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3,205,238

THIENYL PHOSPHOROTHIOATES

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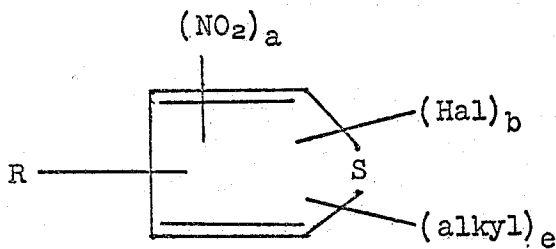
No Drawing. Continuation of application Ser. No. 20,561, Apr. 7, 1960. This application Oct. 16, 1964, Ser. No. 404,522

8 Claims. (Cl. 260-332.5)

The present application is a continuation of copending application, Serial Number 20,561, filed April 7, 1960, now abandoned.

This invention relates to new and useful phosphorothioates, to methods of making same, and to insecticidal compositions containing same as an active ingredient.

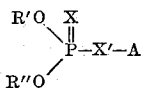
The new phosphorothioates can be termed thienyl phosphorothioates and employing the skeleton of the thiophene radical can be represented by the structure



wherein a is an integer from 0 to 1, inclusive; wherein b is an integer from 0 to 2, inclusive; wherein "Hal" means a halogen having an atomic number above 9 but not higher than 35 (i.e. chlorine or bromine);

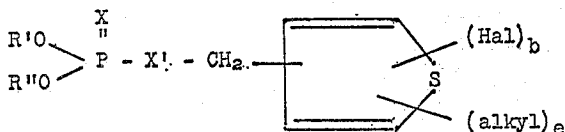
wherein e is an integer from 0 to 2, inclusive; wherein "alkyl" means an alkyl radical containing from 1 to 4 carbon atoms (i.e. methyl, ethyl, propyl, butyl, and the various isomeric forms thereof) but preferably containing not more than 2 carbon atoms (i.e. methyl or ethyl);

wherein R is



wherein R' and R'' are like or unlike lower alkyl radicals (i.e. alkyl radicals containing from 1 to 5 carbon atoms such as methyl, ethyl, propyl, butyl, amyl, and the various isomeric forms thereof) but preferably alkyl radicals containing not more than two carbon atoms, wherein X and X' are chalcogens of atomic weight less than 40 (i.e. sulfur or oxygen) but wherein at least one of X and X' is sulfur, and wherein A is an aliphatic hydrocarbon radical having the empirical formula C_nH_{2n} wherein n is a whole number from 1 to 3 but preferably 1; and wherein the sum total of a , b and e (i.e. $a+b+e$) is an integer from 0 to 3, inclusive, but preferably an integer from 0 to 2, inclusive.

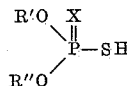
The preferred thienyl phosphorothioates of this invention are the thienyl phosphorothioates of the structure



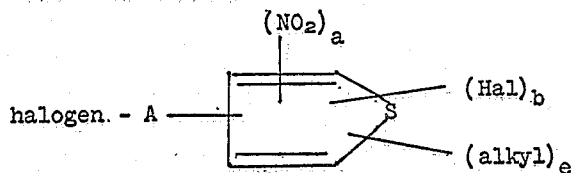
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wherein R' and R'' are alkyl radicals containing not more than two carbon atoms; wherein X and X' are chalcogens of atomic weight less than 40 but wherein at least one of X and X' is sulfur; wherein "Hal" means a halogen having an atomic number above 9 but not higher than 35 (i.e. chlorine or bromine); wherein "alkyl" means an alkyl radical containing not more than two carbon atoms; wherein b is an integer from 0 to 2, inclusive; wherein e is an integer from 0 to 2, inclusive; and wherein the sum total of b and e is an integer from 0 to 2, inclusive.

