in which the bond breaking is more important to the formation of the transition state than is bond making.[18]

This concept is in agreement with the known facts concerning the reaction: **1. Effect of Changing R.**—It has been shown that in the reactions of various Grignard reagents with hexyne-1,[4] the rate of reaction is proportional to the number of β-hydrogens of R. It has been proposed that this represents a stabilization of the incipient carbanion, R:⁻, by anionic hyperconjugation[19]
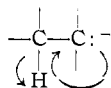
2. Effect of Changing R′.—In the reactions of ethylmagnesium bromide with various terminal acetylenes,[3] the rate of reaction is dependent upon the electron-withdrawing power (inductive effect) of R′ when steric factors are not important. Such inductive effects would render the terminal acetylenic hydrogen more labile, increasing the rate of reaction. However, when R′ is capable of preventing the "close approach" of the two reactants, because of steric factors, the formation of the transi-

(18) It should be noted that the present information does not exclude a three-center reaction, in which the first products are the alkane and an ion pair, provided that the collapse of the latter to give a covalent bond takes place rapidly, and is not in any way rate determining.

(19) The term hydridization was suggested for such resonance by J. H. Wotiz, C. A. Hollingsworth and R. E. Dessy, Abstracts of Papers, American Chemical Society Meeting, Kansas City, Mo., 1954, page 11N. Recently Seubold [*J. Org. Chem.*, **21**, 156 (1956)] has published a paper on the infrared absorption spectra of some sodium alkoxides, in which he describes some additional evidence for such anionic hyperconjugation.

tion state would be more difficult, thus decreasing the observed rate of reaction.

3. The Deuterium Isotope Effect.—A large deuterium isotope effect is noted in such reactions, indicating that the cleavage of the ≡C—H bond is involved in the rate-determining step and that bond breaking is more important than bond making in determining the activation energy.

4. The Kinetic Picture.—The rate laws obeyed by the various reactions are in agreement with the proposed reaction mechanism and with the equilibrium picture illustrated by equation 11.

5. The Effect of Dioxane.—The results obtained by adding dioxane to solutions of ethylmagnesium bromide[6] are in agreement with equation 11, indicating a shift in the equilibrium to the left. It was found that the rate of reaction of hexyne-1 with ethylmagnesium bromide in the presence of dioxane was dependent upon both the concentration of dioxane used and the time of contact between the Grignard reagent and the dioxane. The reactivity of such mixtures eventually approached that of diethylmagnesium.

6. The Effect of Magnesium Bromide.—The results obtained by adding magnesium bromide to solutions of diethylmagnesium[7] are in agreement with equation 11, indicating a shift in equilibrium to the right. It was found that the rate of reaction of hexyne-1 with diethylmagnesium in the presence of magnesium bromide was dependent upon the concentration of magnesium bromide used and on the time of contact between the Grignard reagent and the magnesium bromide. The reactivity of solutions with Br/Mg ratios of unity eventually approached that of ethylmagnesium bromide.

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Organic Sulfur Derivatives. I. Addition of Mercaptoacetic Acid to Long-chain Monounsaturated Compounds

BY N. H. KOENIG AND DANIEL SWERN

Sulfides are formed by the free-radical addition of mercaptoacetic acid to oleic acid, methyl oleate, methyl ricinoleate or 10-undecenoic acid. Diesters have been prepared by esterifying the product from oleic acid, 9(10)-(carboxymethylthio)-stearic acid and by treating n-butyl oleate with ethyl mercaptoacetate. The addition products are centrally branched long-chain molecules, except for 11-(carboxymethylthio)-undecanoic acid, and can be purified by separating the unreacted linear starting materials as urea complexes. In developing optimum reaction conditions, the yield of urea complexes serves as a key method of determining the extent of reaction. Supporting evidence for the structure of the products is provided by molecular refraction, infrared and X-ray data.

