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PATENT SPECIFICATION

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 (72) Inventors HANS-JOCHIM RIEBEL, INGEBORG HAMMANN
 and WILHELM STENDEL



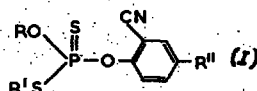
(54) 2-CYANOPHENYLDITHIOPHOSPHORIC ACID ESTERS,
 PROCESS FOR THEIR PREPARATION AND THEIR USE AS
 INSECTICIDES OR ACARICIDES

(71) We, BAYER AKTIENGESELLSCHAFT, a body corporate, organised under the laws of Germany, of Leverkusen, Germany, 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 relates to certain 2-cyanophenyldithiophosphoric acid esters, to a process for their preparation and to their use as insecticides or acaricides.

It has already been disclosed that 2-cyanophenylthiophosphoric acid esters, for example O,O - diethyl - O - (2 - cyanophenyl) - thionophosphoric acid ester, possess good insecticidal and acaricidal properties (compare Belgian Patent Specification 627,817). However, these compounds have a high toxicity to warm-blooded animals.

The present invention provides 2-cyanophenyldithiophosphoric acid esters of the general formula



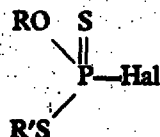
in which

R and R' are the same or different alkyls each with 1 to 6 carbon atoms, and R'' is hydrogen or bromine.

R and R', which may be straight chain or branched alkyl, preferably each have 1 to 4 carbon atoms.

These compounds exhibit a very good insecticidal and acaricidal activity and in addition a low toxicity to warm-blooded animals.

The invention also provides a process for the production of a 2-cyanophenyl-dithiophosphoric acid ester of the formula (I) in which a dithiophosphoric acid ester-halide of the general formula

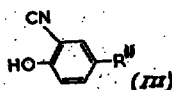


(II)

in which

R and R' have the abovementioned meanings, and

Hal is halogen (preferably chlorine) is reacted with a 2-cyanophenol of the general formula

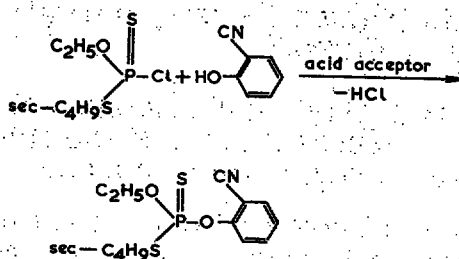


in which

R" has the abovementioned meaning optionally in the presence of an acid acceptor, or in the form of an alkali metal salt, alkaline earth metal salt or ammonium salt, and optionally in the presence of a solvent.

Surprisingly, the 2-cyanophenyldithiophosphoric acid esters (I) according to the invention, whilst having a very low toxicity to warm-blooded animals, exhibit a better insecticidal and acaricidal action than previously known compounds. The compounds according to the invention thus represent a genuine enrichment of the art.

If, for example, O - ethyl - S - sec. - butyl - thionothiophosphoric acid ester-chloride and 2-cyanophenol are used, the course of the reaction can be represented by the following equation:



The formulae (II) and (III) provide an unambiguous general definition of the starting materials which can be used in the process of the invention.

The O,S - dialkyl - thionothiophosphoric acid ester halides (II) to be used as starting materials can be prepared by conventional methods (compare USSR Patent Specification 184,863 and published Japanese Patent Application 5536/72).

The following are specific examples of such compounds: O - ethyl - S - n-propyl-, O - ethyl - S - n - butyl-, O - ethyl - S - sec. - butyl-, O - ethyl - S - tert-butyl-, O - n - propyl - S - n - propyl-, O - n - propyl - S - sec. - butyl-, O - n-propyl - S - iso - butyl-, O - n - propyl - S - tert. - butyl-, O - iso - propyl - S - n-butyl- and O - iso - propyl - S - sec. - butyl - thionothiophosphoric acid ester chloride.

