United States Patent Office

3,230,244
Patented Jan. 18, 1966

3,230,244

2-SULFOALKYL SULFATES AND METHOD OF PREPARATION

Alexander J. Stirton, Philadelphia, Frank D. Smith, Huntingdon Valley, and James K. Weil, North Wales, Pa., assignors to the United States of America as represented by the Secretary of Agriculture

No Drawing. Original application Jan. 16, 1963, Ser. No. 251,985. Divided and this application Aug. 26, 1963, Ser. No. 311,933

6 Claims. (Cl. 260—458)

(Granted under Title 35, U.S. Code (1952), sec. 266)

This application is a division of application bearing Serial No. 251,985, filed January 16, 1963.

This invention relates to 1-hydroxy-2-alkanesulfonates, derivatives thereof, and method of preparation. The compounds of this invention are useful as chemical intermediates, surface active agents, detergents, and lime soap dispersing agents.

An object of the present invention is to provide a process for the preparation of 1-hydroxy-2-alkanesulfonates of the formula $RCH(SO_3M)CH_2OH$, wherein R is a normal alkyl group having 7 to 16 carbon atoms and M is sodium, potassium, lithium, or hydrogen.

Another object of this invention is to prepare compounds of the formula $RCH(SO_3M')CH_2OSO_3M'$, wherein R is a normal alkyl group having 7 to16 carbon atoms and M' is sodium, potassium, or lithium.

A further object is to prepare compounds for use as the active ingredient in products such as solid detergent compositions, liquid syndet compositions, detergent bars, or in soap-detergent combinations.

Other objects and a fuller understanding of the present invention may be had by referring to the following description and claims.

In general according to the present invention an ester of the Formula I

$$RCH(SO_3M)CO_2R' \quad (I)$$

wherein R is a normal alkyl group containing 7 to 16 carbon atoms, R' is methyl, ethyl, n-propyl or isopropyl and M is sodium, potassium or lithium, a substantially anhydrous solvent and dispersing medium consisting of a low molecular weight primary or secondary alcohol, particularly an alkanol, and a metal borohydride such as sodium borohydride or lithium borohydride, are combined, and the mixture is heated until the reaction is substantially complete, to form a 1-hydroxy-2-alkanesulfonate of the Formula II

$$RCH(SO_3M)CH_2OH \quad (II)$$

wherein R and M remain unchanged.

The discovery that an alkali metal salt of an alkyl ester of a long chain α-sulfo fatty acid could be smoothly and selectively reduced at the carboxylic ester group to give the corresponding primary alcohol group was unexpected. The inertness of the sulfo group under the conditions of the reaction was not predictable. Even more surprising, and contrary to previously reported information, is the discovery that sodium borohydride is an effective reducing agent for the carboxyl function in the ester group.

The esters of Formula I are prepared by well known procedures, sulfonating a fatty acid with SO_3 or $ClSO_3H$, as illustrated by the equation,

$$RCH_2CO_2H+SO_3\rightarrow RCH(SO_3H)CO_2H \quad (1)$$

esterifying the α-sulfo fatty acid product at the carboxyl group:

$$RCH(SO_3H)CO_2H+R'OH\rightarrow RCH(SO_3H)CO_2R'+H_2O \quad (2)$$

and then neutralizing as follows:

$$RCH(SO_3H)CO_2R'+MOH\rightarrow RCH(SO_3M)CO_2R'+H_2O \quad (3)$$

where R, R' and M are as previously described. Alternatively, the α-sulfo fatty acid may be first selectively neutralized at the sulfonic acid group and then esterified to give the same product, as illustrated by Equations 4 and 5:

$$RCH(SO_3H)CO_2H+MOH\rightarrow RCH(SO_3M)CO_2H+H_2O \quad (4)$$

$$RCH(SO_3M)CO_2H+R'OH\rightarrow RCH(SO_3M)CO_2R'+H_2O \quad (5)$$

The reaction to produce the 1-hydroxy-2-alkanesulfonates of the present invention is considered to proceed according to the following equation:

$$2RCH(SO_3M)CO_2R'+MBH_4+(2H^++2OH^-)\rightarrow 2RCH(SO_3M)CH_2OH+2R'OH+MBO_2 \quad (6)$$

While the reaction gives high yields of the indicated product, a side reaction proceeds as follows:

$$RCH(SO_3M)CO_2H+R'HOH\rightarrow RCH(SO_3M)CO_2H+R'OH \quad (7)$$

Since this product, the salt of the α-sulfo fatty acid, may be recovered and used again in the esterification and reduction reactions, the yield of 1-hydroxy-2-alkanesulfonate from starting material is substantially 100%.

