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UNITED STATES PATENT OFFICE

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ORGANIC PHOSPHATE ESTERS AND METHODS OF PREPARATION

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13 Claims. (Cl. 260—461)

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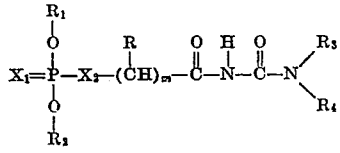
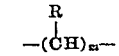
The present invention relates to new and useful organic phosphate compounds and methods of preparation thereof.

These new compounds are phosphate esters which conform to the general formula



wherein X_1 and X_2 are members of the group consisting of sulfur and oxygen, R is a member of the group consisting of hydrogen and an alkyl radical, R_1 and R_2 are members of the group consisting of alkyl, aralkyl and aryl radicals, (in this specification and claims where the words aralkyl and aryl are used, they are intended to mean aralkyl hydrocarbon and aryl hydrocarbon respectively) R_3 and R_4 are members of the group consisting of hydrogen, alkyl and aryl radicals, and m represents a small whole number. In the specification and claims where the symbol group

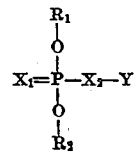


occurs, it is to be understood that the R is also subject to the subscript m.

In the new compounds R_1 and R_2 may be the same or different radicals. Furthermore, it is to be understood that when R_1 and R_2 stand for alkyl radicals, they represent both the straight chain and branch chain, the saturated and unsaturated, and the cycloaliphatic hydrocarbon radicals. The R_1 and R_2 radicals may also carry halogen substituents, particularly chlorine and bromine. Typical examples of these radicals are methyl, ethyl, n-propyl, isopropyl, isobutyl, sec.-amyl, n-hexyl, 2-ethylhexyl, n-octyl, n-decyl, n-dodecyl, oleyl, cetyl, ceryl, allyl, bromomethyl, 2-chloroethyl, cyclohexyl, benzyl, phenyl, p-chlorophenyl, o-, m-, and p-nitrophenyl.

The compounds of this invention possess general pest-control characteristics, including insecticidal, rodenticidal, and fungicidal properties. They may also be employed as corrosion inhibitors, plasticizers, flotation agents, and petroleum additives.

The phosphate esters of the above general formula may be readily prepared by reacting a phosphate of the general formula



in which R_1, R_2, X_1, and X_2 have the meaning

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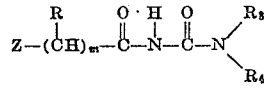
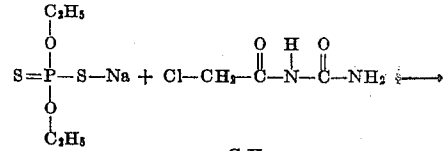
shown above, and Y represents an alkali-forming metal, with a haloacylurea of the general formula

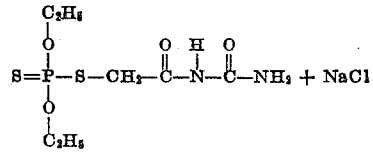


in which R, R_3, R_4, and m have the meaning shown above, and Z is a member of the group consisting of chlorine and bromine.

The term "alkali-forming metal" as used in this specification and in the appended claims is intended to cover the alkali metals (including ammonium), and the alkaline earth metals.

A typical reaction in which sodium O,O-diethyl dithiophosphate is reacted with chloroacetylurea to produce O,O-diethyl mercaptoacetylurea dithiophosphate may be illustrated as follows:





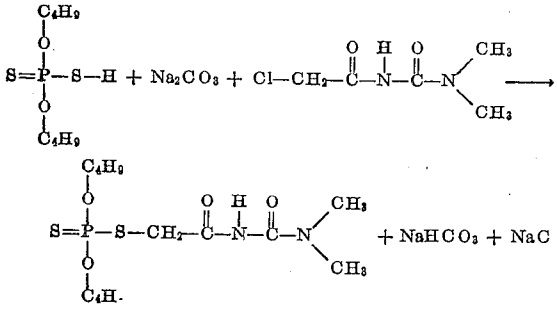
High yields of the desired products are obtained by carrying out the reaction in the presence of a solvent. Such solvents include water, the low molecular weight aliphatic monohydric alcohols, the ketones such as, for example, acetone, methyl ethyl ketone, methyl isobutyl ketone, methyl benzyl ketone, cyclohexanone, acetophenone, and the like; aliphatic esters such as ethyl acetate. amyl acetate, 2-ethylhexyl acetate, methyl propionate, methyl butyrate, ethyl butyrate, and isopropyl butyrate; saturated aliphatic nitriles such as acetonitrile and propionitrile; dioxane, nitrobenzene, chlorobenzene, toluene, xylene, chloroform, carbon tetracholoride, 1,2-dimethoxyethane, and the trialkyl phosphates such as trimethyl phosphate, triethyl phosphate, and triisopropyl phosphate.