The patent literature contains many references to reactions of fats and their long-chain derivatives with sulfur, hydrogen sulfide, mercaptans, sulfur halides and phosphorus sulfides. The products have commercial value as lubricant additives, coatings and rubber substitutes, but little is known about their structure and chemistry. The aim of this program is to prepare and study clearly defined sulfur derivatives, starting with well characterized fatty compounds. The reaction selected

(1) A laboratory of the Eastern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.
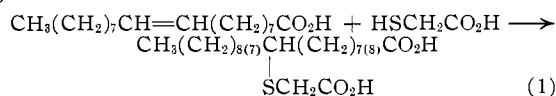
for initial study is the addition of a reactive mercaptan (mercaptoacetic acid) to the olefinic linkage of monounsaturated fatty acids or their esters. The addition of mercaptans to olefins is a well known reaction and generally follows a free-radical mechanism.[2]

Present Investigation.—Oleic acid reacts with mercaptoacetic acid to give a sulfide (thioether),

(2) F. R. Mayo and C. Walling, *Chem. Revs.*, **27**, 351 (1940); J. I. Cunneen, *J. Chem. Soc.*, 36 (1947); J. T. Hackmann and R. Berkenbosch, *Rec. trav. chim.*, **68**, 745 (1949); M. S. Kharasch, W. Nudenberg and G. J. Mantell, *J. Org. Chem.*, **16**, 524 (1951); B. Smith and S. Hernestam, *Acta Chem. Scand.*, **8**, 1111 (1951).

9(10)-(carboxymethylthio)-stearic acid (equation 1).

$$CH_3(CH_2)_7CH=CH(CH_2)_7CO_2H + HSCH_2CO_2H \longrightarrow$$
$$CH_3(CH_2)_{8(7)}CH(CH_2)_{7(8)}CO_2H$$
$$|$$
$$SCH_2CO_2H \qquad (1)$$

As predicted, the same addition product is obtained from elaidic acid. In a similar fashion, compounds containing both an acid group and an ester group are formed by the reaction of mercaptoacetic acid with fatty acid esters. The addition product with methyl oleate is methyl 9(10)-(carboxymethylthio)-stearate and with methyl ricinoleate is methyl 9(10)-carboxymethylthio-12-hydroxystearate.

Some diester derivatives are made by esterifying 9(10)-(carboxymethylthio)-stearic acid with the appropriate alcohol to form the dimethyl, dibutyl or di-(2-ethylhexyl) ester. A mixed diester, *n*-butyl 9(10)-(carbethoxymethylthio)-stearate (I), is formed by the reaction of *n*-butyl oleate with ethyl mercaptoacetate.

$$CH_3(CH_2)_{8(7)}CH(CH_2)_{7(8)}COOC_4H_9$$
$$|$$
$$SCH_2COOC_2H_5 \qquad (I)$$
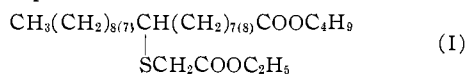
Mercaptoacetic acid also reacts very readily with terminally unsaturated 10-undecenoic acid. Whereas the preceding compounds are all liquids, the product from 10-undecenoic acid is a crystalline solid of sharp melting point. Depending on the mode of addition, it could be either a linear molecule, 11-(carboxymethylthio)-undecanoic acid (II) or a branched structure (III, the 10-isomer).

$$CO_2HCH_2S(CH_2)_{10}CO_2H \qquad CH_3CH(CH_2)_8CO_2H$$
$$II \qquad\qquad\qquad |$$
$$III \quad SCH_2CO_2H$$
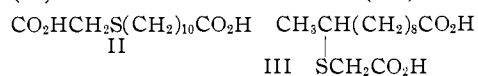
Infrared and X-ray data show that the linear isomer II is the chief or only product.

The above reaction is one of the two lines of evidence that support a free-radical mechanism for the addition of mercaptoacetic acid to monounsaturated fatty materials. In accordance with a radical mechanism, the carboxymethylthio group adds to the terminal carbon of 10-undecenoic acid, contrary to Markownikoff's rule. The other evidence is the enhancement of the rate of addition of mercaptoacetic acid to oleic acid by catalytic amounts of lauroyl peroxide.

