

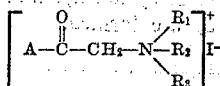
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QUATERNARY AMMONIUM IODIDES

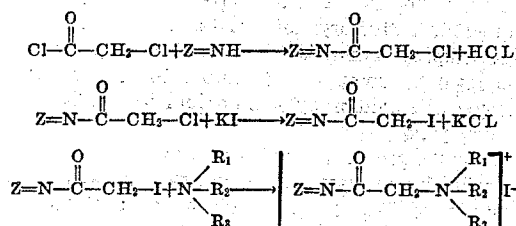
No Drawing. Filed Oct. 21, 1960, Ser. No. 63,972

8 Claims. (Cl. 260—347.3)

The compounds of this invention are characterized by the following structural formula,



All of the new compounds are quaternary ammonium iodides, which can be synthesized from alpha-chloroacetyl chloride by first reacting it with a primary or secondary amine containing an organic cyclic nucleus and thereafter replacing the alpha-chlorine atom with an iodine atom by digesting the product with a water-soluble salt of hydro-iodic acid, for example, potassium iodide. The resulting iodoacetamide is then condensed with a tertiary alkyl amine. These reactions may be represented by the following structural equations:



Representative examples of the novel quaternary ammonium iodides of this invention include the following:

(Cyclohexylmethylcarbamoylmethyl) trimethyl ammonium iodide

N-methyldiethyl (thenylcarbamoylmethyl) ammonium iodide
 N-methyldiethyl (3-propyl-2-furylcarbamoylmethyl) ammonium iodide
 N-methyldiethyl (N-ethylthienylcarbamoylmethyl) ammonium iodide

The first step, i.e., the reaction of alpha-chloroacetyl chloride with the amine containing the cyclic nucleus, is carried out by combining stoichiometric equivalent amounts of the two reactants, preferably at reduced temperatures, e.g., under refrigerated conditions so as to prevent an excessive rate of reaction and in the presence of a stoichiometric amount of sodium hydroxide. It is usually desirable to carry out the reaction in the presence of a suitable solvent, such as ethylene dichloride, from which the solid material may be crystallized. If desired, the composition may be recrystallized from the same or other solvents.

The second reaction involves the reaction at reflux temperatures of the composition obtained above with a water-soluble salt of hydro-iodic acid in the presence of a suitable solvent, such as acetone. When the reaction is complete, the mixture is cooled to room temperature and the N-cyclic alpha-iodoacetamide is recovered by filtration and drying. If desired, the composition may be recrystallized from suitable solvents.

The final reaction involves the addition of the desired tertiary amine to the N-cyclic alpha-iodoacetamide in the presence of a suitable solvent, such as benzene. Although the reaction proceeds at room temperature, it may be desirable to warm the reaction mixture to temperatures of from about 30° C. to about 100° C. to accelerate the reaction. When the reaction is complete, the solvent is removed by distillation. If desired, the product may be further purified by recrystallizing it from a suitable solvent, such as an ethyl acetate-ethanol mixture.

The following examples are offered in illustration of the invention, but are not to be considered a limitation thereof.

Example I.—Triethyl (N-furfurylcarbamoylmethyl) ammonium iodide

To a suitable reaction vessel is charged 39 g. of furfurylamine, 120 ml. of 20 percent sodium hydroxide solution, and 150 ml. of ethylene dichloride and the mixture is cooled to -10° C.; 67.2 g. of chloroacetyl chloride is added over a period of one hour and the mixture is stirred for 30 minutes. The organic phase is then separated and washed with water, 5% sodium bicarbonate solution and water, and dried over anhydrous magnesium sulfate. The ethylene dichloride is removed by vacuum distillation and the resulting product is recrystallized twice from a mixture of water and methanol and once from a benzene solution. The alpha-chloro-N-(2-furfuryl)acetamide so obtained is then refluxed with 33.2 g. of potassium iodide in 300 ml. of dry acetone for 3 hours. The mixture is then cooled to room temperature, filtered, and washed with dry acetone. The solvent is removed by evaporation and there remains 47.5 g. of crude iodoacetamide. The crude iodoacetamide is recrystallized from a mixture of 150 ml. Skellysolve B and 75 ml. of ethanol, and 39 g. of the intermediate compound, N-furfuryl-alpha-iodoacetamide, are obtained.

