

UNITED STATES PATENT OFFICE

2,547,965

REACTION OF ALKYLPHENOL, TERTIARY AMINE, AND EPIHALOHYDRIN

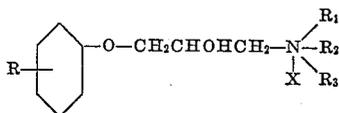
John F. Olin, Grosse Ile, Mich., assignor to Sharples Chemicals Inc., a corporation of Delaware

No Drawing. Application June 23, 1948, Serial No. 34,811

12 Claims. (Cl. 260-567.6)

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This invention pertains to a new process for producing compounds having the formula:



wherein R represents an alkyl radical having from 5 to 18 carbon atoms; wherein X represents halogen, that is, chlorine, bromine, iodine or fluorine; wherein R₁ represents an alkyl radical having from 1 to 3 carbon atoms; wherein R₂ represents an alkyl radical having from 1 to 3 carbon atoms; wherein R₃ represents one of the group consisting of the allyl radical, the benzyl radical and alkyl radicals having from 1 to 3 carbon atoms.

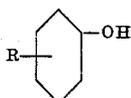
I have discovered that compounds coming within the scope of the above-mentioned formula have outstanding properties when used as surface active agents or bactericides, and that these properties are imparted to these new compounds by the particular molecular structure thereof.

When these compounds are to be employed primarily as surface active agents, as, for example in textile treating baths, I prefer those in which the alkyl radical represented by R contains from 8 to 16 carbon atoms and in which the radicals represented by R₁, R₂ and R₃, taken individually, are selected from the group consisting of methyl and ethyl radicals.

On the other hand, when these compounds are to be employed primarily as bactericides, I prefer those in which the alkyl radical R contains from 6 to 12 carbon atoms, in which the radicals represented by R₁ and R₂ are selected from the group consisting of methyl and ethyl radicals, and in which the radical represented by R₃ is selected from the group consisting of the allyl radical and the benzyl radical.

In the production of these compounds, I bring together either simultaneously or in any desired order of addition, three reactants as follows:

1. A phenol having the formula



wherein R represents an alkyl radical having from 5 to 18 carbon atoms.

2. Epihalohydrin, for example, epichlorhydrin or epibromohydrin.

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3. A tertiary amine having the formula



wherein R₁ represents an alkyl radical having from 1 to 3 carbon atoms; wherein R₂ represents an alkyl radical having from 1 to 3 carbon atoms; wherein R₃ represents a radical selected from the group consisting of the allyl radical, the benzyl radical and alkyl radicals having from 1 to 3 carbon atoms.

In order that the reaction may proceed at a reasonable rate, I prefer to have the reaction take place at a temperature above 20° C., and in order to limit the percentage of by-products produced, I prefer to have reaction take place at a temperature below 120° C. However, it is to be understood that, if desired for any reason, the temperature of the reaction mixture may be taken above or below the range of from 20° C. to 120° C. such as for a part of the reaction period without departing from the spirit of the invention, and bearing in mind that a reduced temperature will slow up the reaction and that an elevated temperature is likely to result in the production of considerable quantities of undesired by-products. Particularly excellent results may be attained by conducting at least the major portion of the reaction while maintaining the temperature of the reaction mixture within the range of from 50° C. to 90° C.

Any convenient or desirable expedient may be employed for maintaining the temperature of the reaction within the desired range, such as, the use of a jacketed reaction vessel, or the use of heat exchange coils within the reaction mixture, or otherwise.

The reaction is carried out in liquid phase with or without the presence of a solvent or diluent which is inert to the reaction under the conditions obtaining, the presence of a solvent in any suitable or desired quantity being preferred in many instances. Thus, I frequently prefer to use from 25 to 100% by volume of solvent based on the volume of reactants employed.

Although in general any non-reacting solvent or diluent may be employed such as an aromatic hydrocarbon, an aliphatic hydrocarbon or an ether, I have found that very satisfactory results are obtained by use, as a solvent, of a lower saturated aliphatic monohydric alcohol, i. e. an alkanol. Among the alcohols which may be so employed, for example, are methanol, ethanol,

propanol, butanol, pentanol and hexanol, including the various isomeric forms thereof.

Obviously any suitable pressure may be employed, such as atmospheric, subatmospheric or superatmospheric, while causing the reaction to take place in the liquid phase. In many instances it is convenient to employ a solvent which boils at or near the desired reaction temperature under the pressure conditions obtaining, and to maintain a reflux of said solvent, thereby causing a uniform temperature to be maintained in the reaction mixture. Isopropanol serves admirably for this purpose when operating near atmospheric pressure.

