Sulfur Derivatives of Long-Chain Acids

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EARLY LITERATURE describing sulfur derivatives of fatty materials is vague; e.g., a patent (1) issued in 1939 describes reactions between various unsaturated glycerides and sulfur in the presence of iodine. The products of these reactions apparently contain sulfur, and claims have been made that they are useful insecticides. However, no structures were proposed for these materials, and no product properties were described.

One of the early significant contributions to the sulfur chemistry of fatty materials was made in 1939 by Ralston and co-workers (2). In that year they reported a series of thiol esters of lauric, myristic, palmitic, stearic and oleic acids. I say that this is a significant contribution, because prior to this work, thiol esters of long-chain acids were considered to be unstable (3).

Thiol esters of long-chain acids cannot be prepared by direct esterification of acids and thiols; however, these compounds may be prepared very conveniently by treating an acyl chloride with an alkane thiol or a benzene thiol.

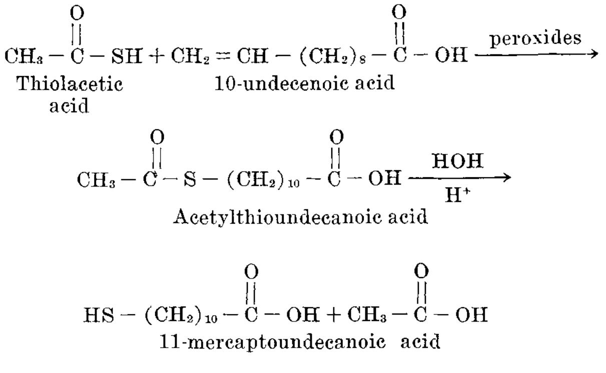
Thiol esters of long-chain acids are stable compounds. This is evidenced by the fact that these compounds may be distilled under diminished pressure without excessive decomposition. Later, other investigators (4, 5) synthesized a variety of long-chain thiol esters, and their findings regarding the stability of thiol esters coincide with Ralston's findings.

Thiol esters of long-chain dibasic acids are known (6). These compounds have been prepared by treating the acyl chlorides of the dibasic acid with two moles of a mercaptan.

Similarly, thioglycols have been prepared. In this case, however, dithiols instead of thiols are treated with long-chain acyl chlorides in the presence of pyridine (7).

Thiol esters upon hydrolysis do not yield a thiol acid and an alcohol, but instead, an acid and a thiol (8).

This reaction has been applied successfully in preparing long-chain mercaptoacids (9, 10).



$$CH_3-\overset{O}{\overset{\|}{C}}-SH + CH_2=CH-(CH_2)_8-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{\text{peroxides}}$$

Thiolacetic acid 10-undecenoic acid

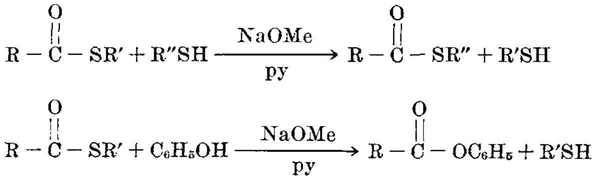
$$CH_3-\overset{O}{\overset{\|}{C}}-S-(CH_2)_{10}-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[H^+]{HOH}$$

Acetylthioundecanoic acid

$$HS-(CH_2)_{10}-\overset{O}{\overset{\|}{C}}-OH + CH_3-\overset{O}{\overset{\|}{C}}-OH$$

11-mercaptoundecanoic acid

Thiol esters undergo ester interchange reactions (11). The following equilibria may be forced to the right by the use of a slight excess of a higher mol thiol, a benzene thiol or phenol in the presence of sodium methoxide and using pyridine as a solvent.

