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3,444,200

ARYL-ALKYL QUATERNARY AMMONIUM COMPOUNDS

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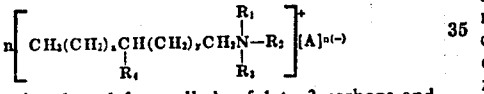
No Drawing. Filed Oct. 21, 1965, Ser. No. 500,203
Int. Cl. C07c 87/30
U.S. Cl. 260—567.6 15 Claims

ABSTRACT OF THE DISCLOSURE

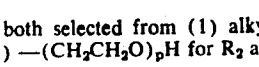
Aryl-substituted aliphatic quaternary ammonium compounds having one or two long chain alkyl groups to which an aryl group is attached to an internal carbon atom, useful as cationic bituminous emulsifiers and for fabric treating and in textile processing.

This invention relates to a novel class of aryl-substituted aliphatic quaternary compounds, and more particularly, this invention relates to quaternary compounds containing one or more long chain aliphatic groups to which an aryl group is attached as a side chain, thereby providing an aralkyl group. The compounds of this invention have utility as cationic emulsifiers for preparing asphalt or other bituminous emulsions. The compounds may also be used for other purposes, such as for fabric treatment and in textile processing.

The quaternary compounds of the present invention can be represented by the following structural formula



wherein R_1 is selected from alkyls of 1 to 3 carbons and



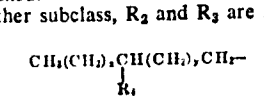
R_2 and R_3 are both selected from (1) alkyls of 1 to 3 carbons, and (2) $-(CH_2CH_2O)_pH$ for R_2 and

$$-(CH_2CH_2O)_wH$$

for R_3 with p and w being integers from 1 to 40 and with the total of p and w not exceeding 60, A is an anion having a valence of 1 to 2, n is an integer from 1 to 2, x and y are integers from 0 to 19 and the total of x and y is an integer from 8 to 19, and R_4 is selected from phenyl, naphthyl, and phenyl substituted with from 1 to 2 groups selected from methyl, hydroxy, and methoxy.

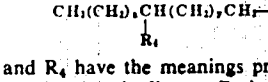
In one subclass, R_1, R_2 and R_3 are methyl. In another subclass, R_1 is methyl, R_2 is $-(CH_2CH_2O)_pH$, and R_3 is $-(CH_2CH_2O)_wH$ with p and w being integers from 1 to 20 and with the total of p and w not exceeding 30. In these subclasses, the other variables have the meanings previously defined.

In still another subclass, R_2 and R_3 are methyl and R_1 is



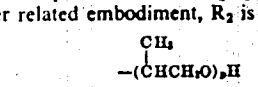
where x, y, and R_4 have the meanings previously defined.

In a further subclass, R_2 is methyl, R_3 is $-(CH_2CH_2O)_wH$ with w being an integer from 1 to 20, and R_1 is

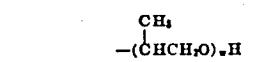


where x, y and R_4 have the meanings previously defined.

In another related embodiment, R_2 is



R_3 is



with p and w being integers from 1 to 20 and with the total of p and w not exceeding 30. The other variables have the meetings previously defined, or R_4 is phenyl, R_1 is methyl, n is 1, and A is chloride.

It will be noted from the foregoing formula that the quaternary compounds contain at least one long chain aryl-substituted aliphatic group, or, more specifically, an aralkyl group. In one specific embodiment the alkyl portion of the aralkyl group contains a total of 18 carbons. In other specific embodiments, the alkyl portion of the aralkyl groups contain 11, 16 or 22 carbons. More generally, the total of x and y, which is three less than the total of carbons in the alkyl portion of the aralkyl, may range from 8 to 19. The compounds also contain at least one, or up to three, short chain alkyl groups which are bonded to the nitrogen atom. While methyl groups are preferred, the alkyl groups may also comprise ethyl, propyl, etho-, or propo-, or mixtures thereof.

