Branched Chain Fatty Acids and Sulfonated Derivatives[1]

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Abstract

Several 2-alkyl fatty acids containing 18–21 carbon atoms, were synthesized by tertiary butyl peroxide catalyzed addition of linear aliphatic carboxylic acids to normal terminal olefins. The products obtained in 35–70% yields were purified by fractional distillation. The acids were sulfonated with sulfur trioxide·dioxane adduct and isolated as the disodium salts in 60–80% yields.

$$R{-}CH_2CO_2H + R'CH{=}CH_2 \xrightarrow[125\text{–}160C]{Peroxide} R'CH_2CH_2{-}CH(R)CO_2H$$

$$R'CH_2CH_2CH(R)CO_2H + SO_3 \xrightarrow{CCl_4} R'CH_2CH_2C(SO_3H)(R)CO_2H$$

Surface active properties of the sodium salts of the 2-alkyl carboxylic acids and the corresponding sulfonated products were evaluated. Good wetting properties were observed for those sulfonated acids where the hydrophilic portion of the molecule was equidistant from the ends of the hydrocarbon chain.

Introduction

SALTS OF LINEAR CARBOXYLIC ACIDS (1), of 12–18 carbon atoms, and sulfonated derivatives exhibit increasing detergent power and decreasing solubility with increase in chain length. Useful surface active properties have been found when these materials are incorporated in detergent bars (2) and compositions (3). Previous studies have also shown that the sodium salts of α-sulfonated linear aliphatic carboxylate esters (4,5), $R{-}CH(SO_3Na)CO_2R'$ where R and R′ are equivalent or nearly so, exhibit excellent wetting properties in both hard and soft water, stable foams and good calcium ion stability. Branching would therefore be expected to increase the solubility of carboxylic acid salts and derivatives while central location of the hydrophilic group should lead to enhanced wetting properties. These studies have now been extended to determine the surface active properties of sodium 2-alkyl carboxylates and their corresponding 2-sulfonated derivatives.

The general synthesis of these acids is conveniently expressed in the following equations where R and R′ are linear alkyl groups.

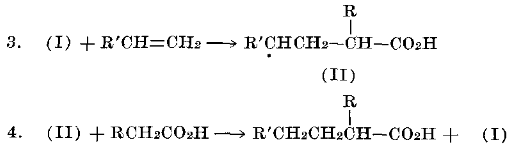
$$R{-}CH_2CO_2H + R'CH{=}CH_2 \xrightarrow[125\text{–}160C]{Peroxide} R'CH_2CH_2{-}CH(R)CO_2H$$

$$R'CH_2CH_2CH(R)CO_2H + SO_3 \xrightarrow{CCl_4} R'CH_2CH_2C(SO_3H)(R)CO_2H$$

Numerous investigations have shown that the addition of acids (6), esters (7,8), amides (9), and ketones (10, 11) to olefins occurs at the carbon atom alpha to the carbonyl group. These peroxide induced additions are believed to proceed via a free radical chain reaction involving a complex stepwise sequence.

$$1.\quad (CH_3)_3C{-}O{-}O{-}C(CH_3)_3 \xrightarrow{\Delta} 2(CH_3)_3CO\cdot$$

$$2.\quad (CH_3)_3CO\cdot + RCH_2CO_2H \longrightarrow (CH_3)_3C{-}OH + \underset{(I)}{R{-}\underset{\bullet}{C}HCO_2H}$$



$$3.\quad (I) + R'CH{=}CH_2 \longrightarrow \underset{(II)}{R'\underset{\bullet}{C}HCH_2{-}\overset{\overset{\displaystyle R}{|}}{C}H{-}CO_2H}$$

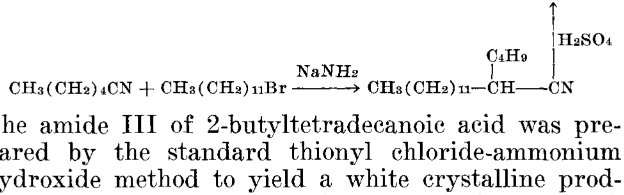
$$4.\quad (II) + RCH_2CO_2H \longrightarrow R'CH_2CH_2\overset{\overset{\displaystyle R}{|}}{C}H{-}CO_2H + (I)$$

Chain initiation is represented by steps 1 and 2, while chain propagation occurs via steps 3 and 4. Chain termination can occur by dimerization of radicals I and II with themselves or each other. Telomerization involving successive additions of olefin molecules to radical II (actually a polymerization) is thought to be the most important side reaction observed in this process. High ratios of carboxylic acid to olefin minimize telomer formation.