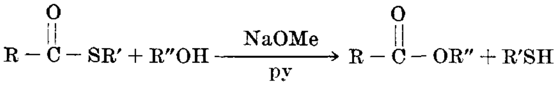


$$R-\overset{O}{\overset{\|}{C}}-SR' + R''SH \xrightarrow[py]{NaOMe} R-\overset{O}{\overset{\|}{C}}-SR'' + R'SH$$

$$R-\overset{O}{\overset{\|}{C}}-SR' + C_6H_5OH \xrightarrow[py]{NaOMe} R-\overset{O}{\overset{\|}{C}}-OC_6H_5 + R'SH$$

The above reactions are essentially complete in about 1 hr and the yields are in the order of 60–70%.

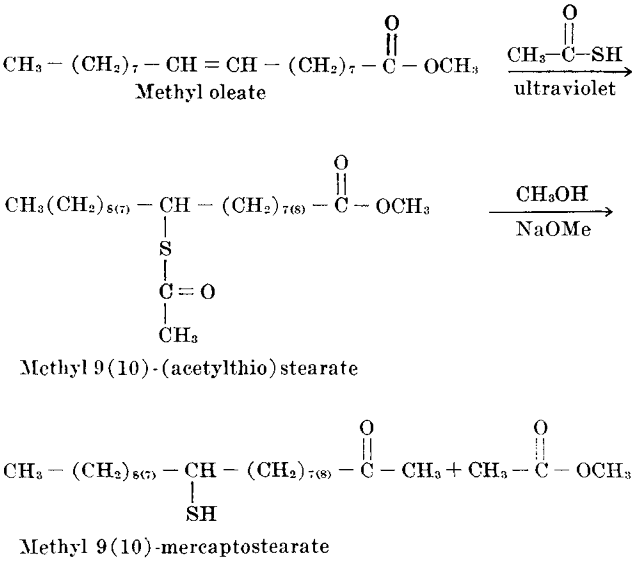
Under similar conditions, but in the presence of large excesses of alcohols, thiol esters are converted to oxygen esters (11).



$$R-\overset{O}{\overset{\|}{C}}-SR' + R''OH \xrightarrow[py]{NaOMe} R-\overset{O}{\overset{\|}{C}}-OR'' + R'SH$$

This reaction, however, is more sluggish than the previous ones. For example, it was found that ethyl thiostearate was converted to methyl stearate in 3 hr, to ethyl stearate in about 24 hr and to n-butyl stearate in about 48 hr.

This reaction has been applied in preparing methyl 9(10)-mercaptostearate (10).



$$CH_3-(CH_2)_7-CH=CH-(CH_2)_7-\overset{O}{\overset{\|}{C}}-OCH_3 \xrightarrow[\text{ultraviolet}]{CH_3-\overset{O}{\overset{\|}{C}}-SH}$$

Methyl oleate

$$CH_3(CH_2)_{8(7)}-\underset{\underset{\underset{CH_3}{|}}{\underset{C=O}{|}}}{\underset{S}{\underset{|}{CH}}}-(CH_2)_{7(8)}-\overset{O}{\overset{\|}{C}}-OCH_3 \xrightarrow[NaOMe]{CH_3OH}$$

Methyl 9(10)-(acetylthio)stearate

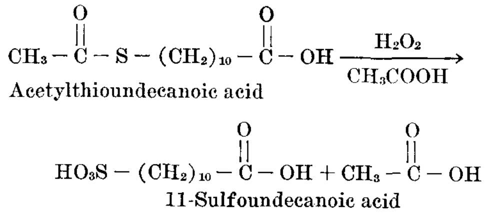
$$CH_3-(CH_2)_{8(7)}-\underset{SH}{\underset{|}{CH}}-(CH_2)_{7(8)}-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3-\overset{O}{\overset{\|}{C}}-OCH_3$$

Methyl 9(10)-mercaptostearate

Conversion of an oxygen ester to a thiol ester by ester interchange has not been successful (11). Prolonged heating of methyl stearate with excesses of benzenethiol, p-toluenethiol or dodecanethiol in the presence of sodium methoxide or an acid catalyst resulted in no reaction.

