United States Patent Office

3,660,459
Patented May 2, 1972

3,660,459

BORATE QUATERNARY AMMONIUM COMPOUNDS DERIVED FROM BORATE ESTERS OF AMINO SECONDARY ALKANOLS

Graham K. Hughes, Hackettstown, N.J., assignor to Ashland Oil, Inc., Houston, Tex.

No Drawing. Original application May 16, 1966, Ser. No. 550,157, now Patent No. 3,465,026, dated Sept. 2, 1969. Divided and this application Apr. 23, 1969, Ser. No. 818,833

Int. Cl. C07c *141/04*

U.S. Cl. 260—459 7 Claims

ABSTRACT OF THE DISCLOSURE

Quaternary ammonium salts of borate esters of 1-dialkylamino-2-alkanols are disclosed; such compounds having particular utility as fabric softeners and sanitizers.

CROSS REFERENCE TO RELATED APPLICATION

This application is a division of Ser. No. 550,157, filed May 16, 1966, now Pat. No. 3,465,026.

BACKGROUND OF THE INVENTION

Field of the invention

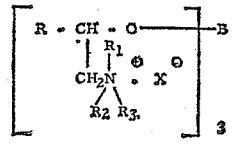
This invention relates to a process for the preparation of quaternary ammonium derivatives of borate esters of amino secondary alkanols. In a further aspect, it relates to the preparation of quaternary ammonium salts of borate esters of 1-dialkylamino-2-alkanols.

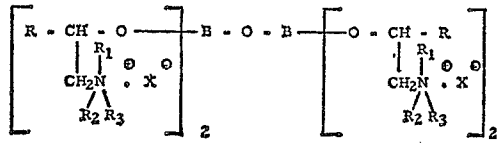
Description of the prior art

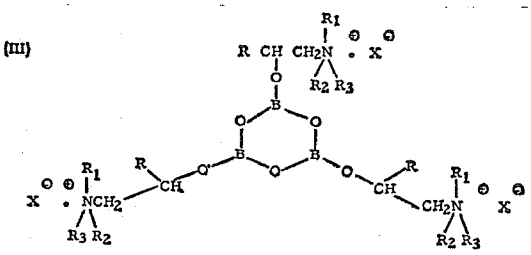
In my application Ser. No. 550,101, filed May 16, 1966, now abandoned, there are disclosed borate esters of amino secondary alkanols and methods for preparing the same. In accordance with the present invention, novel quaternary ammonium derivatives of the aforesaid borate esters and processes for the preparation thereof are disclosed and claimed.

SUMMARY OF THE INVENTION

In accordance with this invention, a new class of compounds is provided, which compounds are the quaternary ammonium salts of borate esters of amino-substituted secondary alkanols, said compounds having the general formulae:

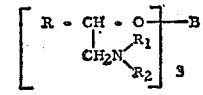
(I) 

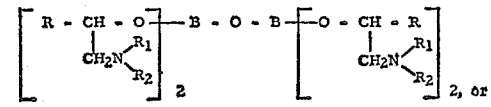
(II) 

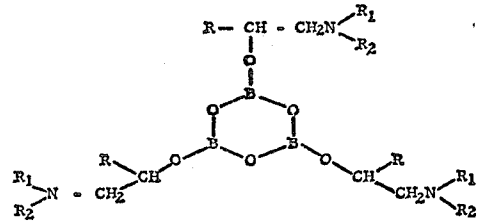
(III) 

where R_1 and R_2 are alkyl groups having 1 to 22 carbon atoms, preferably 1 to 8 carbon atoms, or are lower alkyl groups substituted with aryl, cyclo alkyl, cyclo alkenyl, alkaryl, alkylcycloalkyl or alkylcycloalkenyl groups having 6 to 10 carbon atoms, or R_1 and R_2 together with the nitrogen atom form a heterocyclic nitrogen group having 2 to 6 ring carbon atoms; and R is an alkyl group, either straight or branched chain having from 6 to 22 carbon atoms, preferably 9–16 carbon atoms, or R is an alkoxy-substituted alkyl having from 8–22, preferably from 9–16 carbon atoms; R_3 is a hydrocarbon radical selected from the group consisting of alkyl of 1 to 15 carbon atoms or aryl, e.g., benzyl, and X is a quaternizing anion, e.g., chloride, bromide, iodide, sulfate, and the like.