Thienyl phosphorothioates of the foregoing structure wherein X' is sulfur can be prepared by reacting a salt (i.e. ammonium or alkali metal such as sodium, potassium or lithium) of a phosphorothioic acid of the structure

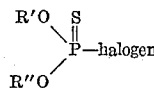


wherein R' , R'' and X have the aforescribed significance, with a substantially equimolecular proportion of a halide of the structure

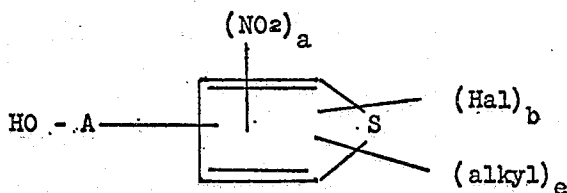


wherein A , a , b , "Hal," e and "alkyl" have the aforescribed significance and wherein the term "halogen" means a halogen having an atomic number above 9 but not higher than 35 (i.e. chlorine or bromine) in the presence of an inert organic liquid or solvent (e.g. acetone, butanone, dioxane, benzene, toluene, xylene, ethyl alcohol, isopropyl alcohol, etc.). While a wide range of reaction temperatures can be employed provided the reaction system is fluid (i.e. a temperature above the freezing point of the system and up to and including the boiling point of the system), it is preferred to employ a reaction temperature in the range of 20° C. to 120° C.

Thienyl phosphorothioates of the foregoing structure wherein X is sulfur and wherein X' is oxygen can be prepared by reacting a phosphorohalidithioate of the structure



wherein "halogen" means a halogen having an atomic number above 9 but not higher than 35 (i.e. chlorine or bromine), with an equimolecular proportion of a thienyl substituted alcohol of the structure



wherein A , a , b , "Hal," e and "alkyl" have the aforescribed significance in the presence of an inert organic liquid or solvent (e.g. benzene, toluene, xylene, acetone, butanone, dioxane, etc.) and a hydrogen halide scaveng-

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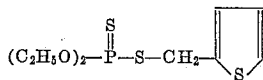
ing agent (e.g. sodium carbonate, potassium carbonate, the tertiary organic amines such as triethylamine, tributylamine, dimethylaniline, lutidine, pyridine, etc.) in an amount sufficient to absorb the hydrogen halide by-product. While a wide range of reaction temperatures can be employed provided the system is fluid (i.e. a temperature above the freezing point of the system and up to and including the boiling point of the system) it is preferred to employ a temperature in the range of 20° C. to 120° C.

As illustrative of the new phosphorothioates of this invention is the following

S-(2-thenyl) O,O-dimethyl phosphorothioate
 O-(2-thenyl) O,O-dimethyl phosphorothioate
 S-(2-thenyl) O,O-dimethyl phosphorodithioate
 S-(3-thenyl) O,O-dimethyl phosphorothioate
 S-(3-thenyl) O,O-diisopropyl phosphorodithioate
 S-(2-thenyl) O,O-di-n-butyl phosphorothioate
 S-(2-thenyl) O,O-diisoamyl phosphorodithioate
 O-(3-thenyl) O,O-diethyl phosphorothioate
 O-(5-chloro-2-thenyl) O,O-diethyl phosphorothioate
 S-(5-chloro-2-thenyl) O,O-dimethyl phosphorothioate
 S-(5-chloro-2-thenyl) O,O-diethyl phosphorodithioate
 S-(5-bromo-2-thenyl) O,O-diethyl phosphorothioate
 S-(2-nitro-3-thenyl) O,O-diethyl phosphorodithioate
 S-(3-nitro-2-thenyl) O,O-dimethyl phosphorodithioate
 S-(2,5-dichloro-3-thenyl) O,O-diethyl phosphorothioate
 O-(5-n-butyl-2-thenyl) O,O-diethyl phosphorothioate
 O-(5-ethyl-2-thenyl) O,O-diisopropyl phosphorothioate
 S-(3-methyl-2-thenyl) O,O-dimethyl phosphorodithioate
 S-(2,5-diethyl-3-thenyl) O,O-diethyl phosphorodithioate
 S-(2-methyl-3-thenyl) O,O-diethyl phosphorothioate
 S-(5-chloro-4-methyl-2-thenyl) O,O-dimethyl phosphorodithioate
 S-(2-bromo-3-thenyl) O,O-dimethyl phosphorodithioate
 S-(2,5-dimethyl-3-thenyl) O,O-diethyl phosphorothioate
 S-(2,5-dibromo-3-thenyl) O,O-diethyl phosphorothioate
 S-(5-isopropyl-2-thenyl) O,O-diethyl phosphorothioate
 S-(4-chloro-3-thenyl) O,O-diethyl phosphorodithioate
 S-(2,5-diethyl-3-chloro-4-thenyl) O,O-diethyl phosphorothioate
 S-(2-methyl-3-chloro-5-tert.butyl-4-thenyl) O,O-diethyl phosphorothioate
 S-(2,5-dimethyl-3-chloro-4-thenyl) O,O-diethyl phosphorodithioate
 S-[1-(2-thienyl)ethyl] O,O-diethyl phosphorodithioate
 S-[2-(2-thienyl)ethyl] O,O-diethyl phosphorodithioate
 S-[2-(2-thienyl)propyl] O,O-diethyl phosphorothioate
 S-[1-(5-chloro-2-thienyl)ethyl] O,O-dimethyl phosphorodithioate

