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COMPLETE SPECIFICATION

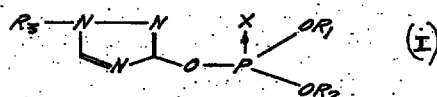
Phosphoric and Thionophosphoric Acid Esters, manufacture thereof and their use as Insecticides

We: **FARBWERKE HOECHST AKTIENGESELLSCHAFT**. Vornals Meister Lucius & Brüning, a Body Corporate recognised under German law, of, 6230 Frankfurt (M)-Hoechst, 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 new phosphoric and thionophosphoric acid esters, a process for their manufacture and their use as insecticides and pesticides.

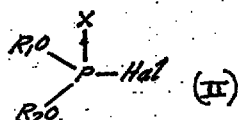
British Patent No. 713,278 discloses phosphoric acid esters that contain an enolizable heterocycle, which esters can be used for the control of pests.

The present invention provides phosphoric and thionophosphoric acid esters of the general formula I



in which R_1 and R_2 each represents an alkyl radical having 1 to 4 carbon atoms, preferably the ethyl radical, R_3 represents a phenyl radical or phenyl radicals substituted by chlorine atoms, and X represents an oxygen atom or a sulphur atom.

The present invention also provides a process for the manufacture of phosphoric and thionophosphoric acid esters of the general formula I, which comprises reacting phosphoric or thiophosphoric acid halides of the general formula II

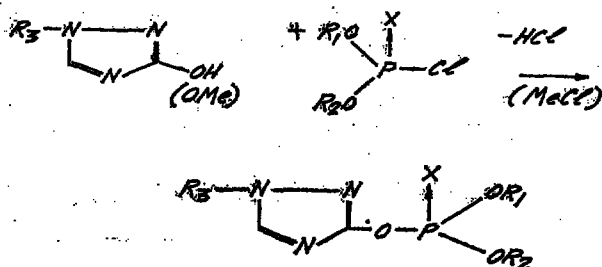


in which X , R_1 and R_2 have the meanings given above, and Hal represents a halogen atom, preferably a chlorine atom; with 3-hydroxy-triazols substituted by R_3 according to the above formula, or the metal salts of the 3-hydroxy-triazols, preferably the sodium- or potassium salts thereof.

In the first instant, the reaction is carried out in the presence of acid-binding agents, for example, alkali metal carbonates, for example, sodium carbonate, alkaline earth metal carbonates, or tertiary amines, for example, triethyl amine, dimethyl aniline or pyridine.

The reaction is illustrated by the following scheme: (Me=metal)

[Price 5s. 0d.]



The reaction may be carried out with or without using solvents. As solvents, there are suitable all usual organic liquids which are inert under the reaction conditions, for example, acetone, methylethyl ketone, acetonitrile, acetic acid ethyl ester, butyl acetate, tetrahydrofuran, dioxane, methylene chloride, carbon tetrachloride, benzene, xylene and chlorobenzene.

The reaction is generally carried out at a temperature within the range of from about 20—25°C to the boiling points of the individual solvents, preferably within the range of from 50 to 90°C. Copper powder may be added in an amount of from 1 to 20 mol-%, and this may have a favourable effect on the reaction velocity.

Some of the novel compounds are obtained as oils, some as crystals. They cannot be distilled without decomposition.

Further the present invention provides pesticidal compositions comprising, as the active ingredient a phosphoric or thionophosphoric acid ester of the general formula I together with a carrier. These novel phosphoric and thionophosphoric acid esters exhibit an excellent pesticidal activity, especially insecticidal activity by penetrating into the tissue of the plants, for example, they are effective as contact and stomach poisons, especially against herbivorous and plant-sucking arthropods. Owing to their low toxicity to warm blooded animals, the phosphoric and thionophosphoric acid esters of the formula I are, moreover, suitable for the control of ecto- and endo-parasites on and in animals. In contradistinction to known compounds of a similar constitution, the phosphoric and thionophosphoric acid esters I are effective against arthropods that are resistant to known phosphoric acid esters. The duration of activity of the phosphoric and thionophosphoric acid esters I is also superior to that of the known compounds.