Urea Complexes.—The formation of urea complexes is useful for purifying the crude reaction products.[3] Since the starting materials are long, linear molecules, and the products, except for 11-(carboxymethylthio)-undecanoic acid are centrally branched molecules too large to fit the urea channels, good separations are usually obtained. Urea also complexes with saturated fatty impurities in the starting materials and with *trans* unsaturated reaction by-products. The unsaturates separated as complexes are largely *trans*, although the starting materials are *cis*. Infrared spectra show that the *trans* unsaturates are present in the crude reaction products prior to the urea treatment.

Urea complexes were prepared in methanol solution, resulting in some methyl ester contamination in the case of 9(10)-(carboxymethylthio)-stearic

acid. Urea complex formation was only partially successful in purifying methyl ricinoleate reaction products. The hydroxyl group on the ricinoleate chain may have been responsible.

Reaction Variables.—In developing optimum reaction conditions, urea complex formation was a key method of determining the extent of reaction. Neutralization equivalents, elementary analyses for sulfur and refractive indices also served as general criteria of product purity, although these values were somewhat affected by variable side reactions.

The rate of mercaptan addition at 60° to a given fatty compound is generally increased by adding lauroyl peroxide or by increasing the excess of mercaptoacetic acid; conversion is increased by lengthening the reaction time. With 1% of lauroyl peroxide and 100% molar excess of mercaptoacetic acid, the conversion of oleic acid is essentially complete in 1 hr. Under these conditions, the conversion of elaidic acid is 87%, while that of methyl oleate is only 66%. Moreover, addition to methyl ricinoleate, whose sluggishness in addition reactions has been noted with formic acid,[4] is only one-third complete. An 89% conversion of methyl ricinoleate is achieved in 8 hr. with 2% of lauroyl peroxide and 133% excess of mercaptoacetic acid. On the other hand, the addition to 10-undecenoic acid, which has a double bond in the terminal position, is strikingly rapid. The conversion is at least 90% in 0.5 hr. with only a 20% excess of commercial mercaptoacetic acid and without catalyst.

Proof of Structure.—The structures of the (carboxymethylthio)-stearates were demonstrated by elementary analyses, functional group analyses, molecular refraction data and infrared spectra. The data for the esters of 9(10)-(carboxymethylthio)-stearic acid are given in Table I. The acid itself was obtained in at least 95% purity and was unequivocally characterized by conversion to ester derivatives. The structure of 11-(carboxymethylthio)-undecanoic acid was established by analytical data, the infrared spectrum and X-ray diffraction data. The purity of methyl 9(10)-carboxymethylthio-12-hydroxystearate was estimated at 85% from analytical and infrared data.

The infrared spectra of the dialkyl (carboxymethylthio)-stearates show two peaks that suggest a previously unreported structural correlation. These peaks are in the range 1271-1276 and 1128-1132 cm.$^{-1}$ in the four diesters and occur at 1276 and 1132 cm.$^{-1}$ in the dimethyl ester. Methyl oleate, *n*-butyl oleate and 9(10)-(carboxymethylthio)-stearic acid do not have peaks in these locations. They appear to be characteristic of the carbalkoxymethylthio group. The esters also show the usual absorption common to fatty esters,[5] as well as some differences arising from the alkyl groups; for example, the 1437 cm.$^{-1}$ carbomethoxy peak[6] occurs only in the dimethyl ester.

The best evidence for the linear structure of 11-(carboxymethylthio)-undecanoic acid is its infrared spectrum. This molecule, unlike the branched 10-isomer, has no methyl group. The spectrum

(4) H. B. Knight, R. E. Koos and D. Swern, This Journal, **75**, 6212 (1953).

(5) R. T. O'Connor, J. Am. Oil Chemists' Soc., **33**, 1 (1956).

(6) R. N. Jones and A. R. H. Cole, This Journal, **74**, 5648 (1952).