The cyanophenols (III) which are also used as starting materials are described in the literature and are obtainable by conventional methods [compare Berichte der deutschen Chemischen Gesellschaft 26, 2623 (1893); 31, 3042 (1898)].

The reaction according to the present invention is preferably carried out in the presence of a solvent (this term includes a mere diluent). Practically all inert organic solvents can be employed for this purpose. These include, in particular, aliphatic and aromatic (optionally chlorinated) hydrocarbons, for example benzene, toluene, xylene, benzine, methylene chloride, chloroform, carbon tetrachloride and chlorobenzene; ethers, for example diethyl ether, dibutyl ether and dioxan; ketones, for example acetone, methyl ethyl ketone, methyl isopropyl ketone and methyl isobutyl ketone; and nitriles, for example acetonitrile and propionitrile.

All customary acid-binding agents can be used as acid acceptors. Alkali metal carbonates and alkali metal alcoholates, such as sodium carbonate and potassium carbonate, sodium methylate and ethylate and potassium methylate and ethylate, have proved particularly suitable, as have aliphatic, aromatic or heterocyclic amines, for example triethylamine, dimethylaniline, dimethylbenzylamine and pyridine.

The reaction temperature can be varied within a wide range. In general, the reaction is carried out at 0 to 100, preferably at 15 to 60°C.

The reaction is in general allowed to take place under normal pressure.

To carry out the process, the starting materials are in most cases employed in equimolar ratio. An excess of one or other reactant seems to produce no significant advantages. The reaction is in general carried out in a solvent in the presence of an acid acceptor and is completed by stirring for between one and several hours at elevated temperatures. The mixture is then cooled and poured into an organic solvent, for example toluene. The organic phase may then be washed with saturated sodium carbonate solution and subsequently with water and dried, the solvent distilled off under reduced pressure and the residue purified by "slight distillation".

Some of the new compounds are obtained in the form of oils which in most cases cannot be distilled without decomposition but can be freed from remaining volatile impurities by so-called "slight distillation", that is to say prolonged heating under reduced pressure to moderately elevated temperatures, and they can be purified in this

way. They are characterised by their refractive index.

As already mentioned, the 2-cyanophenyldithiophosphoric acid esters (I) according to the invention are distinguished by a very good insecticidal and acaricidal activity coupled with very low toxicity to warm-blooded animals. They possess a good action both against sucking and biting insects and against mites (*Acarina*). For this reason, the compounds according to the invention can be employed with success as pesticides in plant protection, in the hygiene field and in the field of protection of stored products and/or in the veterinary medicine field against animal ectoparasites.

To the sucking insects there belong, in the main, aphids (*Aphididae*) such as the green peach aphid (*Myzus persicae*), the bean aphid (*Doralis fabae*), the bird cherry aphid (*Rhopalosiphum padi*), the pea aphid (*Macrosiphum pisi*) and the potato aphid (*Macrosiphum solanifolii*), the currant gall aphid (*Cryptomyzus korschelti*), the rosy apple aphid (*Sappaphis mali*), the mealy plum aphid (*Hyalopteris arundinis*) and the cherry black-fly (*Myzus cerasi*); in addition, scales and mealybugs (*Coccina*), for example the oleander scale (*Aspidiotus hederæ*) and the soft scale (*Lecanium hesperidum*) as well as the grape mealybug (*Pseudococcus maritimus*); thrips (*Thysanoptera*), such as *Hercinothrips femoralis*, and bugs, for example the beet bug (*Piesma quadrata*), the red cotton bug (*Dysdercus intermedius*), the red bug (*Cimex lectularius*), the assassin bug (*Rhodnius prolixus*) and Chavas' bug (*Triatoma infestans*) and, further cicadas, such as *Euscelis bilobatus* and *Nephotettix bipunctatus*.

