

PATENT SPECIFICATION

(11) 1 419 131

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- (21) Application No. 56818/72 (22) Filed 8 Dec. 1972
 (31) Convention Application No. 18065/71 (32) Filed 10 Dec. 1971
 (31) Convention Application No. 14693/72 (32) Filed 6 Oct. 1972 in
 (33) Switzerland (CH)
 (44) Complete Specification published 24 Dec. 1975
 (51) INT CL³ C07F 9/65; A01N 9/36//C07D 249/08
 (52) Index at acceptance

C2P 1L1 1L2 1L3 2E13 2E18B 2E18C 2E19C 2E23 2E24
 2E25A 2E25B 2E26D 2L13 2L18B 2L18C 2L19C
 2L25A 2L25B 2L26D 2L30A 2L30B 3B13 3B14A
 3B15A 3B18B 3B18C 3B18D 3B19C 3B21 3C13
 3C18B 3C18C 3C19C 3C21 3C27 3C28 3C29A
 3C29B 3C30A 3C30B 7 B1 B
 C2C 1175 1450 215 220 221 225 226 22Y 247 250 252
 25Y 311 313 314 31Y 337 338 365 366 368 36Y
 373 37X 37Y 396 397 43X 440 464 613 623 624
 628 662 668 672 67X 694 697 699 BK QM WK

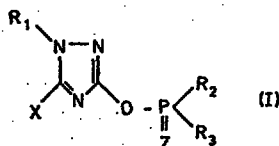


(54) TRIAZOLYLGORGANOPHOSPHORUS DERIVATIVES AND THEIR USE IN PEST CONTROL

(71) We, CIBA-GEIGY A.G., a Swiss body corporate of 4002 Basle, Switzerland, 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 triazolyorgano-phosphorous derivatives, a process for their manufacture and their use in pest control.

The compounds of the invention have the formula I



wherein

- 10 X represents a fluorine, chlorine or bromine atom, 10
 Z represents an oxygen or sulphur atom
 R₁ represents an alkyl group optionally substituted by one or more halogen atoms and containing maximally 19 carbon atoms, a cycloalkyl group containing from 3 to 8 ring carbon atoms, an optionally substituted aryl or an optionally substituted aralkyl group, 15
 R₂ represents an alkoxy or alkylthio group each being optionally substituted by one or more halogen atoms and each containing maximally 19 carbon atoms, an amino group, or a mono- or di-alkyl-amino group in which the alkyl moieties each contain maximally 19 carbon atoms, and
 20 R₃ represents an alkyl, alkoxy, or alkylthio group each being optionally substituted by one or more halogen atoms and each containing maximally 19 carbon atoms, a phenyl, phenoxy or amino group, or a mono- or di-alkyl-amino group in which the alkyl moieties each contain maximally 19 carbon atoms, 20
 25 with the proviso that when X represents a chlorine atom, Z represents a sulphur atom, and R₁ represents an isopropyl group, R₂ and R₃ are not both ethoxy groups. 25
 The alkyl, alkoxy and alkylthio groups and the alkyl moieties present in the mono- and di-alkylamino groups represented by R₁ to R₃ contain preferably 1 to 6 carbon atoms and may be straight-chained or branched. The halogen atoms optionally present as substituents in the alkyl, alkoxy and alkylthio groups are fluorine, chlorine, bromine and/or iodine atoms. Examples of such groups include 30

[Price 33p]

Price 75p

the methyl, methoxy, methylthio, ethyl, ethoxy, ethylthio, 2-chloroethyl, propyl, 3,3,3-tri-chloropropyl, propoxy, propylthio, isopropyl, n-, i-, sec. and tert. butyl, 4-chloro-(n)-butyl, n-pentyl, n-dodecyl or (n)-nonadecyl group.

The cycloalkyl groups represented by R_1 contain preferably 5 or 6 ring carbon atoms. Such groups are the cyclopentyl and cyclohexyl group.

The aralkyl groups represented by R_1 are preferably benzyl, α -phenethyl, β -phenethyl or diphenylmethyl groups and the aryl groups are carbocyclic aromatic rings in particular the phenyl ring.

The aralkyl, in particular the benzyl, and the aryl, especially phenyl groups, represented by R_1 may be unsubstituted or mono- or poly-substituted. Possible substituents on these groups are preferably one or more fluorine, chlorine and/or bromine atoms, alkyl and/or haloalkyl groups each containing 1 to 6 carbon atoms, in particular $-\text{CF}_3$, alkoxy, alkylsulphinyl, and alkylsulphonyl groups each containing 1 to 6 carbon atoms, and/or nitro groups.

Compounds preferred by reason of their activity are those of the formula I, wherein

X and Z are as defined above and

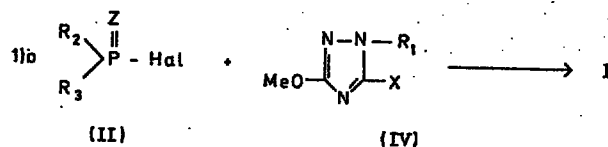
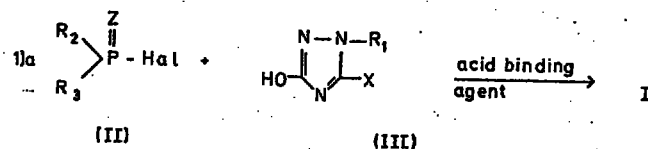
R_1 represents an alkyl group containing maximally 19 carbon atoms, a cycloalkyl group containing from 3 to 8 ring carbon atoms; or a phenyl, benzyl, α -phenethyl, β -phenethyl, or diphenylmethyl group each being optionally substituted in the phenyl ring or rings by one or more members selected from fluorine, chlorine and bromine atoms and alkyl, haloalkyl, alkoxy, alkylthio, alkylsulphinyl and alkylsulphonyl groups each containing maximally 6 carbon atoms and nitro groups,

R_2 represents an alkoxy or alkylthio group each containing maximally 6 carbon atoms, an amino group or a mono- or di-alkyl-amino group in which the alkyl moieties each contain maximally 6 carbon atoms, and

R_3 represents an alkyl, alkoxy or alkylthio group each containing maximally 6 carbon atoms, a phenyl, phenoxy or amino group, or a mono- or di-alkyl-amino group in which the alkyl moieties each contain maximally 6 carbon atoms,

with the proviso that when X represents a chlorine atom, Z represents a sulphur atom, and R_1 represents an isopropyl group, R_2 and R_3 are not both ethoxy groups. Preferably R_1 represents an alkyl group containing maximally 6 carbon atoms, a cycloalkyl group containing 5 or 6 ring carbon atoms, a phenyl or benzyl group each optionally substituted by one or more members selected from fluorine, chlorine and bromine atoms, and methyl, trifluoromethyl, methoxy, methylthio, ethoxy and nitro groups, or an α -phenethyl, β -phenethyl or diphenylmethyl group; especially an alkyl group containing maximally 6 carbon atoms, or a cyclopentyl, phenyl, trifluoromethyl-phenyl, benzyl, diphenylmethyl or β -phenethyl group. R_2 preferably represents an alkoxy or alkylthio group containing maximally 6 carbon atoms; especially a methoxy, ethoxy or n-propoxy group. R_3 preferably represents a methyl, ethyl, methoxy, ethoxy, amino, methylamino, ethylamino, isopropylamino, dimethylamino, methylthio, ethylthio, n-propylthio, phenyl or phenoxy group, especially a methyl, ethyl, methoxy, ethoxy, propylthio, amino, methylamino or dimethylamino group. X preferably represents a chlorine atom. Z preferably represents a sulphur atom.

The compounds of the formula I can be manufactured analogously to known methods e.g. as shown schematically below.



