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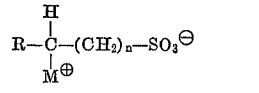
SULFOBETAINE DETERGENTS, AND LUBRICANTS AND COSMETICS CONTAINING SAME

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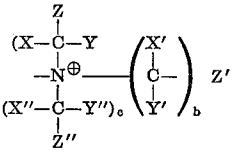
No Drawing. Filed Apr. 25, 1968, Ser. No. 724,290
Int. Cl. C07c *143/14*
U.S. Cl. 260—501.12 4 Claims

ABSTRACT OF THE DISCLOSURE

Novel sulfobetaines, prepared from tertiary amines and sultones, having the structure

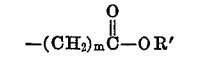


in which R is an alkyl group having from 6 to 23 carbon atoms, *n* is the integer 2 or 3, and M⊕ is a radical having the structure



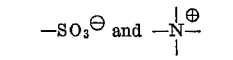
wherein *a*, *b*, and *c* are, independently, integers of from 1 to 6, and the substituents X, X', X'', Y, Y', Y'', Z, Z', and Z'', attached to each carbon atom, are independently, selected from the group consisting of:

(i) hydrogen,
(ii) hydroxyl,
(iii) halogen,
(iv)

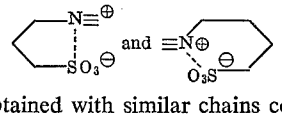


in which *m* is 0 or an integer of from 1 to 5 and R' is H— or an alkyl group having from 1 to 3 carbon atoms,
(v) —NR_2'' in which each R'' is, independently, H— or an alkyl group having from 1 to 4 carbon atoms, and
(vi) —OR''', in which R''' is an alkyl group having from 1 to 4 carbon atoms, at least one of said substituents being other than hydrogen are provided.

The five or six membered chain including the



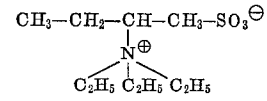
groups provides for ready inner salt or ring formation, giving resistance to degradation, such as



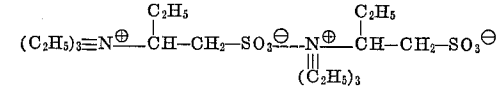
not readily obtained with similar chains containing other numbers of atoms such as ≡N⊕—CH_2—CH_2—SO_3⊖, which would require a highly strained four-membered ring. A more effective detergent is provided than in compounds having the nitrogen atom in the longest chain of the molecule. The detergent compounds are useful, for example, in lubricants and cosmetics, all as is more particularly described in the specification which follows.

This invention relates to novel compounds in the form of particular sulfobetaines, and detergents, cosmetics, and lubricant compositions containing the same.

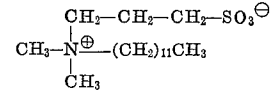
Known sulfobetaines such as



are not effective detergents, and further, because of the four membered chain ≡N⊕—C—C—SO_3⊖ do not readily form inner ring salt compounds. Instead, there is a tendency to form salts or complexes inter-molecularly rather than intramolecularly, as for example

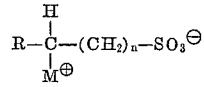


Other known sulfobetaines such as

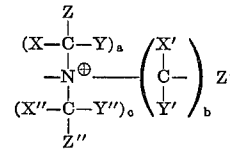


have detergent properties, but the inclusion of the nitrogen atom in the longest chain detracts from such properties.

It has now been found that superior detergent and surface active compositions are the sulfobetaines of the empirical formula

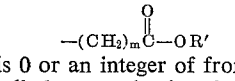


in which R is an alkyl group having from 6 to 23 carbon atoms, *n* is the integer 2 or 3, and M⊕ is a radical having the structure



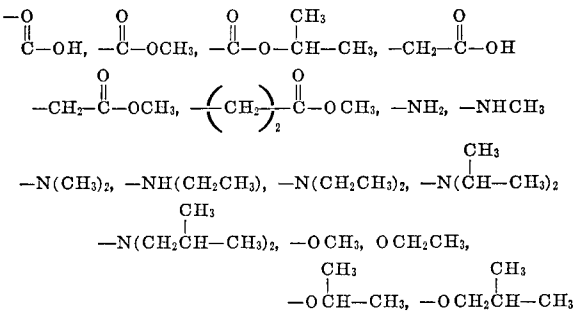
wherein *a*, *b*, and *c* are, independently, integers of from 1 to 6, and the substituents X, X', X'', Y, Y', Y'', Z, Z', and Z'', attached to each carbon atom, are, independently, selected from the group consisting of:

(i) hydrogen,
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in which *m* is 0 or an integer of from 1 to 5 and R' is H— or an alkyl group having from 1 to 3 carbon atoms,
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(vi) —OR''', in which R''' is an alkyl group having from 1 to 4 carbon atoms, at least one of said substituents being other than hydrogen.

