

nant formation of X. That such was the case was established by the zinc reduction of the chief product from the rearrangement, affording only 4-methyl-*ar*-2-tetralol-7-acetic acid XII, identified by comparison with an authentic sample recently prepared in this laboratory.³ No evidence for the alternative possible product XII' from X' (R = H) could be found in the reduction, excluding the possibility of path B. Since, in the migration of IV, positions 5 and 6 do not appear to be directly involved, the configurations at these positions may be considered to remain untouched, as shown in X. It is notable that such a lactone ring in the dienone has a remarkable effect on the migration course in forming X, in which the acetic acid residue occupies position (7) dissimilar from that (6) predicted from the migration paths of the dienone-acetic acids (I).³ The variety of the rearrangement courses, including the present result, can hardly be rationalized on the available data.

Experimental¹⁴

All temperatures are uncorrected. Infrared absorption spectra were measured with a Perkin-Elmer Model 21 double beam spectrophotometer.

Lactone of 9-Methyl-5 α -hydroxy- Δ^4 -3-octalone-6 α -acetic Acid (V).—Under the same conditions as reported previously,⁴ *trans*-9-methyl- Δ^4 -3-octalone-6-acetic acid (II, 3.0 g.)⁵ was monobrominated with *N*-bromosuccinimide (2.5 g.) in carbon tetrachloride (200 cc.), except under exposure to diffused sunlight in the absence of peroxide. After removal of the succinimide, the reaction containing the product was mixed with acetic acid (15 cc.) and fused sodium acetate (16 g.). The mixture was heated at 90–100° on a water bath with occasional shaking. The reaction was diluted with water, extracted with ethyl acetate, and the acetate layer washed with saturated aqueous bicarbonate and water. Evaporation of the dried acetate solution furnished 1.21 g. (40%) of the lactone V as colorless crystals, m.p. 132–134°, from ethyl acetate-petroleum ether. Two further crystallizations from benzene-petroleum ether raised the melting point to 134–135°; $\lambda_{\text{max}}^{\text{EtOH}}$ 234.5 μm (ϵ 10,300). Reported,⁴ m.p. 136–137°; $\lambda_{\text{max}}^{\text{EtOH}}$ 235 μm ($\log \epsilon$ 4.14).

Lactone of 3-Keto-9-methyl-5 α -hydroxy- Δ^1 -4-hexahydro-naphthalene-6 α -acetic Acid (IV).—Under the same conditions as described previously for the oxidation of the dimethyl-octalone,⁵ 0.82 g. of the above monoenolactone V was heated to reflux with selenium dioxide (0.50 g.) in a mixture of *tert*-butyl alcohol (110 cc.) and glacial acetic acid (1 cc.). The product, a red-brown sirup, was dissolved in ethyl acetate, and, after washing with aqueous bicarbonate and water, the acetate was evaporated to leave a viscous mass which could not be crystallized. The mass was chromatographed on an alumina column (10 g.) and the elutions with benzene gave 0.26 g. (32%) of the dienone-lactone IV, m.p. 133–136°, from ethyl acetate-petroleum ether. Two further crystallizations from benzene formed yellowish plates, m.p. 136–137°; $\lambda_{\text{max}}^{\text{EtOH}}$ 239 μm (ϵ 15,600); $\nu_{\text{max}}^{\text{Nujol}}$ 1785 (γ -lactone), 1663 (Δ^1 -3-dienone) and 1629 (double bond).⁵

Anal. Calcd. for C₁₃H₁₄O₃: C, 71.54; H, 6.47. Found: C, 71.03; H, 6.11.

