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COMPLEX AMMONIUM SALTS AND PROCESSES FOR PRODUCING THE SAME

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10 Claims. (Cl. 260—448.2)

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This invention relates in general to a new series of chemical compounds which are surface-active or cationic agents. The invention relates in particular to a new series of quaternary ammonium compounds which are adapted for use as antiseptic and germicidal agents, also as wetting, dispersing and emulsifying agents, and to a process for the preparation of such compounds and to compositions containing them.

It is known to prepare quaternary ammonium compounds from tertiary amines in which the nitrogen is initially trivalent by reacting such amines with alkyl halides, the compounds resulting having the general formula

$$R_4N—X$$

and these compounds have been used as surface active agents. However, the known quaternary ammonium compounds which contain four organic radicals attached directly to the nitrogen are characterized by the disadvantages, inter alia (1) the amine complexes are relatively difficult to form with alkyl halides and require a substantial time for complete reaction; (2) the amine complexes obviously are prepared by starting with tertiary amines but not with primary and secondary amines, which increases their cost and limits the number of compounds in the series.

Accordingly, it is a general object of the present invention to provide an entirely new series of quaternary ammonium compounds which can be prepared with both primary and secondary as well as tertiary amines.

It is another object to provide a new series of quaternary ammonium compounds which show an increased stability, a wide range of solubility in water and organic solvents and improved surface active characteristics.

According to the present invention, there is provided a new series of compounds by condensing an amine (containing trivalent nitrogen) with a halide of a tetravalent element of group IV of the periodic system, to produce a complex salt (a quaternary ammonium compound) in which the nitrogen is pentavalent and is linked directly to the element. When the amine is primary and aliphatic, it should contain at least eight carbon atoms in the straight chain, but if it is aromatic, alicyclic or heterocyclic, it may contain less than eight carbon atoms. The tetravalent element is one which forms normal covalent linkages with the halogens and which forms coordination complexes with trivalent nitrogen. In the complex amine thus formed, the nitrogen is pentavalent, that is, the nitrogen has one coordinate covalent

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linkage and three normal covalent linkages per nitrogen atom, at least one of which is common to the nitrogen and the tetravalent element. In the recent literature the term "quaternary ammonium compound" is used as a generic term to define a nitrogen compound which contains, for each nitrogen atom, four covalent linkages and one electrovalent linkage, the covalent linkages joining the nitrogen to one, two or three radicals other than hydrogen, such for example as to atoms or radicals, alkyl, aryl, aralkyl, alicyclic and heterocyclic radicals. Thus the radical containing the nitrogen constitutes a cationic radical which is joined to an anion through the electrovalent linkage. The complexes of the present invention may be considered an analogue of such quaternary ammonium compounds in which, however, the nitrogen is linked directly to a tetravalent element. The new compounds have the following general formula:

$$[(R_3N_n)ER'_{4-n}]\cdot nX$$

in which N represents pentavalent nitrogen; E represents a tetravalent element selected from the group consisting of silicon, titanium, germanium, zirconium, tin and lead; R represents at least one hydrocarbon radical and if aliphatic it contains at least eight carbon atoms, the remaining R's being selected from the group consisting of hydrogen, aliphatic, aromatic, alicyclic and heterocyclic radicals, or an amine radical, R' being selected from the group consisting of hydrogen, alkyl, aryl, aralkyl, alicyclic and heterocyclic radicals; X is any anion, and "*n*" is an integer from 1 to 4.

In the preparation of the new quaternary ammonium compounds, the initial amine (containing trivalent nitrogen) can be either an aliphatic, alicyclic, aromatic or heterocyclic amine, and either saturated or unsaturated, and either primary, secondary or tertiary. When the amine is aliphatic it should contain at least 8 carbon atoms. The lower aliphatic amines appear to form only simple addition products which are not invert soaps.