While all of the reactants may be combined simultaneously, I find it expedient for purposes of heat control, the reaction being exothermic, to first mix a part or all of the phenol with a part or all of the amine, and then to add the epihalohydrin, for instance, epichlorhydrin, gradually to the foregoing mixture. If only a part of the phenol or of the amine or both were initially combined, the remainder may be added gradually, or in increments, or in a body, as the reaction proceeds.

For instance, a part of the amine may be added to the phenol followed by the addition of the epihalohydrin gradually or in increments, or as a body if proper heat control facilities are available, and after all or part of the epihalohydrin has been combined, the remainder of the amine may be added to the reaction mixture. Thus, for example, from 1 to 10% or more of the amine may be added to the phenol, followed by the addition of the epihalohydrin, and then the remainder of the amine may be added.

Any other order of addition may be resorted to.

My process fundamentally involves the chemical combination of the phenol, the epihalohydrin and the tertiary amine in stoichiometric proportions to form the corresponding quaternary salt, and the reaction may be conducted by use of the three reactants in substantially stoichiometric amounts. It will be understood, however, that the reactants may be employed in any other desired ratios during the reaction, and the excess may subsequently be removed by any suitable means. As a general rule, I prefer to have all or part of the alkyl phenol present whenever the amine is mixed with the epihalohydrin.

While the foregoing contemplates more particularly addition of the reactants on the batch principle, it includes within its purview operations on the continuous, semi-continuous or other principle, whereby the three reactants are brought together for reaction purposes while preferably maintaining the temperature of the reaction mixture between 20° C. and 120° C.

While I do not wish to be bound by any theory as to the manner in which the reaction proceeds, the amine in addition to reacting to form the desired quaternary ammonium compound apparently also catalyzes the reaction between the phenol and the epihalohydrin, since it is unnecessary to add to the reaction any other compound in order for the reaction to proceed. While the invention does not preclude the addition of any other compound for purposes of assisting the reaction, as above pointed out, such addition is unnecessary for my purposes. Thus, any such other catalyst may be added, if desired. It is preferred, however, that any such addition should not interfere with the reaction, or result in the production of by-products in undesired quantities.

Suitable catalyst for the condensation of the epihalohydrin with the phenol in practice of my invention are, in addition to the tertiary amines employed in the reaction, those organic catalysts for the condensation of phenols with epoxides which are neutral or basic in reaction and which contain chemically bound nitrogen. Epoxide condensation catalysts of this character, including, for example, primary amines such as mono-alkyl amines having from 1 to 5 carbon atoms in the alkyl radical, for instance, monobutyl amine, secondary amines such as dialkyl amines having from 1 to 5 carbon atoms in each alkyl radical, for instance, dibutyl amine, tertiary amines (which may be either aliphatic, aliphatic-aromatic, or aromatic in character) such as the tertiary amines employed as reactants herein, as well as alkyl-aryl amines and aryl amines such as dimethyl aniline and triphenyl amine, amine oxides such as trialkyl amine oxides having from 1 to 5 carbon atoms in each alkyl radical, for instance, triethyl amine oxide, hexamethylene tetramine, urea, substituted ureas such as the alkyl ureas having from 1 to 5 carbon atoms in each alkyl radical of which there may be from 1 to 4 attached to the nitrogen atoms, for instance, tetraethyl urea, guanidine, substituted guanidines, such as the alkyl guanidines having from 1 to 5 carbon atoms in each alkyl radical of which there may be from 1 to 4 attached to the nitrogen atoms of the amine groups, such as symmetrical dibutyl guanidine, etc., are capable of promoting condensation of the alkyl phenol with the epihalohydrin to form condensation products which may readily be converted in high yield into my quaternary ammonium salts by reaction with the appropriate tertiary amines. When practicing my invention by use of organic, nitrogen-containing, epoxide-condensation catalysts other than the tertiary amine to be quaternized, I prefer to employ the catalyst in relatively small proportion, say from 1/2 to 5 per cent by weight based on the phenol, in order to minimize the contamination of the ultimate product.

However, the procedure more particularly described herein is preferred, and results in greatly improved yields and quality of product.

Examples of phenols suitable for use in the practice of my invention are as follows:

The amyl phenols, such as, normal amyl phenol, secondary amyl phenol and tertiary amyl phenol, in which said alkyl radicals may be attached in the ortho, the meta or the para position; and the corresponding hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl and octadecyl phenols.

It is not necessary in practice of my invention that the phenol employed be a relatively pure compound, and in many instances it may be desirable or expedient to employ a homologous or an isomeric mixture of phenols, or both.

