

AMENDED SPECIFICATION

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PATENT SPECIFICATION

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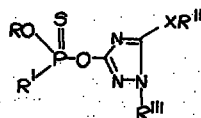
(54) O-TRIAZOLYLTHIONOPHOSPHORIC(PHOSPHONIC) ACID ESTERS AND ESTER-AMIDES, A PROCESS FOR THEIR PREPARATION AND THEIR USE AS INSECTICIDES AND ACARICIDES

(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 new O-triazolylthionophosphoric(phosphonic) acid esters and ester-amides, to a process for their preparation and to their use as insecticides or acaricides.

It is already known that pyrazolothionophosphoric acid esters, for example O,O-dimethyl- and O,O-diethyl-O-[3-methyl-pyrazol(5)yl]-thionophosphoric acid esters, possess insecticidal and acaricidal properties (compare U.S.A. Patent Specification 2,754,244).

The present invention provides O-triazolylthionophosphoric(phosphonic) acid esters and ester-amides of the general formula



in which

- R denotes alkyl with 1 to 6 carbon atoms,
 R' denotes alkyl, alkoxy or mono- or di-alkylamino with 1 to 6 carbon atoms in each alkyl or alkoxy or phenyl,
 R'' denotes alkyl or cyanoalkyl with 1 to 4 carbon atoms in each alkyl or alkenyl with 3 or 4 carbon atoms,
 X denotes oxygen or sulphur, and
 R''' denotes alkyl or cyanoalkyl with 1—6 carbon atoms in each alkyl, provided that R'' and R''' do not both simultaneously denote alkyl.
 Preferably, R denotes alkyl with 1 to 4 carbon atoms, R' denotes alkyl or alkyl-

amino with 1 to 4 carbon atoms or phenyl, R'' denotes alkenyl with 3 carbon atoms or cyanomethyl, and R''' denotes alkyl with 1 to 3 carbon atoms.

The alkyl groups may of course be branched or straight-chain.

The invention also provides a process for the production of an O-triazolythionophosphoric(phosphonic) acid ester or ester-amide of the formula (I) in which a thiono-



in which

R and R' have the abovementioned meanings, and

Hal denotes halogen, preferably chlorine, is reacted with a triazoly derivative of the general formula

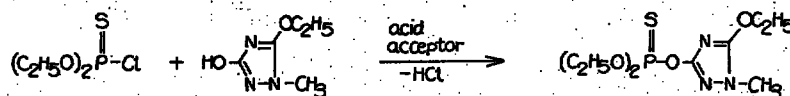


in which

X, R'' and R''' have the abovementioned meanings, in the presence of an acid acceptor or in the form of an alkali metal salt, alkaline earth metal salt or ammonium salt.

Surprisingly, the O-triazolythionophosphoric(phosphonic) acid esters and ester-amides according to the invention display a better insecticidal, especially soil-insecticidal, and acaricidal action than the previously known compounds of analogous structure and of the same type of action. The new products can not only be employed against insects which damage plants but also against hygiene pests and pests of stored products and/or in the veterinary medicine field against animal ectoparasites, for example parasitic fly larvae and ticks. They thus represent a genuine enrichment of the art. Furthermore, the new compounds contribute to reducing the constant demand for new preparations in the field of combating pests. This demand arises from the fact that the commercially available agents have to meet higher and higher standards, especially in respect of the protection of the environment, such as low toxicity to warm-blooded animals and phytotoxicity, rapid degradation in and on the plant with short periods which have to elapse between application of the pesticide and harvesting, and activity against resistant pests.

If, for example, O,O-diethylthionophosphoric acid diester-chloride and 1-methyl-3-hydroxy-5-ethoxytriazole-(1,2,4) are used as starting materials, the course of the reaction can be represented by the following formula scheme:

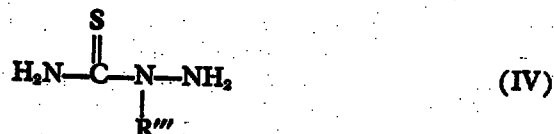


The formulae (II) and (III) provide an unambiguous general definition of the starting compounds to be used.

