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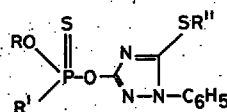
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(71) We, BAYER AKTIENGESellschaft, a body corporate organised under the laws of Germany, of Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to certain new O-triazolylthionophosphoric-(phosphonic) acid esters, to a process for their preparation and to their use as insecticides and acaricides.

It is already known that pyrazolothionophosphoric acid esters, for example O,O-diethyl- or O,O-dimethyl-O-[3-methylpyrazol(5)yl]-thionophosphoric acid ester, and triazolothionophosphoric acid esters, for example O,O-dimethyl- or O,O-diethyl-O-[1-methyl-5-methylmercapto-1,2,4-triazol(3)yl]- or O,O-dimethyl-O-[1-ethyl-5-methylmercapto-1,2,4-triazol(3)-yl]-thionophosphoric acid ester, possess insecticidal and acaricidal properties (see U.S. Patent Specification 2,754,244 and German Offenlegungsschrift (German Published Specification) 2,259,960).

The present invention provides, as new compounds, the O-triazolylthionophosphoric(phosphonic) acid esters of the general formula



(I),

in which

R is alkyl with 1 to 6 carbon atoms,

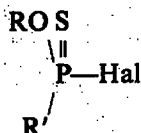
R is alkyl with 1 to 6 carbon atoms,
R' is alkyl or alkoxy with in either case 1 to 6 carbon atoms, and

R' is cyanoalkyl with 1 to 4 carbon atoms in the alkyl part.

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

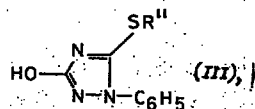
Preferably, R is straight-chain or branched alkyl with 1 to 5, especially 1 to 4, carbon atoms, R' is straight-chain or branched alkyl or alkoxy with in either case 1 to 5, especially 1 to 4, carbon atoms, and R'' is cyanoalkyl with 1 to 3 carbon atoms in the alkyl part.

The present invention also provides a process for the preparation of an O-triazolylthionophosphoric(phosphonic) acid ester of the formula (I), in which a thionophosphoric(phosphonic) acid (di)ester halide of the general formula



(II),

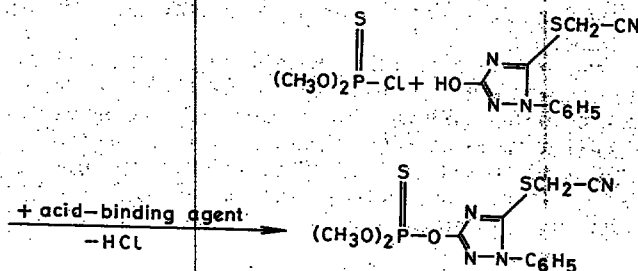
in which
 R and R' have the above-mentioned meanings, and
 Hal is halogen, preferably chlorine,
 is reacted with an hydroxytriazole derivative of the general formula



in which
 R'' has the above-mentioned meaning,
 the latter being reacted as such in the presence of an acid-binding agent, or in
 the form of an alkali metal salt, alkaline earth metal salt or ammonium salt
 thereof.

Surprisingly, the O-triazolythionophosphoric(phosphonic) acid esters
 according to the invention show a better insecticidal and acaricidal action than the
 previously known compounds of analogous structure and of the same type of
 action. They act not only against insects and mites which are harmful to plants, but
 also against ectoparasites, for example parasitic fly larvae, in the veterinary
 medicine field. The compounds according to the invention thus represent a
 genuine enrichment of the art.

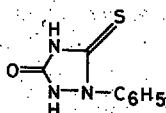
If, for example O,O-dimethylthionophosphoric acid diester chloride and 1-
 phenyl-3-hydroxy-5-cyanomethylmercaptotriazole-(1,2,4) are used as starting
 materials, the course of the reaction can be represented by the following equation:



The thionophosphoric(phosphonic) acid ester halides (II) to be used as
 starting materials are known from the literature and can be prepared according to
 generally customary processes, even on a large industrial scale.

The following may be mentioned as examples thereof: O,O-dimethyl-,
 O,O-diethyl-, O,O-di-n-propyl-, O,O-di-isopropyl-, O,O-di-n-butyl-, O,O-di-iso-
 butyl-, O,O-di-tert.-butyl-, O-ethyl-O-n-propyl-, O-ethyl-O-isopropyl- or O-ethyl-
 O-sec.-butyl-thionophosphoric acid ester chloride and O-methyl-, O-ethyl-,
 O-n-propyl-, O-isopropyl-, O-n-butyl-, O-sec.-butyl-, O-isobutyl- or O-tert.-butyl-
 methane-, -ethane-, -n-propane-, -isopropane-, n-butane-, isobutane-, -sec-
 -butane- or -tert.-butane-thionophosphonic acid ester chloride.