(3) D. Swern, Ind. Eng. Chem., **47**, 216 (1955).

TABLE I SCH₂COOR₂

ESTERS OF 9(10)-(CARBOXYMETHYLTHIO)-STEARIC ACID (CH₃(CH₂)₈₍₇₎CH(CH₂)₇ ₍₈₎ COOR₁)

Ester	Sapn. equiv. Calcd.	Sapn. equiv. Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found	d^{25}_4	n^{30}D	Molecular refraction Calcd.	Molecular refraction Found
R₁ = CH₃, R₂ = H	194	194	65.0	64.8	10.4	10.4	8.27	8.17	0.9860	1.4732	110.5	110.6
R₁ = R₂ = CH₃	201	201	65.6	65.9	10.5	10.8	7.96	8.09	.9688	1.4661	115.1	115.1
R₁ = n-C₄H₉, R₂ = C₂H₅	230	230	68.0	67.8	10.9	11.0	6.97	6.98	.9444	1.4628	133.7	133.7
R₁ = R₂ = n-C₄H₉	244	242	69.1	68.9	11.1	11.2	6.59	6.73	.9354	1.4623	143.1	142.8
R₁ = R₂ = C₄H₉CH(C₂H₅)CH₂	299	302	72.2	71.7	11.7	12.0	5.36	5.37	.9205	1.4645	179.7	179.5

has no peak in the range 1370–1385 cm.⁻¹, characteristic of the methyl group in hydrocarbons[7] and in long-chain fatty acids.[8] 9(10)-(Carboxymethylthio)-stearic acid, on the other hand, has a methyl group absorption at 1380 cm.⁻¹.

Supporting evidence for the linear structure of 11-(carboxymethylthio)-undecanoic acid was obtained from its X-ray diffraction pattern. The long spacing of high intensity was 15.7 Å.; there was also a very weak long spacing of 12.4 Å. The prominent side spacings were at 4.09 and 3.74 Å. These data may be compared to values for the C₁₄-dibasic acid, CO₂H·(CH₂)₁₂·CO₂H, allowing for a carbon-to-sulfur distance of 1.82 Å. instead of a carbon-to-carbon distance of 1.54 Å. Provided the assumption is made that the two molecules are tilted at the same angle, there is good agreement with the values for the C₁₄-dibasic acid (long spacing, 15.4 Å; side spacings, 4.13 and 3.71 Å.).[9]

Experimental

Starting Materials.—Oleic acid (iodine number 86.5, containing 4% saturates and less than 0.2% polyunsaturates) was prepared from olive oil by saponification and low-temperature crystallization.[10] Butyl oleate (sapn. equiv. 336.4, n^{20}D 1.4512) was made by esterifying oleic acid of 93% purity. Methyl oleate (iodine number 85.4, 99% purity) was prepared from methyl esters of olive oil by multiple fractional distillation and low-temperature crystallization from acetone. Methyl ricinoleate (iodine number 83.0) was obtained from castor oil by methanolysis and fractional distillation.[11] Elaidic acid (m.p. 44°, iodine number 84.6, 6% saturates) was prepared by isomerization of oleic acid with selenium.[12] Mercaptoacetic acid, ethyl mercaptoacetate and 10-undecenoic acid were purified by fractional distillation of the best commercial materials. In the reaction with 10-undecenoic acid, however, commercial mercaptoacetic acid, b.p. 104–107° at 10 mm., was used as received. Lauroyl peroxide was technical grade.[13]

9(10)-(Carboxymethylthio)-stearic Acid.—In a typical experiment, 8.9 g. of oleic acid (0.031 mole), 5.8 g. of mercaptoacetic acid (0.063 mole) and 0.1 g. of lauroyl peroxide were heated under nitrogen at 60–65° for 6 hr. (Occasionally the initial reaction was very exothermic.) The reaction mixture was diluted with an equal volume of ether. It was then washed with 30-ml. portions of water, adding ether to maintain the volume of the organic phase, until the water washings were essentially free of acid. Only 0.5 ml. of 0.1 N alkali was required to neutralize the seventh wash.