The phosphoric and thionophosphoric acid esters I are far superior to O,O-dimethyl-(5-ethyl-1,2,4-triazol-3-yl)-thionophosphate disclosed in British Patent Specification No. 713,278, Number 19 in the Table, as well as to the corresponding undisclosed O,O-diethyl-(5-ethyl-1,2,4-triazol-3-yl)-thionophosphate with respect to their biological activity, as is shown in the following Examples 6 to 9. The phosphoric and thionophosphoric acid esters I are very compatible with plants and possess fungicidal properties in addition to their insecticidal and parasitocidal actions. Therefore, they can be used for protecting plants and stocks as well as for combating parasites on and in animals.

In order to obtain pesticidal compositions, the phosphoric and thionophosphoric acid esters I may be mixed with inert solid or liquid carrier materials, with adhesives, wetting agents, dispersing agents and grinding auxiliaries to be used as wettable powders, emulsions, suspensions, dusting powders, granules, fly-catchers, strewing powders and detergents. Such compositions may also be combined with other insecticides, fungicides, nematocides and herbicides.

As inert carrier materials, there may be used mineral substances for example, aluminium silicates, alumina, kaolin, chalks, siliceous chalks, talcum, kieselguhr, or hydrated silicic acids or preparations of these mineral substances with special additives, for example, chalk greased with sodium stearate. As inert carrier materials for liquid preparations there may be used all the usual and suitable inert organic solvents, for example, toluene, xylene, diacetone alcohol, cyclohexanone, isophorone, gasolines, paraffin oils, dioxane, dimethyl formamide, dimethyl sulphoxide, ethyl acetate, butyl acetate, tetrahydrofuran and chlorobenzene.

As adhesives, there may be used glutinous cellulose products or polyvinyl alcohols.

As wetting agents, there may be used all suitable emulsifiers, for example, hydroxy-ethylated alkylphenols, salts of aryl- or alkyl-aryl sulphonic acid salts, of methyl-taurine, salts of phenylcogaine sulphonic acids or soaps.

As dispersing agents there may be used salts of dried cellulose sulphite liquors, e.g. potassium ligninsulphonate, salts of naphthalene-sulphonic acid and, if required, hydrated silicic acids or even kieselguhr.

As grinding auxiliaries there may be used suitable inorganic or organic salts of sodium sulphate, ammonium sulphate, sodium carbonate, sodium bicarbonate, sodium thiosulphate, sodium stearate, sodium acetate.

Pesticidal compositions obtained according to the invention may preferably be used in the form of an emulsion concentrate containing from 10 to 70% by weight of a phosphoric or thionophosphoric acid ester I and from 5 to 20% by weight of a wetting agent, whereas the rest making up 100% by weight, is a suitable organic solvent.

In the so-called ultra-low-volume method, where highly concentrated mixtures are sprayed through valves from planes, there may be used insecticidal compositions containing from 70 to 90% by weight of a phosphoric or thionophosphoric acid ester I and from 30 to 10% by weight of an aromatic and/or aliphatic mineral oil, having a boiling point higher than 120°C.

The following Examples illustrate the invention.

EXAMPLE 1

32.2 Grams (0.2 mol) of 1-phenyl-3-hydroxy-1,2,4-triazol were suspended in 250 millilitres of acetone and 38 grams (0.2 mol) of O,O-diethyl-thionophosphoric acid chloride were added thereto. Subsequently, 22 grams (0.22 mol) of triethylamine were added drop by drop and the mixture was stirred for 6 hours at about 50°C. After cooling, the triethylamine hydrochloride was filtered off, and the solvent was evaporated from the filtrate. 60 grams of O,O-diethyl-(1-phenyl-1,2,4-triazol-3-yl)-thionophosphate were obtained as a light-brown oil.