The reaction is preferably carried out at a temperature within the range of from about 20° to 150° C. However, temperatures outside of this range may be employed depending upon the type of reactants and solvents utilized.

An alternative method of preparing the above compounds consists in employing in lieu of the alkali-forming metal phosphate the corresponding acid and a basic alkali-forming metal compound, the latter having sufficient alkalinity to neutralize said acid. Obviously, this procedure

avoids the initial preparation and isolation of the alkali-forming metal phosphate. Such basic alkali-forming metal compounds include sodium carbonate, potassium carbonate, barium carbonate, magnesium carbonate, lithium carbonate, sodium hydroxide, potassium hydroxide, calcium hydroxide, strontium hydroxide, magnesium hydroxide, sodium hydrosulfide, sodium borate, tripotassium arsenate, tripotassium arsenite, sodium pyrophosphate, magnesium pyrophosphate, potassium pyrophosphate, barium phosphate, trisodium phosphate, and the like.

Employing the above procedure in the preparation of O,O-di-n-butyl 1-mercaptoacetyl-3,3-dimethylurea dithiophosphate, the reaction may be illustrated as follows:



The haloacylureas utilized in the preparation of the compounds of the present invention are known compounds prepared by well-known methods, for example, chloroacetylurea is produced by reacting chloroacetyl chloride with urea.

The following examples in which the parts are by weight further illustrate the invention.

Example 1

50 parts of O,O-diethyl dithiophosphoric acid (93%) were added slowly to a well-agitated mixture of 26.5 parts of anhydrous sodium carbonate suspended in 100 parts of methyl isobutyl ketone. The temperature of the mixture rose spontaneously to about 40° C. 34.1 parts of chloroacetylurea were added slowly and the resulting mixture was maintained at 60°–65° C. with continued stirring for a period of 6 hours. The warm reaction mixture was filtered through a sintered glass funnel. The filtrate was heated under vacuum to distill off the methyl isobutyl ketone, and the resulting solid was recrystallized from carbon tetrachloride. The product, O,O-diethyl mercaptoacetylurea dithiophosphate, was a colorless crystalline material melting at 93°–95° C.

Example 2

The procedure of Example 1 was employed using 43.8 parts of O,O-dimethyl dithiophosphoric acid (90%), 26.5 parts of anhydrous sodium carbonate, 100 parts of methyl isobutyl ketone, and 34.1 parts of chloroacetylurea. The product, O,O-dimethyl mercaptoacetylurea dithiophosphate, after recrystallization from carbon tetrachloride was a colorless crystalline material melting at 117°–118° C.

Example 3

The procedure of Example 1 was employed using 40 parts of O,O-diethyl dithiophosphoric acid (93%), 21.2 parts of anhydrous sodium carbonate, 150 parts of methyl isobutyl ketone, and 44.6 parts of alpha-bromoisovalerylurea. The product, O,O-diethyl alpha-mercaptoisovalerylurea dithiophosphate, after recrystallization from a carbon tetrachloride-hexane mixture (equal parts by volume) was a colorless crystalline material melting at 96°–97° C.

Example 4

The procedure of Example 1 was employed using 23.3 parts of O,O-diisopropyl dithiophosphoric acid (92%), 11.6 parts of anhydrous sodium carbonate, 75 parts of methyl isobutyl ketone, and 15 parts of 1-chloroacetyl-3-methylurea. 31 parts (95% yield) of O,O-diisopropyl 1-mercaptoacetyl-3-methylurea dithiophosphate were obtained. After recrystallization from hexane, the product was a colorless crystalline material melting at 97°–98° C.

Example 5

31.9 parts of O,O-di-n-amyl dithiophosphoric acid (85%) were added slowly to a well-agitated mixture of 11.6 parts of anhydrous sodium carbonate suspended in 100 parts of methyl isobutyl ketone. 13.7 parts of chloroacetylurea were added and the resulting mixture was held at 60°–70° C. with stirring for 3 hours. The reaction mixture was washed three times with cold water, dried over anhydrous sodium sulfate, and filtered. The methyl isobutyl ketone was removed from the filtrate by distillation under vacuum, leaving 35 parts (95% yield) of O,O-di-n-amyl mercaptoacetylurea dithiophosphate, an oily residue which rapidly set to a waxy solid. After recrystallization, first from hexane and then from petroleum ether, the product was a colorless, waxy solid melting at 47°–48° C.