Tertiary alkyl phenols are preferred, particularly when the tertiary alkyl radical is derived from an open chain polymer olefin resulting from the polymerization of an open chain olefin of lower carbon content, such as propylene, butene-1, butene-2, isobutene, any of the isomeric pentenes, any of the isomeric hexenes, or of mixtures of two or more of the foregoing.

Methods of polymerizing olefins of lower carbon content to form polymer olefins of higher carbon content are well known in the art, as are methods for the alkylation of benzene ring com-

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pounds, including phenols, employing such polymer olefins as the source of the alkyl radicals.

Some examples of amines which may be quaternized in the practice of my invention are as follows:

Trimethylamine, triethylamine, trinormalpropylamine, dimethylethylamine, methyl-diethylamine, dimethylbenzylamine, diethylbenzylamine, dimethylallylamine, diethylallylamine, methylethylallylamine, and mixtures thereof.

My preferred process has outstanding advantages in that the highly desirable quaternary compounds of my invention may be prepared in excellent yield and quality, from available and relatively inexpensive raw materials, by a simple method and with the use of conventional equipment. In addition the reaction may take place, if desired, in a single vessel, and without necessitating the separation of intermediate reaction products or intermediate by-products, such as catalyst residues, unused catalysts, etc.

The reaction proceeds smoothly and fairly rapidly.

Further features of the invention are illustrated in examples as follows:

EXAMPLE 1

3-(*p*-*tert*-dodecylphenoxy)-2-hydroxypropyl-triethylammonium chloride

384 grams (1.5 moles) of *p*-tertiary-dodecyl phenol and 152 grams (1.5 moles) triethylamine were placed in a reaction flask, equipped with a reflux condenser, together with 200 grams of isopropanol as solvent and the mixture was brought to reflux temperature. 139 grams (1.5 moles) of epichlorhydrin was introduced and the reaction mixture was refluxed for sixteen hours. For purposes of purification, the crude product was then diluted with 1500 ml. of water to give a clear solution. The aqueous solution was treated with sufficient toluene (3 liters) to cause separation of an oil layer of about 1 liter. The separated oil layer was discarded and the aqueous layer was again washed with about 1500 ml. of toluene and was subjected to a flash-evaporation procedure in vacuo to eliminate volatiles. The solvent-free product which amounted to 640 grams of viscous oil was taken up in isopropanol to facilitate handling. The product was a good dispersing agent, an excellent surface and interfacial tension depressant and possessed a high phenol coefficient. On a solvent free basis it contained 3.1% N, 7.8% total Cl and 7.7% ionizable Cl as compared with theoretical values of 3.08% N, 7.9% Cl and 7.9% Cl, respectively.

EXAMPLE 2

3-(*p*-*tert*-octadecylphenoxy)-2-hydroxypropyl-triethylammonium chloride

By the procedure of Example 1, 346 grams (1 mole) of tertiary octadecyl phenol, prepared by alkylation of phenol with propylene hexamer, 92.5 grams (1 mole) of epichlorhydrin and 101 grams (1 mole) of triethylamine were reacted for thirty hours in isopropanol solution. It was observed that 93% of the amine had reacted at the end of twenty hours and that the additional ten hours of reaction effected substantially no further conversion. After purification the product was obtained in an amount corresponding to 85% yield. Its surface activity and detergency as shown by standard tests was slightly lower than in the case of the corresponding compound

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derived from tertiary dodecyl phenol. It possessed great emulsifying power.

EXAMPLE 3

3-(*p*-*tert*-octadecylphenoxy)-2-hydroxypropyl-trimethylammonium chloride

692 grams (2 moles) of tertiary octadecyl phenol was reacted with 185 grams (2 moles) of epichlorhydrin and trimethylamine in the presence of isopropanol in the following manner. The phenol and the solvent were placed in a flask and the trimethylamine was introduced at a slow uniform rate below the surface of the reaction mixture, the latter being maintained at about 90° C. throughout the reaction period. Any amine which escaped from the reaction system was recondensed in a suitable reservoir and was reintroduced into the system, thus providing a uniform flow of amine through the reaction vessel. The epichlorhydrin was added dropwise over a period of fifty minutes, and circulation of the trimethylamine was continued for five hours at the end of which period approximately the theoretical quantity of the amine (2 moles) had been consumed in the reaction. After extraction of minor amounts of impurities the product was concentrated and taken up in diluted alcohol. Its dilute aqueous solutions foamed strongly and were efficient washing agents and germicides.