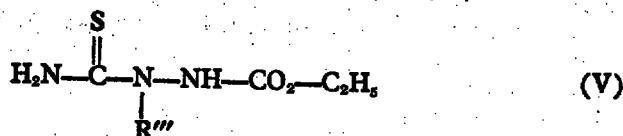
The thionophosphoric(phosphonic) acid derivatives (II) are known from the literature and can be prepared according to customary processes. As examples thereof, the following may be mentioned individually: O,O-dimethyl-, O,O-diethyl-, O,O-di-n-propyl-, O,O-di-iso-propyl-, O,O-di-n-butyl-, O,O-di-tert.-butyl-, O-ethyl-O-n-propyl-, O-ethyl-O-isopropyl- and O-ethyl-O-n-butyl-thionophosphoric acid ester-chloride, and also O-methyl-, O-ethyl-, O-n-propyl-, O-iso-propyl-, O-n-butyl-, O-iso-butyl-, O-sec.-butyl- and O-tert.-butyl-methane or -ethane-, -propane- or -phenyl-thionophosphonic acid ester-chloride, as well as O-methyl-N-methyl-, O-ethyl-N-methyl-, O-n-propyl-N-methyl-, O-iso-propyl-N-methyl-, O-n-butyl-N-methyl-, O-methyl-N-ethyl-, O-ethyl-N-n-propyl-, O-ethyl-N-iso-propyl-, O-n-propyl-N-ethyl-, O-iso-propyl-N-ethyl- and O-n-propyl-N-ethyl-thionophosphoric acid ester-amide-chloride.

The triazoles of the formula (III), some of which are new, can be prepared by processes which are known in principle, in particular:

(a) If X represents sulphur, the known thiosemicarbazide derivatives of the general formula

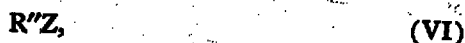


may be reacted, for example, with pyrocarbonic acid diethyl ester, to give intermediate products of the following general formula



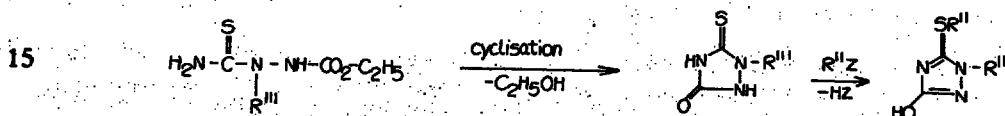
in which

R''' has the abovementioned meaning; the compounds of the formula (V) may be cyclised and reacted with a compound of the formula

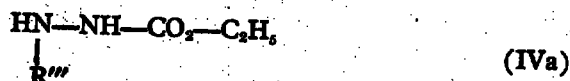


wherein

Z is a radical which is easily removed, for example halogen. This method is illustrated by the following formula scheme:



By an alternative method the intermediate products of formula (V) may be prepared by reacting of N-alkylcarbonic acid ethyl ester hydrazids of the formula



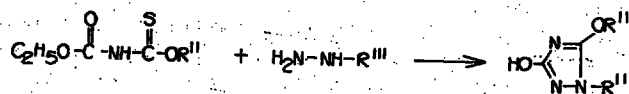
with potassium thiocyanate.

(b) If X represents oxygen, chloroformic acid ethyl ester may be reacted with potassium thiocyanate and subsequently with an alcohol to give a compound of the general formula



wherein

R'' has the abovementioned meaning, and this intermediate product may be cyclised in the presence of a hydrazine derivative in accordance with the following reaction scheme:



The following may be mentioned individually as examples of triazolyl derivatives (III) to be used in the process of the invention: 1-methyl-, 1-ethyl-, 1-n-propyl- and 1-iso-propyl-3-hydroxy-5-methoxytriazole-(1,2,4) and also the corresponding -5-ethoxy-, -5-n-propoxy-, -5-iso-propoxy-, -5-methylthio-, -5-ethylthio-, -5-n-propylthio-, -5-iso-propylthio-, -5-allyloxy-, -5-allylthio-, -5-cyanomethyloxy- and -5-cyanomethylthio derivatives.

The process of the invention is preferably carried out with the use of a solvent (this term includes a mere diluent). Practically all inert organic solvents can be used for this purpose. These in particular include aliphatic and aromatic (optionally chlorinated) hydrocarbons, e.g. benzene, toluene, xylene, benzine, methylene chloride, chloroform, carbon tetrachloride and chlorobenzene; ethers, e.g. diethyl ether, dibutyl ether and dioxan; ketones, e.g. acetone, methyl ethyl ketone, methyl isopropyl ketone and methyl isobutyl ketone; and nitriles, e.g. 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, and also aliphatic, aromatic or heterocyclic amines, especially triethylamine, dimethylamine, dimethylaniline, dimethylbenzylamine and pyridine, have proved particularly suitable.