In the formula, R_4 represents the aryl substituent. The carbon to which the aryl group is attached varies with the respective values of x and y. With unsaturated alkylene chains, such as oleyl, under most reaction conditions the double bond migrates up and down the chain (isomerization by hydrogen ion transfer) resulting in a mixture of isomeric products. In arylating oleyl, there is a tendency for the C_8–C_{14} and the C_{17} aryl isomers to predominate, but smaller mole percentages of other isomers, such as the C_6, C_7, C_{15}, and C_{16} isomers are also produced. The mole percent of the C_2–C_5 isomers is usually quite small or even negligible. The relative proportions of the various isomers may vary depending on the arylation process. See J. Org. Chem. 30, 885–888 (1965). However, the total of x and y will remain constant for the particular unsaturated chain, viz. 15 for oleyl, 8 for undecyl, 19 for behenyl, etc. By arylation, oleic acid is converted to aryl-substituted stearic acid. Similarly, palmitoleic, erucic, and 10-undecenoic acids can be converted to the corresponding aryl-substituted carboxylic acids. Ordinary commercial grade oleic acid contains several percent of palmitoleic acid, and therefore a mixture of aryl-substituted stearic and palmitic acids is obtained by arylation.

Among the preferred aryl substituents are phenyl, hydoxphenyl, tolyl, anisyl, and naphthyl. More generally, the phenyl nucleus may be substituted with 1 or 2 groups such as methyl, hydroxy, and methoxy. Other groups coming within this subclass are cresyl, resorcyl, xylyl, etc.

Since quaternaries are in the form of salts, the cationic portion of the molecule will be associated with an anionic portion. The particular anion is not critical, and generally the anion may be any of those which are commonly pres-

ent in quaternary compounds, such as monovalent or divalent anions. To provide for complete neutralization, the formula indicated that *n* will be 1 for monovalent anions and 2 for divalent anions. Chloride salts of the quaternary are particularly desirable where the compounds are to be employed as cationic emulsifiers, but other salts can be used such as hydroxides, sulfates, nitrates, hydrochlorates, perchlorates, hypochlorates, formates, acetates, etc. For certain purposes, the anion should be selected to provide water solubility or water dispersibility.

As previously indicated, the aryl fatty acids such as arylstearic acid or arylpalmitic acid, may be prepared by the arylation of oleic acid or palmitoleic acid. A catalyst is ordinarily required for such arylation, as is well known in the art. For example, aluminum chloride may be employed as the catalyst. With this process, the fatty acid is preferably first converted to the cyano derivative, which is reacted with the arylating agent in the presence of aluminum chloride. The aryl cyano aliphatic compound, by procedures well known in the art, can then be converted to the corresponding primary amine (by hydrogenation), then to the tertiary amine (by alkylation with short chain alkyl groups or alkoxy groups), and finally quaternized by a suitable quaternizing agent such as methyl chloride or dimethyl sulfate.

For direct arylation of fatty acids other catalysts are preferred, such as activated clays, or hydrofluoric acid. A process employing HF as the catalyst is described in Patent 2,275,312, while the use of an activated clay is described in Patent 3,074,983. An improved HF process is described and claimed in copending application, Ser. No. 451,021, filed Apr. 26, 1965, entitled "Process for Arylating Unsaturated Fatty Compounds." The arylated fatty acid can then be used to prepare the quaternary compounds of the present invention. For example, phenylstearic acid (or other aryl-substituted long chain fatty acid) can be converted to the corresponding nitrile, the nitrile converted to the primary amine, the primary amine converted to the tertiary amine, and the tertiary amine quaternized. Alternatively, the primary amine, such as phenylstearyl amine, can be converted to the quaternary by reaction with methyl chloride. The primary amine can also be ethoxylated or propoxylated by reaction with ethylene oxide or propylene oxide before being quaternized. It will be understood that such procedures are well known in the art.

This invention is further illustrated by the following specific examples. From what has been said above, it will be understood that the products of the examples are in the form of isomeric mixtures.

Example I

Phenylstearic acid, hydroxyphenylstearic acid, and tolylstearic acid were prepared from commercial grade oleic acid which contained a few percent of palmitoleic acid by a Friedel-Crafts reaction using aluminum chloride as the catalyst and benzene, phenol, and toluene, respectively, as the arylating agents. Thereafter, phenylstearonitrile was prepared on a continuous nitrile unit over bauxite catalyst at 280–300° C. from 1127 g. phenylstearic acid. A crude yield of 833.5 g. of phenylstearonitrile was obtained comprising a mixture of isomers, predominantly, the C_8 to C_{14}, and the C_{17} isomers with lesser proportions of other isomers.

