

PATENT SPECIFICATION

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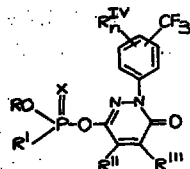
(54) NOVEL (THIONO)(THIOL)PHOSPHORIC(PHOSPHONIC) ACID ESTERS AND ESTER-AMIDES AND THEIR USE AS INSECTICIDES AND ACARICIDES

(71) We, BAYER AKTIENGESSELLSCHAFT, 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 new pyridazinyl (thiono)(thiol)phosphoric(phosphonic) acid esters and ester-amides, to a process for their preparation and to their use as insecticides and acaricides.

It is already known that O,O-dialkyl-O-pyridazinyl-thiophosphoric acid esters, for example O[1-phenyl-1,6-dihydro-6-oxo-pyridazin(3)yl]-, O-[1-hydroxymethyl-1,6-dihydro-6-oxo-pyridazin(3)yl]-, O-[1-(N,N-dimethylaminomethyl)-1,6-dihydro-6-oxo-pyridazin(3)yl]- and O-[1-(p-methylphenyl)-1,6-dihydro-6-oxo-pyridazin(3)yl]-O,O-diethylthionophosphoric acid esters possess insecticidal and acaricidal properties [see U.S. Patent Specification 2,759,937, Japanese published Patent Application 20,025/72 and Journal of Organic Chemistry, volume 26, No.9 (1961), pages 3,382—3,386].

The present invention provides, as new compounds, the pyridazinyl(thiono)(thiol)phosphoric(phosphonic) acid esters and ester-amides of the general formula



(I)

in which
R is alkyl with 1 to 6 carbon atoms,
R' is phenyl, alkyl with 1 to 4 carbon atoms, alkoxy with 1 to 6 carbon atoms, alkylthio with 1 to 6 carbon atoms or monoalkylamino or dialkylamino with 1 to 4 carbon atoms in the or each alkyl group,

R'' and R''', which may be identical or different, are each hydrogen or methyl, and

R''V is hydrogen, halogen, nitro or halogenoalkyl with 1 to 3 carbon atoms, n is an integer from 1 to 4 and X is oxygen or sulphur.

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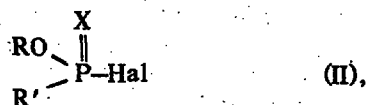
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The compounds of the formula (I) have been found to possess strong insecticidal and acaricidal properties.

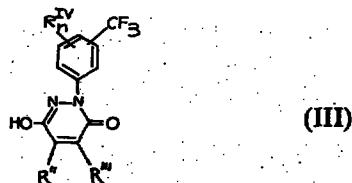
Preferably R is straight-chain or branched alkyl with 1 to 5 (especially 1 to 4) carbon atoms, R' is phenyl, straight-chain or branched alkyl with 1 to 3 (especially 1 or 2) carbon atoms, straight-chain or branched alkoxy or alkylthio, each with 1 to 5 (especially 1 to 4) carbon atoms, or monoalkylamino or dialkylamino with 1 to 3 (especially 1 or 2) carbon atoms per alkyl group, R^{IV} is hydrogen, chlorine, nitro or trifluoromethyl, and n is 1, 2 or 3 (especially 1).

The invention also provides a process for the preparation of a pyridazinyl(thiono)(thiol)phosphoric(phosphonic) acid ester or ester-amide of the formula (I), in which a (thiono)(thiol)phosphoric(phosphonic) acid ester halide or ester-amide halide of the general formula



in which

R, R' and X have the above-mentioned meanings and Hal is halogen, is reacted with a 1-phenyl-3-hydroxy-1,6-dihydro-pyridazinone-(6) derivative of the general formula



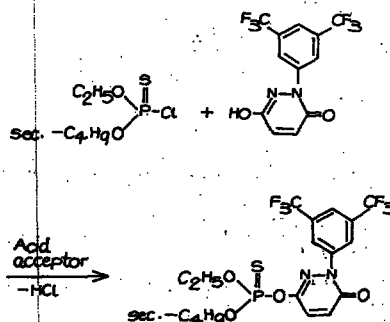
in which

R'', R''', R^{IV} and n have the above-mentioned meanings, if appropriate in the presence of a solvent or diluent, and if appropriate in the presence of an acid acceptor.

Surprisingly, the pyridazinyl(thiono)(thiol)phosphoric(phosphonic) acid esters and ester-amides according to the invention exhibit a better insecticidal and acaricidal action than the previously known O,O-diethyl-O-pyridazinyl-thiono-phosphoric acid ester derivatives of analogous structure and of the same type of action.

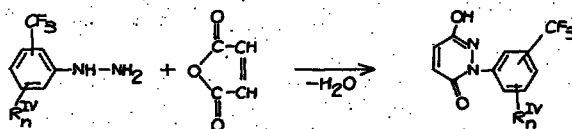
The new compounds are not only active against insects and mites which damage plants but are also active against pests harmful to health and pests of stored products and, in the veterinary medicine field, against animal ectoparasites, for example parasitic fly larvae. Accordingly, they represent an enrichment of the art.

If, for example, O-ethyl-O-sec.-butyl-thionophosphoric acid diester chloride and 1-(3,5-bis-trifluoromethylphenyl)-3-hydroxy-6-oxo-pyridazine are used as starting materials, the course of the reaction can be represented by the following equation:



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The (thiono)(thiol)phosphoric(phosphonic) acid ester halides and ester-amide halides (II) are known and can be prepared according to processes described in the literature, as can the 1-phenyl-3-hydroxy-1,6-dihydro-6-oxo-pyridazine derivatives (III), which can be prepared, for example, from the correspondingly substituted phenylhydrazines, dissolved in dilute hydrochloric acid, by reaction with maleic anhydride in accordance with the following equation:



wherein

R^{IV} and *n* have the above-mentioned meanings.