Examples of the radical R are hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, and tetracosyl. Branched chain hydrocarbon radicals, as the radical R are also useful. These include: 2-ethylhexyl, 3-methylhexyl; 5-ethyl nonyl; 2,5-dimethyl decyl, 2-methyl-10-propyl dodecyl, 6,10-dimethyl-2-tetradecyl, 6-isopropylhexadecyl, 4,8,12,16-tetramethyl-2-octadecyl, 5-methyl docosyl and propylene dimer, trimer and tetramer. As examples of the substituents X, X', X'', Y, Y', Y'', Z, Z', and Z'', the following are representative: hydrogen, hydroxyl, chlorine, bromine,



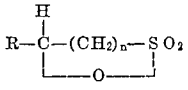
These substituents may be the same or different, i.e., they are independently, any of the described radicals, as long as at least one of them is other than hydrogen. For many purposes, it is preferred that at least one of these substituents is hydroxyl.

In addition to the advantages hereinafter enumerated, the subject sulfobetaines exhibit some properties of each of the nonionic, cationic, and anionic detergents. They are effective in hard water, and are resistant to degradation by chemicals. One reason stable compounds are believed to exist is the stability of the inner salt or ring compounds wherein the ring contains five or six atoms. Rings with this number of atoms are much more stable than rings having a larger or smaller number of atoms. The following represent rings which may be obtained with the compounds of the invention:



In the products having hydroxyl groups, enhanced physiological properties such as skin afterfeel are obtained. Similarly, such products have improved solubility in hydroxylic solvents and improved compatibility with cosmetic bases. Accordingly, they are useful in such solutions as electroplating baths, metal cleaning solutions, and the like. Other uses of particular importance are as ashless detergents in lubricants such as hydrocarbon motor oils, and in cosmetics or salves such as skin creams, as emulsifiers and dispersants. In the latter utility they provide a pleasant, smooth afterfeel on the skin.

Although any known method is useful for preparing the sulfobetaines of the invention, a particularly useful method is by the reaction of a 1,3- or 1,4-alkanesultone with a tri(substituted alkyl)amine. Suitable sultones have the empirical formula

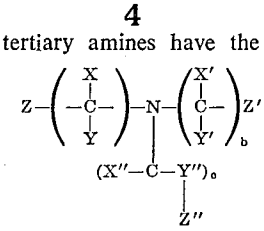


in which R and *n* have the meaning given above.

Useful 1,3- and 1,4-n-alkanesultones are as follows: 1,3-nonanesultone; 1,4-nonanesultone; 1,3-decanesultone; 1,4-decanesultone; 1,3-undecanesultone; 1,4-undecanesultone; 1,3-dodecanesultone; 1,4-dodecanesultone; 1,3-tridecanesultone; 1,4-tridecanesultone; 1,3-tetradecanesultone; 1,4-tetradecanesultone; 1,3-pentadecanesultone; 1,4-pentadecanesultone; 1,3-hexadecanesultone; 1,4-hexadecanesultone; 1,3-heptadecanesultone; 1,4-heptadecanesultone; and the 1,3- and 1,4-alkane sultones of octadecane, nonadecane, eicosane, heneicosane, docosane, tricosane, tetracosane, and pentacosane. Examples of useful branched chain compounds are 8-methyl-1,3-nonanesultone, 7-methyl-1,3-dodecanesultone, 8,12-diethylhexanedecanesultone, 5,8,12-trimethyl-1,4-octadecanesultone; 4-methyl, 9-isopropyl - 1,3 - cosanesultone; and 6,12,16,20-tetramethyl-1,4-tetracosanesultone.