Similarly, hydroxyphenylstearonitrile was obtained in 62% crude yield from the crude acid, and tolylstearonitrile was obtained in 87% crude yield from distilled tolylstearic acid.

Example II

Phenylstearonitrile (591 g.) prepared as described in Example I was reduced in a 1-liter, Parr autoclave over 2% (by wt.) alcohol washed Raney nickel catalyst in the presence of ammonia (150 p.s.i./30–40° C.) and hydrogen (800 p.s.i. total pressure at 125° C. for 4–5 hours). The product was obtained as a light amber oil, 582.3 g. (97% crude yield). Pure phenyloctadecylamine was obtained in 67% yield upon distillation at 183–190°/0.3 mm.

Similarly, hydroxyphenyloctadecylamine was prepared in 91.5% crude yield and 81% distilled yield from distilled hydroxyphenylstearonitrile prepared as described in Example I. Tolyloctadecylamine was prepared in 97% crude yield from the distilled nitrile.

Example III

Phenyloctadecylamine (50 g., 0.145 mole) prepared as described in Example II and $NaHCO_3$ (25 g., 0.31 mole) in 50 ml. isopropanol were treated with methyl chloride at 75–80°/70 p.s.i. in a 300 cc. stirred autoclave for 3.5–4 hours. Carbon dioxide was removed by periodic venting of the reaction vessel. The reaction mixture was then diluted to an approximately 50% solution of quaternary in isopropanol.

Analysis.—Percent quaternary, 43.6; free amine, nil; amine.HCl, nil.

The product was a mixture of isomers of N,N,N-trimethyl-N-phenyloctadecylammonium chloride.

Similarly, the hydroxyphenyl- and tolyloctadecyl trimethylammonium chlorides were prepared from the reactants of Example II.

Hydroxyphenyl derivative: 78.5% quaternary; amine.HCl nil; free amine, 0.9%.

Tolyloctadecyl derivative: 64.3% quaternary; amine.HCl 2.8; Free amine, nil.

Example IV

Tolylstearonitrile (806.8 g., 2.27 moles) was reduced in a two-liter Parr autoclave over 2% (by wt.) alcohol Raney nickel catalyst in the presence of ammonia (360 p.s.i./135° C.) and hydrogen (800 p.s.i. total pressure/135–135° C.) in five hours. The crude amine was obtained as an amber oil, 800 g. (98% crude yield).

Analysis.—Neut. equivalent, 362 (Calcd. 359.6); Primary amine, 88.1%; Secondary amine, 0.31 meq./g.

Distillation at 201–202° C./0.7–1.0 mm. afforded a 68.8% yield of tolyloctadecylamine.

Analysis.—Neut. equivalent, 362 (Calcd. 359.6); Primary amine, 98.8 %.

Example V

Xylylstearonitrile (579.1 g., 1.56 moles) was reduced in a one-liter Magnedash autoclave over 2% (by wt.) alcohol washed Raney nickel catalyst in the presence of ammonia (480 ps.i./135° C.) and hydrogen (800 p.s.i. total pressure/135–140° C.) in eight hours. The crude amine was obtained as an amber oil, 576.4 g. (99% crude yield).

Analysis.—Neut. equivalent, 366.0 (Calcd. 375.7); Primary amine, 100.5%; Secondary amine, 3.14%.

Distillation at 180–196° C./0.07–0.1 mm. afforded 75% yield of xylyloctadecylamine.

Analysis.—Neut. equivalent, 374 (Calc'd 373.7); Primary amine, 99.9%.

Example VI

"Tolyltallownitrile" (868.7 g., 2.85 moles) was reduced in a two-liter Parr autoclave over 2% (by wt.) alcohol washed Raney nickel catalyst in the presence of ammonia (550 p.s.i./135–140° C.) and hydrogen (800 p.s.i. total pressure/135–138° C.) in six hours. The crude amine was obtained as an amber oil which solidified on cooling, 878.4 g. (99.8% crude yield).

