

sodium dissolved in 10 ml. of absolute ethanol was added 3.98 g. (0.0195 mole) of diethyl formamidomalonate. To this solution was added 4.92 g. (0.0195 mole) of VIIId in 15 ml. of ethanol. The mixture was refluxed for 5 hr. and then evaporated to dryness under reduced pressure. One hundred ml. of water was added with stirring, the solid removed by filtration and recrystallized from ethanol; yield 4.6 g. (63%), m.p. 236–240°. A sample was recrystallized from dioxane–heptane for analysis, m.p. 239–240°.

*p*-Sulfamylphenylalanine (VII).—The amino acid hydrochloride was obtained by refluxing 21 g. (0.056 mole) of

VIIe with 200 ml. of concentrated hydrochloric acid for 5 hr. The solution was evaporated to dryness under reduced pressure. The hydrochloride salt was dissolved in 100 ml. of water and the solution passed through a column of Duolite A-2 ion-exchange resin to obtain the free amino acid. The resulting solution was evaporated to 125 ml. under reduced pressure and 100 ml. of acetone added. The solution was cooled overnight and the crude product was collected; yield 10.5 g. (76%), m.p. 248–249° dec. A sample was recrystallized from water–acetone for analysis, m.p. 251–252° dec.

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[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY<sup>1</sup>]

## Organic Sulfur Derivatives. II.<sup>2</sup> Sulfides, Sulfoxides and Sulfones from Thiols and 10-Undecenoic Acid

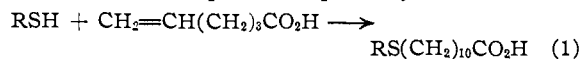
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Sulfides are formed by the addition of thiols (RSH) to 10-undecenoic acid (equation 1). The reactions proceed moderately rapidly at temperatures below 100° under free-radical conditions, often with the assistance of ultraviolet light. The acids [RS(CH<sub>2</sub>)<sub>10</sub>CO<sub>2</sub>H] have a terminal substituent R, which is alkyl (propyl, butyl, hexyl, heptyl, octyl, undecyl or dodecyl), hydroxyethyl, carboxymethyl, acetyl, benzyl, phenyl or 2-naphthyl. Some of the sulfides have been oxidized to sulfoxides by bromate–bromide solution; many have been oxidized to sulfones by peracetic acid. However, an attempt to prepare the sulfone of 11-(acetylthio)-undecanoic acid yielded 11-sulfoundecanoic acid. Other compounds prepared include diesters of 11-(carboxymethylthio)-undecanoic acid and a sulfonium salt, methyl-*n*-octyl-10-carboxydecylsulfonium iodide.

This investigation continues our systematic study of the preparation of long-chain sulfur compounds of known structure. In our first paper<sup>2</sup> it was shown that a high yield of 11-(carboxymethylthio)-undecanoic acid readily is obtained by the addition of an equimolar amount of mercaptoacetic acid to 10-undecenoic acid. We have now shown that this reaction is general. It has been extended to include many other thiols; the resulting (alkylthio)- and (arylthio)-undecanoic acids have been converted in many instances to sulfoxides, sulfones, esters and other derivatives. Aside from 11-(carboxymethylthio)-undecanoic acid,<sup>3</sup> 11-(*n*-dodecylthio)-undecanoic acid<sup>3</sup> and 11-sulfoundecanoic acid,<sup>4</sup> all of the compounds described in this paper are new. Some similar alkylthio, alkylsulfinyl and alkylsulfonyl acids, prepared in different ways, have been reported.<sup>5,6</sup>

Alkanethiols add moderately rapidly to 10-undecenoic acid as shown in equation 1. Previous evidence,<sup>2</sup> as well as infrared and X-ray diffraction studies to be reported separately, indicates that



R = *n*-propyl, butyl, hexyl, heptyl, octyl, undecyl or dodecyl.

the addition products isolated have an unbranched structure, *i.e.*, the sulfur atom is attached at the 11-(terminal) rather than at the 10-position, and

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(2) Paper I, N. H. Koenig and D. Swern, *THIS JOURNAL*, **79**, 362 (1957).

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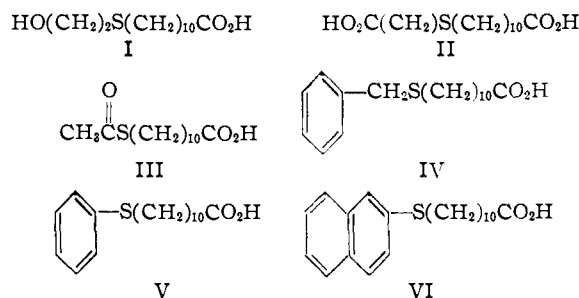
(4) W. Rigby, *J. Chem. Soc.*, 2560 (1956).