$C_{12}H_{18}N_3O_3P$ S calculated: N 13.5%; P 9.9%
molecular weight: 313 found: N 12.5%; P 9.9%

EXAMPLE 2

36.6 Grams (0.2 mol) of the sodium salt of 1-phenyl-3-hydroxy-1,2,4-triazol were suspended in 200 millilitres of acetonitrile and 32.2 grams (0.2 mol) of O,O-dimethyl-thionophosphoric acid chloride were added thereto. After the suspension had been stirred for 12 hours at 50–60°C, the sodium chloride was filtered off and the solvent was evaporated from the filtrate. Thus, 55 grams of O,O-dimethyl-(1-phenyl-1,2,4-triazol-3-yl)-thionophosphate were obtained.

$C_{10}H_{12}N_3O_3P$ S calculated: N 14.75%; P 10.85%
molecular weight: 285 found: N 14.2%; P 10.8%

EXAMPLE 3

400 Millilitres of tetrahydrofuran and 69 grams (0.4 mol) of O,O-diethyl-phosphoric acid chloride were added to 64.4 grams (0.4 mol) of 1-phenyl-3-hydroxy-1,2,4-triazol. 44 Grams (0.44 mol) of triethylamine were added dropwise to the mixture. For completing the exothermic reaction, stirring was continued for 3 hours at 50°C. Then the triethylamine-hydrochloride was filtered off. The filtrate was evaporated, the residue was dissolved in benzene and washed with water. After evaporating the benzene, there were obtained 117 grams of O,O-diethyl-(1-phenyl-1,2,4-triazol-3-yl)phosphate as a light-brown oil.

$C_{12}H_{18}N_3O_4P$ calculated: N 14.1%; P 10.4%
molecular weight: 297 found: N 13.9%; P 10.0%

EXAMPLE 4

A mixture of 25 Grams (0.127 mol) of 1-(3-chlorophenyl)-3-hydroxy-1,2,4-triazol, 24 grams (0.127 mol) of O,O-diethyl-thionophosphoric acid chloride, 15 grams (0.15 mol) of triethylamine and 250 millilitres of benzene were stirred for 10 hours at 60°C. After filtration, the residue was washed with water and the benzene was evaporated. There were obtained 39 grams of O,O-diethyl-[1-(3-chlorophenyl)-1,2,4-triazol-3-yl]-thionophosphate.

$C_{12}H_{15}ClN_3O_3P$ S calculated: N 12.1%; P 8.9%
molecular weight: 347.5 found: N 12.1%; P 8.7%

EXAMPLE 5

A suspension of 43.4 Grams (0.2 mol) of the sodium salt of 1-(4-chlorophenyl)-3-hydroxy-1,2,4-triazol in 300 millilitres of benzene was refluxed with 38 grams (0.2

mol) of O,O-diethyl-thionophosphoric acid chloride. The sodium chloride was filtered off and the benzene was evaporated. 64 Grams of O,O-diethyl-[1-(4-chlorophenyl)-1,2,4-triazol-3-yl]-thionophosphate were obtained as a yellow oil.

$C_{12}H_{15}ClN_3O_3P S$ calculated: N 12.1%; P 8.9%
molecular weight: 347.5 found: N 12.0%; P 8.9%

EXAMPLES 6 to 9

The following Tables show the actions of the active ingredients according to the invention on a considerable number of pests. The active ingredients of the invention are designated hereinafter as follows:

O,O-diethyl-(1-phenyl-1,2,4-triazol-3-yl)-thionophosphate as AI 1;

O,O-diethyl-(1-phenyl-1,2,4-triazol-3-yl)-phosphate as AI 2;

O,O-diethyl-[1-(3-chlorophenyl)-1,2,4-triazol-3-yl]-thionophosphate as AI 3;

O,O-diethyl-[1-(4-chlorophenyl)-1,2,4-triazol-3-yl]-thionophosphate as AI 4;

