

1.149.563



# PATENT SPECIFICATION

NO. DRAWINGS

1.149.563

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Int. Cl.:—C 07 f 9/16

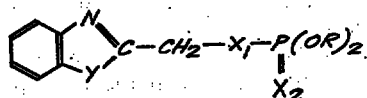
## COMPLETE SPECIFICATION

### Dithiophosphoric Acid Esters, their preparation and use as Pesticides

We, FARBWERKE HOECHST A.G., vormalis Meister Lucius & Brüning, a Company recognised by 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:—

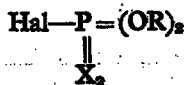
The present invention relates to dithio phosphoric acid esters, to their manufacture and their use as agents for combating noxious organisms.

Specification No. 819,850 describes and claims a phosphoric ester of the general formula

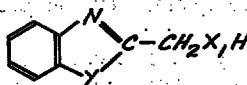


wherein Y, X<sub>1</sub> and X<sub>2</sub> are each selected from oxygen and sulphur atoms, at least one of X<sub>1</sub> and X<sub>2</sub> being a sulphur atom, and R represents an alkyl group containing from 1 to 4 carbon atoms and wherein the fused benzene nucleus may contain one or more chlorine or bromine atoms.

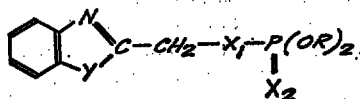
The said Specification also describes and claims a process which comprises reacting a phosphoric acid halide of the general formula



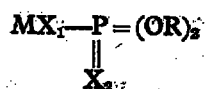
(wherein Hal represents a halogen atom) with a benzoxazole or benzthiazole of the general formula



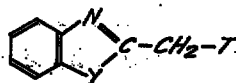
(wherein the fused benzene ring may contain one or more substituents in the form of halogen atoms, alkyl or alkoxy groups containing 1 to 4 carbon atoms or nitro groups, and R, X<sub>1</sub>, X<sub>2</sub>, and Y have the meanings set forth above) whereby to produce a phosphoric ester of the general formula



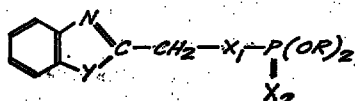
and a process which comprises reacting a phosphorus derivative of the general formula



with a benzoxazole or benzthiazole of the general formula

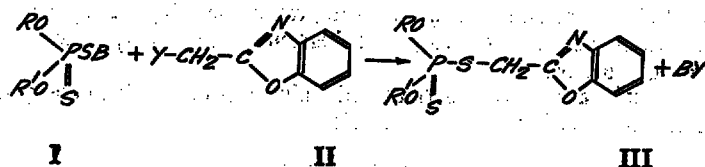


whereby to produce a phosphoric ester of the general formula



(wherein the fused benzene ring may contain one or more substituents in the form of halogen atoms, alkyl or alkoxy groups containing 1 to 4 carbon atoms, or nitro groups, and R, X<sub>1</sub>, X<sub>2</sub> and Y have the meanings set forth above; T represents a reactive ester residue for example a halogen atom or a sulphuric or sulphonic ester residue, and M represents an alkali metal atom).

The present invention provides processes for the manufacture of the novel phosphoric acid esters 2-O,O-diethyldithiophosphorylmethyl-5-chlorobenzoxazole, 2-O,O-diethyldithiophosphorylmethyl-6-chlorobenzoxazole and 2-O,O-diethyldithiophosphorylmethyl-5,7-dichlorobenzoxazole by reacting salts of O,O-diethyl-(di)-thiophosphoric acid of the formula I with the corresponding chlorobenzoxazoles carrying the chlorine substituents in the benzene nucleus and having the formula II according to the following scheme:



in which B represents an alkali metal, alkaline earth metal or ammonium cation or a cation of an organic base, R and R' each stands for an ethyl radical, Y stands for a halogen atom or a reactive acid radical, for example a sulphonic acid radical, and in which the benzene nucleus of the benzoxazole is substituted in the 5- or 6-position or in the 5,7-position by chlorine atoms, preferably in an organic solvent that is inert to the reactants and at a temperature in the range of from 20 to 100°C.

Not one of these three compounds or the preparation thereof is disclosed in Specification No. 819,850.

It is a further object of the present invention to use the compounds as pesticides. (Some of which are described and claimed in co-pending application No. 38857/68, Serial No. 1,149,564).

The 2-halogen-methyl-benzoxazoles of formula II mentioned above and sulphonic acid esters of corresponding 2-hydroxymethyl-benzoxazoles are new.

The 2-chloromethyl-benzoxazoles of general formula II used as starting products may be prepared for example, as follows:

66 grams of 2-chloroacetamino-4-chlorophenol are heated for 30 minutes with 0.5 gram of zinc chloride in 300 millilitres of *o*-dichlorobenzene under such conditions that *o*-dichlorobenzene distills off slowly and until water no longer passes over with the *o*-dichlorobenzene. The reaction mixture is cooled to room temperature, the solution is shaken with water and separated. The *o*-dichlorobenzene is separated from the solution by distillation under reduced pressure. The residue which solidifies at about 47°C. is recrystallized from methanol. 56 grams of 2-chloromethyl-5-chlorobenzoxazole having a melting point of 54 to 55°C. are obtained.