As illustrative of the preparation of the phosphorothioates of this invention is the following:

Example I

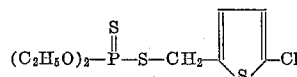


To a suitable reaction vessel equipped with a thermometer, agitator and reflux condenser is charged 55.8 parts by weight (substantially 0.3 mole) of O,O-diethyl phosphorodithioic acid and 99.0 parts by weight of a 20.8% solution of sodium ethylate (substantially 0.3 mole) in ethyl alcohol. To this ethyl alcohol solution of sodium O,O-diethyl phosphorodithioate is added 39.8 parts by weight (substantially 0.3 mole) of 2-thenyl chloride. The reaction mass is then heated for 2.5 hours at about 80 °C. The resulting reaction mass is then cooled to room temperature and quenched with water. The organic layer is removed and washed first with 3% aqueous sodium carbonate and then with water. The so-washed organic solution is then heated at 100° C. at 25 mm. pressure to remove the volatiles. The residue, 78.1 parts by weight of an amber liquid, is S-(2-thenyl) O,O-di-

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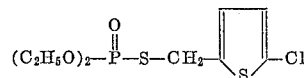
ethyl phosphorodithioate, which is soluble in benzene, ethyl ether and chloroform but insoluble in water. *Analysis*.—Theory: 34.0% S. Found: 33.8% S.

Example II



To a suitable reaction vessel equipped with a thermometer, agitator and reflux condenser is charged 71.0 parts by weight (substantially 0.35 mole) of ammonium O,O-diethyl phosphorodithioate, approximately 160 parts by weight of acetone, and 50.1 parts by weight (substantially 0.30 mole) of 5-chloro-2-thenyl chloride. The mass is then heated slowly to the reflux temperature and then refluxed for 1.25 hours. The resulting reaction mass is then cooled to room temperature and quenched with water. The organic layer is removed and washed first with 3% aqueous sodium carbonate and then with water. The so-washed organic solution is then dissolved in benzene and then dried by distilling off the volatiles by heating to final conditions of 105° C. at 20 mm. pressure. The residue, 91.0 parts by weight of an amber liquid, is S-(5-chloro-2-thenyl) O,O-diethyl phosphorodithioate which is soluble in chloroform, ethyl alcohol and ethyl acetate but insoluble in water. *Analysis*.—Theory: 9.8% P, 11.2% Cl. Found: 10.0% P, 10.9% Cl.

Example III



Employing the procedure of Example II but replacing ammonium O,O-diethyl phosphorodithioate with an equimolar amount of ammonium O,O-diethyl phosphorothioate there is obtained in a 98.2% yield S-(5-chloro-2-thenyl) O,O-diethyl phosphorothioate, an oil, which is soluble in ethyl alcohol, ethyl acetate, and chloroform but insoluble in water. *Analysis*.—Theory: 11.8% Cl, 10.3% P. Found: 11.7% Cl, 10.8% P.

Example IV

Employing the procedure of Example II but replacing ammonium O,O-diethyl phosphorodithioate with an equimolar amount of ammonium O,O-diisopropyl phosphorodithioate there is obtained in an 88.6% yield S-(5-chloro-2-thenyl) O,O-diethyl phosphorodithioate, an oil, which is soluble in ethyl alcohol and carbon tetrachloride but insoluble in water.