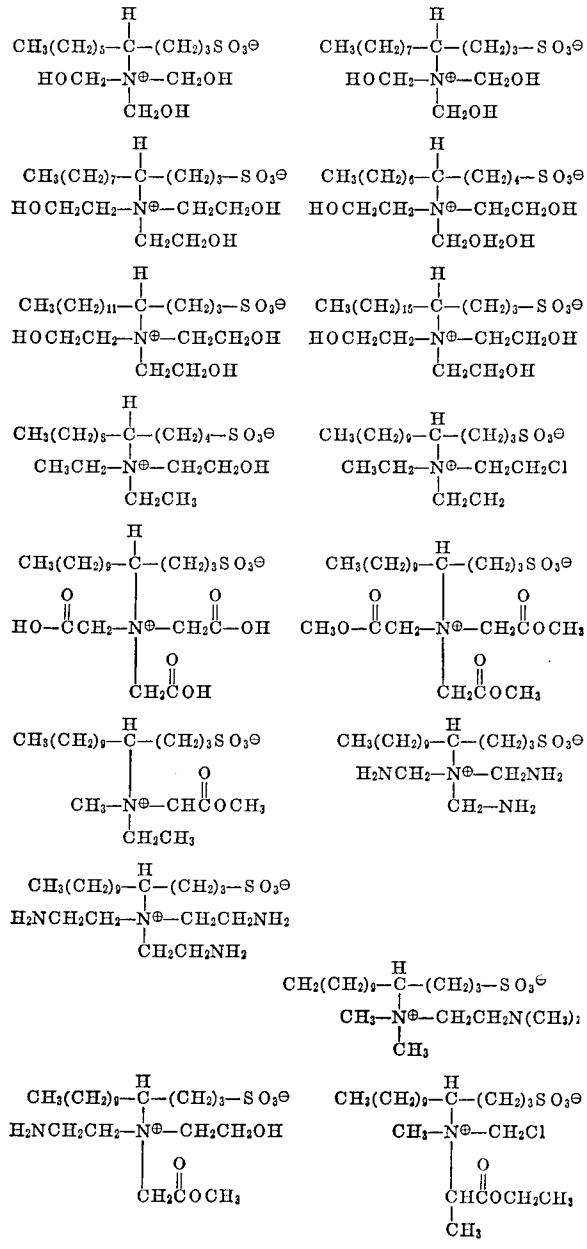
The sultones employed can be obtained in any suitable manner. One method involves bringing together an alpha olefin with SO_3 in gaseous form in an inert medium, such as nitrogen, at a temperature of about 10° to about 25° C. at about atmospheric pressure, for about 0.1 to 0.5 second.

The useful tertiary amines have the formula

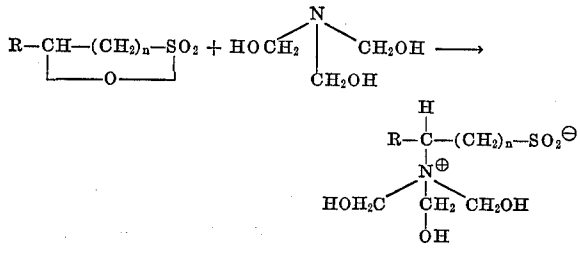


in which X, X', X'', Y, Y', Y'', Z, Z', and Z'' and *a*, *b* and *c* have the meaning given above. Among the tri(substituted alkyl)-amines, the following are given as examples: trimethanol amine; triethanol amine; tripropan-3-ol amine; trihexan-6-olamine; N,N-dimethanol alanine; methyl ester of N,N-dimethanol-β-alanine; N,N-diethanol - 3 - aminopropionic acid; 2-chloro-N,N-diethylethyl amine; 2-chloro-N,N-dimethylethyl amine; N,N-dimethyl-2-amino-1-butanol; methyldiethanolamine; dimethylethanolamine, triisopropanolamine; dimethylaminomethyl-amine; N,N - dimethyl - (N',N'-diethyl)aminomethylamine; methyldiisopropanolamine; dimethylaminomethylamine; N, N - dinolamine.

Examples of sulfobetaines falling within the invention are:



The reaction of a sultone with a (substituted trialkyl) amine, taking trimethanol amine as an example, may be represented by the following equation:



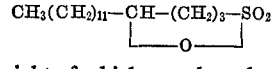
No by-products are formed in this reaction.