The following may be mentioned as examples of (thiono)(thiol)phosphoric(phosphonic) acid ester halides to be reacted in accordance with the process: O,O-dimethyl-, O,O-diethyl-, O,O-di-n-propyl-, O,O-di-isopropyl-, O,O-di-n-butyl-, O,O-di-isobutyl-, O,O-di-sec-butyl-, O,O-di-tert-butyl-, O-ethyl-O-n-propyl-, O-ethyl-O-isopropyl-, O-n-butyl-O-ethyl-, O-ethyl-O-sec-butyl- and O-ethyl-O-methylphosphoric acid diester chlorides and the corresponding thiono analogues; O-methyl-, O-ethyl-, O-n-propyl-, O-isopropyl-, O-n-butyl-, O-sec-butyl- and O-tert-butyl-methane-, ethane-, n-propane-, isopropane-, and phenylphosphoric acid ester chlorides and the corresponding thiono analogues; O,S-dimethyl-, O,S-diethyl-, O,S-di-n-propyl-, O,S-di-isopropyl-, O,S-di-n-butyl-, O,S-di-isobutyl-, O,S-di-tert-butyl-, O-ethyl-S-n-propyl-, O-ethyl-S-isopropyl-, O-ethyl-S-n-butyl-, O-ethyl-S-sec-butyl-, O-n-propyl-S-ethyl-, O-n-propyl-S-isopropyl-, O-n-butyl-S-n-propyl- and O-sec-butyl-S-ethylthiolophosphoric acid diester chlorides and the corresponding thiono analogues; and O-methyl-N-methyl-, O-ethyl-N-methyl-, O-n-propyl-N-methyl-, O-isopropyl-N-methyl-, O-n-butyl-N-methyl-, O-sec-butyl-N-methyl-, O-methyl-N-ethyl-, O-ethyl-N-ethyl-, O-n-propyl-N-ethyl-, O-isopropyl-N-ethyl-, O-n-butyl-N-ethyl-, O-sec-butyl-N-ethyl-, O-methyl-N-n-propyl-, O-ethyl-N-n-propyl-, O-n-propyl-N-n-propyl-, O-isopropyl-N-ethyl- and O-tert-butyl-N-ethyl-phosphoric acid ester-amide chlorides, the corresponding thiono analogues and the corresponding dialkylamides.

The following may be mentioned as examples of the 1-phenyl-3-hydroxy-1,6-dihydro-6-oxo-pyridazine derivatives (III) to be employed: 1-(2- and 3-trifluoromethyl-, 3,5-bis-trifluoromethyl-, 2-trifluoromethyl-4-chloro-, 2-chloro-5-trifluoromethyl-, 2-nitro-4-trifluoromethyl- and 5-chloro-3-trifluoromethylphenyl)-3-hydroxy-1,6-dihydro-6-oxo-pyridazines, as well as the corresponding 4- and 5-methyl derivatives.

The process for the preparation of the compounds according to the invention is preferably carried out in the presence of a suitable solvent or diluent. Practically all inert organic solvents can be used for this purpose, especially aliphatic and aromatic optionally chlorinated hydrocarbons, such as 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, such as 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, 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, trimethylamine, dimethylaniline, dimethylbenzylamine and pyridine.

The reaction temperature can be varied within a fairly wide range. In general, the reaction is carried out at between 0° and 120° C, preferably at 40° to 60°.

To carry out the process, the starting materials are in general employed in substantially equimolar amounts. An excess of one or other component in general produces no significant advantages. The reaction is preferably carried out in the presence of one of the above-mentioned solvents, if appropriate in the presence of an acid acceptor, at the indicated temperatures. After a reaction time of one or more hours, in most cases at elevated temperatures, the reaction batch is cooled to

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room temperature, an organic solvent, for example toluene, is added, and the organic phase is worked up in accordance with customary methods, for example washing, drying and distillation.

The new compounds are frequently obtained in the form of oils which mostly cannot be distilled without decomposition but are freed from the last volatile constituents by so-called "slight distillation", that is to say by prolonged heating under reduced pressure to moderately elevated temperatures, and are purified in this way. They are characterised by the refractive index. Some of the products are obtained in a crystalline form; in that case, they can be characterised by their melting point.

As has already been mentioned, the pyridazinyl-(thiono)(thiol)phosphoric(phosphonic) acid esters and ester-amides according to the invention are distinguished by an excellent insecticidal and acaricidal activity. They are not only active against plant pests, pests harmful to health and pests of stored products but also, in the veterinary medicine field, against animal parasites (ectoparasites), such as parasitic fly larvae. They combine a low phytotoxicity with a good action against both sucking and biting insects and against mites.

For this reason, the compounds according to the invention can be employed with success as pesticides in plant protection and in the hygiene field, the field of protection of stored products and the veterinary field.

The economically important pests in agriculture and forestry, as well as pests of stored products, pests destructive of materials and pests harmful to health, include: from the order of the *Isopoda*, for example, *Oniscus asellus*, *Armadillidium vulgare* and *Porcellio scaber*; from the order of the *Diploda*, for example, *Blaniulus guttulatus*; from the order of the *Chilopoda*, for example, *Geophilus carpophagus* and *Scutigera* spec.; from the order of the *Symphyla*, for example, *Scutigera immaculata*; from the order of the *Arachnida*, for example, *Scorpio maurus* and *Latrodectus mactans*; from the order of the *Acarina*, for example, *Acarus siro*, *Argas reflexus*, *Ornithodoros moubata*, *Dermanyssus gallinae*, *Eriophyes ribis*, *Phyllocoptura oleivora*, *Boophilus microplus*, *Rhipicephalus eversti*, *Sarcoptes scabiei*, *Tarsonemus* spec., *Bryobia praetiosa*, *Panonychus citri*, *Panonychus ulmi*, *Tetranychus tumidus* and *Tetranychus urticae*; from the order of the *Thysanura*, for example, *Lepisma saccharina*; from the order of the *Collembola*, for example, *Onychiurus armatus*; from the order of the *Orthoptera*, for example, *Blatta orientalis*, *Periplaneta americana*, *Leucophaea maderae*, *Blattella germanica*, *Acheta domesticus*, *Gryllotalpa* spec., *Locusta migratoria migratorioides*, *Melanoplus differentialis* and *Schistocerca gregaria*; from the order of the *Dermaptera*, for example, *Forficula auricularia*; from the order of the *Isotera*, for example, *Reticulitermes* spec.; from the order of the *Anoptura*, for example, *Phylloxera vastatrix*, *Pemphigus* spec. and *Pediculus humanus corporis*; from the order of the *Thysanoptera*, for example, *Hercinothrips femoralis* and *Thrips tabaci*; from the order of the *Heteroptera*, for example, *Eurygaster* spec., *Dysdercus intermedius*, *Piesma quadrata*, *Cimex lectularius*, *Rhodnius prolixus* and *Triatoma* spec.; from the order of the *Homoptera*, for example, *Aleurodes brassicae*, *Bemisia tabaci*, *Trialeurodes vaporariorum*, *Aphis gossypii*, *Brevicoryne brassicae*, *Cryptomyces ribis*, *Doralis fabae*, *Doralis pomi*, *Eriosoma lanigerum*, *Hyalopterus arundinis*, *Macrosiphum avenae*, *Myzus cerasi*, *Myzus persicae*, *Phorodon humuli*, *Rhopalosiphum padi*, *Empoasca* spec., *Euscelis bilobatus*, *Nephotettix cincticeps*, *Lecanium corni*, *Saissetia oleae*, *Laodelphax striatellus*, *Nilaparvata lugens*, *Aonidiella aurantii*, *Aspidiotus hederae*, *Pseudococcus* spec. and *Psylla* spec.; from the order of the *Lepidoptera*, for example, *Pectinophora gossypiella*, *Bupalus piniarius*, *Cheimatobiabrumata*, *Lithocolletis blancardella*, *Hyponomeuta padella*, *Plutella maculipennis*, *Malacosoma neustria*, *Euproctis chrysorrhoea*, *Lymantria* spec., *Buccatrix thurberiella*, *Phyllocnistis citrella*, *Agrotis* spec., *Euxoa* spec., *Feltia* spec., *Earias insulana*, *Heliothis* spec., *Laphygma exigua*, *Mamestra brassicae*, *Panolis flammea*, *Prodenia litura*, *Spodoptera* spec., *Trichoplusia ni*, *Carpocapsa pomonella*, *Pieris* spec., *Chilo* spec., *Pyrausta nubilalis*, *Ephestia kühniella*, *Galleria mellonella*, *Cacoecia podana*, *Capua reticulana*, *Choristoneura fumiferana*, *Clysia ambiguella*, *Homona magnanima*, and *Tortrix viridana*; from the order of the *Coleoptera*, for example, *Anobium punctatum*, *Rhizopertha dominica*, *Bruchidius obtectus*, *Acanthoscelides obtectus*, *Hylotrupes bajulus*, *Agelastica alni*, *Leptinotarsa decemlineata*, *Phaedon cochleariae*, *Diabrotica* spec., *Psylliodes chrysocephala*, *Epilachna varivestis*, *Atomaria* spec., *Oryzaephilus surinamensis*, *Anthonomus* spec., *Sitophilus* spec., *Otiorrhynchus sulcatus*, *Cosmopolites sordidus*, *Ceuthorrhynchus assimilis*, *Hypera postica*, *Dermestes* spec., *Trogoderma* spec.,