In a preferred embodiment of the present invention a compound of the Formula I, where M is sodium or lithium, and R' is methyl or isopropyl, is combined in isopropanol with about a 1.2 to 2.4 molar ratio of sodium borohydride or lithium borohydride, the mixture is heated at reflux temperature for several hours, and a 1-hydroxy-2-alkanesulfonate separated from the reaction mixture.

The 1-hydroxy-2-alkanesulfonate is a useful chemical intermediate, detergent and surface active agent. It may be sulfated at the primary alcohol group:

$$RCH(SO_3M)CH_2OH + ClSO_3H \rightarrow RCH(SO_3M)CH_2OSO_3H + HCl \quad (8)$$

or the primary alcohol group may be employed in esterification reactions with organic carboxylic acids or sulfocarboxylic acids.

In another embodiment of the invention the reduction product is separated as the free sulfonic acid by the use of ion exchange techniques, as illustrated in the equation:

$$RCH(SO_3M)CH_2OH + H^+ \rightarrow RCH(SO_3H)CH_2OH + M^+ \quad (9)$$

then sulfated and isolated as the salt

$$RCH(SO_3M)CH_2OSO_3M$$

usually as the less expensive disodium salt. Sulfation is preferably carried out on isolated 1-hydroxy-2-alkanesulfonic acid in chloroform by means of a 1.4 to 1.7 molar ratio of chlorosulfonic acid.

While the invention is exemplified with esters derived from commercially available fatty acids such as pelargonic, lauric, myristic, palmitic and stearic acids, the process is considered applicable to esters derived from fatty acids having 9 to 18 carbon atoms, or mixtures thereof.

Preferred esters are those in which the alcohol moiety is obtained from methanol or isopropanol, but R' may be derived from other short carbon chain primary or secondary alcohols such as ethanol, n-propanol, n-butanol, or isobutanol.

Although other types of metal borohydride reductions, such as reduction of ketones with sodium borohydride, are reported to proceed satisfactorily in aqueous systems, the process of the present invention is, at least for all practical purposes, operative only in anhydrous systems.

The solvent is preferably a low molecular weight primary or secondary alkanol, several of which are listed above. Isopropanol is the especially preferred solvent because its solubility and boiling point characteristics are conducive to higher yields of the desired product than those obtainable with other low molecular weight alcohols.

Yield of the 1-hydroxy-2-alkanesulfonate is also improved by using an excess of the reducing agent, preferably a ratio of 1.2 to 2.4 moles of sodium borohydride or lithium borohydride per mole of ester.

The reaction mixture is heated, conveniently to the reflux temperature of the solvent, until the reaction is considered substantially complete. Various factors, such as solubility of substrate and reducing agent in the solvent, boiling point of the solvent, and choice of reducing agent, affect the time required to obtain optimum yield of 1-hydroxy-2-alkanesulfonate. While many reductions are complete in a few hours, some were allowed to continue 24 hours to provide ample time for complete reaction.

Since the 1-hydroxy-2-alkanesulfonates of Formula II are not very soluble in water, especially when M is sodium, a convenient means of separating the product from the reaction mixture is to evaporate most of the solvent and add water, thus converting the borohydride reducing agent to water soluble products and precipitating the 1-hydroxy-2-alkanesulfonate so that it may be recovered as a solid.

The product may be further purified, as by recrystallization from methanol.

In operating the process to obtain definite chemical compounds for purposes of comparative evaluation the same metal (M) was selected for the ester and for the reducing agent. In many instances the production of 1-hydroxy-2-alkanesulfonates which are a mixture of salts of potassium, sodium and lithium may be more practical or desirable. Regardless of the particular ester or reducing agent in the reaction mixture, the inclusion of the ion exchange step using a strongly acidic cation exchange resin, producing the free sulfonic acid derivative, makes it possible to prepare the desired 1 hydroxy-2-alkanesulfonates or mixture of alkanesulfonates, by neutralizing with a particular base or a mixture of basic materials.

