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N,N-DIFATTY ALKYLSUBSTITUTED MORPHOLINIUM HALIDES

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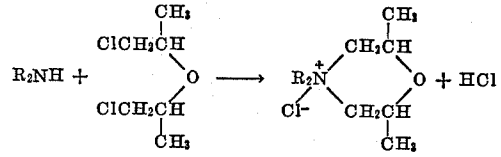
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8 Claims. (Cl. 260—247)

The present invention relates to new compounds which are N,N-difatty morpholinium halides containing at least one other aliphatic hydrocarbon substituent on the ring. The fatty groups on the nitrogen may each contain from 8 to 22 carbon atoms. These compounds are useful as bactericides and detergents.

It is, therefore, an object of the present invention to provide novel morpholinium compounds of the above type. It is another object of the present invention to provide a process of producing such compounds.

These compounds are prepared by the reaction of a secondary fatty amine and with a beta halo ether, the ether containing at least one aliphatic hydrocarbon substituent attached to either the alpha or the beta carbon atom. While a variety of ethers may be employed, the invention will be described particularly with reference to 1-chloro-2-propyl ether. This reaction is indicated in the following equation:

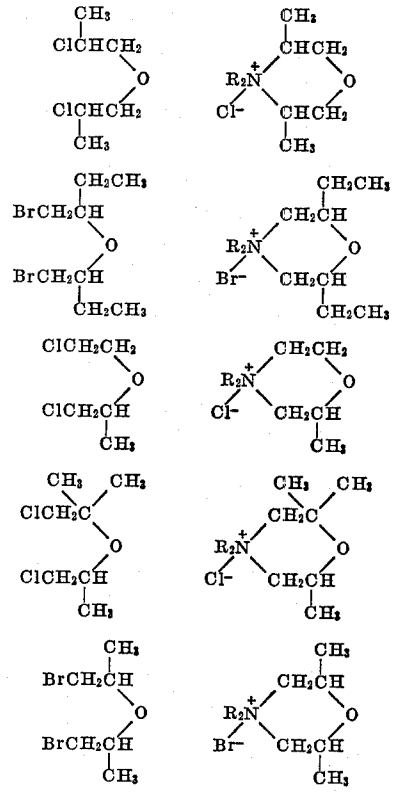


in which R is a fatty group containing from 8 to 22 carbon atoms.

The reaction may be carried out by simply heating the reactants together. Since, however, the acid which is liberated tends to form a salt with some of the amine, it is preferred to employ an inorganic alkali such as the alkali metal hydroxides and carbonates for the purpose of neutralizing this acid. Likewise, the use of a solvent is preferred. Any inert solvent may be employed, but particularly useful are the lower aliphatic alcohols containing from 1 to 8 carbon atoms. Since a somewhat elevated temperature is required, the use of an alcohol boiling at a suitable reaction temperature is preferred. Thus, the reaction should be carried out at temperatures of from 100 to 200° C. Where lower boiling alcohols are employed, it may be necessary to carry the reaction out under pressure in order to obtain a suitable reaction temperature. A readily available alcohol which may be used is n-butyl alcohol which boils at 115–118° C. By carrying out the reaction with n-butyl alcohol at reflux temperatures, the reaction proceeds to a substantial extent in from 70 to 100 hours. At 150° C. the reaction proceeds to a satisfactory extent in 30 to 40 hours. Temperatures up to 200° C. may be used, but the product tends to decompose above this temperature, and, accordingly, temperatures above 200° C. are not desirable.

A wide variety of secondary fatty amines containing from 8 to 22 carbon atoms in the fatty groups may be employed. These fatty amines are customarily derived from fatty acids and, accordingly, it will be appreciated that a single isolated fatty amine or the mixed fatty amines derived from the mixed fatty acids of a fat or oil or from any selected group of such fatty acids may be used. The fatty acids, and consequently the amines, may be either saturated or unsaturated. In addition, where a mixture of fatty acids is employed for the preparation of the secondary amine, it will be appreciated that the fatty groups in a single amine molecule may not be the same.

A variety of beta halo ethers may be employed for the present invention. These ethers are customarily prepared from olefins by reaction with a halogen and water. For this purpose pure olefins may be employed, or mixtures thereof. Where mixtures of olefins are employed, for preparation of the ethers, it will be apparent that a mixture of ethers may result, the mixture containing both symmetrical and asymmetrical ethers. For the purpose of the present invention the ethers must contain an aliphatic hydrocarbon substituent containing from 1 to 3 carbon atoms attached to either the alpha or beta carbon atom. Typical ethers include the following which are shown with the fatty morpholinium compounds prepared therefrom:



The halogens which may be used in these ethers include chlorine, bromine and iodine.