Table I summarizes the physical properties and pertinent experimental data obtained in the synthesis of some 2-alkyl carboxylic acids. Purities of better than 95% are indicated by carbon, hydrogen analyses and neutral equivalents. The yields of alkylated acetic acids based on the quantity of olefins used range from 35–70% with the most highly branched product 2,2-dimethylhexadecanoic acid being obtained in the lowest yield. The ratio of nondistillable residue to product ranges from 0.30–0.40 with all of the acids except 2,2-dimethylhexadecanoic acid where this ratio equals 0.60. This effect of branching at the 2-carbon atom of the acid has been noted previously by Nikishin et al. (6,7) and attributed to steric hindrance.

Sulfonation of the 2-alkyl carboxylic acids proceeds smoothly with sulfur trioxide·dioxane adduct in carbon tetrachloride leading to product formation in 60–80% yields. Analyses of carbon, hydrogen, and sodium summarized in Table II indicate better than 95% purity in all samples. Some difficulties were encountered in determining sulfur by the oxygen flask combustion method were relatively high and low values were observed for these compounds. All of the sulfonated dialkyl acetic acids were isolated as the disodium salts in view of the ease of purification in this form. Attempts to sulfonate 2,2-dimethylhexadecanoic acid resulted in the formation of a complex mixture of products.

In this study we desired to establish the structure of the dealkyl acetic acids by synthesizing one of the acids or a derivative by a known and different reaction.



$$CH_3{-}(CH_2)_{11}{-}\overset{\overset{\displaystyle C_4H_9}{|}}{C}HCO_2H \xrightarrow{SOCl_2/NH_4OH} \underset{(III)}{CH_3(CH_2)_{11}{-}\overset{\overset{\displaystyle C_4H_9}{|}}{C}H{-}\overset{\overset{\displaystyle O}{\|}}{C}NH_2}$$

$$CH_3(CH_2)_4CN + CH_3(CH_2)_{11}Br \xrightarrow{NaNH_2} CH_3(CH_2)_{11}{-}\overset{\overset{\displaystyle C_4H_9}{|}}{C}H{-}CN \xrightarrow{H_2SO_4} (III)$$

The amide III of 2-butyltetradecanoic acid was prepared by the standard thionyl chloride-ammonium hydroxide method to yield a white crystalline product mp 108C, % nitrogen 4.94, theory % nitrogen 4.95. Hexanenitrile was alkylated with dodecyl bromide using sodium amide (12) to form 2-hutyltetradecanenitrile bp 126.5C at 0.25 mm; $n_D^{20°}$ 1.4458. The nitrile, exhibiting a sharp band 4.39 μ and a purity better than 95% by gas-liquid chromatography was

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TABLE I

Experimental Data 2-Alkyl Carboxylic Acids[a]

