane was distilled off from the filtrate, and the residue was recrystallized from benzene to give distearoyl sulfide (14 g.); m. p. 79.5—80.5°C, colorless plate crystals, N. V. 100.4 (Calcd. by $C_{36}H_{70}O_2S$: KOH= 1 : 1 mol., 98.95).

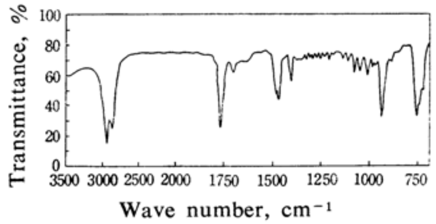


Fig. 2. Infrared absorption spectrum of distearoyl sulfide in KBr disk (1.05 mg./200 mg. KBr).

Found: C, 76.08; H, 12.33; S, 0·S(J), 5.68 $S(J)_{NV}$, 5.70 S(K)%. Calcd. for $C_{36}H_{70}O_2S$: C, 76.26; H, 12.44; S, 5.65%.

UV (cf. Fig. 1): $\lambda_{max}^{cyclohexane}$ 240 mμ (ε=4030); inflection 280—320 mμ. IR (KBr disk, cf. Fig. 2): $\nu_{C=O}$ 1766 cm^{-1}.

The Reaction of Distearoyl Sulfide with Absolute Methanol by Heating.—A solution of distearoyl sulfide (3 g.) in absolute methanol (300 ml.) was refluxed for 30 hr., and the following product I was obtained by distilling off the methanol under reduced pressure; m. p. 33.5—34.5°C, N. V. 68.3, S(J) 3.33%, $S(J)_{NV}$ 3.58%, S(K) 3.58%.

Its ultraviolet absorption spectrum (curve a, Fig. 3) exhibits a low-intensity absorption maximum at 221 mμ, but the absorption maximum at 240 mμ due to distearoyl sulfide is not seen.

The product I (2.8 g.) was recrystallized several times from hexane and benzene; the properties and the ultraviolet absorption spectrum of each fraction are shown in Table I and Fig. 3 respectively. The composition of each fraction was thus found to be as follows:

[*6] All melting points are uncorrected. The ultraviolet absorption spectra were measured with a Shimadzu quartz-spectrophotometer, model QB-50, and silica cells (1 cm.), while the infrared absorption spectrum was measured with a Hilger-H-800 infrared spectrophotometer.

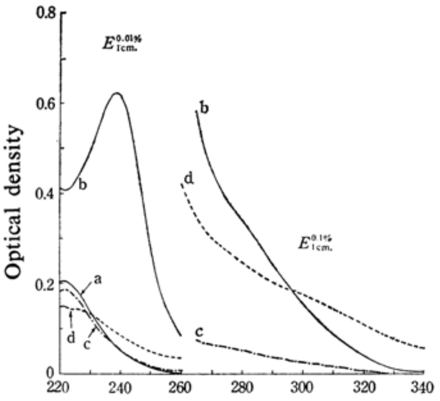


Fig. 3. Ultraviolet absorption spectra in cyclohexane.
a: Product I
b: Fraction 1 in Table I
c: Fraction 3 in Table I
d: Fraction N-2 in Table II

TABLE I. THE PROPERTIES OF FRACTIONS OBTAINED FROM THE PRODUCT I (2.8 g.)

	Yield g.	M. p. °C	N. V.	$S(J)_{NV}$	S(K)
(1)	0.1	79—80	—	—	6.02
(2)	0.05	71—77	—	—	—
(3)	0.8	34.5—35.5	62.7	3.11	3.14
(4)	1.8	33—34	74.9	3.90	3.92

(1): Unreacted and reformed distearoyl sulfide
(2): Mainly distearoyl sulfide
(3) and (4): Thiostearic acid and ester (RCOOR′ or RCOSR′)

It was difficult to purify fractions 3 and 4 further by recrystallization. The mixture of 3 and 4 (1.6 g.) was neutralized with ethanolic potassium hydroxide in ethanol[*7] and separated into an acidic part A and a neutral part N by the usual method. Each part was then recrystallized; the results of recrystallization are shown in Table II. The fractions A and N-1 were identified as thiostearic acid and methyl stearate respectively. (Neither of them showed any depression of melting point upon admixture with an authentic sample, and the ultraviolet spectrum of A was identical with that of thiostearic acid.) The fraction N-2 was slightly yellow and exhibited the weak absorption in the 260—400 mμ region. This fraction was found to consist mainly of methyl stearate, together with a small amount of an unidentified substance.

TABLE II. THE PROPERTIES OF FRACTIONS OBTAINED FROM THE MIXTURE (1.6 g.) OF (3) AND (4) IN TABLE I

	Yield g.	M. p. °C	N. V.	$S(J)_{NV}$	S(K)
(A)	0.6	39.5—40.5	186.4	10.54	10.57
(N-1)	0.9	38.5—39.0	1.5[a)]	0.09	0.08
(N-2)	0.1	39.5—40.5	41.2[b)]	1.81	—

Saponification value (S. V.): a), 185.5; b), 179.5 (calcd. for methyl stearate: 188.0).