Example 1

A mixture of 35.3 parts of didodecylamine, 20.6 parts of 1-chloro-2-propyl ether, 12.7 parts of anhydrous sodium carbonate and 160 parts of butyl alcohol was stirred and refluxed for 72 hours. It was then cooled and filtered. The filtrate was evaporated under reduced pressure. The residue was dissolved in methanol; this solution was chilled and filtered to remove unreacted didodecylamine. The filtrate was again evaporated and the residue recrystallized from ethyl acetate, yielding 4,4-didodecyl-2,6-dimethylmorpholinium chloride, a white solid, M. P. approximately 175–180° C.

Example 2

A mixture of 84.1 parts of dioctadecylamine, 33 parts of 1-chloro-2-propyl ether, 20.5 parts of anhydrous sodium carbonate and 320 parts of butyl alcohol was stirred and refluxed for 20 hours. It was then filtered, chilled, and filtered again. The filtrate was evaporated to dryness under reduced pressure. Unreacted amine was removed by dissolving the residue in methanol. Evaporation of the methanol, followed by recrystallization of the residue from ethyl acetate, gave 4,4-dioctadecyl-2,6-dimethylmorpholinium chloride as a white solid, M. P. 172.5–175.5° C.

A solution of this compound in isopropyl alcohol, added to an aqueous dispersion of bentonite, produced a flocculent precipitate. This was filtered off and washed with water and acetone. When this bentonite-morpho-

linium chloride reaction product was stirred with toluene, a grease-like gel formed.

I claim as my invention:

1. A morpholinium halide having two alkyl groups, each containing from 8–22 carbon atoms, attached to the nitrogen atom, and having attached to the ring at least one alkyl group containing from one to three carbon atoms, the ring being unsubstituted except for said alkyl groups.

2. A morpholinium halide having two alkyl groups, each containing from 8–22 carbon atoms, attached to the nitrogen atom, and having attached to the No. 2 and No. 6 positions on the ring an alkyl group containing from one to three carbon atoms, the ring being unsubstituted except for said alkyl groups.

3. 4,4-didodecyl-2,6-dimethylmorpholinium chloride.

4. 4,4-dioctadecyl-2,6-dimethylmorpholinium chloride.

5. Process of producing a morpholinium halide having two alkyl groups, each containing from 8–22 carbon atoms, attached to the nitrogen atom, and having attached to the ring at least one alkyl group containing from one to three carbon atoms, the ring being unsubstituted except for said alkyl groups, which comprises reacting a secondary amine containing two alkyl groups each containing from 8–22 carbon atoms, with a $\beta\beta'$ dihaloether containing said alkyl substituent of from 1–3 carbon atoms, at a temperature within the approximate range of 100–200° C.

6. Process according to claim 5 in which the reaction is carried out in the presence of an inorganic alkali.

7. Process according to claim 5 in which the reaction is carried out in the presence of a lower alkanol.

8. Process of producing 2,6-dimethyl morpholinium chlorides containing 2 alkyl groups, each containing from 8–22 carbon atoms, attached to the nitrogen atom which comprises reacting a secondary amine containing 2 alkyl groups each containing from 8–22 carbon atoms, with beta chloro isopropyl ether in the presence of sodium carbonate and n-butanol at approximately reflux temperature.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,096,441	Wilson	Oct. 19, 1937
2,129,805	Wilson	Sept. 13, 1938
2,295,504	Shelton	Sept. 8, 1942
2,380,325	Niederl et al.	July 10, 1945

FOREIGN PATENTS

Number	Country	Date
438,452	Great Britain	Nov. 18, 1935

OTHER REFERENCES

Chem. Abstr., vol. 19, pp. 634 and 1413.
Chem. Abstr., vol. 28, p. 1704.
Chem. Abstr., vol. 35, p. 4385.
Chem. Abstr., vol. 40, p. 4022.
Chem. Abstr., vol. 44, p. 635.
Beilstein, vol. XXVII, first suppl., p. 203.
Morton: "Chemistry of Heterocyclic Compounds" (1946), pp. 231–2.