Thiol esters, like oxygen esters undergo acidolysis (12), e.g., upon heating a mixture of n-decyl thioacetate and palmitic acid in the presence of 100% sulfuric acid and mercuric acetate results in the formation of n-decyl thiopalmitate and acetic acid (12).

When a thiol ester is subjected to an oxidation, a Keto sulfones do not form, but instead oxidative cleavage occurs (13).



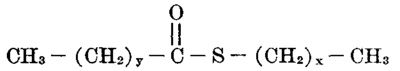
$$CH_3-\overset{O}{\overset{\|}{C}}-S-(CH_2)_{10}-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[CH_3COOH]{H_2O_2} HO_3S-(CH_2)_{10}-\overset{O}{\overset{\|}{C}}-OH+CH_3-\overset{O}{\overset{\|}{C}}-OH$$

Acetylthioundecanoic acid

11-Sulfoundecanoic acid

This is a convenient method for the preparation of aliphatic sulfonic acids.

The normal thiol esters, like most homologous series, show an alternation of melting points, but unlike most homologous series, the odd members melt at a higher temp than the even members (5). Figure 1 represents the plot of melting points of thiomyristates against the number of carbon atoms in the thiol portion of the ester. The melting points of the even members fall on a single ascending curve while the melting points of the odd members fall on two distinct and separate ascending curves. The melting points of thiol esters prepared from alkane thiols containing fewer carbon atoms than the alkyl radical belonging to the acid fall on ascending curves, which are lower than the melting points of thiol esters prepared from alkane thiols containing an equal or greater number of carbon atoms than the alkyl radical belonging to the acid. Thus the compounds:



$$CH_3-(CH_2)_y-\overset{O}{\overset{\|}{C}}-S-(CH_2)_x-CH_3$$

form a lower melting series if the value of x is smaller than the value of y and form a higher melting series if the value of x is equal to or higher than the value of y. Similar results have been observed with thiolaurates, thiopalmitates and thiostearates.

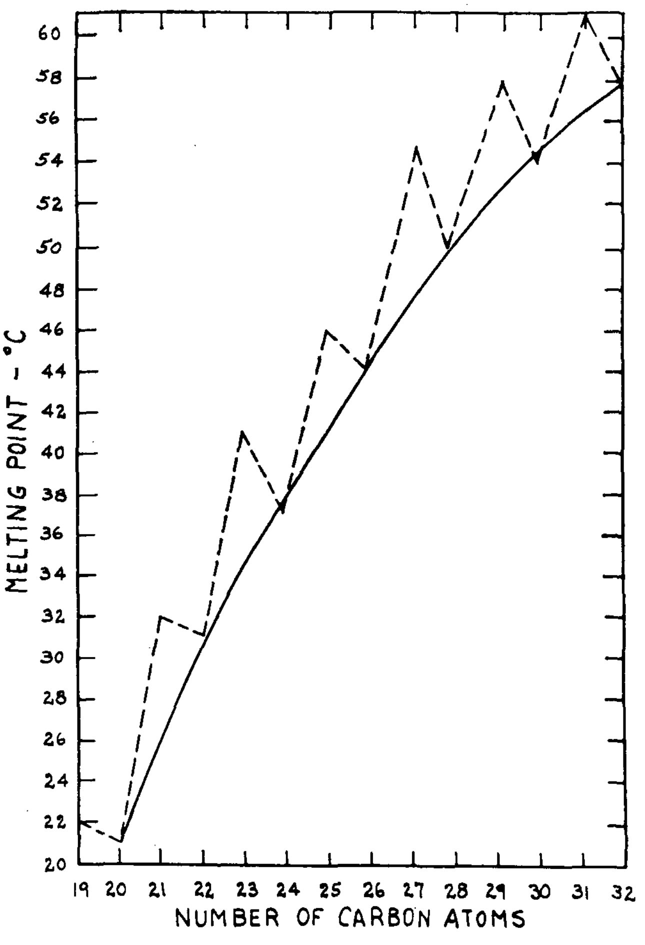
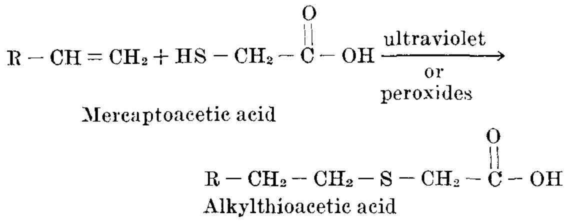