The ether phase was evaporated in a stream of nitrogen at 100° and 15 mm. pressure, yielding 6.3 g. of a colorless liquid, neut. equiv. 194, n^{30}D 1.4787.

To determine the extent of reaction, 5.00 g. of the above liquid was dissolved in a hot solution of 7.5 g. of urea in 19 ml. of methanol. The precipitate that formed on cooling was filtered and washed with five 1-ml. portions of urea-saturated methanol. The precipitate (5.2 g.) was dissolved in a mixture of 10 ml. of water and 4 ml. of carbon tetrachloride. The aqueous layer was discarded, and the organic layer was washed with three 10-ml. portions of water. Subsequent evaporation of the organic phase at 50° and 15 mm. gave 0.16 g. of a white solid.

The filtrate from the urea complex was evaporated to one-half volume, diluted with carbon tetrachloride and washed with water until the organic phase was free of urea. Evaporation at reduced pressure gave 4.65 g. of crude 9(10)-(carboxymethylthio)-stearic acid (neut. equiv., 202; sapn. equiv., 181).

For purification by low temperature crystallization,[11] 1.00 g. of 9(10)-(carboxymethylthio)-stearic acid (94% pure, 9.4% sulfur, neut. equiv. (193) was diluted to 2.0 ml. with acetone, cooled to −20° and centrifuged. The supernatant liquid was rejected, and the precipitate was diluted with acetone to 2.6 ml. This solution was cooled to −20° and centrifuged. The supernatant liquid was decanted and evaporated to give 0.53 g. of liquid residue, purified 9(10)-(carboxymethylthio)-stearic acid.

Anal. Calcd. for C₂₀H₃₈O₄S: C, 64.2; H, 10.2; S, 8.56. Found: C, 63.3; H, 10.1; S, 8.94.

Occasionally, excess mercaptan was removed by reduced-pressure distillation, although this usually gave less pure products than those obtained by the water-washing procedure. A larger-scale preparation of 9(10)-(carboxymethylthio)-stearic acid illustrates the distillation procedure. Oleic acid (293 g., 1.0 mole) was added dropwise with stirring to 1.3 moles (116 g.) of mercaptoacetic acid. The mixture was heated for 1 hr. at 100°, and excess mercaptoacetic acid was distilled off under reduced pressure. Portions of the product (380 g., purity 74%) were used to prepare the dimethyl, dibutyl and di-(2-ethylhexyl) esters described later.

Treatment of 5.0 g. of the above product (8.63% sulfur, neut. equiv. 200) by the urea method gave the following fractions: From urea complex: 1.3 g. of solid, m.p. 37°; neut. equiv., 299; sulfur, 0.68%; iodine number, 75; *trans* double bond by infrared analysis,[15] 79%; non-complex: 3.7 g. of liquid; neut. equiv., 218; sapn. equiv., 185; sulfur, 8.12%.

Elaidic acid (11.3 g., 0.04 mole) was treated with mercaptoacetic acid (7.4 g., 0.08 mole) for 1 hour at 60° with 1% of lauroyl peroxide. The product (10.2 g.) was chiefly 9(10)-(carboxymethylthio)-stearic acid, as shown by the infrared spectrum of the non-complex fraction from the urea separation. The product from the urea complex was a solid with an iodine number of 89 and 67% of *trans* double bond.

Methyl 9(10)-(Carboxymethylthio)-stearate.—Fifty-six grams (0.21 mole) of methyl oleate, 30 g. (0.33 mole) of mercaptoacetic acid and 0.5 g. of lauroyl peroxide were heated at 60° for 4 hr. During this time, 15 g. of the mixture was removed for analysis and an additional 1.0 g. of lauroyl peroxide was added. The remaining mixture, after washing and evaporation, gave 46 g. of liquid, n^{30}D 1.4725.

Anal. Calcd. for C₂₁H₄₀O₄S: S, 8.27; neut. equiv., 389. Found: S, 8.26; neut. equiv., 386.