In the formulae II to IV, R_1 , R_2 , R_3 , X and Z, have the meanings given for the formula I. Hal represents a halogen, preferably chlorine or bromine atom, and Me represents a monovalent metal atom, preferably an alkali-metal atom, in particular a sodium or potassium atom.

The following bases, for example, are suitable as acid binding agents, tertiary amines, such as triethylamine, dimethylaniline, pyridine, inorganic bases, such as hydroxides and carbonates of alkali and alkaline earth metals, preferably sodium or potassium hydroxide.

The reactions are preferably carried out in solvents or diluents which are inert towards the reactants or in an excess of a tertiary amine, e.g. pyridine. Suitable inert solvents or diluents are, for example, the following: aromatic hydrocarbons, such as benzene, toluene, benzines, halogenated hydrocarbons such as chlorobenzene, polychlorobenzenes, bromobenzene; chlorinated alkanes with 1 to 3 carbon atoms; ethers, such as dioxan, tetrahydrofuran; esters, such as ethyl acetate; ketones, such as methyl ethylketone, diethyl ketone, or nitriles.

The starting materials of the formulae III and IV are new and can be manufactured, for example, by halogenation of a 3-hydroxy-triazole derivative which is unsubstituted in the 5-position, or an ester thereof, or by trans-halogenation of a 5-halo-3-hydroxy-triazole derivative or an ester thereof, followed in each case by hydrolysis when an ester is used.

The compounds of the formula I have insecticidal, nematocidal and acaricidal activity. Accordingly the invention provides a method of combating insects, nematodes or acarina which method comprises applying to a locus infested or liable to be infested with the insects, nematodes or acarina a compound of the formula I. The compounds may be used against all development stages of the insects, nematodes and acarina. The compounds are particularly effective against insects, nematodes and acarina which are harmful to seeds, tubers, plants and plant parts.

The compounds of the formula I may be used as pure active substance or in composition form together with a solid extender, a solid extender and a surfactant, or a liquid diluent and a surfactant. The compositions can be solid or liquid and can contain substances conventionally used in formulation technique such, for example, as solvents, dispersants, wetting agents, adhesives, thickeners, binders and/or fertilisers.

For application, the compounds of the formula I may be processed to dusts, emulsifiable concentrates, granulates, dispersions, sprays, solutions, or suspensions in the conventional formulation which is commonly employed in application technology. Mention may also be made of cattle dips and spray races, in which aqueous preparations are used.

The compositions according to the invention may be manufactured in known manner e.g. by intimately mixing and/or grinding active substances of the formula I with a suitable solid extender, optionally with the addition of dispersants or solvents which are inert towards the active substances. The active substances may take and be used in the following forms:

Solid forms:

Dusts, tracking agents, granules, coated granules, impregnated granules and homogeneous granules.

Liquid forms:

a) active substances which are dispersible in water: wettable powders, pastes, emulsions;

b) solutions.

To manufacture solid forms (dusts, tracking agents), the active substances are mixed with solid extenders. Suitable extenders are, for example: kaolin, talcum, bolus, loess, chalk, limestone, ground limestone, attaclay, dolomite, diatomaceous earth, precipitated silica, alkaline earth metal silicates, sodium and potassium aluminium silicates (feldspar and mica), calcium and magnesium sulphates, magnesium oxide, ground synthetic materials, fertilisers, for example ammonium sulphate, ammonium phosphate, ammonium nitrate, urea, ground vegetable products, such as corn meal, bark dust, sawdust, nutshell meal, cellulose powder, residues of plant extractions, and activated charcoal. These substances can either be used alone or in admixture with one another.

Granules can be very easily manufactured by dissolving an active substance of the formula I in an organic solvent and applying the resulting solution to a granulated material, for example attapulgit, SiO_2 , granicalcium, or bentonite and then evaporating the solvent.

Polymer granules can also be manufactured by mixing the active substances of the formula I with polymerisable compounds (urea/formaldehyde; dicyandiamide/formaldehyde; melamine/formaldehyde or others), whereupon a mild polymerisation is carried out that does not affect the active substances and in the process of which the granulation is carried out during the gel formation. It is more advantageous to impregnate finished, porous polymer granules (urea/formaldehyde, polyacrylonitrile, polyester or others) which have a specific surface area and a favourable predeterminable adsorption/desorption ratio, with the active substances, for example in the form of their solutions (in a low boiling solvent) and to remove the solvent. Polymer granules of this kind in the form of microgranules having a bulk density of 300 g/litre to 600 g/litre can also be manufactured with the aid of atomisers. The dusting can be carried out from aircraft over extensive areas of cultures of useful plants.

It is also possible to obtain granules by compacting the extender with the active substance and subsequently comminuting the product.

To these mixtures can also be added additives which stabilize the active substance and/or non-ionic, anionic and cationic surface active substances, which, for example, improve the adhesion of the active ingredients on plants or parts of plants (adhesives and agglutinants) and/or ensure a better wettability (wetting agents) and dispersibility (dispersing agents). Examples of suitable adhesives are the following: olein/chalk mixture, cellulose derivatives (methyl cellulose, carboxymethyl cellulose), hydroxyethyl glycol ethers of monoalkyl and dialkyl phenols having 5 to 15 ethylene oxide radicals per molecule and 8 to 9 carbon atoms in the alkyl radical, lignin sulphonic acids, their alkali metal and alkaline earth metal salts, polyethylene glycol ethers, e.g. Carbowaxes ("Carbowax" is a registered Trade Mark), fatty alcohol polyethylene glycol ethers having 5 to 20 ethylene oxide radicals per molecule and 8 to 18 carbon atoms in the fatty alcohol moiety, condensation products of ethylene oxide/propylene oxide, polyvinyl pyrrolidones, polyvinyl alcohols, condensation products of urea and formaldehyde, and also latex products.

The water-dispersible concentrates of the active substance, i.e. wettable powders, pastes and emulsifiable concentrates, are agents which can be diluted with water to any concentration desired. They consist of active substance, extender, optionally additives which stabilize the active substance, surface-active substance and anti-foam agents and, optionally, solvents.

Wettable powders and pastes may be obtained by mixing and grinding the active substances with dispersing agents and pulverulent extenders in suitable apparatus until homogeneity is attained. Suitable extenders are, for example, those mentioned for the solid forms of application. In some cases it is advantageous to use mixtures of different extenders. As dispersing agents there can be used, for example, condensation products of sulfonated naphthalene and sulfonated naphthalene derivatives with formaldehyde, condensation products of naphthalene or naphthalene sulfonic acids with phenol and formaldehyde, as well as alkali, ammonium and alkaline earth metal salts of lignin sulfonic acid, in addition, alkylaryl sulfonates, alkali and alkaline earth metal salts of dibutyl naphthalene sulfonic acid, fatty alcohol sulfates such as salts of sulfated hexadecanols, heptadecanols, octadecanols, and salts of sulfated fatty alcohol glycol ethers, the sodium salt of oleoyl ethionate, the sodium salt of oleoyl methyl tauride, ditertiary acetylene glycols, dialkyl dilauryl ammonium chloride and fatty acid alkali and alkaline earth metal salts.

Suitable anti-foam agents are silicones.

The active substances may be mixed, ground, sieved and strained with the additives cited hereinabove in such a manner that, in wettable powders, the solid particle size of from 0.02 to 0.04 mm and in pastes of 0.03 mm is not exceeded. To produce emulsifiable concentrates and pastes, dispersing agents such as those cited above, organic solvents and water are used. Examples of suitable solvents are: alcohols, benzene, xylene, toluene, dimethyl sulfoxide, and mineral oil fractions boiling between 120 and 350°C. The solvents must be practically odourless, not phytotoxic, and inert to the active substances.

