

PATENT SPECIFICATION

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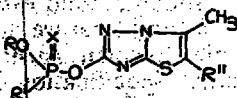
(54) TRIAZOLOTHIAZOLYL-(THIONO)-PHOSPHORIC
 (PHOSPHONIC) ACID ESTERS, PROCESS FOR THEIR
 PREPARATION AND THEIR USE AS INSECTICIDES AND
 ACARICIDES (INCLUDING TICKICIDES)

(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 triazolothiazolyl-(thiono)-phosphoric(phosphonic) acid esters, to a process for their preparation and to their use as insecticides and acaricides (including tickicides).

It is already known that pyrazolyl-thionophosphoric acid esters, for example O,O-diethyl-O-[3-methyl-pyrazolyl(5)]-thionophosphoric acid ester, possess an insecticidal and acaricidal action (compare US Patent Specification 2,754,244).

The present invention provides triazolothiazolyl-(thiono)-phosphoric(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 4 carbon atoms or alkoxy with 1 to 6 carbon atoms or phenyl,
 R'' is alkyl with 1 to 3 carbon atoms or alkylmercapto with 1 to 3 carbon atoms, and
 X is oxygen or sulphur.

Such compounds are distinguished by strong insecticidal and acaricidal (including tickicidal) activity.

Preferably, R is straight-chain or branched alkyl with 1 to 3 carbon atoms, R' is straight-chain or branched alkyl with 1 to 3 carbon atoms or alkoxy with 1 to 3 carbon atoms or phenyl, and R'' is methyl, ethyl, methylmercapto or ethylmercapto.

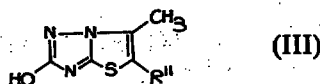
The invention also provides a process for the preparation of a triazolo-

thiazolyl-(thiono)-phosphoric(phosphonic) acid ester of the formula (I) in which a (thiono)-phosphoric (phosphonic) acid ester halide of the general formula



in which

R, R' and X have the above mentioned meanings, and Hal is halogen is reacted with a triazolothiazole derivative of the general formula



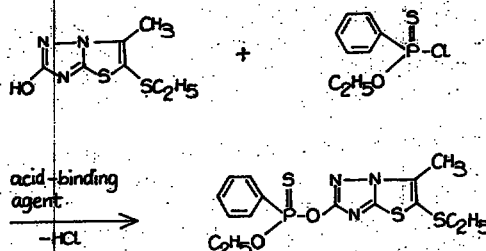
in which

R'' has the abovementioned meaning, optionally in the presence of an acid acceptor or in the form of a salt (preferably an alkali metal salt, alkaline earth metal salt or ammonium salt).

Preferably, Hal is chlorine.

Surprisingly, the triazolothiazolyl-(thiono)-phosphoric(phosphonic) acid esters according to the invention have a substantially better insecticidal and acaricidal (for example tickicidal) action than previously known compounds of analogous structure and of the same type of action. The compounds according to the invention thus represent a genuine enrichment of the art.

If, for example, 2-ethylmercapto-3-methyl-6-hydroxy-1,2,4-triazole-(2,3-b)-thiazole and O-ethyl-thionophenylphosphonic acid ester chloride are used as starting materials, the course of the reaction can be represented by the following formula scheme:

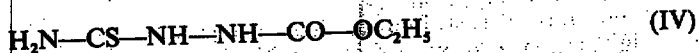


The formulae (II) and (III) provide an unambiguous general definition of the starting materials to be employed.

The (thiono)-phosphoric(phosphonic) acid ester halides (II) used as starting materials are already described in the literature and are accessible according to customary methods (for example German Auslegeschrift (German Published Specification) 1,067,017; US Patent Specification 3,167,574).