(7) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954.

(8) O. D. Shreve, M. R. Heether, H. B. Knight and D. Swern, *Anal. Chem.*, **22**, 1498 (1950).

(9) A. R. Normand, J. D. M. Ross and E. Henderson, *J. Chem. Soc.*, 2632 (1926).

(10) H. B. Knight, E. F. Jordan, Jr., E. T. Roe and D. Swern, *Biochem. Preparations*, **2**, 100 (1952).

(11) D. Swern and E. F. Jordan, Jr., *ibid.*, **2**, 104 (1952).

(12) D. Swern, H. B. Knight, O. D. Shreve and M. R. Heether, *J. Am. Oil Chemists' Soc.*, **27**, 17 (1950).

(13) Alperox C, Lucidol Division, Wallace and Tiernan Incorporated, Data Sheet 3. Reference to a company name is intended to be descriptive only and does not constitute a recommendation of the product of the company mentioned.

(14) J. B. Brown, *J. Am. Oil Chemists' Soc.*, **32**, 646 (1955).

(15) O. D. Shreve, M. R. Heether, H. B. Knight and D. Swern, *Anal. Chem.*, **22**, 1261 (1950).

Treatment with urea removed 1% of material as complex and raised the refractive index slightly (n^{30}D 1.4732) but did not change the neutralization equivalent (see Table I for other analyses).

In another run, an almost pure product was obtained by a distillation procedure. Methyl oleate (8.9 g., 0.03 mole) and mercaptoacetic acid (5.6 g., 0.06 mole) were heated at 95° for 0.5 hr. Excess mercaptoacetic acid was distilled off at 140° at 0.5 mm., leaving 12.0 g. of residue (neut. equiv., 386; sapn. equiv., 185). Distillation at 0.2 mm. in an alembic apparatus gave 6.8 g. of methyl 9(10)-(carboxymethylthio)-stearate.

Anal. Calcd.: C, 65.0; H, 10.4; S, 8.27; neut. equiv., 389; sapn. equiv., 194. Found: C, 64.4; H, 10.2; S, 8.66; neut. equiv., 387; sapn. equiv., 188.

Methyl 9(10)-Carboxymethylthio-12-hydroxystearate.—Methyl ricinoleate (9.4 g., 0.03 mole), mercaptoacetic acid (6.0 g., 0.07 mole) and lauroyl peroxide (0.1 g.) were heated at 60° for 4 hr. Another 0.1 g. of lauroyl peroxide was added and heating was continued for 4 hr. longer. After washing and evaporation, 12.2 g. of liquid remained (n^{30}D 1.4809; sulfur, 8.13%; neut. equiv., 470; sapn. equiv., 200). Urea treatment removed 12% of product as complex, leaving crude methyl 9(10)-carboxymethylthio-12-hydroxystearate (n^{30}D 1.4832) in the filtrate.

Anal. Calcd. for $C_{21}H_{40}O_5S$: S, 7.93; neut. equiv., 405; sapn. equiv., 202. Found: S, 8.48; neut. equiv., 446; sapn. equiv., 191.

Dimethyl 9(10)-(Carboxymethylthio)-stearate.—Ninety-seven grams (0.26 mole) of 9(10)-(carboxymethylthio)-stearic acid (74% pure), 2% by weight (1.9 g.) of naphthalene-2-sulfonic acid catalyst and 153 g. (4.8 moles) of methanol were refluxed for 8 hr. The reaction mixture was washed with water until neutral and dried at 100° under moderate vacuum. The product, 97 g., was fractionated by the urea method. The fraction isolated from the urea complex, 23 g., was chiefly methyl elaidate. The non-complex fraction, 57 g., was further purified by distillation through a heated 2-foot Vigreux column attached to a diffusion pump. The fraction boiling at 209° at 1 mm. weighed 37 g. (see Table I for analysis).

