

UNITED STATES PATENT OFFICE

2,202,864

QUATERNARY AMMONIUM SALTS

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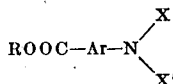
No Drawing. Application February 9, 1937, Serial No. 124,922. In Great Britain February 12, 1936

14 Claims. (Cl. 260—456)

This invention relates to the manufacture of new quaternary ammonium salts.

This invention has as an object to devise a method of manufacturing new aromatic quaternary ammonium compounds. A further object is to produce new aromatic quaternary ammonium compounds. A further object is to produce new reagents from which the new quaternary ammonium compounds can be prepared. Further objects will appear hereafter.

These objects are achieved by the following invention. We have found that we can manufacture new quaternary ammonium salts by interacting a dialkylaminobenzoate of the general formula



where Ar represents a residue of the benzene series, X and X' each represent a lower alkyl (methyl to butyl) radicle and R represents a long chain aliphatic hydrocarbon radicle having 10 to 20 carbon atoms, with an alkyl ester of an inorganic acid or of an organic sulfonic acid.

In manufacturing the new quaternary ammonium salts of the present invention, interaction is conveniently brought about by heating the defined reagents together at moderately raised temperatures, for example, 90°–100° C. In most cases the reaction mixture is fluid at such temperatures and the use of an inert liquid diluent is not necessary but such a diluent, for example, a hydrocarbon such as toluene, may be present if desired.

The reagents of the general formula hereinbefore given are, as will be seen, esters of aliphatic alcohols having 10–20 carbon atoms. These alcohols, which are used as starting materials in the making of the intermediates to be used according to the invention, comprise dodecyl alcohol, otherwise known as dodecanol, tetradecyl alcohol, hexadecyl alcohol, octadecyl alcohol, all of which are saturated. Hexadecyl alcohol is the main or sole component of the alcohols obtained by the saponification of spermaceti. If the alcohol obtained by the saponification of spermaceti is regarded as hexadecyl alcohol, its purity will depend upon the purity of the spermaceti which has been saponi-

fied. With low grade spermaceti the alcohol obtained is a mixture which may contain also oleyl alcohol. When the term cetyl alcohol is used in this specification, it will be understood that it does not necessarily refer to pure cetyl alcohol.

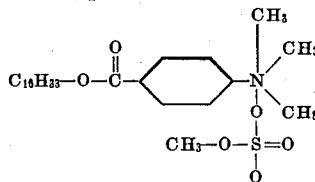
The reagents of the given general formula which are new compounds are readily prepared by applying the methods hereinafter indicated. The new dialkylaminobenzoates disclosed herein are claimed in a division of this application, Serial No. 219,096 filed July 13, 1938.

The new quaternary ammonium salts manufactured according to the present invention are solids which dissolve in water to give foaming solutions. On warming these aqueous solutions with alkali the foaming power disappears and the solutions become turbid or opalescent. The salts are unstable to alkali and slowly decompose under the conditions of alkalinity and temperature usually prevailing in the application of a vat dyestuff.

The invention is illustrated but not limited by the following examples, in which the parts are by weight.

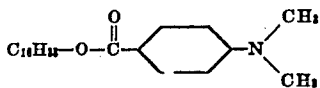
Example 1

39 parts of cetyl p-dimethylaminobenzoate are mixed with 14 parts of neutral dimethyl sulfate and heated in a closed vessel at 90–95° C. until a sample of the reaction mixture is completely soluble in water; this requires about 15 minutes. The reaction product may be purified, if desired, by recrystallisation from acetone, when a colorless solid m. p. 112–113° C. is obtained. The new quaternary ammonium salt so obtained is readily soluble in water to give colorless, foaming solutions and has the formula



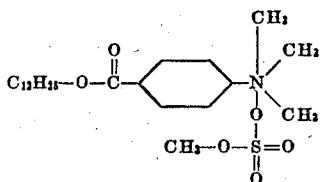
The cetyl p-dimethylaminobenzoate used in the above example may be made by reacting 18.4 parts of p-dimethylaminobenzoyl chloride with 25 parts of cetyl alcohol in the presence of 70 parts of dimethylaniline at 100° C. for 18 hours

and then removing the dimethylaniline from the reaction product by washing with dilute hydrochloric acid. When crystallized from methanol, cetyl p-dimethylaminobenzoate is a crystalline solid m. p. 66-67° C. and has the formula

