

PATENT SPECIFICATION

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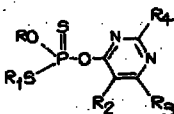
(54) SUBSTITUTED PYRIMIDINE-
 THIONOTHIOLPHOSPHORIC ACID ESTERS, PROCESS FOR
 THEIR PREPARATION AND THEIR USE AS INSECTICIDES
 OR ACARICIDES

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

The present invention relates to certain new pyrimidine-thionothiophosphoric acid esters and a process for their preparation, as well as their use as insecticides or acaricides.

It is already known that pyrimidin(4)yl-thionophosphoric acid esters, for example O,O-diethyl-O-[2-methylmercapto-6-methyl-pyrimidin(4)yl]-thionophosphoric acid ester, exhibit insecticidal and acaricidal properties (compare German Patent Specification 910,652).

The present invention provides new pyrimidine-thionothiophosphoric acid esters of the general formula



(I) 15

in which

R and R₁ are the same or different alkyl radicals each with 1 to 6 carbon atoms,

R₂ is hydrogen or alkylmercapto with 1 to 4 carbon atoms,

R₃ is hydrogen or methyl, and

R₄ is alkyl or alkylmercapto with 1 to 6 carbon atoms or alkylmercaptoalkylmercapto with 1 to 4 carbon atoms per alkyl moiety or carbalkoxymethylmercapto with 1 to 4 carbon atoms in the alkyl moiety.

Preferably, R and R₁ are straight or branched alkyl radicals each with 1 to 4 carbon atoms, R₂ is hydrogen, methylmercapto or ethylmercapto, and R₄ is methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert.-butyl, methylmercapto, ethylmercapto, n-propylmercapto, iso-propylmercapto, methylmercaptomethylmercapto, ethylmercaptoethylmercapto, methylmercaptoethylmercapto, carbomethoxymethylmercapto, carboethoxymethylmercapto or carbo-n-propoxymethylmercapto.

These compounds exhibit an excellent insecticidal and acaricidal action.

The invention also provides a process for the production of a pyrimidine-thionothiophosphoric acid ester of formula (I) in which an O,S-dialkylthionothiophosphoric acid diester halide of the general formula



in which

R and R₁ have the abovementioned meanings and
Hal is halogen (preferably chlorine)
is reacted with a 4-hydroxy-pyrimidine derivative of the general formula

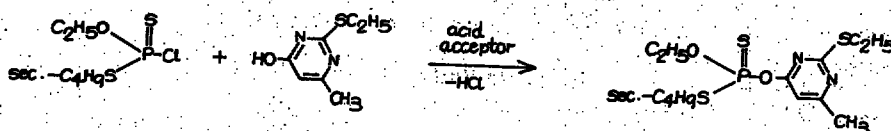


in which

R₂, R₃ and R₄ have the abovementioned meanings, optionally in the form of an alkali metal salt, alkaline earth metal salt or ammonium salt, or in the presence of an acid acceptor.

Surprisingly, the pyrimidine-thionothiophosphoric acid esters (I) according to the invention couple a low toxicity to warm-blooded animals with a substantially higher insecticidal and acaricidal action than the previously known compounds of analogous structure and of the same type of action. Hence, the compounds according to the invention represent a genuine enrichment of the art.

If, for example, O-ethyl-S-sec.-butyl-thionothiophosphoric acid diester chloride and 2-ethylmercapto-4-hydroxy-6-methylpyrimidine 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 O,S-dialkylthionothiophosphoric acid ester halides and 4-hydroxypyrimidine derivatives which are used as starting materials.

The majority of the O,S-dialkylthionothiophosphoric acid diester halides (II) are described in the literature and can be prepared according to conventional processes (compare USSR Patent Specification 184,863 and published Japanese Patent Application 5536/72).

The following are specific examples thereof: O,S-diethyl-, O,S-di-n-propyl-, O,S-di-iso-propyl-, O,S-di-n-butyl-, O,S-di-iso-butyl-, O,S-di-tert.-butyl-, O,S-di-sec.-butyl-, O-ethyl-S-n-propyl-, O-ethyl-S-iso-propyl-, O-ethyl-S-n-butyl-, O-ethyl-S-sec.-butyl-, O-ethyl-S-tert.-butyl-, O-ethyl-S-iso-butyl-, O-n-propyl-S-n-butyl-, O-n-propyl-S-sec.-butyl-, or O-n-butyl-S-n-propyl-thionothiophosphoric acid ester chloride.

