[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

1-DODECANESULFINIC ACID

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In connection with a study of aliphatic sulfinic acids as activators for Redox type polymerization (1) we have had occasion to prepare for the first time a pure crystalline aliphatic sulfinic acid, 1-dodecanesulfinic acid. Autenrieth (2) has reported the isolation of pure benzenesulfinic acid, but he found that the aliphatic acids were unstable, and did not accomplish their isolation. 1-Dodecanesulfinic acid appears to be considerably more stable than the lower alkanesulfinic acids but on standing for two months or on heating to 100° for a few hours it undergoes the disproportionation reaction reported for aliphatic sulfinic acids by von Braun and Weissbach (3) to yield 1-dodecyl 1-dodecanethiolsulfonate (I) and 1-dodecanesulfonic acid. When an excess of sulfur dioxide was used in the

$$3C_{12}H_{25}SO_2H \rightarrow \underset{\text{I}}{C_{12}H_{25}SO_2SC_{12}H_{25}} + C_{12}H_{25}SO_3H + H_2O$$

preparation of the magnesium salt of the sulfinic acid from 1-dodecylmagnesium bromide by the procedure of Houlton and Tartar (4), the free sulfinic acid was formed and underwent disproportionation. The magnesium salt of the sulfinic acid was slowly oxidized in the air to the corresponding sulfonic acid salt.

We also investigated the Ziegler and Connor (5) cleavage of ethane disulfones by sodium cyanide as a route to the salts of the higher aliphatic sulfinic acids. This reaction gave a good yield of sodium 1-dodecanesulfinate but was unsatisfactory as a method of preparation of sodium 6-dodecanesulfinate.

1-Dodecanesulfinic acid reacted with 1-dodecanethiol in boiling ether to produce a high yield of 1-dodecyl 1-dodecanethiolsulfonate. von Braun and Weissbach (3) write the equation for the reaction of *n*-butanesulfinic acid and benzyl mercaptan as follows:

$$2C_4H_9SO_2H + 2C_6H_5CH_2SH \rightarrow C_4H_9SO_2SC_4H_9 + C_6H_5CH_2SSCH_2C_6H_5 + 2H_2O$$

In the case of our reaction between 1-dodecanethiol and 1-dodecanesulfinic acid this equation does not seem to account for the products isolated. When equal molar quantities of the two reactants were used the yield of thiol ester was double that which should be obtained on the basis of the von Braun equation. Also when 0.02 mole of acid and 0.0067 mole of mercaptan were used the yield was more than twice that possible in the von Braun reaction. No dodecyl disulfide was obtained in either experiment. Heating the sulfinic acid under the same conditions in the absence of the mercaptan did not yield the thiolsulfonate.

These results support the views of Kharasch, Potempa, and Wehrmeister (6) that sulfenic acids are probable intermediates in reactions which involve sulfinic

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acids. The formation of thiolsulfonate from a free sulfinic acid has been attributed to the combination of two simpler reactions:

$$2RSO_2H \rightarrow RSOH + RSO_3H$$

$$RSO_2H + RSOH \rightarrow RSO_2SR + H_2O$$

It is also reported that sulfenic acids disproportionate in similar fashion to give a number of products including disulfides.

$$2RSOH \rightarrow RSH + RSO_2H$$

$$RSOH + RSH \rightarrow RSSR + H_2O$$

Consideration of the above relations leads to the suggestion that a sulfinic acid could react with a mercaptan to yield a sulfenic acid.

$$RSO_2H + RSH \rightleftarrows 2RSOH$$

The products which von Braun and Weissbach isolated could then be explained by the following sequence of reactions:

$$C_6H_5CH_2SH + C_4H_9SO_2H \rightarrow C_6H_5CH_2SOH + C_4H_9SOH$$

$$C_6H_5CH_2SH + C_6H_5CH_2SOH \rightarrow C_6H_5CH_2SSCH_2C_6H_5 + H_2O$$

$$C_4H_9SO_2H + C_4H_9SOH \rightarrow C_4H_9SO_2SC_4H_9 + H_2O$$

If the combination of sulfenic acid with sulfinic acid to yield thiolsulfonate is more rapid than the reaction between sulfenic acid and mercaptan to give disulfide in the case of dodecyl derivatives, these reactions would account for the yields and the products which we have obtained in our experiments.

