PATENT SPECIFICATION

772,213

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International Classification:—A61l. C07f.

COMPLETE SPECIFICATION

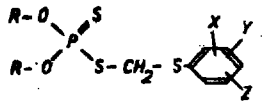
Improvements in and relating to Dithiophosphoric Acid Esters

We, J. R. GEIGY A.-G., a body corporate organised according to the laws of Switzerland, of 215, Schwarzwaldallee, Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with new dithiophosphoric acid esters, with the production thereof and with their use in pest control, in particular for the control of mites.

Alkylmercaptoalkyl-, arylmercaptoalkyl- and aralkylmercaptoalkyl-O.O-dialkyl esters of monothiophosphoric acid have been described in the German patent specification No. 830,509. (β-Ethylmercapto-ethyl)-O.O - diethyl monothiophosphate which belongs to this group, has also become of practical importance as a systemic insecticide, but its toxicity is high for warm blooded animals. The aromatic analogues embraced by the above patent specification have neither been given further notice nor have they been used in practice.

The surprising observation has now been made that the S-arylmercaptomethyl-O.O-dialkyl esters of dithiophosphoric acid which have not been known up to now, corresponding to the general formula:



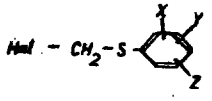
I

wherein R represents alkyl radicals with at most 3 carbon atoms,

X and Y represent hydrogen, halogen atoms, alkyl or alkoxy groups containing 1 to 4 carbon atoms or nitro groups, and

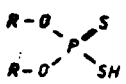
Z represents hydrogen, a halogen atom or an alkyl group, containing 1 to 4 carbon atoms, have an excellent acaricidal activity. At the same time, they have a relatively low toxicity for warm blooded animals so that they are excellently suitable for the control of mites, in particular in plant protection. Compared with the acaricidal activity, the insecticidal activity is relatively slight. However, the new dithiophosphoric acid esters according to the above definition can be used as additives to insecticides which have a long duration of action such as, for example, dichlorodiphenyl-trichloroethane, as their action also continues for a long time on plants and other substrata.

The new dithiophosphoric acid esters according to the above definition may be produced in a simple manner by condensing a halogen methyl aryl sulphide of the general formula:



II

wherein Hal represents chlorine or bromine and X, Y and Z have the meanings given above, with an alkali salt of an acid dithiophosphoric acid-O.O-dialkyl ester of the general formula:



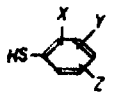
III

wherein R has the meaning given above. It is advantageous to perform the reaction in an indifferent solvent such as water, alcohol, acetone or aliphatic or aromatic hydrocarbons at a normal or slightly raised temperature.

The halogen methyl aryl sulphides of the general formula II may be obtained by react-

[Price 3s. 6d.]

ing an arylmercaptan of the general formula:



IV

wherein X, Y and Z have the meanings given above, with formaldehyde in the presence of hydrogen halide, e.g. in a hydrochloric acid or hydrobromic acid aqueous solution.

Apart from thiophenol, for example, 2-chloro-, 3-chloro-, 4-chloro-, 2:4-dichloro-, 2:5-dichloro-, 2:3:4-trichloro-, 2:4:5-trichloro-, 2:4:6-trichloro-, 3-bromo-, 4-bromo- and 4-fluorothiophenol; 2-methyl-, 3-methyl-, 4-methyl-, 2-ethyl-, 2-*iso*propyl-, 4-*iso*propyl-, 4-tertiary butyl-, 2-methyl-4-bromo-2-methyl-5-chloro-, 2-methyl-5-bromo-, 3-methyl-6-chloro- and 3-methyl-4:6-dichloro-, thiophenol, 2-methoxy-, 2:4-dimethoxy-, 2:5-dimethoxy- and 3:4-dimethoxy-thiophenol, 2-nitro-, 3-nitro-, 4-nitro-, 2:4-dinitro-, 4-chloro-2-nitro- and 2-nitro-4-methyl-thiophenol can be used as arylmercaptans of the general formula IV all of which are known. The greater part of those of the above compounds which have no nitro groups may be produced by reduction of the corresponding sulpho-chlorides, for example by means of zinc and sulphuric acid, whilst 2-nitro-thiophenol, 4-nitro-thiophenol, 2:4-dinitro-thiophenol and the substitution products thereof are also easily attainable by reacting nitrobenzenes or *m*-dinitrobenzenes halogen substituted in the ortho- or para-position with alkali hydrogen sulphides. Further substituted thiophenols such as, for example, 3:4-dichloro-thiophenol can be produced by analogous processes. In particular, dithiophosphoric acid-O.O - dimethyl ester, -O-methyl-O-ethyl ester, -O.O-diethyl ester, -O.O-di-*n*-propyl ester, -O-methyl-O-*iso*propyl ester and -O.O-di-*iso*propyl ester can be used as acid dithiophosphoric acid dialkyl esters of the general formula III. The following examples serve to illustrate the production of the new compounds. Parts are given as parts by weight and their relationship to parts by volume is as that of grammes to cubic centimetres.

