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2,459,088

ALIPHATIC AMIDE-SUBSTITUTED PROPYL QUATERNARY AMMONIUM COMPOUNDS

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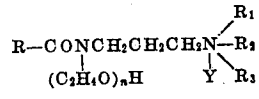
No Drawing. Application May 24, 1947, Serial No. 750,368

3 Claims. (Cl. 260—404.5)

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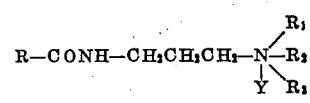
The present invention relates to new organic ammonium compounds and relates more particularly to novel quaternary ammonium compounds which are suitable for use as wetting and detergent agents, germicides, fungicides, flotation agents, and the like uses.

The novel quaternary ammonium compounds of the invention are defined by the general formula:



wherein R is a member of the group consisting of aliphatic and alicyclic radicals containing at least 7 carbon atoms such as nonyl, undecyl, tridecyl, heptadecyl and the like radicals; R_1 and R_2 are members of the group consisting of alkyl and hydroxyalkyl radicals of 1–3 carbon atoms such as, for example, methyl, ethyl, propyl, isopropyl, hydroxyethyl, dihydroxypropyl, and the like radicals; R_3 is an aralkyl radical such as benzyl, phenethyl, para xylyl, naphthyl methyl, methyl xylyl, etc.; n is an integer of 1–10; and Y is an anion such as halogen, hydrogen sulfate, thiocyanate, etc.

This invention is a continuation-in-part of our copending application Serial No. 521,588 filed February 8, 1944. In that application several remarkably effective quaternary ammonium wetting and detergent agents were disclosed. The compounds possess desirable disinfectant and antiseptic properties and are particularly suitable for use as germicidal and fungicidal agents. In general, the compounds corresponded to the formula



wherein R, R_1, R_2, R_3 and Y are substantially as defined above.

Our present invention is directed to improvements in the class of compounds described in our earlier application and has for its principal object a modification therein which increases greatly the range of surface-active agents that can be prepared. We have found that a close adjustment of the hydrophile-hydrophobe ratio can be obtained, while varying within wide limits the molecular weight of the radicals R and R_3 in the above formula, by condensing ethylene oxide into the compounds in such a manner that the substitution occurs at the amido nitrogen atom.

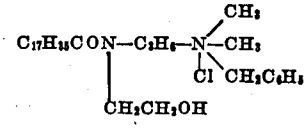
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By increasing the water-solubilizing characteristics of the amido propyl-quaternary ammonium radical we are thus enabled to employ aliphatic or alicyclic radicals of substantially greater molecular weight in preparing our compounds.

The new compounds are for the most part thick liquids or amorphous solids having no definite melting points and which are soluble or dispersible in water and form stable aqueous solutions. The compounds are also readily soluble in the ordinary organic solvents such as ethanol, acetone, dioxane, toluene and the like. Because of their excellent dispersing properties they exert a remarkable action as wetting and emulsifying agents, and have also been found to be particularly suitable for rewetting uses, flotation agents, germicidal and fungicidal agents, and the like.

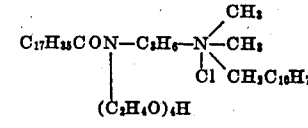
Representative examples of the quaternary ammonium compounds embraced in the present invention are:

(1)



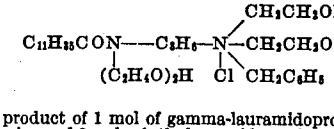
Reaction product of 1 mol of gamma-stearamidopropyldimethylbenzylammonium chloride and 1 mol of ethylene oxide

(2)



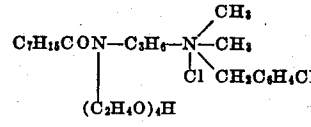
Reaction product of 1 mol of gamma-stearamidopropyldimethylalphanaphthylmethylammonium chloride and 4 mols of ethylene oxide

(3)



Reaction product of 1 mol of gamma-lauramidopropyl-di(hydroxyethyl) amine and 2 mols of ethylene oxide, and quaternarizing with 1 mol of benzyl chloride

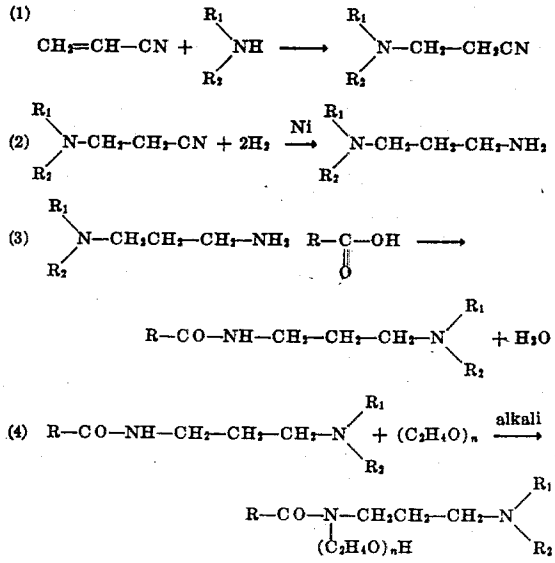
(4)



Reaction product of 1 mol of gamma-caprylamidopropyl-dimethly para-xylylammonium chloride and 4 mols of ethylene oxide

The preferred method of preparing the novel quaternary ammonium salts of this invention

may be expressed by the following equations and description:



where R_1, R_2, and n are as defined above.

