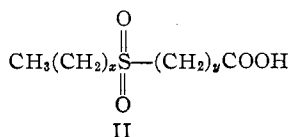


[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

A Series of ω -Alkylmercapto and ω -Alkylsulfonyl Acids¹BY LORENCE RAPOPORT,² ALLEN SMITH AND MELVIN S. NEWMAN

In the course of an investigation of the surface activity of various organic acids a series of twelve-carbon ω -alkylmercapto fatty acids and ω -alkylsulfonyl fatty acids of the general formulas $\text{CH}_3(\text{CH}_2)_x\text{S}-(\text{CH}_2)_y\text{COOH}$ and

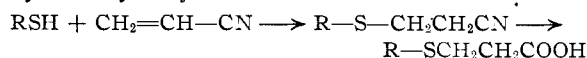
I



II

were prepared. In addition to the twelve-carbon acids certain homologs containing more or fewer carbon atoms were also synthesized.

addition of a mercaptan to acrylonitrile followed by acid hydrolysis⁴ of the resultant nitrile.



While the addition of the thiophenols to acrylic acid⁵ and acrylic esters,⁶ and the addition of mercaptans to olefins⁷ and hydrogen sulfide to acrylonitrile⁸ have been reported, this appears to be the first case of the use of acrylonitrile and aliphatic mercaptans. The reaction is analogous to the addition of aliphatic alcohols to acrylonitrile which has been described previously.⁹ The reaction proceeds smoothly in dioxane solution at 40–50° in the presence of a catalytic amount of

TABLE I

ω -ALKYLMERCAPTO FATTY ACIDS $\text{CH}_3(\text{CH}_2)_x\text{S}(\text{CH}_2)_y\text{COOH}$													
X	Y	M. p., °C.	B. p., °C.	mm.	Formula	Neut. equiv.		% Carbon ^a		% Hydrogen		% Sulfur	
						Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
9	1	52–53			$\text{C}_{12}\text{H}_{24}\text{O}_2\text{S}$	232	235	62.0	61.9	10.4	10.4	13.8	13.7
8	2	52–53	180–185	3.5	$\text{C}_{12}\text{H}_{24}\text{O}_2\text{S}$	232	233	62.0		10.4		13.8	14.1
7	3	35–36	155–158	0.5	$\text{C}_{12}\text{H}_{24}\text{O}_2\text{S}$	232	240	62.0	61.8	10.4	10.6	13.8	14.0
6	4	27–28	163.5–165	1	$\text{C}_{12}\text{H}_{24}\text{O}_2\text{S}$	232	236	62.0	62.3	10.4	10.4	13.8	13.9
5	5	28	164–166	1	$\text{C}_{12}\text{H}_{24}\text{O}_2\text{S}$	232	235	62.0	61.4	10.4	10.4	13.8	13.3
2	8	27–28	165–170	2	$\text{C}_{12}\text{H}_{24}\text{O}_2\text{S}$	232	232	62.0		10.4		13.8	
0	10	43–45	165–168	1	$\text{C}_{12}\text{H}_{24}\text{O}_2\text{S}$	232	236	62.0	61.8	10.4	10.4	13.8	13.5
7	1	36–37	150–154	2	$\text{C}_{10}\text{H}_{20}\text{O}_2\text{S}$	204	208	58.7		9.9		15.6	
7	2	40–41			$\text{C}_{11}\text{H}_{22}\text{O}_2\text{S}$	218	219	60.5		10.1		14.7	
11	1	61–62			$\text{C}_{14}\text{H}_{28}\text{O}_2\text{S}$	260	262	64.6	64.8	10.8	10.8	12.3	12.3
11	2	61–62			$\text{C}_{15}\text{H}_{30}\text{O}_2\text{S}$	275	283	65.6	65.7	11.0	11.4	11.7	11.7

^a All analyses by Arlington Laboratories, Fairfax, Virginia.