The majority of the 4-hydroxypyrimidines (III) are described in the literature and can be prepared according to conventional processes.

The following are specific examples thereof: 2-methyl-, 2-ethyl-, 2-n-propyl-, 2-iso-propyl-, 2-n-butyl-, 2-iso-butyl-, 2-sec.-butyl-, 2-tert.-butyl-, 2-methylmercapto-, 2-ethylmercapto-, 2-n-propylmercapto-, 2-iso-propylmercapto-, 2-methylthiomethylmercapto-, 2-ethylthioethylmercapto-, 2-methylthioethylmercapto-, 2-carbomethoxymethylmercapto-, 2-carboethoxymethylmercapto- and 2-carbo-n-propoxymethylmercapto-4-hydroxy-6-methylpyrimidine and the compounds which are additionally substituted by methylmercapto or ethylmercapto in the 5-position.

The reaction 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. They 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 or heterocyclic amines, for example triethylamine, dimethylaniline, dimethylbenzylamine and pyridine.

The reaction temperature can be varied within a wide range. In general, the reaction is carried out at 0 to 100°C, preferably at 30 to 60°C.

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

In carrying out the process, the starting materials are in most cases employed in an equimolar ratio. An excess of one or other reactant seems to produce no significant advantage. In general, the reaction is carried out in a solvent in the presence of an acid acceptor. To complete the reaction, the mixture is in most cases stirred for from one to several hours at elevated temperatures, and cooled, and the reaction mixture is poured into an organic solvent, for example toluene. After washing with saturated sodium bicarbonate solution and water, the organic phase may be dried and the solvent distilled off under reduced pressure. The residue may be generally purified by "slight distillation".

The new compounds are generally obtained in the form of oils which can in most cases not 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.

As has already been mentioned, the pyrimidine-thionothiophosphoric acid esters (I) according to the invention are distinguished by an outstanding insecticidal and acaricidal action against plant pests, hygiene pests and pests of stored products, coupled with very low toxicity to warm-blooded animals. They possess a good action against sucking and against biting insects and mites (*Acarina*). Furthermore, some of the compounds also exhibit a soil insecticidal and/or nematocidal action.

For this reason, the compounds according to the invention are employed successfully in plant protection as well as in the field of hygiene and of the protection of stored products.

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 cutworm (*Agrotis segetum*), the large white butterfly (*Pieris brassicae*), the small winter moth (*Cheimatobia brumata*), the green oak tortrix moth (*Tortrix viridana*), the fall armyworm (*Laphygma frugiperda*) and cotton worm (*Prodenia litura*), the ermine moth (*Hyponomeuta padella*), the Mediterranean flour moth (*Ephestia kühniella*) and greater wax moth (*Galleria mellonella*).

Also to be classed with the biting insects are beetles (*Coleoptera*), for example the granary weevil (*Sitophilus granarius* = *Calandra granaria*), the Colorado beetle (*Leptinotarsa decemlineata*), the dock beetle (*Gastrophysa viridula*), the mustard beetle (*Phaedon cochleariae*), the blossom beetle (*Meligethes aeneus*), the raspberry beetle (*Byturus tomentosus*), the bean weevil (*Bruchidius* = *Acanthoscelides obtectus*), the leather beetle (*Dermestes frischi*), the khapra beetle (*Trogoderma granarium*), the flour beetle (*Tribolium castaneum*), the northern corn billbug (*Calandra* or

Sitophilus zeamais), the drugstore beetle (*Stegobium paniceum*), the yellow mealworm (*Tenebrio molitor*) and the saw-toothed grain beetle (*Oryzaephilus surinamensis*), and also species living in the soil, for example wireworms (*Agriotes spec.*) and larvae of the cockchafer (*Melolontha melolontha*); cockroaches, such as the German cockroach (*Blatella 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 limited substrates.