Example V

Employing the procedure of Example II but replacing ammonium O,O-diethyl phosphorodithioate with an equimolecular amount of ammonium O,O-diisopropyl phosphorodithioate there is obtained in a 100% yield S-(5-chloro-2-thenyl) O,O-diisopropyl phosphorodithioate an amber liquid which is soluble in diethyl ether, and chloroform but insoluble in water. *Analysis*.—Theory: 9.0% P. Found: 9.3% P.

Example VI

Employing the procedure of Example II but replacing 5-chloro-2-thenyl chloride with an equimolar amount of 2-thenyl bromide and replacing ammonium O,O-diethyl phosphorodithioate with an equimolar amount of sodium O,O-diethyl phosphorothioate there is obtained S-(2-thenyl) O,O-diethyl phosphorothioate, an oil which is soluble in chloroform and ethyl acetate but insoluble in water.

Example VII

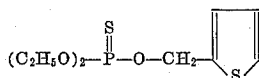
Employing the procedure of Example II but replacing 5-chloro-2-thenyl chloride with an equimolar amount of 2,5-dichloro-3-thenyl chloride there is obtained S-(2,5-dichloro-3-thenyl) O,O-diethyl phosphorodithioate, an oil which is soluble in chloroform but insoluble in water.

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Example VIII

Employing the procedure of Example I but replacing 2-thenyl chloride with an equimolar amount of 2-(2-bromoethyl) thiophene there is obtained S-[2-(2-thienyl)-ethyl] O,O-diethyl phosphorodithioate, an oil which is soluble in chloroform but insoluble in water.

Example IX



To a suitable reaction vessel equipped with a thermometer, agitator and reflux condenser is charged approximately 200 parts by weight of benzene, 18.8 parts by weight (substantially 0.1 mole) of O,O-ethyl phosphorochlorodithioate, 11.4 parts by weight (substantially 0.1 mole) of 2-thienylmethanol, and 7.9 parts by weight (substantially 0.1 mole) of pyridine. The mixture is refluxed for 8 hours, cooled to room temperature and filtered. The filtrate is then washed first with 3% aqueous sodium carbonate and then with water. The so-washed organic solution is then subjected to vacuum distillation to remove the benzene. The residue, a liquid, is O-(2-thienyl) O,O-diethyl phosphorothioate which is soluble in acetone, ethyl alcohol, and ethyl acetate but insoluble in water.

Example X

Employing the procedure of Example II but replacing 5-chloro-2-thenyl chloride with an equimolar amount of 2-nitro-3-thenyl bromide there is obtained S-(2-nitro-3-thenyl) O,O-diethyl phosphorodithioate which is soluble in acetone but insoluble in water.

Example XI

Employing the procedure of Example II but replacing 5-chloro-2-thenyl chloride with an equimolar amount of 5-chloro-4-methyl-2-thenyl chloride there is obtained S-(5-chloro-4-methyl-2-thenyl) O,O-diethyl phosphorodithioate, an oil which is insoluble in water.

Example XII

Employing the procedure of Example IX but replacing 2-thienyl methanol with an equimolar amount of 2-(2-thienyl)ethanol there is obtained O-[2-(2-thienyl)ethyl] O,O-diethyl phosphorothioate, an oil which is water insoluble.

Example XIII

Employing the procedure of Example I but replacing 2-thenyl chloride with an equimolar amount of 1-(2-thienyl)-1-chloroethane there is obtained S-[1-(2-thienyl)-ethyl] O,O-diethyl phosphorodithioate, an oil, which is soluble in benzene but insoluble in water.

The methods by which the phosphorothioates of this invention are isolated will vary slightly with the reactants employed and the product produced. Further purification by selective solvent extraction or by absorptive agents such as activated carbon or clays can precede the removal of the inert organic liquid or solvent. Additionally an inert organic solvent can be added to and in the purification by absorptive agents. However, the product is generally satisfactory for insecticidal purposes without further purification.