Furthermore, the agents according to the invention can be applied in the form of solutions. For this purpose the active substance or several active substances of the general formula I are dissolved in suitable organic solvents, mixtures of solvents or in water. Aliphatic and aromatic hydrocarbons, chlorinated derivatives thereof, alkyl naphthalenes, and mineral oils singly or in admixture with each other, can be used as organic solvents.

The content of active substance in the above described agents is generally between 0.1% to 95%, in which connection it should be mentioned that, in the case of application from aircraft or some other suitable means of application, it is possible to use concentrations of up to 99.5% or even pure active substance. (Throughout this specification parts and percentages are by weight unless otherwise specified).

The active substances of the formula I can, for example, be formulated as follows:

Dusts

The following substances are used to manufacture a) a 5% and b) a 2% dust:

a) 5 parts of active substance
95 parts of talcum

b) 2 parts of active substance
1 part of highly disperse silica
97 parts of talcum.

The active substances are mixed with the extenders and ground.

Granulate

The following substances are used to produce 5% granulate:

5 parts of active substance,
0.25 parts of epichlorohydrin,
0.25 parts of cetyl polyglycol ether,
3.50 parts of polyethylene glycol,
91 parts of kaolin (particle size 0.3—0.8 mm).

The active substance is mixed with epichlorohydrin and dissolved with 6 parts of acetone; the polyethylene glycol and cetyl polyglycol ether are then added. The thus obtained solution is sprayed on to kaolin, and the acetone subsequently evaporated in vacuo.

Wettable powder:

The following constituents are used for the preparation of a) a 40%, b) and c) a 25%, and d) a 10% wettable powder:

a) 40 parts of active substance,
5 parts of sodium lignin sulphonate,
1 part of sodium dibutyl-naphthalene sulphonate,
54 parts of silica acid.

b) 25 parts of active substance,
4.5 parts of calcium lignin sulphonate,
1.9 parts of Champagne chalk/hydroxyethyl cellulose mixture (1:1),
1.5 parts of sodium dibutyl naphthalene sulphonate,
19.5 parts of silica acid,
19.5 parts of Champagne chalk,
28.1 parts of kaolin.

c) 25 parts of active substance,
2.5 parts of isooctylphenoxy-polyoxyethylene-ethanol,
1.7 parts of Champagne chalk/hydroxyethyl cellulose mixture (1:1),
8.3 parts of sodium aluminium silicate,
16.5 parts of kieselguhr,
46 parts of kaolin,

d) 10 parts of active substance,
3 parts of a mixture of the sodium salts of saturated fatty alcohol sulphates,
5 parts of naphthalenesulphonic acid/formaldehyde condensate,
82 parts of kaolin.

The active substances are intimately mixed, in suitable mixers, with the additives, the mixture being then ground in the appropriate mills and rollers. Wettable powder are obtained which can be diluted with water to give suspensions of any desired concentration.

5 *Emulsifiable concentrate*

The following substances are used to produce a 25% emulsifiable concentrate:

- 25 25 parts of active substance,
2.5 parts of epoxidised vegetable oil,
10 10 parts of an alkylarylsulphonate/fatty alcoholpolyglycol ether mixture,
5 5 parts of dimethylformamide,
57.5 parts of xylene.

From this concentrate it is possible to produce, by dilution with water, emulsions of desired concentration.

Spray:

15 The following constituents are used to prepare a 5% spray:

- 5 parts of active substance,
1 part of epichlorohydrin,
94 parts of benzene (boiling limits 160°—190°C).

20 Other biologically active ingredients can be included in the compositions according to the invention. For the widening of their sphere of action, the compositions may thus contain, in addition to the compounds of the general formula I, for example, insecticides, fungicides, bactericides, fungistatics, bacteriostatics or nematocides.

25 The invention further provides a compound of formula I in a container which bears instructions to use the compound in combating insects, nematodes or acarina.

The invention is further illustrated in the following Examples.

Example 1.

Manufacture of the Starting Material.

- 30 a) *1-isopropyl-3-hydroxy-5-chloro-1,2,4-triazole*.
127 g of 1-isopropyl-3-hydroxy-1,2,4-triazole and 276 ml of triethylamine are dissolved in 1200 ml of absolute alcohol. The solution turns cloudy yellow. While cooling (26° to 30°C), 106.5 g of chlorine (dried by concentrated sulphuric acid) are passed in within 30 minutes whereby the yellow solution initially becomes clear. Subsequently triethylamine hydrochloride precipitates as crystalline product, which is filtered off after stirring for 1 further hour. The filtrate is concentrated to dryness in a rotary evaporator. The brown residue is dissolved in 1 litre of water and 1 litre of ether. The mixture is extracted and separated in a separating funnel. The aqueous phase is extracted three times with 500 ml of ether on each occasion. The combined ether phases are dried over sodium sulphate, the drying agent is filtered off and the filtrate is concentrated to dryness. The light brown residue is dissolved in 500 ml of carbon tetrachloride containing activated charcoal, whereupon the mother liquor is concentrated to 1/3 of its volume and then cooled. The active substance crystallises out and is dried in vacuo for 15 hours at 60° C/15 mm Hg.

Yield: 96.3 g (60 % of theory); m.p.: 103°—105° C.

- b) *1-phenyl-3-hydroxy-5-chloro-1,2,4-triazole*.
32.2 g of 1-phenyl-3-hydroxy-1,2,4-triazole and 40.5 g of triethylamine are dissolved in 300 ml of absolute alcohol. While cooling, 21.3 g of chlorine are passed in (20° to 30° C). The precipitated triethylamine hydrochloride is filtered off and the filtrate is concentrated in a rotary evaporator. The residue is treated with 300 ml of water and extracted 4 times with 200 ml of ether each time. The combined ethereal extracts are dried over sodium sulphate. The drying agent is filtered off and the filtrate concentrated. The solid residue is recrystallised from 70 ml of acetonitrile.

Yield: 11.4 g (29.2 % of theory); m.p. 147—149° C.

c) *1-phenyl-3-hydroxy-5-chloro-1,2,4-triazole.*

32.2 g of 1-phenyl-3-hydroxy-1,2,4-triazole and 40.5 g of triethylamine are dissolved in 300 ml of dimethyl formamide. While cooling with ice, 21.3 g of chlorine gas are passed in at 20° to 30° C. The resulting triethylamine hydrochloride is filtered off and the solvent is distilled off in vacuo. The residue is taken up in 300 ml of water and extracted 4 times with 200 ml of ether. The combined ethereal extracts are dried over sodium sulphate and, after the solvent has been filtered off, concentrated in vacuo. The residue is recrystallised from acetonitrile. Yield: 15.0 g (38.4 % of theory); m.p. 146—147° C.

d) *1-ethyl-3-hydroxy-5-chloro-1,2,4-triazole.*

71.5 g of chlorine are passed into a solution of 75.5 g of 1-ethyl-3-hydroxy-1,2,4-triazole and 185 ml of triethylamine in 800 ml of absolute ethanol. The exothermic reaction is kept at 20° to 30° C by cooling. Triethylamine hydrochloride precipitates. The batch is stirred for a further 2 hours whereupon the residue is dissolved in 500 ml of ether and 500 ml of water. The phases are separated and the aqueous phase is extracted 3 times with 300 ml of ether each time. The ethereal extracts are dried over sodium sulphate. The drying agent is filtered off and the filtrate concentrated. The residue is recrystallised from a mixture of 400 ml of xylene and 250 ml of ligroin and dried in vacuo. Yield: 28.7 g (29 % of theory); m.p. 108—110° C.

e) *1-isobutyl-3-hydroxy-5-chloro-1,2,4-triazole.*

241 g of 1-isobutyl-3-hydroxy-1,2,4-triazole and 475 ml of triethylamine are dissolved in 2100 ml of absolute ethanol and 182 g of chlorine are passed into the solution while cooling at 20—30° C. The solution is stirred for 1½ hours at room temperature, after which the precipitated triethylamine hydrochloride is filtered off. The filtrate is concentrated in a rotary evaporator, the residue dissolved in 1000 ml of ether and 1000 ml of water are added. The phases are separated and the aqueous phase is extracted 3 times with 300 ml of ether each time. The ether phases are combined, dried and concentrated. The residue is recrystallised from ligroin/xylene. Yield: 104.7 g (34 % of theory); m.p. 84—86° C.