In the case of the biting insects, above all there should be mentioned butterfly and moth caterpillars (*Lepidoptera*) such as the diamond-back moth (*Plutella maculipennis*), the gipsy moth (*Lymantria dispar*), the brown-tail moth (*Euproctis chrysorrhoea*) and tent caterpillar (*Malacosoma neustria*); further, the cabbage moth (*Mamestra brassicae*) and the cutworm (*Agrotis segetum*), the large white butterfly (*Pieris brassicae*), the small winter moth (*Cheimatobia brumata*), the green oak tortrix moth (*Tortrix viridana*), the fall armyworm (*Laphygma frugiperda*) and cotton worm (*Prodenia litura*), the ermine moth (*Hyponomeuta padella*), the Mediterranean flour moth (*Ephestia kühniella*) and greater wax moth (*Galleria mellonella*).

Also to be classed with the biting insects are beetles (*Coleoptera*), for example the granary weevil (*Sitophilus granarius*=*Calandra granaria*), the Colorado beetle (*Leptinotarsa decemlineata*), the dock beetle (*Gastrophysa viridula*), the mustard beetle (*Phaedon cochleariae*), the blossom beetle (*Meligethes aeneus*), the raspberry beetle (*Byturus tomentosus*), the bean weevil (*Bruchidius*=*Acanthoscelides obtectus*), the leather beetle (*Dermestes frischi*), the khapra beetle (*Trogoderma granarium*), the flour beetle (*Tribolium castaneum*), the northern corn billbug (*Calandra* or *Sitophilus zeamais*), the drugstore beetle (*Stegobium paniceum*), the yellow mealworm (*Tenebrio molitor*) and the saw-toothed grain beetle (*Oryzaephilus surinamensis*), but also species living in the soil, for example wireworms (*Agriotes spec.*) and larvae of the cockchafer (*Melolontha melolontha*); cockroaches, such as the German cockroach (*Blattella germanica*), American cockroach (*Periplaneta americana*), Madeira cockroach (*Leucophaea* or *Rhyparobia maderae*), oriental cockroach (*Blatta orientalis*), the giant cockroach (*Blaberus giganteus*) and the black giant cockroach (*Blaberus fuscus*) as well as *Henschoutedenia flexivitta*; further, *Orthoptera*, for example the house cricket (*Gryllus domesticus*); termites such as the eastern subterranean termite (*Reticulitermes flavipes*) and *Hymenoptera* such as ants, for example the garden ant (*Lasius niger*).

The *Diptera* comprise essentially the flies, such as the vinegar fly (*Drosophila melanogaster*), the Mediterranean fruit fly (*Ceratitidis capitata*), the house fly (*Musca domestica*), the little house fly (*Fannia canicularis*), the black blow fly (*Phormia regina*) and bluebottle fly (*Calliphora erythrocephala*) as well as the stable fly (*Stomoxys calcitrans*); further, gnats, for example mosquitoes such as the yellow fever mosquito (*Aedes aegypti*), the northern house mosquito (*Culex pipiens*) and the malaria mosquito (*Anopheles stephensi*).

With the mites (*Acari*) there are classed, in particular, the spider mites (*Tetranychidae*) such as the two-spotted spider mite (*Tetranychus urticae*) and the European red mite (*Paratetranychus pilosus*=*Panonychus ulmi*), gall mites, for example the blackcurrant gall mite (*Eriophyes ribis*) and tarsonemids, for example the broad mite (*Hemitarsonemus latus*) and the cyclamen mite (*Tarsonemus pallidus*); finally, ticks, such as the relapsing fever tick (*Ornithodoros moubata*).

When applied against hygiene pests and pests of stored products, particularly flies and mosquitoes, the compounds of the invention are also distinguished by an

outstanding residual activity on wood and clay, as well as a good stability to alkali on limed substrates.