Acid	Formula	MP[c] °C	BP[c] °C/mm	$n_D^{20°}$	Neut. equival. Found	Neut. equival. Theory	Analysis Found C	Analysis Found H	Analysis Theory C	Analysis Theory H	Reactants Olefin	Reactants Acid	Reaction[d] temp °C	Yield per cent
2-Methyleicosanoic	$C_{18}H_{37}CH(CH_3)CO_2H$	60–1	172–4/0.2	....	331	326	77.46	13.05	77.30	12.90	Octadecene-1	Propionic	140	57
2-Methyloctadecanoic	$C_{16}H_{33}\overset{CH_3}{\overset{\vert}{C}}HCO_2H$	54–5	164–8/0.2	....	305	298	76.58	12.72	76.50	12.75	Hexadecene-1	Propionic	138	56
2-Butyltetradecanoic	$C_{12}H_{25}\overset{C_4H_9}{\overset{\vert}{C}}H—CO_2H$	26	152–3/0.3	1.4500	282	284	75.05	12.33	76.05	12.69	Dodecene-1	Hexanoic	160	63
2-Heptylundecanoic	$C_9H_{21}\overset{C_7H_{15}}{\overset{\vert}{C}}H—CO_2H$	18–9	151/0.3	1.4500	283	284	75.94	12.43	76.05	12.69	Nonene-1	Nonanoic	160	60
2-Octyldecanoic	$(C_8H_{17})_2CHCO_2H$	33–4	162–3/0.5	1.4445[b]	287	284	75.89	12.64	76.05	12.69	Octene-1	Decanoic	160	68
2,2-Dimethylhexadecanoic	$C_{14}H_{29}\overset{CH_3}{\underset{CH_3}{\overset{\vert}{\underset{\vert}{C}}}}—CO_2H$	46.5–7.5	144–6/0.2	....	287	284	76.17	12.59	76.05	12.69	Tetradecene-1	Isobutyric	145	36

[a] Properties of octadecanoic acids previously reported (11).
[b] Determined at 35C.
[c] All melting points and boiling points are uncorrected.
[d] Reaction temperatures are indicated as the median of a 3–6° range.

hydrolyzed with sulfuric acid (12) to an amide mp 108–109C; % nitrogen 5.00, theory % nitrogen 4.95. A mixed melting point of this amide with the amide from 2-butyl tetradecanoic acid resulted in no melting point depression.

Experimental

Reagents

Tertiary butyl peroxide $n_D^{20°} = 1.3889$ was obtained from the Monomer-Polymer Corp., Philadelphia, Pa., and used as received. Reagent carbon tetrachloride was passed through a 12 in. silica gel column and stored over anhydrous sodium sulfate. Dioxane (Eastman yellow label) was distilled through a 24 in. vacuum jacketed column filled with protruded packing. The center cut was passed through a 12 in. column of silica gel and stored over anhydrous sodium sulfate. Sulfur trioxide (Sulfan-Allied Chemical Corp.) was freshly distilled immediately prior to use. The olefins (Humphrey-Wilkinson, petroleum derived) and aliphatic acids (Eastman Organic Chemicals) were distilled through a 24 in. column of protruded packing. Boiling points and refractive indices of the center cuts checked closely with the literature values.

2-Alkyl Carboxylic Acids (6). Carboxylic acid, olefin and t-butyl peroxide were used in the molar ratio of 10/1/0.25, respectively. To an appropriate sized four-neck round-bottom flask equipped with a condenser, stirrer, dropping funnel and thermometer was added two-thirds of the acid to be used. The remaining one-third of the acid was added to the olefin-peroxide mixture and placed in the dropping funnel. After heating the acid to the reaction temperature (125–160C), the acid-olefin-peroxide mixture was added dropwise over a 6-hr period with efficient stirring. After complete addition, the mixture was held at the reaction temperature for one hour to complete the reaction. Simple distillation at reduced pressure separated the mixture into crude fractions which were successively distilled through a 24-in. spinning band column.

2-Sulfo-2-Alkyl Carboxylic Acids. To a 500-ml round-bottom flask equipped with a bar magnet condenser and drying tube was added 240 ml of dry carbon tetrachloride and 0.17 mole dry dioxane. The stirred mixture was cooled to 15C and 0.15 mole of freshly distilled sulfur trioxide in 30 ml of carbon tetrachloride was added to form a white crystalline slurry. After stirring the sulfur trioxide-dioxane slurry for 10 min, 0.1 mole of pure dialkyl acetic acid in 30 ml of carbon tetrachloride was added. The