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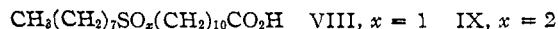
that they are formed *via* free-radical intermediates. The free-radical addition mechanism is also supported by the activating influence of ultraviolet light.

Other types of terminally substituted undecanoic acids, (I–VI) are formed by the addition of mercaptoethanol, mercaptoacetic acid, thiolacetic acid,  $\alpha$ -toluenethiol, benzenethiol or 2-naphthalenethiol, respectively.



The pure acids, RS(CH<sub>2</sub>)<sub>10</sub>CO<sub>2</sub>H, are odorless, white, crystalline solids. They are insoluble in water, sparingly soluble in petroleum ether at room temperature or 0° and moderately soluble in more polar solvents such as acetone and ethanol. Other characteristics of these compounds are given in Table I.

The chemical behavior of these sulfides is illustrated by some reactions of 11-(*n*-octylthio)-undecanoic acid, CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>S(CH<sub>2</sub>)<sub>10</sub>CO<sub>2</sub>H (VII). Controlled oxidation with bromate–bromide solution gives the sulfoxide VIII, while excess peracetic acid forms the sulfone IX. Methyl iodide adds to



VII to give the sulfonium salt, methyl-*n*-octyl-10-carboxydecylsulfonium iodide (X). The carboxyl



and  $\alpha$ -toluenethiol, which were Practical Grade. Peracetic acid (approximately 40%) in acetic acid was used as received.

**Sulfides (Table I).** 11-(*n*-Heptylthio)-undecanoic Acid (XIII).—The following reaction conditions are typical. 10-Undecenoic acid (45.6 g., 0.25 mole) and *n*-heptanethiol (33.3 g., 0.25 mole) were mixed in a quartz flask. No noticeable change occurred in 16 hr. The solution was then irradiated at a distance of 1 inch by a 140 watt ultraviolet lamp (high pressure quartz mercury arc). Within 3 minutes, a precipitate formed on the walls of the flask (internal temperature, 35°). After 1 hr., during which the temperature rose to 80°, the extent of reaction was checked by cooling the solution to room temperature. Since the mixture was only about one-fifth solid, it was irradiated for 2 more hr. The reaction product, which appeared entirely solid at room temperature, was crystallized three times at 4° from 600-ml. portions of petroleum ether, yielding 49 g. of XIII as transparent crystals, m.p. 53–54° (62% yield). All melting points were obtained with a micro hot-stage.

Ultraviolet irradiation was unnecessary in the addition of mercaptoethanol, which resembles mercaptoacetic acid in being an unusually reactive thiol.<sup>2</sup> Compound I was formed simply by stirring mercaptoethanol and 10-undecenoic acid for 1.5 hr. at 60°. The crude product was recrystallized three times from acetone-petroleum ether and once from acetonitrile (m.p. 69°). An additional recrystallization from carbon tetrachloride yielded the analytical sample, m.p. 70°.

In the preparation of V, 1% of lauroyl peroxide catalyst was substituted for ultraviolet irradiation, and the mixture was heated overnight at 60° (yield 61%). This reaction was the only one conducted under a nitrogen atmosphere.

**Methyl-*n*-octyl-10-carboxydecylsulfonium Iodide (X).**—A solution of VII (1.0 g., 0.003 mole) in methyl iodide (4.9 g., 0.035 mole) was sealed and left in the dark for 8 days. The resulting precipitate was washed with ether and dissolved in 5 ml. of methanol. Addition of 85 ml. of ether precipitated an oil that changed to a solid when rubbed with a glass rod. Filtration and drying gave 0.55 g. of X as a pale yellow solid, m.p. 68–70°.

*Anal.* Calcd. for C<sub>20</sub>H<sub>41</sub>IO<sub>2</sub>S: I, 26.9; S, 6.79; neut. equiv., 473. Found: I, 27.1; S, 7.07; neut. equiv., 453.

***p*-Bromophenacyl 11-(*n*-Octylthio)-undecanoate.**—VII was converted to the *p*-bromophenacyl ester by the conventional procedure.<sup>11</sup> Recrystallization of the ester from ethanol gave white platelets, m.p. 73°.

*Anal.* Calcd. for C<sub>27</sub>H<sub>43</sub>BrO<sub>2</sub>S: Br, 15.2; S, 6.08. Found: Br, 14.9; S, 5.71.