FIG. 1. Melting points of thiomyristates.

Long-chain sulfur-containing acids have been prepared by the addition under free radical conditions of mercaptoacetic (14) or β-mercaptopropionic acid (15) to long-chain terminally unsaturated olefins.



$$R-CH=CH_2+HS-CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\text{or peroxides}]{\text{ultraviolet}} R-CH_2-CH_2-S-CH_2-\overset{O}{\overset{\|}{C}}-OH$$

Mercaptoacetic acid

Alkylthioacetic acid

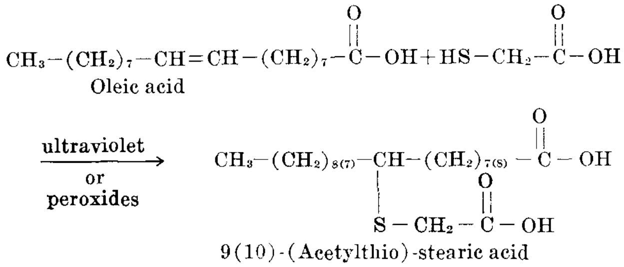
The addition under these conditions results in the formation of anti-Markownikoff configuration products. The sulfide acids which result from these reactions are readily oxidized to the corresponding sulfoxides and sulfones.

Also, these acids undergo typical acid reactions, i.e., these compounds can be converted to esters, amides, acyl halides, thiol esters, etc. (15).

Other sulfur-containing long-chain acids have been prepared by the addition of various thiols to 10-undecenoic acid (13).

These sulfide acids have also been oxidized to the corresponding sulfoxides and sulfones.

Sulfur-containing dicarboxylic long-chain acids have been prepared by the addition of mercaptoacetic acid, under free radical conditions, to such unsaturated compounds as 10-undecenoic or oleic acids (13, 16).

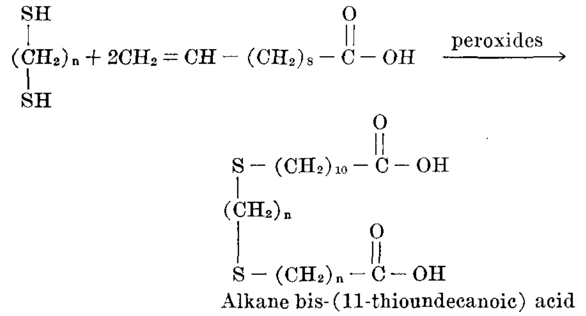


$$CH_3-(CH_2)_7-CH=CH-(CH_2)_7-\overset{O}{\overset{\|}{C}}-OH+HS-CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\text{or peroxides}]{\text{ultraviolet}} CH_3-(CH_2)_{8(7)}-\underset{\underset{S-CH_2-\overset{O}{\overset{\|}{C}}-OH}{|}}{CH}-(CH_2)_{7(8)}-\overset{O}{\overset{\|}{C}}-OH$$

Oleic acid

9(10)-(Acetylthio)-stearic acid

Another route to the formation of sulfur-containing long-chain dicarboxylic acids involves the addition of dithiols to unsaturated acids. When dithiols are added to such compounds as 11-undecenoic acid or vinyl acetic acid in the presence of peroxides anti-Markownikoff products are formed (17).