The reaction temperature can be varied over a wide range. In general, the reaction is carried out at 0 to 120°C, preferably at 20 to 70°C. It is allowed in general to take place under normal pressure.

To carry out the process, the starting compounds are generally employed in equimolar ratios. An excess of one or other component in general does not appear to result in any significant advantage. The reaction is preferably carried out in the presence of one of the abovementioned solvents, optionally in the presence of an acid acceptor, at the indicated temperatures. After a reaction time of one or more hours, in most cases at raised temperatures, the batch may be cooled and the reaction mixture poured into water and taken up in an organic solvent, for example benzene. Thereafter, the mixture may be worked up in the usual manner by drying the organic phase, evaporating the solvent and optionally distilling the residue.

Most of the new compounds are obtained in the form of oils which can in some cases not be distilled without decomposition but can be freed of the last volatile constituents by so-called "slight distillation", that is to say prolonged heating under reduced pressure to moderately elevated temperatures, and they can in this way be purified. They are characterised, above all, by the refractive index.

The O-triazolylthionophosphoric(phosphonic) acid esters and ester-amides according to the invention are distinguished by an excellent insecticidal, especially soil-insecticidal, and acaricidal activity against plant pests, hygiene pests and pests of stored products and, in the veterinary medicine field, by an excellent activity against animal ectoparasites, such as parasitic fly larvae and ticks. They couple a low phytotoxicity with a good action both against biting and against sucking insects.

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

To the sucking insects there belong, in the main, aphids (*Aphidae*) 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 (*Hyalopterus arundinis*) and the cherry black-fly (*Myzus cerasi*); in addition, scales and mealybugs (*Coccinea*), for example the oleander scale (*Aspidiotus hederae*) 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 bed bug (*Cimex lectularius*), the assassin bug (*Rhodnius prolixus*) and Chagas' 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 cut-worm (*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 kuehniella*) and the 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 (*Lepidotarsa 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 frischii*), 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 (*Ceratitis 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 process products 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 (including 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, 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 of 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 use 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, sprinkling, 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 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.

Example A.

Phaedon larvae 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.

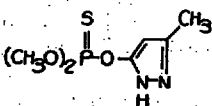
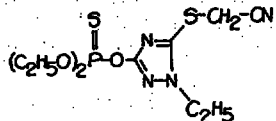
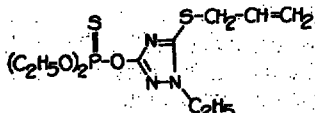
Cabbage plants (*Brassica oleracea*) were sprayed with the preparation of the active compound until dripping wet and were then infested with mustard beetle larvae (*Phaedon cochleariae*).

After the specified periods of time, the degree of destruction was determined in %: 100% means that all beetle larvae were killed whereas 0% means that none of the beetle larvae were killed.

The active compounds, the concentrations of the active compounds, the evaluation times and the results can be seen from the following Table 1:

TABLE 1

(Phaedon larvae test)

Active compound	Active compound concentration in % by weight	Degree of destruction in % after 3 days
 (known)	0.1	0
	0.1 0.01	100 100
	0.1 0.01	100 100

Example B.

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 2:

TABLE 2

(Plutella test)

Active compound	Active compound concentration in % by weight	Degree of destruction in % after 3 days
$\begin{array}{c} \text{S} \\ \parallel \\ (\text{CH}_3\text{O})_2\text{P}-\text{O}-\text{C}_5\text{H}_4\text{N} \\ \text{H} \end{array}$ (known)	0.1	0
$\begin{array}{c} \text{S} \\ \parallel \\ (\text{C}_2\text{H}_5\text{O})_2\text{P}-\text{O}-\text{C}_5\text{H}_4\text{N}-\text{CH}_2\text{CN} \\ \text{C}_2\text{H}_5 \end{array}$	0.1 0.01	100 100
$\begin{array}{c} \text{S} \\ \parallel \\ (\text{C}_2\text{H}_5\text{O})_2\text{P}-\text{O}-\text{C}_5\text{H}_4\text{N}-\text{CH}_2\text{CH}=\text{CH}_2 \\ \text{C}_2\text{H}_5 \end{array}$	0.1 0.01 0.001	100 100 50

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.