Analysis.—Neut. equivalent, 316; Primary amine, 101.5%; Secondary amine, 0.224 meq./g.

Distillation at 127–202° C./0.05–0.3 mm. afforded an 89.9% yield of "tolyltallowamin "

Analysis.—Neut. equivalent, 292.5; Primary amine, 99.8%.

Example VII

A 500 ml. glass reactor was charged with 43 g. (0.116 mole) of anisyloctadecylamine, 19.5 g. (9.232 mole) of sodium bicarbonate and 200 ml. of isopropanol. The reactor was sealed and the reaction mixture heated to 60–70° C. Gaseous methyl chloride was introduced at 60–70 p.s.i.g. and the reaction mixture maintained at 60–70° C./60–70 p.s.i.g. for six hours with periodic venting. Sodium chloride and excess sodium bicarbonate were removed by filtration and the isopropanol solution of N,N,N-trimethyl - N-anisyloctadecylammonium chloride concentrated to about 40% active.

Analysis.—Percent quaternary, 41.1; Free amine, trace; Amine.HCl, 0.14%.

Example VIII

A 500 ml. glass reactor was charged with 15 g. (0.032 mole) of naphthyloctadecylamine, 10.1 g. (0.12 mole) of sodium bicarbonate and 150 ml. of isopropanol. The reactor was sealed and the reaction mixture heated to 60–70° C. Gaseous methyl chloride was introduced at 60–70 p.s.i.g. and the reaction mixture maintained at 60–70° C./60–70 p.s.i.g. for 4.5 hours with periodic venting. Sodium chloride and excess sodium bicarbonate were removed by filtration and the isopropanol solution of N,N,N-trimethyl - N-naphthyloctadecylammonium chloride concentrated.

Analysis.—Percent quaternary, 14; Free amine, 0.4%; Aamine.HCl, nil.

Example IX

A two-liter Parr autoclave was charged with 425.2 g. (1.14 moles) of xylyloctadecylamine, 234.5 g. (2.79 moles) of sodium bicarbonate and 500 ml. of isopropanol. The reactor was sealed and the temperature of the reaction mixture was raised to 65–75° C. Gaseous methyl chloride was introduced at 70–75 p.s.i.g. and the reaction mixture maintained at 65–75° C./70–75 p.s.i.g. for fourteen hours with periodic venting. Sodium chloride and excess sodium bicarbonate were removed by filtration and the isopropanol solution of N,N,N-trimethyl-N-xylyloctadecylammonium chloride concentrated.

Analysis.—Percent quaternary, 83.7; Free amine, 0.32%; Amine.HCl, nil.

Example X

A 500 ml. glass reactor was charged with 47.2 g. (0.117 mole) of phenyldocosanylamine, 22.0 g. (0.247 mole) of sodium bicarbonate and 60.0 ml. of isopropanol. The reactor was sealed and heated to 70–75° C. Gaseous methyl chloride was introduced to 60–70 p.s.i.g. and the reaction mixture maintained at 70–75° C./60–70 p.s.i.g. for four hours with periodic venting. Sodium chloride and excess sodium bicarbonate were removed by filtration and the isopropanol solution of N,N,N-trimethyl-N-phenyldocosanylammonium chloride was obtained as a yellow liquid having the following analysis: Percent quaternary, 48.7; Free amine, nil; Amine.HCl, nil.

Example XI

A 500 ml. glass reactor was charged with 50.0 g. (0.203 mole) of phenylundecylamine, 37.9 g. (0.45 mole) of sodium bicarbonate and 50 g. of isopropanol. The reactor was sealed and heated to 70–75° C. Gaseous methyl chloride was introduced to 70 p.s.i.g. and the reaction mixture maintained at 70–75° C./60–70 p.s.i.g. for 2.5 hours with periodic venting. Sodium chloride and excess sodium bicarbonate were removed by filtration and the isopropanol solution of N,N,N-trimethyl-N-phenylundecylammonium chloride was obtained as a clear colorless liquid having the following analysis: Percent quaternary, 57.0; Free amine, nil; Amine.HCl, nil.