Rearrangement of the Above Dienone-Lactone (IV) in Acetic Anhydride.—This reaction was carried out under the customary conditions.³ IV (0.16 g.) was dissolved in acetic anhydride (1 cc.) containing a trace of concentrated sulfuric acid and kept at room temperature for 6 hr. The reaction

was not exothermic and the color changed from a pale yellow to an orange yellow. The mixture was poured into ice water and no crystals separated even after standing in a refrigerator overnight. The aqueous solution was extracted with ether and the ethereal layer washed with aqueous bicarbonate and water. Drying and evaporation of the ether left a neutral sirup (0.15 g.), which could not be induced to crystallize. The sirup was heated to reflux in a mixture of ethanol (5 cc.) and 10% aqueous sodium carbonate (3 cc.) for 30 min. After evaporation of the alkaline solution *in vacuo*, the residue was mixed with water, acidified, and extracted with ethyl acetate. The acetate extract was washed as usual, and evaporated to leave 0.11 g. (69%) of lactone of 4-methyl-8 α -hydroxy-1-*ar*-tetralol-7 α -acetic acid X (R = H), m.p. 168°, from ethyl acetate-petroleum ether. Two further crystallizations from the same solvents furnished microscopic white plates, m.p. 174–175°; $\lambda_{\text{max}}^{\text{EtOH}}$ 289 μm (ϵ 3430); $\nu_{\text{max}}^{\text{Nujol}}$ 3317 (OH), 1738 (γ -lactone),¹² and 816 and 809 (adjacent hydrogens on a benzene ring).^{3,9}

Anal. Calcd. for C₁₃H₁₄O₃: C, 71.54; H, 6.47. Found: C, 71.65; H, 6.34.

Reduction of the Above Tetralol-Lactone (X) with Zinc.—As described for the reduction of the acetoxytetrahydro-santonin,¹³ a solution of 50 mg. of X (R = H) in 5 cc. of acetic acid was heated with 0.5 g. of zinc dust on a water bath for 6 hr. Worked up as usual, the bicarbonate soluble portion of the product afforded 30 mg. of the crude acid (XII), m.p. 118–120°, from benzene-petroleum ether. Two further crystallizations from the same solvents formed prisms, m.p. 121–122°, showing no depression on admixture with an authentic sample of 4-methyl-1-*ar*-tetralol-7-acetic acid (XII).³ The light absorption spectra are practically identical with those reported for XII; $\lambda_{\text{max}}^{\text{EtOH}}$ 280 μm (ϵ 2140); $\nu_{\text{max}}^{\text{Nujol}}$ 3330 (OH), 1700 (COOH), and 817 and 804 (adjacent hydrogens on a benzene ring).^{3,9}

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(12) Ref. 7, p. 186.

(13) K. Yamakawa, *J. Org. Chem.*, **24**, 897 (1959).

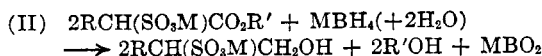
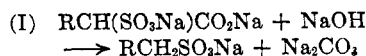
Alkanesulfonates and Hydroxyalkane-sulfonates from α -Sulfo Fatty Acids¹

J. K. WEIL, F. D. SMITH, AND A. J. STIRTON

Eastern Regional Research Laboratory,²
Philadelphia 18, Pennsylvania

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Continuation of research on long chain α -sulfo fatty acids has led to a decarboxylation (I) and a reduction method (II) as shown by the equations:



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(2) Eastern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.

(11) Microanalyses were carried out by Miss K. Shimamura and ultraviolet measurement by Miss M. Suzuki, both of this school.

TABLE I
 SODIUM ALKANESULFONATES

Compound	Method ^a	Yield, %	Krafft point ^b	% Na		% C		% H		% S	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
C ₁₁ H ₂₃ SO ₂ Na	D	8	21.5°	8.90	8.94	51.13	50.98	8.97	9.07	12.41	12.50
C ₁₂ H ₂₅ SO ₂ Na	S	53	38°	8.44	8.37	52.91	52.51	9.25	9.35	11.77	11.28
C ₁₃ H ₂₇ SO ₂ Na	D	39	35.5°	8.03	7.86	54.51	54.17	9.50	9.63	11.20	11.14
C ₁₄ H ₂₉ SO ₂ Na	S	56	48°	7.65	7.55	55.97	55.89	9.73	10.08	10.67	10.79
C ₁₅ H ₃₁ SO ₂ Na	D	52	48°	7.31	7.35	57.29	57.33	9.94	10.15	10.20	9.90
C ₁₆ H ₃₃ SO ₂ Na	S	65	57°	7.00	6.78	58.50	58.25	10.13	10.24	9.76	9.76
C ₁₇ H ₃₅ SO ₂ Na	D	40	62°	6.71	6.51	59.61	59.68	10.30	10.37	9.36	9.07
C ₁₈ H ₃₇ SO ₂ Na	S	53	70°	6.45	6.20	60.63	60.65	10.46	10.56	8.99	9.05

