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QUATERNARY AMMONIUM SULFONE HALIDES

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5 Claims. (Cl. 260—543)

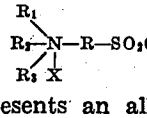
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This invention relates to a new class of organic quaternary ammonium compounds and more particularly refers to quaternary ammonium sulfone halides and processes for their production and use.

This application is a continuation in part of my copending application Serial No. 451,682 filed on July 20, 1942, and bearing the same title, now Patent No. 2,359,863.

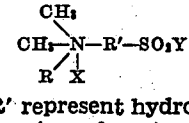
It is an object of this invention to produce a new class of organic quaternary ammonium compounds having particular value as surface-active agents, textile agents, auxiliary agents in making fungicides, insecticides, waterproofing agents, and as intermediates in the production of the aforesaid compounds, as well as in the production of dyes, pharmaceuticals and related products. A further object is to produce a new class of quaternary ammonium compounds comprising quaternary ammonium sulfone halides. Additional objects will become apparent from a consideration of the following description and claims.

These objects are attained in accordance with the present invention wherein quaternary ammonium sulfone halides are produced and employed as hereinafter described. In a more restricted sense this invention is concerned with quaternary ammonium sulfone chlorides, particularly those conforming to the following formula:



wherein R represents an alkylene, arylene or aralkylene group, particularly an ethylene, phenylene or benzylene radical. R_1 and R_2 represent alkyl groups, particularly those containing less than eight carbon atoms, R_3 represents an alkyl, aryl or aralkyl group, particularly an alkyl group of less than eighteen carbon atoms, a phenyl group or benzyl group. (Likewise, R_1, R_2 and R_3 may together form a heterocyclic ring.) X represents an anion, particularly an anion of a strong acid.

In a still more restricted embodiment this invention is directed to quaternary ammonium sulfone halides having the following formula:



wherein R and R' represent hydrocarbon groups, X represents an anion of a strong acid, and Y represents a halogen atom.

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In its preferred embodiment this invention is concerned with compounds conforming to the general formula just described wherein Y represents chlorine, particularly compounds such as N-chloro N-trimethyl amino ethane sulfone chloride.

Compounds of the aforementioned type may be produced by various methods. For instance, an organic sulfonic acid containing as a substituent a pentavalent nitrogen atom, unsubstituted by hydrogen, may be condensed with halogenating agents such as phosphorous pentachloride, chloro sulfonic acid, and the like. In this reaction some heating is usually advisable in order to carry it to completion. An inert diluent is frequently helpful, although it may be omitted. Likewise, an amount of one of the reactants in excess of that required for the reaction may be employed in order to reduce the fusion point of the reaction mixture. Condensation is customarily carried out under atmospheric pressure and the product recovered by decantation, filtration, etc.; or the excess halogenating agent and by-products may be removed by lowering the pressure on the reaction vessel.

In place of the foregoing general process it is also to be understood that a sulfone halide group may be introduced into a quaternary ammonium derivative capable of sulfonation. This reaction is conducted along similar lines to that mentioned previously, except the sulfone halide group is introduced into the compound rather than the halogen atom alone. In this reaction the quaternary ammonium substituted derivative may be mixed with a halogeno sulfonic acid either directly or in the presence of inert diluents, and heat applied, if necessary, until reaction is complete. The desired reaction product may be separated from the remaining components of the reaction mixture in the usual manner.

The invention may be more readily understood by a consideration of the following illustrative examples wherein the quantities are stated in parts by weight.

Example 1

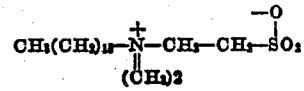
N-chloro N-trimethyl amino ethane sulfone chloride

Twenty-five parts of N-trimethyl amino ethane sulfonic acid inner anhydride (prepared by con-

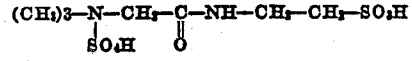
densing beta-bromo-ethane sodium sulfonate with trimethylamine in methyl alcohol at 160° C.) is mixed with 49.2 parts of phosphorus pentachloride. Reaction begins at once and the mixture is rapidly reduced to a viscous syrup with the evolution of heat. The reaction mixture is heated to 115° C., allowing the phosphorus oxy chloride to distill off. The temperature is held at 110–115° C. for one hour; then the pressure is reduced on the reaction vessel to remove last traces of volatile by-products. A nearly quantitative yield of N-chloro N-trimethyl amino ethane sulfone chloride is recovered after drying in vacuo.