The comparative substances are designated hereinafter as follows:

O,O-dimethyl-(5-ethyl-1,2,4-triazol-3-yl)thionophosphate (known from British Patent Specification No. 713,278) as comp. I;

O,O-diethyl-(5-ethyl-1,2,4-triazol-3-yl)-thionophosphate as comp. II;

O,O-diethyl-S[(2,5-dichloro-phenyl)-thiomethyl]-dithiophosphate (known from German Patent No. 957,213) as comp. III;

O,O-dimethyl-S[2-(ethyl-mercapto)-ethyl]thiophosphate (known from German Patent No. 836,349) as comp. IV;

O,O-dimethyl(1-hydroxy-2,2,2-trichloroethyl)-phosphonate (known from Chem. Abstr. 50, 9673 (1956)) as comp. V.

The symbol $\emptyset$ indicated in the Tables means that the respective substance showed no activity at the tested concentration.

EXAMPLE 6

Tables 1, 2a and 2b show examples for the use and the activity of different compositions applied by different methods.

Table 1 shows the effects of the active ingredients of the invention and that of comparative substances I and II on a series of arthropodes. The insects were either dusted directly with the active ingredient or sprayed with a solution thereof, or the substrates on which the insects were found were treated with a solution of the active ingredient; in further tests, both the insects and the forage were sprayed with a solution of the active ingredient and in a final test only the forage was treated.

Table 2a shows the effects on different pests with different concentrations of the active ingredients and of the comparative substances.

Table 2b shows the activity against a stock of spinning mites (*metatetranychus ulmi* Dardar) which is resistant to known phosphoric acid esters.

According to the above Tables, the active ingredients of the invention are superior to the comparative substances.

EXAMPLE 7

The data given in Table 3 were determined by applying the active ingredients per os using a micro-applicator manufactured by Messrs. Makers Burkhard MFG. Co. Ltd., Rickmansworth, England. The amounts of the active ingredients and comparative substances were administered to the insects in a solution with acetone. The active ingredients of the invention are superior to the comparative substances.

EXAMPLE 8

In order to examine the prolonged activity of the active ingredients of the invention in comparison with known substances, common house-flies, some of them normal, some resistant to known phosphoric acid esters, were treated at 20—22°C on dead materials, for example glass, wood, cotton fabric, polyvinyl chloride sheets, with active ingredients of the invention and with the comparative substance V. For this purpose, 1 millilitre each of a solution having the given concentration (0.1% by weight) was spread onto 65 cm² of surface of the dead material. Table 4a shows that a layer of active ingredients of the invention on dead material preserved its activity both against the normal house-flies (*musca domestica*) and the house-flies that were resistant to phosphoric acid esters, over a prolonged period of time. The effective time (TL 100), i.e. the time required for completely (100%) killing the house-flies, was increased only slightly. In contrast thereto, the effective time was essentially prolonged with the known comparative substance V. In this latter case, the activity was, moreover, already neutralized after 40 days whereas in the active ingredients of the invention it was still per-

fectly the same as at the beginning. The known comparative substances I and II were not considered in this test since, according to Table I, they have an only weak activity against house-flies.

EXAMPLE 9

5 As a model for flies, for example, *Glossina*, living in the bushes, a test was carried out with house-flies on citrus plants as a sclerophyllous plant. *Table 4b* shows that the prolonged activity of the active ingredients of the invention against normally sensitive house-flies on leaves of citrus trees was substantially superior to the activity of the comparative substance V; the time required for a 100%-killing of the flies (TL 100) was only slightly increased with the active ingredients of the invention. The activity of the comparative substance V was neutralized after 51 days whereas the activity of the active ingredients of the invention was still perfectly the same as at the beginning.

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TABLE 1

Treatment of insects and substrates or forage

The numbers show the percentage of active ingredients at which 100% of the arthropodes cited were killed.

