

[54] **PROCESS FOR THE PREPARATION OF QUATERNARY AMMONIUM SALTS**

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[22] Filed: **Nov. 6, 1972**

[21] Appl. No.: **304,128**

[30] **Foreign Application Priority Data**

Nov. 9, 1971 Japan..... 46-892257

[52] **U.S. Cl.**..... **260/404**, 260/468 G, 260/468 R, 260/486 R, 260/490, 252/8.8

[51] **Int. Cl.**..... **C11c 1/00**

[58] **Field of Search**..... 260/404, 468 G, 468 R, 260/486 R, 490

[56] **References Cited**

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[57] **ABSTRACT**

A quaternary ammonium salt containing an ester linkage in the cationic moiety is prepared by reacting an epihalohydrin with a salt of an alkyl or alkenyl tertiary amine and a carboxylic acid.

5 Claims, No Drawings

PROCESS FOR THE PREPARATION OF QUATERNARY AMMONIUM SALTS

BACKGROUND OF THE INVENTION

This invention relates to a new process for preparing quaternary ammonium salts which are useful as detergents, emulsifying agents and wetting agents, particularly as textile treating agents.

DESCRIPTION OF THE PRIOR ART

A conventional method of preparing quaternary ammonium salts, which is usually adopted in the art, comprises reacting an alkyl amine with an alkyl halide. Recently, methods using an epihalohydrin are adopted sometimes. The most typical method using an epihalohydrin comprises reacting an epihalohydrin directly with a tertiary amine. However, in this method it is difficult to prepare quaternary ammonium salts having a complicated structure. It is especially difficult to introduce a reactive group into the cationic moiety.

As disclosed in U.S. Pat. Nos. 2,547,965 or 2,548,679, it has been known that when an adduct of a tertiary amine with an alkyl phenol or mercaptan synthesized in advance is quaternarized by an epihalohydrin, the alkyl phenol or mercaptan is introduced in the cationic moiety in the form of a phenyl ether or thioether. However, since the linkage introduced into the cationic moiety is an ether linkage, its reactivity is relatively low. Also, a method comprising synthesizing in advance a salt of a tertiary amine with a mineral acid such as hydrochloric acid and then reacting an epihalohydrin with the salt has been known in the art. However, according to this method it is impossible to introduce a reactive group into the cationic moiety.

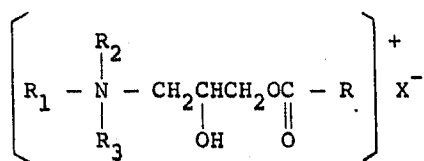
DETAILED DESCRIPTION

This invention is based on the discovery of a process for preparing quaternary ammonium salts having a reactive ester group in the cationic moiety, which are useful as textile-treating agents. The products obtained by the process of this invention are useful as textile-softening agents having an antistatic property, or as level-dyeing or dyeing-retarding agents of the decomposition type.

More specifically, this invention is to provide a process for the preparation of quaternary ammonium salts having an ester linkage in the cationic moiety, characterized by reacting an epihalohydrin with a salt of an alkyl or alkenyl tertiary amine and a carboxylic acid.

The salt of an alkyl tertiary amine and a carboxylic acid may be prepared in an ordinary solvent such as benzene and lower aliphatic alcohols by a customary method. The kind of the epihalohydrin is appropriately chosen depending on whether the intended quaternary ammonium salt is a chloride or bromide.

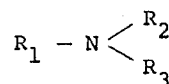
Quaternary ammonium salts to be obtained by the process of the present invention are represented by a chemical formula as follows:



in which R is an alkyl, alkenyl or cycloalkyl radical of from 1 to 17 carbon atoms; in which N is a quaternary nitrogen atom; in which X is halogen, such as chlorine, bromine and fluorine; and in which each of R₁, R₂ and R₃ is an alkyl or alkenyl radical having 1 to 18 carbon atoms.

In the production of these compounds, the following three reactants are used:

1. An alkyl or alkenyl tertiary amine having the formula



wherein each of R₁, R₂ and R₃ is an alkyl or alkenyl radical having 1 to 18 carbon atoms.

- Some examples of alkyl or alkenyl tertiary amines which may be quaternized in the practice of the present invention are as follows:

Trimethylamine, triethylamine, trinormalpropylamine, dimethylethylamine, methyldiethylamine, dimethylallylamine, diethylallylamine, dimethyldodecylamine, dimethyloctadecylamine, trioctylamine, trioctadecylamine and trioleylamine and mixtures thereof.