EXAMPLE 1.

Hydrogen chloride is introduced until saturation at 25—35° into a well stirred mixture of 17.9 parts of 3:4-dichloro-thiophenol, 100 parts by volume of 36% hydrochloric acid and 9 parts by volume of 37% aqueous formaldehyde solution. About 14 parts of hydrogen chloride are used. The reaction mixture is then diluted with ice water and ethered out, the ether extracts are washed with cold diluted caustic soda lye and water and evaporated. On distillation of the residue, 3:4-dichlorophenyl-chloromethyl sulphide passes over at 106—109° under 0.1 mm pressure. The yield is 18.5 parts.

20.8 Parts of the sodium salt of diethyl dithiophosphoric acid are dissolved in 200 parts by volume of acetone, the solution is filtered and the filtrate is boiled under reflux with 21 parts of 3:4-dichlorophenyl chloromethyl sulphide for 14 hours. The mixture is diluted with water, ethered out and the ether extracts are washed with diluted soda solution and water. The ether residue is dried until the weight is constant. 36 Parts of dithiophosphoric acid-S-(3:4-dichloro-phenylmercapto-methyl)-O.O-diethyl ester are obtained as a colourless oil which distills without decomposition on molecular distillation at 150° at 0.01 mm pressure.

The following aryl halogen methyl sulphides and the corresponding dithiophosphoric acid-S-(arylmercapto-methyl)-O.O-dialkyl esters for example are produced in an analogous manner:

phenyl-chloromethyl sulphide, B.P.$_{12}$ 106—109°, dithiophosphoric acid-S-phenylmercaptomethyl-O.O-diethyl ester, B.P.$_{0.04}$ 85°;

(4-methyl-phenyl)-chloromethyl sulphide, B.P.$_{12}$ 116—118°, Dithiophosphoric acid-S-(4-methyl-phenylmercaptomethyl)-O.O-diethyl ester, B.P.$_{0.04}$ 120°;

(4-tertiarybutyl-phenyl)-chloromethyl sulphide, B.P.$_{0.4}$ 96—98°, dithiophosphoric acid-S-(4-tertiary butyl-phenylmercaptomethyl)-O.O-diethyl ester, B.P.$_{0.04}$ 120°;

(4-methoxy-phenyl)-chloromethyl sulphide, B.P.$_{12}$ 141—142°, dithiophosphoric acid-S-(4-methoxy-phenylmercaptomethyl)-O.O-diethyl ester, B.P.$_{0.04}$ 130°;

(4-fluoro-phenyl)-chloromethyl sulphide, B.P.$_{12}$ 104—108° dithiophosphoric acid-S-(fluoro-phenylmercaptomethyl)-O.O-diethyl ester, B.P.$_{0.04}$ 120°;

(4-chloro-phenyl)-chloromethyl sulphide, B.P. 79—81°, dithiophosphoric acid-S-(4-chloro-phenylmercaptomethyl)-O.O-dimethyl ester, B.P.$_{0.4}$ 130°, dithiophosphoric acid-S-(4-chloro-phenylmercaptomethyl)-O.O-diethyl ester, B.P.$_{0.04}$ 130°;

(2:4-dichloro-phenyl)-chloromethyl sulphide, M.P. 61—62°, dithiophosphoric acid-S-(2:4-dichloro-phenylmercaptomethyl)-O.O-diethyl ester, B.P.$_{0.04}$ 130°, dithiophosphoric acid-S-(2:4-dichloro-phenylmercaptomethyl)-O.O-di-*iso*propyl-ester, B.P.$_{0.04}$ 150°;