The borate esters can be prepared by reacting amino-substituted secondary alkanols with boric acid as disclosed in application Ser. No. 550,101, supra. Depending upon the mole ration of alkanol to acid, the borate esters having the following general formulae are produced:

(IV) 

(V) 

(VI) 

It will be apparent that the esters corresponding to Formula IV above can be quaternized to obtain the compounds corresponding to Formula I. Further, esters V and VI can be quaternized to obtain the compounds structurally shown by Formulas II and III, respectively.

The amino-substituted secondary alkanols can be prepared by reacting 1,2-epoxides of long-, straight-, or branched-chain, terminally unsaturated mono-olefins, such as those having 8 to 24 carbon atoms, preferably 11 to 18 carbon atoms, per molecule, with a secondary amine or secondary hydroxy amine, such as dimethylamine, diethylamine, dipropylamine, dioctylamine, methyl

ethylamine, ethyl butylamine, ethyl ethanolamine, diethanolamine, diisopropanolamine, diglycerolamine, cyclohexylmethylamine, morpholine, piperidine, 3,5-bis(hydroxymethyl)morpholine, pyrrolidine, pyrrole, azepine, aziridine, azetidine, hexahydroazepine, methyl benzylamine, ethylphenethylamine, methyl 1-naphthalene methylamine, and the like.

The 1,2-epoxides used in preparing such amino secondary alkanols can, in turn, be prepared by the epoxidation of said terminal olefins with an aliphatic peracid, such as peracetic acid. Such terminal olefins can be used singly or in admixture, and they can be straight-chain or branched-chain terminal olefins. Long, straight-chain terminal mono-olefins can be obtained from petrochemical sources, for example, by cracking of petroleum waxes or by polymerization of ethylene using Ziegler catalysts such as trialkylaluminum. Representative 1-olefins which can be used to prepare the 1,2-epoxide precursors include 1-decene, 1-hendecene, 1-dodecene, 1-hexadecene, 1-octadecene, 1-eicosene, and the like, including mixtures thereof. Table I sets forth a description and specifications for some long chain, terminal mono-olefin mixed fractions commercially available from petrochemical sources which can be epoxidized to prepare the precursor 1,2-epoxides of said amino secondary alkanols. Where such terminal mono-olefins are used as the initial precursors of the amino-substituted alkanols, the borate esters, prepared in this invention, will be mixtures of said esters, the various carbon chain lengths of the beta-substituted group attached to the nitrogen atom corresponding to that of the olefin fraction.

TABLE I

	C_9–C_{11}	C_{11}–C_{15}	C_{12}–C_{16}	C_{15}–C_{20}	C_{15}–C_{18}	C_{20+}
Total straight chain alpha olefins, percent	87	87	93.5	86	88.8	69
Carbon No. distributing, percent:						
C_8	1					
C_9	22					
C_{10}	55	1	0.7			
C_{11}	21	13				
C_{12}	1	24	41.3			
C_{13}		24				
C_{14}		24	31.9	1	1	
C_{15}		13		12	27	
C_{16}		1	25.6	19	29	
C_{17}				18	28	
C_{18}				18	15	
C_{19}				17		
C_{20-26}			0.5	15		77
C_{26-42}						23
Specific gravity, 20° C. g/ml	0.747	0.769	0.769	0.790	0.784	0.865

Representative amino secondary alkanols which are converted to the borate esters by reaction with boric acid and according to this invention include: beta hydroxy-C_{11-14}-alkyldimethylamine, beta - hydroxy-C_{15-19}-alkyldimethylamine, and the like, including their polypropoxylated derivatives, e.g., polypropoxylated distearyl ethanolamine, polypropoxylated beta - hydroxy - C_{11-14}-alkyldimethylamine, and the like. Also, included among representative amino secondary alkanols are:

3-hydroxybutyl dimethylamine,
9-hydroxystearyl dimethylamine,
1-dimethylamino-2-decanol,
1-dimethylamino-2-hendecanol,
1-(N-methyl-N-ethylamino)-2-dodecanol,
1-dipropylamino-2-tridecanol,
1-(N-ethyl-N-butyl)-amino-2-tetradecanol,
1-(N-pentyl-N-hexyl) amino-2-pentadecanol,
1-(N-methyl-N-heptyl) amino-2-hexadecanol,
1-(N-heptyl-N-octyl)-amino-2-octadecanol,
1-dioctylamino-2-eicosanol,
1-dibutylamino-2-heneicosanol,
1-dimethyl amino-2-nonadecanol,
1-diethylamino-2-eicosanol,
1-dipentyl-amino-2-docosanol,
1-(N-methyl-N-ethyl) amino-2-tricosanol,
1-dioctylamino-2-tricosanol
N-(2-hydroxydecyl) pyrrolidine,
N-(2-hydroxyoctyl)-piperidine,
N-(2-hydroxyeicosyl) decahydroquinoline,
1-(bis-2-hydroxyethyl)amino-2-decanol,
1-(methyl-2-hydroxyethyl)amino-2-dodecanol,
1-(bis-2-hydroxypropyl)amino-2-tetradecanol,
1-(methyl-2-hydroxypropyl)-amino-2-octadecanol,
1-(N-methyl-N-butyl) amino-2-eicosanol,

and the like, including mixtures thereof.

The quaternary ammonium salts are prepared according to this invention by quaternizing said borate esters of said amino-substituted alkanols at temperatures in the range of 40 to 80° C. with a quaternizing agent, such as methyl chloride, benzyl chloride, dodecenyl chloride, methyl sulfate, and the like. In general, the quaternizing agent is an alkyl, chloride, bromide, iodide or sulfate, an arylalkyl halide, an alkyl ester of an aromatic sulfonic acid or the like. In this process the quaternizing agent is, preferably, slowly added to a heated mixture of the borate ester, water and a solvent, such as a lower alkanol, e.g., methanol, ethanol, propanol, or butanol. The amount of quaternizing agent added is usualy about 1 to 25% in excess of the stoichiometric amount. The quaternaries are generally water-soluble and can be used, for example, as fabric softeners. Further, the quaternaries, especially those obtained when an aromatic halide, e.g., benzyl chloride, is used as the quaternizing agent, are useful as disinfectants and/or sanitizers.

Representative quaternary ammonium salts of the borate esters of amino-secondary alkanols which can be made according to this invention, include the quaternary ammonium salts of the borate esters of any of the aforementioned amino-secondary alkanols, such as the quaternary ammonium chloride of the borate ester of beta-hydroxy-C_{11-14}-alkyldimethylamine.

The following working examples are illustrative of the best mode contemplated for carrying out the present invention.

EXAMPLE I

In this example 100 grams of the borate ester of beta-hydroxy-C_{15-16}-alkyl dimethylamine (prepared by reacting 3 moles of the hydroxyamine with 1 mole of boric acid) were reacted with 51.7 grams of benzyl chloride in an isopropanol-water system to prepare the benzyl chloride quaternary ammonium salt.

To obtain the quaternary, the borate ester, 40.3 grams of isopropanol and 10.1 grams of water were charged to a reactor. The reactor and its contents were then heated to 60–70° C. after which 51.7 grams of benzyl chloride were dripped in over a one-half hour period. The reaction mixture was then held at 65° C. for 2 days. The reaction was substantially quantitative, there being 0.57% free amine in the product.

The quaternary ammonium compound is readily dispersed in cold water and, when employed at a 0.1% level in the rinse water of a washing machine cycle, improves the fluffiness and softness of towels to a greater extent than similarly treated towels employing a commercially available fabric softener. Further, the quaternary shows disinfecting and/or sanitizing properties.

EXAMPLE II

In this example, 79.5 grams of the borate ester used in Example I were reacted with 73.7 grams of dodecenyl chloride in an isopropanol-water system to prepare the dodecenyl chloride quarternary ammonium salt of the borate ester. The procedure was similar to that of Example I. 3.16 grams of isopropanol and 9.8 grams of water were used. After 4 days the reaction was complete, these

being 0.89% free amine in the product. This quaternary shows similar fabric-softening and sanitizing properties.

EXAMPLE III

In this example, 100 grams of the borate ester of beta-hydroxy-C_{11-14}-dimethylamine (prepared by reacting 3 moles of the hydroxy amine with 1 mole of boric acid) were reacted with 48.6 grams of benzyl chloride to prepare the quaternary ammonium salt in a manner quite similar to that used in Example I. 39.6 grams of isopropanol and 99 grams of water were used as the solvent system. After 2 days, at 50° C., the reaction was substantially complete, there being 0.53% free amine in the product. The quaternary ammonium compound showed surprising germicidal properties when used as a fabric softener.