Di-*n*-butyl 9(10)-(Carboxymethylthio)-stearate.—Seventy-five grams (0.2 mole) of 9(10)-(carboxymethylthio)-stearic acid (74% pure), 1.9 g. of naphthalene-2-sulfonic acid and 89 g. (1.2 moles) of *n*-butyl alcohol were mixed with 250 ml. of benzene as entraining agent. The mixture was refluxed with azeotropic removal of water (6 hr.). After the product had been washed free of acid, benzene and excess butanol were distilled off at reduced pressure. The residue was distilled in an alembic type flask connected to a diffusion pump. The fractions boiling at 150–200° at 0.08 mm. weighed 56 g. (see Table I for center cut analysis).

Di-(2-ethylhexyl) 9(10)-(Carboxymethylthio)-stearate.—Seventy-five grams (0.2 mole) of 9(10)-(carboxymethyl-thio)-stearic acid (74% pure), 1.5 g. of naphthalene-2-sulfonic acid, 130 g. (1.0 mole) of 2-ethyl-1-hexanol and 200 ml. of toluene were refluxed for 4 hr. with azeotropic removal of water. Further treatment by the procedure for dibutyl ester gave 65 g. of product boiling at 204–210° at 0.01 mm. (Table I for analysis).

Butyl 9(10)-(Carbethoxymethylthio)-stearate.—Eighty grams (0.24 mole) of *n*-butyl oleate was added dropwise to 35 g. (0.29 mole) of ethyl mercaptoacetate containing a trace of ascaridole. During the addition of the first 25 ml. of butyl oleate, no significant temperature rise was noted as evidence of reaction. Therefore, 0.8 g. of lauroyl peroxide was added, causing a 10° temperature rise. The temperature was raised to 75° while adding the remaining butyl oleate and kept at 75° for an additional 16 hr. The solution was then heated for 7 hr. at 110°, and excess ethyl mercaptoacetate was distilled off at reduced pressure. Subsequent distillation in an alembic apparatus gave 35 g. of a fraction boiling at 128–152° at 0.003 mm. (Table I for analysis).

11-(Carboxymethylthio)-undecanoic Acid.—Ten grams (0.054 mole) of 10-undecenoic acid and 6.0 g. (0.065 mole) of mercaptoacetic acid were stirred for a few minutes (air atmosphere). Heat was evolved and a solid began to separate. The mixture was liquefied by heating and kept at 90° for 0.5 hr.; then 25 ml. of carbon tetrachloride was added. The precipitate that separated on cooling was filtered with suction and washed with small portions of chilled carbon tetrachloride and petroleum ether. Vacuum drying gave 13.4 g. of white solid, m.p. 96-98°, neut. equiv., 143. Two recrystallizations from carbon tetrachloride gave a granular solid, m.p. 99°, recovery 87%. A final recrystallization from acetonitrile gave a crystalline product, m.p. 99°.

Anal. Calcd. for $C_{13}H_{24}O_4S$: C, 56.5; H, 8.75; S, 11.6. Found: C, 56.4; H, 8.72; S, 11.7.

Analytical and Physical Data.—Under conventional procedures, the present compounds tend to flash during the carbon–hydrogen analysis, giving low values. Satisfactory results were achieved by adding tungstic oxide.[16] The spectra of the liquid compounds were recorded as thin films with a Beckman IR-3 infrared spectrophotometer, using sodium chloride optics. The infrared spectrum of 11-(carboxymethylthio)-undecanoic acid was run on a pressed potassium bromide disk (preground in a mechanical vibrator[17]) in a Perkin–Elmer model 21 spectrophotometer equipped with a sodium chloride prism. The X-ray diffraction pattern was obtained with a direct recording General Electric diffraction unit, using filtered CuKα radiation. The crystalline sample was finely ground to reduce orientation effects.

PHILADELPHIA 18, PENNA.

(16) R. Belcher, J. E. Fildes and A. J. Nutten, *Anal. Chim. Acta,* **13**, 431 (1955).

(17) J. J. Kirkland, *Anal. Chem.,* **27**, 1537 (1955)