5 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. 5

The active compounds, the concentrations of the active compounds, the evaluation times and the results can be seen from the following Table 3:

TABLE 3

(Myzus test)

Active compound	Active compound concentration in % by weight	Degree of destruction in % after 1 day
$\text{(CH}_3\text{O)}_2\text{P(=S)-O-}\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{N} \\ \diagdown \\ \text{H} \end{array}$ (known)	0.1	0
$\text{(C}_2\text{H}_5\text{O)}_2\text{P(=S)-O-}\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{N} \\ \diagdown \\ \text{H} \end{array}$ (known)	0.1 0.01 0.001	99 40 0
$\text{(C}_2\text{H}_5\text{O)}_2\text{P(=S)-O-}\begin{array}{c} \text{S-CH}_2\text{-CN} \\ \diagup \\ \text{N} \\ \diagdown \\ \text{N-C}_2\text{H}_5 \end{array}$	0.1 0.01 0.001	100 100 100
$\text{(C}_2\text{H}_5\text{O)}_2\text{P(=S)-O-}\begin{array}{c} \text{S-CH}_2\text{-CH=CH}_2 \\ \diagup \\ \text{N} \\ \diagdown \\ \text{N-C}_2\text{H}_5 \end{array}$	0.1 0.01 0.001	100 100 99

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Example D.

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Critical concentration test/soil insects

Test insect: *Tenebrio molitor*

Solvent: 3 parts by weight of acetone

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

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

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The preparation of active compound was intimately mixed with soil. The concentration of the active compound in the preparation was of practically no importance; only the amount by weight of active compound per unit volume of soil, which is given in ppm (mg/l) was decisive. The soil was filled into pots and the pots were left to stand at room temperature. After 24 hours, the test animals were introduced into the treated soil and after a further 48 hours the degree of effectiveness of the active compound was determined in % by counting the dead and live test insects. The degree of destruction was 100% if all test insects were killed and was 0% if just as many test insects were still alive as in the case of the control.

The active compounds, the amounts used and the results can be seen from Table 4 which follows:

TABLE 4

Critical concentration test/soil insecticides

(Tenebrio molitor)

Degree of destruction in % at an active compound concentration of

Active compound	20	10	5	2.5	1.25 ppm
<chem>COP(=S)(OC)Oc1c[nH]c(C)c1</chem> (known)	0				
<chem>CCOP(=S)(OCC)Oc1c[nH]c(C)c1</chem> (known)	0				
<chem>CCOP(=S)(OCC)Oc1c[nH]c(C)nc1SCC=C</chem>	100	100	95	50	

Example E.

Tetranychus 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 so obtained 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 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 from the following Table 5:

TABLE 5

(Tetranychus test)

Active compound	Active compound concentration in % by weight	Degree of destruction in % after 2 days
$\begin{array}{c} \text{S} \\ \parallel \\ (\text{CH}_3\text{O})_2\text{P}-\text{O}-\text{N} \begin{array}{c} \diagup \text{CH}_3 \\ \diagdown \text{H} \end{array} \end{array}$ (known)	0.1	0
$\begin{array}{c} \text{S} \\ \parallel \\ (\text{C}_2\text{H}_5\text{O})_2\text{P}-\text{O}-\text{N} \begin{array}{c} \diagup \text{CH}_3 \\ \diagdown \text{H} \end{array} \end{array}$ (known)	0.1 0.01	50 0
$\begin{array}{c} \text{S} \\ \parallel \\ (\text{C}_2\text{H}_5\text{O})_2\text{P}-\text{O}-\text{N} \begin{array}{c} \diagup \text{S}-\text{CH}_2-\text{CN} \\ \diagdown \text{N}-\text{C}_2\text{H}_5 \end{array} \end{array}$	0.1 0.01	100 90
$\begin{array}{c} \text{S} \\ \parallel \\ (\text{C}_2\text{H}_5\text{O})_2\text{P}-\text{O}-\text{N} \begin{array}{c} \diagup \text{S}-\text{CH}_2-\text{CH}=\text{CH}_2 \\ \diagdown \text{N}-\text{C}_2\text{H}_5 \end{array} \end{array}$	0.1 0.01	100 100

Example F.