The N-furfuryl-alpha-iodoacetamide is then added to 100 ml. of dry benzene, and 24.4 g. of triethylamine in 30 ml. of dry benzene are added over a period of 10 minutes. The mixture is heated at 60–65° C. for 4 hours and then distilled to remove the benzene. The crude solid residue thus obtained is then recrystallized from an ethyl acetate-ethanol mixture to yield 35 g. of triethyl (N-furfurylcarbamoylmethyl) ammonium iodide, M.P. 142–144° C.

Analysis.—Calculated: 34.66% I. Found: 34.40% I.

Example II.—Tributyl (p-methoxyphenylcarbamoylmethyl) ammonium iodide

The procedure of Example I is repeated, except an equimolar amount of p-methoxyaniline is substituted for furfurylamine and an equimolar amount of tributyl amine is substituted for the triethylamine. The resulting compound, tributyl (p-methoxyphenylcarbamoylmethyl) ammonium iodide, has a melting point of 100–101° C.

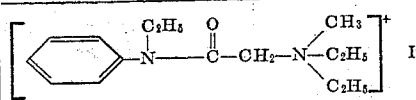
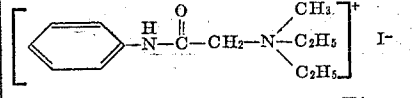
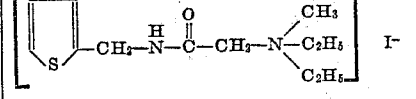
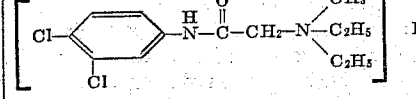
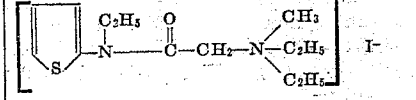
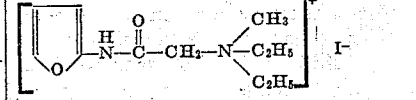
Analysis.—Calculated: 26.64% I. Found: 26.40% I.

Example III.—(Cyclohexylcarbamoylmethyl) methyldiethyl ammonium iodide

The procedure of Example I is repeated, except that an equimolar amount of cyclohexylamine is substituted for the furfurylamine and an equimolar amount of N-methyldiethylamine is substituted for the triethylamine. The resulting compound, (cyclohexylcarbamoylmethyl) methyldiethyl ammonium iodide, has a melting point of 74–76° C.

Analysis.—Calculated: 35.8% I. Found: 35.3% I.

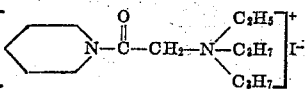
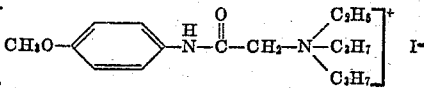
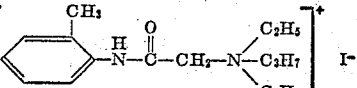
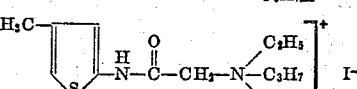
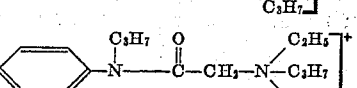
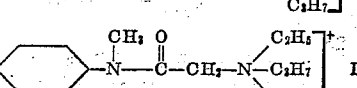
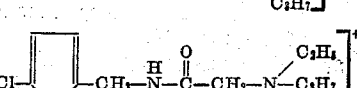
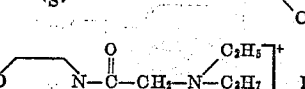
Using the procedure of the preceding example, except by utilizing the following primary and secondary amines (column 1) in place of cyclohexylamine, analogous compounds (column 2) are formed.