(5) The substituted amidopropylamines of (4) are then quaternarized by reaction thereof with the desired quaternarizing agents such as benzyl chloride, ethyl benzyl chloride, alpha naphthyl methyl chloride, para-methyl benzyl chloride, xylyl methyl chloride, etc.

If desired, the quaternarizing reaction may precede the ethylene oxide substitution reaction. In such cases, the amidopropylamine is reacted with the appropriate aralkyl halide, and thereafter the quaternary salt is made alkaline by adding excess sodium hydroxide or other alkali and is then reacted with 1–10 mols of ethylene oxide as in step (4) above.

As noted above, R may be any aliphatic or alicyclic radical containing a sufficient number of carbon atoms to provide a hydrophobic radical which will produce orientation of the compounds at an oil-water interface. It is an advantage of the invention that a wide variety of monocarboxylic acids may be used for this purpose such, for example, as caproic acid, decenoic acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, oleic acid and other more highly unsaturated fatty acids of 14–18 carbon atoms obtained from vegetable and animal oil and fats such as soya bean oil, cottonseed oil, coconut oil, linseed oil, castor oil, dehydrated castor oil, and the like, or from other commercial sources such as talloil. Alicyclic monocarboxylic acids which may be used include abietic acid, petroleum naphthenic acid of 7–14 carbon atoms having boiling points within the range of 215°–310° C., as described in Ellis, "Chemistry of Petroleum Derivatives," (1934 edition) pages 1062–1085, and the like. It will be apparent that the number of carbon atoms contained by the aliphatic or alicyclic radicals is largely dependent on the purpose to which the quaternarized compound is to be put. Where compounds having good detergency and emulsifying properties are desired R may contain in excess of 20 carbon atoms. Where a high degree of wetting power is needed it is more desirable that R shall contain not more than about 19–20 carbon atoms and preferably about 11–17 carbon atoms.

The invention will be further illustrated by the following examples in which the parts are by weight unless otherwise specified.

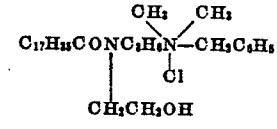
Example 1

Into 545 gm. of a 25% aqueous solution of dimethylamine, cooled with ice and water, were added 170 gm. of acrylonitrile, the rate of addition of the nitrile being controlled so that the temperature in the reaction vessel remained below 20° C. After the cooled reaction mixture had stood for one hour, it was poured into 350 cc. of 10% aqueous sodium hydroxide solution, the oily layer collected and the aqueous layer extracted with ether. The extract and the oily layer were dried over sodium sulfate and distilled. 218 gm. of beta-dimethylaminopropionitrile were collected at 73°–74° C. at 22 mm.

207 gm. of beta-dimethylaminopropionitrile were hydrogenated in an autoclave under a pressure of about 90 atmospheres at 100° C. in the presence of 72.4 gm. of anhydrous ammonia, using Raney nickel as the catalyst. The product was dried over solid potassium hydroxide and vacuum distilled. There were collected 204.5 gm. of gamma-dimethylaminopropylamine having a boiling point of 134° C. at atmospheric pressure.

49 gm. of stearyl chloride were added drop-wise to a solution of 15.5 gm. of gamma-dimethylaminopropylamine in 160 gm. of benzene. After one hour of stirring, the benzene solution was washed with 10% aqueous sodium hydroxide. The benzene layer was then washed with water and the solvent was removed by vacuum distillation. The residue was distilled at 208°–215° C. at 1 to 2 mm. giving a solid distillate of gamma-stearamidopropyldimethylamine.

0.4 mol of gamma-stearamidopropyldimethylamine was reacted with ethylene oxide in the presence of 0.93 gm. of sodium hydroxide in t-butanol at a temperature of about 65° C. Following this operation, the alkali was neutralized by the addition of 1.9 cc. of 38% hydrochloric acid. The N-(hydroxy ethyl) stearamidopropyldimethylamine was quaternarized by reaction with 51 gm. (0.4 mol) of benzyl chloride at about 75° C. for 2 hours. The solution was then filtered and the solvent removed by vacuum distillation. The product:

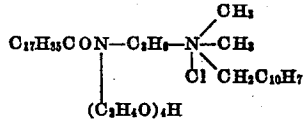


was a crystalline solid at room temperature having no odor of benzyl chloride. It was soluble in water or carbonate solution indicating that quaternarization was essentially complete.