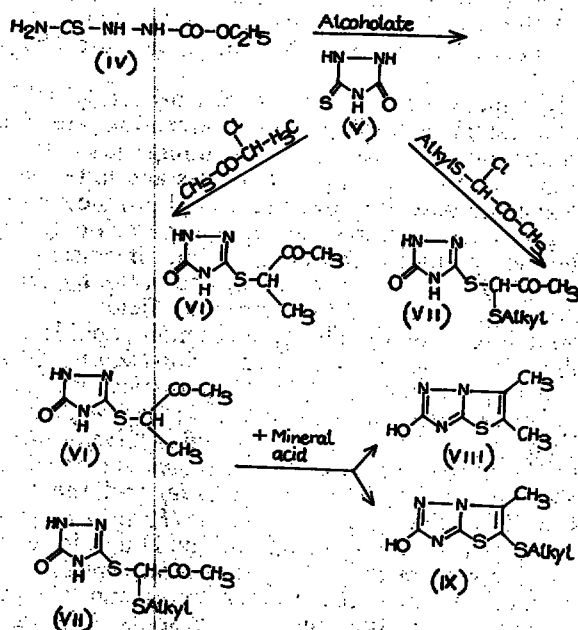
The following are specific examples thereof: O,O-dimethyl-, O,O-diethyl-, O,O-di-n-propyl-, O,O-di-isopropyl-, O-ethyl-O-n-propyl-, O-ethyl-O-iso-propyl- and O-n-propyl-O-methylphosphoric acid ester chloride and the corresponding thiono compounds and also O-methyl-, O-ethyl-, O-n-propyl- and O-iso-propyl-methane-, -ethane-, -propane- and -phenylphosphonic acid ester chloride and the corresponding thiono analogues.

The triazolothiazole derivatives (III) also required as starting materials are new, but they can be prepared by processes of known type, for example by reacting thiosemicarbazide with pyrocarbonic acid ethyl ester to give an intermediate of the formula



then cyclising the latter in the presence of alkali metal alcoholate and thereafter reacting the product, for example with 2-chlorobutanone-(3) or

alkylmercaptochloroacetone, and closing the thiazole ring, in the presence of a mineral acid, for example sulphuric acid, in accordance with the following formula scheme:



The following are specific examples of triazolothiazole derivatives (III): 2-methyl-, 2-ethyl-, 2-methylmercapto- and 2-ethylmercapto-3-methyl-6-hydroxy-1,2,4-triazolo(2,3-b)-thiazole.

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

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

Instead of carrying out the reaction in the presence of an acid-binding agent, one may prepare a salt, preferably an alkali metal salt or ammonium salt, of the triazolothiazole derivative (III) in the undiluted form, and then react the salt with the ester halide (II).

The reaction temperature can be varied within a wide range. In general, the reaction is carried out at 0 to 100°C, preferably at 25 to 50°C.

The reaction is in general carried out under normal pressure.

To carry out the process, preferably equimolar amounts of the reactants are combined at the indicated temperatures, optionally in the presence of an acid acceptor and of one of the abovementioned solvents. After stirring the mixture for between one and several hours at elevated temperature, the reaction is complete. Either the reaction mixture is poured into water and extracted by shaking with an organic solvent, for example benzene, and the organic phase is separated off, or it suffices, in some cases, merely to cool the reaction mixture and filter it and then to work up the organic phase in the usual manner by washing, drying and subsequent distillation under reduced pressure. The residue may be subjected to "slight distillation" and at times solidifies to crystals.

Some of the new compounds are obtained in the form of oils which in most cases cannot be distilled without decomposition but can be freed from 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 be purified in this way. They are characterised by their refractive index. If the compounds are obtained in a crystalline form, they are characterised by their melting point.

As already mentioned, the triazolothiazolyl-(thiono)-phosphoric-(phosphonic) acid esters according to the invention are distinguished by an outstanding insecticidal and acaricidal (including tickicidal) action. The new products not only have an action against insects and mites which damage plants but also against hygiene pests and pests of stored products and, in the veterinary medicine field, against ectoparasites, for example parasitic fly larvae and ticks. 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-black 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 kuehniella*) and greater wax moth (*Galleria mellonella*).