The active compounds according to the present invention can be converted into the usual formulations, such as solutions, emulsions, suspensions, powders, pastes and granulates. These may be produced in known manner, for example by mixing the active compounds with extenders, that is, liquid or solid or liquefied gaseous diluents or carriers, optionally with the use of surface-active agents, that is, emulsifying agents and/or dispersing agents, and/or foam-forming agents. In the case of the use of water as an extender, organic solvents can, for example, also be used as auxiliary solvents.

As liquid diluents or carriers, there are preferably used aromatic hydrocarbons, such as xylenes, toluene, benzene or alkyl naphthalenes, chlorinated aromatic or aliphatic hydrocarbons, such as chlorobenzenes, chloroethylenes or methylene chloride, aliphatic hydrocarbons, such as cyclohexane or paraffins, for example mineral oil fractions, alcohols, such as butanol or glycol as well as their ethers and esters, ketones, such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, or strongly polar solvents, such as dimethyl formamide, dimethyl sulphoxide or acetonitrile, as well as water.

By liquefied gaseous diluents or carriers are meant liquids which would be gaseous at normal temperatures and pressures, e.g. aerosol propellants, such as halogenated hydrocarbons, e.g. Freon "Freon" is a Registered Trade Mark.

As solid diluents or carriers, there are preferably used ground natural minerals, such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, or ground synthetic minerals, such as highly-dispersed silicic acid, alumina or silicates.

Preferred examples of emulsifying and foam-forming agents include non-ionic and anionic emulsifiers, such as polyoxyethylene-fatty acid esters, polyoxyethylene-fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkyl sulphonates, alkyl sulphates and aryl sulphonates as well as albumin hydrolyzation products; and preferred examples of dispersing agents include lignin, sulphite waste liquors and methyl cellulose.

The active compounds according to the invention can be used as a mixture with other active compounds.

The formulations in general contain from 0.1 to 95 per cent by weight of active compound, preferably 0.5 to 90%.

The active compounds can be used as such or in the form of their formulations or the application forms prepared therefrom, such as ready-to-use solutions, emulsions, foams, suspensions, powders, pastes, soluble powders, dusting agents and granules. They may be applied in the customary manner, for example by squirting, spraying, atomising, dusting, scattering, fumigating, gassing, watering, dressing or encrusting.

The compositions may be diluted for actual application, and the active compound concentrations in the ready-to-use preparations can be varied within wide ranges. In general, they are from 0.0001 to 10%, preferably 0.01 to 1%, by weight.

The active compounds can also be used with good success in the ultra-low volume (ULV) method where it is possible to apply formulations of up to 95% strength or even the 100% strength active compound by itself.

The invention therefore provides an insecticidal or acaricidal composition containing as active ingredient a compound according to the invention in admixture with a solid or liquefied gaseous diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.

The invention also provides a method of combating insect or acarid pests which comprises applying to the pests or a habitat thereof a compound according to the invention alone or in the form of a composition containing as active ingredient a compound according to the invention in admixture with a diluent or carrier.

The invention also provides a method of combating animal ectoparasites which comprises applying to the animal a compound according to the invention alone or in the form of a composition containing as active ingredient a compound according to the invention in admixture with a diluent or carrier.

The invention also provides crops protected from damage by insects or acarids by being grown in areas in which, immediately prior to and/or during the time of the growing, a compound according to the invention was applied alone or in admixture with a diluent or carrier. It will be seen that the usual methods of providing a harvested crop may be improved by the present invention.

The compounds according to the invention and the preparation and use of the

compounds according to the invention, are illustrated by the following Examples.

In Examples A to D, the active compounds according to the invention were tested for their activity against various pests of plants and animals, in comparison to the previously known O,O - diethyl - O - (2 - cyanophenyl) - thionophosphoric acid ester, which is referred to as (A) in these Examples. In these Examples the compounds according to the invention were identified by the numbers shown in brackets, which correspond to those of the preparation Examples 1 and 2 in which these compounds were prepared.

Example A.

Plutella test

Solvent: 3 parts by weight of acetone

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of the active compound was mixed with the stated amount of solvent containing the stated amount of emulsifier and the concentrate was diluted with water to the desired concentration.