Koenigs (7) reported that nitrous acid converts benzenesulfinic acid to N,N-di(benzenesulfonyl)hydroxylamine (II).

$$2C_6H_5SO_2H + HONO \rightarrow \underset{\text{II}}{(C_6H_5SO_2)_2\,NOH} + H_2O$$

Since we were using nitrous acid titration to determine the sulfinic acid content of our various materials (2) we have determined the products of the reaction in the case of 1-dodecanesulfinic acid. When exactly equivalent amounts of nitrous acid and sulfinic acid were used, the principal product of the reaction was N,N-di(1-dodecanesulfonyl)hydroxylamine (III) with a trace of a byproduct tri-(1-dodecanesulfonyl)amine oxide (IV). When an excess of nitrous acid was used with the sulfinic acid, the amine oxide derivative (IV) became the major product.

$$\underset{\text{III}}{(C_{12}H_{25}SO_2)_2NOH} \qquad \underset{\text{IV}}{(C_{12}H_{25}SO_2)_3NO}$$

Treatment of the hydroxylamine derivative with nitric acid in glacial acetic acid also gave the amine oxide derivative. Zuckschwerdt (8) and Koenigs (9) have reported similar amine oxide derivatives by treatment of aliphatic and aromatic sulfinic acids with fuming or concentrated nitric acid. We have observed that the hydroxylamine derivative (III) decomposes on standing at room temperature to yield the amine oxide derivative (IV) and oxides of nitrogen.

In seeking a solid derivative for the identification of 1-dodecanesulfinic acid we have treated its sodium salt with chloroacetic acid and thus obtained 1-dodecanesulfonyl acetic acid which is easily purified and melts sharply at 108–109°.

EXPERIMENTAL

1-Dodecanesulfinic acid. The Grignard reagent prepared from 125 g. (0.5 mole) of 1-bromododecane in 500 cc. of ether was treated with 32 g. (0.5 mole) of sulfur dioxide at −40° to −35° as described by Houlton and Tartar (4a) and Allen (4b). The reaction mixture was poured into a cold aqueous ammonium chloride solution and the insoluble magnesium 1-dodecanesulfinate was thoroughly washed with water. The salt was air dried and extracted with ether and with carbon tetrachloride. Evaporation of the ether extracts yielded 8 g. of a waxy hydrocarbon which melted at 51–51.5° after crystallization from 95% ethanol. Krafft (10) has reported the melting point of *n*-tetracosane as 51.1°. The magnesium salt was further washed thoroughly with hot 95% ethanol to remove any magnesium 1-dodecanesulfonate. The yield of magnesium 1-dodecanesulfinate dihydrate thus obtained was 105 g. (80%).

Two grams of freshly prepared magnesium 1-dodecanesulfinate dihydrate was ground to a fine powder and extracted first with two 50-cc. portions of boiling 95% ethanol and then with two 50-cc. portions of diethyl ether. The remaining powder was shaken with 100 cc. of 2% aqueous hydrochloric acid and 50 cc. of diethyl ether. The ether layer was separated, washed with two 100-cc. portions of water and filtered. The ether was distilled under reduced pressure and the crystalline residue was dried in a desiccator at 0.15 mm. pressure. The yield was 1.7 g. (96%) of 1-dodecanesulfinic acid, m.p. 29–30°. The material was analyzed within twenty-four hours of its preparation.

Anal. Calc'd for $C_{12}H_{26}O_2S$: C, 61.49; H, 11.18; S, 13.75.
Found: C, 61.92; H, 11.36; S, 13.66.

Conversion of 1-dodecanesulfinic acid to 1-dodecyl 1-dodecanethiolsulfonate. A 1-g. sample of pure sulfinic acid, m.p. 29–30°, was allowed to stand in a stoppered bottle at room temperature (22–25°). The solid gradually changed to an oil and was completely liquid in two weeks. After a month of standing the oil began to resolidify and in two months it became completely solid, m.p. 37–40°. A sample of this material recrystallized from ethanol melted at 42–44° and did not depress the melting point of a known sample of 1-dodecyl 1-dodecanethiolsulfonate (see below).