Spray Tests													
	Dusting powder tests 1)			Musca domestica 3)		Treatment of substrate 2)				Treatment of Insects and forage			Treatment of forage
				Substrate 2)	Insects and Substrate	Cimex lect.	Ornithodor. moubata	Derma-nyssus gall.	Epi-lachna variv.	Pachytilus migrat.	Prode-nia litura		
	Peri-planeta americ.	Blatta orient.	Blat-tella germ.										
												AI 1	0.5
AI 2	>0.05	>0.05	0.012	0.0025	0.008	0.006	0.0025	0.00015	0.01	0.01	0.05	0.05	0.1
AI 3	0.1	0.05	0.025	0.0025	0.05	0.006	0.025	0.0005	0.005	0.02	0.01	0.01	0.1
AI 4	0.05	0.025	0.012	0.0025	0.05	0.012	<0.05	0.00025	0.005	0.05	0.01	>0.05	
Comp. II				0.1	1.0	0.1	0.1	0.001					
Comp. I				0.1	1.0	0.1	0.1	0.001					

1) gram of active ingredient per square meter.

2) test on glass substrate (Petri dishes) 1 cc of solution having the active ingredient content given was spread on 65 cm² of substrate.

3) 2 cc of solution having the active ingredient content given were sprayed per cubic meter.

TABLE 2a

The active ingredients were sprayed on:

	Doralis fabae, Myzodes Persicae on Vicia Faba or Cinnearia		Pseudococcus citri on citrus trees		Oncopeltus fasciatus, then put on untreated plants		Doralis fabae on underside of leaf while only upperside of leaf treated: penetration activity	
	% concentration in the spraying mixture	% Killing	% concentration in the spraying mixture	% Killing	% concentration in the spraying mixture	% Killing	% concentration in the spraying mixture	% Killing
AI 1	0.003	100	0.025	100	0.0125	100	0.025	100
AI 2	0.006	100	0.05	95	0.0125	100		
AI 3	0.006	100	0.1	95	0.0125	100	0.05	100
AI 4	0.0125	100	0.05	95	0.0125	100		
Comp. II	0.05	50	0.1	40	0.1	φ	0.1	φ
Comp. I	0.05	φ	0.1	φ	0.1	φ	0.1	φ

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TABLE 2b
 Spraying of *Metatetranychus ulmi* Dardar (resistant to known phosphoric acid esters) on apple trees planted in pots

	% concentration in spraying mixture	degree of activity in % (Abbott)	ovicidal activity estimated in %
AI 1	0.05	100	100
	0.025	100	85—90
	0.0125	96	70
	0.006	88	30
Comp. I	0.1	φ	φ
Comp. II	0.1	φ	φ
Comp. III	0.06	40	φ
	0.04	φ	φ
	0.02	φ	φ
Comp. IV	0.05	φ	φ

TABLE 3

Test by oral administration. Concentration of active-ingredient in milligram per kilogram of animal species/mortality in %.

	Musca domestica	Onithodoros moubata
AI 1	6.0/100	60/100
AI 2	6.0/100	60/100
AI 4	66/100	100/40
Comp. II	50/10	200/0
Comp. I	50/10	200/40

TABLE 4a

Tests as to prolonged activity against normal house-flies and house-flies resistant to known phosphoric acid esters, on materials such as glass, wood, cotton fabrics, polyvinyl chloride sheets, at 20–22 °C.
1 milliliter of the solution having the given concentration, was spread on 65 cm²

	Stock of flies	Concentration of active-ingredient in spraying mixture	(TL 100) in minutes									
			after 0	1	5	12	21	28	40	62	94 days	
AI 1	normal	0.1%	30'	45'	45'	60'	60'	60'	60'	60'	90'	
	resistant	0.1%	45'	90'	90'	70'	60'	60'	60'	60'	120'	
AI 2	normal	0.1%	30'	45'	45'	90'	90'	80'	90'	80'	90'	
	resistant	0.1%	30'	60'	80'	90'	90'	90'	90'	90'	120'	
Comp. V	normal	0.1%	60'	120'	120'	150'	150'	180'	180'	—	—	
	resistant	0.1%	60'	120'	300'	180'	180'	180'	180'	—	—	