The triazoles of the formula (III), which in some cases are new, can be
 prepared according to processes which are known in principle. For example,
 halogenocarbonic acid alkyl esters are reacted with potassium thiocyanate and
 subsequently with phenylhydrazine to give the intermediate of the formula



which can then be converted to the desired hydroxytriazoles (III) by reaction with
 halogenoalkanecarboxylic acid nitriles in the presence of alcohols.

The following may be mentioned as examples of the triazole derivatives (III)
 to be used as starting materials: 5-cyanomethylmercapto-, 5-(2-cyanoethyl-
 mercapto)-, 5-(1-cyanoethylmercapto)- or 5-(3-cyanopropylmercapto)-3-hydroxy-
 1-phenyltriazole-(1,2,4).

The preparative process is preferably carried out with conjoint use of suitable

solvents and diluents. 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-acceptors can be used as acid-binding agents. Alkali metal carbonates and alkali metal alcoholates, such as sodium carbonate, methylate and ethylate, and potassium carbonate, 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 from 15° to 80°C.

In general, the starting components are employed in substantially equimolar amounts in carrying out the process. An excess of one or other reactant produces no significant advantages. The reaction is preferably carried out in one of the above-mentioned solvents in the presence of an acid-acceptor at the indicated temperatures, whilst stirring the mixture, and after a period of reaction of one or more hours—in most cases at elevated temperatures—the reaction mixture is worked up in accordance with customary methods. In general, the reaction solution is poured into water and taken up in an organic solvent, for example benzene, the organic phase is washed and dried, and the solvent is distilled off under reduced pressure.

The new compounds are frequently obtained in the form of oils which in most cases cannot be distilled without decomposition but can be 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 can be purified in this way. They are characterised by the refractive index. Others of the products are obtained in a crystalline form with sharp melting point.

As has already been mentioned, the O-triazolylthionophosphoric(phosphonic) acid esters according to the invention are distinguished by an outstanding insecticidal and acaricidal activity. They act not only 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. The products possess low phytotoxicity and a good action both against sucking and against biting insects. In addition, some of the compounds show a nematocidal activity.

For this reason, the new compounds 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 (*Aphididae*) such as the green peach aphid (*Myzus persicae*), the bean aphid (*Doralis fabae*), the bird cherry aphid (*Rhopalosiphum padi*), the pea aphid (*Macrosiphum pisi*) and the potato aphid (*Macrosiphum solanifolii*), the currant gall aphid (*Cryptomyzus korschelti*), the rosy apple aphid (*Sappaphis mali*), the mealy plum aphid (*Hyalopterus arundinis*) and the cherry black-fly (*Myzus cerasi*); in addition, scales and mealybugs (*Coccina*), 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 box 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 cutworm (*Agrotis segetum*), the large white butterfly (*Pieris brassicae*), the small winter moth (*Cheimatobia brumata*), the green oak tortrix moth (*Tortrix viridana*), the fall armyworm (*Laphygma frugiperda*) and cotton worm (*Prodenia litura*), the ermine moth (*Hyponomeuta padella*), the

Mediterranean flour moth (*Ephestia kühniella*) and greater wax moth (*Galleria mellonella*).

Also to be classed with the biting insects are beetles (*Coleoptera*) for example the granary weevil (*Sitophilus granarius*=*Calandra granaria*), the Colorado beetle (*Leptinotarsa decemlineata*), the dock beetle (*Gastrophysa viridula*), the mustard beetle (*Phaedon cochleariae*), the blossom beetle (*Meligethes aeneus*), the raspberry beetle (*Byturus tomentosus*), the bean weevil (*Bruchidius*=*Acanthoscelides obiectus*), the leather beetle (*Dermestes frischeri*), 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 (*Acarina*) 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 black currant 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 pests harmful to health 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 or 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 sulfoxide 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 aerosol propellants, such as halogenated hydrocarbons, for example Freon (registered trade mark).

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

Preferred examples of emulsifying and foam-forming agents include non-ionic and anionic emulsifiers, such as polyoxyethylene-fatty acid esters, polyoxyethylene-fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkyl sulphonates, alkyl sulphates and aryl sulphonates as well as albumin hydrolyzation

products; and preferred examples of dispersing agents include lignin sulphite waste liquors and methyl cellulose.