Tick test

Solvent: 35 parts by weight of ethylene glycol monomethyl ether

Emulsifier: 35 parts by weight of nonylphenyl polyglycol ether

To prepare a suitable formulation, 3 parts by weight of active compound were mixed with 7 parts of the above-mentioned solvent-emulsifier mixture and the emulsion concentrate thus obtained was diluted with water to the particular desired concentration.

Example H.

Critical concentration test

Test nematode: *Meloidogyne incognita*

Solvent: 3 parts by weight of acetone

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

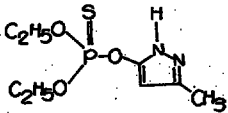
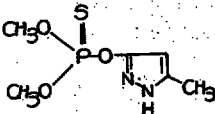
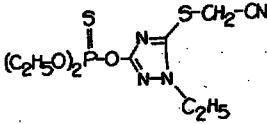
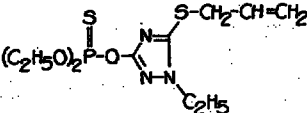
To produce a suitable preparation of active compound, 1 part by weight of active compound was mixed with the stated amount of solvent, the stated amount of emulsifier was added and the concentrate was diluted with water to the desired concentration.

The preparation of active compound was intimately mixed with soil which was heavily infested with the test nematodes. The concentration of the active compound in the preparation was of practically no importance; only the amount of active compound per unit volume of soil, which is given in ppm(w/v), was decisive. The soil was filled into pots, lettuce was sown in and the pots were kept at a greenhouse temperature of 27°C. After 4 weeks, the lettuce roots were examined for infestation with nematodes, and the degree of effectiveness of the active compound was determined as a percentage. The degree of effectiveness is 100% when infestation was completely avoided; it is 0% when the infestation was exactly the same as in the case of the control plants in untreated soil which had been infested in the same manner.

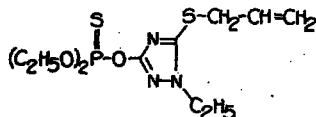
The active compound, the amounts applied and the results can be seen from the following Table 8:

TABLE 8

(Meloidogyne incognita test)

Active compound	Degree of destruction in % at an active compound concentration of					
	20	10	5	2.5	1.25	0.525 ppm
 (known)	0					
 (known)	0					
	100	97	50			
	100	100	98	97	50	

Example 1.



19 g (0.1 mole) of O,O-diethylthionophosphoric acid diester chloride were added dropwise to a mixture of 19 g (0.1 mole) of 1-ethyl-3-hydroxy-5-allylmercapto-1,2,4-triazole and 15 g of potassium carbonate in 200 ml of acetonitrile, during which addition the internal temperature of the mixture slowly rose from 22 to 30°C. After stirring the mixture for three hours at 80°C, it was cooled and poured into water, and the batch was taken up in benzene. The organic phase was washed and dried, the solvent was evaporated under reduced pressure and the residue was subjected to "slight distillation". 29 g (86% of theory) of O,O-diethyl-O-[1,ethyl-5-allylmercapto-1,2,4-triazolyl-(3)] thionophosphoric acid ester of refractive index n_D^{24} : 1.5160 were obtained.

Examples 2.

The following compound was prepared analogously to Example 1:

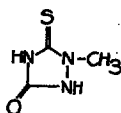
Compound	Physical properties (refractive index)	Yield (% of theory)
(2)	n_D^{24} : 1.5184	71

The compounds in the following Table 9 were prepared by a process analogous to that of Example 1. In the table, the compounds are identified by the meanings of the symbols R, R', R'' and R''' in formula (I).