(2:5-dichloro-phenyl)-chloromethyl sulphide, M.P. 34—35°, B.P.$_{12}$ 116—119°, dithiophosphoric acid-S-(2:5-dichloro-phenylmercaptomethyl)-O.O-diethyl ester, B.P.$_{0.04}$ 120°;

dithiophosphoric acid-S-(3:4-dichloro-phenylmercaptomethyl)-O.O-di-*iso*propyl ester, B.P.$_{0.04}$ 150°;

(2:4:5-trichloro-phenyl)-chloromethyl sulphide, M.P. 57—59°, dithiophosphoric

acid-S-(2:4:5 - trichloro - phenylmercaptomethyl)-O.O-diethyl ester, B.P.$_{0.005}$ 135—140°;

(4 - nitro-phenyl) - chloromethyl sulphide, M.P. 65—66°, B.P.$_{1}$ 110—112°, dithiophosphoric acid-S-(4-nitro - phenylmercaptomethyl)-O.O-diethyl ester, M.P. 58—59°;

dithiophosphoric acid - S-(4-nitro-phenylmercaptomethyl) - O.O - di - *iso*propyl ester, B.P.$_{0.005}$ 140° (on decomposition);

(2-nitro-phenyl) - chloromethyl sulphide, M.P. 93—95°, dithiophosphoric acid-S-(2-nitro-phenylmercaptomethyl) - O.O - diethyl ester, M.P. 44—45°;

(2:4-dinitro-phenyl) - chloromethyl sulphide, M.P. 100—102°, dithiophosphoric acid-S-(2:4-dinitro - phenylmercaptomethyl)-O.O-diethyl ester (unstable);

(2-chloro-4 - nitro - phenyl) - chloromethyl sulphide, M.P. 74—75°, dithiophosphoric acid-S-(2-chloro-4 - nitro - phenylmercaptomethyl)-O.O-diethyl ester, B.P.$_{0.005}$ 170°.

The boiling points given for the dithiophosphoric acid esters all refer to the bath temperature on molecular distillation.

The new compounds can be used as such for the control of pests, in particular of mites, which are injurious to plants. However, generally it is more advantageous to adapt them more closely to the intended use by combining them with the usual pulverulent, semi-solid (ointments), liquid or gaseous carriers. Both solutions and also emulsions and suspensions are suitable as combinations with liquid carriers. When we refer to combination with a gaseous carrier we are concerned with an aerosol. The aerosol is obtained by mixing the active ingredient, if necessary with the aid of an auxiliary solvent, with a propellant, which is gaseous at normal pressure and temperature such as difluorodichloromethane or methyl chloride.

The active component itself can consist of one or more compounds of the defined formula. Also it can be used combined with other acaricidal, insecticidal, ovicidal, fungicidal or bactericidal substances. Examples of such are: α:α-bis-(chlorophenyl) - β:β:β-trichlorethane or -β:β-dichloroethane, 1:2:4:5:6:7:8:8 - octachloro-3a:4.7:7a - tetrahydro-4·7-endomethylene indan, diethyl-*p*-nitro-phenyl thiophosphate, diethyl-[2-*iso*propyl-4-methyl-pyrimidyl - (6)] - thiophosphate, 5:5-dimethyl - dihydroresorcinol - dimethyl carbamate, dinitrocresol, nitrated naphthylamines, mercury compounds or inorganic substances such as copper compounds, corrosive sublimate, sulphur, etc. Combined preparations having a great range of action are obtained in this way.

In the further examples below, the various forms of the agents for the control of mites and their use are described.

EXAMPLE 2.

1—5 Parts of dithiophosphoric acid-S-(3:4-dichlorophenyl-mercaptomethyl) - O.O-diethyl ester are rubbed and ground with 99—95 parts of talc until the active substance is equally distributed over the carrier. The dusting agent so obtained has a good action against the imagines and larvae of red spiders, e.g. Paratetranychus pilosus, Tetranychus urticae, etc., it can however, also be used for the control of ticks. If a mixture of talcum, kaolin and ground limestone is used as carrier, products with a similar action are obtained.

EXAMPLE 3.