The active compounds according to the invention can be present in the formulations as a mixture with other active compounds.

In general, the formulations contain from 0.1 to 95 per cent by weight of active compound, preferably from 0.5 to 90 per cent by weight.

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

The active compound concentrations in their 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.

The present invention also provides an insecticidal or acaricidal composition containing as active ingredient a compound of the present 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 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 compounds of this invention is illustrated by the following biotest Examples, wherein the active compounds of this invention are each identified by the number of the corresponding preparative Example hereinafter.

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:

TABLE A

(Phaedon larvae test)

Active compound	Active compound concentration in %	Degree of destruction in % after 3 days
<chem>CC1=CN(C1)OP(=S)(OC)OC</chem> (known)	0.1	0
<chem>CC1=CN(C1)OP(=S)(OCC)OCC</chem> (known)	0.1 0.01 0.001	100 100 0
<chem>CSC1=NC(C1)OP(=S)(OC)OC</chem> (known)	0.1 0.01 0.001	100 100 0
<chem>CCN1C(C1)OP(=S)(OC)OC</chem> (known)	0.1 0.01 0.001	100 100 0
<chem>CCN1C(C1)OP(=S)(OCC)OCC</chem> (known)	0.1 0.01 0.001	100 100 0
(2)	0.1 0.01 0.001	100 100 70
(1)	0.1 0.01 0.001	100 100 95
(3)	0.1 0.01 0.001	100 100 100
(4)	0.1 0.01 0.001	100 100 100

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:

TABLE B

(Plutella test)

Active compound	Active compound concentration in %	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{CH}_3 \end{array} $	0.1	0
(known)		
(2)	0.1	100
	0.01	100
	0.001	70
(1)	0.1	100
	0.01	100
	0.001	100
(3)	0.1	100
	0.01	100
	0.001	100
(4)	0.1	100
	0.01	100
	0.001	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.

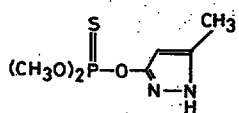
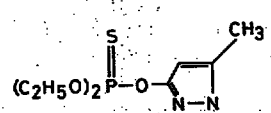
After the specified periods of time, the degree of destruction was determined

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:

TABLE C

(Myzus test)

Active compound	Active compound concentration in %	Degree of destruction in % after 1 day
 (known)	0.1	0
 (known)	0.1 0.01	99 40
(1)	0.1 0.01	100 90
(3)	0.1 0.01	100 100
(4)	0.1 0.01	100 99

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 effectiveness of the preparation of active compound was determined by counting the dead mites. The degree of destruction thus obtained is 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:

TABLE D

(Tetranychus test)

Active compound	Active compound concentration in %	Degree of destruction in % after 2 days
<chem>CC1=CN(C(=O)OP(=O)(OC)OC)C=C1</chem> (known)	0.1	0
<chem>CC1=CN(C(=O)OP(=O)(OCC)OCC)C=C1</chem> (known)	0.1 0.01	50 0
(3)	0.1 0.01	100 55

Example E.

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

Solvent: 35 parts by weight of ethylene polyglycol monomethyl 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* res.) were introduced into a test tube which contained approximately 2 ml of horse muscle. 0.5 ml of the preparation of active compound was applied to this horse meat. After 24 hours, the degree of destruction in % was determined. 100% means that all larvae were killed and 0% means that no larvae were killed.

The test results obtained can be seen from the table which follows:

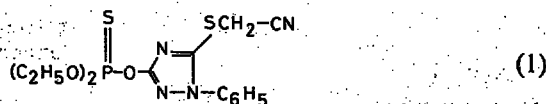
TABLE E

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

Active compound	Active compound concentration in ppm	Degree of destruction in %
(1)	100	100
	30	100
	10	100
	3	>50
	1	0

The process of this invention is illustrated in and by the following preparative Examples.

Example 1.



19 g (0.1 mole) of O,O-diethylthionophosphoric acid diester chloride were added to a mixture of 23 g (0.1 mole) of 1-phenyl-3-hydroxy-5-cyanomethylmercaptotriazole-(1,2,4) in 300 ml of acetonitrile and 15 g of potassium carbonate. After stirring for 4 hours at 80°C, the reaction mixture was poured into water and taken up in benzene. The organic phase was washed and dried. The solvent was then distilled off under reduced pressure. The residue was subjected to "slight distillation". This gave 29 g (76% of theory) of O,O-diethyl-O-[1-phenyl-5-cyanomethylmercapto-1,2,4-triazol(3)yl]-thionophosphoric acid ester having a refractive index n_D^{20} of 1.5589.