Anthrenus spec., *Attageus spec.*, *Lyctus spec.*, *Meligethes aeneus*, *Ptinus spec.*, *Niptus hololeucus*, *Gibbium psyllodes*, *Tribolium spec.*, *Tenebrio molitor*, *Agriotes spec.*, *Conoderus spec.*, *Melolontha melolontha*, *Amphimallus solstitialis* and *Costelytra zealandica*; from the order of the Hymenoptera, for example *Diprion spec.*, *Hoplocampa spec.*, *Lasius spec.*, *Monomorium pharaonis* and *Vespa spec.*; from the order of the Diptera, for example, *Aedes spec.*, *Anopheles spec.*, *Culex spec.*, *Drosophila melanogaster*, *Musca domestica*, *Fannia spec.*, *Stomoxys calcitrans*, *Hypoderma spec.*, *Bibio hortulans*, *Oscinella frit*, *Phormia spec.*, *Pegomya hyoscyami*, *Calliphora erythrocephala*, *Lucilia spec.*, *Chrysomya spec.*, *Ceratitis capitata*, *Dacus oleae* and *Tipula paludosa*; and from the order of the Siphonaptera, for example, *Xenopsylla cheopis*.

The active compounds can be converted to the customary formulations, such as solutions, emulsions, wettable powders, suspensions, powders, dusting agents, foams, pastes, soluble powders, granules, aerosols, suspension-emulsion concentrates, seed-treatment powders, natural and synthetic materials impregnated with active compound, very fine capsules in polymeric substances, coating compositions, for use on seed, and formulations used with burning equipment, such as fumigating cartridges, fumigating cans and fumigating coils, as well as ULV cold mist and warm mist formulations.

These formulations are 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 and alicyclic 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, for example propellants, such as halogenated hydrocarbons, for example Freon (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 present in the formulations 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 from 0.5 to 90 per cent.

The active compounds can be employed as such, in the form of their formulations or as the use forms prepared therefrom. They may be used in the customary manner, for example by squirting, spraying, atomising, dusting, scattering, fumigating, gassing, watering, dressing or encrusting.

The active-compound concentrations in the ready-to-use preparations can be varied within fairly wide ranges. In general they are from 0.0001 to 10%, preferably from 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% active compound or even to use the active compound by itself.

When used against pests harmful to health and pests of stored products, the active compounds are distinguished by an excellent residual action on wood and clay, as well as a good stability to alkali on limed substrates.

The present invention also provides an insecticidal or acaricidal composition containing as active ingredient a compound of the present invention in admixture

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with a solid or liquefied gaseous diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.

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

The present invention further 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 of the present 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 pesticidal activity of the present compounds is illustrated in the following biotest Examples.

Example A

Plutella test

Solvent: 3 parts by weight of acetone

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

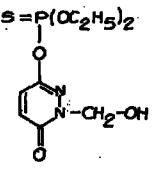
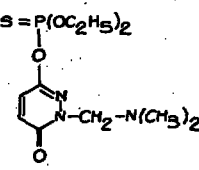
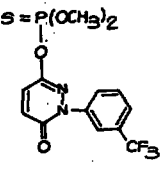
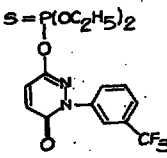
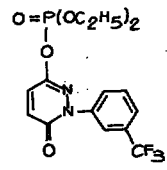
To produce a suitable preparation of active compound, 1 part by weight of the active compound was mixed with the stated amount of solvent containing the stated amount of emulsifier and the concentrate was diluted with water to the desired concentration.

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 from the following table:

TABLE A
(Plutella test)

Active compound	Active compound concentration in %	Degree of destruction in % after 3 days
<chem>S=P(OC2H5)2</chem>  (known)	0.1 0.01	100 0
<chem>S=P(OC2H5)2</chem>  (known)	0.1 0.01	100 0
<chem>S=P(OCH3)2</chem>  (6)	0.1 0.01	100 100
<chem>S=P(OC2H5)2</chem>  (1)	0.1 0.01	100 100
<chem>O=P(OC2H5)2</chem>  (5)	0.1 0.01	100 95

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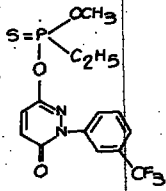
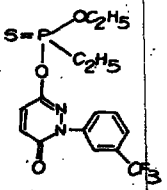
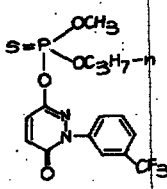
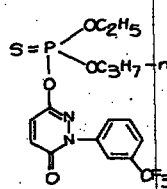
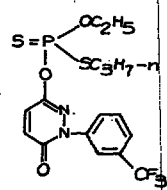
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TABLE A (Continued)

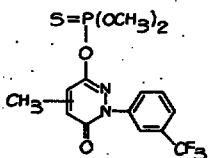
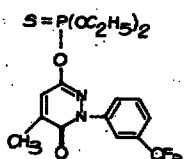
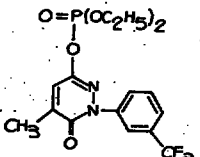
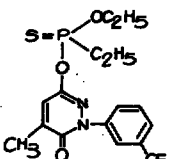
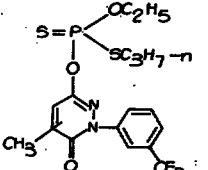
(*Plutella* test)