In a similar manner, N-substitution and C-substitution products of quaternary ammonium sulfonic acids and their derivatives in general can be converted to the corresponding quaternary ammonium sulfone chlorides or bromides. The following compounds are a representative few of the quaternary sulfonic acids and derivatives which may be treated in accordance with this invention:

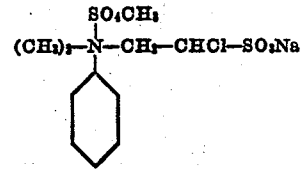
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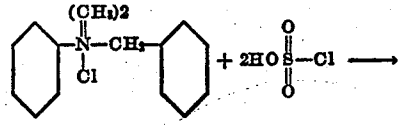


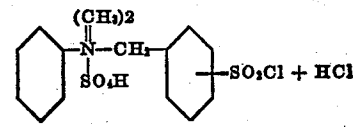
3. Trimethyl ammonium bromo cetane sulfonate (obtained by bromination of cetene sulfonic acid followed by a reaction with trimethylamine).
4. Dimethyl cetyl ammonium butane sulfonate.
5.



EXAMPLE 2

Phenyl benzyl dimethyl ammonium sulfate sulfone chloride

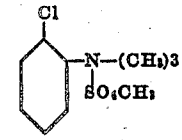




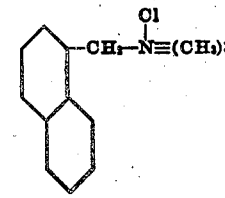
Fifty parts of phenyl benzyl dimethyl ammonium chloride (prepared by condensing benzyl chloride with dimethylaniline in alcohol) is suspended in 240 parts of tetrachloroethane. Fifty-nine parts of chlorosulfonic acid is run into this suspension under good agitation during 10 minutes time interval. The reaction is exothermic and hydrogen chloride is released. The mixture is heated to 56° C. during 1½ hours and held at 56–62° C. for 1½ hours. The mixture is cooled to room temperature and the two liquid phases separated. The lower solvent layer is discarded, or used in a subsequent chlorination. The product is freed of solvent under vacuum on a steam bath. A theoretical yield of phenyl benzyl dimethyl ammonium sulfate sulfone chloride is obtained as an oil. By substituting bromosulfonic acid or fluorosulfonic acid in place of chloro-sulfonic acid, the corresponding phenyl benzyl dimethyl ammonium sulfate sulfone bromide or fluoride is obtained. Other inert solvents such as carbon tetrachloride, orthodichlorobenzene, dioxane, nitrobenzene, kerosene, etc., produce equally good results.

The above method for the manufacture of quaternary ammonium sulfone halides is applicable in general to derivatives susceptible of sulfonation. The following compounds are a representative few of the many which may be treated in accordance with this invention:

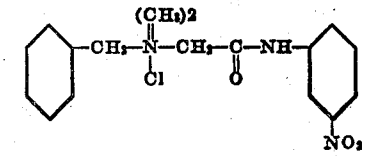
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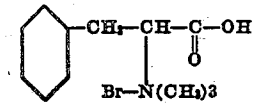
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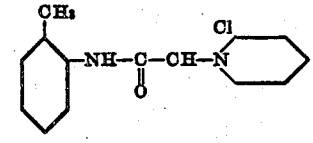
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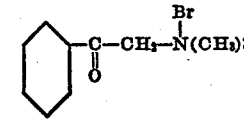
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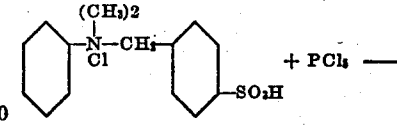
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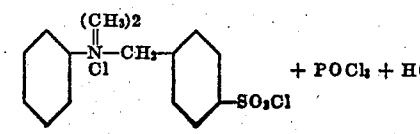


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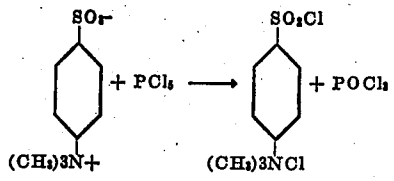


However, the methods for the preparation of aryl quaternary ammonium sulfon chloride is not confined to the use of chlorosulfonic acid as a chlorosulfonating agent with aryl quaternary ammonium derivatives. Equally good results are obtained by condensing aryl quaternary ammonium sulfonic acids with agents, such as phosphorus pentachloride, usually employed in producing sulfone halides. For exampie, dimethyl phenyl parasulfobenzyl ammonium chloride (prepared by condensing parachloromethyl benzene sulfonic acid with dimethyl anyline) heated with phosphorus pentachloride yields the corresponding dimethyl phenyl benzyl ammonium chloride sulfone chloride, i. e.,

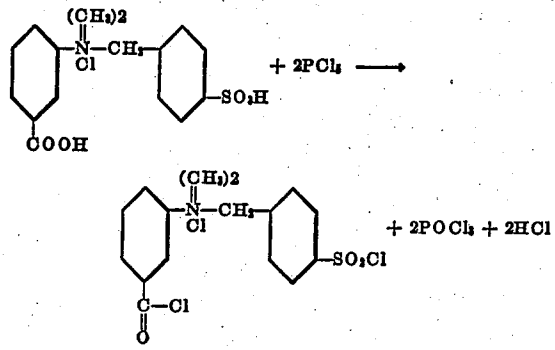




or anhydro para-sulfophenyl trimethyl ammonium hydroxide heated with phosphorus pentachloride yields para-chloro-sulfonyl phenyl trimethyl ammonium chloride, i. e.,