The following compounds of the general formula

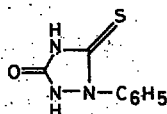


could be prepared by methods analogous to that of Example 1:

Example No.	R	R'	R''	Physical properties (refractive index or melting point)
2	CH ₃	CH ₃ O	NC-CH ₂	melting point 82°C.
3	C ₂ H ₅	C ₂ H ₅	NC-CH ₂	n_D^{22} : 1.5840
4	C ₂ H ₅	C ₂ H ₅ O	NC-CH ₂ -CH ₂	n_D^{22} : 1.5640

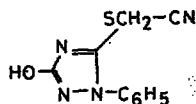
The hydroxytriazole derivatives (III) used as starting materials could be prepared, for example, as follows:

(a)



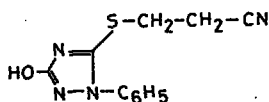
109 g of chlorocarbonic acid ethyl ester were added to a suspension of 96 g (1 mole) of dried potassium thiocyanate in 500 ml of acetone, whilst keeping the exothermic reaction at a temperature of between 30° and 40°C by external cooling of the mixture or by an appropriately slow addition of the ester. The reaction solution was then stirred for approx. 4 hours at 25° to 30°C and was subsequently added to a solution of 100 g of phenylhydrazine in 200 ml of acetone, which solution had beforehand been stirred for 3 hours. The reaction was slightly exothermic. The batch was stirred overnight, the precipitate which had separated out was filtered off, the solvent was evaporated off, a mixture of 800 ml of water and 100 ml of concentrated hydrochloric acid was added to the distillation residue, the batch was boiled for 2 hours and cooled, and the product was filtered off. The product thus obtained could be used directly for further operations without having to undergo additional purification processes. 100 to 110 g (52 to 55% of theory) of a crude product of melting point 218–225°C were obtained. A sample of 1-phenyl-3-oxo-5-thio-triazolidine-(1,2,4) recrystallised from acetonitrile melted at 235°C.

(b)



0.2 mole of sodium methylate, followed by 16 g of chloroacetonitrile, was added to 39 g of (0.2 mole) of the product obtained as described under (a), in 200 ml of methanol. The reaction mixture was stirred for 4 hours at 50° to 60°C, cooled and poured into water; the residue was filtered off, dried and recrystallised from acetonitrile. This gave 36 g (78% of theory) of 1-phenyl-3-hydroxy-5-cyanomethylmercaptotriazole-(1,2,4) of melting point 178°C.

The compound of the formula



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could be prepared analogously in 53% yield; the product had a melting point of 183°C.

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WHAT WE CLAIM IS:—

1. O-Triazolylthionophosphoric(phosphonic) acid esters of the general formula:



(I),

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in which

R is alkyl with 1 to 6 carbon atoms,

R' is alkyl or alkoxy with in either case 1 to 6 carbon atoms, and

R'' is cyanoalkyl with 1 to 4 carbon atoms in the alkyl part.

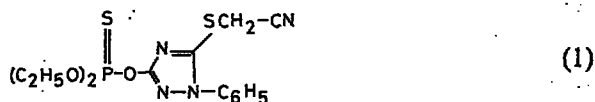
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2. Compounds according to claim 1, in which R is straight-chain or branched alkyl with 1 to 5 carbon atoms, R' is straight-chain or branched alkyl or alkoxy with in either case 1 to 5 carbon atoms, and R'' is cyanoalkyl with 1 to 3 carbon atoms in the alkyl part.

20

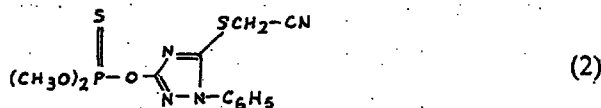
3. The compound of the formula



(1)

25

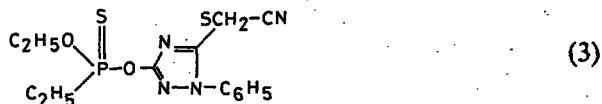
4. The compound of the formula



(2)

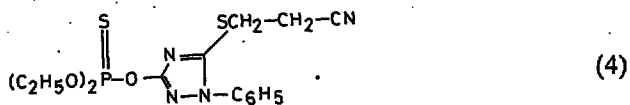
25

5. The compound of the formula



(3)