Active compound	Active compound concentration in %	Degree of destruction in % after 3 days
	(3) 0.1 0.01	100 100
	(8) 0.1 0.01	100 100
	(4) 0.1 0.01	100 100
	(2) 0.1 0.01	100 100
	(7) 0.1 0.01	100 100

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TABLE A (Continued)

(*Plutella* test)

Active compound	Active compound concentration in %	Degree of destruction in % after 3 days
 (18) (isomer mixture)	0.1 0.01	100 100
 (12)	0.1 0.01	100 100
 (16)	0.1 0.01	100 90
 (14)	0.1 0.01	100 100
 (17) (isomer mixture)	0.1 0.01	100 100

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TABLE A (Continued)

(Plutella test)

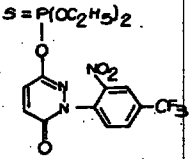
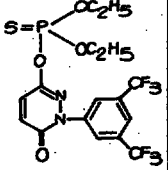
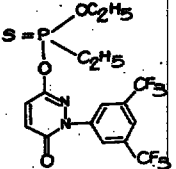
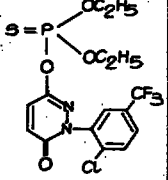
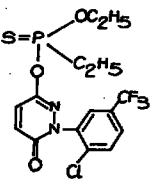
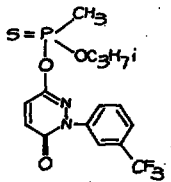
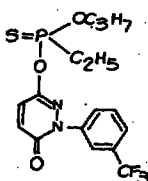
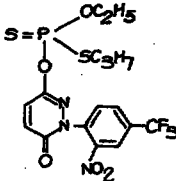
Active compound	Active compound concentration in %	Degree of destruction in % after 3 days
	(23) 0.1 0.01	100 100
	(21) 0.1 0.01	100 100
	(25) 0.1 0.01	100 100
	(20) 0.1 0.01	100 100
	(22) 0.1 0.01	100 100

TABLE A (Continued)

(Plutella test)

Active compound	Active compound concentration in %	Degree of destruction in % after 3 days
 (24)	0.1 0.01	100 100
 (28)	0.1 0.01	100 100
 (27)	0.1 0.01	100 100

Example B

Laphygma 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 and the stated amount of emulsifier and the concentrate was diluted with water to the desired concentration.

Cotton leaves (*Gossypium hirsutum*) were sprayed with the preparation of the active compound until dew-moist and were then infested with caterpillars of the owl moth (*Laphygma exigua*).

After the specified periods of time, the degree of destruction in % was determined. 100% means that all caterpillars had been killed whilst 0% indicates that no caterpillars had been killed.

The active compounds, the concentrations of the active compounds, the evaluation times and the results can be seen from the table which follows:

(23)

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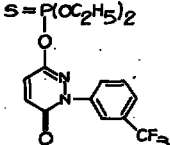
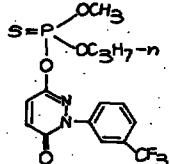
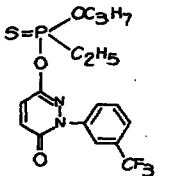
12

TABLE B
(Laphygma test)

Active compound	Active compound concentration in %	Degree of destruction in % after 3 days
$\begin{array}{c} \text{S}=\text{P}(\text{OC}_2\text{H}_5)_2 \\ \\ \text{O} \\ \\ \text{C}_5\text{H}_4\text{N}-\text{CH}_2-\text{OH} \\ \\ \text{O} \end{array}$ (known)	0.1 0.01 0.001	100 40 0
$\begin{array}{c} \text{S}=\text{P}(\text{OC}_2\text{H}_5)_2 \\ \\ \text{O} \\ \\ \text{C}_5\text{H}_4\text{N}-\text{CH}_2-\text{N}(\text{CH}_3)_2 \\ \\ \text{O} \end{array}$ (known)	0.1 0.01	100 0
$\begin{array}{c} \text{S}=\text{P}(\text{OC}_2\text{H}_5)_2 \\ \\ \text{O} \\ \\ \text{C}_5\text{H}_4\text{N}-\text{C}_6\text{H}_5 \\ \\ \text{O} \end{array}$ (known)	0.1 0.01 0.001	100 100 0
$\begin{array}{c} \text{S}=\text{P}(\text{OC}_2\text{H}_5)_2 \\ \\ \text{O} \\ \\ \text{C}_5\text{H}_4\text{N}-\text{C}_6\text{H}_4-\text{CH}_3 \\ \\ \text{O} \end{array}$ (known)	0.1 0.01 0.001	100 100 0

24

TABLE B
(Laphygma test)

Active compound	Active compound concentration in %	Degree of destruction in % after 3 days
 (1)	0.1 0.01 0.001	100 100 95
 (4)	0.1 0.01 0.001	100 100 100
 (28)	0.1 0.01 0.001	100 100 100

Example C

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 from the following table:

(25)

14

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TABLE C

(Myzus test)

Active compound	Active compound concentration in %	Degree of destruction in % after 1 day
$\begin{array}{c} \text{S}=\text{P}(\text{OC}_2\text{H}_5)_2 \\ \\ \text{O} \\ \\ \text{C}_6\text{H}_3\text{N}(\text{CH}_2\text{OH})\text{C}_2\text{O} \end{array}$	0.1 0.01 0.001	100 75 0
(known)		
$\begin{array}{c} \text{S}=\text{P}(\text{OC}_2\text{H}_5)_2 \\ \\ \text{O} \\ \\ \text{C}_6\text{H}_3\text{N}(\text{CH}_2\text{N}(\text{CH}_3)_2)\text{C}_2\text{O} \end{array}$	0.1 0.01 0.001	100 50 0
(known)		
$\begin{array}{c} \text{S}=\text{P}(\text{OC}_2\text{H}_5)_2 \\ \\ \text{O} \\ \\ \text{C}_6\text{H}_3\text{N}(\text{C}_6\text{H}_5)\text{C}_2\text{O} \end{array}$	0.1 0.01 0.001	100 95 0
(known)		
$\begin{array}{c} \text{S}=\text{P}(\text{OC}_2\text{H}_5)_2 \\ \\ \text{O} \\ \\ \text{C}_6\text{H}_3\text{N}(\text{C}_6\text{H}_4\text{CH}_3)\text{C}_2\text{O} \end{array}$	0.1 0.01 0.001	100 95 0
(known)		

26

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TABLE C (Continued)

(Myzus test)

Active compound	Active compound concentration in %	Degree of destruction in % after 1 day
 (3)	0.1 0.01 0.001	100 99 98
 (8)	0.1 0.01 0.001	100 100 100

Example D

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 two-spotted spider mite (*Tetranychus urticae*) in all stages of development.