Cabbage leaves (*Brassica oleracea*) were sprayed with the preparation of the active compound until dew moist and were then infested with caterpillars of the diamond-back moth (*Plutella maculipennis*).

After the specified periods of time, the degree of destruction was determined as a percentage: 100% means that all the caterpillars were killed whereas 0% means that none of the caterpillars were killed.

The active compounds, the concentrations of the active compounds, the evaluation times and the results can be seen in Table A.

TABLE A

(Plutella test)

Active compound	Active compound concentration in % by weight	Degree of destruction in % after 3 days
(A)	0.1	100
	0.01	100
	0.001	0
(2)	0.1	100
	0.01	100
	0.001	95
(1)	0.1	100
	0.01	100
	0.001	100
	0.0001	100

Example B.

Myzus test (contact action)

Solvent: 3 parts by weight of acetone

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of the active compound was mixed with the stated amount of solvent containing the stated amount of emulsifier and the concentrate was diluted with water to the desired concentration.

Cabbage plants (*Brassica oleracea*) which had been heavily infested with peach aphids (*Myzus persicae*) were sprayed with the preparation of the active compound until dripping wet.

After the specified periods of time, the degree of destruction was determined as a percentage: 100% means that all the aphids were killed whereas 0% means that none of the aphids were killed.

The active compounds, the concentrations of the active compounds, the evaluation times and the results can be seen in Table B.

TABLE B

(Myzus test)

Active compound	Active compound concentration in % by weight	Degree of destruction in % after 1 day
(A)	0.1	100
	0.01	50
	0.001	0
(2)	0.1	100
	0.01	100
	0.001	95
(1)	0.1	100
	0.01	100
	0.001	100
	0.0001	50

Example C.

Tetranychus test (resistant)

Solvent: 3 parts by weight of acetone

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of the active compound was mixed with the stated amount of solvent containing the stated amount of emulsifier and the concentrate was diluted with water to the desired concentration.

Bean plants (*Phaseolus vulgaris*), which had a height of approximately 10—30 cm, were sprayed with the preparation of the active compound until dripping wet. These bean plants were heavily infested with the common or two-spotted spider mite (*Tetranychus urticae*) in all stages of development.

After the specified periods of time, the effectiveness of the preparation of active compound was determined by counting the dead mites. The degree of destruction thus obtained was expressed as a percentage: 100% means that all the spider mites were killed whereas 0% means that none of the spider mites were killed.

The active compounds, the concentrations of the active compounds, the evaluation times and the results can be seen in Table C.

TABLE C

(Tetranychus test/resistant)

Active compound	Active compound concentration in % by weight	Degree of destruction in % after 2 days
(A)	0.1	0
(2)	0.1	100
	0.01	85
(1)	0.1	99
	0.01	45

Example D.

Test with parasitic fly larvae

Solvent: 35 parts by weight of ethylene polyglycol monomethyl ether
35 parts by weight of nonylphenol polyglycol ether

5 To produce a suitable preparation of active compound, 30 parts by weight of the active substance in question were mixed with the stated amount of solvent which contained the abovementioned proportion of emulsifier and the concentrate thus obtained was diluted with water to the desired concentration.

10 About 20 fly larvae (*Lucilia cuprina*) were introduced into a test tube which contained approximately 2 cm³ of horse muscle. 0.5 ml of the preparation of active compound was applied to this horse meat. After 24 hours, the degree of destruction in % was determined. 100% means that all larvae had been killed and 0% means that no larvae had been killed.

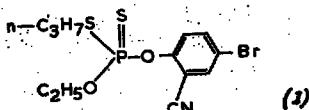
The results obtained can be seen in Table D.

TABLE D

(Test with parasitic fly larvae/*Lucilia cuprina*, resistant)

Active compound	Active compound concentration in ppm by weight	Degree of destruction in %
(2)	100	100
	30	100
	10	100
	3	100
	1	100
	0.3	0

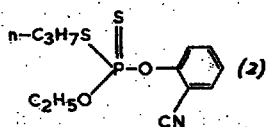
Example 1.