The following compounds are manufactured in analogous manner:

1-methyl-3-hydroxy-5-chloro-1,2,4-triazole		
1-n-propyl-3-hydroxy-5-chloro-1,2,4-triazole		
1-n-butyl-3-hydroxy-5-chloro-1,2,4-triazole	m.p. 26—30° C	
1-sec.-butyl-3-hydroxy-5-chloro-1,2,4-triazole	m.p. 41—45° C	35
1-n-pentyl-3-hydroxy-5-chloro-1,2,4-triazole	m.p. 77—79° C	
1-sec.-pentyl-3-hydroxy-5-chloro-1,2,4-triazole		
1-n-hexyl-3-hydroxy-5-chloro-1,2,4-triazole	m.p. 25—35° C	
1-(2',2',2'-trimethyl-propyl)-3-hydroxy-5-chloro-1,2,4-triazole		
1-cyclopentyl-3-hydroxy-5-chloro-1,2,4-triazole	m.p. 154—160° C	40
1-cyclohexyl-3-hydroxy-5-chloro-1,2,4-triazole	m.p. 128—130° C	
1-(1'-methyl-decyl)-3-hydroxy-5-chloro-1,2,4-triazole		
1-(1'-n-nonyl-decyl)-3-hydroxy-5-chloro-1,2,4-triazole		
1-phenyl-3-hydroxy-5-chloro-1,2,4-triazole		
1-(α -phenethyl)-3-hydroxy-5-chloro-1,2,4-triazole	m.p. 139—141° C	45
1-diphenylmethyl-3-hydroxy-5-chloro-1,2,4-triazole	m.p. 112—114° C	
1-(2'-chlorophenyl)-3-hydroxy-5-chloro-1,2,4-triazole		
1-(3'-chlorophenyl)-3-hydroxy-5-chloro-1,2,4-triazole		
1-(4'-chlorophenyl)-3-hydroxy-5-chloro-1,2,4-triazole		
1-(2',5'-dichlorophenyl)-3-hydroxy-5-chloro-1,2,4-triazole		
1-(3',5'-dichlorophenyl)-3-hydroxy-5-chloro-1,2,4-triazole	m.p. 153—158° C	50
1-(3',4'-dichlorophenyl)-3-hydroxy-5-chloro-1,2,4-triazole		
1-(2,4'-dichlorophenyl)-3-hydroxy-5-chloro-1,2,4-triazole		
1-(2',4',5'-trichlorophenyl)-3-hydroxy-5-chloro-1,2,4-triazole		
1-(4'-bromophenyl)-3-hydroxy-5-chloro-1,2,4-triazole		
1-(4'-fluorophenyl)-3-hydroxy-5-chloro-1,2,4-triazole		55
1-(2',3',4',5',6'-pentafluorophenyl)-3-hydroxy-5-chloro-1,2,4-triazole		
1-(3'-tolyl)-3-hydroxy-5-chloro-1,2,4-triazole		
1-(4'-tolyl)-3-hydroxy-5-chloro-1,2,4-triazole		
1-(3'-chloro-4'-tolyl)-3-hydroxy-5-chloro-1,2,4-triazole		60
1-(3'-trifluoromethyl-phenyl)-3-hydroxy-5-chloro-1,2,4-triazole		

1-(4'-methylmercapto-phenyl)-3-hydroxy-5-chloro-1,2,4-triazole
 1-(4'-methanesulphinyl-phenyl)-3-hydroxy-5-chloro-1,2,4-triazole
 1-(4'-methanesulphonyl-phenyl)-3-hydroxy-5-chloro-1,2,4-triazole
 1-(4'-ethoxyphenyl)-3-hydroxy-5-chloro-1,2,4-triazole
 1-(3'-nitrophenyl)-3-hydroxy-5-chloro-1,2,4-triazole.

f) *1-isopropyl-3-hydroxy-5-bromo-1,2,4-triazole.*

63.9 g of 1-isopropyl-1,2,4-triazolyl-(3)-benzoate with a melting point of 55—57°C (manufactured from 1-isopropyl-3-hydroxy-1,2,4-triazole and benzoyl chloride), 53.4 g of N-bromosuccinimide and 0.2 g of azoisobutyronitrile in 550 ml of carbon tetrachloride are heated together for 48 hours to reflux. After the reaction mixture has been cooled to 0°C, the precipitate which has formed is filtered off under suction and heated to 75°C in 600 ml of water. The undissolved portion is filtered off and dried in vacuo, to give 40 g of 1-isopropyl-5-bromo-1,2,4-triazolyl-(3)-benzoate in the form of crystals melting at 125—130°C.

361 g of this intermediate product are treated with 1950 ml of 2N NaOH and the mixture is heated to 60°C. The solution is cooled to 20°C, filtered clear with activated charcoal over "Hyflo", and the filtrate is acidified with 390 ml of concentrated hydrochloric acid in 2000 ml of water. White crystals of 1-isopropyl-3-hydroxy-5-bromo-1,2,4-triazole (m.p. 155—157°C) are obtained. ("Hyflo" is a registered Trade Mark).

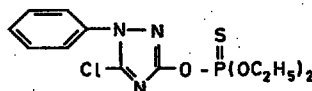
g) *isopropyl-3-hydroxy-5-fluoro-1,2,4-triazole.*

16.2 g of 1-isopropyl-3-hydroxy-5-chloro-1,2,4-triazole, 29 g of dry potassium fluoride and 150 ml of sulpholane are heated together for 16 hours to 160—200°C. The solvent is evaporated off in a high vacuum and the residue then treated with 10% acetic acid and extracted with ethyl acetate. The ethyl acetate is evaporated off and the residual solid is recrystallised from water, in the process of which 1-isopropyl-3-hydroxy-5-fluoro-1,2,4-triazole is obtained in the form of white crystals with a melting point of 80—95°C. The product can be recrystallised from an organic solvent in order to purify it further.