10 Parts of dithiophosphoric acid - S-(4-nitrophenylmercaptomethyl) - O.O - diethyl ester are homogeneously ground with 82.5 parts of carrier and 7.5 parts of auxiliary substance. Kaolin, bentonite, chalk, etc. can be used as carriers. Examples of auxiliary substances are sulphite waste liquor, the sodium salt of dibutylnaphthalene sulphonic acid as well as other wetting and adhesive agents. Such a water dispersible powder is used in a concentration of 0.1—1%, and it has a good action against the imagines and larvae of red spiders.

If, for example, bean plants are treated with a 0.1% concentration of this water dispersible powder, then all spider mites of the genus Tetranychus urticae placed thereon are destroyed within 24 hours. The complete activity lasts for longer than 14 days.

EXAMPLE 4.

Suspension-spraying agents (water dispersible powders) with insecticidal and acaricidal activity are obtained if 25—50 parts of dichlorodiphenyltrichlorethane are mixed thoroughly with 5—10 parts of dithiophosphoric acid-S-(4-fluorophenylmercaptomethyl)-O.O-diethyl ester and a porous, absorbent, voluminous carrier, e.g. bentonite, kaolin or precipitated magnesium carbonate. Sulphite waste liquor, blood albumin and the sodium salt of dibutylnaphthalene sulphonic acid in amounts of from 5—10 parts can be used as additives. Used in a concentration of 0.05—0.5%, these spraying agents have a good action against the imagines and larvae of red spiders and at the same time they have an insecticidal activity.

EXAMPLE 5.

10—25 Parts of dithiophosphoric acid-S-(2.5 - dichlorophenylmercaptomethyl) - O.O-diethyl ester are dissolved in a ratio of 1:2 in 85—65 parts of a mixture of diacetone alcohol and xylene and the solution is mixed with 5—10 parts of an emulsifying agent. An example of an emulsifier is a high molecular ethylene oxide condensation product. This mixture is emulsifiable in water and, used in a concentration of 0.1—1%, has a good action against the imagines and larvae of the red spider. If the solvent is replaced by 10—30

parts of mineral oil, then agents with an increased acaricidal and ovicidal action are obtained

EXAMPLE 6.

0.1 Part of dithiophosphoric acid-S-(2:4-dichlorophenylmercaptomethyl) - O.O - diethyl ester is dissolved in 5—10 parts of xylene and 94.9—89.9 parts of petroleum (B.P. 180—220°). A spray with an acaricidal action is obtained.

EXAMPLE 7.

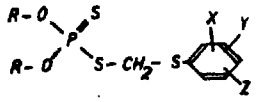
1 Part of dithiophosphoric acid-S-(4-chlorophenylmercaptomethyl) - O.O - diethyl ester is homogenously ground with 5 parts of dichlorodiphenyltrichlorethane and 94 parts of talcum. This mixture as well as similar combinations, e.g. with 5:5-dimethyl-dihydroresorcinol dimethyl carbamate or other contact insecticides or also fungicides, are excellently suitable for the simultaneous control of the red spider, injurious insects and fungal diseases.

EXAMPLE 8.

20—25 Parts of dichlorodiphenyltrichlorethane and 4—6 parts of dithiophosphoric acid-S-(3:4 - dichlorophenylmercaptomethyl)-O.O-diethyl ester are dissolved in a ratio of 1:2 in a mixture of diacetone alcohol and and xylene and the solution is mixed with 5—10 parts of an emulsifying agent of the ethylene oxide condensation product type. The solution obtained is emulsifiable and, used in a concentration of 0.3—0.5%, has a good action against red spiders and at the same time it has excellent insecticidal activity.

What we claim is:—

1. Dithiophosphoric acid esters of the general formula:

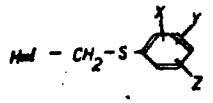


wherein R represents an alkyl group with at most 3 carbon atoms, X and Y represent hydrogen, halogen atoms, alkyl or alkoxy groups containing 1 to 4 carbon atoms or nitro groups, and Z represents hydrogen, a halogen atom or an alkyl group containing 1 to 4 carbon atoms.

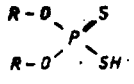
2. Dithiophosphoric acid esters of the general formula given in claim 1 wherein R represents an ethyl radical.

