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ALKYL ESTERS OF SULPHATO-CARBOXYLIC ACIDS

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This invention relates to new chemical compounds, their methods of manufacture, and their technical uses, and more particularly to the production and utilization of alkyl esters of branched-chain, aliphatic mono-sulphato-monocarboxylic acids wherein the alkyl radical contains at least 4 carbon atoms and the monocarboxylic acid radical contains at least 4 carbon atoms.

This invention has as an object the preparation of a number of new chemical compounds which have surface active properties. A further object is to manufacture these new compounds by novel and easily conducted processes which give high yields of products of relatively high quality. A still further object is to use these new compounds in various technical processes wherein surface active compounds are commonly employed. Other objects will appear hereinafter.

These objects are accomplished by the following invention which relates in a general way to the production of alkyl esters of branched-chain, aliphatic mono-sulphato-monocarboxylic acids wherein the alkyl radical contains at least 4 carbon atoms—preferably from 6 to 16 carbon atoms—and the monocarboxylic acid radical contains at least 4 carbon atoms—preferably from 6 to 12 carbon atoms. In the preferred embodiments of this invention the alkyl radicals of these esters are derived from branched, open chain alcohols, and the sulphato group is attached to the carbon atom in the monocarboxylic acid radical which is in alpha position to the carboxyl group. These alkyl esters of branched-chain aliphatic sulphato-monocarboxylic acids may be made by sulphating alkyl esters of monohydroxy or mono-unsaturated, branched-chain, aliphatic monocarboxylic acids. The products of this invention may also be obtained by esterifying a branched-chain aliphatic sulphato-monocarboxylic acid with an aliphatic alcohol.

The following examples illustrate but do not limit the invention. All parts are given by weight.

Example I

Beta-ethylhexyl alpha-(sodium sulphato)-beta-ethyl-heptoate

Fourteen and three-tenths parts of 2-ethylhexyl alpha-hydroxy-beta-ethyl-heptoate was dissolved in 72 parts of anhydrous ethyl ether and cooled to 0° C. Six and four-tenths parts of chlorosulphonic acid was added slowly, and the solution was stirred for three hours. Two hundred parts of ice was then added to the reaction mixture, which was neutralized with 4% aqueous sodium hydroxide solution. The ether layer was separated, and the aqueous layer was extracted four times with ether. The combined ether extracts were dried with sodium sulphate, filtered and the ether evaporated. The soft, viscous, yellow oil, after drying over phosphorus pentoxide in a vacuum desiccator, amounted to 14 parts. The product, beta-ethylhexyl alpha-(sodium sulphato)-beta-ethylheptoate, formed foaming aqueous solutions which wet powdered sulphur. Dilute aqueous solutions of this product wet skeins of cotton thread very rapidly when tested by the method of Draves and Clarkson (American Dyestuffs Reporter 20, 201 (1931)).

Example II

Octyl alpha-(sodium sulphato)-beta-ethyl-valerate

Twenty-five and eight-tenths parts of n-octyl alpha-hydroxy-beta-ethylvalerate was dissolved in 72 parts of anhydrous ethyl ether and cooled to 0° C. Twelve and eight-tenths parts of chlorosulphonic acid was slowly added to the reaction mixture which was then stirred for 3 hours. Two hundred parts of ice was then added to the reaction mixture, which was neutralized with 4% aqueous sodium hydroxide solution. At this stage the product was a clear solution, so the ether layer was salted out with sodium chloride. The aqueous layer was then extracted four times with ethyl ether, the ether extracts dried with sodium sulphate, filtered and the ether evaporated. The product was dried over phosphorus pentoxide and was isolated as a viscous white syrup (36.5 parts). Dilute aqueous solutions of n-octyl alpha-(sodium sulphato)-beta-ethylvalerate wet powdered sulphur rapidly and are very good wetting agents for cotton thread when tested by the method of Draves and Clarkson. On an equal active ingredient basis this product with the straight-chain octyl group is somewhat inferior as a wetting agent to the product of Example I which has the branched-chain 2-ethylhexyl group.