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

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

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

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

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

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

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

The active compounds can be used as such or in the form of their formulations or the application forms prepared therefrom, such as ready-to-use solutions, emulsions, foams, suspensions, powders, pastes, soluble powders, dusting agents and granules. They may be applied in the customary manner, for

example by squirting, spraying, atomising, dusting, scattering, fumigating, gassing, watering, dressing or encrusting.

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

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

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

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

The invention also provides 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 the test Examples A and B, the activity of compounds according to the invention against certain pests of plants was tested in comparison to the known O,O-diethyl-O-[2-methylmercapto-6-methylpyrimidin(4)yl]-thionophosphoric acid ester, which is designated (A) in these examples. The compounds according to the invention are designated by the figure shown in each case in brackets, which corresponds to that of the preparative Examples for that compound.

Example A. Plutella test

Solvent: 3 parts by weight of acetone
Emulsifier: 1 part by weight of alkylaryl polyglycol ether

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

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

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

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

TABLE A
(Plutella test)

Active compound	Active compound concentration in % by weight	Degree of destruction in % after 3 days
[A]	0.1	100
	0.01	0
[1]	0.1	100
	0.01	100
[4]	0.1	100
	0.01	100
	0.001	90
[6]	0.1	100
	0.01	100
[5]	0.1	100
	0.01	100
[3]	0.1	100
	0.01	100
[2]	0.1	100
	0.01	100

Example B.

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.

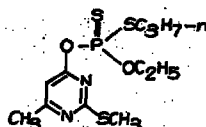
The active compounds, the concentrations of the active compounds, the evaluation times and the results can be seen in Table B.

TABLE B

(Tetranychus test/resistant)

Active compound	Active compound concentration in % by weight	Degree of destruction in % after 2 days
[A]	0.1	0
[1]	0.1	100
	0.01	100
	0.001	60
[4]	0.1	98
[6]	0.1	99
[5]	0.1	100
	0.01	99
[3]	0.1	100
	0.01	90

Example 1.

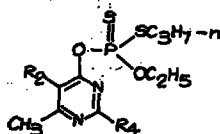


(1)

21.8 g (0.1 mol) of O-ethyl-S-n-propyl-thionothiophosphoric acid ester chloride were added dropwise to a mixture of 15.6 g (0.1 mol) of 2-methylmercapto-4-hydroxy-6-methylpyrimidine, 20.7 g (0.15 mol) of potassium carbonate and 300 ml of acetonitrile and the batch was allowed to react for a further 3 hours at 45—50°C. The reaction mixture was then cooled, poured into 500 ml of toluene and washed with saturated sodium bicarbonate solution and with water. The organic phase was then dried over sodium sulphate and freed from the solvent under reduced pressure, and the residue was subjected to "slight distillation". 28 g (83% of theory) of O-ethyl-S-n-propyl-O-[2-methylmercapto-6-methylpyrimidin(4)yl]-thionothiophosphoric acid ester were obtained in the form of a yellow oil of refractive index n_D^{25} : 1.5694.

Examples 2—6.

The following compounds of the formula

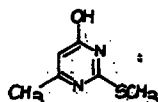


were obtained analogously to Example 1.

Example	R ₁	R ₂	Yield (% of theory)	Refractive index
2	-S-CH ₂ -CO-OC ₂ H ₅	H	85	n _D ²³ : 1.5520
3	-S-CH ₂ -CH ₂ -SC ₂ H ₅	H	80	n _D ²³ : 1.5719
4	-C ₃ H ₇ -iso	H	81	n _D ²¹ : 1.5208
5	-S-C ₃ H ₇ -iso	H	87	n _D ²³ : 1.5606
6	-C ₃ H ₇ -iso	SC ₂ H ₅	48	n _D ²³ : 1.5403

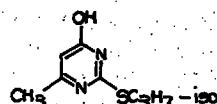
The following illustrates the preparation of the 4-hydroxy-pyrimidine derivatives (III) used as starting materials for the process of the invention.