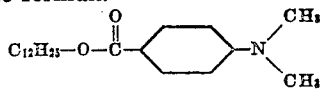


Example 2

105 parts of dodecyl p-dimethylaminobenzoate and 43 parts of dimethyl sulfate are heated together at 100° C. under a reflux condenser until a sample of the reaction mixture is completely soluble in water. The total reaction product, which consists of crude dodecyl p-dimethylaminobenzoate methosulfate, is purified by crystallization from acetone. The purified material which is a white crystalline solid m. p. 104°-107° C. dissolves readily in warm water to give clear foaming solutions and has the formula

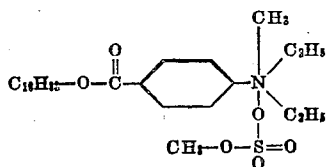


The dodecyl p-dimethylaminobenzoate used in the above example is a new compound and was prepared as follows: A solution of p-dimethylamino benzoyl chloride in dimethylaniline was prepared by passing phosgene into 976 parts of dimethylaniline at below 20° C. until the increase in weight indicated that 200 parts of phosgene had been taken up. After standing for 18 hours, during which time the temperature of the solution rose to 80° C. and then slowly fell to room temperature, 488 parts of dimethylaniline and 221 parts of dodecyl alcohol were added and the mixture heated at 100° C. for 4 hours. The reaction mixture was then poured into 5,000 parts of aqueous 2N hydrochloric acid and the whole was then cooled to atmospheric temperature and extracted with ether. The ether extract was washed with water, then with dilute aqueous sodium carbonate to remove any traces of excess hydrochloric acid, finally dried with anhydrous magnesium sulfate, and the ether evaporated off. The oily residue was purified by crystallization from methyl alcohol whereby dodecyl p-dimethylaminobenzoate was obtained in the form of colorless crystals, m. p. 50° C. having the formula

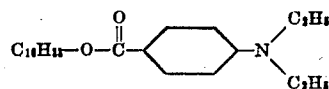


Example 3

8.6 parts of cetyl p-diethylaminobenzoate was heated at 100° C. with 3 parts of dimethyl sulfate until a sample of the reaction mixture was completely soluble in water. By crystallizing the reaction product from acetone, cetyl p-diethylaminobenzoate methosulfate was obtained as a white solid m. p. 76°-77° C. having the formula

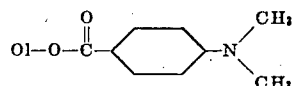


Cetyl p-diethylaminobenzoate, m. p. 46°-48° C. is prepared from diethylaniline, phosgene and cetyl alcohol in a similar manner to that already described for the preparation of dodecyl p-dimethylaminobenzoate and has the formula

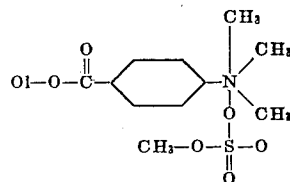


Example 4

40 parts of oleyl p-dimethylaminobenzoate (golden yellow oil, b. p. 240°-275° C./3 mm., prepared by reacting technical oleyl alcohol with p-dimethylaminobenzoyl chloride in dimethylaniline and having the formula



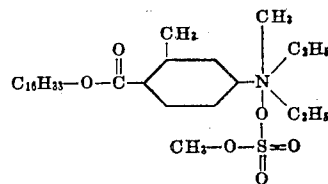
where Ol stands for the radicle of oleyl alcohol) and 13.0 parts of dimethyl sulfate are heated together and the product isolated as described in Example 2. Oleyl p-dimethylaminobenzoate methosulfate is thus obtained as a pale yellow semi-crystalline mass which dissolves in hot water to give foaming solutions having the formula



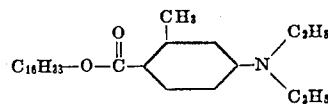
where Ol stands for the radicle of oleyl alcohol.

Example 5

6 parts of cetyl p-diethylamino-o-toluate m. p. 51°-53° C. were heated for two hours at 90°-100° C. with 2 parts of dimethyl sulfate. The reaction product solidifies on cooling to atmospheric temperature and is purified by crystallization from acetone. There is thus obtained cetyl p-diethylamino-o-toluate methosulfate, m. p. 87°-89° C. and having the formula



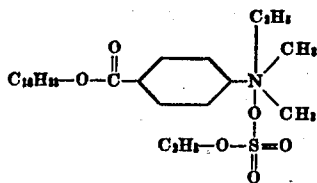
The cetyl p-diethylamino-o-toluate used in the above example is prepared by first interacting phosgene with an excess of 3-diethylaminotoluene and then reacting the product with cetyl alcohol. It has the formula