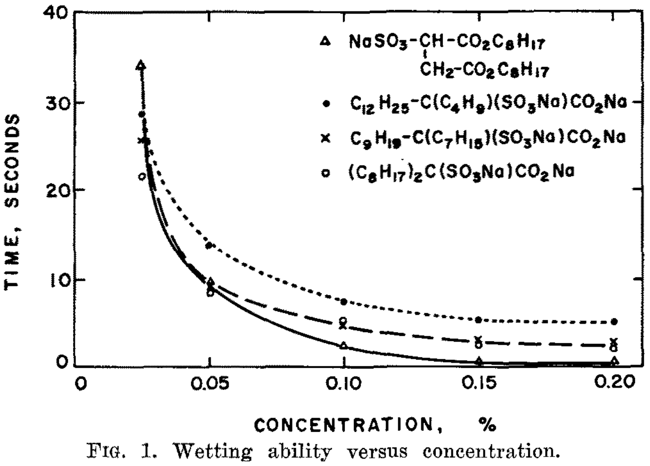

FIG. 1. Wetting ability versus concentration.

TABLE II

Analysis of Disodium 2-Sulfo-2-Alkyl Carboxylates

$RR'C(CO_2Na)SO_3Na$

Compounds	Substituents		Analysis							
			Found				Theory			
	R	R′	C	H	S	Na	C	H	S	Na
Disodium 2-sulfo-										
2-methyleicosanoate	CH_3	$C_{18}H_{37}$	55.74	9.22	6.53	9.89	56.00	8.90	7.12	10.02
2-methyloctadecanoate	CH_3	$C_{16}H_{33}$	54.07	8.65	7.26	10.63	54.03	8.53	7.58	10.90
2-butyltetradecanoate	C_4H_9	$C_{12}H_{25}$	53.40	8.40	8.30	11.28	52.94	8.33	7.84	11.27
2-heptylundecanoate	C_7H_{15}	C_9H_{19}	52.68	8.28	7.57	11.40	52.94	8.33	7.84	11.27
2-octyldecanoate	C_8H_{15}	C_8H_{17}	52.12	8.26	8.68	11.58	52.94	8.33	7.84	11.27

mixture was stirred at room temp for 15 min, 45C for 45 min, and 60C for an additional hour. The final light amber mixture was filtered to remove insolubles and evaporated under vacuum (0.2 mm/1 hr) to remove volatiles. The residue was dissolved in 250 ml of absolute ethanol and neutralized with a slight excess of 6 *N* sodium hydroxide. The precipitate formed was filtered and recrystallized two or three times from ethanol-water mixtures.

Discussion

Pertinent surface active properties of the sodium salts of the 2-alkyl carboxylic acids and 2-sulfonated derivatives are summarized in Table III. The compounds are arranged in the order of increasing size of the 2-alkyl group with the properties of sodium octadecanoate and disodium 2-sulfooctadecanoate (disodium α-sulfostearate) being included for purposes of comparison.

For both mono- and disodium salts, the Krafft point decreases as size of the 2-alkyl group increases. This is a reflection of the degree of molecular symmetry. Within a given series of isomeric compounds, the Krafft point decreases reaching a minimum for the most unsymmetrical molecule and then increases as the symmetry of the molecule approaches a maximum (compare compounds 1, 4, 5 and 6 or the corresponding disodium salts). The Krafft point for the most symmetrically branched molecules, however, is considerably below that of the linear molecule. Early workers in the field found that the Krafft point of soaps of linear carboxylic acids were roughly comparable to the melting points of the corresponding free acids. This is not true for the soaps of the branched chain acids (compare data in Table III with Table I).

In most cases the critical micelle concentration (cmc) of the monosodium soaps could not be measured because clear micellar solutions were not obtained in the presence of pinacyanol chloride. For the disodium salts the homologs disodium 2-sulfo-2-methyloctadecanoate and disodium 2-sulfo-2-methyleicosanoate show an expected decrease to one-fourth of the value (0.97 compared to 0.24) for an increase in chain length by two carbon atoms (18). The good wetting agents, the last 3 compounds of Table III, are characterized by high cmc and high interfacial tension.