(a)

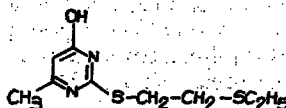


- 5 A solution of 120 g of sodium hydroxide (3 mols) in 250 ml of water was added dropwise at room temperature to a mixture of 195 g (1.5 mols) of acetoacetic acid ethyl ester, 210 g (0.76 mol) of S-methylisothiourea sulphate and 300 ml of water and the batch was allowed to react for a further 18 hours at room temperature. The reaction mixture was then acidified with acetic acid and the product which had crystallised out was filtered off and rinsed thoroughly with water. 224 g (96% of theory) of 2-methylmercapto-4-hydroxy-6-methyl-pyrimidine were obtained in the form of a colourless powder of melting point 219°C.

The following compounds were prepared analogously to (a):

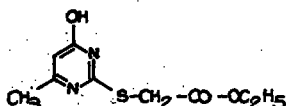


- 15 of melting point 149°C, yield 75% of theory.



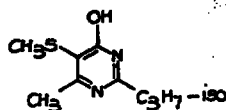
- of melting point 94°C, yield 91% of theory.

(b)



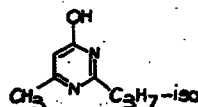
- 20 175 g (1.05 mols) of bromoacetic acid ethyl ester were added dropwise at 50–60°C to a suspension of 142 g (1 mol) of 4-methyl-2-thiouracil and 71.5 g (1.05 mols) of sodium ethylate in 1 litre of ethanol. The reaction mixture was allowed to complete reacting for 2½ hours at 70–80°C and was then poured into 2 litres of water. The product which had crystallised out was filtered off and well rinsed with ether. 173 g (76% of theory) of 2-carboethoxy-methylmercapto-4-hydroxy-6-methylpyrimidine were obtained in the form of a beige powder of melting point 139°C.

(c)



A mixture of 19 g (0.15 mol) of isobutyramidine hydrochloride, 35 ml of methanol, 8.1 g (0.15 mol) of sodium methylate and 27 g (0.15 mol) of 2-methylmercaptoacetoacetic acid ethyl ester was stirred for 4 hours at 60–70°C. The solvent was then distilled off under reduced pressure, the residue was dissolved in warm water and the solution was neutralised with acetic acid. The product which had crystallised out was filtered off. 13 g (44% of theory) of 2-isopropyl-4-hydroxy-5-methylmercapto-6-methylpyrimidine were obtained in the form of a colourless powder of melting point 156°C.

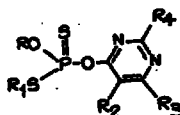
The following compound was obtained analogously to (c):



of melting point 173°C, yield 66% of theory.

WHAT WE CLAIM IS:—

1. Pyrimidine-thionothiophosphoric acid esters of the general formula



(I)

in which

R and R₁ are the same or different alkyl radicals each with 1 to 6 carbon atoms,

R₂ is hydrogen or alkylmercapto with 1 to 4 carbon atoms,

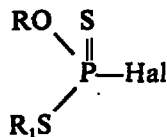
R₃ is hydrogen or methyl, and

R₄ is alkyl or alkylmercapto with 1 to 6 carbon atoms or alkylmercaptoalkylmercapto with 1 to 4 carbon atoms per alkyl moiety or carbalkoxymethylmercapto with 1 to 4 carbon atoms in the alkyl moiety.

2. Compounds according to claim 1 in which R and R₁ are straight or branched alkyl radicals each with 1 to 4 carbon atoms, R₂ is hydrogen, methylmercapto or ethylmercapto, and R₄ is methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert.-butyl, methylmercapto, ethylmercapto, n-propylmercapto, isopropylmercapto, methylmercaptomethylmercapto, ethylmercaptoethylmercapto, methylmercaptoethylmercapto, carbomethoxymethylmercapto, carboethoxymethylmercapto or carbo-n-propoxymethylmercapto.