By way of illustrating but not by way of limitation, there will be given examples of the classes of amines suitable for use in the reaction:

(*a*) Primary amines as a class, such, for example, as octyl amine, lauryl amine, stearyl amine, oleyl amine, cyclohexylamine, benzyl amine, aniline, phenylene diamine, and their analogues and homologues, and the alkanolamines of this class.

(*b*) Secondary amines as a class, including in

this definition the heterocyclic nitrogen compounds which have a secondary amine structure such, for example, as di-octyl, dicetyl amine, dilauryl amine, dodecylmethyl amine, dicyclohexyl amine, methyl aniline, also piperidine, morpholine, and the like, and the alkanolamines of this class.

(c) Tertiary amines as a class, such for example as tripropyl amine, dimethyl benzyl amine, trilauryl amine, pyridine, dimethyl lauryl amine, dimethyl aniline, methyl dicyclohexyl amine, quinoline, 8-hydroxyl quinoline, glyceryl diethylamine, cyclohexyldiethylamine, and the alkanolamines and acid amines of this class and the analogues and homologues.

The invention also contemplates the use of compounds containing more than one trivalent nitrogen, such as diamines and triamines as a class, such for example, as trimethylene diamine, hexamethylene diamine, melamine, cyclohexyl triamine and the like.

In the preferred embodiment of the invention, at least one of the R hydrocarbon radicals attached to the nitrogen atom or one of the R' hydrocarbon radicals attached to the metal is an aliphatic hydrocarbon radical of the fatty series, that is an aliphatic chain having twelve or more carbon atoms, because the new quaternary compounds containing such two long chain groups are characterized by superior detergent and germicidal properties.

Halides used in the reaction

In general, any fluoride, chloride, bromide or iodide of one of the tetravalent elements selected from the class consisting of silicon, titanium, germanium, zirconium, tin and lead and mixtures of these salts may be used as the other reagent in the formation of the quaternary compound. Further, when the halide contains less than 4 halogen atoms, the remaining valences can be occupied by hydrogen or organic radicals selected from the class consisting of alkyl, aryl, aralkyl, alicyclic and heterocyclic radicals. Thus, the halides of the tetravalent elements have the following general formula:

$$R'_{4-n}EX_n$$

in which X is halogen and R' is hydrogen or an organic radical, in which "*n*" is an integer from 1 to 4. Of the various halides, it is preferred to employ the halides of silicon, including the organo-silicon halides containing an organic radical in which carbon is directly linked to silicon, because these reagents produce quaternary ammonium compounds characterized by superior stability and greater availability. Of the various halogens, it is preferred to employ the chlorides because of their cheapness, non-corrosiveness and availability, combined with their high reactivity. By way of illustration but not by way of limiting the invention, there will be given the following examples of specific halides useful in the reaction: silicon tetrafluoride, silicon tetrabromide, silicon tetrachloride, methyltrichlorosilane, diethyldichlorosilane, triphenylmonochlorosilane, trimethylmonochlorosilane, monocyclohexyltrifluorosilane, benzylmethyldifluorosilane. The corresponding halides of titanium, germanium, zirconium, tin and lead may be employed.

Carrying out the reaction

With halides of tetravalent elements there may be employed from one to four mols of the amine depending upon the number of halogen atoms initially attached to the tetravalent elements. In general, reaction is effected by mixing the amine and the halide, but preferably in a common inert solvent, such, for example, as benzene, acetone, carbontetrachloride, xylene, toluene, and the like; in some cases, however, as with solid reagents, the reagents may be melted or dissolved in a common solvent with or without subjecting the mixture to heat and pressure to bring about the condensation to form the quaternary compounds. The temperatures employed can be up to the boiling point of the lowest boiling fraction when the reaction is carried out in an open vessel or under reflux, but higher temperatures can be employed when a closed reaction vessel is used. By use of pressure, reaction can be effected at temperatures which are below the thermal decomposition temperatures of the reaction mixture or of the product. The condensation reaction appears to occur according to the following general equation:

$$nR_3N + R'_{4-n}EX_n \rightarrow [(R_3N)_nER'_{4-n}] \cdot nX$$

Specific examples

By way of illustration, but not by way of limiting the invention, the following specific examples will be given:

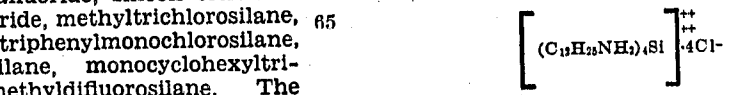
1. To 117.3 g. (0.4 mol) of 9-octadecenyl-dimethylamine dissolved in 200 cc. of acetone, there was added, in small portions with frequent stirring, 31.4 g. (0.2) mol of diethyldichlorosilane. An immediate exothermic reaction takes place. In about 3 minutes after all the silane had been added the entire mass caked. The product was then recrystallized from acetone. The yield was practically quantitative. The product is believed to have the following formula:



2. To 84.48 g. (0.4 mol) of lauryldimethylamine dissolved in 200 cc. of benzene there was added, slowly with stirring, 17 grams (0.1 mol) of silicon tetrachloride. The product precipitated almost immediately from the solvent. The benzene was evaporated in a hood without heat. The product was dried by standing overnight. The yield was practically quantitative. The product is believed to have the following formula:

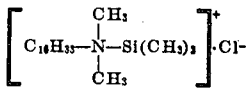


3. To 74.0 g. (0.4 mol) of dodecylamine dissolved in 200 cc. of benzene there was added, slowly with stirring, 17 g. (0.1 mol) of $SiCl_4$. A rapid, exothermic reaction took place with the formation of a precipitate. The product was evaporated to dryness in a hood, without heat. The yield was practically quantitative. The product is believed to have the following formula:

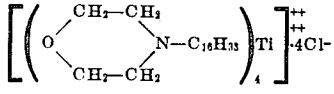


4. To 106.8 g. (0.4 mol) of cetyldimethylamine dissolved in 250 cc. of benzene was added slowly, with stirring, 43.4 g. (0.4 mol) of trimethylchlorosilane. The reaction proceeded rapidly and some precipitate formed. The benzene was evaporated off in the hood, without heat, and the product recrystallized from acetone. The yield was prac-

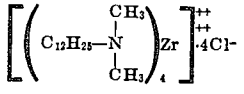
tically quantitative. The product is believed to have the following formula:



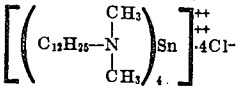
5. To a solution of 24 g. (0.08 mol) of N-cetylmorpholine in 100 cc. of toluene, was added 3.8 g. (0.02 mol) of titanium tetrachloride ($TiCl_4$). The solution gradually turned red in color and some heat was evolved when mixing occurred. The solution was heated to about 90° C. and poured into an evaporating dish. The toluene was evaporated in the hood, without further heating, leaving a practically quantitative yield of waxy crystals of the quaternary ammonium compound. The crystals are pink in color as obtained, but white when pure. These crystals dissolve in water and the resulting solution foams to a considerable degree when agitated. The product is believed to have the following formula:



6. To 9.8 g. (0.04 mol+1.3 g. excess) of lauryldimethylamine dissolved in 25 cc. of benzene, there was added slowly, with frequent shaking, 2.3 g. (0.01 mol) of zirconium tetrachloride (C. P.). The halide rapidly reacted and the solution became warm. The solution was shaken occasionally over a period of ten minutes and then poured onto a plate and allowed to evaporate in the hood. Fatty crystals were obtained. A small portion added to about 5 cc. of water in a test tube partially dissolved and soaped when agitated. The solubility appears to be low. The addition of methyl alcohol does not enhance solubility to any appreciable extent. The yield of the zirconium invert soap was practically equal to the theoretical yield. The product is believed to have the following formula:



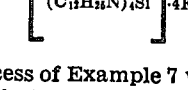
7. To 9.8 g. (0.04 mol+1.3 g. excess) of lauryldimethyl amine there was added 25 cc. of benzene. To this solution was slowly added 2.6 g. of anhydrous stannic chloride ($SnCl_4$) with occasional shaking. The reaction took place rapidly and heat was generated. The solution was shaken occasionally for 5–10 minutes, and then poured onto a flat plate and the benzene evaporated in the hood. Crystals with a pale brown tint were obtained. The crystals, waxy or fatty-like, were broken up and left to dry. Yield was 11.1 g. The product is believed to have the following formula:



8. To 14.5 g. (0.1 mol) of 8-hydroxyquinoline in 100 cc. of benzene was added slowly, with good mixing, 10.9 g. (0.1 mol) of trimethylchlorosilane. A greenish-yellow solid precipitated immediately. The product was poured onto a flat plate and dried in the hood. The yield was practically quantitative. The product is believed to have the structure:

$$[HOC_9H_6N—Si(CH_3)_3]^+ \cdot Cl$$

9. 74 grams (0.4 mol) of laurylamine were dissolved in 500 cc. of acetone. While this solution was stirred, silicon tetrafluoride vapor was passed over the surface. An immediate clouding of the solution occurred, followed, in about 5 minutes, by a white precipitate, which increased rapidly in quantity as the reaction progressed. The solvent was evaporated and the white solid recrystallized from acetone. The yield was practically quantitative. The product is believed to have the following formula:



10. The process of Example 7 was repeated with the exception that a mol equivalent of germanium tetrachloride was substituted for the tin tetrachloride. A similar reaction took place and the corresponding invert soap of germanium was produced in a substantially quantitative yield.

11. The process of Example 7 was repeated with the exception that a mol equivalent of lead tetrafluoride was substituted for the tin tetrachloride. A similar reaction took place and the corresponding invert soap of lead was produced in a substantially quantitative yield.

12. 0.6 mol of cetyl dimethyl amine was dissolved in 75 cc. of acetone and there was then added to the solution, while cooling the solution 0.3 mol of diethyl difluoro silane. An exothermic reaction occurred. The resulting solution was evaporated to dryness and there was obtained a substantially quantitative yield of an invert silicon soap. This product, when dispersed in water, produced a marked lowering of the surface tension and also exhibited good wetting and emulsifying properties.

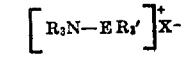
In the above examples it must be understood that instead of using chlorine or fluorine, other halides may be employed with similar results. Further, it should be understood that while most of the examples show the step of dissolving the amine in a solvent, such as acetone or benzene, such solvents are merely used by way of example and that the amine may be dissolved in any of its solvents. On the other hand, when the amine is itself liquid, the use of an inert solvent is unnecessary, since the halide of the group IV element can be added directly to the liquid amine. It is also possible to carry out the reaction in the gas phase by vaporizing both the amine and the halide.

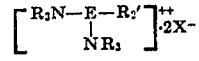
Variations

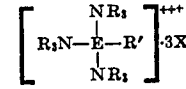
In the general formula, column 2, line 21, any or all R's may be a radical which contains an amino group either in the chain or in a heterocyclic ring. These nitrogen atoms may be a part of a primary, secondary or tertiary amino group. If these groups are primary or secondary, then further quaternization may be caused by any of the halogen derivatives of elements of group IV, or by inorganic acids. If, however, the amino group is tertiary, then alkyl halides as well may be used to form the complex salts. Such a case would alter the total electrostatic charge on the complex cation. Thus, there are a large number of combinations possible by using R' radicals which themselves contain trivalent nitrogen atoms (amino radical). These other nitrogen atoms may or may not be united to a long chain hydrocarbon radical (of the higher fatty series). Therefore, the ratio of the number of charges on the cation to the number of long chain radicals, can be considerably varied.