Example 6

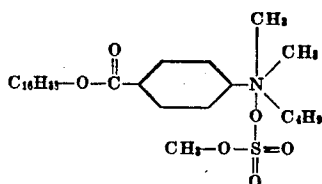
Equal weights of cetyl p-dimethylaminobenzoate and diethyl sulfate are heated together for 6 hours at 90° C. in a closed vessel. The water-soluble reaction product is purified by crystallization from acetone whereby cetyl p-dimethyl-

aminobenzoate ethosulfate m. p. 78°-80° C. is obtained and has the formula

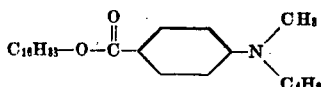


Example 7

15 15 parts of cetyl p-methylbutylaminobenzoate m. p. 50°-52° C. and 7.5 parts of dimethyl sulfate are heated together at 100° C. until (about one hour) a sample of the reaction mixture is soluble in water. The main reaction product on crystallisation from acetone yields cetyl p-methylbutylaminobenzoate methosulfate m. p. 88°-89° C. 20 which is readily soluble in hot water to give foaming solutions and has the formula

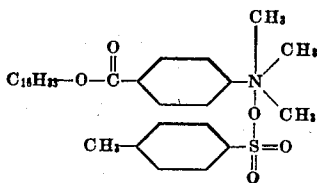


30 Cetyl p-methylbutylaminobenzoate is obtained
by reacting phosgene with an excess of N-methyl-
butylaniline and then reacting the so-obtained
N-methylbutylaniline solution of p-N-methyl-
35 butylaminobenzooyl chloride with cetyl alcohol.
It has the formula



Example 8

20 parts of cetyl p-dimethylaminobenzoate and 10 parts of methyl p-toluenesulfonate are heated together at 90°-100° C. for six hours. On crystallizing the reaction product from a mixture of acetone and methanol, cetyl p-dimethylaminobenzoate metho-p-toluenesulfonate is obtained in the form of colorless crystals, m. p. 251°-252° C., which dissolve in warm water to give foaming solutions and has the formula



10 The new quaternary ammonium compounds disclosed herein are valuable assistants for use in connection with the application of vat dyestuffs to cellulosic textile materials. Their use for this
 65 purpose is illustrated by Examples 2, 3, and 11 to 17 of applicants' British Patent 470,346, which correspond with examples which have been deleted from the present application.

Further examples of suitable alkyl esters of inorganic acids and organic sulfonic acids are methyl bromide, methyl iodide, ethyl bromide, diethyl sulfate, isopropyl bromide, butyl chloride, amyl chloride, allyl bromide, ethyl p-toluenesulfonate methyl benzene sulfonate, etc.

75 The invention is not limited to the use of esters

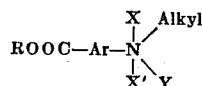
of the alcohols mentioned above altho for economic reasons we prefer to use alcohols with an even number of carbon atoms. Dodecyl and tetradecyl alcohols are obtainable by reduction of the fatty acids obtained from coconut oil and palm oil. Other alcohols, e. g. "olein" or oleyl alcohol (better to be known as octadecenol) are likewise obtainable by reduction of the fatty acids of natural fats and oils (see here, for instance, Bouveault and Blanc, Bull. Soc. Chim., Series 3, vol. 31, page 1, pages 674 and 1210). The invention contemplates the use of the said esters of any of these alcohols, whether in the pure state or as obtained as mixtures from the fatty acids of natural fats and oils. Convenient alternative description of the said esters is accordingly that they are those of primary alcohols resulting from the reduction of the fatty acid radicles of natural fats and oils or from the saponification of waxes.

This invention is a valuable advance in the art 20 as it extends the range of compounds which can be used with vat dyestuffs to build up level shades and discloses new compounds more effective than those known in the prior art.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that we do not limit ourselves to the specific embodiments thereof except as defined in the appended claims.

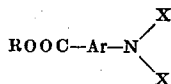
We claim:

1. New quaternary ammonium salts having the general formula:



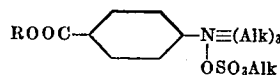
wherein R represents a long chain aliphatic hydrocarbon group containing from 10 to 20 carbon atoms, Ar denotes an aromatic radical of the benzene series selected from the class consisting of phenylene and methylphenylene radicals, X and X' each represent a lower alkyl group containing from 1 to 4 carbon atoms, and Y represents the anion of an acid selected from the class consisting of inorganic acids and organic sulfonic acids.