It will be understood that the terms "insect" and "insecticide" are used herein in their broad common usage to include spiders, mites, ticks, and like pests which are not in the strict biological sense classed as insects. Thus, the usage herein conforms to the definitions provided by Congress in Public Law 104, the "Federal Insecticide, Fungicide, and Rodenticide Act" of 1947, Section 2, subsection h, wherein the term "insect" is used to refer not only to those small invertebrate animals belonging mostly to the class Insecta, comprising six-legged, usually winged forms, as beetles, bugs, bees, flies, and so forth, but also to other

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allied classes of arthropods whose members are wingless and usually have more than six legs, as spiders, mites, ticks, centipedes, and wood lice.

The phosphorothioates of this invention are effective against a wide variety of insect pests. As illustrative of the activity but not limitative thereof is the following:

One gram of S-(2-thenyl) O,O-diethyl phosphorodithioate is dissolved in sufficient acetone to make a concentrate solution thereof. Approximately 0.1 cc. of sorbitan monolaurate polyoxyethylene derivative (a commercial water-soluble non-ionic emulsifying agent) is then mixed with the concentrate. To this mixture and with agitation is added sufficient water to provide an aqueous emulsion having a concentration of 0.05% by weight of S-(2-thenyl) O,O-diethyl phosphorodithioate. Thereupon lima bean plant leaves previously infested with the two spotted spider mite, *Tetranychus telarius* (L.), are dipped in the aqueous emulsion, withdrawn, and set aside for observation. At the end of 48 hours a 100% kill of the mobile stage of the mite was noted. Seven days after setting the test specimen aside residual activity was confirmed, a 100% kill of the resting stage and a 97% kill of the ova stage being noted. Similar results against the mobile resting and ova stages of the same mite were obtained employing S-(5-chloro-2-thenyl) O,O-diethyl phosphorodithioate instead of S-(2-thenyl) O,O-diethyl phosphorodithioate at a concentration of 0.1%. Similar results were obtained employing S-(5-chloro-2-thenyl) O,O-diethyl phosphorothioate.

Contact activity was also observed employing the compounds of this invention against larvae of the Mexican bean beetle, e.g. at a concentration of 0.05% by weight. S-(2-thenyl) O,O-diethyl phosphorodithioate gave a 90% kill.

Employing S-(2-thenyl) O,O-diethyl phosphorodithioate and S-(5-chloro-2-thenyl) O,O-diethyl phosphorodithioate, respectively, at a concentration of 0.0005% by weight against yellow fever mosquito larvae, *Aedes aegypti*, 100% kill in each instance was observed.

Systemic activity was also observed against a wide variety of insects. For example against the two-spotted spider mite, *Tetranychus telarius* (L.), a 100% kill was observed employing S-(5-chloro-2-thenyl) O,O-diethyl phosphorothioate at a concentration of 0.004% by weight.

Although the phosphorothioates of this invention are useful per se in controlling a wide variety of insect pests, it is preferable that they be supplied to the pests or to the environment of the pest or pests in a dispersed form in a suitable extending agent.

In the instant specification and appended claims it is to be understood that the term "dispersed" is used in its widest possible sense. When it is said that the phosphorothioates of this invention are dispersed, it means that the particles of the phosphorothioates of this invention may be molecular in size and held in true solution in a suitable organic solvent. It means further, that the particles may be colloidal in size and distributed throughout a liquid phase in the form of suspensions or emulsions or in the form of particles held in suspension by wetting agents. It also includes particles which are distributed in a semi-solid viscous carrier such as petrolatum or soap or other ointment base in which they may be actually dissolved in the semi-solid or held in suspension in the semi-solid with the aid of suitable wetting or emulsifying agents. The term "dispersed" also means that the particles may be mixed with and distributed throughout a solid carrier providing a mixture in particulate form, e.g. pellets, granules, powders, or dusts. The term "dispersed" also includes mixtures which are suitable for use as aerosols including solutions, suspensions, or emulsions of the phosphorothioates of this invention in a carrier such as dichlorodifluoromethane and like fluorochloroalkanes which boil below room temperature at atmospheric pressure.

