

PATENT SPECIFICATION

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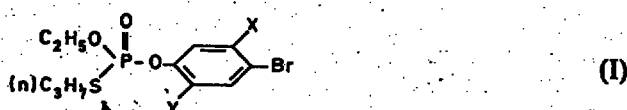


(54) PESTICIDAL O,S-DIALKYL-O-PHENYL THIOPHOSPHORIC ACID ESTERS

(71) We, CIBA-GEIGY A.G., a Swiss body corporate, of 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:—

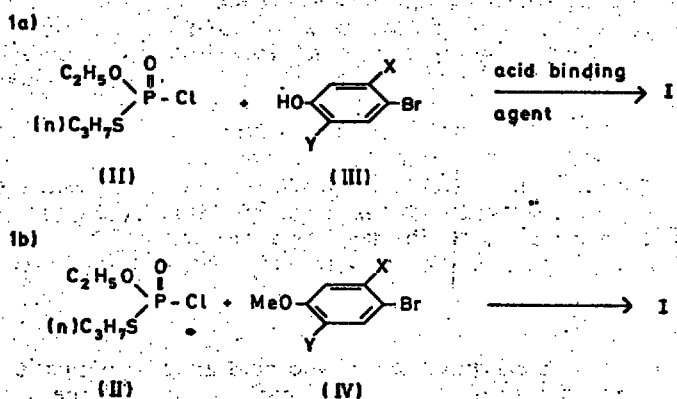
This invention relates to O,S-dialkyl-O-phenyl thiophosphoric acid esters, their preparation and their use in pest control.

According to the present invention there are provided compounds of the formula



wherein X represents a hydrogen atom and Y represents a chlorine atom or X represents a chlorine atom and Y represents a bromine atom.

The compounds of formula I may be prepared by the following processes:



[Price 33p]

price 75p



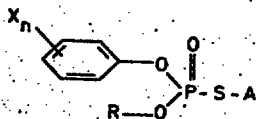
5.

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15

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2.



wherein R is alkyl having up to 5 carbon atoms;

A is alkyl having 3 or 4 carbon atoms, haloalkyl having up to 3 carbon atoms, alkenyl having up to 4 carbon atoms, alkynyl having up to 4 carbon atoms, phenylthioalkyl having up to 9 carbon atoms, phthalimidoalkyl having up to 11 carbon atoms or phenylalkyl having 8 to 10 carbon atoms;

X is halogen or alkyl having up to 5 carbon atoms; and n is 0 or an integer of 1 to 5 inclusive.

It has now been found that the compounds of formula I have surprisingly better action against insects which are phytopathogenic pests and household pests, particularly against cotton pests, compared to similar compounds disclosed in British Patent Specification No. 1214188, Swiss Patent Specification No. 414597 and Canadian Patent Specification No. 833,039. The compounds of formula I also have acaricidal action.

Accordingly the invention further provides a method of combating household pests and/or phytopathogenic pests which are insects or members of the order *Acarina* at a locus, which method comprises applying to the locus a compound of formula I.

The compounds of formula I may be used particularly against phytopathogenic pests. The compounds act above all as contact and stomach poisons. They may be used for combating all development stages such as eggs, larvae, nymphs, pupae and adults of sucking, chewing and boring insects and mites. Thus the compounds of formula I may be used to combat for example household and/or phytopathogenic insect pests of the families: Tettigoniidae, Gryllidae, Gryllotalpidae, Blattidae, Reduviidae, Pyrrhocoridae, Cimicidae, Delphacidae, Aphididae, Diaspididae, Pseudococcidae, Scarabaeidae, Dermestidae, Coccinellidae, Tenebrionidae, Chrysomelidae, Bruchidae, Tineidae, Noctuidae, Lymantriidae, Pyralidae, Culicidae, Tipulidae, Stomoxidae, Trypetidae, Muscidae, Calliphoridae and Pulicidae, as well as *Acarina* especially of the family Tetranychidae which are household and/or phytopathogenic pests.

The compounds of formula I may especially be used in the combating of the pests on cotton plants and vegetables.

The insecticidal and/or acaricidal action can be substantially broadened and matched to given circumstances by the addition of other insecticides or acaricides. Such additional active ingredients may be selected from the group of organophosphorus compounds, nitrophenols and derivatives thereof, ureas, carbamates, chlorinated hydrocarbons, pyrethrin compounds and amidines especially formamidines, especially preferred of which is 1,1-dimethyl-2-(2'-methyl-4'-chlorophenyl)formamide.