^a D = decarboxylation, S = Strecker reaction. ^b Ref. 6.

Desulfonation rather than decarboxylation occurred on heating α -sulfopalmitic acid in *o*-dichlorobenzene at the reflux temperature. Palmitic acid was recovered in a yield of 77%. Attempts to use a recent method³ for the decarboxylation of sodium α -sulfostearic acid simply by heating the monosodium salt at 265° under a nitrogen atmosphere gave in our case similar desulfonation to stearic acid.

Alkaline fusion of the disodium salt of the α -sulfo acid gave 35–50% yield of sodium alkanesulfonate of one less carbon atom, according to equation I. The disodium salt was heated and stirred under nitrogen with excess sodium hydroxide to ensure a stirrable paste near the fusion temperature (300–320°). The product contained the sodium alkanesulfonate, unconverted disodium salt, and a by-product identified as the fatty acid of two less carbon atoms, apparently formed by conversion of the disodium salt to the soap of an α -olefinic acid, followed by chain degradation by the Varrentrapp reaction⁴: $\text{RCH}_2\text{CH}(\text{SO}_3\text{Na})\text{CO}_2\text{Na} + \text{NaOH} \rightarrow \text{RCH}=\text{CHCO}_2\text{Na} + \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{RCO}_2\text{Na} + \text{CH}_3\text{CO}_2\text{Na}$.

For comparison, sodium alkanesulfonates of an even number of carbon atoms were prepared by the Strecker reaction⁵ from the alkyl bromide and sodium sulfite. All sodium alkanesulfonates are recorded in Table I. The Krafft point, the temperature at which a 1% aqueous dispersion changes sharply to a clear solution, is related to melting point⁶ and serves to characterize these compounds. Alternations in Krafft point, shown in Figure 1, are similar to alternations in melting point in the fatty acid series.

Hydroxyalkanesulfonates, isolated as the sodium salt, were generally prepared by the lithium borohydride reduction of lithium methyl α -sulfolaurate, myristate, palmitate, or stearate. Sodium borohydride gave lower yields but higher than that previously indicated for use in ester reductions.⁷ In all cases the only products were the

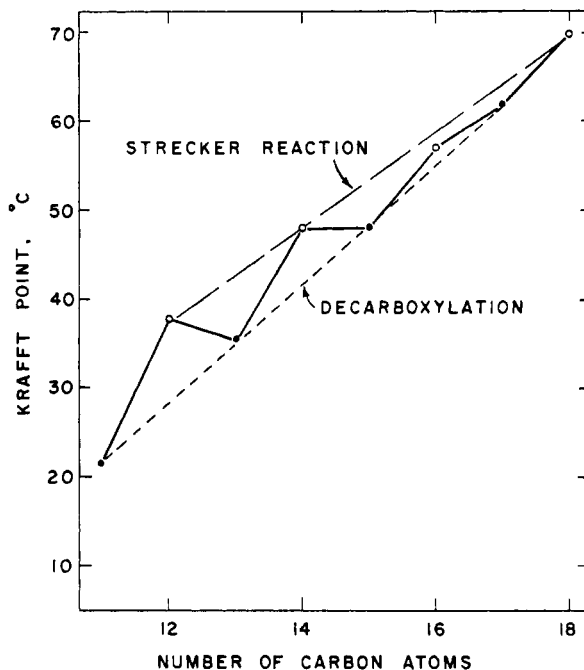


Fig. 1.—Krafft points for sodium alkanesulfonates as a function of chain length.