In the instant specification and appended claims it is to be understood that the expression "extending agent" includes any and all of those substances in which the phosphorothioates of this invention are dispersed. It includes, therefore, the solvents of a true solution, the liquid phase of suspensions, emulsions or aerosols, the semi-solid carrier of ointments and the solid phase of particulate solids, e.g. pellets, granules, dusts and powders.

The exact concentration of the phosphorothioates of this invention employed in combatting or controlling insect pests can vary considerably provided the required dosage (i.e., toxic or lethal amount) thereof is supplied to the pests or to the environment of the pests. When the extending agent is a liquid or mixture of liquids (e.g. as in solutions, suspensions, emulsions, or aerosols) the concentration of the phosphorothioate employed to supply the desired dosage generally will be in the range of 0.001 to 50 percent by weight. When the extending agent is a semi-solid or solid, the concentration of the phosphorothioate employed to supply the desired dosage generally will be in the range of 0.1 to 25 percent by weight. From a practical point of view, the manufacturer must supply the agriculturist with a low-cost concentrate or spray base or particulate solid base in such form that, by merely mixing with water or solid extender (e.g., powdered clay or talc) or other low-cost material available to the agriculturist at the point of use, he will have an easily prepared insecticidal spray or particulate solid. In such a concentrate composition, the phosphorothioate generally will be present in a concentration of 5 to 95 percent by weight, the residue being any one or more of the well-known insecticidal adjuvants, such as the various surface active agents (e.g., detergents, a soap or other emulsifying or wetting agent, surface-active clays), solvents, diluents, carrier media, adhesives, spreading agents, humectants, and the like.

There are a large number of organic liquids which can be used for the preparation of solutions, suspensions, or emulsions of the phosphorothioates of this invention. For example, isopropyl ether, acetone, methyl ethyl ketone, dioxane, cyclohexanone, carbon tetrachloride, ethylene dichloride, tetrachloroethane, hexane, heptane and like higher liquid alkanes, hydrogenated naphthalenes, solvent naphtha, benzene, toluene, xylene, petroleum fractions (e.g. those boiling almost entirely under 400° F., at atmospheric pressure and having a flash point above about 80° F., particularly kerosene), mineral oils having an unsulfonatable residue above about 80 percent and preferably above about 90 percent. In those instances wherein there may be concern about the phytotoxicity of the organic liquid extending agent a portion of same can be replaced by such low molecular weight aliphatic hydrocarbons as dipentene, diisobutylene, propylene trimer, and the like or suitable polar organic liquids such as the aliphatic ethers and the aliphatic ketones containing not more than about 10 carbon atoms as exemplified by acetone, methyl ethyl ketone, diisobutyl ketone, dioxane, isopropyl ether, and the like. In certain instances, it is advantageous to employ a mixture of organic liquids as the extending agent.

When the phosphorothioates of this invention are to be supplied to the insect pests or to the environment of the pests as aerosols, it is convenient to dissolve them in a suitable solvent and disperse the resulting solution in dichlorodifluoromethane or like chlorofluoroalkane which boils below room temperature at atmospheric pressure.

The phosphorothioates of this invention are preferably supplied to the insect pests or to the environment of the insect pests in the form of emulsions or suspensions. Emulsions or suspensions are prepared by dispersing the phosphorothioate of this invention either per se or in the form of an organic solution thereof in water with the aid of a water-soluble surfactant. The term "sur-