After the specified periods of time, the degree of destruction was determined 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 from the following table:

27

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TABLE D
(Tetranychus test)

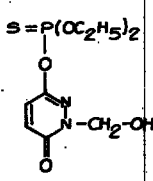
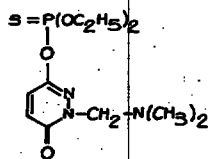
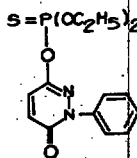
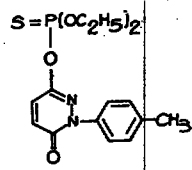
Active compound	Active compound concentration in %	Degree of destruction in % after 2 days
 (known)	0.1 0.01	95 0
 (known)	0.1 0.01	90 0
 (known)	0.1 0.01	98 0
 (known)	0.1 0.01	40 0

TABLE D (Continued)

(Tetranychus test)

Active compound	Active compound concentration in %	Degree of destruction in % after 2 days
$\begin{array}{c} \text{S}=\text{P}(\text{OCH}_3)_2 \\ \\ \text{O} \\ \\ \text{C}_6\text{H}_3\text{N} \end{array}$ (6)	0.1 0.01	100 95
$\begin{array}{c} \text{S}=\text{P}(\text{OC}_2\text{H}_5)_2 \\ \\ \text{O} \\ \\ \text{C}_6\text{H}_3\text{N} \end{array}$ (1)	0.1 0.01	100 70
$\begin{array}{c} \text{S}=\text{P} \begin{array}{l} \text{OCH}_3 \\ \text{C}_2\text{H}_5 \end{array} \\ \\ \text{O} \\ \\ \text{C}_6\text{H}_3\text{N} \end{array}$ (3)	0.1 0.01	100 100
$\begin{array}{c} \text{S}=\text{P} \begin{array}{l} \text{OC}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{array} \\ \\ \text{O} \\ \\ \text{C}_6\text{H}_3\text{N} \end{array}$ (8)	0.1 0.01	100 100
$\begin{array}{c} \text{S}=\text{P} \begin{array}{l} \text{OC}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{array} \\ \\ \text{O} \\ \\ \text{C}_6\text{H}_3\text{N} \end{array}$ (14)	0.1 0.01	100 100

29

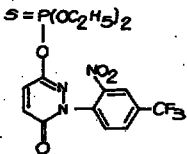
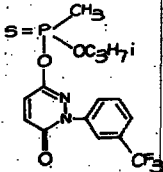
18

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TABLE D (Continued)

(Tetranychus test)

Active compound	Active compound concentration in %	Degree of destruction in % after 2 days
	(23) 0.1 0.01	100 95
	(24) 0.1 0.01 0.001	100 99 95

Example E

LD₁₀₀ test

Test animals: *Sitophilus granarius*

Solvent: Acetone

2 parts by weight of the active compound was taken up in 1,000 parts by volume of the solvent. The solution so obtained was diluted with further solvent to the desired concentrations.

2.5 ml of the solution of the active compound were pipetted into a Petri dish. On the bottom of the Petri dish there was a filter paper with a diameter of about 9.5 cm. The Petri dish remained uncovered until the solvent had completely evaporated. The amount of active compound per m² of filter paper varied with the concentration of the solution of active compound. About 25 test animals were then placed in the Petri dish and it was covered with a glass lid.

The condition of the test animals was observed 3 days after the commencement of the experiments. The destruction, in %, was determined. 100% denotes that all the test animals had been killed; 0% denotes that no test animals had been killed.

The active compounds, the concentrations of the active compounds, the test animals and the results can be seen from the following table:

TABLE E

(LD₁₀₀ test/*Sitophilus granarius*)

Active compound	Active compound concentration in %	Degree of destruction in %
$\begin{array}{c} \text{S}=\text{P}(\text{OC}_2\text{H}_5)_2 \\ \\ \text{O} \\ \\ \text{C}_6\text{H}_3\text{N}(\text{CH}_2\text{N}(\text{CH}_3)_2) \\ \\ \text{O} \end{array}$ (known)	0.2	0
$\begin{array}{c} \text{S}=\text{P}(\text{OC}_2\text{H}_5)_2 \\ \\ \text{O} \\ \\ \text{C}_6\text{H}_3\text{N}(\text{CH}_2\text{OH}) \\ \\ \text{O} \end{array}$ (known)	0.2	90
$\begin{array}{c} \text{S}=\text{P}(\text{OC}_2\text{H}_5)_2 \\ \\ \text{O} \\ \\ \text{C}_6\text{H}_3\text{N}(\text{C}_6\text{H}_5) \\ \\ \text{O} \end{array}$ (known)	0.2 0.02	100 0
$\begin{array}{c} \text{S}=\text{P}(\text{OC}_2\text{H}_5)_2 \\ \\ \text{O} \\ \\ \text{C}_6\text{H}_3\text{N}(\text{C}_6\text{H}_4\text{CF}_3) \\ \\ \text{O} \end{array}$ (1)	0.2 0.02	100 100
$\begin{array}{c} \text{S}=\text{P}(\text{OC}_2\text{H}_5)_2 \\ \\ \text{O} \\ \\ \text{C}_6\text{H}_3\text{N}(\text{C}_6\text{H}_4\text{CF}_3) \\ \\ \text{O} \end{array}$ (3)	0.2 0.02	100 100

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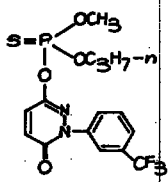
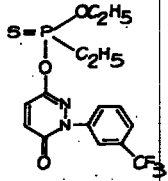
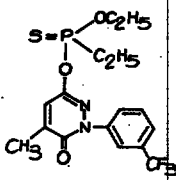
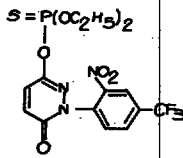
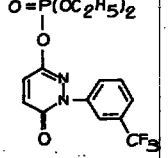
20

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20

TABLE E (Continued)

(LD₁₀₀ test/*Sitophilus granarius*)

Active compound	Active compound concentration in %	Degree of destruction in %
 (4)	0.2 0.02	100 100
 (8)	0.2 0.02	100 100
 (14)	0.2 0.02	100 100
 (23)	0.2 0.02	100 100
 (5)	0.2 0.02	100 100

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Example F

LT₁₀₀ test for *Diptera*

Test animals: *Aedes aegypti*

Solvent: Acetone

2 parts by weight of active compound were dissolved in 1,000 parts by volume of solvent. The solution so obtained was diluted with further solvent to the desired lower concentrations.