**Di-*n*-butyl 11-(Carboxymethylthio)-undecanoate.**—II was esterified with *n*-butyl alcohol by a published procedure,<sup>3</sup> giving an 84% yield of product, b.p. 138° at 0.003 mm.

*Anal.* Calcd. for C<sub>21</sub>H<sub>40</sub>O<sub>4</sub>S: C, 64.9; H, 10.4; S, 8.25. Found: C, 65.0; H, 10.9; S, 8.09.

**Di-(2-ethylhexyl) 11-(Carboxymethylthio)-undecanoate.**—Esterification of II with 2-ethylhexyl alcohol gave a 58% yield of product, b.p. 168° at 0.0005 mm.

*Anal.* Calcd. for C<sub>29</sub>H<sub>56</sub>O<sub>4</sub>S: C, 69.5; H, 11.3; S, 6.40. Found: C, 69.6; H, 11.5; S, 6.13.

**Sulfoxides.**—The (sulfinyl)-undecanoic acids (Table II) were prepared by dissolving or suspending the sulfide in

glacial acetic acid acidified with hydrochloric acid and adding 0.5 *N* bromate-bromide solution dropwise.<sup>4</sup>

**11-(*n*-Octylsulfinyl)-undecanoic Acid (VIII).**—Crude VIII (m.p. 79–86°, neut. equiv. 345, yield 91%) was dissolved in boiling acetone-petroleum ether (4:1) and crystallized at 4° to yield analytically pure VIII as white platelets, m.p. 88°.

**11-(Carboxymethylsulfinyl)-undecanoic Acid.**—This sulfide was fairly soluble in aqueous acetic acid and was recovered in low yield. The best material was a white powder or needles, m.p. 91–92°.

**11-(Phenylsulfinyl)-undecanoic Acid.**—The crude product was purified by dissolving it in acetone and adding 5 volumes of petroleum ether. The resulting oil, when rubbed with a glass rod, gave a white powder, m.p. 60–61°, in 90% yield.

**Sulfones.** 11-(*n*-Heptylsulfonyl)-undecanoic Acid (XIV).—Most of the sulfones (Table II) were prepared by slight modifications of the following procedure. XIII (15.8 g., 0.05 mole) was suspended in 100 ml. of acetic acid. Peracetic acid (20 ml. of 40% acid, 0.12 mole) was added, with stirring, over a 15-minute period. The rate of addition was controlled so that the maximum temperature of the resulting solution was 70°. Little or no heat was evolved during the addition of the last 5 ml. of peracetic acid. A positive starch-iodide paper test for excess peracetic acid was obtained a few minutes after its addition was completed. As the solution cooled, a heavy precipitate formed; it was stirred with 400 ml. of water, filtered through a coarse fritted disk, washed with water and vacuum dried. The product, a microcrystalline solid, weighed 17.1 g. (yield 98%), neut. equiv. 346, m.p. 110–111°. One gram of this solid was recrystallized from 80 ml. of acetonitrile, yielding 0.45 g. of white needles of analytically pure XIV, m.p. 111–112°.

**11-(2-Hydroxyethylsulfonyl)-undecanoic Acid (XV).**—The gel-like original product was dissolved in ethyl acetate, and the solution was dried with sodium sulfate. Addition of petroleum ether precipitated XV as a white powder, m.p. ca. 94–96°.

**11-(Carboxymethylsulfonyl)-undecanoic Acid.**—The solid that precipitated from aqueous acetic acid was gelatinous. It was difficult to filter and dry, and it melted at 122–126°. Three recrystallizations from acetonitrile gave the analytical sample, a granular crystalline solid, m.p. 140–141°.

**11-(Benzylsulfonyl)-undecanoic Acid.**—Water was not added after the peracetic acid. Instead, the mixture was evaporated to constant weight in a vacuum desiccator containing excess sodium hydroxide and a dehydrating agent. The crude solid (m.p. 104–112°) was recrystallized from acetone-petroleum ether, forming a white powder, m.p. 126–127° (93% yield).

**11-Sulfoundecanoic Acid (XVI).**—After adding peracetic acid to the acetic acid solution of III, the reaction mixture was dried over sodium hydroxide under vacuum at 25°. The crude product, m.p. 59–62°, neut. equiv. 141, corresponded to 11-sulfodecanoic acid hemihydrate, m.p. ca. 65°, neut. equiv. 138.<sup>4</sup> An ether-insoluble fraction was separated and discarded; the ether-soluble acid was purified by recrystallization from ether-benzene. Vacuum desiccation at room temperature gave anhydrous XVI, m.p. ca. 94° (reported<sup>4</sup> ca. 99° and 95–99° by two other methods of preparation).

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