Example 2

0.4 mol of stearamidopropyldimethylamine was reacted with 4 mols of ethylene oxide in the presence of 0.93 gm. of sodium hydroxide in t-butanol at a temperature of about 70° C. Thereafter the alkali was neutralized by the addition to the solution of 1.9 cc. of 38% hydrochloric acid. The N-(hydroxy ethyl) stearamidopropyldimethylamine was then quaternarized by reaction with 70.5 gm. (0.4 mol) of alpha-naphthyl methyl chloride at a temperature of 70°–80° C. for 3 hours. The solution was then

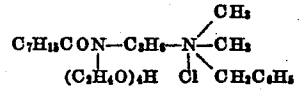
filtered and the solvent removed by vacuum distillation. The product:



was a brown solid at room temperature, and was soluble in warm water, ethanol, toluene, acetone, and the like organic solvents.

Example 3

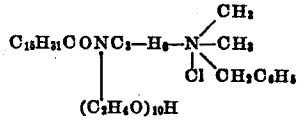
A mixture consisting of 30 parts of benzene, 8.1 parts of gamma-caprylamidopropyldimethylamine, and 5 parts of benzyl chloride was heated at reflux temperature for 6 hours. After removing the benzene, the gamma-caprylamidopropyldimethyl benzylammonium chloride was obtained as a viscous syrup. This material was thereafter dissolved in t-butanol containing about 2 parts of sodium hydroxide, and ethylene oxide was passed into the solution under reflux conditions. The reaction was carried out for 2.5 hours at a temperature of 70°–80° C., after which the solvent was removed by vacuum distillation. Analyses indicated that 4 mols of ethylene oxide had reacted with each mol of the quaternary ammonium and that the product had the formula



This product was readily soluble in water and had excellent wetting properties.

Example 4

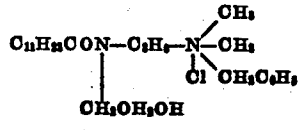
Two parts of benzyl chloride were gradually added to a solution of 4.5 parts of gamma-palmitamidopropyldimethylamine dissolved in 30 parts of benzene. The resulting solution was refluxed for about 4 hours. Thereafter the solution was adjusted to about 8.5–9 pH by the addition of sodium hydroxide. The quaternary ammonium salt was then reacted with ethylene oxide in an amount equal to 10 mols of ethylene oxide for each mol of the salt, at a temperature of 70°–80° C. for 3 hours. Upon neutralization, filtering and removal of the solvent a product was obtained having the formula



This product was a brown solid at room temperature; it was soluble in warm water and the ordinary organic solvents, and had very good detergent and wetting properties, and was quite satisfactory as a germicidal agent.

Example 5

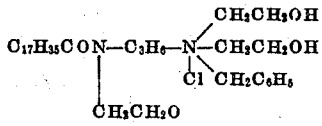
A solution of 6.9 parts of gamma-lauramidopropyldimethylamine and 4.5 parts of benzyl chloride in 75 parts of benzene was refluxed during a period of 4 hours. Thereafter the solvent was removed, the residue was dissolved in 100 parts of t-butanol containing 2 parts of NaOH. Ethylene oxide was passed into the solution over a period of 0.5 hour, and the reaction was continued for 2.5 hours at 70°–75° C. The product



was a light tan solid, soluble in water, and had good germicidal properties.

Example 6

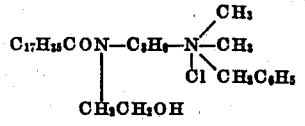
42.8 parts gamma-stearamidopropyldiethanolamine was dissolved in 150 parts of isopropanol containing about 0.9 part of sodium hydroxide and about 4.4 parts of ethylene oxide was passed into the solution. The reaction was carried out at a temperature of 70°–75° C. for about 2.5 hours. Thereafter the alkali was neutralized by the addition of hydrochloric acid, after which about 9.1 parts of benzyl chloride was added thereto. The mixture was heated to about 75° C. and this temperature was maintained for about 6 hours. After filtering and removing the solvent, a product was obtained having the formula



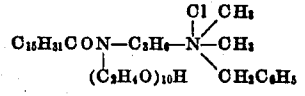
The material was a brown solid which was readily soluble in water and had very good wetting and detergent properties.

What we claim is:

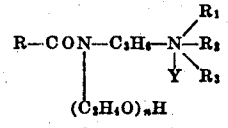
1. The quaternary ammonium compound having the formula



2. The quaternary ammonium compound having the formula



3. A quaternary ammonium compound having the general formula



wherein R is a member of the group consisting of aliphatic and alicyclic radicals containing from 7 to 17 carbon atoms, R_1 and R_2 are alkyl radicals of 1–3 carbon atoms, R_3 is an aralkyl radical, n is an integer of 1–10, and Y is halogen.

PHILIP H. MOSS.
ELMER W. COOK.

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