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2.5 ml of the solution of active compound were pipetted into a Petri dish. On the bottom of the Petri dish there was a filter paper with a diameter of about 9.5 cm. The Petri dish remained uncovered until the solvent had completely evaporated. The amount of active compound per m² of filter paper varied with the concentration of the solution of active compound. About 25 test animals were then placed in the Petri dish and it was covered with a glass lid.

10

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The condition of the test animals was continuously observed. The time which was necessary for 100% destruction was determined.

15

The test animals, the active compounds, the concentrations of the active compounds and the times at which there was 100% destruction can be seen from the following table:

33

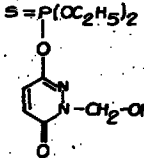
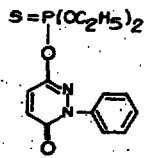
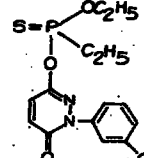
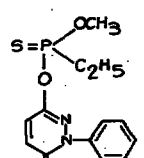
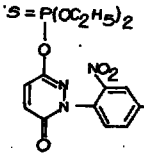
22

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22

TABLE F

(LT₁₀₀ test for diptera/*Aedes aegypti*)

Active compound	Active compound concentration in the solution, in %	LT ₁₀₀ in minutes (¹) or hours (hrs)
<chem>S=P(OC2H5)2</chem>  (known)	0.2 0.02	180' 3 hrs 0%
<chem>S=P(OC2H5)2</chem>  (known)	0.2 0.02	120' 3 hrs 0%
<chem>S=P(OC2H5)2</chem>  (8)	0.2 0.02	120' 180'
<chem>S=P(OC2H5)2</chem>  (3)	0.2 0.02 0.002	120' 120' 3 hrs 70%
<chem>S=P(OC2H5)2</chem>  (23)	0.2 0.02 0.002	60' 120' 180'

Example G

LT₁₀₀ test for *Diptera*Test animals: *Musca domestica*

Solvent: Acetone

2 parts by weight of active compound were dissolved in 1,000 parts by volume of solvent. The solution so obtained was diluted with further solvent to the desired lower concentrations.

2.5 ml of the solution of active compound were pipetted into a Petri dish. On the bottom of the Petri dish there was a filter paper with a diameter of about 9.5 cm. The Petri dish remained uncovered until the solvent had completely evaporated. The amount of active compound per m² of filter paper varied with the concentration of the solution of active compound. About 25 test animals were then placed in the Petri dish and it was covered with a glass lid.

The condition of the test animals was continuously observed. The time which was necessary for 100% destruction was determined.

The test animals, the active compounds, the concentrations of the active compounds and the times at which there was 100% destruction can be seen from the following table:

TABLE G

(LT₁₀₀ test for *diptera/Musca domestica*)

Active compound	Active compound concentration in the solution, in %	LT ₁₀₀ in minutes (¹) or hours (hrs)
$\begin{array}{c} \text{S}=\text{P}(\text{OC}_2\text{H}_5)_2 \\ \\ \text{O} \\ \\ \text{C}_6\text{H}_4-\text{N} \\ \\ \text{C}_6\text{H}_4-\text{CH}_3 \end{array}$	0.2 0.02	60' 6 hrs.
(known)		
$\begin{array}{c} \text{S}=\text{P}(\text{OC}_2\text{H}_5)_2 \\ \\ \text{O} \\ \\ \text{C}_6\text{H}_4-\text{N} \\ \\ \text{C}_6\text{H}_5 \end{array}$	0.2 0.02	100' 6 hrs
(known)		
$\begin{array}{c} \text{S}=\text{P}(\text{OC}_2\text{H}_5)_2 \\ \\ \text{O} \\ \\ \text{C}_6\text{H}_4-\text{N} \\ \\ \text{C}_6\text{H}_3(\text{NO}_2)(\text{CH}_3) \end{array}$	(23) 0.2 0.02	30' 80'

Example H

Test with parasitic fly larvae

Solvent: 35 parts by weight of ethylene polyglycol mono-methyl ether

Emulsifier: 35 parts by weight of nonylphenol polyglycol ether

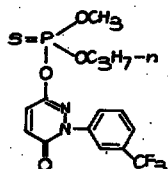
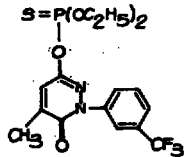
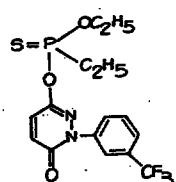
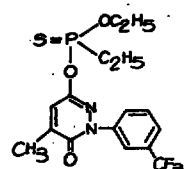
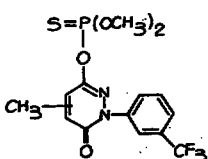
To produce a suitable preparation of active compound, 30 parts by weight of the active substance in question were mixed with the stated amount of solvent which contained the above-mentioned proportion of emulsifier and the concentrate thus obtained was diluted with water to the desired concentration.

About 20 fly larvae (*Lucilia cuprina*) were introduced into a test tube which contained approx. 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 the larvae had been killed and 0% means that no larvae had been killed.

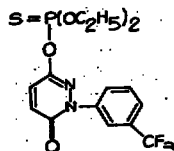
The active compounds investigated, the concentrations of the active compounds used and the results obtained can be seen from the table which follows:

TABLE H

(Test with parasitic fly larvae/*Lucilia cuprina* res.)

Active compound	Active compound concentration in ppm	Degree of destruction in %
 (4)	100 30 10	100 100 100
 (12)	100 30	100 >50
 (8)	100 30	100 >50
 (14)	100 30 10	100 100 100
 (18) (isomer mixture)	100 30 10	100 100 100

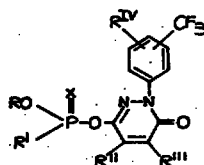
The process of this invention is illustrated in the following Preparative Examples:



(I)

A mixture of 25.6 g (0.1 mole) of 1-(3-trifluoromethyl-phenyl)-3-hydroxy-1,6-dihydropyridazinone-(6), 20.7 g (0.15 mole) of potassium carbonate, 18.8 g (0.1 mole) of O,O-diethyl-thionophosphoric acid diester chloride and 300 ml of acetonitrile was stirred for 4 hours at 50° C. It was then cooled to room temperature and, after addition of 400 ml of toluene, was extracted by shaking with twice 30 ml of water. The organic phase was separated off, dried over sodium sulphate and freed from the solvent *in vacuo*. The residue was subjected to slight distillation. This gave 33.4 g (82% of theory) of O,O-diethyl-O-[1-(3-trifluoromethylphenyl)-1,6-dihydropyridaz-(6)-on-(3-yl)]-thionophosphoric acid ester in the form of a yellow oil having a refractive index n_D^{22} of 1.5240.