Many ion exchange resins which are suitable for use in the process are available from commercial sources.

Yields of recrystallized 1-hydroxy-2-alkanesulfonate are usually about 60% or higher and the by-product salt of the hydrolyzed ester is recovered for recycling.

Sulfation of the 1-hydroxy-2-alkanesulfonate to the 2-sulfoalkyl sulfate likewise proceeds in good yield, which could not have been predicted in view of possible dehydration and polymerization reactions.

Properties of the products of our invention are shown in Tables I, II, III, IV.

The Krafft point, a convenient indication of relative solubility, may be defined as the temperature at which a 1% turbid aqueous dispersion changes sharply to a clear solution on gradual heating. The critical micelle concentration, abbreviated as "CMC", is the concentration at which simple ions or molecules aggregate to form colloidal micelles.

The alkali metal salts of 1-hydroxy-2-alkanesulfonic acids particularly those of 14 or more carbon atoms, have limited solubility, attributable to hydrogen-bonding. The corresponding free acids formed by ion exchange are, in contrast, easily soluble, as can be seen in Table II. Isolation of the free acid permits the easy formation of more readily soluble salts with aqueous ammonia, lower molecular weight amines and alkanolamines.

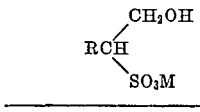
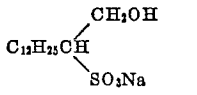
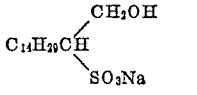
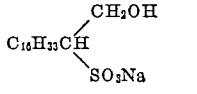
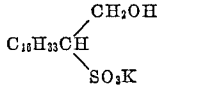
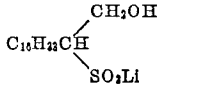
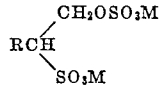
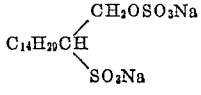
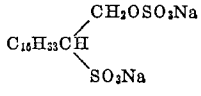
As can be seen from Table I the lithium salt is more soluble than the corresponding sodium 1-hydroxy-2-alkanesulfonate and the reduction of the lithium salt of an alkyl ester of an α-sulfo fatty acid can be carried out with $LiBH_4$ and the product can be isolated as the soluble lithium salt $RCH(SO_3Li)CH_2OH$ without the necessity of ion exchange.

TABLE I

1-hydroxy-2-alkanesulfonates and 2-sulfoalkyl sulfates

$RCH(CH_2OH)SO_3M$	Krafft point,[a] ° C.	CMC[b]		Elemental analysis, found/theo.			
		Percent	Mmoles per liter	Percent Na	Percent C	Percent H	Percent S
$C_7H_{15}CH(CH_2OH)SO_3Na$	<3	No micelles, 1%, 25°.		9.29/9.34			
$C_{16}H_{21}CH(CH_2OH)SO_3Na$	56	.43	15.0	8.01/7.97	50.09/49.98	8.77/8.74	11.13/11.12

TABLE I—Continued

	Kraft point,[a] ° C.	CMC [b]		Elemental analysis, found/theo.			
		Percent	Mmoles per liter	Percent Na	Percent C	Percent H	Percent S
	71	.11	3.4	7.25/7.27	53.13/53.14	9.09/9.24	10.21/10.13
	84	.010	.3	6.72/6.68	56.13/55.78	9.65/9.66	9.27/9.31
	93	.0037	.1	6.12/6.17	58.08/58.03	10.02/10.01	8.99/8.61
	73.5			[c] 9.83/10.06			
	33			[d] 2.00/1.96			
							
	Solubility >30% at 25°.	.4	8.9	10.17/10.30	43.19/43.03	7.33/7.22	14.35/14.36
	Solubility >15% at 25°.	.17	3.6	9.65/9.69	45.51/45.55	7.61/7.65	13.60/13.51

[a] Temperature at which a 1% turbid dispersion becomes clear on gradual heating.
[b] Critical micelle concentration.
[c] Percent K.
[d] Percent Li.