Also to be classed with the biting insects are beetles (*Coleoptera*), for example the granary weevil (*Sitophilus granarius* = *Calandra granaria*), the Colorado beetle (*Leptinotarsa decemlineata*), the dock beetle (*Gastrophysa viridula*), the mustard beetle (*Phaedon cochleariae*), the blossom beetle (*Meligethes aeneus*), the raspberry beetle (*Byturus tomentosus*), the bean weevil (*Bruchidius* = *Acanthoscelides obtectus*), the leather beetle (*Dermestes 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 *Henshouedenia flexivitta*; further, *Orthoptera*, for example the house cricket (*Gryllus domesticus*); termites such as the eastern subterranean termite (*Reticulitermes flavipes*) and *Hymenoptera* such as ants, for example the garden ant (*Lasius niger*).

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

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

When applied against hygiene pests and pests of stored products, particularly flies and mosquitoes, the 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 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 sulphates, alkyl sulphates and aryl sulphates as well as albumin hydrolyzation products; and preferred examples of dispersing agents include lignin, sulphite waste liquors and methyl cellulose.

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

In general, the formulations contain 1.0 to 29 per cent by weight of active compound, preferably 0.5 to 90%.

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

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

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

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

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

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

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

The compounds according to the invention, and the preparation and use of the compounds according to the invention, are illustrated by the following Examples.

In Examples A to F, the active compounds according to the invention are tested for their activity against various pests of plants and animals, in comparison to a known compound. In these Examples the compounds according to the invention are identified by the numbers shown in each case in brackets, which correspond to those of the preparation Examples in which these compounds are prepared.

Example A. Plutella test

Solvent: 3 parts by weight of acetone

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

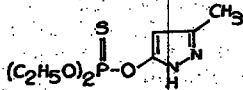
To produce a suitable preparation of active compound 1 part by weight of the active compound was mixed with the stated amount of solvent containing the stated amount of emulsifier and the concentrate was diluted with water to the desired concentration.

Cabbage leaves (*Brassica oleracea*) were sprayed with the preparation of the active compound until dew moist and were then infested with caterpillars of the diamond-black 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 time and the results can be seen in Table A.

Table A
(Plutella test)

Active compound	Active compound concentration in % by weight	Degree of destruction in % after 3 days
	0.1	100
	0.01	60
	0.001	0
(known)		
(3)	0.1	100
	0.01	100
	0.001	70
(4)	0.1	100
	0.01	100
	0.001	100

Example B.

Myzus test (contact action)

Solvent: 3 parts by weight of acetone

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

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

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

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

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

Table B

(Myzus test)

Active compound	Active compound concentration in % by weight	Degree of destruction in % after 1 day
$\begin{array}{c} \text{S} \\ \parallel \\ (\text{C}_2\text{H}_5\text{O})_2\text{P}-\text{O}-\text{N} \begin{array}{c} \diagup \text{CH}_3 \\ \diagdown \end{array} \\ \text{H} \end{array}$	0.1	99
	0.01	40
	0.001	0
(known)		
(1)	0.1	100
	0.01	100
	0.001	99
(3)	0.1	100
	0.01	100
	0.001	100
(2)	0.1	100
	0.01	100
	0.001	80
(4)	0.1	100
	0.01	100
	0.001	100

Example C.

Tetranychus test (resistant)

Solvent: 3 parts by weight of acetone

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

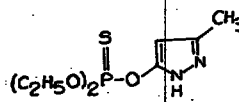
To produce a suitable preparation of active compound, 1 part by weight of the active compound was mixed with the stated amount of solvent containing the stated amount of emulsifier and the concentrate was diluted with water to the desired concentration.

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

After the specified periods of time, the effectiveness of the preparation of active compound was determined by counting the dead mites. The degree of destruction thus obtained 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 compound, the concentrations of the active compound, the evaluation time and the results can be seen in Table C.