The free sulfinic acid from 5.3 g. of magnesium 1-dodecanesulfinate dihydrate was heated in a nitrogen atmosphere on a steam-bath for two and one-third hours. The dark oily material thus obtained was poured into a solution of 1 g. of sodium acetate in 200 cc. of water. The portion insoluble in water was extracted with ether, the ether solution treated with decolorizing carbon (Norit) and the solvent was removed. The white crystalline residue was recrystallized from 95% ethanol, m.p. 41–42°. A mixture with an authentic sample of 1-dodecyl 1-dodecanethiolsulfonate melted at the same temperature. The yield was 2 g. (69%). The above aqueous sodium acetate solution was evaporated to dryness and the solid residue recrystallized from 95% ethanol to give 1 g. of sodium 1-dodecanesulfonate (identified as a sulfur containing salt which did not react with sodium nitrite solution).

Air oxidation of magnesium 1-dodecanesulfinate. A sample of dry powdered magnesium 1-dodecanesulfinate dihydrate was exposed on a watch glass and the sulfinate content was checked during one hundred nineteen days by titrating with 0.1 normal nitrite solution. The results are summarized in Table I.

A sample of unpurified magnesium 1-dodecanesulfinate (85% sulfinate by nitrite titration) was allowed to stand in an open dish for six months. Nitrite titration showed that only a trace of sulfinate remained. The magnesium salt was soluble in hot water and hot 95% ethanol. These are properties of the sulfonate and not the sulfinate.

Reaction of excess sulfur dioxide with 1-dodecanemagnesium bromide. The Grignard reagent prepared from 200 g. of 1-bromododecane was treated at about −35° with approximately a three-fold excess of sulfur dioxide over that required to yield the salt of the sulfinic acid. Hydrolysis of this reaction mixture with cold aqueous ammonium chloride solution and isolation of the product as before gave 100 g. of solid melting at 39–41°. Crystallization of a sample from chloroform gave a small amount of tetracosane, m.p. 51–52°. The chloroform solution fraction was recrystallized from low-boiling petroleum ether to give a solid m.p. 44–45° which proved to be 1-dodecyl 1-dodecanethiolsulfonate.

Anal. Calc'd for $C_{24}H_{50}O_2S_2$: C, 66.30; H, 11.59.
Found: C, 66.73; H, 11.82.

Hydrolysis of 35 g. of the crude ester with 10 g. of sodium hydroxide in 400 cc. of 95% ethanol at the boiling point for three hours gave 16 g. of sodium 1-dodecanesulfinate. Titration with standard nitrite indicated the salt was at least 86% sulfinate.

Anal. Calc'd for $C_{12}H_{25}NaO_2S$: C, 56.24; H, 9.83; Na, 8.97.
Found: C, 56.30; H, 9.99; Na, 8.88.

TABLE I

AIR OXIDATION OF MAGNESIUM 1-DODECANESULFINATE

DAYS OF STANDING	% SULFINATE CONTENT
0	96
25	89
54	82
91	74
119	66

1,2-Bis(1-dodecylthio)ethane. The procedure used was a modification of that described by Ziegler and Connor (5) for the *n*-butyl analog. In a 1-liter three-necked, round-bottomed flask equipped with a mechanical stirrer, reflux condenser, and dropping-funnel was placed 150 cc. of absolute ethanol. Six grams (0.26 g. atom) of sodium was added in small pieces followed by 50.5 g. (0.25 mole) of *n*-dodecyl mercaptan. The mixture was brought to reflux temperature, the source of heat withdrawn, and a solution of 18.8 g. (0.1 mole) of ethylene bromide in 100 cc. of absolute ethanol added with stirring at such a rate that moderate refluxing was maintained. The addition was complete in one-half hour and the mixture was then heated under reflux for four hours. When the reaction mixture was cooled, a solid crystallized which was washed with water, and extracted with diethyl ether. The insoluble salt was removed, the ether distilled under diminished pressure, and the residue recrystallized twice from absolute ethanol, m.p. 54–55°; the yield was 35 g. or 81%.