3. Each of the compounds according to claim 1 hereinbefore identified in Examples 1–6.

4. A process for the production of a pyrimidine-thionothiophosphoric acid ester according to any of claims 1–3 in which an O,S-dialkylthionothiophosphoric acid diester halide of the general formula



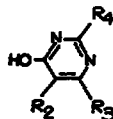
(II)

in which

R and R₁ have the meanings given in claim 1, and

Hal is halogen

is reacted with a 4-hydroxy-pyrimidine derivative of the general formula



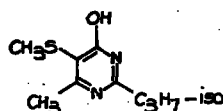
(III)



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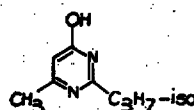
(18)

(c)



A mixture of 19 g (0.15 mol) of isobutyramidine hydrochloride, 35 ml of methanol, 8.1 g (0.15 mol) of sodium methylate and 27 g (0.15 mol) of 2-methylmercaptoacetoacetic acid ethyl ester was stirred for 4 hours at 60–70°C. The solvent was then distilled off under reduced pressure, the residue was dissolved in warm water and the solution was neutralised with acetic acid. The product which had crystallised out was filtered off. 13 g (44% of theory) of 2-isopropyl-4-hydroxy-5-methylmercapto-6-methylpyrimidine were obtained in the form of a colourless powder of melting point 156°C.

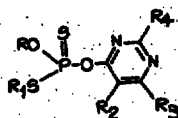
The following compound was obtained analogously to (c):



of melting point 173°C, yield 66% of theory.

WHAT WE CLAIM IS:—

1. Pyrimidine-thionothiophosphoric acid esters of the general formula



(I)

in which

R and R₁ are the same or different alkyl radicals each with 1 to 6 carbon atoms,

R₂ is hydrogen or alkylmercapto with 1 to 4 carbon atoms,

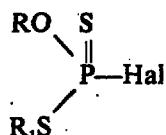
R₃ is hydrogen or methyl, and

R₄ is alkyl or alkylmercapto with 1 to 6 carbon atoms or alkylmercaptoalkylmercapto with 1 to 4 carbon atoms per alkyl moiety or carbalkoxymethylmercapto with 1 to 4 carbon atoms in the alkyl moiety.

2. Compounds according to claim 1 in which R and R₁ are straight or branched alkyl radicals each with 1 to 4 carbon atoms, R₂ is hydrogen, methylmercapto or ethylmercapto, and R₄ is methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert.-butyl, methylmercapto, ethylmercapto, n-propylmercapto, isopropylmercapto, methylmercaptomethylmercapto, ethylmercaptoethylmercapto, methylmercaptoethylmercapto, carbomethoxymethylmercapto, carboethoxymethylmercapto or carbo-n-propoxymethylmercapto.

3. Each of the compounds according to claim 1 hereinbefore identified in Examples 1–6.

4. A process for the production of a pyrimidine-thionothiophosphoric acid ester according to any of claims 1–3 in which an O,S-dialkylthionothiophosphoric acid diester halide of the general formula



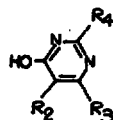
(II)

in which

R and R₁ have the meanings given in claim 1, and

Hal is halogen

is reacted with a 4-hydroxy-pyrimidine derivative of the general formula



(III)



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in which

R_2 , R_3 and R_4 have the meanings given in claim 1.

5. A process according to claim 4 in which the reaction is carried out in the presence of an acid acceptor or the pyrimidine derivative is used in the form of an alkali metal salt, alkaline earth metal salt or ammonium salt.

6. A process according to claim 4 or 5 in which Hal is chlorine.

7. A process according to any of claims 4—6 in which the compound of the formula (II) is any of those hereinbefore specifically identified.

8. A process according to any of claims 4—7 in which the compound of the formula (III) is any of those hereinbefore specifically identified.

9. A process according to any of claims 4—8 in which the reaction is carried out in the presence of a solvent.

10. A process according to any of claims 4—9 in which the reaction is carried out at 30—60°C.

11. A process for the production of a compound according to claim 1 substantially as hereinbefore described in any of Examples 1—6.

12. Compounds according to claim 1 whenever prepared by a process according to any of claims 4—11.

13. An insecticidal or acaricidal composition containing as active ingredient a compound according to any of claims 1—3 or 12 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.

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

15. 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—3 or 12 alone or in the form of a composition containing as active ingredient a compound according to any of claims 1—3 or 12 in admixture with a diluent or carrier.

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

17. 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—3 or 12 was applied alone or in admixture with a diluent or carrier.

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