Manufacture of the new phosphorus compounds.

a) *O,O-diethyl-O-[1-phenyl-5-chloro-1,2,4-triazolyl-(3)]-phosphorothionate.*

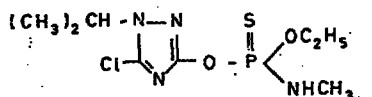
11.4 g of 1-phenyl-3-hydroxy-5-chloro-1,2,4-triazole and 8.0 g of potassium carbonate in 250 ml of methyl ethyl ketone are heated for 2 hours under reflux and the mixture is subsequently cooled to room temperature. 10.8 g of diethylthiophosphoric chloride are added dropwise and the solution is heated again for 1½ hours under reflux. It is then stirred overnight at room temperature. The salts are filtered off using Hyflo and the clear filtrate is evaporated in vacuo, to give O,O-diethyl-O-[1-phenyl-5-chloro-1,2,4-triazolyl-(3)]-phosphorothionate of the formula:—



n_D^{20} : 1.5449. (Compound No.1)

b) *O-ethyl-O-[1-isopropyl-5-chloro-1,2,4-triazolyl-(3)]-N-methyl-phosphoramidothionate.*

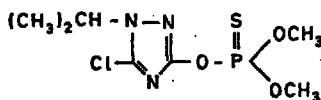
32.2 g of 1-isopropyl-3-hydroxy-5-chloro-1,2,4-triazole and 27.6 g of potassium carbonate were heated under reflux for 2 hours in 400 ml of methyl ethyl ketone. The resulting slurry was cooled to room temperature and 34.7 g of O-ethyl-S-methylamino-dithiophosphoric chloride in 100 ml of methyl ethyl ketone were added dropwise. The batch was heated to reflux once more for 2 hours and subsequently stirred overnight at room temperature. The salts were filtered off using Hyflo and the solvent distilled off from the filtrate in vacuo. The residue was purified by chromatography over a short silica gel column with chloroform as eluant, giving O-ethyl-O-[1-isopropyl-5-chloro-1,2,4-triazolyl-(3)]-N-methyl-phosphoramidothionate of the formula


 $n_D^{20}: 1.5130.$

(Compound No.2)

c) *O,O*-dimethyl-*O*-[1-isopropyl-5-chloro-1,2,4-triazolyl-(3)]-phosphorothionate.

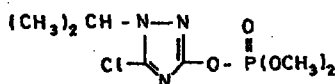
33 g of 1-isopropyl-3-hydroxy-5-chloro-1,2,4-triazole and 27 g of potassium carbonate are heated under reflux for 2 hours in 400 ml of methyl ethyl ketone. The solution is cooled to room temperature and 32 g of dimethylthiophosphoric chloride are added dropwise. The batch is subsequently stirred for 5 hours at 60° C and then overnight at room temperature. The salts are filtered off and the filtrate is concentrated in vacuo. The oily residue is purified by chromatography over a short silica gel column with chloroform as eluant, to give *O,O*-dimethyl-*O*-[1-isopropyl-5-chloro-1,2,4-triazolyl-(3)]-phosphorothionate of the formula:—


 $n_D^{20}: 1.4970.$

(Compound No.3)

d) *O,O*-dimethyl-*O*-[1-isopropyl-5-chloro-1,2,4-triazolyl-(3)]-phosphate.

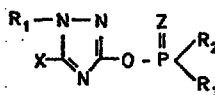
32.2 g of 1-isopropyl-3-hydroxy-5-chloro-1,2,4-triazole and 27.6 g of potassium carbonate are heated under reflux for 2 hours in 400 ml of methyl ethyl ketone and the mixture is subsequently cooled to room temperature. 28.9 g of dimethylphosphoric chloride in 100 ml of methyl ethyl ketone are added dropwise and the solution is heated again under reflux for 2 hours. The batch is then stirred overnight at room temperature. The salts are then filtered off using Hyflo and the filtrate is concentrated in vacuo. The oily, dark residue is purified by chromatography over a short silica gel column with chloroform/1 % methanol, to give *O,O*-dimethyl-*O*-[1-isopropyl-5-chloro-1,2,4-triazolyl-(3)]-phosphate of the formula:—

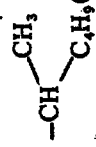

 $n_D^{20}: 1.4650.$

(Compound No.4)

25 The following compounds were manufactured in analogous manner:

25

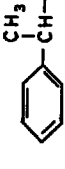


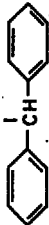
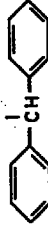
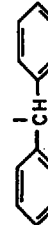
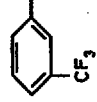
Compound No.	R ₁	R ₂	R ₃	X	Z	Physical Data
5		-OC ₂ H ₅	-NH-CH(CH ₃) ₂	Cl	O	n _D ²⁰ : 1.5273
6	-C ₃ H ₇ (i)	-OC ₂ H ₅	-NH-CH(CH ₃) ₂	Cl	S	Mp. : 50-52°C
7	-C ₃ H ₇ (i)	-OC ₂ H ₅	-N(CH ₃) ₂	Cl	S	n _D ²⁰ : 1.5016
8	-C ₃ H ₇ (i)	-OC ₂ H ₅	-NHCH ₃	Br	S	n _D ²⁰ : 1.5237
9	-C ₃ H ₇ (i)	-OC ₂ H ₅	-NH ₂	Cl	S	n _D ²⁰ 1.5192
10		-OC ₂ H ₅	-NHCH ₃	Cl	S	n _D ²⁰ : 1.4988
11	-C ₂ H ₅	-OC ₂ H ₅	-OC ₂ H ₅	Cl	S	n _D ²⁰ : 1.5032
12	-C ₄ H ₉ (sec.)	-OC ₂ H ₅	-OC ₂ H ₅	Cl	S	n _D ²⁰ : 1.4871
13	-C ₄ H ₉ (i)	-OC ₂ H ₅	-OC ₂ H ₅	Cl	S	n _D ²⁰ : 1.4882
14	-C ₂ H ₅	-OCH ₃	-OCH ₃	Cl	S	n _D ²⁰ : 1.4939
15	-C ₄ H ₉ (sec.)	-OCH ₃	-OCH ₃	Cl	S	n _D ²⁰ : 1.4953
16	-C ₄ H ₉ (i)	-OCH ₃	-OCH ₃	Cl	S	n _D ²⁰ : 1.4966

Compound No.	R ₁	R ₂	R ₃	X	Z	Physical Data
17		-OCH ₃	-OCH ₃	Cl	S	n _D ²⁰ : 1.5666
18	-C ₃ H ₇ (i)	-OC ₂ H ₅	-C ₂ H ₅	Cl	S	n _D ²⁰ : 1.4968
19	-C ₃ H ₇ (i)	-OC ₃ H ₇ (n)	-CH ₃	Cl	S	n _D ²⁰ : 1.5000
20	-C ₃ H ₇ (i)	-OC ₂ H ₅		Cl	S	n _D ²⁰ : 1.5498
21	-C ₄ H ₉ (sec.)	-OC ₂ H ₅	-C ₂ H ₅	Cl	S	n _D ²⁰ : 1.5002
22	-C ₄ H ₉ (i)	-OC ₃ H ₇ (n)	-CH ₃	Cl	S	n _D ²⁰ : 1.4992
23		-OC ₂ H ₅	-C ₂ H ₅	Cl	S	n _D ²⁰ : 1.5620
24	-C ₃ H ₇ (i)	-OC ₂ H ₅	-OC ₂ H ₅	Cl	O	n _D ²⁰ : 1.4604
25	-C ₃ H ₇ (i)	-OC ₂ H ₅	-SC ₃ H ₇ (n)	Cl	O	n _D ²⁰ : 1.4931
26	-C ₃ H ₇ (i)	-OC ₂ H ₅	-SC ₃ H ₇ (n)	Cl	S	n _D ²⁰ : 1.5243