On the basis of the above results, the compositions of the product I were as follows: unreacted or reformed distearoyl sulfide 5%, methyl stearate 60%, and thiostearic acid 35%.

The Reaction of Distearoyl Sulfide in Benzene or Benzene-Ether with Ethanolic Potassium Hydroxide.—A solution of distearoyl sulfide (1.07 g.) in benzene (30 ml.) or benzene (20 ml.) - ether (10 ml.) was neutralized with 0.1 N ethanolic potassium hydroxide; the neutralization value was determined to be 100.5. The reaction mixture was then allowed to stand at room temperature for 2 hr., after which the solvent was distilled off under reduced pressure and water (200 ml.) was added to the residue. The resulting mixture was acidified with dilute hydrochloric acid and extracted with ether. The following product II was obtained by distilling off the ether: m. p. 30.0—31.0°C, N. V. 98.1, S(J) 5.60%, $S(J)_{NV}$ 5.60%.[*7]

A solution of this product II (0.94 g.) in ether (20 ml.) was neutralized with 0.5 N ethanolic potassium hydroxide (3.25 ml.), and the reaction mixture was allowed to stand at room temperature for 1 hr. Then the deposit part was filtered off. The filtrate (ether solution) was washed with water, and the neutral part N was obtained by distilling off the ether. The above deposit part, combined with washings of the filtrate, was acidified, and the mixture was extracted with ether. The acidic part A was obtained by washing the ether solution with water, followed by distilling off the ether. The same procedures were repeated for three times in each part in order to separate the neutral part from the acidic part as much as possible. The properties of each part are shown in Table III. It was deduced from the above results that almost equal amounts of potassium thiostearate and ethyl stearate are formed by the neutralization reaction of distearoyl sulfide in benzene or benzene-ether with ethanolic potassium hydroxide.

TABLE III. THE PROPERTIES OF FRACTIONS OBTAINED FROM THE PRODUCT II (0.94 g.)

	Yield g.	M. p. °C	N. V.	$S(J)_{NV}$
(A)	0.43	39.5—40.5	184.8	10.28
(N)	0.45	34.5—35.5	1.0[a)]	0

S. V.: a) 180.9 (calcd. for ethyl stearate: 179.5).

The Neutralization Reaction of Distearoyl Sulfide in Benzene with Aqueous Potassium Hydroxide.—a) A solution of distearoyl sulfide (1 g.) in methanol (equal mole to distearoyl sulfide) and benzene (50 ml.) was titrated with 0.1 N aqueous potassium hydroxide, using phenolphthalein as an indicator. The titre was less than 0.03 ml.

b) To a solution of distearoyl sulfide (2 g.) in benzene (50 ml.), 36 ml. (calcd. value as 1 : 1 mol. ratio, 35.18 ml.) of 0.1 N (f=1.073) aqueous potassium hydroxide was added drop by drop, and then

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[*7] Since no difference is found between the S(J) and $S(J)_{NV}$ values, it can be said that no distearoyl sulfide exists in the product, and that no new products are formed by the neutralization of the product.

the mixture was heated while being vigorously stirred at 50°C for 2 hr. Then it was acidified with dilute hydrochloric acid. The benzene layer separated was washed with water and dried, and the benzene was distilled off. The product obtained was distearoyl sulfide.

The Reaction of Distearoyl Sulfide in Benzene-Ethanol with Aqueous Potassium Hydroxide.—To a solution of distearoyl sulfide (1 g.) in benzene (80 ml.) and ethanol (20 ml.), 0.15 ml. of 0.5 N aqueous potassium hydroxide was added (distearoyl sulfide : potassium hydroxide=1 mol.: ca. 0.02mol.). The mixture was heated at 40—50°C for 3 hr. and then allowed to stand overnight at room temperature. It was then acidified with dilute hydrochloric acid. The benzene layer separated was washed with water and dried, and the following product III was obtained by distilling off the benzene; m. p. 29.5—30.5°C, N. V. 97.6, S(J) 5.41%, $S(J)_{NV}$ 5.41%.[*7] A solution of the product III (0.91 g.) in benzene was repeatedly washed with aqueous potassium hydroxide, and the acidic part A and the neutral part N were obtained from the washings and the benzene layer respectively in the usual way. The results are shown in Table IV. It may be deduced from the results that almost equal amounts of thiostearic acid and ethyl stearate were formed by the reaction of distearoyl sulfide in benzene-ethanol with aqueous potassium hydroxide.

TABLE IV. THE PROPERTIES OF FRACTIONS OBTAINED FROM THE PRODUCT III (0.91 g.)

	Yield g.	M. p. °C	N. V.	$S(J)_{NV}$	S(K)
(A)	0.45	39—40	186.6	10.32	10.38
(N)	0.46	34.5—35.5	1.3a)	0	0

S. V.: a) 181.8.

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