The compounds of the formula I may be used as pure active substances or, in composition form together with a solid extender; a solid extender and a surface active agent; or a liquid diluent and a surface active agent. The compositions may be solid or liquid and may contain substances conventionally used in formulation technique such, for example, as solvents, dispersants, wetting agents, adhesives, thickeners, binders and/or fertilisers.

For application, the compounds of the formula I may be processed to conventionally formulated preparations commonly employed in application technology. They may be used as concentrates or dilutions according to circumstances. Examples of such preparations are

in solid form:

dusts, scattering agents or granules,

in liquid form:

a) concentrates of active ingredient dispersible in water:
wettable powders, pastes or emulsifiable concentrates;

b) solutions.

The compositions according to the invention may be manufactured in known manner e.g. by intimately mixing and/or grinding active substances of the formula

I with the suitable extenders, optionally with the addition of dispersants or solvents which are inert towards the active substances.

To manufacture dusts and scattering agents, the active substance is mixed with solid extenders. Suitable extenders are, for example: kaolin, talcum, bolus, loess, chalk, limestone, ground limestone, attaclay, dolomite, diatomaceous earth, precipitated silica, alkaline earth metal silicates, sodium and potassium aluminium silicates (feldspar and mica), calcium and magnesium sulphates, magnesium oxide, ground synthetic materials, fertilisers, for example ammonium sulphate, ammonium phosphate, ammonium nitrate, urea, ground vegetable products, such as corn meal, bark dust, sawdust, nutshell meal, cellulose powder, residues of plant extractions and activated charcoal. These substances can either be used alone or in admixture with one another.

Granular preparations can also readily be manufactured by known methods.

To these mixtures may also be added stabilizers for the active substance and/or non-ionic, anionic and cationic surface active substances, which for example improve the adhesion of the active ingredients on plants or parts of plants (adhesives and agglutinants) and/or ensure a better wettability (wetting agents) and dispersibility (dispersing agents). Suitable adhesives are for example olein/chalk mixture, cellulose derivatives (methyl cellulose, carboxymethyl cellulose), hydroxyethyl glycol ethers of monoalkyl and dialkyl phenols having 5 to 15 ethylene oxide radicals per molecule and 8 to 9 carbon atoms in the alkyl radical, lignin sulfonic acids, their alkali metal and alkaline earth metal salts, polyethylene glycol ethers (Carbowaxes—Carbowax is a Registered Trade Mark), fatty alcohol polyethylene glycol ethers having 5 to 20 ethylene oxide radicals per molecule and 8 to 18 carbon atoms in the fatty alcohol moiety, condensation products of ethylene oxide/propylene oxide, polyvinyl pyrrolidones, polyvinyl alcohols, condensation products of urea and formaldehyde, and also latex products.

The water-dispersible concentrates of the active substance, i.e. wettable powders, pastes and emulsifiable concentrates, are agents which can be diluted with water to any concentration desired. They consist of active substance, extender, optionally additives which stabilize the active substance, surface-active substance and anti-foam agents (e.g. silicone oils) and, optionally, solvents. These concentrates may be manufactured by known methods.

For the manufacture of solutions, the active substance of formula I is dissolved in a suitable organic solvent, mixture of solvent or in water.

The content of active substance in the above described preparation is generally from 0.1% to 95%, preferably between 2 and 40%. In this connection it should be mentioned that if the application is carried out from an aircraft or with some other suitable means, it is possible to use concentrations of up to 99.5% or even pure active substance.

(Parts and percentages throughout this specification are by weight unless otherwise specified.)

The active substances of the formula I can, for example, be formulated as follows:

Dusts

The following substances are used to manufacture a) a 5% and b) a 2% dust:

- a) 5 parts of active substance
95 parts of talcum
- b) 2 parts of active substance
1 part of highly disperse silica
97 parts of talcum.

The active substances are mixed with the extenders and ground.

Granulate

The following substances are used to produce a 5% granulate:

- 5 parts of active substance
- 0.25 parts of epichlorohydrin
- 0.25 parts of cetyl polyglycol ether
- 3.50 parts of polyethylene glycol
- 91 parts of kaolin (particle size 0.3—0.8 mm).