Compound No.	R ₁	R ₂	R ₃	X	Z	Physical Data
27	-C ₃ H ₇ (i)	-OC ₂ H ₅	-OC ₂ H ₅	Br	S	n _D ²⁰ : 1.4977
28	-C ₃ H ₇ (i)	-OCH ₃	-OC ₂ H ₅	Cl	S	n _D ²⁰ : 1.4888
29	-C ₃ H ₇ (i)	-OCH ₃	-OCH ₃	Br	S	n _D ²⁰ : 1.5133
30	-C ₃ H ₇ (i)	-OC ₃ H ₇ (n)	-CH ₃	Br	S	n _D ²⁰ : 1.5135
31	-C ₃ H ₅	-OC ₂ H ₅	-C ₂ H ₅	Cl	S	n _D ²⁰ : 1.5087
32	-C ₄ H ₉ (n)	-OC ₂ H ₅	-OC ₂ H ₅	Cl	S	n _D ²⁰ : 1.4896
33	-C ₄ H ₉ (n)	-OC ₂ H ₅	-C ₂ H ₅	Cl	S	n _D ²⁰ : 1.5017
34	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}-\text{C}_3\text{H}_7(\text{n}) \end{array}$	-OC ₂ H ₅	-OC ₂ H ₅	Cl	S	n _D ²⁰ : 1.4858
35	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}-\text{C}_3\text{H}_7(\text{n}) \end{array}$	-OCH ₃	-OCH ₃	Cl	S	n _D ²⁰ : 1.4919
36	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}-\text{C}_4\text{H}_9(\text{tert.}) \end{array}$	-OC ₂ H ₅	-OC ₂ H ₅	Cl	S	n _D ²⁰ : 1.4880
37	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}-\text{C}_4\text{H}_9(\text{tert.}) \end{array}$	-OCH ₃	-OCH ₃	Cl	S	n _D ²⁰ : 1.4930

Compound No.	R ₁	R ₂	R ₃	X	Z	Physical Data
38		-OC ₂ H ₅	-OC ₂ H ₅	Cl	S	$n_D^{20} : 1.5044$
39		-OC ₂ H ₅	-S-C ₃ H ₇ (n)	Cl	S	$n_D^{20} : 1.4971$
40		-OCH ₃	-OCH ₃	Cl	S	
41	-C ₃ H ₇ (i)	-OC ₂ H ₅	-SCH ₃	Cl	S	
42	-C ₄ H ₉ (sec.)	-OC ₂ H ₅	-SC ₃ H ₇ (n)	Cl	S	
43	C ₄ H ₉ (i)	-OC ₂ H ₅	-SC ₃ H ₇ (n)	Cl	S	
44	-C ₃ H ₇ (n)	-OC ₂ H ₅	-OC ₂ H ₅	Cl	S	
45	-C ₃ H ₇ (n)	-OCH ₃	-OCH ₃	Cl	S	
46		-OC ₂ H ₅	-OC ₂ H ₅	Cl	S	$n_D^{20} : 1.5344$
47		-OCH ₃	-OCH ₃	Cl	S	$n_D^{20} : 1.5498$

Compound No.	R ₁	R ₂	R ₃	X	Z	Physical Data
48		-OC ₂ H ₅	-NHCH ₃	Cl	S	n _D ²⁰ : 1.5554
49		-OC ₂ H ₅	-SC ₃ H _{7(n)}	Cl	S	n _D ²⁰ : 1.5648
50		-OC ₂ H ₅	-OC ₂ H ₅	Cl	S	n _D ²⁰ : 1.5289
51		-OCH ₃	-OCH ₃	Cl	S	n _D ²⁰ : 1.5437
52		-OC ₂ H ₅	-NHCH ₃	Cl	S	n _D ²⁰ : 1.5517
53		-OC ₂ H ₅	-SC ₃ H _{7(n)}	Cl	S	n _D ²⁰ : 1.5590

Compound No.	R ₁	R ₂	R ₃	X	Z	Physical Data
54		-OC ₂ H ₅	-OC ₂ H ₅	Cl	S	
55		-OCH ₃	-OCH ₃	Cl	S	
56		-OC ₂ H ₅	-C ₂ H ₅	Cl	S	
57		-OC ₂ H ₅	-OC ₂ H ₅	Cl	S	
58		-OC ₂ H ₅	-NHCH ₃	Cl	S	m.p. : 51-59°C
59	-C ₃ H ₇ (i)	-OC ₂ H ₅	-NH-CH(CH ₃) ₂	Cl	O	m.p. : 53-56°C

Example 2.

A) Insecticidal ingest poison action.

Tobacco and potato plants were sprayed with a 0.05 % aqueous emulsion (obtained from a 10 % emulsifiable concentrate).

After the coating had dried, the tobacco plants were populated with Egyptian cotton leaf worms (*Spodoptera littoralis*) and the potato plants with Colorado potato beetle larvae (*Leptinotarsa decemlineata*). The tests was carried out at 24° C and 60 % relative humidity. In the above test, the compounds Nos. 4, 30 to 34 and 47 to 51 displayed ingest poison action against *Spodoptera littoralis* and *Leptinotarsa decemlineata*.

Example 3.

Action against *Aulacophora femoralis* larvae.

Sterilised compost earth was homogeneously mixed with a wettable powder containing 25 % of active substance so that there resulted a rate of application of 8 kg of active substance per hectare.

Young zucchini plants (*Cucumis pepo*) were put into plastic pots with the treated soil (3 plants per pot; diameter of pot=7 cm). Each pot was infected immediately afterwards with 5 *Aulacophora femoralis* larvae. The control was carried out 4, 8, 16 and 32 days after depositing the larvae.

At 80—100% kill after the first control, a fresh infestation with 5 larvae each was carried out in the same soil sample with 3 new zucchini plants. If the activity was less than 80 %, the remaining larvae remained in the soil sample until the control immediately following. If an active substance at a rate of application of 8 kg/ha still effected a 100 % kill, a further control with 4 and 2 kg of active substance per hectare was carried out.

In the above test, the compounds Nos. 1 to 3, 11 to 13, 27 and 28 displayed action against *Aulacophora femoralis* larvae.

Example 4.

Action against ticks.

A) *Rhipicephalus bursa*

Five adult ticks and 50 tick larvae were counted into a glass tube and immersed for 1 to 2 minutes in 2 ml of an aqueous emulsion from an emulsion series each containing 100, 10, 1 and 0.1 ppm of test substance. The tube was then sealed with a standardised cotton wool plug and placed on its head, so that the active substance emulsion could be adsorbed by the cotton wool.

In the case of the adults evaluation took place after 2 weeks, and in that of the larvae after 2 days. Each test was repeated twice.

B) *Boophilus microplus* (larvae).

Tests were carried out in each case with 20 OP-sensitive larvae using an analogous dilution series as in the case of test A. (The resistance refers to the tolerability of Diazinon).

The compounds Nos. 11 to 13, 15, 17, 22, 23, 34, 44 and 46 acted in the above test against adults and larvae of *Rhipicephalus bursa* and sensitive and OP-resistant larvae of *Boophilus microplus*.

Example 5.

Acaricidal action.

Phaseolus vulgaris (dwarf beans) have an infested piece of leaf from a mass culture of *Tetranychus urticae* placed on them 12 hours before the test for the acaricidal action. The mobile stages which have migrated are sprayed with the emulsified test preparations from a chromatography atomiser so that the spray broth does not run off. The number of living and dead larvae and adults are evaluated after 2 to 7 days under a stereoscopic microscope.

During the "interim", the treated plants are kept in greenhouse compartments at 25° C.

The compounds Nos. 11 to 13, 33, 34 and 46 to 53 are active in the above test against larvae and adults of *Tetranychus urticae*.

Example 6.

Action against soil nematodes.

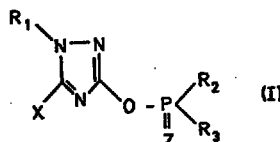
To test the action against soil nematodes, the active substance (in varied concentrations) is applied to and intimately mixed with soil infected with root gall

nematodes (*Meloidgyne avenaria*). Immediately afterwards, tomato cuttings are planted in the thus prepared soil in a series of tests and after a waiting time of 8 days tomato seeds are sown in another test series.

In order to assess the nematocidal action, the galls present on the roots are counted 28 days after planting and sowing respectively. The compounds Nos. 8, 12, 18, 21, 44 and 46 display good action against *Meloidgyne avenaria*.