2. Epihalohydrin, for example, epichlorohydrin or epibromohydrin.

3. A saturated or unsaturated aliphatic carboxylic acid, or alicyclic acid having from 2 to 18 carbon atoms and represented by the formula of RCOOH, wherein R is an alkyl, alkenyl or cycloalkyl radical such as cyclohexyl and adamantyl having from 1 to 17 carbon atoms.

- Some examples of carboxylic acids which may be used in the practice of the present invention are as follows:

Acetic acid, lauric acid, crotonic acid, acrylic acid, methacrylic acid, oleic acid, 1-adamantyl carboxylic acid and cyclohexyl carboxylic acid.

- Our process involves the preparation of a salt of an alkyl or alkenyl tertiary amine and a carboxylic acid by neutralizing the carboxylic acid with the amine in substantially stoichiometric amounts. Then, the salt is reacted with epihalohydrin. The reaction may be carried out at any suitable temperature and pressure, temperatures between 50°C and 150°C and pressures at or near atmospheric being suitable. Conveniently, the reaction is carried out in the presence of a solvent such as benzene and a lower aliphatic alcohol, for example, methanol, ethanol, propanol, butanol, pentanol, etc. The temperature of the reaction may be very conveniently controlled by conducting the reaction under reflux conditions. We have found that the use of benzene is highly satisfactory.

- Epihalohydrin can be used in a substantially stoichiometric amount, but it may be preferably employed in a slight excess, for example, 20 percent excess over its stoichiometric amount.

- After the reaction, the solvent employed is first distilled off. Purification is largely by way of removal of small quantities of unreacted reactants by any suitable means such as extraction with a suitable solvent, for example, diethyl ether and/or recrystallization from a suitable solvent, for example, acetone and diethyl ether.

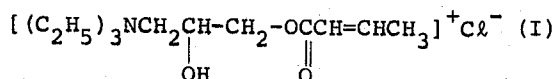
Our process has outstanding advantages in that the highly desirable quaternary compounds may be pre-

pared in excellent yield and quality, from available and relatively inexpensive raw materials, by a simple method and with the use of conventional equipment.

This invention will now be illustrated more detailedly with reference to Examples.

EXAMPLE 1

25.8 g (0.3 mole) of crotonic acid was dissolved in 150 g of benzene, and the solution was neutralized by addition of 30.4 g (0.3 mole) of triethylamine. Then, 33.4 g (0.36 mole) of epichlorohydrin was added to the solution, and the reaction was conducted at 80°C. for 15 hours. After completion of the reaction, benzene was distilled off under reduced pressure and unreacted reactants contained in the residue were removed by extraction with diethyl ether to obtain 50.4 g of a grayish brown, jelly-like product having a structure expressed by the following formula (I):

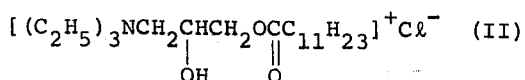


The yield was 60 percent, and results of the analysis are as follows:

	Found Values	Calculated Values
N	4.8%	5.0%
Cl	12.7%	12.7%
Cl ⁻	12.0%	12.7%
hydroxyl number	210	200
saponification number	200	200

EXAMPLE 2

50.1 g (0.25 mole) of lauric acid was dissolved in 80 g of benzene, and neutralization was accomplished by addition of 25.3 g (0.25 mole) of triethylamine. Then, 27.8 g (0.3 mole) of epichlorohydrin was added to the neutralized product and the reaction was conducted at 80°C. for 15 hours. Purification were carried out in the same manner as in Example 1 to obtain 45.4 g of a faintly yellow, transparent, viscous liquid product having a structure expressed by the following formula (II), the yield being 46%:



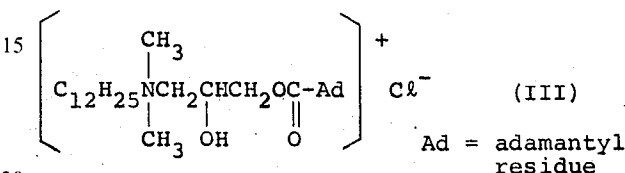
Results of the analysis are as follows:

	Found Values	Calculated Values
N	4.0%	3.6%
Cl	10.5%	9.0%
Cl ⁻	9.4%	9.0%
hydroxyl number	150	143
saponification number	140	143

EXAMPLE 3

27 g (0.15 mole) of 1-adamantyl carboxylic acid was

dissolved in 80 g of benzene, and it was neutralized by addition of 32 g (0.15 mole) of dimethyl n-dodecylamine. Then, 16.7 g (0.18 mole) of epichlorohydrin was added to the neutralized product, and the reaction was conducted at 80°C. for 15 hours. After completion of the reaction, benzene was distilled off under reduced pressure and a large excess of diethyl ether was added to the residue, then the mixture was cooled to precipitate crystals. Thus, there was obtained 34.7 g of a white powdery product having a structure expressed by the following formula (III) and melting at 132.5°C., the yield being 47.6%:

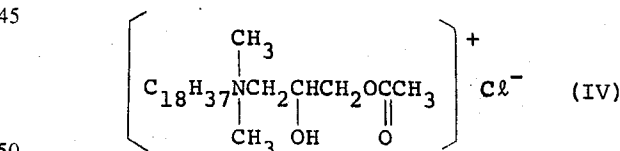


Results of the elementary analysis are as follows:

	Found Values	Calculated Values
C	69.20%	69.27%
H	10.70%	10.71%
N	2.88%	2.88%
Cl	7.70%	7.31%

EXAMPLE 4

74.3 g (0.25 mole) of dimethyl n-octadecylamine was dissolved in 80 g of benzene, and it was neutralized by addition of 15 g (0.25 mole) of acetic acid. Then, 27.8 g (0.30 mole) of epichlorohydrin was added to the neutralized product, and the reaction was conducted at 80°C. for 15 hours. After completion of the reaction, benzene was distilled off under reduced pressure, and the residue was recrystallized from acetone several times to obtain 80 g of a white powdery product having a structure expressed by the following formula (IV) and melting at 102.5°C., the yield being 71.2%:



Results of the elementary analysis are as follows:

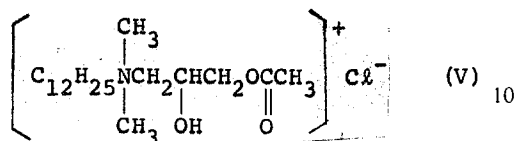
	Found Values	Calculated Values
C	66.35%	66.74%
H	11.49%	11.57%
N	3.19%	3.11%
Cl	7.55%	7.90%

EXAMPLE 5

53.3 g (0.25 mole) of dimethyl n-dodecylamine was dissolved in 75 g of benzene, and it was neutralized by addition of 15 g (0.25 mole) of acetic acid. Then, 27.8 g (0.30 mole) of epichlorohydrin was added to the neutralized product and the reaction was conducted at

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80°C. for 15 hours. After completion of the reaction, purification was carried out in the same manner as in Example 1 to obtain 88.4 g of a brown viscous liquid product having a structure expressed by the following formula (V), the yield being 96.5%:

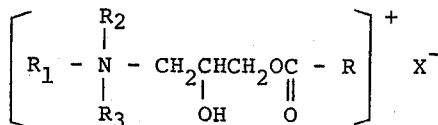


Results of the analysis are as follows:

	Found Values	Calculated Values
N	3.9%	3.8%
Cl	10.0%	9.7%
Cl ⁻	9.5%	9.7%
hydroxyl number	160	153
saponification number	155	153

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

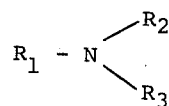
1. A process for preparing quaternary ammonium salts containing an ester linkage in the cationic moiety, of the formula



in which R is alkyl, alkenyl or cycloalkyl having 1 to 17 carbon atoms, X is halogen and each of R₁, R₂

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and R₃ is alkyl or alkenyl having 1 to 18 carbon atoms which comprises neutralizing a carboxylic acid of the formula RCOOH with a substantially stoichiometric amount of a tertiary amine of the formula



to form a salt and then reacting said salt with a stoichiometric amount or a slight excess of an epichlorohydrin to form a compound of the first-mentioned formula.

2. A process according to claim 1, in which the reaction is carried out at a temperature of 50° to 150°C in the presence of a solvent.

3. A process according to claim 1, in which said tertiary amine is selected from the group consisting of trimethylamine, triethylamine, trinormalpropylamine, dimethylethylamine, methyldiethylamine, dimethylallylamine, diethyallylamine, dimethyldodecylamine, dimethyloctadecylamine, trioctylamine, trioctadecylamine and trioctylamine and mixtures thereof and said carboxylic acid is selected from the group consisting of acetic acid, lauric acid, crotonic acid, acrylic acid, methacrylic acid, oleic acid, 1-adamantyl carboxylic acid and cyclohexyl carboxylic acid.

4. The process of claim 3, in which said epichlorohydrin is epichlorohydrin.

5. A process according to claim 1, in which each of R₁, R₂ and R₃ is alkyl having 1 to 18 carbon atoms and R is selected from the group consisting of alkyl having 1 to 17 carbon atoms, alkenyl having from 2 to 17 carbon atoms, adamantyl and cyclohexyl.

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