TABLE II

1-hydroxy-2-alkanesulfonic acids

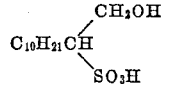
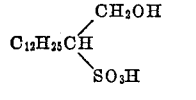
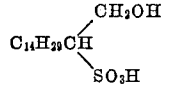
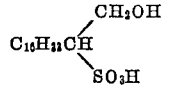
	Neutralization equivalent, found/theo.	Melting point, ° C.	Krafft point, ° C.	Critical micelle concentration	
				Percent	Millimoles/l.
	265.9/266.4	108	Easily soluble below 25°.	.35	16.1
	294.0/294.4	111.5	----do----	.057	2.61
	322.9/322.5	114.6	----do----	.021	0.58
	350.0/350.6	115	28.5----	.0078	0.21

TABLE III

Detergency and foam

	Detergency, Terg-O-Tometer, standard soiled cotton, 10 swatches/liter, 60° C., ΔR=increase in reflectance after washing			Foam height, Ross-Miles test, 60° C., mm.	
	0.25%, distd. water	0.25%, 300 p.p.m.	0.25% built,[a] 300 p.p.m.	.25% distd.	.25% 300 p.p.m.
$C_{12}H_{25}CH(CH_2OH)SO_3Na$	14.8	----------	----------	----------	----------
$C_{14}H_{29}CH(CH_2OH)SO_3Na$	25.0	----------	----------	----------	----------
$C_{16}H_{33}CH(CH_2OH)SO_3Na$	26.2	----------	----------	----------	----------
$C_{18}H_{37}CH(CH_2OH)SO_3Na$	24.8	----------	----------	----------	----------
$RCH(CH_2OSO_3Na)SO_3Na$					
$C_{14}H_{29}CH(CH_2OSO_3Na)SO_3Na$	13.2	16.0	15.9	155	190
$C_{16}H_{33}CH(CH_2OSO_3Na)SO_3Na$	26.8	22.3	22.1	200	205

[a] Concentration of .05% active ingredient, 0.2% inorganic polyphosphate-phosphate sulfate builder.

TABLE IV

Surface active properties of disodium 2-sulfoalkyl sulfates

	Solubility, 25° C., percent	CMC,[a] percent	Surface tension, dynes per cm., 25° C., .2%	Wetting time, seconds Draves test [b]		Ca^{++} stability,[c] p.p.m. $CaCO_3$	Metal ion stability [d]	Stability to Hydrolysis [e]	Lime soap dispersing power,[f] percent
				.1% distd. water	.1% 300 p.p.m.				
$C_{14}H_{29}CH(CH_2OSO_3Na)SO_3Na$	>30	.4	55.4	180	84	>1,800	Values of 100 (excellent) for Ni^{++}, Mg^{++}, Ca^{++}, Cu^{++}, Zn^{++}, Al^{+++}, Fe^{++}. Value of 75 for Pb^{++}, 15 for Ba^{++}.	Stable to alkaline hydrolysis. Hydrolyzed in N/10 HCl in 1 hour at 100° C.	85
$C_{16}H_{33}CH(CH_2OSO_3Na)SO_3Na$	>15	.17	40.2	28	42	>1,800			5

[a] Critical micelle concentration.
[b] A.A.T.C.C. Tech. Manual 36, 161-3 (1960), standard test method.
[c] Wilkes and Wickert, Ind. Eng. Chem. 29 1234-9 (1937). A value as high as 1,800 means complete stability to hard water.
[d] "Detergency Evaluation and Testing," by J. C. Harris, pages 22-7 (1954). A value as high as 100 means complete stability to this metal ion.
[e] The disodium 2-sulfoalkyl sulfates like the sodium alkyl sulfates are not hydrolyzed in alkali but can be hydrolyzed in hot acid solutions.
[f] Borghetty and Bergman, J. Am. Oil Chemists' Soc. 27, 88-90 (1950). A value of 5% is excellent and means that 5 grams will disperse the Ca soap formed from 100 grams of Na oleate.