Column 1	Column 2
N-ethylaniline.....	
aniline.....	
thenylamine.....	
3,4-dichloroaniline.....	
N-ethylthienylamine.....	
furfurylamine.....	

Example IV.—(3-chloro-2-furfurylcarbamoylmethyl) ethyldipropyl ammonium iodide

The procedure of Example I is repeated, except that an equimolar amount of 3-chloro-2-furfurylamine is substituted for the furfurylamine and an equimolar amount of N-ethyldipropylamine is substituted for the triethylamine. The resulting compound (3-chloro-2-furfurylcarbamoylmethyl) N-ethyldipropyl ammonium iodide, is obtained in good yield.

Using the procedure of Example IV, except by utilizing the following primary and secondary amines (column 1) in place of 3-chloro-2-furfurylamine, analogous compounds (column 2) are formed.

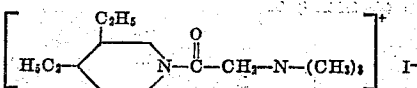
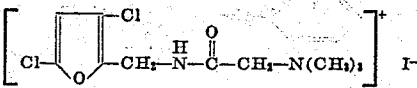
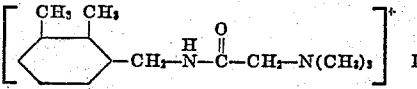
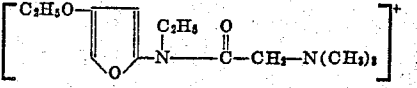
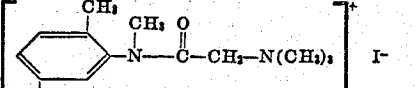
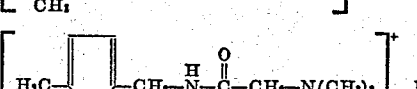
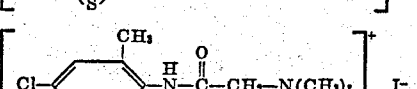
Column 1	Column 2
piperidine.....	
p-methoxyaniline.....	
o-toluidine.....	
4-methyl-2-thienylamine.....	
N-propylaniline.....	
N-methylcyclohexylamine.....	
5-chloro-2-thienylamine.....	
morpholine.....	

Example V.—Trimethyl (thienylcarbamoylmethyl) ammonium iodide

The procedure of Example I is repeated, except that an equimolar amount of thienylamine is substituted for the furfurylamine and an equimolar amount of trimethylamine is substituted for the triethylamine. The resulting

compound, trimethyl (thienylcarbamoylmethyl) ammonium iodide, is obtained in good yield.

Using the procedure of the preceding example, except by utilizing the following primary and secondary amines (column 1) in place of thienylamine, analogous compounds (column 2) are formed.

Column 1	Column 2
3,4-diethylpiperidine.....	
3,5-dichloro-2-furfurylamine.....	
2,3-dimethylcyclohexylmeth- ylamine.	
N-ethyl-4-ethoxy-2-furyl- amine.	
N-methyl-2,5-dimethylaniline.	
5-methyl-2-thienylamine.....	
2-methyl-4-chloroaniline.....	

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The new compounds have biological toxicity and may be used as bacteriostats and as antiseptic agents. Since they are water-soluble and ionize in contact with water, they are useful cationic emulsion stabilizers especially effective in preserving in aqueous suspension substances subject to bacterial attack. The compounds are also useful in precipitating solids from aqueous colloids, for example, paper pulp, and especially in preventing discoloration by fungal action.

The utility of the compounds of this invention in defoliating plants is effectively demonstrated by the data in the following table wherein the activity of triethyl (2,6-dimethylphenylcarbamoylmethyl) ammonium iodide is compared with its chloride and bromide analogs. The experiments were conducted by spraying bean plants with solutions containing varying concentrations of the compounds such that the concentration data is convertible directly into the indicated pounds per acre rating.