Table C.
(Tetranychus test/resistant)
Mites which damage plants

Active compound	Active compound concentration in % by weight	Degree of destruction in % after 2 days
 (known) (4)	0.1	50
	0.01	0
	0.1	100
	0.01	98

Example D.
LD₁₀₀ test

Test animals: *Sitophilus granarius*

Solvent: Acetone

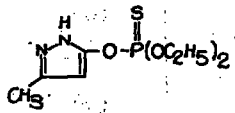
2 parts by weight of the active compound were dissolved in 1,000 parts by volume of the solvent. The solution so obtained was diluted with further solvent to the desired concentration.

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.

The active compounds, the concentrations of the active compounds, the test animals and the results can be seen in Table D.

Table D
(LD₁₀₀ test/*Sitophilus granarius*)

Active compound	Active compound concentration of the solution in % by weight	Degree of destruction in %
 (known)	0.2	100
	0.02	0
(3)	0.2	100
	0.02	100
(4)	0.2	100
	0.02	100
	0.002	100
(1)	0.2	100
	0.02	100
(2)	0.2	100
	0.02	100

Example E.

Test with parasitic fly larvae

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 abovementioned 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 approximately 2 cm³ of horse muscle. 0.5 ml of the preparation of active compound was applied to this horse meat. After 24 hours, the degree of destruction in % was determined. 100% means that all larvae were killed and 0% means that no larvae were killed.

The results obtained can be seen in Table E.

Table E
(Test with parasitic fly larvae/*Lucilia cuprina*)

Active compound	Active compound concentration in ppm by weight	Degree of destruction in %
(4)	100	100
	10	100
	1	100
(1)	100	100
	10	100
	1	>50
(3)	100	100
	10	100
	1	100
(2)	100	100
	10	100
	1	100

Example F.

Tick Test

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

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

Adult fully bloated female ticks of the species *Boophilus microplus* (sensitive or resistant) were dipped into these active compound preparations for one minute. After dipping 10 female specimens of the various species of ticks, the specimens were transferred into Petri dishes, the bottom of which was covered with a filter disc of appropriate size.

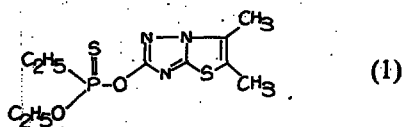
After 10 days, the activity of the active compound preparation was assessed by determining the inhibition of deposition of eggs compared to untreated control ticks. The action is expressed in per cent, with 100% denoting that eggs were no longer being laid and 0% denoting that the ticks laid eggs in normal amount.

The active compound investigated, the concentration tested, the parasites tested and the results obtained can be seen in Table F.

Table F
(Tick test/*Boophilus microplus*)

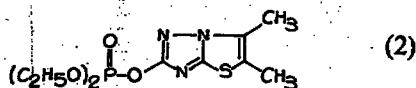
Active compound	Active compound concentration in ppm by weight	Inhibition of deposition of eggs eggs in % (<i>Boophilus microplus</i> Biarra strain)
(4)	10,000	100
	1,000	100
	100	100
(1)	10,000	100
	1,000	100
	100	100
(3)	10,000	100
	1,000	100
	100	100
(2)	10,000	100
	1,000	100
	100	100

Example 1.