Tables I, III and IV demonstrate that sulfation of the 1-hydroxy-2-alkanesulfonates of our invention improves solubility, detergent and foaming properties, particularly in the 18 carbon compound, increases the critical micelle concentration, and greatly improves resistance to precipitation by hard water and various metal ions. The 2-sulfoalkyl sulfates are easily soluble detergents and surface active agents, stable to alkaline hydrolysis and about as stable to acid hydroylsis as hte related sodium alkyl sulfates. In particular the 18 carbon compound, disodium 2-sulfooctadecyl sulfate, is an excellent lime soap dispersing agent and therefore can be used effectively with soap in hard water to make useful soap-detergent combinations.

The following examples further demonstrate the products and the process of our invention.

EXAMPLE

$LiBH_4$ *reduction of* Li *isopropyl α-sulfostearate.*—A solution of 22.6 grams (54.8 millimoles) of

$$C_{16}H_{33}CH(SO_3Li)CO_2CH(CH_3)_2$$

in 270 ml. of isopropanol was heated and 50 ml. of the solvent was distilled to remove traces of moisture. Lithium borohydride (1.48 grams, 68.5 millimoles) was added during 3 minutes, the solution was refluxed 24 hours, 300 ml. of water was added and the mixture was refluxed an additional hour.

The aqueous isopropanol solution was poured through an ion exchange column containing 400 ml. of a strongly acidic cation exchange resin (Dowex 50W–X8), the eluate 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 $C_{16}H_{33}CH(SO_3Na)CH_2OH$, yield 61% with the analysis and properties shown in Tables I and III.

EXAMPLE II

$NaBH_4$ *reduction of* Na *methyl α-sulfostearate.*—A solution of 8.0 grams (20.0 millimoles) of

$$C_{16}H_{33}CH(SO_3Na)CO_2CH_3$$

in 150 ml. of isopropanol was heated and 25 ml. of solvent was distilled to remove traces of water. Sodium borohydride (1.76 grams, 46.5 millimoles) was added during 3 minutes and the mixture was refluxed for 24 hours. Separation of the 1-hydroxy-2-alkanesulfonate from hydrolyzed ester gave 44% yield of

$$C_{16}H_{33}CH(SO_3Na)CH_2OH$$

and 56% recovery of disodium α-sulfostearate.

EXAMPLE III

$LIBH_4$ *reduction of* Li *methyl α-sulfomyristate.*—A solution of 41.4 grams (126 millimoles) of

$$CC_{12}H_{25}CH(SO_3Li)CO_2H_3$$

was dissolved in 450 ml. of isopropanol and 50 ml. was distilled to remove traces of moisture. Lithium borohydride (3.44 grams, 158 millimoles) was added during 3 minutes and the mixture was refluxed 24 hours. Separation as described in Example I gave 74% yield of

$$C_{12}H_{25}CH(SO_3Na)CH_2OH$$

and 26% recovery of disodium α-sulfomyristate.

EXAMPLE IV

1-hydroxy-2-alkanesulfonic acids.—Sodium 1-hydroxy-2-hexadecanesulfonate, 2.9 grams, was dissolved in 150 ml. of isopropanol by heating and stirring in the presence of 100 ml. of a strongly acidic cation exchange resin (Dowex 50W–X8), passed through a column containing 300 ml. of the exchange medium and eluted with 900 ml. of isopropanol.

The isopropanol solution was evaporated in a rotary evaporator at 80° C. and 10 mm. the residue was dissolved in 100 ml. of chloroform and water was removed azeotropically. Crystallization from chloroform at −20° C. and drying for 1 hour in a vacuum oven gave 1-hydroxy-2-hexadecanesulfonic acid with the analysis and properties shown in Table II. The 1-hydroxy-2-alkanesulfonic acids of our invention are hygroscopic crystals which soften and pass through a glassy stage before melting sharply at the temperatures listed in Table II.