EXAMPLE 4

3-(*tert*-nonylphenoxy)-2-hydroxypropyltriethylammonium chloride

A mixture of 280 grams (1.27 moles) of tertiary nonyl phenol, 200 grams of anhydrous ethyl alcohol and 3 grams of triethylamine was brought to reflux temperature and 120 grams (1.30 moles) of epichlorhydrin was introduced over a twenty minute period. The mixture was refluxed for an additional two hours resulting in condensation of approximately 50% of the phenol with the epichlorhydrin. 138 grams (1.39 moles) of triethylamine was then introduced and refluxing was continued. After 3.5 hours, 0.41 equivalent of amine remained unreacted. After sixteen hours, when the reaction was discontinued, all but 0.124 equivalent of the amine had been consumed. The product was isolated in good yield and proved to be a highly effective wetting agent and wool detergent and a moderately effective germicide. It was furthermore found that its surface activity could be extended (i. e., it could be "built") by incorporating substantial proportions of inorganic salts such as sodium sulfate or sodium pyrophosphate.

EXAMPLE 5

3-(undecylphenoxy)-2-hydroxypropyltriethylammonium chloride

744 grams (3.0 moles) of a mixed monoalkyl phenol having an alkyl group averaging 11 carbon atoms, 450 grams of solvent naphtha and 12 grams of triethylamine oxide were mixed and held at reflux temperature during gradual addition of 291 grams (3.14 moles) of epichlorhydrin. Reflux temperature was maintained for an additional 2.5 hours after which 3.30 moles of triethylamine were introduced, the mixture being then further reacted for twenty hours. Purification in this instance was accomplished by passing steam at 100° C. through the viscous product contained in a stainless steel mixer which was operated to provide sufficient heat and vacuum to prevent condensation of the steam and suffi-

cient agitation of the product to effect intimate contacting with the steam. The desired quaternary salt was thereby obtained in high purity in 78% yield.

EXAMPLE 6

3-(*p*-*tert*-nonylphenoxy)-2-hydroxypropyldimethylbenzylammonium chloride

400 grams (1.82 moles) of nonyl phenol derived by the alkylation of phenol with propylene trimer, 300 grams of isopropanol and 10 ml. of dimethylbenzylamine were brought to reflux and 168 grams (1.82 moles) of epichlorhydrin was added over a period of one hour. Refluxing was continued for five hours. Another 300 grams of isopropanol and the remainder of 246 grams (1.82 moles) of the dimethylbenzylamine was introduced. This mixture was refluxed for twenty hours. Titration showed that only .03 equivalent of free amine remained. 1200 ml. of toluene was added and the mixture was then extracted once with 500 ml. and twice with 300 ml. of water.

The toluene layer was evaporated to 705 grams and was diluted with 800 ml. of isopropanol and 3200 ml. of water. The combined aqueous solutions were then extracted with three portions of hexane to provide an aqueous layer containing 745 grams of the desired quaternary salt.

EXAMPLE 7

3-(*p*-*tert*-octylphenoxy)-2-hydroxypropyldimethylbenzylammonium chloride

A mixture consisting of 2 moles of epichlorhydrin, 1 mole of *p*-*tert*-octylphenol, 7 grams of dimethylaniline and 200 cc. of isopropyl alcohol was refluxed at atmospheric pressure for sixteen hours. The solvent, together with the excess epichlorhydrin, was then vaporized out of the reaction mixture by application of a temperature of 100° C. and a pressure of 25 mm. absolute. The residual condensation product was quaternized with 1 mole of dimethylbenzylamine by refluxing the mixture for two hours in methanol solution. Naphtha was then added and the mixture was distilled through a column until the overhead temperature reached 90° C. to effect removal of methanol. About 50 cc. of water was added to the residue at about 60° C. after which crystallization was induced by further reducing the temperature. The precipitate, which was segregated by filtration, washed with water and dried at a moderate temperature, was a white crystalline monohydrate of the desired quaternary salt. It melted at 110° C. and was found upon analysis to contain 7.8% ionizable chlorine and 3.1% nitrogen as compared with corresponding theoretical values of 7.8% and 2.9% respectively. The melting point of the anhydrous product was approximately 162-164° C.

The following example illustrates an alternative method for the preparation of my compounds.

EXAMPLE 8

3-(*tert*-nonylphenoxy)-2-hydroxypropyldiethylbenzylammonium chloride

220 parts of nonylphenol were reacted with 92.5 parts of epichlorhydrin in 200 parts of isopropanol with 5 parts of dimethylaniline as catalyst by refluxing for four hours. This product was then reacted with 146 parts of diethylamine by adding the diethylamine to the above solution and refluxing for 20 hours. Titration

showed the reaction to have proceeded 98%. 200 cc. of 10 normal sodium hydroxide was added and the organic layer which formed was separated and washed twice with water. This product was then steamed and dried. The final product had a neutral equivalent of 347 (calculated 349).