TABLE II

ω -ALKYLSULFONYL FATTY ACIDS, $\text{CH}_3(\text{CH}_2)_x\text{SO}_2(\text{CH}_2)_y\text{COOH}$													
X	Y	M. p., °C.	Formula	Neut. equiv.		% Yield (from sulfide)	% Carbon		% Hydrogen		% Sulfur		
				Calcd.	Found		Calcd.	Found	Calcd.	Found	Calcd.	Found	
9	1	104–105	$\text{C}_{12}\text{H}_{24}\text{O}_4\text{S}$	264	267	81	54.5	54.7	9.2	9.2	12.1	12.5	
8	2	130.5–131.5	$\text{C}_{12}\text{H}_{24}\text{O}_4\text{S}$	264	268	38 ^a	54.5		9.2		12.1	12.4	
7	3	125–126	$\text{C}_{12}\text{H}_{24}\text{O}_4\text{S}$	264	266	97	54.5	53.8	9.2	9.2	12.1	11.8	
6	4	112.5–113	$\text{C}_{12}\text{H}_{24}\text{O}_4\text{S}$	264	263	80	54.5	54.7	9.2	9.3	12.1	12.1	
5	5	113–113.5	$\text{C}_{12}\text{H}_{24}\text{O}_4\text{S}$	264	262	85	54.5	54.0	9.2	9.3	12.1	12.0	
0	10	95.5–96	$\text{C}_{12}\text{H}_{24}\text{O}_4\text{S}$	264	262	78	54.5	54.4	9.2	9.1	12.1	12.3	
11	2	134–135	$\text{C}_{15}\text{H}_{30}\text{O}_4\text{S}$	307	311	92	58.8	58.6	9.9	9.9	10.5	10.5	

^a Low yield due to mechanical loss during violent reaction.

Three general methods were used in the preparation of the alkylmercapto acids: (1) the condensation of a mercaptan with the appropriate haloacids, halo-ester, or halo-nitrile followed by hydrolysis where necessary³; (2) the alkylation of a ω -mercapto acid with an alkyl iodide; (3) the

sodium methoxide. The β -(alkylmercapto)-propionic acids are obtained easily after hydrolysis of the nitriles in over-all yields in excess of 60%.

(4) The presence of the negative group β to the sulfur linkage causes cleavage during alkaline hydrolysis; cf. Connor in Gilman, "Organic Chemistry," Vol. I, 2d ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 860.

(5) Posner, *Ber.*, **40**, 4788 (1907).

(6) U. S. Patent 2,199,799, C. A., **34**, 5968 (1940).

(7) Nicolet, *THIS JOURNAL*, **57**, 1098 (1935); Jones and Reid, *ibid.*, **60**, 2452 (1938); Ipatieff and Friedman, *ibid.*, **61**, 71 (1939).

(8) German Patent 669,961, C. A., **33**, 5415 (1939).

(9) Koelsch, *THIS JOURNAL*, **65**, 437 (1943); Utermohlen, *ibid.*, **67**, 1505 (1945); MacGregor and Pugh, *J. Chem. Soc.*, 535 (1945).

(1) The work described in this paper was carried out under a contract between the B. F. Goodrich Company and The Ohio State Research Foundation.

(2) Present address: American Cyanamid Company, Stamford, Connecticut.

(3) (a) Hill and Fager, *THIS JOURNAL*, **65**, 2300 (1943); (b) French Patent 748,460, *Chem. Zentr.*, **33**, II, 2210 (1933).

The alkylsulfonyl acids were prepared in excellent yield by the oxidation of the alkylmercapto acids with 30% hydrogen peroxide in acetic acid.

The properties of the compounds prepared are summarized in Tables I and II.