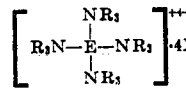
By way of illustrating but not by way of limiting the invention, the various general formulas

will be given of different classes of quaternary ammonium compounds, which can be produced according to the present invention.

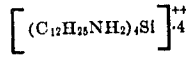
(1) 

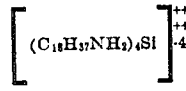
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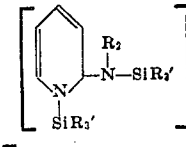
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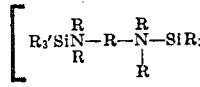
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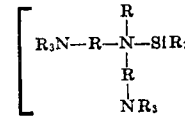
The above series of compounds, numbered 1 to 4, will illustrate the feature that by increasing the number of pentavalent nitrogen radicals in the cation, the number of charges on this ion may be increased by integers from 1 to 4.

(5) 

(6) 

(7) 

(8) 

(9) 

The compounds designated 7, 8, and 9 illustrate compounds capable of being formed from di- and triamines. In this connection, it should be noted that the nitrogen may be in a straight chain on an aromatic ring or in a heterocyclic ring. Where there is more than one nitrogen atom present, it is to be understood that a tetravalent element such as silicon may be united directly to one or more of these additional nitrogen atoms. In all the above formulas, it is to be

understood that any of the tetravalent elements may be substituted for silicon, and likewise chlorine may be substituted by any anion such as another halogen, SO_4CH_3, NO_3, SO_4, PO_4, OH, acetate and lactate and the like. It is also to be understood that in the above formulas the hydrocarbon radical designated by R or R′ may be the same or different, and that the number of long chain fatty hydrocarbon radicals may also be varied, as desired.

Characteristics and properties

The new compounds provided by the present invention are characterized by being, in general, viscous liquids, or solids. They normally exhibit an appreciable water solubility, but the solubility will depend in part upon the nature and chain length of the hydrocarbon radicals.

The products are also soluble in a wide variety of organic solvents. A valuable feature is the fact that the compounds are generally soluble in warm acetone, benzene, ethyl acetate and ethyl alcohol, but are insoluble in these solvents at room temperature. This permits purification by re-crystallization from such solvents.

In order to illustrate some of the technologically important characteristics, the following table will be given:

Table

No.	Quaternary Ammonium Compound formed by Condensing Silicon Compounds	Amine	Surface Tension Lowering of Water at 20° C. 1% solution	Phenol Co-efficient at 20° C.
1	$(CH_3)_3SiCl$	Lauryl Morpholine	38.1	30
2	$C_2H_5SiCl_3$	do	43.5	1
3	$SiCl_4$	do	43.3	20
4	$(C_2H_5)_2SiCl_2$	do	48.2	10
5	$SiCl_4$	Dodecyl amine	40.4	25
6	$SiCl_4$	Mixt. of chemically pure octadecenyl, hexadecyl and octadecadienyl amines.[1]	31.0	200
7	$SiCl_4$	Octadecyl amine	38.4	100
8	$SiCl_4$	Coconut oil amines	30.0	200
	Water		72.8	
Control:	Alkyldimethylbenzyl ammonium chloride			180

[1] Chemically pure amines corresponding in alkyl chain links to the fatty acids normally obtained from coconut oil and containing more than 98% of a mono-amine having an average molecular weight of 200.

Referring to the above table, it will be noted that the surface tension lowering of water even in .1% solution is very marked. It is the unique properties of these compounds which make them useful as wetting, dispersing and emulsifying agents, as well as increases their efficiency in bacteriologic, pharmacopedic, and therapeutic uses.