Anal. Calc'd for $C_{26}H_{54}S_2$: C, 72.48; H, 12.64.
Found: C, 72.30; H, 12.63.

1,2-Bis(1-dodecylsulfonyl)ethane. A solution of 30 g. (0.07 mole) of 1,2-bis(1-dodecylthio)ethane in 1200 cc. of glacial acetic acid was warmed to 70° and a solution of 44 g. (0.28 mole) of potassium permanganate in 400 cc. of water was slowly added with stirring. The reaction was complete in about fifteen minutes, and the mixture was cooled to 25°. The solid precipitate was washed with water, suspended in 1500 cc. of ice water, and bleached with sulfur dioxide. The white solid was washed with a large quantity of water, dried at room temperature, and extracted with warm diethyl ether. The yield of the insoluble material which melted at 160–161° was 28 g. or 81%. A sample was recrystallized from a glacial acetic acid-absolute ethanol mixture, m.p. 161–162° (165–166° corr.).

The melting point of 1,2-*bis*(1-dodecylsulfonyl)ethane prepared by a different procedure is reported in the literature (4b) at 165.8–166.8°.

Anal. Calc'd for $C_{26}H_{54}O_4S_2$: C, 63.15; H, 10.93.
Found: C, 63.03; H, 10.99.

Hydrolysis of 1,2-bis(1-dodecylsulfonyl)ethane. A modification of the method of Ziegler and Connor (5) was used. In a 3-l., three-necked, round-bottomed flask equipped with a mechanical stirrer, a reflux condenser and dropping-funnel were placed 1200 cc. of 95% ethanol and 24.7 g. (0.05 mole) of 1,2-*bis*(1-dodecylsulfonyl)ethane. The mixture was heated under reflux and a solution of 16.5 g. (0.25 mole) of potassium cyanide in 70 cc. of water was added with stirring. After the mixture was refluxed for thirty minutes, all of the disulfone had gone into solution. An additional 100 cc. of water was added, and the solution stirred and heated under reflux for twenty hours. Most of the solvent was removed by distillation under diminished pressure, leaving about 200 cc. of liquid residue.

The reflux condenser was replaced by an outlet tube which was connected through a sodium hydroxide trap to a water-pump. The cold residue was then acidified under diminished pressure by slow addition of a solution of 40 cc. of concentrated hydrochloric acid in 300 cc. of water. The acidified residue was extracted with 300 cc. of ether and the ether evaporated under diminished pressure to remove any remaining hydrogen cyanide. The residue, which was a solid below room temperature, was then dissolved in 100 cc. of absolute ethanol and added to a solution of 4 g. (0.1 mole) of sodium hydroxide in 400 cc. of 95% ethanol. A solid immediately crystallized and the mixture was cooled to 0°. After recrystallization from ethanol the yield of sodium 1-dodecanesulfinate monohydrate was 22 g. or 80%. The analysis of this material by nitrite titration showed a 92% sulfinate content.

1,2-Bis(6-dodecylthio)ethane. In a 1-liter, three-necked, round-bottomed flask equipped with a mechanical stirrer, reflux condenser, and dropping-funnel were placed 14.7 g. (0.066 mole) of 90% 6-dodecyl mercaptan,[2] 5.6 g. (0.03 mole) of ethylene bromide, and 100 cc. of 95% ethanol. The mixture was heated under reflux and with stirring, and a solution of 1.8 g. of sodium in 50 cc. of 95% ethanol was added over the period of one hour. After stirring and refluxing the resulting solution for an additional hour, it was concentrated to 50 cc. by removal of the solvent under diminished pressure. To this concentrate was added 100 cc. of water and the mixture extracted with three 50-cc. portions of low-boiling petroleum ether. The extracts were combined, dried over sodium sulfate, and the ether distilled under diminished pressure, leaving 15.3 g. of clear oily residue.

A 12.8-g. sample of the crude oil product was distilled through an electrically heated 10-in. Vigreux column to give a fraction of 10.3 g., b.p. 170–180° (0.1 mm.); n_D^{20} 1.4808. Redistillation of this fraction gave 7.5 g. of liquid which boiled at 180° (0.1 mm.); n_D^{20} 1.4818. The yield of 1,2-*bis*(6-dodecylthio)ethane thus obtained was 70%.