factant" as employed here and in the appended claims is used as in volume II of Schwartz, Perry and Berch's "Surface Active Agents and Detergents" (1958, Interscience Publishers, Inc., New York), in place of the expression "emulsifying agent" to connote generically the various "emulsifying agents," "dispersing agents," "wetting agents" and "spreading agents" that are adapted to be admixed with the active compounds of this invention in order to secure better wetting and spreading of the active ingredients in the water vehicle or carrier in which they are insoluble through lowering the surface tension of the water (see also Frear, "Chemistry of Insecticides, Fungicides and Herbicides," second edition, page 280). These surfactants include the well-known capillary-active substances which may be anion-active (or anionic), cation active (or cationic), or non-ionizing (or non-ionic) which are described in detail in volumes I and II of Schwartz, Perry and Berch's "Surface Active Agents and Detergents" (1958, Interscience Publishers, Inc., New York), and also in the November 1947 issue of Chemical Industries (pages 811-824) in an article entitled "Synthetic Detergents" by John W. McCutcheon and also in the July, August, September and October 1952 issues of Soap and Sanitary Chemicals under the title "Synthetic Detergents." The disclosures of these articles with respect to surfactants, i.e. the anion active, cation-active and non-ionizing capillary active substances, are incorporated in this specification by reference in order to avoid unnecessary enlargement of this specification. The preferred surfactants are the water-soluble anionic surface-active agents and the water soluble non-ionic surface-active agents set forth in U.S. 2,846,398 (issued August 5, 1958). In general it is preferred that a mixture of water-soluble anionic and water-soluble non-ionic surfactants be employed.

The phosphorothioates of this invention can be dispersed by suitable methods (e.g., tumbling or grinding) in solid extending agents either of organic or inorganic nature and supplied to the insect pest environment in particulate form. Such solid materials include for example, tricalcium phosphate, calcium carbonate, kaolin, bole, kieselguhr, talc, bentonite, fuller's earth, pyrophyllite diatomaceous earth, calcined magnesite, volcanic ash, sulfur and the like inorganic solid materials, and include, for example, such materials of organic nature as powdered cork, powdered wood, and powdered walnut shells. The preferred solid carriers are the adsorbent clays, e.g. bentonite. These mixtures can be used for insecticidal purposes in the dry form, or, by addition of water-soluble surfactants or wetting agents the dry particulate solids can be rendered wettable by water so as to obtain stable aqueous dispersions or suspensions suitable for use as sprays.

For special purposes the phosphorothioates of this invention can be dispersed in a semi-solid extending agent such as petrolatum or soap (e.g., sodium stearate or oleate or palmitate or mixtures thereof) with or without the aid of solubility promoters and/or surfactants or dispersing agents.

In all of the forms described above the dispersions can be provided ready for use in combatting insect pests or they can be provided in a concentrated form suitable for mixing with or dispersing in other extending agents. As illustrative of a particularly useful concentrate is an intimate mixture of phosphorothioates of this invention with a water-soluble surfactant which lowers the surface tension of water in the weight proportions of 0.1 to 15 parts of surfactant with sufficient of the phosphorothioate of this invention to make 100 parts by weight. Such a concentrate is particularly adapted to be made into a spray for combatting various forms of insect pests (particularly mites) by the addition of water thereto. As illustrative of such a concentrate is an intimate mixture of 95 parts by weight of S-(5-chloro-2-thenyl) O,O-diethyl phosphorodithioate and 5 parts by weight of a water-soluble

nonionic surfactant such as the polyoxyethylene derivative of sorbitan monolaurate.

Another useful concentrate adapted to be made into a spray for combatting insect pests (particularly mites) is a solution (preferably as concentrated as possible) of a phosphorothioate of this invention in an organic solvent therefor. The said liquid concentrate preferably contains dissolved therein a minor amount (e.g. 0.5 to 10 percent by weight of the weight of the new insecticidal agent) of a surfactant (or emulsifying agent), which surfactant is also water-soluble. As illustrative of such a concentrate is a solution of S-(5-chloro-2-thenyl) O,O-diethyl phosphorothioate in benzene which solution contains dissolved therein a water-soluble polyoxyethylene glycol nonionic surfactant and a water-soluble alkarylsulfonate anionic surfactant.

Of the surfactants aforementioned in preparing the various emulsifiable, wettable or dispersible compositions or concentrates of this invention, the anionic and nonionic surfactants are preferred. Of the anionic surfactants, the particularly preferred are the well-known water-soluble alkali metal alkarylsulfonates as exemplified by sodium decylbenzene sulfonate and sodium dodecylbenzene sulfonate. Of the nonionic surfactants, the particularly preferred are the water-soluble polyoxyethylene derivations of alkylphenols (particularly isooctylphenol) and the water-soluble polyoxyethylene derivatives of the mono-higher fatty acid esters of hexitol anhydrides such as mannitan or sorbitan.