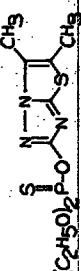
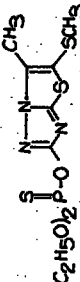
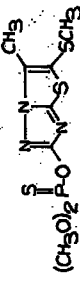
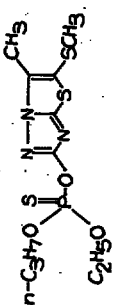
18 g (0.1 mol) of O-ethyl-thionoethanephosphonic acid ester chloride were added to a mixture of 17 g (0.1 mol) of 2,3-dimethyl-6-hydroxy-1,2,4-triazole-(2,3-b)-thiazole and 15 g of potassium carbonate in 200 ml of acetonitrile and the mixture was warmed to 40°C for 4 hours whilst stirring, then poured into water and extracted by shaking with benzene; after separating the layers, the organic phase was washed and dried and the solvent was distilled off under reduced pressure. The residue solidified to a crystalline mass which was recrystallised from glacial acetic acid/ligroin. 14 g (46% of theory) of O-ethyl-O-[2,3-dimethyl-1,2,4-triazole-(2,3-b)-thiazol(6)-yl]-thionoethanephosphonic acid ester of melting point 76°C were obtained.

Example 2.



18 g (0.1 mol) of O,O-diethylphosphoric acid diester chloride were added to a mixture of 21 g (0.1 mol) of 2,3-dimethyl-6-hydroxy-1,2,4-triazole-(2,3-b)-thiazole, 15 g of potassium carbonate and 200 ml of acetonitrile, the mixture was warmed to 40°C for 4 hours whilst stirring and then cooled and freed from the solid constituents, and the solvent was evaporated off under reduced pressure. The residue solidified to a crystalline mass and was recrystallised from glacial acetic acid/ligroin. 19 g (62% of theory) of O,O-diethyl-O-[2,3-dimethyl-1,2,4-triazole-(2,3-b)-thiazol(6)-yl]-phosphoric acid ester of melting point 52°C were obtained.

Examples 3 — 6.
The following compounds were prepared analogously to Example 1 and 2.

Structure	Physical data (refractive index, melting point °C)	Yield (% of theory)
 (3)	79	56
 (4)	$n_D^{23} : 1.5680$	79
 (5)	83	
 (6)	$n_D^{22} : 1.5543$	

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



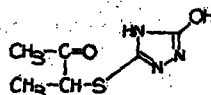
A mixture of 162 g of pyrocarbonic acid diethyl ester, 91 g of thiosemicarbazide and 300 ml of chloroform was boiled for 3 hours under reflux. After cooling the batch, the precipitate which had separated out was filtered off and recrystallised from ethanol. 121 g (74% of theory) of the product of the above formula, of decomposition point 165 to 168°C were obtained.

(b)



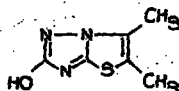
0.5 mol of sodium methylate was added to 82 g (0.5 mol) of the product prepared as described under (a), in 300 ml of methanol. After heating for 5 hours under reflux, the mixture was cooled and evaporated, the residue was taken up in water and hydrochloric acid was added to the reaction mixture. The precipitate which had separated out was filtered off and dried on clay. 24 g (41% of theory) of the above product, of melting point 193°C (with decomposition) were obtained.

(c)



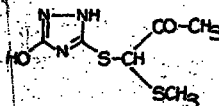
107 g of 2-chlorobutanone-(3) were added to 140 g (1 mol) of the sodium salt of the product prepared as described under (b), in 400 ml of ethanol, at 30 to 50°C. The reaction mixture was stirred overnight. It was then poured into 1,000 ml of water and the precipitate which had separated out was filtered off and dried on clay. 78 g (42% of theory) of the above product, of melting point 153°C, were obtained.

(d)



75 g (0.4 mol) of the product prepared as described under (c) were introduced, in portions, into 140 ml of pure concentrated sulphuric acid, in the course of which the reaction temperature rose to 80°C. The batch was stirred until the solid had dissolved and the reaction solution was then left to stand overnight, poured onto ice and buffered with sodium acetate. The precipitate was filtered off and dried on clay. 27 g (40% of theory) of 2,3-dimethyl-6-hydroxy-1,2,4-triazole-(2,3-b)-thiazole of melting point 218 to 220°C were obtained.