20 21.8 g (0.1 mol of O - ethyl - S - n - propyl - thionothiophosphoric acid diester chloride were added dropwise to a mixture of 19.8 g (0.1 mol) of 2 - cyano - 4 - bromophenol and 14.5 g (0.105 mol) of potassium carbonate in 200 ml of acetonitrile. The mixture was allowed to react for a further 3 hours at 50 to 60°C and was then cooled, and the batch was poured into 500 ml of toluene. The organic phase was washed with saturated sodium carbonate solution and with water and dried over sodium sulphate. The solvent was then evaporated off under reduced pressure and the residue was subjected to "slight distillation". 25 g (65.5% of theory) of O - ethyl - S - n - propyl - O - (2 - cyano - 4 - bromophenyl) - thionothiophosphoric acid ester were obtained in the form of a yellow oil of refractive index $n_D^{21} = 1.5796$.

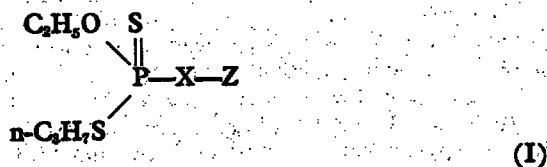
Example 2.

30 The following compound was prepared by a method analogous to that of Example 1.



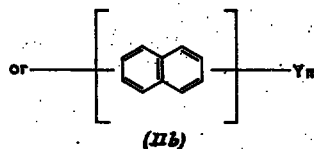
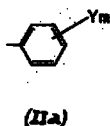
Refractive index: $n_D^{22}=1.5558$ Yield: 68% of theory.

Our Patent 1,295,418 describes and claims phosphoric acid esters of the general formula



in which

X is an oxygen or sulphur atom, and
Z is a group of the formula



in which

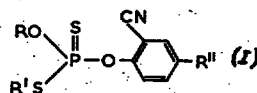
Y is a halogen atom or a C_{1-4} alkyl, C_{1-4} alkoxy, C_{1-4} alkylmercapto, C_{1-4} alkylsulphinyl, nitro, cyano or phenyl group, and

m is 0, 1, 2 or 3, the radicals Y being selected independently when m is 2 or 3.

Patent 1,295,418 also describes and claims an insecticidal, acaricidal or nematocidal composition containing as active ingredient a compound as claimed above in admixture with a diluent or carrier.

WHAT WE CLAIM IS:—

1. 2-Cyanophenyldithiophosphoric acid esters of the general formula

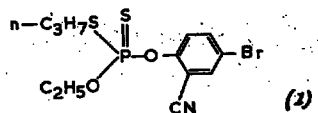


in which

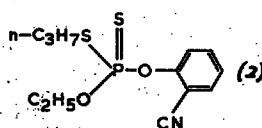
R and R' are the same or different alkyls each with 1 to 6 carbon atoms, and
R'' is hydrogen or bromine.

2. Compounds according to claim 1 in which R and R' each have 1 to 4 carbon atoms.

3. The compound of the formula



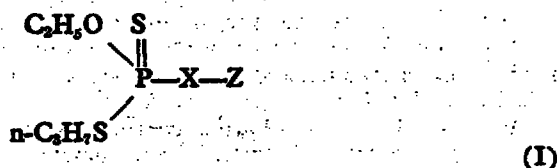
4. The compound of the formula



5. A process for the preparation of a 2-cyanophenyldithiophosphoric acid ester according to any of claims 1—4 in which a dithiophosphoric acid ester halide of the general formula

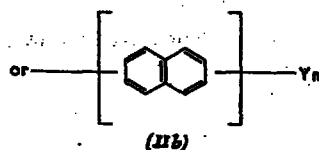
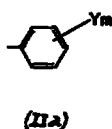
Refractive index: $n_D^{25} = 1.5558$ Yield: 68% of theory.