The following compounds of the formula



(I)

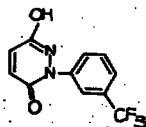
could be prepared analogously:

Example No.	R	R'	R''	R'''	R ^{IV}	Position of CF ₃ group	X	Yield (% of theory)	Physical data (refractive index, melting point °C)
2	-C ₂ H ₅	-OC ₃ H _{7-n}	H	H	H	3	S	71	n _D ²¹ :1.5212
3	-CH ₃	-C ₂ H ₅	H	H	H	3	S	65	n _D ²¹ :1.5413
4	-CH ₃	-OC ₃ H _{7-n}	H	H	H	3	S	87	n _D ²¹ :1.5290
5	-C ₂ H ₅	-OC ₂ H ₅	H	H	H	3	O	74	n _D ²⁶ :1.4946
6	-CH ₃	-OCH ₃	H	H	H	3	S	61	58
7	-C ₂ H ₅	-SC ₃ H _{7-n}	H	H	H	3	S	53	n _D ²⁶ :1.5475
8	-C ₂ H ₅	-C ₂ H ₅	H	H	H	3	S	56	n _D ²⁴ :1.5338
9	-C ₂ H ₅	-C ₆ H ₅	H	H	H	3	S	40	n _D ²⁴ :1.5741
10	-C ₂ H ₅	-NH-C ₃ H _{7-iso}	H	H	H	3	S	30	n _D ²⁴ :1.5309
11	-C ₂ H ₅	-OC ₂ H ₅	CH ₃	H	H	3	S	76	86
12	-C ₂ H ₅	-OC ₂ H ₅	H	CH ₃	H	3	S	66	n _D ²⁰ :1.5251
13	-C ₂ H ₅	-C ₂ H ₅	CH ₃	H	H	3	S	62	80
14	-C ₂ H ₅	-C ₂ H ₅	H	CH ₃	H	3	S	84	n _D ²⁰ :1.5385
15	-C ₂ H ₅	-OC ₂ H ₅	CH ₃	H	H	3	O	64	72
16	-C ₂ H ₅	-OC ₂ H ₅	H	CH ₃	H	3	O	84	n _D ²⁰ :1.4987

Example No.	R	R'	R''	R'''	R ^{IV}	Position of CF ₃ group	X	Yield (% of theory)	Physical data (refractive index, melting point °C)
17	-C ₂ H ₅	-SC ₃ H _{7-n}	CH ₃ H	H CH ₃	H	3	S	86	n _D ²⁰ :1.5486 (isomer mixture)
18	-CH ₃	-OCH ₃	CH ₃ H	H CH ₃	H	3	S	54	n _D ²⁴ :1.5375 (isomer mixture)
19	-CH ₃	-OC ₃ H _{7-n}	CH ₃ H	H CH ₃	H	3	S	59	n _D ²⁴ :1.5300 (isomer mixture)
20	-C ₂ H ₅	-OC ₂ H ₅	H	H	6-Cl	3	S	41	n _D ²⁴ :1.5330
21	-C ₂ H ₅	-OC ₂ H ₅	H	H	5-CF ₃	3	S	72	n _D ²⁴ :1.5009
22	-C ₂ H ₅	-C ₂ H ₅	H	H	6-Cl	3	S	70	n _D ²⁵ :1.5473
23	-C ₂ H ₅	-OC ₂ H ₅	H	H	2-NO ₂	4	S	38	n _D ²² :1.5431
24	-C ₃ H _{7-iso}	-CH ₃	H	H	H	3	S	63	n _D ²⁵ :1.5348
25	-C ₂ H ₅	-C ₂ H ₅	H	H	5-CF ₃	3	S	44	n _D ²³ :1.5084
26	-C ₂ H ₅	-SC ₃ H _{7-n}	H	H	5-CF ₃	3	S	46	n _D ²³ :1.5185
27	-C ₂ H ₅	-SC ₃ H _{7-n}	H	H	2-NO ₂	4	S	80	n _D ²⁶ :1.5332
28	-C ₃ H _{7-n}	-C ₂ H ₅	H	H	H	3	S	62	n _D ²⁴ :1.5277
29	-C ₃ H _{7-iso}	-C ₃ H _{7-iso}	H	H	H	3	S	60	n _D ²³ :1.5173

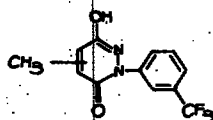
39

The 1-phenyl-3-hydroxy-6-oxo-pyridazine derivatives (III) required as starting materials can be prepared, for example, as follows:

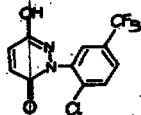


176 g (1 mole) of 3-trifluoromethylphenylhydrazine (for preparation, see German Auslegeschrift (German Published Specification) 1,116,534) were dissolved in a mixture of 1,000 ml of water and 250 ml of concentrated hydrochloric acid and then 98 g (1 mole) of maleic anhydride were added at approx. 90° C. The mixture was then stirred for a further hour at 95—100° C and after the reaction mixture had cooled, the product which had crystallised out was filtered off. It could be purified by dissolving it in dilute sodium hydroxide solution and reprecipitating with hydrochloric acid. This gave 210 g (82% of theory) of 1-(3-trifluoromethylphenyl)-3-hydroxy-1,6-dihydropyridazinone-(6) in the form of a pale yellow-coloured powder of melting point 176° C.

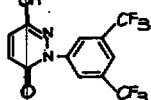
The following compounds could be prepared analogously:



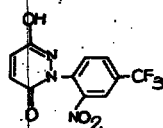
88% yield; melting point 245° C (isomer mixture).



65% yield; melting point 230° C



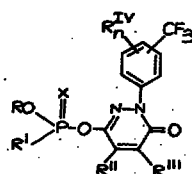
69% yield; melting point 174° C



40% yield; melting point 208° C

WHAT WE CLAIM IS:—

1. Pyridazinyl(thiono)(thiol)phosphoric(phosphonic) acid esters and ester-amides of the general formula

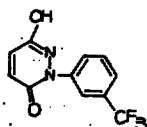


(I)

in which

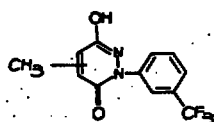
R is alkyl with 1 to 6 carbon atoms,
R' is phenyl, alkyl with 1 to 4 carbon atoms, alkoxy with 1 to 6 carbon atoms, alkylthio with 1 to 6 carbon atoms or monoalkylamino or dialkylamino with 1 to 4 carbon atoms in the or each alkyl group.

