# NOTES

## Studies of Thio Acids. II.[1] The Reaction of Stearic Esters with Sodium Hydrosulfide*1

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Thio acids can be synthesized as follows: (1) By heating carboxylic acids with phosphorus pentasulfide.[2,3] (2) By saponifying phenyl esters of carboxylic acids with sodium hydrosulfide in absolute alcohol.[4] (3) By treating acid chlorides with alkali hydrosulfide.[1] (4) By treating carbon oxysulfide with a Grignard reagent. (5) By treating carboxylic acid anhydrides with phosphorus sulfide.

It was reported that thio acids were not obtained, while carboxylic acids and mercaptans were obtained, by method 2 when alkyl esters of carboxylic acids were used in place of phenyl esters.[4] The present authors have now treated phenyl, methyl, β-chloroethyl, and cetyl stearates with sodium hydrosulfide in absolute ethanol, and obtained ethyl stearate and stearic acid from alkyl stearates, and thiostearic acid, distearoyl disulfide, ethyl stearate, and a trace of stearic acid from phenyl stearate.

### Experimental and Results

**Stearic Acid Esters.**—Methyl stearate was prepared by the reaction of stearic acid with methanol in the presence of concentrated sulfuric acid as a catalyst; it was then purified by recrystallization (m. p. 38.0—39.0°C).

Phenyl stearate and β-chloroethyl stearate were prepared by the reactions of stearoyl chloride[1] with phenol and ethylene chlorohydrine respectively, and were purified by recrystallization (m. p. 52.0—52.5°C for phenyl stearate and 49.5—50.5°C for β-chloroethyl stearate).

Cetyl stearate was prepared from stearoyl chloride, cetyl alcohol and polished magnesium ribbon according to the directions of Paquot and Boquet;[5] it was then recrystallized from ethanol (m. p. 60.5—61.5°C, saponification value 110.2 (110.2 by calcd.)).

TABLE I. ACID VALUES AND SULFUR CONTENTS OF PRODUCT

| Product | Acid value | Sulfur content, % (iodine method) |
|---|---|---|
| I | 106.4 | 5.2 |
| II | 108.5 | 0 |
| III | 138.5 | 1.4 |
| IV | 29.6 | 0 |

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*1 Most of this study was presented at the Symposium of Oils and Fats of the Chemical Society of Japan, Nagoya, October, 1957.

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1) Part I of this series: Y. Hirabayashi, M. Mizuta and T. Mazume, This Bulletin, 37, 1002 (1964).

2) F. A. Kekulé, *Ann.*, **90**, 311 (1854).

3) R. Kitamura, *J. Pharm. Soc. Japan*, **57**, 31 (1937).

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

5) C. Paquot and F. Boquet, *Bull. soc. chim. France*, **1947**, 321.

TABLE II. COMPOSITION OF PRODUCTS OBTAINED BY REACTION OF STEARIC ACID ESTERS WITH ETHANOL - SODIUM HYDROSULFIDE

| Stearic acid ester ($R=C_{17}H_{35}-$) | Composition of product |
|---|---|
| $RCOOC_6H_5$ | RCOOH(10%), $RCOOC_2H_5$(20%), RCOSH(50%), RCOSSOCR(20%) |
| $RCOOCH_3$ | RCOOH(54%), $RCOOC_2H_5$(46%) |
| $RCOOCH_2CH_2Cl$ | RCOOH(75%), $RCOOC_2H_5$(20%), sulfur compound[a] |
| $RCOOC_{16}H_{33}$ | RCOOH, $RCOOC_2H_5$, $C_{16}H_{33}OH$, $RCOOC_{16}H_{33}$[b] |

a) A trace of a compound with SH group, confirmed to be not thiostearic acid, was detected in some ethyl stearate-fraction.

b) Too much losses were inevitable during the process of isolation, and an attempt to determine material balance among the components was unsuccessful.

**An Ethanol Solution of Sodium Hydrosulfide.**—This was prepared by the method described in the previous paper.[1)]

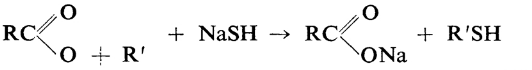
**The Reaction of Phenyl, Methyl, β-Chloroethyl, Cetyl Stearates with Sodium Hydrosulfide.**—About a 2 N sodium hydrosulfide-ethanol solution (80 ml., or 0.167 mol. NaSH (50 ml., or 0.1 mol. NaSH to the cetyl ester only)) was added to the phenyl ester (12.4 g.), the methyl ester (9.9 g.), the β-chloroethyl ester (11.6 g.) (0.033 mol. for each), or the cetyl ester (10.2 g., or 0.02 mol.). Each mixture was refluxed for 3 hr. under a current of dried nitrogen. The ethanol was then distilled off under reduced pressure, and water was added to the residue. The mixture was acidified with dilute hydrochloric acid and extracted with ether. The ether layer was washed with water and dried over anhydrous sodium sulfate, and the ether was distilled off. The acid value[*3] and sulfur content of the products are shown in Table I, in which I refers to the product from phenyl ester, II refers to that from methyl ester, III refers to that from β-chloroethyl ester, and IV refers to that from cetyl ester.