EXAMPLE V

Sulfation of 1-hydroxy-2-alkanesulfonic acids. Disodium 2-sulfooctadecyl sulfate.—Chlorosulfonic acid (12.2 ml., 21.5 grams, 185 millimoles) was added slowly in 1.7 molar ratio to a stirred slurry of 37.9 grams (108 millimoles) of $C_{16}H_{33}CH(SO_3H)CH_2OH$ in 500 ml. of carbon tetrachloride at 23° C. A clear solution developed during the addition, HCl was evolved and the temperature dropped to 20° C. The mixture was stirred and heated at 20–45° C. for 20 minutes, with a slight color development.

The sulfation mixture was cooled to 0° C., 200 ml. of 95% ethanol was added, and the mixture was made slightly alkaline with aqueous 18 N sodium hydroxide. The precipitated solids were filtered off, treated with 60% ethanol, and filtered. Crystallization of the aqueous alcohol filtrate at 0° C. gave an 82% yield of disodium 2-sulfooctadecyl sulfate, purity 92%, further purified by crystallization from 80% ethanol at 0° C. to give disodium 2-sulfooctadecyl sulfate in a pure state, yield 77%, with the analysis and properties shown in Table I, III, and IV. Disodium 2-sulfohexadecyl sulfate was obtained in a similar manner.

We claim:

1. A compound of the formula

$$RCH(SO_3M')CH_2OSO_3M'$$

wherein R is a normal alkyl group containing 7 to 16 carbon atoms, and M' is selected from the group consisting of sodium, potassium and lithium.

2. Disodium 2-sulfohexadecyl sulfate.

3. Disodium 2-sulfooctadecyl sulfate.

4. A process for the preparation of a metal salt of a 2-sulfoalkyl sulfate comprising combining (a) an ester of the formula

$$RCH(SO_3M)CO_2R'$$

wherein R is a normal alkyl group containing 7 to 16 carbon atoms, R' is a lower alkyl group, and M is selected from the group consisting of sodium, potassium and lithium, and (b) a metal borohydride selected from the group consisting of sodium borohydride and lithium borohydride, in (c) a substantially anhydrous low molecular weight alkanol, heating the mixture until the reduction is substantially complete, thereby producing a 1-hydroxy-2-alkanesulfonate of the formula

$$RCH(SO_3M)CH_2OH$$

wherein R and M have the same significance as above, mixing the reaction mixture with water, contacting the 1-hydroxy-2-alkanesulfonate contained in the resulting aqueous alcohol solution with an excess of a strongly acidic cation exchange resin in the acid cycle, separating from the aqueous alcohol solution a 1-hydroxy-2-alkanesulfonic acid of the formula

$$RCH(SO_3H)CH_2OH$$

wherein R has the same significance as above, sulfating said 1-hydroxy-2-alkanesulfonic acid, mixing sufficient alkaline hydroxide of the formula M'OH wherein M' is a metal selected from the group consisting of sodium, potassium, and lithium with the sulfation reaction mixture to provide a pH of at least 7.0, and separating from the neutralized sulfation reaction mixture a metal salt of a 2-sulfoalkyl sulfate of the formula

$$RCH(SO_3M')CH_2OSO_3M'$$

wherein R is a normal alkyl group containing 7 to 16 carbon atoms and M' is selected from the group consisting of sodium, potassium and lithium.

5. The process of claim 4 in which R is tetradecyl and M' is sodium.

6. The process of claim 4 in which R is hexadecyl and M' is potassium.

(References on following page)

References Cited by the Examiner

UNITED STATES PATENTS

2,267,731	12/1941	Guenther et al.	260—513
2,909,554	10/1950	Doerr	260—458
2,923,728	2/1960	Falk et al.	260—459
2,938,872	5/1960	Cowan et al.	260—458 X

OTHER REFERENCES

Calmon et al., "Ion Exchangers in Organic and Biochemistry," pp. 136–137 (1957).

Gaylord, "Reduction With Complex Metal Hydrides," pp. 500–509 (1956).

Kunin, "Ion Exchange Resins," 2nd Ed., pp. 106–108 (1958).

Nachod et al., "Ion Exchange Technology," pp. 96–97 (1956).

Suter et al., "J.A.C.S.," vol. 60, pp. 538–540 (1938).

CHARLES B. PARKER, *Primary Examiner.*

JOSEPH P. BRUST, FLOYD D. HIGEL,
Assistant Examiners.