EXAMPLE IV

In this example, 100 grams of the borate ester used in Example III were reacted with 84.2 grams of dodecenyl chloride to prepare the dodecenyl chloride quaternary ammonium salt of the ester. The procedure used was similar to that of Example I. The solvent system used comprised 12.3 grams of water and 49.1 grams of isopropanol. The reaction mixture was held at 60° C. for about 12 hours at which time the percentage of free amine was about 0%. The quaternary so obtained showed excellent germicidal activity and is used as a fabric softener.

EXAMPLE V

In this example, 165 grams of the borate ester of beta-hydroxy-C_{15-18}-alkyl dimethylamine (prepared by reacting 3 moles of the hydroxy amine with 1 mole of boric acid) were reacted with 64.2 grams of methyl sulfate, by a procedure similar to that observed in the previous examples, to obtain the methyl sulfate quaternary ammonium salt of the ester. The solvent system comprised 61.2 grams of isopropanol and 15.3 grams of water. The reaction mixture was held at 60–70° C. for 2 days after which time the percent total amine nitrogen (T.A.N.) was 0.018% and the percent free amine was 0.417%. Accordingly, the reaction was substantially complete.

The quaternary so obtained is readily dispersed in cold water, and, when employed at a 0.1% level in the rinse water of a washing machine cycle, improves the fluffiness and softness of towels to a greater extent than similarly-treated towels employing a commercially-available fabric softener.

EXAMPLE VI

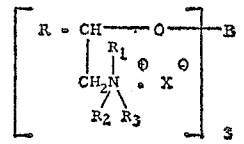
In this example, 128 grams of the borate ester of beta-hydroxy-C_{11-14}-alkyldimethylamine (prepared by reacting 1 mole of the hydroxy amine with ½ mole of boric acid) were reacted with 193 grams of dodecenyl chloride. The solvent system comprised 256 grams of isopropanol and 64 grams of water. After about 2½ hours the reaction was complete in that the total amine nitrogen was approximately zero.

The quaternary so obtained is evaluated as a fabric softener and shown to possess good softening properties and compatibility with zinc nitrate.

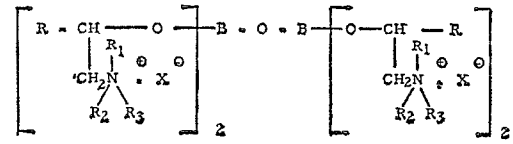
I claim:

1. A class of compounds having the general formula:

(I)

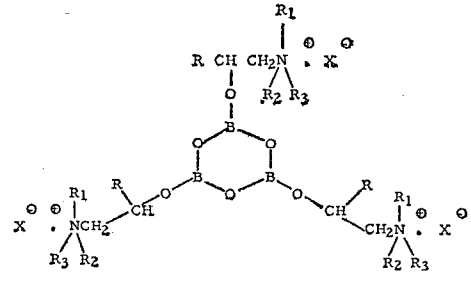


(II)



or

(III)



where R is an alkyl group having 6 to 22 carbon atoms; R_1 and R_2 are alkyl groups having 1 to 8 carbon atoms; R_3 is dodecenyl, benzyl or alkyl having not in excess of 15 carbon atoms and X is an anion selected from the group consisting of chloride, bromide, iodide and methyl sulfate.

2. Quaternary ammonium compounds according to claim 1 where R_1 and R_2 are methyl groups.

3. Quarternary ammonium compounds according to claim 2 where R is an alkyl group having 9 to 16 carbon atoms.

4. Quarternary ammonium compounds according to claim 1 where X is a chloride or a methyl sulfate anion.

5. Quarternary ammonium compounds according to claim 4 where R_3 is benzyl.

6. Quaternary ammonium compounds according to claim 4 where R_3 is dodecenyl.

7. Quaternary ammonium compounds according to claim 4 where R_3 is methyl.

References Cited

UNITED STATES PATENTS

2,259,175	10/1941	Paul	260—462 X
3,072,737	1/1963	Chen	260—462 X

LEON ZITVER, Primary Examiner

L. B. DECRESCENTE, Assistant Examiner

U.S. Cl. X.R.

260—462 R