Example 6

45.5 parts of O,O-di-n-decyl dithiophosphoric acid (90%) were added slowly to a well-agitated mixture of 11.6 parts of anhydrous sodium carbonate suspended in 100 parts of methyl isobutyl ketone. 21.3 parts of 1-chloroacetyl-3-phenylurea were added and the resulting mixture maintained at 60°–65° C. with continued stirring for 8 hours. The reaction mixture was cooled to room temperature and filtered. The filtrate was washed three times with water, dried over anhydrous sodium sulfate, and then stripped of solvent by distillation under vacuum. The residual product, O,O-di-n-decyl 1-mercaptoacetyl-3-phenylurea dithiophosphate, was obtained in a 90% yield as an amber-colored, viscous liquid having a refractive index n_D^{25} 1.5222.

Example 7

A mixture consisting of 20.5 parts of potassium O,O-diethyl monothiophosphate and 13.5 parts of chloroacetylurea dissolved in 75 parts of methyl isobutyl ketone was heated at 60°–70° C. for 10 hours with stirring, and then filtered. The filtrate was washed twice with water, dried over anhydrous sodium sulfate, filtered, and stripped of solvent by distillation under vacuum. The residual product, O,O-diethyl mercaptoacetylurea monothiophosphate, after recrystallization, first from carbon tetrachloride and then from benzene, was a colorless crystalline material melting at 74°–75° C.

Example 8

The procedure of Example 1 was employed using 28.2 parts of O,O-diphenyl dithiophosphoric acid, 11 parts of anhydrous sodium carbonate, 100 parts of acetone, and 13.7 parts of chloroacetylurea. 35.4 parts (93% yield) of O,O-di-

phenyl mercaptoacetylurea dithiophosphate were obtained. After recrystallization from benzene, the product was a colorless needle-like crystalline material melting at 99°–100° C.

Example 9

34.6 parts of diethyl chlorophosphate were added dropwise during a period of one hour to a well-agitated solution of 25.2 parts of potassium hydroxide (89%) in 160 parts of ethanol maintained at 10°–15° C. The mixture was held at 20°–25° C. for 1½ hours, followed by the removal of 90 parts of ethanol by distillation under vacuum. 100 parts of acetone and 27.4 parts of chloroacetylurea were added, and the mixture was maintained at 25°–35° C. for 6 hours. The reaction mixture was filtered, and the acetone and ethanol were removed from the filtrate by distillation under vacuum. The residual product (48.6 parts, 96% yield), diethyl glycolylurea phosphate, was a straw-colored liquid having a refractive index n_D^{25} 1.4382.

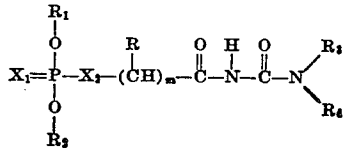
The phosphate esters of this invention may be employed in controlling many types of insects and mites such as, for example, the black bean aphid, green peach aphid, pea aphid, chrysanthemum aphid, greenhouse thrips, California red scale, citrus red spider, greenhouse red spider, milkweed bug, mealy bug, sow bug, German cockroach, southern army worm, yellow fever mosquito, malarial mosquito, Mexican bean beetle, confused flour beetle, and black carpet beetle.

These new compounds may also be used in combination with insecticides such as lead arsenate, nicotine, rotenone, pyrethrum, benzene hexachloride, 1,1,1-trichloro-2,2-di(p-chlorophenyl)-ethane, dodecyl thiocyanate, phenothiazine, and the like; with fungicides such as sulfur, various copper compounds, mercury salts, and the like; and with various types of plant foods and fertilizers.

While the invention has been described with particular reference to specific embodiments, it is to be understood that it is not to be limited thereto, but is to be construed broadly and restricted solely by the scope of the appended claims.

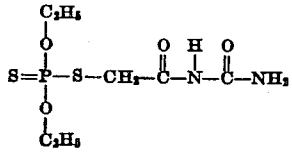
I claim:

1. Organic phosphate esters of the general formula

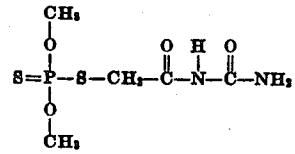


wherein X_1 and X_2 are members of the group consisting of sulfur and oxygen, R is a member of the group consisting of hydrogen and an alkyl radical, R_1 and R_2 are members of the group consisting of alkyl, aralkyl, and aryl radicals, R_3 and R_4 are members of the group consisting of hydrogen, alkyl, and aryl radicals, and m represents a small whole number.