The above table also demonstrates that as compared to a well known quaternary ammonium compound, the phenol coefficients of the present series increase with the number and lengths of the fatty acid chains. The phenol coefficient tests were conducted by the standard Dunn method, using *Eberthella typhii*. As pointed out above, the present compounds have many applications in the fields of bacteriology, pharmacology, and therapeutics of which a few may be mentioned, merely by way of example. Since the compounds themselves are highly germicidal in high dilutions, they are especially adapted for use as a general antiseptic and germicide, for use on the human skin, wearing apparel, leather; for the disinfection of surgical instruments, drinking vessels, milk dispensing equipment; for

deodorizing and for retarding and preventing putrefaction of organic material; for control of slime and algae in swimming pools, water storage tanks, aqueous treating baths and paper manufacture. In the paper industry, these products may be used as penetrants in the liquors used for cooking rags and pulp, and as assistants in paper softening, filling, and processes to increase absorbency, also for the control of slime in foul water and lowering the bacteria count in the finished products. They are also adapted for control of athlete's foot and other fungus diseases, for sterilization of the skin preparatory to surgery; for the disinfection of wounds, burns, and mucous membranes. In these latter uses, the compounds are preferably employed in combination with aqueous solutions of alcohol and acetone, as a tincture and finally for the prevention of rust on metal articles. In addition, when mixed with common germicides these compounds increase the efficiency of the former.

A few representative uses of these new products as textile assistants will be mentioned. They may be used alone or in combination with suitable detergents for cleansing and scouring vegetable and animal fibers. When added to flax retting baths, they function as wetting and penetrating agents. They may be employed as assistants in fulling and felting processes. They may be used in sizing preparations in combination with the usual materials such as starches or gelatine or their equivalents and as the penetrating agents for removing sizing from textile materials. They improve the absorption capability of fibrous materials when such materials are subjected to treatments for creaseproofing, finishing, softening, stiffening, coloring, impregnating, waterproofing, and mildewproofing. They may be used for lustering or delustering fabrics and to oil or lubricate textile materials and as assistants in processes of weighting or loading fabrics. They may be used as assistants in silk degumming liquors.

The products may be employed alone or together with protective colloids, such as glue, or albuminous degradation products. They are especially suitable for washing and cleansing textile and like materials, for the emulsification of substances which are insoluble in water, as for example oils, fats and waxes, resins, cellulose esters and ethers, and as wetting agents. The products may also frequently be employed as softening agents for textiles. The addition of the products to dyebaths causes a good wetting of the goods to be dyed and also frequently an improvement in the levelness and fastnesses.

Another important class of uses of these new compositions is as assistants in the preparation and application of dyestuffs. They may be used in the preparation of dyestuffs in readily dispersible form and for the production of inorganic pigments or pigments of dyes in a finely divided condition. As penetrants and wetting agents, they assist in producing level dyeings. In printing pastes they assist in the dispersion of the dye or dye component and facilitate its penetration into natural or synthetic fibers.

In the leather industry, these compositions function as useful wettings agents in soaking, deliming, bating, tanning, and dyeing baths and in printing. They are useful in softening and treating baths for hides, furs and skins, particularly in baths used for fat-liquoring leather, and dyeing. Solutions of these compounds are useful for pretreating leather prior to dyeing.

The dispersing and emulsifying powers of these new compositions give rise to many interesting uses. They may be utilized for converting liquid or solid substances normally insoluble in water, such as hydrocarbons, higher alcohols, pitches, and pitchy substances, and synthetic resins into stable emulsions or dispersions. They are useful in preparing emulsions of wax and wax-like compositions which are used as leather dressings or floor polishes. They may be used to prepare artificial dispersions of crude, vulcanized, or reclaimed rubber. They may be used as emulsifiers in the manufacture of cosmetic preparations such as cold creams and lip sticks, shampoos and shaving creams. They may be employed for preparing emulsions of the water-in-oil type such as emulsions of water in such organic solvents as are used in the dry cleaning industry.

These compositions may be used for enhancing the spreading and penetrating power of parasiticides. They may be employed in agricultural sprays alone and in combination with the ordinary insecticides and fungicides and germicides. They are useful for promoting the penetrating power of wood preservatives.