The process can be carried out by bringing the reactants together at a temperature of from about 100° to about 200° C., preferably about 125° to about 175° C., at autogenous pressure of about atmospheric pressure to about 500 pounds per square inch gauge, or even higher, for about two to about twenty hours, preferably for about six to about ten hours. Solvents are not necessary, but any inert solvent, particularly polar solvents, for example, lower alcohols, such as methanol, cyclic ethers, such as dioxane, ketones, such as acetone, amides, such as dimethylformamide, etc. can be employed. The sulfobetaine can be recovered from the reaction product in any convenient manner. For example, one method involves decolorization of an isopropanol solution of the reaction product with activated carbon, extraction with hexane, evaporation to dryness, and recrystallization from methanol or isopropanol.

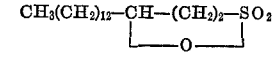
The following examples illustrate the invention.

EXAMPLE 1

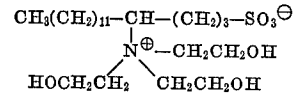
Six and one-half grams of a mixture of sultones, 75% by weight of which was the sultone



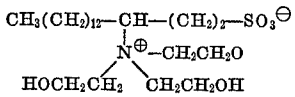
and 25% by weight of which was the sultone



was refluxed with slightly less than one equivalent (on sultone)of triethanol amine in fifty milliliters of dodecane at atmospheric pressure and a temperature of 215° to 220° C. over a period of five to six hours. The reaction mixture was cooled to room temperature, hexane added and extracted with water. The aqueous solution was evaporated to dryness to give 8.5 grams of a mixture containing the following compounds:



and



EXAMPLE 2

The detergent properties of the mixture obtained above, and of a standard detergent, tridecylbenzenesulfonate (TDBS), were compared with each other. The data are presented below in Table 1.

TABLE 1

	Sulfobetaines of Ex. 1	TDBS
Surface tension (dynes/cm. at 25° C.) 0.01 percent aqueous solution	32	29
Interfacial tension against merusol (dynes/cm. at 25° C.) 0.1 percent aqueous solution	2	9
Cotton detergent Terg-o-tometer [percent increase in brightness of fabric using 0.2 percent of a built formulation (20 percent active) at 120° F. in hard water]	28.9	26.5

EXAMPLE 3

The sulfobetaine of Example 1 makes an excellent detergent, in the following formulation:

Ingredient:	Parts by weight
Sodium tripolyphosphate	20–50
Sulfobetaine of Example 2	5–20
Sodium silicate	5–15
Sodium sulphate	10–20
Carboxylmethyl cellulose, i.e. sodium salt thereof	0.1–1

Tarnish inhibitors and other conventional additives are of benefit. When dissolved in water, a liquid detergent is obtained.

EXAMPLE 4

Ingredient:	Parts by weight
Refined mineral oil, API gravity 249° and viscosity SUS 210° F. of 76	99
Sulfobetaine of Example 1	1
Antioxidants such as trialkyl phenols or naphthylamine, anti-wear agent such as P_2S_5-terpene reaction product, pour point depressors, and the like	Usual amounts

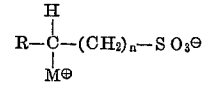
EXAMPLE 5

A sun screening lotion is provided by emulsifying the following materials:

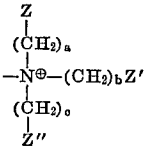
Ingredient:	Parts by weight
P-aminobenzoate	2
Polyethylene glycol	20
Menthol	0.1
Ethanol or isopropanol	35
Perfume	0.2
Sulfobetaine of Example 1	0.5
Water	45

We claim:

1. Sulfobetaines of the empirical formula

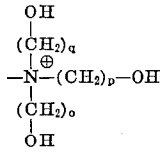


in which R is an alkyl group having from 6 to 23 carbon atoms, *n* is the integer 2 or 3, and M⊕ is a radical having the structure



wherein *a*, *b* and *c* are, independently, integers of from 1 to 6, Z is hydroxyl and Z' and Z'' are, independently, hydrogen or hydroxyl.

2. The composition of claim 1 in which $M^{\oplus}$ is



in which *o*, *p* and *q* are, independently, integers of from 1 to 6, and R contains from 8 to 17 carbon atoms.

3. The composition of claim 2 in which *o*, *p* and *q* are, independently, integers of from 1 to 3.

4. The composition of claim 1 in which R is a branched chain alkyl radical.

References Cited

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JOHN D. RANDOLPH, Primary Examiner

M. W. GLYNN, Assistant Examiner

U.S. Cl. X.R.

252—33.4, 152; 260—327, 481; 424—60