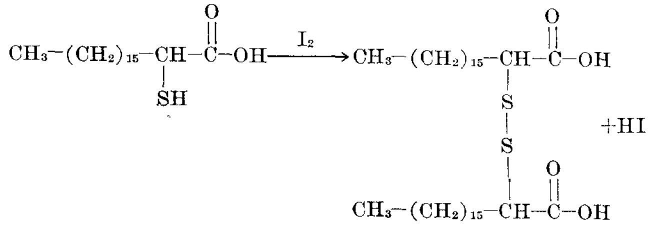


$$\begin{matrix}SH\\|\\(CH_2)_n\\|\\SH\end{matrix}+2CH_2=CH-(CH_2)_8-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{\text{peroxides}} \begin{matrix}S-(CH_2)_{10}-\overset{O}{\overset{\|}{C}}-OH\\|\\(CH_2)_n\\|\\S-(CH_2)_n-\overset{O}{\overset{\|}{C}}-OH\end{matrix}$$

Alkane bis-(11-thioundecanoic) acid

These dicarboxylic acids differ from the other dicarboxylic acids in that they contain two sulfur atoms, but like the other compounds, these acids are readily converted to the corresponding sulfones and esters (17).

Other sulfur-containing dicarboxylic long-chain acids are readily formed by mild oxidation of long-chain mercaptoacids to form the corresponding disulfide acids (10).



2,2′-dithiodistearic acid

Similarly, methyl 9(10) mercaptostearate has been converted to the corresponding disulfide (10).

Sulfur-containing polymers have been prepared from some of these dicarboxylic acids, i.e., heating at 90°C of 11-(acetylthio)-undecanoic acid with hexamethylene diamine results in the formation of polyamides (18). These polyamides (Mol Wt 11,000–20,000) have been converted into fibers.

Uses of Sulfur Derivatives of Long-Chain Acids. Patent literature contains references describing the commercial value of sulfur derivatives of long-chain acids. Some of these products are useful as lubricant additives, coatings, and rubber substitutes; however, from the point of view of an organic chemist, a great deal of work remains to be done. Studies of relationships of structures to properties must be continued before we can expect much greater benefits of these materials to the fat and oil industry.

REFERENCES

1. Dearborn, F. E., U. S. 2,169,793 (1939).
2. Ralston, A. W., E. W. Segebrecht, and S. T. Bauer, J. Org. Chem. *4*, 502 (1939).
3. Pratt, L. S., and E. E. Reid, J. Am. Chem. Soc. *37*, 1934 (1915).
4. Sasin, G. S., Richard Sasin, and N. Capron, J. Org. Chem. *21*, 852 (1956).
5. Sasin, Richard, W. F. Ashley, J. W. Manning, Jr., A. Paolinini, Jr., and G. S. Sasin, JAOCS *35*, 192 (1958).
6. Sasin, Richard, G. S. Weiss, A. E. Wilfond, and G. S. Sasin, J. Org. Chem. *21*, 1304 (1956).
7. Sasin, G. S., F. R. Longo, O. T. Chortyk, P. A. Gwinner, and Richard Sasin, J. Org. Chem. *24*, 2022 (1959).
8. Markley, K. S., Fatty Acids, Interscience Publishers, Inc., N.Y., 1947, page 521.
9. Kabayashi, F., and H. Susuki, U. S. 2,273,379 (1961).
10. Koenig, N. H., G. S. Sasin, and Daniel Swern, J. Org. Chem. *23*, 1525 (1958).
11. Sasin, G. S., P. R. Schaeffer, and Richard Sasin, J. Org. Chem. *22*, 1138 (1957).
12. Sasin, Richard, G. S. Binns, R. M. Haff, and G. S. Sasin, J. Org. Chem. *24*, 1143 (1959).
13. Koenig, N. H., and Daniel Swern, J. Am. Chem. Soc. *79*, 4235 (1957).
14. Henkel & Cie, G.m.b.H., Brit. Pat. 470,717 (1937).
15. Sasin, G. S., Sally Dym, L. Cerankowski, and Richard Sasin, unpublished results.
16. Koenig, N. H., and Daniel Swern, J. Am. Chem. Soc., *79*, 362 (1957).
17. Sasin, G. S., F. R. Longo, Richard Berger, Wm. DeSantis, and Richard Sasin, J. Org. Chem. *26*, 3538 (1961).
18. Champetier, G., and J. Khaladji, Bull. Soc. Chim., 823 (1958).