sodium 1-hydroxy-2-alkanesulfonate and the hydrolyzed unreduced ester isolated as the disodium salt. Use of the isopropyl ester, which is more resistant to hydrolysis than the methyl ester⁸ gave no improvement in yield of the reduction product. The high Krafft points and limited solubility are attributed to hydrogen bonding. Hydrogen bonding may also account for the limited solubility of the corresponding sodium α -sulfolauric, myristic, palmitic, and stearic acids, the Krafft points of which are 52°, 68°, 83°, and 94°, respectively.

The free acids, 1-hydroxy-2-hexadecanesulfonic acid and 1-hydroxy-2-octadecanesulfonic acid, were prepared from the sodium salts by ion exchange.

Experimental

Decarboxylation. Alkali Fusion of Disodium α -Sulfo-myristate.—Sodium hydroxide pellets (53 g.) were added to a resin flask containing a paste of 27 g. of disodium α -sulfo-

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(7) H. C. Brown, E. J. Mead, and C. Subba Rao, *J. Am. Chem. Soc.*, **77**, 6209 (1955).

(8) A. J. Stirton, J. K. Weil, and R. G. Bistline, Jr., *J. Am. Oil Chemists' Soc.*, **31**, 13 (1954).

TABLE II
 SODIUM 1-HYDROXY-2-ALKANESULFONATES

Compound	Yield, ^a %	Krafft point ^b	% Na		% C		% H		% S	
			Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
C ₁₀ H ₂₁ CH CH ₂ OH SO ₃ Na	68	59°	7.97	8.01	49.98	50.09	8.74	8.77	11.12	11.13
C ₁₂ H ₂₅ CH CH ₂ OH SO ₃ Na	74	73°	7.27	7.25	53.14	53.13	9.24	9.09	10.13	10.21
C ₁₄ H ₂₉ CH CH ₂ OH SO ₃ Na	64	84°	6.68	6.72	55.78	56.13	9.66	9.65	9.31	9.27
C ₁₈ H ₃₃ CH CH ₂ OH SO ₃ Na	61 ^c	93°	6.17	6.12	58.03	58.08	10.01	10.02	8.61	8.99

^a Sum of the yield of the reduction product and the hydrolyzed ester, recovered as the disodium salt RCH(SO₃Na)CO₂Na = 100%. ^b Krafft points for corresponding monosodium salts RCH(SO₃Na)CO₂H are 52, 68, 83, and 94°, respectively, ^c Yield from C₁₈H₃₃CH(SO₃Na)CO₂CH₃ and NaBH₄ = 44%.

myristate⁹ with an equal weight of water. The reactants were stirred with a Hershberg stirrer and heated, leading a slow stream of nitrogen over the surface to remove water vapor and exclude oxygen. As the temperature increased and water was removed, the mixture became fusible at 300°. Heating was discontinued when the mixture began to darken above 320°.

The fusion mixture was cooled, taken up in water, and acidified with sulfuric acid. Solids were filtered, washed free of inorganic salts, and taken up in hot 95% ethanol. Insoluble unconverted sodium α -sulfomyristic acid, recovery 20%, was removed by filtration.

The alcoholic solution, treated with water and diethyl ether, formed two phases. Evaporation of the ether layer and crystallization of the residue from chloroform gave lauric acid (3.7 g., yield 23%) neut. equiv. 199.8 (theor. 200.3), m.p. 42.4–43.1°; confirmed by mixed melting point and infrared spectra. A gas-liquid chromatogram showed the purity of the isolated lauric acid by-product to be at least 90%.

Crystallization of the aqueous alcohol solution at 0° gave sodium tridecanesulfonate (6.0 g., yield 39%) with the analysis and Krafft point shown in Table I. Infrared spectra showed the presence of the SO₃⁻ group and absence of CO and COO⁻ groups. Sodium alkanesulfonates of 11, 15, and 17 carbon atoms prepared in the same way are recorded in Table I.