TABLE A
Defoliation (Percent)

Compound	9 lbs./acre	4 lbs./acre	11 lbs./acre
triethyl-2,6-dimethyl phenyl-carbamoylmethyl ammonium iodide	Percent 100	Percent 51-75	Percent 26-50
triethyl-2,6-dimethyl phenyl-carbamoylmethyl ammonium bromide	0	—	—
triethyl-2,6-dimethyl phenyl-carbamoylmethyl ammonium chloride	0	—	—

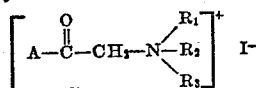
NOTE.—The dash mark indicates that this compound was not tested at the indicated rate.

The foregoing data effectively demonstrates the unique defoliant activity of the quaternary ammonium iodides of this invention.

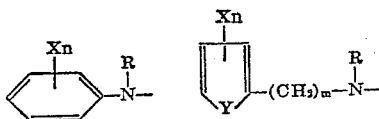
This application is a continuation-in-part of application Serial No. 597,077, filed July 11, 1956, now abandoned.

What is claimed is:

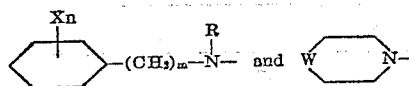
1. A quaternary ammonium compound of the formula



wherein R_1 , R_2 , and R_3 are alkyl radicals containing from 1 to 4 carbon atoms; A is a radical selected from the group consisting of

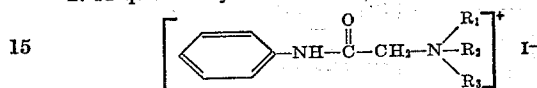


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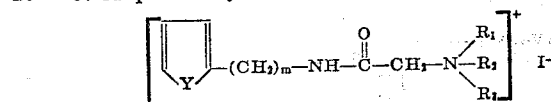
wherein R is selected from the group consisting of hydrogen and lower alkyl, X is selected from the group consisting of Cl, Br, I and of alkyl and alkoxy radicals containing from 1 to 4 carbon atoms, Y is a divalent chalcogen atom having an atomic weight of less than 33, W is selected from the group consisting of $-\text{O}-$, $-\text{S}-$, and $-\text{CH}_2-$; m is an integer of from 0 to 1 and n is an integer of from 0 to 3.

2. A quaternary ammonium compound of the formula



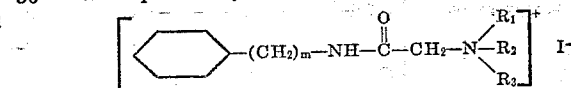
wherein R_1 , R_2 , and R_3 are alkyl radicals containing from 1 to 4 carbon atoms.

3. A quaternary ammonium compound of the formula



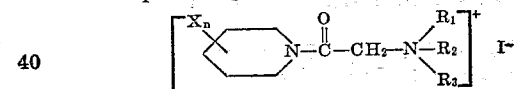
wherein R_1 , R_2 , and R_3 are alkyl radicals containing from 1 to 4 carbon atoms, m is an integer of from 0 to 1, and Y is a divalent chalcogen atom having an atomic weight of less than 33.

4. A quaternary ammonium compound of the formula



wherein R_1 , R_2 , and R_3 are alkyl radicals containing from 1 to 4 carbon atoms and m is an integer of from 0 to 1.

5. A quaternary ammonium compound of the formula



wherein n is an integer of from 0 to 3 and X, R_1 , R_2 , and R_3 are alkyl radicals having from 1 to 4 carbon atoms.

6. Triethyl (N-furfurylcarbamoylmethyl) ammonium iodide.

7. Tributyl (p-methoxyphenylcarbamoylmethyl) ammonium iodide.

8. (Cyclohexylcarbamoylmethyl) methyldiethyl ammonium iodide.

No references cited.