Experimental

A. ω -Alkylmercapto Acids

General Procedure.—The purification of the reaction products was accomplished after acidification of the reaction mixtures, by distillation under reduced pressure and for solids melting above 35° recrystallization from Skellysolve-B or Skellysolve-F. The physical constants are listed in Table I. Mechanical stirring was used to prevent bumping when inorganic halides precipitated during the reaction.

The alkylmercaptoacetic acids were made by converting the mercaptans to their potassium derivatives with potassium hydroxide in alcoholic solution and subsequent addition of an equivalent of aqueous potassium chloroacetate solution. The mixture was refluxed¹⁰ and most of the alcohol was then removed under reduced pressure. The yield of purified alkylmercapto acids from *n*-octyl, *n*-decyl and lauryl mercaptans were 81, 72 and 35% (because of the poor quality of the lauryl mercaptan used), respectively.

β -(Octylmercapto)-propionic Acid, I ($x = 7, y = 2$).—To a stirred solution of 98 g. (0.67 mole) of octyl mercaptan and 2 g. of sodium methoxide in 100 cc. of dioxane was added dropwise (one hour) 40 g. (0.70 mole) of acrylonitrile. The temperature of the reaction mixture was maintained at 40–50° during the addition by means of a cooling bath. After standing overnight the acidified reaction mixture was poured into a large volume of water. The organic layer was separated, and refluxed for ten hours with a mixture of 400 cc. of glacial acetic acid, 180 cc. of concentrated sulfuric acid and 350 cc. of water. The product was isolated on cooling and dilution of the reaction mixture. The yield was 92 g. (63%).

In the same way, nonyl and lauryl mercaptans gave β -nonylmercaptopropionic acid ($x = 8, y = 2$, 48% yield) and β -laurylmercaptopropionic acid ($x = 11, y = 2$, 62% yield).

γ -(Octylmercapto)-butyric Acid, I ($x = 7, y = 3$).—A solution of 160 g. (0.82 mole) of γ -iodobutyronitrile in 160 cc. of absolute ethanol was added dropwise over two hours to a boiling solution of 120 g. (0.82 mole) of octyl mercaptan and 46 g. of potassium hydroxide in 450 cc. of absolute ethanol. The mixture was refluxed for eighteen hours¹⁰ following which most of the alcohol was removed under reduced pressure. The residue was diluted with water and the crude nitrile separated and hydrolyzed for fourteen hours as above. The product isolated in the usual way was obtained in 83% yield (157.5 g.).

δ -(Heptylmercapto)-valeric Acid, I ($x = 6, y = 4$).—A solution of 57.5 g. (0.44 mole) of heptyl mercaptan and 23.5 g. of sodium methoxide in 150 cc. of absolute ethyl alcohol was added dropwise over a period of two hours to a boiling solution of 91 g. of ethyl δ -bromovalerate¹¹ in 100 cc. of absolute alcohol. The mixture was refluxed for eighteen hours and the ester isolated by pouring the reaction mixture into water and extracting with benzene. On distillation there was obtained 92 g. (81.5%) of a colorless oil, b. p. 128–130° at 0.5 mm. The acid was obtained by hydrolysis (acetic-water-sulfuric mixture) in 98% yield (81 g.).

ϵ -(Hexylmercapto)-caproic Acid, I ($x = 5, y = 5$).— ϵ -Bromocaproitrile was prepared by the following method

(10) It was pointed out by the Referee that both the use of alcohol and the long period of refluxing (four to eighteen hours) were probably unnecessary, see Y. Uyeda and E. E. Reid, *THIS JOURNAL*, **42**, 2385 (1920); O. R. Quayle and E. E. Royals, *ibid.*, **64**, 226 (1942).