Example XII

A 200 ml. 3-neck round bottom flask, equipped with an addition funnel, thermometer, redux condenser and magnetic stirred, was charged with 25.8 (0.052 mole) of N,N-di-(Beta-hydroxyethyl)tolyloctadecylamine and 30 ml. of a 50% by volume mixture of benzene and toluene. The solution was heated, with stirring, to 70° C. and 6.5 g. (0.052 mole) of dimethyl sulfate were added over a half hour period at 70–85° C. An additional 40 ml. of 50% benzene-toluene mixture was added during the addition of dimethyl sulfate to reduce the viscosity of the mixture. After the addition was complete the reaction mixture was refluxed at 105° C. for 1.5 hours. The resultant amber solution was concentrated to about 60% active quaternary, being N-methyl-N,N-di-(Beta-hydroxyethyl)-N-tolyloctadecylammonium methyl sulfate.

Analysis.—Percent quaternary, 59.4; Free amine, 4.1%; Amine sulfate, 2.2%.

Example XIII

A 500 ml. glass reactor was charged with 12.7 g. (0.027 mole) of N,N-di-(Beta-hydroxyethyl)tolyloctadecylamine and 41.6 g. of isopropanol. The reactor was sealed and heated to 80° C. Gaseous methyl chloride was introduced to about 50 p.s i.g. and the reaction mixture maintained at 70–80° C./45–50 p.s.i.g. for twelve hours. The isopropanol solution of the quaternary had the following analysis. Percent quaternary, 29.4; Free amine, 1.3%; Amine.HCl, nil.

Example XIV

Similarly, the ethoxylation product of 5 moles of ethylene oxide with tolyloctadecylamine was quaternized using methyl chloride at 70–80° C./45–50 p.s.i.g. to yield an isopropanol solution of the quaternary ammonium salt having the following analysis: Percent quaternary, 28.0; Free amine, nil; Amine.HCl, nil.

Example XV

In like manner, the ethoxylation product of 15 moles of ethylene oxide with tolyloctadecylamine was quaternized. The resulting quaternary ammonium salt had the following analysis: Percent quaternary, 21.7; Free amine, nil; Amine.HCl, nil.

Example XVI

A 500 ml. glass reactor was charged with 48.1 g. (0.1 mole) of di-(phenylundecyl)amine, 9.24 g. (0.11 mole) of sodium bicarbonate and 200 ml. of isopropanol. The reactor was sealed and the temperature raised to 70° C. Gaseous methyl chloride was introduced at 70 p.s.i.g. and the reaction mixture maintained at 60–70° C./60–70 p.s.i.g. for four hours with periodic venting. Sodium chloride and excess sodium bicarbonate were removed by filtration and the N,N-dimethyl-N,N-di(phenylundecyl)ammonium chloride was obtained as an isopropanol solution having the following analysis: Percent quaternary, 33.3; Free amine, 0.34%; Amine.HCl, 0.05%.

Example XVII

A 500 ml. glass reactor was charged with 50 g. (0.063 mole) of di-(phenyldocosyl)amine, 5.85 g. (0.07 mole) of sodium bicarbonate and 200 ml. of isopropanol. The reactor was sealed and the temperature raised to 70° C. Gaseous methyl chloride was introduced at 70 p.s.i.g. and the reaction mixture maintained at 60–70° C./60–70 p.s.i.g. for four hours with periodic venting. Sodium chloride and excess sodium bicarbonate were removed by filtration and the N,N - dimethyl-N,N-di(phenyldocosyl) ammonium chloride was obtained as an isopropanol solution having the following analysis: Percent quaternary, 26.4; Free amine, 0.2%; Amine.HCl, 2.99%.

Example VIII

A two-liter Parr autoclave was charged with 445 g. (0.614 mole) of di-(tolyloctadecyl)amine, 60.0 g (0.674 mole) of sodium bicarbonate, and 500 ml. of isopropanol. The reactor was sealed and the temperature raised to 75° C. Gaseous methyl chloride was introduced at 75 p.s.i.g. and the reaction mixture maintained at 70–80° C./70–80

p.s.i.g. for six hours with periodic venting. Sodium chloride and excess sodium bicarbonate were removed by filtration and the isopropanol solution of quaternary was concentrated under reduced pressure. The resultant product had the following analysis: Percent quaternary, 88.9; Free amine, 0.9%; Amine·HCl, nil.