174 parts of the above product, 63.5 parts of benzyl chloride and 100 parts of isopropanol were refluxed together for 20 hours. Water was then added to the reaction mixture slowly until a faint turbidity developed. An additional amount of water was added slowly (about 10 cc.) until 25 grams of oil had separated. The oil was discarded. The remaining solution contained the desired quaternary substantially free from unreacted reagents. The desired quaternary was obtained by evaporating the solvent. It was a very viscous amber liquid, only slightly soluble in water.

Examples of other quaternary salts which have been prepared in accordance with the process of my invention include:

- 3 - (*t* - amylophenoxy) - 2 - hydroxypropyldimethylbenzyl ammonium chloride
- 3 - (*t* - octylphenoxy) - 2 - hydroxypropyldimethylallyl ammonium chloride
- 3 - (*t* - octylphenoxy) - 2 - hydroxypropyldiethylbenzyl ammonium chloride
- 3 - (*s* - decylphenoxy) - 2 - hydroxypropyltripropylammonium chloride
- 3 - (*n* - dodecylphenoxy) - 2 - hydroxypropyltrimethyl ammonium bromide
- 3 - (*t* - hexadecylphenoxy) - 2 - hydroxypropyldimethylethyl ammonium chloride

The foregoing examples are merely illustrative of various embodiments of my invention and I do not wish to be limited except by the scope of the following claims.

I claim:

1. A process comprising mixing in liquid phase and under temperature conditions between 20° C. and 120° C. a monoalkyl phenol having from 5 to 18 carbon atoms in the alkyl radical, an epihalohydrin, and a tertiary amine having the formula:



in which each of R_1 and R_2 is an alkyl radical having from 1 to 3 carbon atoms, and in which R_3 is one of a group consisting of the allyl radical, the benzyl radical and alkyl radicals having from 1 to 3 carbon atoms; and maintaining the foregoing in mutual contact for stoichiometric reaction until the corresponding quaternary ammonium reaction product is obtained.

2. The process of claim 1 in which the reaction is carried out in the presence of a solvent which is inert to the reaction.

3. The process of claim 2 in which the solvent is an alkanol containing from 1 to 6 carbon atoms.

4. A process comprising mixing in liquid phase and under temperature conditions between 20° C. and 120° C. a monoalkyl phenol having from 5 to 18 carbon atoms in the alkyl radical, epichlorhydrin, and a tertiary alkyl amine having from 1 to 3 carbon atoms in each alkyl radical, and maintaining the foregoing in mutual contact for stoichiometric reaction until the corresponding quaternary ammonium reaction product is obtained.

5. The process of claim 4 in which the phenol is a tertiary alkyl phenol.

6. A process comprising mixing in liquid phase and under temperature conditions between 20° C. and 120° C. a monoalkyl phenol having from 5 to 18 carbon atoms in the alkyl radical, epichlorhydrin, and a monoallyl dialkyl amine having from 1 to 3 carbon atoms in each alkyl radical, and maintaining the foregoing in mutual contact for stoichiometric reaction until the corresponding quaternary ammonium reaction product is obtained.

7. The process of claim 6 in which the phenol is a tertiary alkyl phenol.

8. The process of claim 6 in which the phenol is tertiary octyl phenol, and the amine is dimethylallyl amine.

9. A process comprising mixing in liquid phase and under temperature conditions between 20° C. and 120° C. a monoalkyl phenol having from 5 to 18 carbon atoms in the alkyl radical, epichlorhydrin, and a monobenzyl dialkyl amine having from 1 to 3 carbon atoms in each alkyl radical, and maintaining the foregoing in mutual contact for stoichiometric reaction until the cor-

responding quaternary ammonium reaction product is obtained.

10. The process of claim 9 in which the phenol is tertiary alkyl phenol.

11. The process of claim 9 in which the phenol is tertiary octyl phenol, and the amine is dimethylbenzyl amine.

12. The process of claim 9 in which the phenol is tertiary octyl phenol, and the amine is diethylbenzyl amine.

JOHN F. OLIN.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,087,131	Taub et al. -----	July 13, 1937

FOREIGN PATENTS

Number	Country	Date
228,205	Germany -----	Nov. 7, 1910
484,906	Great Britain -----	May 9, 1938
493,865	Great Britain -----	Oct. 17, 1938