Example III

Dodecyl alpha-(sodium sulphato)-beta-ethyl-valerate

Twenty-five and two-tenths parts of n-dodecyl alpha-hydroxy-beta-ethyl-valerate was dissolved in 72 parts of anhydrous ethyl ether and sulphated with 11.6 parts of chloro-sulphonic acid at 0° C. After stirring 3 hours, ice was added to the reaction mixture, which was then neutralized with 4% sodium hydroxide solution. The reaction mixture was extracted with ethyl ether and the ether extracts dried with sodium sulphate, filtered and the ether evaporated. After drying over phosphorus pentoxide in a vacuum desiccator, 35 parts of a white viscous syrup was obtained which analyzed 7.6% sulphur. The theoretical sulphur content of dodecyl alpha-(sodium sulphato)-beta-ethylvalerate is 7.5%. The product gives foaming solutions in water

which wet powdered sulphur. Dilute aqueous solutions of the product are very good wetting agents for cotton thread when tested by the method of Draves and Clarkson.

EXAMPLE IV

A mixture of alkyl esters is prepared by esterifying a mixture of acids comprising alpha-hydroxy isovaleric acid, alpha-hydroxy-beta-ethyl-valeric acid and alpha-hydroxy-beta-ethyl-heptoic acid with a fraction boiling from 180–200° C. of the mixture of higher aliphatic alcohols obtained in the catalytic synthesis of methanol from carbon monoxide and hydrogen. This fraction of these alcohols contains some 4- or 5-methyl heptanol-1 and various unidentified primary and secondary branched, open-chain alcohols of higher carbon content. Fifteen parts of this mixture of esters is dissolved in 85 parts of ethyl acetate and sulphated at −10° to −20° C. by adding 7 parts of chlorosulphonic acid. The mixture of sulphated esters is neutralized with an aqueous solution of sodium hydroxide and the product is isolated and purified as described in Example I.

It is to be understood that the aforementioned examples are illustrative merely of the many modifications of the present invention. The individual components, the proportion of such components and conditions for reacting them may vary widely without departing from the scope of the invention. The products contain not more than one sulphate group on the residue of the acid, since it has been observed that more than one sulphate group tends to disturb the balance between the lipophile and the hydrophile portions of the molecule and renders the products less efficient, especially when they are to be employed as wetting agents.

The esters to be sulphated may be prepared from branched or straight, open-chain, saturated aliphatic alcohols containing at least 4 carbon atoms, such as the straight and branched-chain primary and the various isomeric secondary butyl alcohols, amyl alcohols, hexyl alcohols, heptyl alcohols, octyl alcohols, nonyl alcohols, decyl alcohols, undecyl alcohols, dodecyl alcohols, tridecyl alcohols, tetradecyl alcohols, pentadecyl alcohols, hexadecyl alcohols, octadecyl alcohols, etc.

These alcohols may be obtained by the hydrogenation of acids or esters of animal, vegetable or synthetic origin, or by the chemical or catalytic reduction of aldehydes or ketones. A few of the alcohols which can be used in preparing the esters to be sulphated are isobutyl alcohol, hexanol-1, 2-ethylbutanol, heptanol-1, 2,4-dimethylpentanol-1, 2,4-dimethylhexanol-3, octanol-3, octanol-2, 5-ethylheptanol-2, decanol-1, 5-ethylnonanol-2, 3-ethyldecanol-6, 3-ethylundecanol-6, tridecanol-2, tetradecanol-1, pentadecanol-8, 3,9-diethylundecanol-6, hexadecanol-1, octadecanol-1, 4,6 - dimethylheptanol - 1,2,4,6 - trimethyloctanol-1, 2,4,6,8-tetramethyldecanol-1, 7-ethyl-2-methylundecanol-4, the branched-chain alcohols obtained in the catalytic synthesis of methanol by the hydrogenation of carbon monoxide, etc. In place of individual alcohols, mixtures thereof may be used, the various components of which may vary from traces to major fractions. In general I prefer to use primary alcohols and especially branched-chain primary alcohols of which 2-ethylhexanol-1 is the preferred example.