TABLE 4b

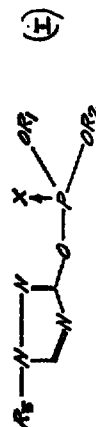
Tests as to the prolonged activity against house-flies on citrus plants as model for flies, such as Glossina, living in the bushes

The plants were sprayed with the mixture until this mixture began to drop off from the leaves

	Active-ingredient-concentration in spraying mixture	(TL 100)* in minutes				
		after 0	4	11	24	27
AI 1	0.1%	45'	60'	60'	60'	180'
AI 3	0.1%	45'	60'	60'	60'	150'
Comp. V	0.1%	60'	90'	180'	240'	400'
						—

WHAT WE CLAIM IS:—

1. Phosphoric and thionophosphoric acid esters of the general formula I



in which R₁ and R₂ each represents an alkyl radical having 1 to 4 carbon atoms, R₃ represents the phenyl radical or phenyl radicals substituted by chlorine atoms and X represents oxygen or sulphur.

2. Phosphoric and thionophosphoric acid esters of the general formula I as claimed in claim 1, wherein R₁ and R₂ each represents an ethyl radical.

3. O,O-diethyl-(1-phenyl-1,2,4-triazol-3-yl)-thionophosphate.

4. O,O-dimethyl-(1-phenyl-1,2,4-triazol-3-yl)-thionophosphate.

5. O,O-diethyl-(1-phenyl-1,2,4-triazol-3-yl)-phosphate.

6. O,O-diethyl-[1-(3-chlorophenyl)-1,2,4-triazol-3-yl]-thionophosphate.

7. O,O-diethyl-[1-(4-chlorophenyl)-1,2,4-triazol-3-yl]-thionophosphate.

8. A pesticidal composition, which comprises, as the active ingredient, a phosphoric or thionophosphoric acid ester of the general formula I

TABLE 4b

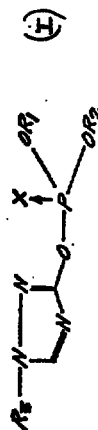
Tests as to the prolonged activity against house-flies on citrus plants as model for flies, such as Glossina, living in the bushes

The plants were sprayed with the mixture until this mixture began to drop off from the leaves

	Active-ingredient-concentration in spraying mixture	(TL 100) in minutes					
		after 0	4	11	24	27	51 days
AI 1	0.1%	45'	60'	60'	60'	180'	180'
AI 3	0.1%	45'	60'	60'	60'	150'	150'
Comp. V	0.1%	60'	90'	180'	240'	400'	—

WHAT WE CLAIM IS:—

1. Phosphoric and thionophosphoric acid esters of the general formula I



5 in which R₁ and R₂ each represents an alkyl radical having 1 to 4 carbon atoms, R₃ represents the phenyl radical or phenyl radicals substituted by chlorine atoms and X represents oxygen or sulphur.

2. Phosphoric and thionophosphoric acid esters of the general formula I as claimed in claim 1, wherein R₁ and R₂ each represents an ethyl radical.

3. O,O-diethyl-(1-phenyl-1,2,4-triazol-3-yl)-thionophosphate.

4. O,O-dimethyl-(1-phenyl-1,2,4-triazol-3-yl)-thionophosphate.

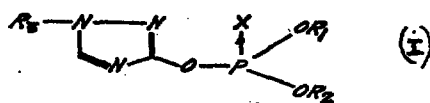
5. O,O-diethyl-(1-phenyl-1,2,4-triazol-3-yl)-phosphate.