R	R'	R''	R'''
CH ₃	CH ₃ O	CH ₂ -CH=CH ₂	CH ₃
C ₂ H ₅	C ₂ H ₅ O	CH ₂ -CH=CH ₂	CH ₃
CH ₃	CH ₃ O	CH ₂ -CH=CH ₂	CH(CH ₃) ₂
C ₂ H ₅	C ₂ H ₅ O	CH ₂ -CH=CH ₂	CH(CH ₃) ₂
CH ₃	C ₂ H ₅	CH ₂ -CH=CH ₂	CH ₃
C ₂ H ₅	C ₂ H ₅	CH ₂ -CH=CH ₂	C ₂ H ₅
C ₂ H ₅	C ₂ H ₅	CH ₂ -CH=CH ₂	CH(CH ₃) ₂
C ₂ H ₅	C ₂ H ₅ O	CH ₂ -CH=CH ₂	CH ₂ -CH ₂ -CN
C ₂ H ₅	C ₂ H ₅ O	CH ₂ -CH=CH-CH ₃	CH ₃
C ₂ H ₅	C ₂ H ₅	CH ₂ -CH=CH ₂	CH ₂ -CH ₂ -CN
CH ₃	CH ₃ O	CH ₂ -CH=CH-CH ₃	CH(CH ₃) ₂
CH ₃	CH ₃ O	CH ₂ -CN	CH ₃
C ₂ H ₅	C ₂ H ₅ O	CH ₂ -CN	CH(CH ₃) ₂
C ₂ H ₅	C ₂ H ₅	CH ₂ -CN	C ₂ H ₅
CH ₃	CH ₃ O	CH ₂ -CH ₂ -CN	CH ₃
C ₂ H ₅	C ₂ H ₅ O	CH ₂ -CH ₂ -CN	CH(CH ₃) ₂
CH ₃	CH ₃ O	CH ₃	CH ₂ -CH ₂ -CN
C ₂ H ₅	C ₂ H ₅	CH ₃	CH ₂ -CH ₂ -CN
CH ₃	CH ₃ O	C ₂ H ₅	CH ₂ -CH ₂ -CN
C ₂ H ₅	C ₂ H ₅ O	C ₂ H ₅	CH ₂ -CH ₂ -CN
C ₂ H ₅	CH ₃	CH ₃	CH ₂ -CH ₂ -CN
CH ₃	CH ₃	CH ₃	CH ₂ -CH ₂ -CN
CH ₃	CH ₃ NH	CH ₃	CH ₃
CH ₃	C ₂ H ₅ NH	CH ₃	CH(CH ₃) ₂
C ₂ H ₅	(CH ₃) ₂ N	CH ₃	CH ₂ -CH ₂ -CN
C ₂ H ₅	(CH ₃) ₂ CH-NH	CH ₂ -CH=CH ₂	CH ₃
C ₂ H ₅	(CH ₃) ₂ CH-NH	CH ₂ -CH=CH ₂	CH(CH ₃) ₂
C ₂ H ₅	(CH ₃) ₂ CH-NH	CH ₂ CN	CH(CH ₃) ₂
C ₂ H ₅	(CH ₃) ₂ CH-NH	CH ₂ -CH=CH ₂	CH ₂ -CH ₂ -CN
C ₂ H ₅	C ₂ H ₅ O	CH ₃	CH(CN)CH ₃
C ₂ H ₅	C ₂ H ₅ O	CH ₂ -CH=CH ₂	CH(CN)CH ₃

The triazolyl derivatives (III) used as starting substances were prepared as exemplified below.

Example a1.



5 35.4 g (0.2 mol) of



5

10 (prepared from methylthiosemicarbazide and pyrocarbonic acid diethyl ester, melting point 170°C) and 0.2 mol of sodium methylate — dissolved in 100 ml of methanol — were heated for 5 hours under reflux and subsequently evaporated under reduced pressure and the residue was dissolved in water and again precipitated with hydrochloric acid. 17 g (65% of theory) of the compound of the above formula, of melting point 250°C, were obtained.

10

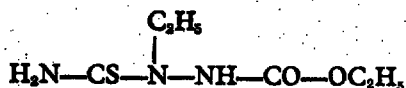
Analogously, the following compounds were obtained from



15

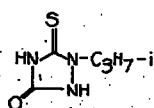
(prepared from N-iso-propylcarbonic acid ethyl ester hydrazide and potassium thiocyanate, melting point 168°C) or from

15



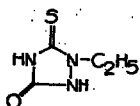
(obtained from N-ethylcarbonic acid ethyl ester hydrazide and potassium thiocyanate, melting point 133°C), respectively:

20



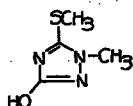
Melting point 228°C;
Yield: 60% of theory

20



Melting point 222°C;
Yield: 76% of theory

Example a2.

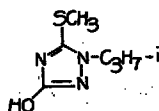


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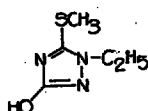
13.1 g (0.1 mol) of the compound obtained in Example a1 and 6 g of potassium hydroxide were dissolved in 50 ml of water and 12.6 g of dimethyl sulphate were added. The batch was stirred for 2 hours at 25°C and the reaction solution was extracted with methylene chloride and worked up in the usual manner. 143 g (98% of theory) of 1-methyl-3-hydroxy-5-methylmercapto-1,2,4-triazole of melting point 130°C were obtained.