These compositions may be employed as detergents in several different relations. They may be used in the washing of fruits and vegetables for spray residue removal. They may be used in combination with metal cleaning compounds in neutral or acid liquors. They may be used for paint, varnish, and lacquer cleaners. They may advantageously be employed as cleansing agents in hard water and where a fatty or oily film resists the ordinary cleansing media. They may be used as soaps in hard water baths, since these compositions do not form precipitates so readily in hard waters as soaps and Turkey red oils.

These compositions may be used as aids in various chemical reactions. They may be used to control particle size and shape during precipitation or crystallization of compounds from reaction mixtures.

These compositions also have several miscellaneous uses. They may be employed as foam stabilizing agents, especially for use in air-foam fire extinguishing compositions. They may be used to stabilize rubber latex. They may also be used as frothing and collecting agents in ore flotation processes, and in other processes such as the recovery of fixed oil from the oil sands. These compounds may be used in tooth paste and in non-spattering margarines.

These compounds may be employed as emulsifying agents for the preparation of artificial latices containing synthetic rubber, in view of their capillary active polymerization of polymerizable compounds, such as chloroprene.

Having described our invention, what we claim as new and desire to secure by Letters Patent is:

1. The quaternary ammonium compounds having the generic formula:

$$[(R_3N)_nER'_{4-n}]\cdot nX$$

in which at least one R attached to each nitrogen atom is an aliphatic hydrocarbon radical selected from the group consisting of alkyl, alkenyl and dialkenyl radicals, having at least 8 carbon atoms in the longest chain thereof, the remaining R's, if any, being selected from the group consisting of hydrogen and alkyl, monocyclic aromatic, cycloalkyl, phenylalkyl, cycloalkyl hetero-N, and cycloalkyl hetero-N-O radicals, E is a tetravalent element selected from the group consisting of silicon, titanium, germanium, zir-

onium, tin, and lead, R' is at least one substituent selected from the group consisting of hydrogen and alkyl, monocyclic aromatic, cycloalkyl, and phenylalkyl radicals, X is at least one substituent selected from the group consisting of halogen atoms and the acetate and lactate radicals and n is an integer from 1 to 4.

2. The process for the preparation of quaternary ammonium compounds which comprises reacting to form an addition product from 1 to 4 mols of an amine having attached to a trivalent nitrogen atom at least 1 aliphatic hydrocarbon radical selected from the group consisting of alkyl, alkenyl and dialkenyl radicals having at least 8 carbon atoms in the longest carbon chain thereof, the remaining valences of the nitrogen atom, if any, being attached to a substituent selected from the group consisting of hydrogen and alkyl monocyclic aromatic, cycloalkyl, phenylalkyl, cycloalkyl hetero-N, and cycloalkyl hetero-N-O radicals, with a mol of a compound having the generic formula EX_n, in which E is a tetravalent element selected from the group consisting of silicon, titanium, germanium, zirconium, tin and lead, X is a halogen atom and n is an integer from 1 to 4, the remainder of the 4 valences of the tetravalent elements, if any, being occupied by at least one substituent selected from the group consisting of hydrogen and alkyl, monocyclic aromatic, cycloalkyl and phenylalkyl radicals.

3. The process of claim 2 in which the amine is a straight-chain alkyl, primary monoamine.

4. The process of claim 2 in which E is silicon.

5. The process of claim 2 in which X is chlorine.

6. A quaternary ammonium compound having the generic formula

$$[(R_3N)_nER'_{4-n}]\cdot nX$$

in which one R attached to each nitrogen atom is an alkyl radical having at least eight carbon atoms, the remaining R's being hydrogen atoms,

E is silicon, R' is an alkyl radical, X is a halogen atom, and n is an integer from 1 to 4.

7. The compounds of claim 6 in which X is chlorine.

8. The compounds of claim 7 in which n is two.

9. The compounds of claim 7 in which n is three.

10. The compounds of claim 7 in which n is four.

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