Aryl derivatives containing more than one group capable of undergoing conversion to sulfonyl and/or carbonyl chlorides in the presence of an excess of thionyl chloride, phosphorus pentachloride, etc. yield poly acid chloride derivatives, i. e.,



It is to be understood that the foregoing examples are illustrative merely of a representative few of the many modifications to which this invention is susceptible. They may be varied widely with respect to the individual reactants, the amounts thereof and the conditions of reaction without departing from the scope hereof.

Temperatures in the range of —80° C. to 150° C. are generally employed, although this range is not critical. Temperatures within the range of room temperature to 100° C. are preferred for the majority of reactions.

Normal atmospheric pressure is ge erally preferred, but it is to be understood tha the invention contemplates subatmospheric a id superatmospheric pressures. Reduction in he pressure upon completion of the reaction is frequently helpful to facilitate the removal of by-products and excess reagents, especially when diluents are not used. For this purpose, pressures other than atmospheric pressure are sometimes helpful.

The amount of halogenating agent employed to convert the quaternary ammonium compound to the corresponding acid chloride may be varied within wide limits above the stoichiometric amounts required. It is, however, usually advisable to use from 10% to 50% excess halogenating agent in order to assure completion of the reaction and to compensate for mechanical losses and hydrolysis due to contact with the atmosphere. It is, of course, to be understood that if more than one acid group is present on the quaternary ammonium compound more than one molecular equivalent of halogenating agent will be required in order to obtain complete conversion of the acid groups to the corresponding acid chlorides. Complete conversion of acid groups is of course not always essential and if desired some unconverted acid groups may be permitted to remain on the reaction product or in the reaction mixture.

When the sulfone halide group is introduced into the quaternary ammonium compounds it is generally advisable to employ two molecular equivalents of a halogeno-sulfonic acid for each sulfone halide group which is to be introduced. This is particularly true where dehydrating agents are not employed in the reaction, as the by-product, water, produced, hydrolyzes part of the halogeno-sulfonic acid. A large excess of halogeno-sulfonic acid will ordinarily result in the introduction of more than one sulfone halide group.

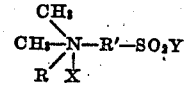
Where reference is made herein to the term "halogen atom" or "halide" it is understood to define the atoms chlorine, bromine or fluorine. Chlorine is the preferred halogen atom and the examples hereof have been primarily directed to the introduction of such atom into the desired compounds. However, in its stead either bromine or fluorine may be employed by suitable changes in the reactants.

By means of the present invention a new class of quaternary ammonium compounds, particularly adapted for employment in the industrial arts, has been discovered. These compounds are especially suitable for use as intermediates in solubilizing existing compounds and synthesizing old compounds. Likewise they are of particular value as intermediates for the production of dyes, pharmaceuticals, insecticides, fungicides, bactericides, surface-active agents, textile agents, auxiliary agents in the manufacture of paper, resist agents for vat printing and other printing agents, waterproofing agents, corrosion inhibitors, etc. So far as known, these quaternary ammonium compounds and those referred to in the parent application are the only materials which can be used for the synthesis of quaternary ammonium substituted acid halide addition compounds with primary, secondary or tertiary amines. Many of these water-soluble addition compounds exhibit unusual properties. These compounds are likewise of value in the production of esters, amides, and other derivatives substituted by pentavalent nitrogen which is unsubstituted by hydrogen.

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

I claim:

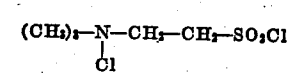
1. A quaternary ammonium sulfone halide represented by the following formula:



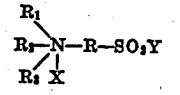
wherein R represents a member selected from the class consisting of alkyl radicals of less than eighteen carbon atoms, phenyl and benzyl radicals, R' represents a member selected from the class consisting of ethylene, phenylene and benzylene radicals, X represents an anion of a strong acid, and Y represents a halogen atom.

2. The products of claim 1 wherein Y represents chlorine.

3. A compound having the following general formula:



4. A quaternary ammonium sulfone halide represented by the following formula:



wherein R represents a member selected from the

class consisting of ethylene, phenylene and benzylene radicals, R_1 and R_2 represent alkyl radicals containing less than eight carbon atoms, R_3 represents a member selected from the class consisting of alkyl radicals of less than eighteen carbon atoms, phenyl and benzyl radicals, X represents an anion of a strong acid, and Y represents a halogen atom.

5. The products of claim 4 wherein Y represents chlorine.

ADRIAN L. LINCH.

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