25

The following were prepared analogously:

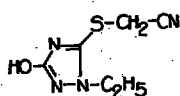


Melting point 94°C;
Yield: 60% of theory



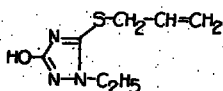
Melting point 91—93°C;
Yield: 33% of theory

Example a3.



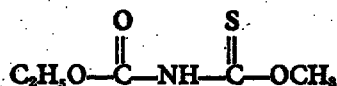
0.5 mol of sodium methylate, followed by 38 g of chloroacetonitrile, were added to a solution of 73 g (0.5 mol) of 1-ethyl-3-hydroxy-triazole-5-thione in 300 ml of methanol, the temperature of the reaction mixture being 30 to 40°C. After stirring for 24 hours the precipitate which had separated out was filtered off, the filtrate was concentrated under reduced pressure and the residue was triturated with water, filtered off and dried. After recrystallisation from acetonitrile, 19 g (20.6% of theory) of 1-ethyl-3-hydroxy-5-cyanomethyl-mercapto-1,2,4-pyrazole of melting point 127°C were obtained.

The following compound was obtained analogously by reaction with allyl bromide:



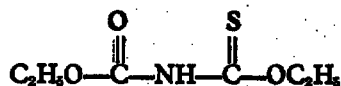
Melting point 76—77°C;
Yield: 35% of theory

Example b1.



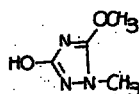
327 g of chloroformic acid ethyl ester were added to a solution or suspension of 300 g (3 mols) of potassium thiocyanate in 800 ml of dry acetone, during which addition the temperature of the mixture rose to 30—40°C; the mixture was stirred for 3 hours and 200 ml of methanol were then added at 50 to 60°C. After further stirring overnight, the solid constituents were filtered off, the filtrate was evaporated under reduced pressure and the residue was stirred up with water. After filtration and drying, 314 g (64% of theory) of N-carboethoxy-thiomethyl-urethane of melting point 48°C were obtained.

The following compound was obtained analogously by reaction with ethanol.



Melting point 46°C;
Yield: 62% of theory

Example b2.



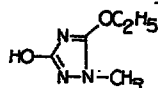
46 g of methylhydrazine were added to 163 g (1 mol) of N-carboethoxy-thiomethylurethane — dissolved in 500 ml of methanol — during which addition the temperature of the reaction solution rose to 20—30°C. The batch was then slowly warmed

to 80°C and was then boiled for 2 hours under reflux. After cooling the mixture, the residue was filtered off and recrystallised from methanol, whereupon 44 g (34% of theory) of 1-methyl-3-hydroxy-5-methoxy-1,2,4-triazole of melting point 216°C were obtained.

5

The following compound was obtained analogously from N-carboethoxy-thioethyl-urethane:

5



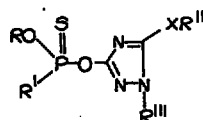
Melting point 162°C;
Yield: 55% of theory

WHAT WE CLAIM IS:—

10

1. O-triazolythiono-phosphoric(phosphonic) acid esters and ester-amides of the general formula

10



(I)

in which

15

R denotes alkyl with 1 to 6 carbon atoms,
R' denotes alkyl, alkoxy or mono- or di-alkylamino with 1 to 6 carbon atoms in each alkyl or alkoxy or phenyl,
R'' denotes alkyl or cyanoalkyl with 1 to 4 carbon atoms in each alkyl or alkenyl with 3 or 4 carbon atoms,

15

20

X denotes oxygen or sulphur, and
R''' denotes alkyl or cyanoalkyl with 1—6 carbon atoms in each alkyl, provided that R'' and R''' do not both simultaneously denote alkyl.

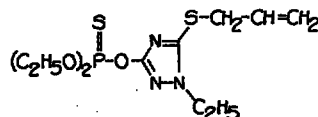
20

25

2. Compounds according to claim 1 in which R denotes alkyl with 1 to 4 carbon atoms, R' denotes alkyl or alkylamino with 1 to 4 carbon atoms or phenyl, R'' denotes alkenyl with 3 carbon atoms or cyanomethyl, and R''' denotes alkyl with 1 to 3 carbon atoms.