The data evidently indicate that mercaptan or thio acid is not contained in products II and III.

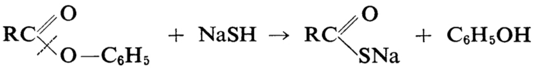
**The Identification of Products.**—Each product was recrystallized repeatedly from hexane, benzene, ether, methanol, or ethanol, giving nine fractions from I, four fractions from II, seven fractions from III and more than ten fractions from IV. The melting points, ultraviolet absorption spectra, neutralization values, saponification values, acetyl values, and sulfur contents (by iodine method and Kitamura's method) of these fractions were measured. The identified products and their yield are shown in Table II.

## Discussion

Auger and Billy[4)] reported that sodium salts of carboxylic acids and mercaptans were formed when alkyl esters of carboxylic acids (RCOOR') were treated with absolute ethanol - sodium hydrosulfide at 180°C, while thio acids were formed when phenyl esters ($RCOOC_6H_5$) were used, and, further, that heating at 80°C or 120°C was insufficient for the achievement of these reactions. Hence, from their experimental results, it is deduced that splitting may occur between O and R' in RCOOR' and between C and O in $RCOOC_6H_5$.



$$\mathrm{RC(=O)O + R' + NaSH \rightarrow RC(=O)ONa + R'SH} \qquad (1)$$



$$\mathrm{RC(=O){\times}O{-}C_6H_5 + NaSH \rightarrow RC(=O)SNa + C_6H_5OH} \qquad (2)$$

However, in the author's experiments, the products shown in Table II were obtained. It was not investigated whether the methyl ester would form methyl mercaptan or not. In order to examine the formation of mercaptans from alkyl esters, the authors investigated the reaction of the cetyl ester, but compounds with an S–H group were not obtained. After all, in these experiments, the reaction shown in Eq. 1 did not occur, though our conditions for the reaction were slightly different from those of Auger's experiments; that is, a trace of water[*4] (principally in alcohol) was present, and heating was at nearly 78°C.

Wiberg[6)] states that, in the mechanism of the hydrolysis of carboxylic acid esters by the base $Y^-$ (Eq. 3), the initial addition depends on the nucleophilicity of $Y^-$, but the partitioning of the addition compound to form reactants or products depends on the relative stabilities of $Y^-$ and $X^-$. If $Y^-$ is a weaker base than $X^-$, the reaction will not proceed, but if $Y^-$ is stronger than $X^-$, the reaction will proceed. Accordingly, ester hydrolysis by a general basic catalysis may be expected to occur when the anion formed from the ester is of a basicity at least comparable to the attacking base; therefore, when such esters are chosen in which the

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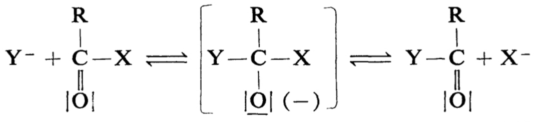
[*3] The acid value of the product varies with the concentration of sodium hydrosulfide added and with the heating time.

[*4] In Auger's experiments, the water content is unknown, since the method of preparing absolute alcohol is not described.

6) K. B. Wiberg, *J. Am. Chem. Soc.*, 77, 2519 (1955).

alcoholic portion (HX) is more acidic than YH, a general basic catalysis will occur.



$$Y^- + \underset{\underset{|O|}{\|}}{\overset{\overset{R}{|}}{C}}-X \rightleftharpoons \left[Y-\underset{\underset{|\underline{O}|\,(-)}{|}}{\overset{\overset{R}{|}}{C}}-X\right] \rightleftharpoons Y-\underset{\underset{|O|}{\|}}{\overset{\overset{R}{|}}{C}} + X^- \tag{3}$$

Although it is not a hydrolysis in the strict sense, the above mechanism will be applied to the authors' reaction.

In these experiments, those substances corresponding to HX are $CH_3OH$, $ClCH_2CH_2OH$, $C_{16}H_{33}OH$, and $C_6H_5OH$, in which phenol is more acidic than in the former three. The bases ($Y^-$) present in the sodium hydrosulfide - ethanol solution are $SH^-$, $C_2H_5O^-$, and $OH^-$ ($NaSH$, $C_2H_5OH$, and $H_2O$) ; for their relative basicities, the sequence $OH^- > C_2H_5O^- (RO^-) > SH^-$ should be taken, while for their nucleophilicities, the sequenee $SH^- > C_2H_5O^- (RO^-) > OH^-$ should be taken.

There is not a great difference between the basicities of $OH^-$ and $OR^-$. Hence, esters of $CH_3OH$, $ClCH_2CH_2OH$, and $C_{16}H_{33}OH$ are replaced by those of $C_2H_5O^-$ or $OH^-$. However, for $SH^-$ basicity ($X^- = (RO^-) > SH^-$), the difference between $X^-$ and $SH^-$ is too large to prompt the reaction. In phenyl ester, it is supposed that $C_6H_5O^-$ is weakly basic and replaced by $SH^-$, $C_2H_5O^-$, $OH^-$, etc.; the quantities of substituted products will depend on their nucleophilicities and concentrations. The results obtained in the experiments are well explained by the above mechanism.

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