As previously mentioned excellent wetting properties are observed for compounds (4,5) of the type $R{-}CH(SO_3Na)CO_2R'$ where the hydrophilic moiety is centrally located. The data in Table III indicate good wetting properties for disodium 2-sulfo-2-alkylcarboxylates in distilled water but with rather poor calcium stability where values are available. These compounds apparently react readily with calcium ion forming insoluble salts. It is expected that esterification of the carboxylate group will result in improved wetting properties and good calcium ion stability. The good wetting ability of the 2-sulfonated derivatives is clearly shown in a plot of wetting time versus concentration (Figure 1) relative to Aerosol-OT.

As is frequently observed, good wetting properties are not necessarily accompanied by good detergency. With the exception of sodium 2-methyleicosanoate, detergency in distilled water is fair at best while for previously mentioned reasons this property is poor in

TABLE III

Surface Active Properties[a]

Sodium Salts of 2-Alkyl Carboxylic Acids and 2-Sulfonated Derivatives

Salt	Krafft point[b] °C	Tension[c]		Critical micelle conc[d] 25C		Calcium ion[e] stability	Wetting time[f] seconds		Detergency terg-o-tometer[g] ΔR		Foam height mm[h]	
		Surface	Interfacial									
		Dynes/cm	Dynes/cm	Mmols/liter	Per cent	ppm $CaCO_3$	Distilled water	300 ppm $CaCO_3$	Distilled water	300 ppm $CaCO_3$	Distilled water	300 ppm $CaCO_3$
Monosodium												
1) Octadecanoate	67.5	......	......	0.50[i]	0.015	....	>300	>300	35	29	238	65
2) 2-Methyleicosanoate	56	35.1	26.3	......	....	....	>300	>300	30	11	149	0
3) 2-Methyloctadecanoate	40.5	26.1	23.4	0.23	0.007	....	>300	>300	29	17	217	15/0
4) 2-Butyltetradecanoate	<1	28.9	13.4	......	....	74	48	>300	21	5	210/130	10/0
5) 2-Heptylundecanoate	12	31.6	14.5	......	....	....	>300	>300	20	6	210/15	115/8
6) 2-Octyldecanoate	17	31.6	15.2	.....	....	....	100	>300	18	6	230/45	140/8
7) 2,2-Dimethylhexadecanoate	39	26.0	10.2	0.50	0.015	258	86	>300	25	11	215	100/25
Disodium												
8) 2-Sulfo octadecanoate	92	......	......	2.45[j]	0.10	....	....	....	20	26	....	....
9) 2-Sulfo-2-methyleicosanoate	53	41.4	9.5	0.24	0.01	....	>300	>300	22	16	193	0
10) 2-Sulfo-2-methyloctadecanoate	43.5	33.8	6.0	0.97	0.04	....	49	>300	22	17	200	45
11) 2-Sulfo-2-butyltetradecanoate	32.5	36.7	12.2	7.0	0.28	95	7.4	>300	8	9	85/5	30/25
12) 2-Sulfo-2-heptylundecanoate	55.5	34.8	13.5	9.1	0.37	36	4.8	85	8	9	0	160/30
13) 2-Sulfo-2-octyldecanoate	67	35.5	15.7	14.1	0.57	31	5.0	>300	8	8	0	95/25

[a] Some properties could not be determined because of the low solubility of some salts.

[b] The temperature at which a 1% dispersion becomes a clear solution on gradual heating.

[c] Determined at 0.1% concentration, 25C with a duNoüy tensiometer.

[d] Determined by pinacyanole method.

[e] Determined on 0.5% solutions (13).

[f] Determined on 0.1% solutions at 25C with a 5 g cotton skein and a 3 g hook (14).

[g] Measured by the increase in reflectance after washing G.D.C. #26 standard soiled cotton in 0.25% solution at 60C.

[h] Measured with 0.25% solutions by the Ross-Miles test at 60C (15). The ratios indicate foam height initially and after 5 minutes.

[i] Conductance method (16).

[j] Solubility method (17).

simulated hard water. Initial foam height for the 2-alkylcarboxylates in distilled water is good; however, where the alkyl groups are of comparable size rapid foam degeneration occurs in 5 min as indicated for monosodium salts (4–6). The remaining data suggest rather poor foaming properties for these salts in simulated hard water and for the sulfonated derivatives in both soft and hard water.