Anal. Calc'd for $C_{26}H_{54}S_2$: C, 72.48; H, 12.64.
Found: C, 72.73; H, 12.58.

1,2-Bis(6-dodecylsulfonyl)ethane. A mixture of 2 g. (0.0046 mole) of 1,2-*bis*(6-dodecylthio)ethane and 50 cc. of glacial acetic acid was warmed to 45° and 3 g. (0.019 mole) of potassium permanganate in 30 cc. of solution added with stirring at this temperature over a period of one hour. The mixture was then treated with sulfur dioxide and the clear oil layer extracted with low-boiling petroleum ether. The ether was removed by distillation under diminished pressure leaving a liquid residue which solidified at about 5°. After several recrystallizations from methanol, the solid melted at 23–24°. The yield of the thus purified product was 1.7 g. or 74%.

Anal. Calc'd for $C_{26}H_{54}O_4S_2$: C, 63.15; H,10.93.
Found: C, 62.70; H, 10.88.

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[2] This material is believed to be contaminated with 6-bromododecane. See Frank, Smith, Woodward, Reynolds, and Canterino, *J. Polymer Sci.*, in press.

Hydrolysis of 1,2-bis(6-dodecylsulfonyl)ethane. The procedure was the same as that described for the hydrolysis of 1,2-*bis*(1-dodecylsulfonyl)ethane. From 1.5 g. (0.003 mole) of 1,2-*bis*(6-dodecylsulfonyl)ethane was obtained 1.6 g. of the crude sodium sulfinate as an amorphous solid. Purification of this salt was not successful. It was shown to be only 35% sulfinate by nitrite titrations.

Action of 1-dodecanethiol on 1-dodecanesulfinic acid. A mixture of 5.3 g. (0.01 mole) of freshly prepared magnesium 1-dodecanesulfinate dihydrate, 100 cc. of 5% hydrochloric acid, and 75 cc. of ether was shaken in a separatory funnel until all of the solid had dissolved. The ether extract was transferred to a flask equipped with a mechanical stirrer and reflux condenser and containing 2 g. (0.01 mole) of 1-dodecanethiol. The mixture was stirred and heated under reflux for one hour and an additional 2 g. (0.01 mole) of 1-dodecanethiol along with two drops of concentrated hydrochloric acid was added. After this mixture had been stirred and heated under reflux for fifteen hours, the ether solvent was removed under diminished pressure, leaving a residue of white solid along with a small amount of oil. The solid was isolated by crystallization from 500 cc. of 95% ethanol, m.p. 43–44°. A mixed melting point with a sample of 1-dodecyl 1-dodecanethiolsulfonate previously identified was not depressed. The yield was 5.6 g.

Anal. Calc'd for $C_{24}H_{50}O_2S_2$: C, 66.30; H, 11.59.
Found: C, 66.51, 66.61; H, 11.37, 11.58.

The alcohol filtrate obtained above was evaporated under diminished pressure, leaving an oil residue which was treated with 50 cc. of 5% sodium carbonate solution and the insoluble oil extracted with ether. The ether left an oil which distilled at 255–265°; n_D^{20} 1.4585. An authentic sample of 1-dodecanethiol was found to distill at 260–265° under the same conditions, n_D^{20} 1.4588. The amount of recovered 1-dodecanethiol was 1.5 g. From the quantity of thiol consumed, the theoretical yield of the thiolsulfonate based upon the equation of von Braun and Weissbach (3) is 2.7 g.

Another run was made using a 3:1 mole ratio of sulfinic acid and mercaptan. From 5.3 g. (0.01 mole) of the magnesium salt and 1.35 g. (0.0067 mole) of 1-dodecanethiol, 3.2 g. of 1-dodecyl 1-dodecanethiolsulfonate was obtained, m.p. 41.5–43°. The theoretical yield by the mechanism of von Braun and Weissbach (3) should be 1.45 g. based on the amount of mercaptan used.