WHAT WE CLAIM IS:—

1. Compounds of the formula I



wherein

X represents a fluorine, chlorine or bromine atom,

Z represents an oxygen or sulphur atom,

R₁ represents an alkyl group optionally substituted by one or more halogen atoms and containing maximally 19 carbon atoms, a cycloalkyl group containing from 3 to 8 ring carbon atoms, an optionally substituted aryl or an optionally substituted aralkyl group.

R₂ represents an alkoxy or alkylthio group each being optionally substituted by one or more halogen atoms and each containing maximally 19 carbon atoms, an amino group, or a mono- or di-alkyl-amino group in which the alkyl moieties each contain maximally 19 carbon atoms, and

R₃ represents an alkyl, alkoxy, or alkylthio group each being optionally substituted by one or more halogen atoms and each containing maximally 19 carbon atoms, a phenyl, phenoxy or amino group, or a mono- or di-alkyl-group in which the alkyl moieties each contain maximally 19 carbon atoms,

with the proviso that when X represents a chlorine atom, Z represents a sulphur atom and R₁ represents an isopropyl group, R₂ and R₃ are not both ethoxy groups.

2. Compounds of the formula I defined in claim 1 wherein X, Z, R₂ and R₃ are as defined in claim 1 and R₁ represents an aryl or aralkyl group optionally substituted by one or more members selected from fluorine, chlorine and bromine atoms and alkyl, haloalkyl, alkoxy, alkylthio, alkylsulphinyl and alkylsulphonyl groups each containing maximally 6 carbon atoms and nitro groups, with the proviso that when X represents a chlorine atom, Z represents a sulphur atom, and R₁ represents an isopropyl group, R₂ and R₃ are not both ethoxy groups.

3. Compounds of the formula I defined in claim 1 wherein X and Z are as defined in claim 1,

R₁ represents an alkyl group containing maximally 19 carbon atoms, a cycloalkyl group containing from 3 to 8 ring carbon atoms, or a phenyl, benzyl, α-phenethyl, β-phenethyl, or diphenylmethyl group each being optionally substituted in the phenyl ring or rings by one or more members selected from fluorine, chlorine and bromine atoms and alkyl, haloalkyl, alkoxy, alkylthio, alkylsulphinyl and alkylsulphonyl groups each containing maximally 6 carbon atoms and nitro groups,

R₂ represents an alkoxy or alkylthio group each containing maximally 6 carbon atoms, an amino group or a mono- or di-alkyl-amino group in which the alkyl moieties each contain maximally 6 carbon atoms, and

R₃ represents an alkyl, alkoxy or alkylthio group each containing maximally 6 carbon atoms, a phenyl, phenoxy or amino group, or a mono- or di-alkyl-amino group in which the alkyl moieties each contain maximally 6 carbon atoms,

with the proviso that when X represents a chlorine atom, Z represents a sulphur atom, and R₁ represents an isopropyl group, R₂ and R₃ are not both ethoxy groups.

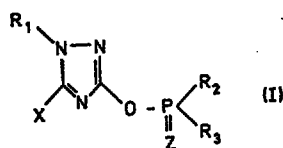
4. Compounds according to claim 3 wherein R₁ represents an alkyl group containing maximally 6 carbon atoms, a cycloalkyl group containing 5 or 6 ring carbon atoms, a phenyl or benzyl group each optionally substituted by one or more members selected from fluorine, chlorine and bromine atoms, and methyl, trifluoromethyl, methoxy, methylthio, ethoxy and nitro groups, or an α-phenethyl, β-phenethyl or diphenylmethyl group.

nematodes (*Meloidgyne avenaria*). Immediately afterwards, tomato cuttings are planted in the thus prepared soil in a series of tests and after a waiting time of 8 days tomato seeds are sown in another test series.

In order to assess the nematocidal action, the galls present on the roots are counted 28 days after planting and sowing respectively. The compounds Nos. 8, 12, 18, 21, 44 and 46 display good action against *Meloidgyne avenaria*.

WHAT WE CLAIM IS:—

1. Compounds of the formula I



wherein

X represents a fluorine, chlorine or bromine atom,

Z represents an oxygen or sulphur atom,

R₁ represents an alkyl group optionally substituted by one or more halogen atoms and containing maximally 19 carbon atoms, a cycloalkyl group containing from 3 to 8 ring carbon atoms, an optionally substituted aryl or an optionally substituted aralkyl group.

R₂ represents an alkoxy or alkylthio group each being optionally substituted by one or more halogen atoms and each containing maximally 19 carbon atoms, an amino group, or a mono- or di-alkyl-amino group in which the alkyl moieties each contain maximally 19 carbon atoms, and

R₃ represents an alkyl, alkoxy, or alkylthio group each being optionally substituted by one or more halogen atoms and each containing maximally 19 carbon atoms, a phenyl, phenoxy or amino group, or a mono- or di-alkyl-group in which the alkyl moieties each contain maximally 19 carbon atoms, with the proviso that when X represents a chlorine atom, Z represents a sulphur atom and R₁ represents an isopropyl group, R₂ and R₃ are not both ethoxy groups.

2. Compounds of the formula I defined in claim 1 wherein X, Z, R₂ and R₃ are as defined in claim 1 and R₁ represents an aryl or aralkyl group optionally substituted by one or more members selected from fluorine, chlorine and bromine atoms and alkyl, haloalkyl, alkoxy, alkylthio, alkylsulphinyl and alkylsulphonyl groups each containing maximally 6 carbon atoms and nitro groups, with the proviso that when X represents a chlorine atom, Z represents a sulphur atom, and R represents an isopropyl group, R₂ and R₃ are not both ethoxy groups.

3. Compounds of the formula I defined in claim 1 wherein X and Z are as defined in claim 1,

R₁ represents an alkyl group containing maximally 19 carbon atoms, a cycloalkyl group containing from 3 to 8 ring carbon atoms, or a phenyl, benzyl, α -phenethyl, β -phenethyl, or diphenylmethyl group each being optionally substituted in the phenyl ring or rings by one or more members selected from fluorine, chlorine and bromine atoms and alkyl, haloalkyl, alkoxy, alkylthio, alkylsulphinyl and alkylsulphonyl groups each containing maximally 6 carbon atoms and nitro groups,

R₂ represents an alkoxy or alkylthio group each containing maximally 6 carbon atoms, an amino group or a mono- or di-alkyl-amino group in which the alkyl moieties each contain maximally 6 carbon atoms, and

R₃ represents an alkyl, alkoxy or alkylthio group each containing maximally 6 carbon atoms, a phenyl, phenoxy or amino group, or a mono- or di-alkyl-amino group in which the alkyl moieties each contain maximally 6 carbon atoms,

with the proviso that when X represents a chlorine atom, Z represents a sulphur atom, and R₁ represents an isopropyl group, R₂ and R₃ are not both ethoxy groups.

4. Compounds according to claim 3 wherein R₁ represents an alkyl group containing maximally 6 carbon atoms, a cycloalkyl group containing 5 or 6 ring carbon atoms, a phenyl or benzyl group each optionally substituted by one or more members selected from fluorine, chlorine and bromine atoms, and methyl, trifluoromethyl, methoxy, methylthio, ethoxy and nitro groups, or an α -phenethyl, β -phenethyl or diphenylmethyl group.