Reduction. Sodium 1-Hydroxy-2-octadecanesulfonate.—The general method was reduction of the lithium salt of the methyl ester of the α -sulfo fatty acid, dissolved in isopropyl alcohol, by addition of a 1.25-molar ratio (theo. 0.5) of lithium borohydride. Variations in the order of addition of reactants or by use of diglyme gave lower yields.

A solution of lithium isopropyl α -sulfostearate (22.6 g., 54.8 mmoles) in 270 ml. of isopropyl alcohol was heated and 50 ml. of the solvent distilled to remove traces of moisture. Lithium borohydride (Metal Hydrides, Inc.,¹⁰ 89.1%; 1.48 g., 68.5 mmoles) was added during 3 min., the solution was refluxed 24 hr., 300 ml. of water was added, and the mixture was refluxed an additional hour.

The aqueous isopropyl alcohol solution was poured through an ion exchange column containing 400 ml. of resin sulfonic acid (Dowex 50W-X8¹⁰), neutralized with sodium hydroxide to pH 10.0, and evaporated to dryness. The residue was taken up with 1200 ml. of water, heated to boiling, allowed to crystallize at room temperature, filtered, washed, dried at 60° in a vacuum oven, and extracted twice with 3 l. of boiling methanol. The residue insoluble in

methanol was the hydrolyzed unreduced ester recovered as disodium α -sulfostearate (yield 39%). Crystallization of the methanol extract gave sodium 1-hydroxy-2-octadecanesulfonate (yield 61%).

Other sodium 1-hydroxy-2-alkanesulfonates recorded in Table II were obtained in a similar manner. Infrared examination of Nujol mulls showed strong OH absorption at 3400 cm.⁻¹ and SO₃⁻ absorption at 1250–1150 and 1060 cm.⁻¹.

1-Hydroxy-2-alkanesulfonic Acids.—Sodium 1-hydroxy-2-hexadecane-sulfonate (2.9 g.) was dissolved in 150 ml. of isopropyl alcohol by heating and stirring in the presence of 100 ml. of resin sulfonic acid, passed through a column containing 300 ml. of the exchange medium, and eluted with 900 ml. of isopropyl alcohol.

The isopropyl alcohol solution was evaporated in a rotary evaporator at 80° and 10 mm., the residue was redissolved in 100 ml. of chloroform, and water was removed azeotropically. Crystallization at -20° and drying at 75° for 1 hr. in a vacuum oven gave 1-hydroxy-2-hexadecanesulfonic acid, neut. equiv. 322.9 (theo. 322.5) as hygroscopic crystals which soften at 106°, pass through a glassy stage and melt sharply at 113°. 1-Hydroxy-2-octadecanesulfonic acid, neut. equiv. 350.8 (theo. 350.5), obtained in a similar manner, softens at 107.5°, becomes glassy and melts sharply at 114.8°.

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Identification of a 3-Benzylidene flavanone as a By-product of a Chalcone Synthesis

MARGARET K. SEIKEL,¹ MARY JANE LOUNSBURY,
AND SU-CHU WANG²

Department of Chemistry, Wellesley College, Wellesley,
Massachusetts, and Forest Products Laboratory, U.S.
Department of Agriculture, Madison 5, Wisconsin

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Although chalcones are most frequently prepared by a condensation reaction in the presence of strong

(1) Present address: Forest Products Laboratory, Madison 5, Wisconsin.

(2) Experimental work on this problem was done at Wellesley College and was started by Ann Fournier and Jane Moss.

(9) A. J. Stirton, J. K. Weil, Anna A. Stawitzke, and S. James, *J. Am. Oil Chemists' Soc.*, **29**, 198 (1952).

(10) Reference to manufactured products does not constitute recommendation by the U.S. Department of Agriculture over similar products not mentioned.