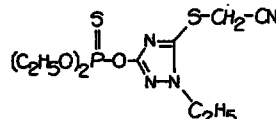
3. A compound of the formula

25



(9)

4. A compound of the formula

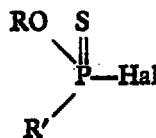


(10)

30

5. A process for the production of a compound according to any of claims 1—18 in which a thionophosphoric(phosphonic) acid ester-halide or ester-amide-halide of the general formula

30



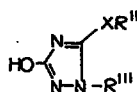
(II)

in which

35

R and R' have the meanings given in claim 1, and
Hal denotes halogen,
is reacted with a triazolyl derivative of the general formula

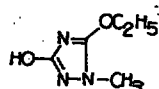
35



(III)

to 80°C and was then boiled for 2 hours under reflux. After cooling the mixture, the residue was filtered off and recrystallised from methanol, whereupon 44 g (34% of theory) of 1-methyl-3-hydroxy-5-methoxy-1,2,4-triazole of melting point 216°C were obtained.

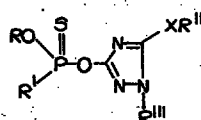
The following compound was obtained analogously from N-carboethoxy-thioethyl-urethane:



Melting point 162°C;
Yield: 55% of theory

WHAT WE CLAIM IS:—

1. O-triazolylthiono-phosphoric(phosphonic) acid esters and ester-amides of the general formula



(I)

in which

R denotes alkyl with 1 to 6 carbon atoms,

R' denotes alkyl, alkoxy or mono- or di-alkylamino with 1 to 6 carbon atoms in each alkyl or alkoxy or phenyl,

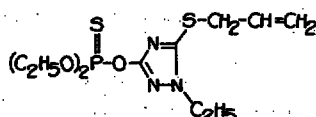
R'' denotes alkyl or cyanoalkyl with 1 to 4 carbon atoms in each alkyl or alkenyl with 3 or 4 carbon atoms,

X denotes oxygen or sulphur, and

R''' denotes alkyl or cyanoalkyl with 1—6 carbon atoms in each alkyl, provided that R'' and R''' do not both simultaneously denote alkyl.

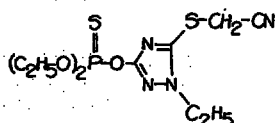
2. Compounds according to claim 1 in which R denotes alkyl with 1 to 4 carbon atoms, R' denotes alkyl or alkylamino with 1 to 4 carbon atoms or phenyl, R'' denotes alkenyl with 3 carbon atoms or cyanomethyl, and R''' denotes alkyl with 1 to 3 carbon atoms.

3. A compound of the formula



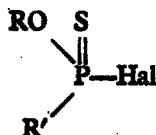
(9)

4. A compound of the formula



(10)

5. A process for the production of a compound according to any of claims 1—18 in which a thionophosphoric(phosphonic) acid ester-halide or ester-amide-halide of the general formula

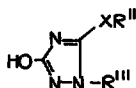


(II)

in which

R and R' have the meanings given in claim 1, and

Hal denotes halogen, is reacted with a triazolyl derivative of the general formula



(III)



in which

X, R'' and R''' have the meanings given in claim 1, in the presence of an acid acceptor or in the form of an alkali metal salt, alkaline earth metal salt or ammonium salt.

5 6. A process according to claim 5 in which the compound of the formula II is any of those hereinbefore specifically identified. 5

7. A process according to claim 5 or 6 in which the compound of the formula III is any of those hereinbefore specifically identified.

10 8. A process according to any of claims 5—7 in which the reaction is carried out in the presence of a solvent. 10

9. A process according to any of claims 5—8 in which the reaction is carried out at 20—70°C.

10. A process for the production of a compound according to claim 1 substantially as hereinbefore described in Examples 1 and 2.

15 11. Compounds according to claim 1 whenever prepared by a process according to any of claims 5—10. 15

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. 20

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—18 or 25 in admixture with a diluent or carrier. 25

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

16. 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—4 or 11 was applied alone or in admixture with a diluent or carrier. 30

17. Each of the compounds according to claim 1 which are hereinbefore identified in Table 9.

18. A composition according to claim 12 or 13 in which the active compound is according to claim 17. 35

19. A method according to claim 14 or 15 in which the active compound is according to claim 17.

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