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

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

\[
R_1-\text{O}-\text{P}-\text{O}-\text{R}_2
\]

in which \( R_1 \) and \( R_2 \) are chosen from the group consisting of alkyl, aralkyl, and aryl radicals, \( X \) is a member of the group consisting of sulfur and oxygen, \( Z \) is a member of the group consisting of halogen and alkyl radicals, and \( m \) represents an integer not greater than 2.

In the new compounds \( R_1 \) and \( R_2 \) may be the same or different radicals. Furthermore, it is to be understood that when the \( R_1 \) 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, and 4-chlorophenyl.

The compounds of this invention possess general pest-control characteristics, including insecticidal, rodenticidal, and fungicidal properties. Many of the members possess desirable flotation properties and have the characteristics of high pressure lubricants when used as oil additives. These compounds may also be employed as corrosion inhibitors.

These phosphate esters may be readily prepared by reacting a chlorophosphate of the general formula

\[
X-\text{O}-\text{P}-\text{O}-\text{Cl}
\]

in which \( X \), \( R_1 \), and \( X \) have the meaning shown above, with an alkali-forming metal phenoxide of the general formula

\[
Y-\text{O}-\text{N}^+\text{Z}^-\text{O}^--\text{R}_2
\]

in which \( Z \) and \( m \) have the meaning shown above, and \( Y \) represents an alkali-forming metal, in the presence of an inert organic solvent.

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.

The chlorophosphate compounds employed in the present process as shown above, namely the organic chlorophosphates and chlorothiophosphates, may be prepared according to the methods described in the Journal of the American Chemical Society, volume 76, No. 10, page 1663.

A typical reaction in which diethyl chlorophosphate is reacted with sodium 4-chloro-2-nitrophenoxide to produce 4-chloro-2-nitrophenyl diethyl phosphate may be illustrated as follows:

\[
\text{Cl}_2\text{H}_2\text{O}^-\text{P}-\text{O}-\text{CH}_2\text{CH}_2\text{Na}^-\text{O}^-\text{N}^+\text{Z}^-\text{O}^--\text{Cl}
\]

High yields of the desired products are obtained by carrying out the reaction in the presence of an inert organic solvent, the latter serving particularly as a solvent for the solid alkali-forming metal phenoxide. Suitable inert solvents include the ketones such as, for example, acetone, methyl ethyl ketone, methyl isobutyl ketone, methyl benzyl ketone, cyclohexanone, acetonaphone, 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, 1,2-dimethoxyethane, and the trialkyl phosphates such as trimethyl phosphate, triethyl phosphate, and triisopropyl phosphate.

Organic liquids which are poor solvents for the alkali-forming metal phenoxides, and hence are less suitable in the present process, include chlorobenzene, toluene, xylene, diethyl ether, chloroform, carbon disulfide, and carbon tetrachloride.

Water and the alcohols in general may be used as solvents for the alkali-forming metal phenoxides. However, they are less satisfactory in the process inasmuch as they tend to react with the
chlorothiophosphate and chlorophosphate compounds.

The reaction is preferably carried out at a temperature within the range of from about 30° 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 compounds of the present invention consists in employing in lieu of the alkali-forming metal phenoxide the corresponding phenol and a basic alkali-forming metal compound, the latter having sufficient alkalinity to neutralize the phenol. Obviously, this procedure avoids the initial preparation and isolation of the alkali-forming metal phenoxide. Such basic alkali-forming metal compounds include sodium carbonate, potassium carbonate, barium carbonate, magnesium carbonate, lithium carbonate, sodium hydroxide, potassium hydroxide, magnesium hydroxide, 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 di-n-butyl 2-nitro-4-tolyl thioephosphate, the reaction may be illustrated as follows:

\[
\text{C}_6\text{H}_5\text{O} = \text{POCH}_3 + \text{HO} = \text{OC}_6\text{H}_5 \rightarrow \text{CH}_3 + \text{Na}_2\text{CO}_3
\]

The following examples will further illustrate the invention.