The 1-phenyl-3-hydroxy-6-oxo-pyridazine derivatives (III) required as starting materials can be prepared, for example, as follows:

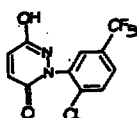


176 g (1 mole) of 3-trifluoromethylphenylhydrazine (for preparation, see German Auslegeschrift (German Published Specification) 1,116,534) were dissolved in a mixture of 1,000 ml of water and 250 ml of concentrated hydrochloric acid and then 98 g (1 mole) of maleic anhydride were added at approx. 90° C. The mixture was then stirred for a further hour at 95—100° C and after the reaction mixture had cooled, the product which had crystallised out was filtered off. It could be purified by dissolving it in dilute sodium hydroxide solution and reprecipitating with hydrochloric acid. This gave 210 g (82% of theory) of 1-(3-trifluoromethylphenyl)-3-hydroxy-1,6-dihydropyridazinone-(6) in the form of a pale yellow-coloured powder of melting point 176° C.

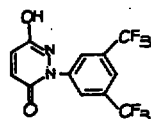
The following compounds could be prepared analogously:



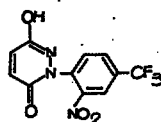
88% yield; melting point 245° C (isomer mixture).



65% yield; melting point 230° C



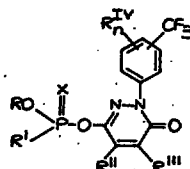
69% yield; melting point 174° C



40% yield; melting point 208° C

WHAT WE CLAIM IS:—

1. Pyridazinyl(thiono)(thiol)phosphoric(phosphonic) acid esters and ester-amides of the general formula



(I)

in which

R is alkyl with 1 to 6 carbon atoms,

R' is phenyl, alkyl with 1 to 4 carbon atoms, alkoxy with 1 to 6 carbon atoms, alkylthio with 1 to 6 carbon atoms or monoalkylamino or dialkylamino with 1 to 4 carbon atoms in the or each alkyl group.



* C L M S *

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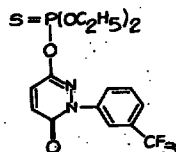
R'' and R''' , which may be identical or different, are each hydrogen or methyl,

R^{IV} is hydrogen, halogen, nitro or halogenoalkyl with 1 to 3 carbon atoms, n is an integer from 1 to 4 and

X is oxygen or sulphur.

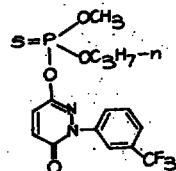
2. Compounds according to claim 1, in which R is straight-chain or branched alkyl with 1 to 5 carbon atoms, R' is phenyl, straight-chain or branched alkyl with 1 to 3 carbon atoms, straight-chain or branched alkoxy or alkylthio, each with 1 to 5 carbon atoms, or monoalkylamino or dialkylamino with 1 to 3 carbon atoms per alkyl group, R^{IV} is hydrogen, chlorine, nitro or trifluoromethyl, and n is 1, 2 or 3.

3. The compound of the formula



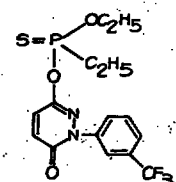
(1)

4. The compound of the formula



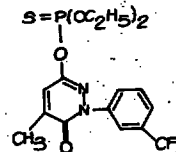
(4)

5. The compound of the formula



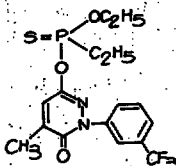
(8)

6. The compound of the formula



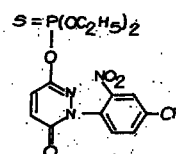
(12)

7. The compound of the formula



(14)

8. The compound of the formula



(23)

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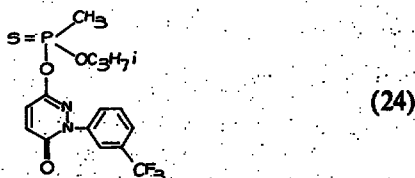


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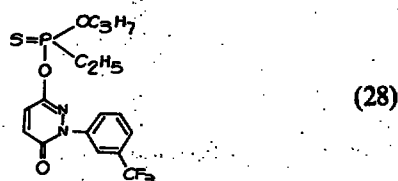
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9. The compound of the formula



10. The compound of the formula

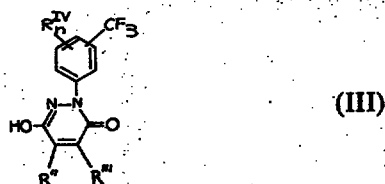


11. The compounds hereinbefore disclosed in Examples 2, 3, 5—7, 9—11, 13, 15—22, 25—27 and 29.

12. A process for the preparation of a pyridazinyl(thiono)(thiol)phosphoric-(phosphonic) acid ester or ester amide according to any of claims 1 to 11, in which a (thiono)(thiol)(phosphoric)(phosphonic) acid ester halide or ester-amide halide of the general formula



in which R, R' and X have the meanings stated in claim 1, and Hal is halogen, is reacted with a 1-phenyl-3-hydroxy-1,6-dihydropyridazinone-(6) derivative of the general formula



in which

R'', R''', R^{IV} and n have the meanings stated in claim 1.

13. A process according to claim 12 in which the reaction is effected in the presence of a diluent or solvent.

14. A process according to claim 12 or 13 in which the reaction is effected in the presence of an acid acceptor.

15. A process according to claim 14 in which the acid acceptor is an alkali metal carbonate, an alkali metal alcoholate or an aliphatic, aromatic or heterocyclic amine.

16. A process according to any of claims 12 to 15, in which the reaction is effected at between 0° and 120° C.

17. A process according to claim 16, in which the reaction is effected at from 40° to 60° C.

18. A process according to any of claims 12 to 17, in which the reactants are employed in substantially equimolar amounts.

19. A process according to any of claims 12 to 18, in which the ester halide or ester-amide halide (II) is one that is hereinbefore specifically mentioned.



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20. A process according to any of claims 12 to 19, in which the pyridazinone derivative (III) is one that is hereinbefore specifically mentioned.

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

22. Compounds according to claim 1 whenever prepared by a process according to any of claims 12 to 21.

23. An insecticidal or acaricidal composition containing as active ingredient a compound according to any of claims 1 to 11 and 22 in admixture with a liquid gaseous diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.

24. A composition according to claim 23 containing from 0.1 to 95% of the active compound, by weight.

25. A composition according to claim 24 containing from 0.5 to 90% of the active compound, by weight.

26. A method of combating insects or acarids which comprises applying to the insects or acarids or to a habitat thereof a compound according to any of claims 1 to 11 and 22 alone or in the form of a composition containing as active ingredient a compound according to any of claims 1 to 11 and 22 in admixture with a diluent or carrier.

27. A method according to claim 26 in which a composition is used containing from 0.0001 to 10% of the active compound, by weight.

28. A method according to claim 27 in which a composition is used containing from 0.01 to 1% of the active compound, by weight.

29. A method according to any of claims 26 to 28 in which the active compound is one of those hereinbefore mentioned in any of Examples A to H.

30. 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 any of claims 1 to 11 and 22 was applied alone or in admixture with a diluent or carrier.

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