Our Patent 1,295,418 describes and claims phosphoric acid esters of the general formula



in which

X is an oxygen or sulphur atom, and
Z is a group of the formula



in which

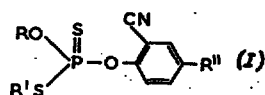
Y is a halogen atom or a C_{1-4} alkyl, C_{1-4} alkoxy, C_{1-4} alkylmercapto, C_{1-4} alkylsulphinyl, nitro, cyano or phenyl group, and

m is 0, 1, 2 or 3, the radicals Y being selected independently when m is 2 or 3.

Patent 1,295,418 also describes and claims an insecticidal, acaricidal or nematocidal composition containing as active ingredient a compound as claimed above in admixture with a diluent or carrier.

WHAT WE CLAIM IS:—

1. 2-Cyanophenyldithiophosphoric acid esters of the general formula

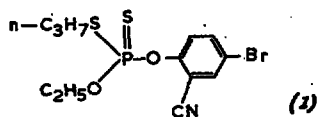


in which

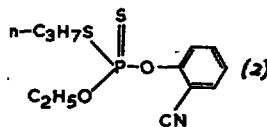
R and R' are the same or different alkyls each with 1 to 6 carbon atoms, and
R'' is hydrogen or bromine.

2. Compounds according to claim 1 in which R and R' each have 1 to 4 carbon atoms.

3. The compound of the formula

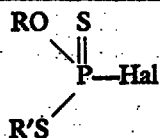


4. The compound of the formula



5. A process for the preparation of a 2-cyanophenyldithiophosphoric acid ester according to any of claims 1—4 in which a dithiophosphoric acid ester halide of the general formula

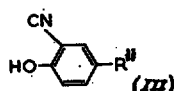




(II)

in which

R and R' have the meanings indicated in claim 1 and
Hal is halogen, is reacted with a 2-cyanophenol of the general formula



in which

R'' has the meaning indicated in claim 1, optionally in the presence of an acid acceptor or in the form of an alkali metal salt, alkaline earth metal salt or ammonium salt.

6. A process according to claim 5 in which the reaction is carried out in the presence of a solvent.

7. A process according to claim 5 or 6 in which Hal is chlorine.

8. A process according to any of claims 5—7 in which the reaction is carried out at 15 to 60°C.

9. A process according to any of claims 5—8 in which the ester halide of formula (II) is any of those hereinbefore specifically identified.

10. A process for the preparation of a compound according to claim 1, substantially as hereinbefore described in Example 1 or 2.

11. Compounds according to claim 1 whenever prepared by a process according to any of claims 5—10.

12. An insecticidal or acaricidal composition containing as active ingredient a compound according to any of claims 1—4 or 11 in admixture with a solid or liquefied gaseous diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.

13. A composition according to claim 12 containing from 0.1 to 95% of the active compound by weight.

14. A method of combating insect or acarid pests which comprises applying to the pests or a habitat thereof a compound according to any of claims 1—4 or 11 alone or in the form of a composition containing as active ingredient a compound according to any of claims 1—4 or 11 in admixture with a diluent or carrier.

15. A method of combating animal ectoparasites which comprises applying to the animal a compound according to any of claims 1—4 or 11 alone or in the form of a composition containing as active ingredient a compound according to any of claims 1—4 or 11 in admixture with a diluent or carrier.

16. A method according to claim 14 or 15 in which a composition is used containing from 0.0001 to 10% of the active compound, by weight.

17. Crops protected from the damage by insects or acarids by being grown in areas in which, immediately prior to and/or during the time of the growing, a compound according to any of claims 1—4 or 11 was applied alone or in admixture with a diluent or carrier.

For the Applicants:
CARPMAELS & RANSFORD,
Chartered Patent Agents,
43 Bloomsbury Square,
London WC1A 2RA.

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