The active substance is mixed with epichlorohydrin and dissolved with 6 parts of acetone; the polyethylene glycol and cetyl polyglycol ether are then added. The

thus obtained solution is sprayed on to kaolin, and the acetone subsequently evaporated in vacuo.

Wettable powder

The following constituents are used for the preparation of a) a 40%, b) and c) and 25%, and d) a 10% wettable powder:

- a) 40 parts of active substance
5 parts of sodium lignin sulphonate
1 part of sodium dibutyl-naphthalene sulphonate
54 parts of silica acid.
- b) 25 parts of active substance
4.5 parts of calcium lignin sulphonate
1.9 parts of Champagne chalk/hydroxyethyl cellulose mixture (1:1)
1.5 parts of sodium dibutyl naphthalene sulphate
19.5 parts of silica acid
19.5 parts of Champagne chalk
28.1 parts of kaolin.
- c) 25 parts of active substance
2.5 parts of isooctylphenoxy-polyoxyethylene-ethanol
1.7 parts of Champagne chalk/hydroxyethyl cellulose mixture (1:1)
8.3 parts of sodium aluminium silicate
16.5 parts of kieselguhr
46 parts of kaolin
- d) 10 parts of active substance
3 parts of a mixture of the sodium salts of saturated fatty alcohol sulphate
5 parts of naphthalenesulphonic acid/formaldehyde condensate
82 parts of kaolin.

The active substances are intimately mixed, in suitable mixers, with the additives, the mixture being then ground in an appropriate mill and roller. Wettable powders are obtained which can be diluted with water to give suspensions of any desired concentration.

Emulsifiable concentrates

The following substances are used to produce a) a 10% and b) a 25% emulsifiable concentrate:

- a) 10 parts of active substance
3.4 parts of epoxidised vegetable oil
3.4 parts of a combination emulsifier consisting of fatty alcohol polyglycol ether and alkylarylsulphonate calcium salt
40 parts of dimethylformamide
43.2 parts of xylene.
- b) 25 parts of active substance
2.5 parts of epoxidised vegetable oil
10 parts of an alkylarylsulphonate/fatty alcohol polyglycol ether mixture
5 parts of dimethylformamide
57.5 parts of xylene.

From these concentrates it is possible to produce, by dilution with water, emulsions of desired concentration.

Sprays

The following substances are used to manufacture 5% spray:

- 5 parts active substance
1 part epichlorohydrin
94 parts petrol (boiling range 160—190°C)

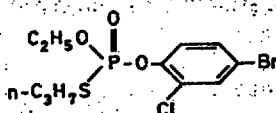
The following Examples further illustrate the present invention.

EXAMPLE 1.

31.1 g (0.15 mole) 2-chloro-4-bromophenol were dissolved in 150 ml benzene and 15.1 g triethylamine were then added. At 10—15°C, 32.0 g of O-ethyl-S-n-propyl-chlorothiophosphate were added dropwise with continuous stirring. Stirring was then continued for 12 hours at room temperature. The mixture was washed with water, 3% Na₂CO₃ solution and water and dried over anhydrous

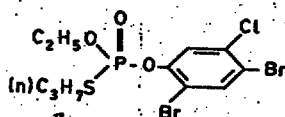
sodium sulphate. The benzene was distilled off and the residue purified by distillation (at 130°C/0.01 torr).

49 g of the ester of the formula



with a refractive index n_D^{20} 1.5466 was obtained.

The following compound was made in analogous fashion:



n_D^{24} 1.5719

EXAMPLE 2.

Insecticidal ingest poison action

Tobacco and potato plants are sprayed with a 0.05% aqueous emulsion (obtained from a 10% emulsifiable concentrate).

After the coating has dried, Egyptian cotton leaf worms (*Spodoptera litoralis*) are settled on the tobacco plants and Colorado potato beetle larvae (*Leptinotarsa decemlineata*) on the potato plants. The test is carried out at 24°C and 60% relative humidity.

The compounds according to Example 1 have an ingest poison action against *Spodoptera litoralis* and *Leptinotarsa decemlineata* in the above test.

EXAMPLE 3.