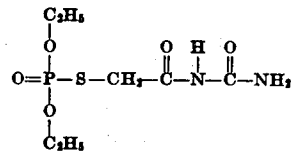
2. O,O-diethyl mercaptoacetylurea dithiophosphate of the formula



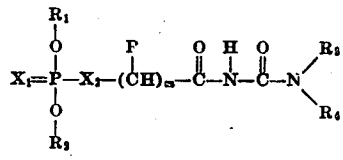
3. O,O-dimethyl mercaptoacetylurea dithiophosphate of the formula



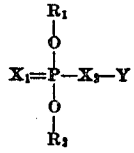
4. O,O-diethyl mercaptoacetylurea monothiophosphate of the formula



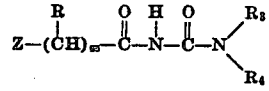
5. A method of preparing an organic phosphate ester of the general formula



wherein X_1 and X_2 are members of the group consisting of sulfur and oxygen, R is a member of the group consisting of hydrogen and an alkyl radical, R_1 and R_2 are members of the group consisting of alkyl, aralkyl, and aryl radicals, R_3 and R_4 are members of the group consisting of hydrogen, alkyl, and aryl radicals, and m represents a small whole number, which includes the step of reacting a phosphate of the general formula



in which R_1 and R_2 are chosen from the group consisting of alkyl, aralkyl, and aryl radicals, X_1 and X_2 are members of the group consisting of sulfur and oxygen, and Y represents an alkali-forming metal, with a haloacylurea of the general formula

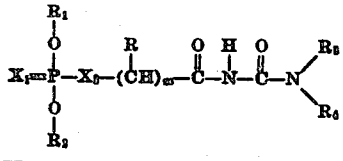


in which R is a member of the group consisting of hydrogen and an alkyl radical, R_3 and R_4 are members of the group consisting of hydrogen, alkyl, and aryl radicals, m represents a small whole number, and Z is a member of the group consisting of chlorine and bromine.

6. The method of claim 5 in which the reaction is carried out in the presence of a solvent.

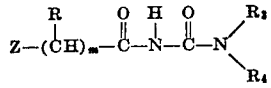
7. The method of claim 5 in which the reaction is carried out at a temperature within the range of from about 20° C. to about 150° C.

8. A method of preparing an organic phosphate ester of the general formula

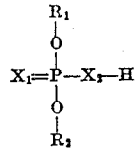


wherein X_1 and X_2 are members of the group consisting of sulfur and oxygen, R is a member

of the group consisting of hydrogen and an alkyl radical, R_1 and R_2 are members of the group consisting of alkyl, aralkyl, and aryl radicals, R_3 and R_4 are members of the group consisting of hydrogen, alkyl, and aryl radicals, and m represents a small whole number, which includes the step of reacting together a haloacylurea of the general formula



in which R is a member of the group consisting of hydrogen and an alkyl radical, R_3 and R_4 are members of the group consisting of hydrogen, alkyl, and aryl radicals, m represents a small whole number, and Z is a member of the group consisting of chlorine and bromine, an acid phosphate of the general formula



in which R_1 and R_2 are chosen from the group consisting of alkyl, aralkyl, and aryl radicals, and X_1 and X_2 are members of the group consisting of sulfur and oxygen, and a basic alkali-forming metal compound having sufficient alkalinity to neutralize the acid phosphate.

9. The method of claim 8 in which the basic alkali-forming metal compound is sodium carbonate.

10. The method of claim 8 in which the reaction is carried out in the presence of a solvent.

11. A method of preparing O,O-diethyl mercaptoacetylurea dithiophosphate which includes the step of reacting together O,O-diethyl dithiophosphoric acid, sodium carbonate, and chloroacetylurea in the presence of a ketone.

12. A method of preparing O,O-dimethyl mercaptoacetylurea dithiophosphate which includes the step of reacting together O,O-dimethyl dithiophosphoric acid, sodium carbonate, and chloroacetylurea in the presence of a ketone.

13. A method of preparing O,O-diethyl mercaptoacetylurea monothiophosphate which includes the step of reacting together potassium O,O-diethyl monothiophosphate and chloroacetylurea in the presence of a ketone.

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