In order to determine if any of the thiolsulfonate had been formed by disproportionation of the sulfinic acid, another run was made. The sulfinic acid, obtained from 5.3 g. (0.01 mole) of the magnesium salt by the same procedure as above, was heated in refluxing ether for sixteen hours with two drops of concentrated hydrochloric acid, but with no mercaptan. The ether was then distilled under diminished pressure as before, leaving a solid residue which melted below room temperature into a clear oil. This oil dissolved in 100 cc. of 5% sodium carbonate with evolution of carbon dioxide, and no insoluble thiolsulfonate was obtained. The solution was evaporated to dryness on a steam cone and the residue extracted with 95% ethanol. The extract was cooled, and yielded 4.1 g. of solid which showed 90% sulfinate by the usual nitrite titration.

N,N-Di(1-dodecylsulfonyl)hydroxylamine. To a solution prepared from 10 cc. of concentrated hydrochloric acid, 60 cc. of water, and 200 cc. of glacial acetic acid was added 2.6 g. (0.005 mole) of freshly prepared magnesium 1-dodecanesulfinate dihydrate. The mixture was shaken at 0° until all of the salt was in solution, and titrated at that temperature with 0.1 normal sodium nitrite. When the end point was reached, using an outside indicator of starch-potassium iodide paper, the addition was stopped. The white solid which crystallized during the nitrite addition was washed with about 1000 cc. of water, and dried. The solid was recrystallized from low-boiling petroleum ether, m.p. 72–74°. The yield of 2.5 g. was quantitative.

The same product was obtained by a procedure similar to that described by Koenigs (7). A solution of 16.5 g. (0.06 mole) of sodium 1-dodecanesulfinate monohydrate and 4.2 g. (0.06 mole) of sodium nitrite in 1000 cc. of water was acidified at 20° with dilute hydrochloric acid. The solid product was washed with water, and dried. After recrystallization from petroleum ether the solid melted at 74–75°. The yield was 12.5 g. or 84% of the theoretical amount. A sample was recrystallized from ethanol, m.p. 76–77°.

Anal. Calc'd for $C_{24}H_{51}NO_5S_2$: C, 57.91; H, 10.33; N, 2.81.
Found: C, 58.02; H, 10.53; N, 2.92.

When only one-half of the equivalent amount of sodium nitrite was added to the dodecanesulfinic acid in acetic acid solution using the titration procedure previously described, a quantitative yield, based on the sodium nitrite used, of the above product was obtained in almost pure form, m.p. 74–75°. Using the same titration procedure, when the sulfinic acid was titrated to the end point with nitrite, the product melted at 72–74° as reported above, and when an excess of nitrite was added, the product melted at 60–70°.

Tri(1-dodecylsulfonyl)amine oxide. A solution of 50 cc. of glacial acetid acid and 1.6 g. (0.003 mole) of freshly prepared N,N-di(1-dodecylsulfonyl)hydroxylamine, m.p. 72–74°, was warmed to 45°, and 5 cc. of concentrated nitric acid (*d.* 1.42) was added with stirring in about five minutes. The flask was stoppered and allowed to stand at room temperature for ten hours. The mixture was then cooled and the solid which had crystallized was washed with a small amount of cold 80% acetic acid. The yield of the dry product, m.p. 60–61°, was 0.4 g. After recrystallization from 90% acetic acid, it melted at 61–62°.

Anal. Calc'd for $C_{36}H_{75}NO_7S_3$: C, 59.22; H, 10.35; N, 1.92.
Found: C, 59.57, 59.35; H, 10.23, 10.40; N, 2.04.

The N,N-di(1-dodecylsulfonyl)hydroxylamine was also oxidized to the amine oxide by the action of an excess of nitrous acid at about 50°. The product was more difficult to purify in this case and after several recrystallizations from ethanol and petroleum ether, it melted at 58–59°. A mixed melting point with the product obtained by nitric acid oxidation was not depressed. A sample of the solid hydroxylamine derivative was also found to decompose spontaneously at room temperature with the evolution of red-brown nitrogen oxides. The amine oxide, m.p. 60–61° was isolated from the decomposition product.