**Example 1**

34.7 grams (0.2 mol) of 4-chloro-2-nitrophenol, 21.2 grams (0.2 mol) of anhydrous sodium carbonate, and 200 cc. of methyl ethyl ketone were mixed together at room temperature with good stirring in a vessel equipped with a reflux condenser. 37.7 grams (0.2 mol) of diethyl chlorothiophosphate were added, and the mixture was stirred and heated at reflux for three hours. After cooling to room temperature, the mixture was filtered to remove the sodium chloride and sodium bicarbonate, and the filtrate heated under reduced pressure to distill off the methyl ethyl ketone. The residual brown oil was dissolved in 200 cc. of toluene, washed with 5% sodium carbonate solution, and then with 10% sodium chloride solution. The toluene extract was dried over Drierite, filtered, and the toluene removed by distillation at reduced pressure. A small amount of unreacted diethyl chlorothiophosphate was also removed by distillation in vacuo. The residual product, 4-chloro-2-nitrophenyl diethyl thioephosphate, weighing 53.5 grams, was a clear light brown liquid having a refractive index \( n_D^{20} = 1.5402 \).

**Example 2**

The procedure of Example 1 was employed using 34.7 grams of 4-chloro-2-nitrophenol, 21.2 grams of anhydrous sodium carbonate, 100 cc. of methyl ethyl ketone, and 34.5 grams of diethyl chlorophosphate. The reaction mixture was stirred for a period of six hours at room temperature, then heated at 55° C. for one hour, followed by heating at reflux for two hours. 39.9 grams of 4-chloro-2-nitrophenyl diethyl phosphate were obtained. The product was a light brown oil having a refractive index \( n_D^{20} = 1.5075 \).

**Example 3**

A mixture consisting of 0.2 mol of 2-nitro-p-cresol and 0.2 mol of anhydrous sodium carbonate was heated in 100 cc. of methyl ethyl ketone until the orange-red sodium salt of 2-nitro-p-cresol was formed. 0.2 mol of diethyl chlorothiophosphate was then added, and the reaction mixture refluxed for four and one-half hours. The resulting mixture was cooled to room temperature, filtered, and the filter cake washed with methyl ethyl ketone. The combined filtrate and washings were heated under reduced pressure to remove the ketone and any unreacted diethyl chlorothiophosphate. The residue was taken up in 77 cc. of benzene, washed twice with dilute sodium hydroxide solution, once with water, and then dried over Drierite. The residue was taken up in 200 cc. of methyl ethyl ketone and heated to 95° C., and distillation, 30 grams of diethyl 2-nitro-4-tolyl thioephosphate were obtained, boiling at 175°-185° C./0.5-1.0 mm., and having a refractive index \( n_D^{20} = 1.5283 \).

**Example 4**

0.12 mol of 2,4-dichloro-6-nitrophenol was heated with concentrated aqueous alkali (containing 5 grams of sodium hydroxide) in 225 cc. of xylene until all the water had distilled azeotropically. 0.12 mol of diethyl chlorothiophosphate in 135 cc. of methyl ethyl ketone was added to the cooled xylene slurry, followed by refluxing the resulting mixture for a period of twelve hours. The reaction mixture was filtered and the filtrate concentrated in vacuo. The residue was taken up in benzene, washed with dilute sodium hydroxide solution, and then with water, and then dried over Drierite. The solution was heated under reduced pressure to remove the benzene and any unreacted diethyl chlorothiophosphate. The residual product, 2,4-dichloro-6-nitrophenyl diethyl thioephosphate, was a dark brown oily liquid.

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 arm 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, 2,4-di(p-chlorophenyl) anthracene, dodecyl thiocyanate, and 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. Additives of high alkalinity are to be avoided, since the organic phosphates are unstable in vehicles having a pH in water greater than about 8.5.

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 re-
In which R₁ and R₂ are chosen from the group consisting of alkyl, aralkyl, and aryl radicals, and X is a member of the group consisting of sulfur and oxygen, Z is a member of the group consisting of halogen and alkyl radicals, and m represents an integer not greater than 2, which includes the step of reacting together a chlorophosphate compound of the general formula

In which R₁ and R₂ are chosen from the group consisting of alkyl, aralkyl, and aryl radicals, and X is a member of the group consisting of sulfur and oxygen, a phenol of the general formula

REFERENCES CITED
The following references are of record in the file of this patent:

UNITED STATES PATENTS

Chemical Abstracts, vol. 7 (1913), pages 987-988, abstracting original publication by Pischinimuka.