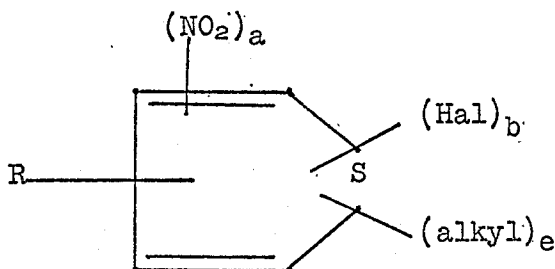
In all of the various dispersions described hereinbefore for insecticidal purposes, the active ingredients can be one or more of the compounds of this invention. The compounds of this invention can also be advantageously employed in combination with other pesticides, including, for example, nematocides, bactericides, and herbicides. In this manner it is possible to obtain mixtures which are effective against a wide variety of pests and other forms of noxious life.

In controlling or combatting insect pests the phosphorothioates of this invention either per se or compositions comprising same are supplied to the insect pests or to their environment in a lethal or toxic amount. This can be done by dispersing the new insecticidal agent or insecticidal composition comprising same in, on or over an infested environment or in, on or over an environment the insect pests frequent, e.g. agricultural soil or other growth media or other media infested with the insect pests or attractable to the pests for habitational or sustenance or propagational purposes, in any conventional fashion which permits contact between the insect pests and the phosphorothioates of this invention. Such dispersing can be brought about by applying the phosphorothioates per se or sprays or particulate solid compositions containing same to a surface infested with the insect pests or attractable to the pests, as for example, the surface of agricultural soil or other media such as the above ground surface of plants by any of the conventional methods, e.g. power dusters, boom and hand sprayers, and spray dusters. Also for sub-surface application such dispersing can be carried out by simply mixing the new insecticidal agent per se or insecticidal spray or particulate solid compositions comprising same with the infested environment or with the environment the insect pests frequent, or by employing a liquid carrier for the new insecticidal agent to accomplish sub-surface penetration and impregnation therein.

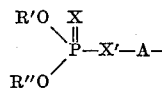
While this invention has been described with respect to certain embodiments, it is to be understood that it is not so limited and that variations and modifications thereof obvious to those skilled in the art can be made without departing from the spirit and scope thereof.

What is claimed is:

1. Thienyl phosphorothioates of the structure

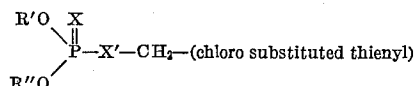


wherein a is an integer from 0 to 1, inclusive;
wherein b is an integer from 1 to 2, inclusive;
wherein "Hal" means a halogen having an atomic number above 9 but not higher than 35;
wherein e is an integer from 0 to 2, inclusive;
wherein "alkyl" means alkyl having from 1 to 4 carbon atoms;
wherein R is



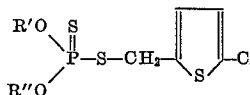
wherein R' and R'' are lower alkyl, wherein X and X' are chalcogens of atomic weight less than 40 but wherein at least one of X and X' is sulfur, and wherein A is of the empirical formula C_nH_{2n} wherein n is a whole number from 1 to 3, inclusive, and wherein the sum total of a , b , and e is an integer from 1 to 3, inclusive.

2. S-(5-chloro-2-thenyl) O,O-diethyl phosphorodithioate.
3. S-(5-chloro-2-thenyl) O,O-dimethyl phosphorodithioate.
4. S-(5-chloro-2-thenyl) O,O-diisopropyl phosphorodithioate.
5. S-(5-chloro-2-thenyl) O,O-diethyl phosphorothioate.
6. Thienyl O,O-dialkyl phosphorothioates of the structure



wherein the chloro substituted thienyl substituent has from 1 to 2 chlorine atoms attached to the ring of the thiophene nucleus, wherein R' and R'' are lower alkyl and wherein X and X' are chalcogens of atomic weight less than 40 but wherein at least one of X and X' is sulfur.

7. S-(5-chloro-2-thenyl) phosphorothioates of the structure



8. S-(2,5-dichloro-3-thenyl) O,O-diethyl phosphorodithioate.

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