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Omega-Formylalkanoates by Ozonization of Unsaturated Fatty Esters[1]

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Abstract

Ozonization of the methyl esters of 11-eicosenoic, linoleic, erucic and linolenic acids gave a number of different homologous methyl ω-formylalkanoates. Complete ozonization of the monounsaturated esters formed C_{11} and C_{13} compounds with 90% conversion; partial ozonization of the polyunsaturated esters gave C_{12} and C_{15} products with maximum conversions at ca. 75% consumption of fatty ester. Thus, methyl linoleate gave 52 and 23% conversions to the 9- and 12-carbon products, and methyl linolenate gave 29, 27 and 19% conversions to the 9-, 12- and 15-carbon products. Yields of aldehyde or acetal esters in distilled products were 70–90% in preparative-scale experiments. Kinetic analysis showed that ozone attack was essentially random. Methanol was used as a participating solvent.

Introduction

RESEARCH AT THE Northern Laboratory has shown that the 9-carbon aldehyde ester, methyl azelaaldehydate, is a highly versatile chemical intermediate having a wide variety of potential applications (11–15), among them nylon-9 (8). World demand for synthetic resins, fibers and plastics has placed great value on polyfunctional materials; consequently, it seemed desirable to investigate the preparation of homologous ω-formylalkanoates as additional potential intermediates.

The formation in 55–60% yields of C_9 through C_{13} ω-formyl compounds by ozonization of unsaturated esters in glacial acetic acid has been reported (7,19). Starting materials included the methyl esters of oleic undecylenic, 11-dodecenoic, 12-tridecenoic and erucic acids, but only products from oleic, undecylenic and erucic acids were described in detail. The others were prepared as intermediates for subsequent syntheses (19). Schmidt and Grafen (16) prepared the 5- through 8- and the 12-carbon ethyl ω,ω-diethoxyalkanoates from cyclic ketones.

In the production of aldehydic compounds by reductive decomposition of ozonolysis products, the solvent has significant effect on yields. We have reported the use of methanol as a participating solvent in making methyl azelaaldehydate in more than 80% yields of isolated product (9). Extension of this study to the preparation of the C_{11} and C_{13} compounds is reported in this paper. We also describe a new technique consisting of partial ozonization to give C_{12} and C_{15} compounds as well. This technique is based on methyl linoleate and methyl linolenate, starting materials that are more readily available than the terminal olefinic esters previously used.

Experimental

Materials. Methyl oleate ($n_D^{30} = 1.4481$, I.V. = 84.3) was obtained from Applied Science Laboratories (20). Gas-liquid chromatographic (GLC) analysis did not indicate any impurities. Methyl linoleate ($n_D^{30} = 1.4574$, I.V. = 162.0) and methyl linolenate ($n_D^{30} = 1.4660$, I.V. = 241.8) were prepared from acids purified by liquid-liquid centrifugal extraction (1,2). Respective GLC analyses indicated purities of 92.6 and 88.4%. Methyl 11-eicosenoate ($n_D^{30} = 1.4505$, I.V. = 79.7) and methyl erucate ($n_D^{30} = 1.4514$) were obtained by fractional distillation through a spinning band column of the methyl esters prepared from crude erucic acid (Eastman Kodak). GLC analyses of the methyl eicosenoate indicated 95.1% of the C_{20} monoene, 1.2% of C_{18} compounds and 3.7% of C_{22} monoene. No impurities were detected for the methyl erucate fraction. New crop research has shown that *Crambe abyssinica* and mustard (5) are two seed oils rich in erucic acid. Accordingly, methyl erucate was also obtained by recrystallization of crude acids from *Crambe abyssinica* seed oil in 4:1 acetone water (4), followed by esterification and distillation. New oilseeds rich in 11-eicosenoic acid have also been reported (5).

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[2] A laboratory of the No. Util. Res. & Dev. Div., ARS, USDA.