3. Dithiophosphoric acid esters of the general formula given in claim 1, wherein R represents an ethyl radical and X and Y represent chlorine.

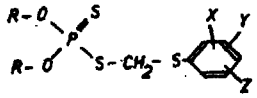
4. Process for the production of new dithiophosphoric acid esters which comprises condensing a halogenmethyl-aryl-sulphide of the general formula



wherein X and Y represent hydrogen, halogen atoms, alkyl or alkoxy groups containing 1 to 4 carbon atoms or nitro groups, Z represents hydrogen a halogen atom or an alkyl group containing 1 to 4 carbon atoms, and Hal represents chlorine or bromine, with an alkali salt of an acid dithiophosphoric acid-O.O-dialkyl ester of the general formula:

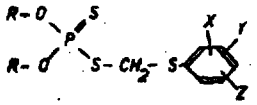


wherein R represents an alkyl group with at most 3 carbon atoms, to form a compound of the general formula:



wherein R, X, Y and Z have the meanings given above.

5. A composition for the control of mites comprising a compound of the general formula:



wherein R represents an alkyl group with at most 3 carbon atoms X and Y represent hydrogen, halogen atoms, alkyl or alkoxy groups containing 1 to 4 carbon atoms or nitro groups, and Z represents hydrogen, a halogen atom or an alkyl group containing 1 to 4 carbon atoms, in combination with suitable carriers or distributing agents.

6. A composition as claimed in claim 5 in which an insecticidal, fungicidal, bactericidal, ovicidal or another acaricidal substance is present.

7. Process for the manufacture of dithio-

parts of mineral oil, then agents with an increased acaricidal and ovicidal action are obtained

EXAMPLE 6.

0.1 Part of dithiophosphoric acid-S-(2:4-dichlorophenylmercaptomethyl) - O.O - diethyl ester is dissolved in 5—10 parts of xylene and 94.9—89.9 parts of petroleum (B.P. 180—220°). A spray with an acaricidal action is obtained.

EXAMPLE 7.

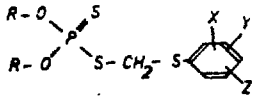
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20—25 Parts of dichlorodiphenyltrichlorethane and 4—6 parts of dithiophosphoric acid-S-(3:4 - dichlorophenylmercaptomethyl) - O.O-diethyl ester are dissolved in a ratio of 1:2 in a mixture of diacetone alcohol and and xylene and the solution is mixed with 5—10 parts of an emulsifying agent of the ethylene oxide condensation product type. The solution obtained is emulsifiable and, used in a concentration of 0.3—0.5%, has a good action against red spiders and at the same time it has excellent insecticidal activity.

What we claim is:—

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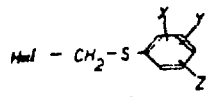


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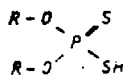
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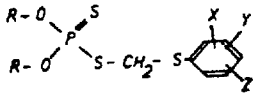
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wherein X and Y represent hydrogen, halogen atoms, alkyl or alkoxy groups containing 1 to 4 carbon atoms or nitro groups, Z represents hydrogen a halogen atom or an alkyl group containing 1 to 4 carbon atoms, and Hal represents chlorine or bromine, with an alkali salt of an acid dithiophosphoric acid-O.O-dialkyl ester of the general formula:

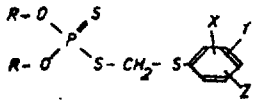


wherein R represents an alkyl group with at most 3 carbon atoms, to form a compound of the general formula:



wherein R, X, Y and Z have the meanings given above.

5. A composition for the control of mites comprising a compound of the general formula



wherein R represents an alkyl group with at most 3 carbon atoms X and Y represent hydrogen, halogen atoms, alkyl or alkoxy groups containing 1 to 4 carbon atoms or nitro groups, and Z represents hydrogen, a halogen atom or an alkyl group containing 1 to 4 carbon atoms, in combination with suitable carriers or distributing agents.

6. A composition as claimed in claim 5 in which an insecticidal, fungicidal, bactericidal, ovicidal or another acaricidal substance is present.

7. Process for the manufacture of dithio-

phosphoric acid esters substantially as herein described.

8. Dithiophosphoric acid esters substantially as herein described.

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