In selecting monocarboxylic branched-chain aliphatic acids for esterification, it should be understood that the acids should contain either one double bond or one hydroxyl group. The esterifying acid containing a double bond or a hydroxyl group may be subjected to treatment with sulphating agents either prior to, simultaneously with, or preferably subsequent to the esterification reaction. Suitable alpha-hydroxy-branched-chain monocarboxylic acids are readily obtained by reacting branched-chain aldehydes or ketones, such as isobutyraldehyde, 2-ethylbutyraldehyde, 2-ethylhexaldehyde, diisopropyl ketone, etc. with hydrogen cyanide and then hydrolyzing the resulting hydroxynitrile. A few examples of suitable acids include alpha-hydroxyisobutyric acid, alpha-hydroxyisovaleric acid, alpha-hydroxy-alpha-methylbutyric acid, alpha-hydroxy-gamma-methylvaleric acid, alpha-hydroxy-alpha-ethylbutyric acid, alpha-hydroxy-alpha-methyl-beta-methylbutyric acid, alpha-hydroxy-beta-methylbutyric acid, alpha-hydroxy-alpha-propylvaleric acid, alpha - hydroxy - alpha - methylundecylic acid, beta-hydroxy-beta-ethylvaleric acid, alpha-methyl-beta-hydroxybutyric acid, beta-hydroxy-beta-methylbutyric acid, alpha-ethyl-beta-hydroxypropionic acid, alpha - dimethyl - beta - hydroxypropionic acid, alpha-ethyl-beta-hydroxybutyric acid, alpha-methyl-beta-hydroxyvaleric acid, beta-hydroxyisocaproic acid, beta-hydroxyisoheptylic acid, etc.

The gamma, delta and epsilon hydroxy branched-chain monocarboxylic acids represent another class of hydroxyacids which may be employed for esterification. These hydroxy acids are usually isolated as lactones. A few examples of this class are alpha-ethyl-gamma-hydroxybutyric acid, beta-methyl-gamma-hydroxyvaleric acid, gamma-methyl-gamma-hydroxyvaleric acid, delta-methyl-gamma-hydroxycaproic acid, alpha, alpha-dimethyl-gamma-hydroxy-valeric acid, alpha-ethyl-gamma-hydroxyvaleric acid, alpha, alpha-dimethyl-delta-hydroxyvaleric acid, gamma-ethyl-delta-hydroxycaproic acid, beta-methyl-epsilon-isopropyl - epsilon - hydroxycaproic acid, etc.

A few examples of branched-chain unsaturated mono-carboxylic acids which may be used for esterification are methacrylic acid, alpha, beta-dimethylacrylic acid, alpha-methylcrotonic acid, alpha-ethylacrylic acid, alpha - ethyl - crotonic acid, alpha-ethylhexenoic acid, etc. Suitable unsaturated branched-chain monocarboxylic acids may also be obtained by the removal of water from many of the above-listed hydroxy monocarboxylic acids.

In place of individual hydroxy monocarboxylic acids or unsaturated monocarboxylic acids, mixtures thereof may be used, the various components of which may vary from traces to major fractions.

The methods of esterifying an acid or acid derivative with an alcohol or alcohol derivative are well known, and need not be described in detail herein. However, mention may be made of the fact that such esterification reactions may be carried out in the presence or absence of solvents, diluents, and/or agents having an avidity for water.

I prefer to employ esters containing from 12 to 22 carbon atoms made from branched-chain acids containing from 6 to 12 carbon atoms with alcohols having from 6 to 16 carbon atoms. In general I prefer to use the branched-chain alcohols for esterification.

The sulphated products described herein are true sulphuric acid esters, wherein the sulphur

atom is connected to the hydrocarbon radical through an oxygen atom. Sulphating agents which may be used in obtaining the products of this invention include concentrated sulphuric acid, fuming sulphuric acid, chlorosulphonic acid, sodium chlorosulphonate, urea sulphuric acid, SO_3 in ether solution, pyridine sulphuric anhydride, pyridine sodium pyrosulphate, etc. Sulphation may be carried out in the presence of solvents or diluents such as water, aliphatic hydrocarbons, esters, ethers, carbon tetrachloride, trichloroethylene, symmetrical dichloroethyl ether, acetic anhydride, nitrobenzene, etc. Ethyl ether, propyl acetate and ethyl acetate are preferred solvents for carrying out the reaction. This reaction is advisedly carried out within the temperature range of from —30° C. to 50° C. and preferably at the lower range of temperature. Esters of hydroxy monocarboxylic acids are preferably sulphated with chlorosulphonic acid in a suitable diluent like ethyl ether, while esters of unsaturated monocarboxylic acids may be sulphated with sulphuric acid, sodium acid sulphate or sodium pyrosulphate or mixtures of these sulphating agents.