6. The compound of the formula

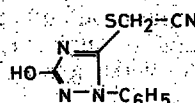


(4)

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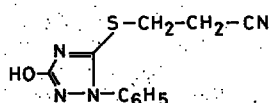
30

(b)



0.2 mole of sodium methylate, followed by 16 g of chloroacetonitrile, was added to 39 g of (0.2 mole) of the product obtained as described under (a), in 200 ml of methanol. The reaction mixture was stirred for 4 hours at 50° to 60°C, cooled and poured into water; the residue was filtered off, dried and recrystallised from acetonitrile. This gave 36 g (78% of theory) of 1-phenyl-3-hydroxy-5-cyanomethylmercaptotriazole-(1,2,4) of melting point 178°C.

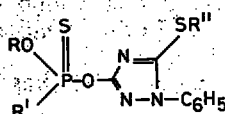
The compound of the formula



could be prepared analogously in 53% yield; the product had a melting point of 183°C.

WHAT WE CLAIM IS:—

1. O-Triazolylthionophosphoric(phosphonic) acid esters of the general formula



(I),

in which

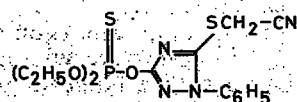
R is alkyl with 1 to 6 carbon atoms,

R' is alkyl or alkoxy with in either case 1 to 6 carbon atoms, and

R'' is cyanoalkyl with 1 to 4 carbon atoms in the alkyl part.

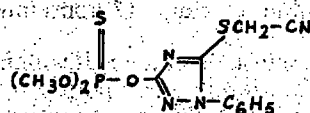
2. Compounds according to claim 1, in which R is straight-chain or branched alkyl with 1 to 5 carbon atoms, R' is straight-chain or branched alkyl or alkoxy with in either case 1 to 5 carbon atoms, and R'' is cyanoalkyl with 1 to 3 carbon atoms in the alkyl part.

3. The compound of the formula



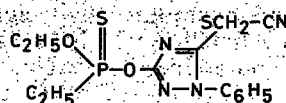
(1)

4. The compound of the formula



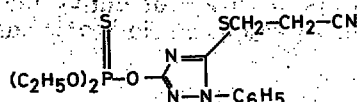
(2)

5. The compound of the formula



(3)

6. The compound of the formula



(4)





* C L M S *

12

1,452,455

12

7. A process for the preparation of an O-triazolythionophosphoric (phosphonic) acid ester according to claim 1, in which a thionophosphoric (phosphonic) acid (di)ester halide of the general formula



in which
R and R' have the meaning stated in claim 1, and
Hal is halogen,
is reacted with an hydroxytriazole derivative of the general formula



in which

R'' has the meaning stated in claim 1, the latter being reacted as such in the presence of an acid-binding agent, or in the form of an alkali metal salt, alkaline earth metal salt or ammonium salt thereof.

8. A process according to claim 7, in which Hal is chlorine.

9. A process according to claim 7 or 8, in which the reaction is effected in the presence of an inert organic solvent.

10. A process according to any one of claims 7 to 9, in which the reaction is effected at between 0° and 120°C.

11. A process according to claim 10, in which the reaction is effected at from 15° to 80°C.

12. A process according to any one of claims 7 to 11, in which the hydroxytriazole derivative is reacted as such in the presence, as an acid-binding agent, of an alkali metal carbonate, an alkali metal alcoholate or an aliphatic, aromatic or heterocyclic amine.

13. A process according to any one of claims 7 to 12, in which the reactants (II) and (III) are employed in substantially equimolar amounts.

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

15. Compounds according to claim 1 whenever prepared by a process according to any one of claims 7 to 14.

16. An insecticidal or acaricidal composition containing as active ingredient a compound according to claim 1 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.

17. A composition according to claim 16 containing from 0.1 to 95% of the active compound, by weight.

18. A composition according to claim 17 containing from 0.5 to 90% of the active compound, by weight.

19. A method of combating insects or acarids which comprises applying to the insects or acarids or to a habitat thereof a compound according to claim 1 alone or in the form of a composition containing as active ingredient a compound according to claim 1 in admixture with a diluent or carrier.

20. A method according to claim 19 in which a composition is used containing from 0.0001 to 10% of the active compound, by weight.

21. A method according to claim 20 in which a composition is used containing from 0.01 to 1% of the active compound, by weight.

22. A method according to any of claims 19 to 21 in which the active compound is one of those hereinbefore mentioned in any of Examples A to E.

23. 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 claim 1 was applied alone or in admixture with a diluent or carrier.



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