Example XIX

A one-liter Magne-drsh autoclave was charged with 518.9 g. (0.73 mole) di-(phenyloctadecyl)amine, 113.3 g. (1.35 moles) sodium bicarbonate, and 50 ml. isopropanol. Methyl chloride gas was add.d and maintained at 70–75 p.s.i.g. at 65–70° C. for 25 hours with a slight, continuous vent. Excess sodium bicarbonate and salt was removed by filtration and the solvent stripped off in vacuo to yield 554.9 g. (98% mass yield) of an amber oil containing N,N - dimethyl - N,N - di-(phenyloctadecyl)ammonium chloride.

Example XX

A 500 ml, glass reactor was charged with 40.8 g. (0.119 mole) of N,N - di(Beta - hydroxyethyl)phenylundecylamine, 2.5 g. (5% by wt.) of sodium bicarbonate and about 100 ml. of isopropanol. The reactor was sealed and the mixture heated to 70° C. Gaseous methyl chloride was introduced to 75 p.s.i.g. and the reaction mixture maintaineo at 75–80° C./70–75 p.s.i.g. for five hours with periodic venting. The sodium chloride and excess sodium bicarbonate was removed by filtration yielding an isopropanol solution of the quaternary ammonium salt.

Analysis.—Percent quaternary, 33.1; Free amine, 0.12%; Amine.HCl, nil.

Example XXI

A 500 ml. glass reactor was charged with 37.1 g. (0.072 mole) of N,N-di(Beta-hydroxyethyl)phenyldocosylamine, 5.0 g. (0.059 mole) of sodium bicarbonate and about 100 ml. of isopropanol. The reactor was sealed and the mixture heated to 75° C. Gaseous methyl chloride was introduced at 70 p.s.i.g. and the reaction mixture maintained at 75–80° C./70–75 p.s.i.g. for five hours with periodic venting. The sodium chloride and excess sodium bicarbonate were removed by filtration, yielding an isopropanol solution of the quaternary ammonium salt.

Analysis.—Percent quaternary, 31.2; Free amine, 1.5%; Amine·HCl, nil.

Example XXII

A two-liter Parr autoclave was charged with 761.0 g. (2.6 moles) of "totyltallowamine," 512.9 g. (5.7 moles) and 150 ml. of isopropanol. The reactor was sealed and the mixture heated to 65–75° C. Gaseous methyl chloride was introduced at 70–75 p.s.i.g. and the reaction mixture maintained at 65–75° C./70–75 p.s.i.g. for about eleven hours. Sodium chloride and excess sodium bicarbonate were removed by filtration with the aid of additional isopropanol. The isopropanol solution containing the N,N,N-trimethyl-N-"tolyltallow" ammonium chloride was then concentrated to the maximum concentration at which it still remained liquid.

Analysis.—Percent quaternary, 73.8; Free amine, 0.25%; Amine·HCl, nil.

Example XXIII

A 500 ml. glass reactor was charged with 69.2 g. (0.1 mole) of di-(xylyloctadecyl)amine, 10.9 g. (0.13 mole) of sodium bicarbonate and 95 ml. of isopropanol. The reactor was sealed and the temperature raised to 80° C. Gaseous methyl chloride was introduced at 85 p.s.i.g. and the reaction mixture maintained at 80–85° C./85–90 p.s.i.g. for three hours with periodic venting. Sodium chloride and excess sodium bicarbonate were removed by filtration and the N,N-dimethyl-N,N-di-(xylyloctadecyl) ammonium chloride was obtained as an isopropanol solution having the following analysis: Percent quaternary, 40.5; Free amine, 1.24%; Amine·HCl, 0.17%.