2. A process of making the quaternary ammonium salts defined in claim 1 which comprises reacting a compound having the general formula: 50



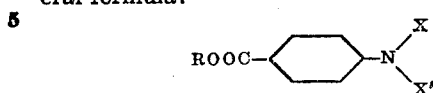
wherein R represents a long chain aliphatic hydrocarbon group containing from 10 to 20 carbon atoms, Ar denotes an aromatic radical of the benzene series selected from the class consisting of phenylene and methylphenylene radicals, and X and X' each represent a lower alkyl group containing from 1 to 4 carbon atoms, with an alkyl ester of an acid selected from the class consisting of inorganic acids and organic sulfonic acids.

3. New quaternary ammonium salts having the general formula:



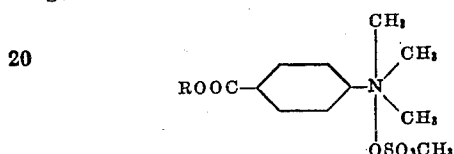
wherein R represents a long chain aliphatic hydrocarbon group containing from 10 to 20 carbon atoms and Alk denotes in each instance an alkyl group containing from 1 to 2 carbon atoms.

4. A process of making the quaternary ammonium salts defined in claim 3 which comprises reacting a dialkylaminobenzoate having the general formula:



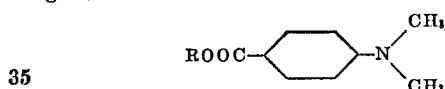
10 wherein R represents a long chain aliphatic hydrocarbon group containing from 10 to 20 carbon atoms, and X and X' each represent an alkyl group containing from 1 to 2 carbon atoms, with a dialkyl sulfate, each of the alkyl groups in which does not contain more than 2 carbon atoms.

15 5. New quaternary ammonium salts having the general formula:



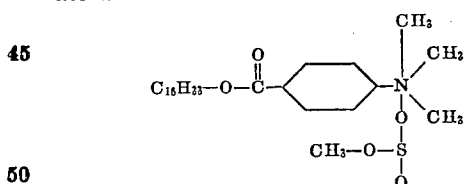
25 wherein R represents a straight chain aliphatic hydrocarbon group containing from 12 to 18 carbon atoms.

30 6. A process of making the quaternary ammonium salts defined in claim 5 which comprises heating a dimethylaminobenzoate having the general formula:



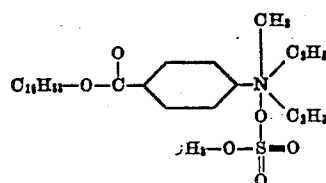
40 wherein R represents a straight chain aliphatic hydrocarbon group containing from 12 to 18 carbon atoms with dimethyl sulfate until a sample of the reaction mixture is soluble in water.

7. Cetyl p-dimethylaminobenzoate methosulfate which has the formula:



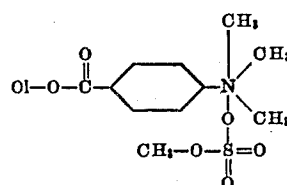
55 8. A process of making cetyl p-dimethylaminobenzoate methosulfate which comprises heating cetyl p-dimethylaminobenzoate with neutral dimethyl sulfate in a closed vessel at 90-95° C. until a sample of the reaction mixture is completely soluble in water.

9. Cetyl p-diethylaminobenzoate methosulfate which has the formula:



10. A process of making cetyl p-diethylaminobenzoate methosulfate which comprises heating cetyl p-diethylaminobenzoate with dimethyl sulfate at about 100° C. until a sample of the reaction mixture is completely soluble in water.

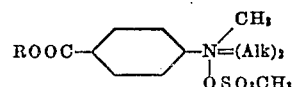
11. Oleyl p-dimethylaminobenzoate methosulfate which has the formula:



wherein Ol stands for the hydrocarbon radical of oleyl alcohol.

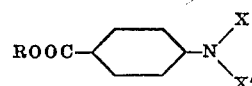
12. A process of making oleyl p-dimethylaminobenzoate methosulfate which comprises heating oleyl p-dimethylaminobenzoate with dimethyl sulfate.

13. New quaternary ammonium salts having the general formula:



wherein R represents a straight chain aliphatic hydrocarbon group containing from 16 to 18 carbon atoms and Alk denotes in each instance an alkyl group containing from 1 to 2 carbon atoms.

14. A process of making the quaternary ammonium salts defined in claim 13 which comprises heating a dialkylaminobenzoate having the general formula:



wherein R represents a straight chain aliphatic hydrocarbon group containing from 16 to 18 carbon atoms, and X and X' each represent an alkyl group containing from 1 to 2 carbon atoms with dimethyl sulfate.

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