6. O,O-diethyl-[1-(3-chlorophenyl)-1,2,4-triazol-3-yl]-thionophosphate.

7. O,O-diethyl-[1-(4-chlorophenyl)-1,2,4-triazol-3-yl]-thionophosphate.

8. A pesticidal composition, which comprises, as the active ingredient, a phosphoric or thionophosphoric acid ester of the general formula I





in which R_1 and R_2 each represents an alkyl radical having 1 to 4 carbon atoms, R_3 represents the phenyl radical or phenyl radicals substituted by chlorine atoms and X represents oxygen or sulphur, together with a carrier material.

9. A pesticidal composition as claimed in claim 8, wherein R_1 and R_2 of the formula I each represents an ethyl radical.

10. A pesticidal composition, wherein the active ingredient is O,O-diethyl-(1-phenyl-1,2,4-triazol-3-yl)-thionophosphate.

11. A pesticidal composition, wherein the active ingredient is O,O-dimethyl-(1-phenyl-1,2,4-triazol-3-yl)-thionophosphate.

12. A pesticidal composition, wherein the active ingredient is O,O-diethyl-(1-phenyl-1,2,4-triazol-3-yl)-phosphate.

13. A pesticidal composition, wherein the active ingredient is O,O-diethyl-[1-(3-chlorophenyl)-1,2,4-triazol-3-yl]-thionophosphate.

14. A pesticidal composition, wherein the active ingredient is O,O-diethyl-[1-(4-chlorophenyl)-1,2,4-triazol-3-yl]-thionophosphate.

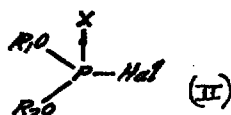
15. A pesticidal composition in the form of a concentrate, which comprises, as active ingredient, from 10 to 70% by weight of a phosphoric or thionophosphoric acid ester of the general formula I, as given in claim 8, and from 5 to 20% by weight of a wetting agent, in an organic solvent.

16. A pesticidal composition as claimed in claim 15, which comprises as active ingredient, 10 to 70% by weight of O,O-diethyl-(1-phenyl-1,2,4-triazol-3-yl)-thionophosphate.

17. A pesticidal composition as claimed in claim 15, which comprises, as active ingredient, from 70 to 90% by weight of O,O-diethyl-(1-phenyl-1,2,4-triazol-3-yl)-thionophosphate and from 30 to 10% by weight of aromatic and/or aliphatic mineral oils having a boiling point of more than 120°C.

18. A pesticidal composition according to claim 8, and substantially as described in any one of Examples 6 to 9 herein.

19. A process for the manufacture of phosphoric and thionophosphoric acid esters of the general formula I, as claimed in claim 1, which comprises reacting phosphoric or thionophosphoric acid halides of the general formula II



in which R_1 , R_2 and X have the meanings given in claim 1 and Hal represents a halogen atom, with 3-hydroxy-1,2,4-triazols substituted by the radical R_3 according to the above formula (I), or with the metal salts thereof, the reaction being carried out in the presence of an acid-binding agent when the free 3-hydroxy-1,2,4-triazols are used.

20. A process as claimed in claim 19, wherein R_1 and R_2 each represents an ethyl radical.

21. A process as claimed in claim 19 or 20, wherein as phosphoric or thionophosphoric acid halides chlorine compounds are used.

22. A process as claimed in any one of claims 19 to 21, wherein the phosphoric or thionophosphoric acid halides are reacted with 3-hydroxy-1,2,4-triazols in the presence of alkali metal carbonates, alkaline earth metal carbonates or tertiary amines.

23. A process as claimed in any one of claims 19 to 21, wherein phosphoric or thionophosphoric acid halides are reacted with sodium- or potassium salts of 3-hydroxy-1,2,4-triazols.

24. A process as claimed in any one of claims 19 to 23, wherein the reaction is carried out at a temperature within the range of from 50 to 90°C.

25. A process as claimed in any one of claims 19 to 24, wherein copper powder is added in an amount of from 1 to 20 mol %.

26. A process as claimed in claim 19, and substantially as described in Examples 1 to 5 herein.



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As Imray