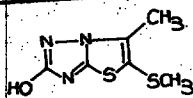
(e)



139 g of 1-chloro-1-methylmercaptoacetone (boiling point 65°C/12 mm Hg) were added to 140 g (1 mol) of the sodium salt of the product prepared as described under (b) in 500 ml of methanol, and the temperature of the mixture was kept at 0 to 10°C by external cooling. The reaction solution was then left to stand overnight whilst stirring, the solvent was distilled off under reduced pressure and the residue was triturated with water and then dried on clay. 179 g (82% of theory) of the desired product, of melting point 82°C, were thus obtained.

14

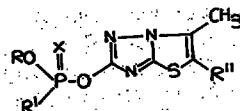
(f)



Hydrogen chloride was passed into a solution of 22 g (0.1 mol) of the product prepared as described under (e), in 200 ml of methanol, for 3 hours and at the same time the temperature of the reaction solution was kept at 60 to 65°C. The mixture was then cooled and filtered, the residue was dissolved in water, the aqueous solution was buffered with sodium acetate and the precipitate was filtered off, dried and recrystallised from acetonitrile. 10 g (50% of theory) of 2-methylmercapto-3-methyl-6-hydroxy-1,2,4-triazole-(2,3-b)-thiazole of melting point 138°C were obtained.

WHAT WE CLAIM IS:—

1. Triazolothiazolyl-(thiono)-phosphoric(phosphonic) acid esters of the general formula



(I)

in which

R is alkyl with 1 to 6 carbon atoms,

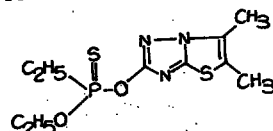
R' is alkyl with 1 to 4 carbon atoms or alkoxy with 1 to 6 carbon atoms or phenyl,

R'' is alkyl with 1 to 3 carbon atoms or alkylmercapto with 1 to 3 carbon atoms, and

X is oxygen or sulphur.

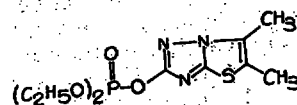
2. Compounds according to claim 1 in which R has 1 to 3 carbon atoms, R' is alkyl or alkoxy with 1 to 3 carbon atoms or phenyl, and R'' is alkyl or alkoxy with 1 to 3 carbon atoms or phenyl, and R'' is methyl, ethyl, methylmercapto or ethylmercapto.

3. The compound of the formula



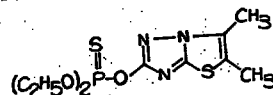
(1)

4. The compound of the formula



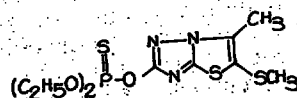
(2)

5. The compound of the formula



(3)

6. The compound of the formula



(4)

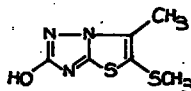
7. A process for the preparation of a triazolothiazolyl-(thiono)-phosphoric(phosphonic) acid ester according to any of claims 1—6 in which a (thiono)-phosphoric(phosphonic) acid ester halide of the general formula

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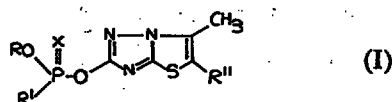
(f)



Hydrogen chloride was passed into a solution of 22 g (0.1 mol) of the product prepared as described under (e), in 200 ml of methanol, for 3 hours and at the same time the temperature of the reaction solution was kept at 60 to 65°C. The mixture was then cooled and filtered, the residue was dissolved in water, the aqueous solution was buffered with sodium acetate and the precipitate was filtered off, dried and recrystallised from acetonitrile. 10 g (50% of theory) of 2-methylmercapto-3-methyl-6-hydroxy-1,2,4-triazole-(2,3-b)-thiazole of melting point 138°C were obtained.