The sulphuric acid esters described herein may be used as such, but generally they are converted to their alkali metal salts by neutralization with an alkali metal hydroxide such as sodium hydroxide. The potassium, ammonium, calcium and magnesium salts may also be prepared and used. Suitable salts of the sulphuric acid esters described herein may also be made from such amines as dimethylamine, ethylamine, diethanolamine, triethanolamine, butylamine, glucamine, methylglucamine, pyridine, piperidine, cyclohexylamine, aniline, toluidine, etc.

The term "esters of branched-chain sulphato-monocarboxylic acids" as used in the description and claims is to be understood to refer generically to the sulphated esters comprehended by the present invention, irrespective of whether or how the sulphated esters may be neutralized.

It has been observed in a study of a homologous series of surface-active agents that the more efficient products are frequently of such a high molecular weight as to have too poor solubility in aqueous solutions for satisfactory commercial application. It has now been noted that esters of sulphated branched-chain monocarboxylic acids have a greater surface-active efficiency than the corresponding esters of sulphated straight-chain monocarboxylic acids. This result is probably due to the fact that a certain amount of branching increases the solubility in water, improves the penetrating power and permits the use of high molecular weight products in a greater variety of commercial applications. The beneficial effect of branching may be still further enhanced by employing a branched-chain alcohol as the esterifying agent.

In the preferred embodiment of the invention, the sulphate group is attached to a carbon atom, alpha, beta, gamma, or delta to the carboxyl group of the ester. This preference is predicated on the fact that the corresponding hydroxy branched-chain acids are more readily available and on the indication that the sulphated products are more efficient as wetting agents than those products which have the sulphate group further removed from the carboxyl group. The markedly improved properties of the surface-active agents of the present invention over older products such as sulphated castor oil are readily indicated by a comparison of the wetting efficiencies of these two types of products. Sulphated castor oil, which is derived from a straight chain acid and has the solubilizing groups 8 and 11 carbons removed from the carboxyl group, is greatly inferior as a wetting agent to the products of the present invention.

The water-soluble salts of the alkyl esters of branched-chain, aliphatic, sulphato-monocarboxylic acids are especially valuable as surface-active or capillary-active materials in that they have colloidal properties and may therefore be advantageously used in any process involving wetting, penetrating, deterging, dispersing, emulsifying, frothing, foaming and kindred phenomena, and therefore they may be utilized in many of the technical applications of surface active agents.

The above description and examples are intended to be illustrative only and not to limit the scope of the invention. Any departure therefrom which conforms to the spirit of the invention is intended to be included within the scope of the appended claims.

I claim:

1. An alkyl ester of a branched-chain, aliphatic mono-sulphato-monocarboxylic acid wherein the alkyl radical contains at least 4 carbon atoms and the monocarboxylic acid radical contains at least 4 carbon atoms.

2. An alkyl ester of a branched-chain, aliphatic alpha-sulphato-monocarboxylic acid wherein the alkyl radical contains at least 4 carbon atoms and the monocarboxylic acid radical contains at least 4 carbon atoms.

3. An alkyl ester of a branched-chain, aliphatic mono-sulphato-monocarboxylic acid wherein the alkyl radical is a branched, open chain containing at least 4 carbon atoms and the monocarboxylic acid radical contains at least 4 carbon atoms.

4. An alkyl ester of a branched-chain, aliphatic alpha-sulphato-monocarboxylic acid wherein the alkyl radical contains from 6 to 16 carbon atoms and the monocarboxylic acid radical contains from 6 to 12 carbon atoms.

5. An alkali metal salt of an alkyl ester of a branched-chain, aliphatic alpha-sulphato-monocarboxylic acid wherein the alkyl radical contains from 8 to 12 carbon atoms and the monocarboxylic acid radical contains from 7 to 9 carbon atoms.

6. An alkali metal salt of an alkyl ester of alpha-sulphato-beta-ethyl-valerate.

7. Octyl alpha-(sodium sulphato)-beta-ethyl valerate.

8. Dodecyl alpha-(sodium sulphato)-beta-ethyl valerate.

9. An alkali metal salt of an alkyl ester of a branched-chain, aliphatic alpha-sulphato-monocarboxylic acid wherein the alkyl radical is a branched, open chain containing from 6 to 16 carbon atoms and the monocarboxylic acid radical contains from 6 to 12 carbon atoms.

10. Beta-ethylhexyl alpha-(sodium sulphato)-beta-ethylheptoate.

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