α-Sulfo Fatty Acids and Derivatives. Synthesis, Properties and Use

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SATURATED long chain fatty acids react with sulfur trioxide, chlorosulfonic acid or dioxane sulfur trioxide to give monosulfonation in the α-position. The reaction is simple, inexpensive and specific. The α-sulfo acid is a versatile intermediate for salts, esters, amides, and other derivatives. Use of α-sulfo compounds has been proposed in ore flotation, as surface active and detergent compositions, detergent bars, wetting agents, lime soap dispersing agents, as paint additives, and in lubricant greases.

The higher fatty acids can be sulfonated directly in the α-position by reaction with sulfur trioxide, chlorosulfonic acid, or dioxane sulfur trioxide. α-Sulfonation can be accomplished less directly by the Strecker reaction of an α-bromo fatty acid with sodium sulfite (23,27). Direct sulfonation of the higher saturated acids is specific and leads only to monosulfonation in the α-position. Reaction of sulfonating agents with unsaturated higher fatty acids is complex (29): the reaction of sulfur trioxide in liquid sulfur dioxide with oleic acid at −10C gives a product estimated to be about

55% $CH_3(CH_2)_7CH{=}CHCH(SO_3Na)(CH_2)_6CO_2Na$,

28% $CH_3(CH_2)_7CHOHCH(SO_3Na)(CH_2)_7CO_2Na$, and

17% $CH_3(CH_2)_7CH(OSO_3Na)CH(SO_3Na)(CH_2)_7CO_2Na$.

Studies on the lower aliphatic sulfocarboxylic acids carried out by Backer and collaborators over a period of several years have been summarized by de Boer (8).

The sulfonation of dicarboxylic acids such as glutaric, adipic, azelaic, or sebacic acids by means of liquid sulfur trioxide, with trichloroacetic acid as the solvent, results in monosulfonation at the α-position (16). Methods also exist for the direct sulfonation of amides, anhydrides, esters (24), soaps (11), and nitriles (6).

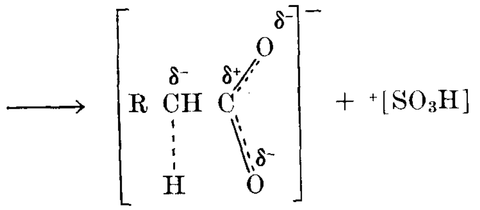
Mechanism of α-Sulfonation

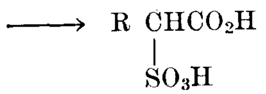
The direct sulfonation of saturated long chain fatty acids by means of the vapor of sulfur trioxide or with the stabilized liquid of sulfur trioxide, in the presence of a relatively inert solvent, appears to take place with the initial formation of a mixed anhydride. Further heating is necessary to convert this to the α-sulfo acid. Some evidence for the existence of the mixed anhydride can be found in the early literature on the lower sulfocarboxylic acids (15), also in the fact that perfluorobutyric acid reacts with SO_3 to form a mixed anhydride sufficiently stable to be purified by distillation (13).

α-Sulfonation apparently occurs as follows:

$$RCH_2CO_2H + SO_3 \longrightarrow RCH_2CO_2SO_3H$$

$$\longrightarrow [RCH_2CO_2]^- + {}^+[SO_3H]$$





$$\longrightarrow R\underset{SO_3H}{CH}CO_2H$$

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