Acaricidal action

Phaseolus vulgaris (dwarf beans) have an infested piece of leaf from a mass culture of *Tetranychus urticae* placed on them 12 hours before the test for the acaricidal action. The occupying mobile stages are sprayed with the emulsified test preparations from a chromatography atomiser so that the spray broth does not run off. The number of living and dead larvae, adults and eggs are evaluated after 7 days under a stereoscopic microscope. During the "interim", the treated plants are kept in greenhouse compartments at 25°C.

The compounds according to Example 1 are active in the above test against eggs, larvae and adults of *Tetranychus urticae*.

EXAMPLE 4.

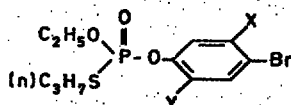
Action against household pests

A dust on a base of talcum and containing 5% active substance was applied to filter paper in concentrations of 200, 100, 50, 25 and 12.6 mg active substance per m². Onto each of the treated substrates were applied 5 *Periplaneta americana*, *Dermestes frischii*, *Tribolium confusum* and *Oryzaephilus surinamensis*. After 24 hours the test was evaluated.

In the above test the compounds of formula I proved effective against *Periplaneta americana*, *Dermestes frischii*, *Tribolium confusum* and *Oryzaephilus surinamensis*.

WHAT WE CLAIM IS:—

1. A compound of the formula

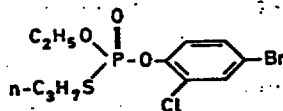


wherein X represents a hydrogen atom and Y represents a chlorine atom or X represents a chlorine atom and Y represents a bromine atom.

2. The compound

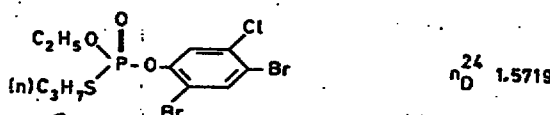
sodium sulphate. The benzene was distilled off and the residue purified by distillation (at 130°C/0.01 torr).

49 g of the ester of the formula



with a refractive index n_D^{20} 1.5466 was obtained.

The following compound was made in analogous fashion:



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The compounds according to Example 1 are active in the above test against eggs, larvae and adults of *Tetranychus urticae*.

EXAMPLE 4.

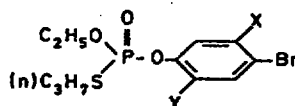
Action against household pests

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In the above test the compounds of formula I proved effective against *Periplaneta americana*, *Dermestes frischii*, *Tribolium confusum* and *Oryzaephilus surinamensis*.

WHAT WE CLAIM IS:—

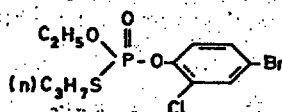
1. A compound of the formula



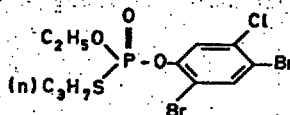
wherein X represents a hydrogen atom and Y represents a chlorine atom or X represents a chlorine atom and Y represents a bromine atom.

2. The compound

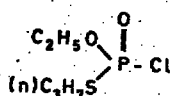




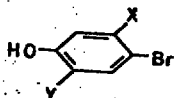
3. The compound



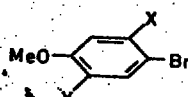
4. A process for preparing a compound as claimed in claim 1 which process comprises reacting a compound of the formula



with a phenol of the formula



in the presence of an acid-binding agent, or with a phenolate of the formula



wherein X and Y are as defined in claim 1 and Me represents an alkali metal atom or an ammonium or alkylammonium group.

5. A process for preparing a compound as claimed in claim 1 substantially as hereinbefore described with reference to Example 1.

6. A compound according to claim 1 prepared by the process claimed in claim 4 or 5.

7. A pesticidal composition which comprises, as active ingredient, a compound as claimed in any one of claims 1 to 3 together with a solid extender; a solid extender and a surface active agent; or a liquid diluent and a surface active agent.

8. A pesticidal composition containing a compound as claimed in claim 1 and in the form of a dust, granulate, wettable powder, emulsifiable concentrate or spray specifically described herein.

9. A method of combating household pests and/or phytopathogenic pests which are insects or members of the order *Acarina* at a locus, with method comprising applying to the locus a compound as claimed in any one of claims 1 to 3.

10. A method according to claim 9 wherein the pests are insects harmful to cotton or vegetables.

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Reference has been directed in pursuance of section 9, subsection (1) of the Patents Act 1949, to Patent No. 1,311,773.

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