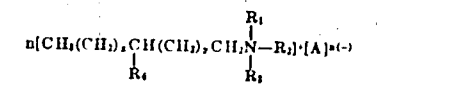
Example XXIV

A 500 ml. glass reactor was charged with 34.9 g. (0.063 mole) of N,N-di - (alpha-methyl - Beta - hydroxyethyl)-phenylbehenylamine, 2.0 g. of sodium bicarbonate and 35 g. of isopropanol. The reactor was sealed and the mixture heated to 75° C. Gaseous methyl chloride was introduced to 75 p.s.i.g. and the reaction mixture maintained at 75–80° C./70–75 p.s.i.g. for ten hours with periodic venting. Sodium chloride and excess sodium bicarbonate was removed by filtration, yielding an isopropanol solution of the quaternary ammonium salt.

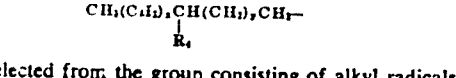
Analysis.—Percent quaternary, 34.2; Free amine, 14.1%; Amine·HCl, nil.

We claim:

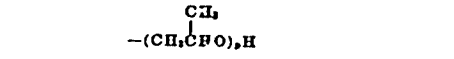
1. Quaternary ammonium compounds represented by the formula



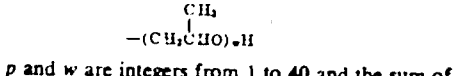
wherein R_1 is selected from the group consisting of alkyl radicals having from 1 to 3 carbon atoms, and



R_2 is selected from the group consisting of alkyl radicals having from 1 to 3 carbon atoms, $-(CH_2CH_2O)_pH$, and



and R_3 is selected from the group consisting of alkyl radicals having from 1 to 3 carbon atoms, $-(CH_2CH_2O)_wH$, and

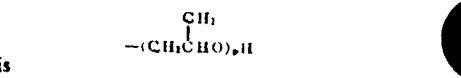


wherein p and w are integers from 1 to 40 and the sum of p and w is less than 60; R_4 is selected from phenyl, naphthyl, and phenyl substituted with from 1 to 2 groups selected from methyl, hydroxy, and methoxy; x and y are integers from 0 to 19 and the sum of x and y is an integer from 8 to 19; A is an anion; and n is an integer from 1 to 2, said compounds comprising isomeric mixtures with respect to the position of R_4 to the alkyl chain.

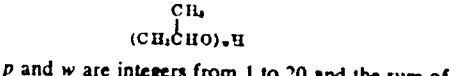
2. The compounds of claim 1 wherein R_1, R_2 and R_3 are each methyl.

3. The compounds of claim 1 wherein R_1 is methyl, R_2 is $-(CH_2CH_2O)_pH$, and R_3 is $-(CH_2CH_2O)_wH$ wherein p and w are integers from 1 to 20 and the sum of p and w is less than 30.

4. The compounds of claim 1 wherein R is methyl, R_2 is

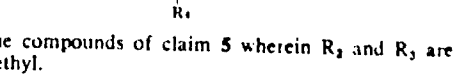


and R_3 is



wherein p and w are integers from 1 to 20 and the sum of p and w is less than 30.

5. The compounds of claim 1 wherein R_1 is



6. The compounds of claim 5 wherein R_2 and R_3 are each methyl.

7. The compounds of claim 1 wherein R_4 is phenyl.

8. The compounds of claim 1 wherein R_4 is xylyl.

9. The compounds of claim 1 wherein R_4 is hydroxyphenyl.

10. The compounds of claim 1 wherein A is selected

from the group consisting of Cl^-, $SO_4^=$, OH^-, NO_3^- and Br^-.

11. The compounds of claim 1 wherein x is an integer from 0 to 11 and y is an integer from 4 to 15 and the sum of x and y is 15.

12. The compounds of claim 11 wherein R_4 is phenyl, and A is selected from the group consisting of Cl^-, $SO_4^=$, OH^-, NO_3^- and Br^-.

13. The compounds of claim 12 wherein R_1, R_2 and R_3 are each methyl and A is Cl^-.

14. The compounds of claim 11 wherein R_4 is hydroxyphenyl, and A is selected from the group consisting of Cl^-, $SO_4^=$, OH^-, NO_3^- and Br^-.

15. The compounds of claim 14 wherein R_1, R_2 and R_3 are each methyl, and R_4 is hydroxyphenyl.

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U.S. Cl. X.R.

252—8.6, 8.8, 311.5; 260—413, 465, 570.8, 999