O-Acetyl N,N-di(1-dodecylsulfonyl)hydroxylamine. One gram (0.002 mole) of N,N-di(1-dodecylsulfonyl)hydroxylamine was added to 25 cc. of acetic anhydride and the solution stirred for one-half hour. The solution was then warmed to 100° with stirring over a period of one-half hour, allowed to cool, and poured into water. After the acetic anhydride was hydrolyzed, the solid residue was recrystallized from 80% acetic acid, m.p. 45–46°. The yield was 0.7 g. or 65%. After further recrystallization from 80% acetic acid the solid melted at 47–48°.

Anal. Calc'd for $C_{26}H_{53}NO_6S_2$: C, 57.85; H, 9.90; N, 2.60.
Found: C, 57.81; H, 10.08; N, 2.66.

1-Dodecylsulfonylacetic acid. The procedure was similar to that described by Gabriel (11). A solution of 1.9 g. (0.02 mole) of monochloroacetic acid in 150 cc. of water was neutralized with 1.7 g. (0.02 mole) of sodium bicarbonate and then treated with a solution of 5.8 g. (0.02 mole) of sodium 1-dodecanesulfinate monohydrate in 100 cc. of water. The mixture was evaporated to about 100 cc. with an open flame, then placed in an evaporating dish and evaporated to dryness on a steam cone. The solid residue was dissolved in 300 cc. of hot water and on cooling, the sodium salt crystallized; the yield was 5.4 g. or 85%.

The sodium salt was dissolved in hot water, neutralized with dilute hydrochloric acid, and the solid which precipitated was recrystallized from an ethanol-water mixture, m.p. 107–109°. It was then recrystallized from high-boiling petroleum ether, m.p. 108–109°. The yield was 4.3 g. or an over-all yield of 74%. After recrystallization from glacial acetic acid, the solid still melted at 108–109°.

Anal. Calc'd for $C_{14}H_{28}O_3S$: C, 57.50; H, 9.65.
Found: C, 57.42; H, 9.47.

SUMMARY

Crystalline 1-dodecanesulfinic acid has been isolated and characterized. On standing, it disproportionates to 1-dodecyl 1-dodecanethiolsulfonate and 1-do-

decanesulfonic acid. On standing in air, the magnesium sulfinate oxidizes to the sulfonate. The reaction of 1-dodecanethiol and 1-dodecanesulfinic acid to give 1-dodecyl 1-dodecanethiolsulfonate has been examined and on the basis of yields it is suggested that 1-dodecanesulfenic acid may be an intermediate in this reaction.

The reaction of nitrous acid with 1-dodecanesulfinic acid has been found to yield di-(1-dodecanesulfonyl)hydroxylamine and tri-(1-dodecanesulfonyl)amine oxide.

1-Dodecanesulfonylacetic acid prepared from sodium 1-dodecanesulfinate and chloroacetic acid is a good derivative for characterization of the sulfinic acid.

URBANA, ILL.

REFERENCES

(1) Office of the Publication Board, U. S. Department of Commerce, Item P. B. No. 1636—Activation of Buna-S Polymerization in Mersolat Emulsion with Reducing Agents by SHERLOCK SWANN, JR. AND N. M. ELIAS.
(2) AUTENRIETH, *Ann.*, **259**, 362 (1890).
(3) VON BRAUN AND WEISSBACH, *Ber.*, **63**, 2836 (1930).
(4) (a) HOULTON AND TARTAR, *J. Am. Chem. Soc.*, **60**, 544 (1938);
(b) ALLEN, *J. Org. Chem.*, **7**, 23 (1942).
(5) ZIEGLER AND CONNOR, *J. Am. Chem. Soc.*, **62**, 2596 (1942).
(6) KHARASCH, POTEMPA, AND WEHRMEISTER, *Chem. Rev.*, **39**, 269 (1946).
(7) KOENIGS, *Ber.*, **11**, 615 (1878).
(8) ZUCKSCHWERDT, *Ann.*, **174**, 308 (1874).
(9) KOENIGS, *Ber.*, **11**, 1588 (1878).
(10) KRAFFT, *Ber.*, **15**, 1687 (1882).
(11) GABRIEL, *Ber.*, **14**, 833 (1881).