5. Compounds according to claim 4 wherein R₁ represents an alkyl group containing maximally 6 carbon atoms, or a cyclopentyl, phenyl, trifluoromethyl-phenyl, benzyl, diphenylmethyl or α -phenethyl group.
- 5 6. Compounds according to any one of claims 3 to 5 wherein R₂ represents an alkoxy or alkylthio group containing maximally 6 carbon atoms.
7. Compounds according to claim 6 wherein R₂ represents a methoxy, ethoxy or n-propoxy group.
8. Compounds according to any one of claims 3 to 7 wherein R₃ represents a methyl, ethyl, methoxy, ethoxy, amino-, methylamino, ethylamino, isopropyl-amino, dimethylamino, methylthio, ethylthio, n-propylthio, phenyl or phenoxy group.
- 10 9. Compounds according to claim 8 wherein R₃ represents a methyl, ethyl, methoxy, ethoxy, propylthio, amino, methylamino or dimethylamino group.
- 10 10. Compounds according to any one of claims 3 to 9 wherein X represents a chlorine atom.
- 15 11. Compounds according to any one of claims 3 to 10 wherein Z represents a sulphur atom.
12. O,O - Diethyl - O - [1 - ethyl - 5 - chloro - 1,2,4 - triazolyl - (3)] - phosphorothionate.
- 20 13. O,O - Diethyl - O - [1 - sec.butyl - 5 - chloro - 1,2,4 - triazolyl - (3)] - phosphorothionate.
14. O,O - Diethyl - O - [1 - phenyl - 5 - chloro - 1,2,4 - triazolyl - (3)] - phosphorothionate.
- 25 15. O - Ethyl - S - n - propyl - O - [1 - isopropyl - 5 - chloro - 1,2,4 - triazolyl - (3)] - phosphorodithioate.
- 25 16. O,O - Diethyl - O - [1 - isopropyl - 5 - bromo - 1,2,4 - triazolyl - (3)] - phosphorothionate.
17. O,O - Diethyl - O - [1 - cyclopentyl - 5 - chloro - 1,2,4 - triazolyl - (3)] - phosphorothionate.
- 30 18. O,O - Diethyl - O - [1 - benzyl - 5 - chloro - 1,2,4 - triazolyl - (3)] - phosphorothionate.
19. O - Ethyl - S - n - propyl - O - [1 - benzyl - 5 - chloro - 1,2,4 - triazolyl - (3)] - phosphorodithioate.
- 35 20. O,O - Diethyl - O - [1 - (α - phenethyl) - 5 - chloro - 1,2,4 - triazolyl - (3)] - phosphorothionate.
- 35 21. O - Ethyl - O - [1 - (α - phenethyl) - 5 - chloro - 1,2,4 - triazolyl - (3)] - N - methyl - phosphoramidothionate.
22. O - Ethyl - O - [1 - isopropyl - 5 - chloro - 1,2,4 - triazolyl - (3)] - N - methyl - phosphoramidothionate.
- 40 23. O - Ethyl - O - [1 - isopropyl - 5 - chloro - 1,2,4 - triazolyl - (3)] - N,N - dimethyl - phosphoramidothionate.
24. O - Ethyl - O - [1 - isopropyl - 5 - chloro - 1,2,4 - triazolyl - (3)] - phosphoramidothionate.
- 45 25. O - Ethyl - O - [1 - (1',2',2' - trimethylpropyl) - 5 - chloro - 1,2,4 - triazolyl - (3)] - N - methyl - phosphoramidothionate.
26. O,O - Diethyl - O - [1 - (1',2',2' - trimethylpropyl) - 5 - chloro - 1,2,4 - triazolyl - (3)] - phosphorothionate.
27. O,O - Dimethyl - O - [1 - (1',2',2' - trimethylpropyl) - 5 - chloro - 1,2,4 - triazolyl - (3)] - phosphorothionate.
- 50 28. O - Ethyl - S - n - propyl - O - [1 - (1',2',2' - trimethylpropyl) - 5 - chloro - 1,2,4 - triazolyl - (3)] - phosphorodithioate.
29. O,O - Dimethyl - O - [1 - benzyl - 5 - chloro - 1,2,4 - triazolyl - (3)] - phosphorothionate.
30. O - Ethyl - O - [1 - benzyl - 5 - chloro - 1,2,4 - triazolyl (3)] - N - methyl - phosphoramidothionate.
- 55 31. O,O - Dimethyl - O - [1 - (α - phenethyl) - 5 - chloro - 1,2,4 - triazolyl - (3)] - phosphorothionate.
32. O - Ethyl - S - n - propyl - O - [1 - (α - phenethyl) - 5 - chloro - 1,2,4 - triazolyl - (3)] - phosphorodithioate.
- 60 33. O,O - Diethyl - O - [1 - n - butyl - 5 - chloro - 1,2,4 - triazolyl - (3)] - phosphorothionate.
34. O - Ethyl - O - [1 - isopropyl - 5 - chloro - 1,2,4 - triazolyl - (3)] - N - isopropyl - phosphoramidothionate.
35. O,O - Diethyl - O - [1 - n - propyl - 5 - chloro - 1,2,4 - triazolyl - (3)] - phosphorothionate.
- 65



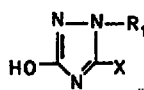
36. O,O - Dimethyl - O - [1 - isopropyl - 5 - chloro - 1,2,4 - triazolyl - (3)] - phosphate.

37. A compound according to claim 1 specifically identified herein.

38. Process for the production of a compound of the formula I as claimed in claim 1, which process comprises reacting a compound of the formula II



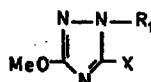
(wherein R_2 , R_3 and Z are as defined in claim 1 and Hal represents a halogen atom) in the presence of an acid binding agent with a compound of the formula III



(III)

(wherein R_1 and X are as defined in claim 1).

39. Process for the production of a compound as claimed in claim 1 which process comprises reacting a compound of formula II as defined in claim 38 with a compound of the formula IV



(IV)

(wherein R_1 and X are as defined in claim 1 and Me represents a monovalent metal atom).

40. A process according to claim 39 wherein, in the compound of formula IV, Me represents an alkali metal atom.

41. A process according to claim 40 wherein Me represents a sodium or potassium atom.

42. A process according to any one of claims 38 to 41 wherein, in the compound of formula II, Hal represents a chlorine or bromine atom.

43. Process for producing a compound claimed in claim 1 substantially as described with reference to Example 1.

44. Compound according to claim 1 produced by the process claimed in any one of claims 38 to 43.

45. A pesticidal composition which comprises, as active ingredient, a compound as claimed in any one of claims 1 to 37 together with a solid extender; a solid extender and a surfactant; or a liquid diluent and a surfactant.

46. A solid composition according to claim 45.

47. A composition according to claim 46 in the form of a granulate.

48. A composition according to claim 47 wherein the granules are coated or impregnated with the active ingredient.

49. A liquid composition according to claim 45.

50. A pesticidal composition containing a compound claimed in claim 1 and in the form of a dust, granulate, wettable powder, emulsifiable concentrate or spray specifically described herein.

51. A composition according to any one of claims 45 to 50 wherein the active ingredient is a compound as claimed in any one of claims 1 to 14, 18, 20, 22 and 33 to 35.

52. A compound as claimed in any one of claims 1 to 37 in a container which bears instructions for the use of the compound in combating insects, nematodes or acarina.



53. A compound as claimed in any one of claims 1 to 14, 18, 20, 22, 26 and 33 to 35 in a container which bears instructions for the use of the compound in combating insects, nematodes or acarina.

5 54. Method of combating insects, nematodes or acarina which method comprises applying to a locus infested with or liable to be infested with the insects, nematodes or acarina a compound as claimed in any one of claims 1 to 37. 5

55. A method according to claim 54 wherein the compound applied is a compound as claimed in any one of claims 1 to 14, 18, 20, 22, 26 and 33 to 35.

10 56. A method according to claim 54 or 55 wherein the insects, nematodes or acarina are harmful to seeds, tubers, plants or plant parts. 10

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1978.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