WHAT WE CLAIM IS:—

1. Triazolothiazolyl-(thiono)-phosphoric(phosphonic) acid esters of the general formula



in which

R is alkyl with 1 to 6 carbon atoms,

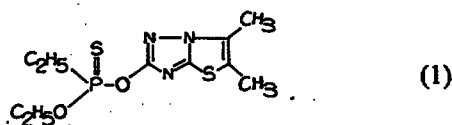
R' is alkyl with 1 to 4 carbon atoms or alkoxy with 1 to 6 carbon atoms or phenyl,

R'' is alkyl with 1 to 3 carbon atoms or alkylmercapto with 1 to 3 carbon atoms, and

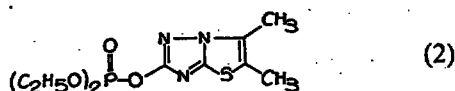
X is oxygen or sulphur.

2. Compounds according to claim 1 in which R has 1 to 3 carbon atoms, R' is alkyl or alkoxy with 1 to 3 carbon atoms or phenyl, and R'' is alkyl or alkoxy with 1 to 3 carbon atoms or phenyl, and R'' is methyl, ethyl, methylmercapto or ethylmercapto.

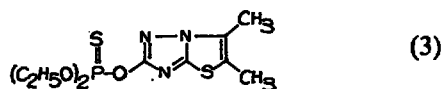
3. The compound of the formula



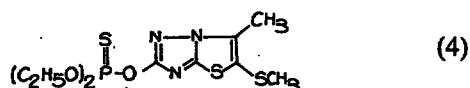
4. The compound of the formula



5. The compound of the formula



6. The compound of the formula



7. A process for the preparation of a triazolothiazolyl-(thiono)-phosphoric(phosphonic) acid ester according to any of claims 1—6 in which a (thiono)-phosphoric(phosphonic) acid ester halide of the general formula



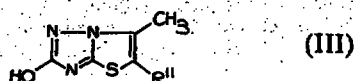
1,451,291

15



in which

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



in which

R'' has the meaning given in claim 1, optionally in the presence of an acid acceptor or in the form of a salt.

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 carried out in the presence of a solvent.

10. A process according to any of claims 7-9 in which the reaction is carried out at 25 to 50°C.

11. A process according to any of claims 7-10 in which the ester halide of formula (II) is any of those hereinbefore specifically identified.

12. A process according to any of claims 7-11 in which the triazolothiazole derivative of formula (III) is any of those hereinbefore specifically identified.

13. A process for the production of a compound according to claim 1, substantially as hereinbefore described in any of Examples 1-4.

14. Compounds according to claim 1 whenever prepared by a process according to any of claims 7-13.

15. An insecticidal or acaricidal composition containing as active ingredient a compound according to any of claims 1-6 or 14 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.

16. A composition according to claim 15 containing from 0.1 to 95% of the active compound by weight.

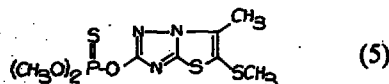
17. A method of combating insect or acarid pests which comprises applying to the pests or a habitat thereof a compound according to any of claims 1-6 or 14 alone or in the form of a composition containing as active ingredient a compound according to any of claims 1-6 or 14 in admixture with a diluent or carrier.

18. A method of combating animal ectoparasites which comprises applying to the animal a compound according to any of claims 1-6 or 14 alone or in the form of a composition containing as active ingredient a compound according to any of claims 1-6 or 14 in admixture with a diluent or carrier.

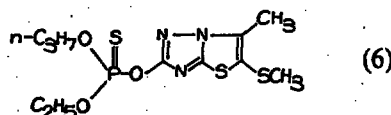
19. A method according to claim 17 or 18 in which a composition is used containing from 0.0001 to 10% of the active compound, by weight.

20. Crops protected from damage by insects or acarids by being grown in areas which, immediately prior to and/or during the time of the growing, a compound according to any of claims 1-6 or 14 was applied alone or in admixture with a diluent or carrier.

21. The compound of the formula



22. The compound of the formula



23. A composition according to claim 15 or 16 in which the active compound is according to claim 21 or 22.



16

1,451,291

16

24. A method according to any of claims 17—19 in which the active compound is according to claim 21 or 22.

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