(11) Linstead and Rydon, *J. Chem. Soc.*, 582 (1933).

which is an improvement over that reported in the literature.¹² A solution of 76 g. (1.17 moles) of potassium cyanide in 150 cc. of water was added dropwise to a well-stirred boiling solution of 300 g. (1.3 moles) of pentamethylene dibromide in 1000 cc. of acetone. The mixture was refluxed for five hours and then most of the acetone removed under reduced pressure. The organic material was isolated in the usual manner, and fractionated under reduced pressure through a three-foot multiple-helices-packed column fitted with a total reflux partial take off head. The two principal fractions consisted of I recovered dibromide, 124.5 g. (41.5%), b. p. 84–85.5° at 7 mm., and II, bromonitrile, 97 g. (42%), b. p. 114–115° at 7 mm.

A solution of the bromo-nitrile (97 g., 0.55 mole) in 100 cc. of absolute alcohol was added to a boiling solution of 65 g. (0.56 mole) of hexyl mercaptan and 36 g. of potassium hydroxide in 350 cc. of absolute alcohol and the mixture refluxed for eighteen hours.¹⁰ The crude product was hydrolyzed by treatment with an acetic-sulfuric-water mixture. There was obtained 93.3 g. (73%) of product.

ω -(Propylmercapto)-pelargonic Acid, I ($x = 2, y = 8$). Methyl- ω -hydroxypelargonate was prepared from methyl oleate by ozonization followed by reduction essentially according to Lycan and Adams.¹³ The over-all yield was 38%. The conversion of the hydroxy compound to ω -bromopelargonic acid (m. p. 35–36°, lit.¹⁴ 36°) was accomplished in 57% yield with 40% hydrobromic and sulfuric acid. This compound has been prepared previously by other methods.¹⁴

The interaction of *n*-propyl mercaptan and ω -bromopelargonic acid essentially as above yielded 57% of desired product.

ω -(Methylmercapto)-undecylic Acid, I ($x = 0, y = 10$). **ω -Mercaptoundecylic Acid.**—A solution of 200 g. (0.75 mole) of ω -bromoundecylic acid (m. p. 49–50°) and 60 g. (0.78 mole) of thiourea in 600 cc. of alcohol was refluxed for two hours. A solution 80 g. of sodium hydroxide in 250 cc. of water was added and the mixture refluxed an additional three hours. The product was isolated by acidification of the reaction mixture and distilled. There was obtained 102 g. (62%) of the desired acid, b. p. 158–161° at 1 mm. Neutral equivalent, calcd. 218, found 219. The compound solidified and remelted at 49–51°, in agreement with Cohen¹⁵ but not with Bauer and Stockhausen.¹⁶

The interaction of ω -mercaptoundecylenic acid and a 90% excess of methyl iodide essentially as in similar cases cited above yielded 66% of desired product.

B. ω -Alkylsulfonyl Acids

General Procedure.—The alkylmercapto acid (0.25 mole) was added slowly with shaking to 100 cc. of 30% hydrogen peroxide in 250 cc. of glacial acetic acid. An exothermic reaction ensued as the compound went into solution. An ice-bath was used when necessary to keep the reaction under control. When the spontaneous reaction had ceased the solution was heated to 90–100° for one hour. The cooled solution was poured into water and the crystals collected and purified by crystallization from benzene-Skellysolve-B. The yields and properties are listed in Table II.

Summary

The preparation of a series of ω -alkylmercapto acids and ω -alkylsulfonyl acids is described.

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(12) Hanower, *ibid.*, 2048 (1931); Breslow and Hauser, *THIS JOURNAL*, **67**, 686–687 (1945).

(13) Lycan and Adams, *THIS JOURNAL*, **51**, 625 (1929).

(14) (a) Chuit and Hauser, *Helv. Chim. Acta*, **12**, 463 (1929);

(b) Gaubert, Linstead and Rydon, *J. Chem. Soc.*, 1974 (1937);

(c) Hünsdieker, *Ber.*, **75B**, 291–297 (1942).

(15) Cohen, *J. Chem. Soc.*, 593 (1932).

(16) Bauer and Stockhausen (*J. prakt. Chem.*, (2) **130**, 35 (1931)) give m. p. 94–95°.