The other 2-chloromethylbenzoxazoles indicated in the Examples can be prepared in analogous manner using the corresponding chlorophenol. If desired, substituents may be subsequently introduced.

The active compounds of formula III may be mixed as is usual for plant protecting agents, with inert substances and used as dusting powders, wettable powders, emulsions e.g. as concentrates or in the form of solutions or granules. They may be used in the form of preparations which contain the active ingredient together with a solid or liquid carrier material and a solvent, an adhesive, wetting, dispersing or grinding auxiliary that enable the noxious organisms to be controlled without greatly injuring the host animals, for example in the control of ectoparasites, or to the host plants, for example in the control of phytopathogenic fungi.

In comparison with the known 2-O,O-diethyl-dithiophosphoryl-methylbenzoxazole unsubstituted in the benzene nucleus, the novel compounds are advantageous in having a higher efficacy to pests as well as a lower toxicity for warm blooded animals as shown by the LD<sub>50</sub> values for rats. These properties enable them to be used for controlling domestic and storage pests as well as other troublesome organisms and ectoparasites.

Surprisingly, the novel compounds have a good fungicidal effect in addition to insecticidal and acaricidal effect, especially with mildew. In Specification No. 819,850 there is no indication that the compounds disclosed therein act otherwise than as pesticides for combatting insects and spider mites on plants whereas the compounds of the present invention are especially intended for combatting ectoparasites on domestic animals.

The following Table illustrates the lower toxicity to warm blooded animals of the 6-chloro and the 5,7-dichloro compounds in comparison with the first mentioned known compound.

| Effective Ingredient                                                                    | LD <sub>50</sub> (rat) |
|-----------------------------------------------------------------------------------------|------------------------|
| 2-O,O-diethyldithiophosphorylmethylbenzoxazole<br>(known compound)                      | 30 mg/kg rat           |
| 2-O,O-diethyldithiophosphorylmethyl-5,7-dichlorobenzoxazole<br>(according to invention) | 105 mg/kg rat          |
| 2-O,O-diethyldithiophosphorylmethyl-6-chlorobenzoxazole<br>(according to invention)     | 110 mg/kg rat          |

The following Examples illustrate the invention.

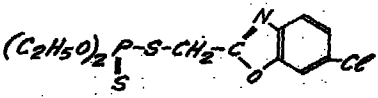
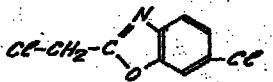
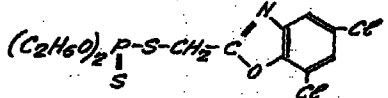
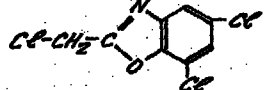
#### EXAMPLE 1

45 Grams of the potassium salt of O,O-diethyldithiophosphoric acid and 41 grams of 2-chloromethyl-5-chloro-benzoxazole (melting point 54—55°C.) were refluxed for 15 minutes in 150 millilitres of ethanol. The reaction mixture was cooled to room temperature and the precipitated potassium chloride was filtered off. The ethanol was removed from the filtrate by distillation. 64 grams of 2-O,O-diethyldithiophosphorylmethyl-5-chlorobenzoxazole remained behind as a brown oil.

| Analysis: | found:        | calculated: |
|-----------|---------------|-------------|
|           | 4.1/4.2% of N | 4.0% of N   |
|           | 8.7/8.8% of P | 8.8% of P   |

#### EXAMPLES 2 and 3

The following phosphoric acid esters were prepared in organic solvents in analogous manner from salts of O,O-diethyldithiophosphoric acid and the corresponding 2-chloromethylchlorobenzoxazoles.

| No. | Formula of product obtained                                                                                                    | Physical properties | Analysis                    |                    | Physical data of 2-chloromethylbenzoxazoles (starting material)                                                                            |
|-----|--------------------------------------------------------------------------------------------------------------------------------|---------------------|-----------------------------|--------------------|--------------------------------------------------------------------------------------------------------------------------------------------|
|     |                                                                                                                                |                     | found                       | calculated         |                                                                                                                                            |
| 2   |  <chem>CCOP(=O)(CC)SCc1cc(Cl)nc1O</chem>      | brown oil           | 4.2/4.0% N<br>8.7/8.8% P    | 4.0% N<br>8.8% P   |  <chem>ClCSc1cc(Cl)nc1O</chem><br>m.p. 58 — 59° C.      |
| 3   |  <chem>CCOP(=O)(CC)SCc1cc(Cl)c(Cl)nc1O</chem> | m.p. 22—24° C.      | 7.8/7.9% P<br>18.4/18.6% Cl | 8.2% P<br>18.9% Cl |  <chem>ClCSc1cc(Cl)c(Cl)nc1O</chem><br>m.p. 60 — 61° C. |

#### EXAMPLE 4

Fattening pigs infested with lice (*Hematophinus suis*) were each sprayed with 0.8 to 1 litre of an aqueous emulsion, containing 0.05 to 0.75% of active ingredient, of the following formulation

- 10% of active ingredient
- 78% of ethanol as solvent
- 10% of an alkyl phenol polyglycol ether as emulsifier
- 2% of epichlorohydrin as stabilizer.

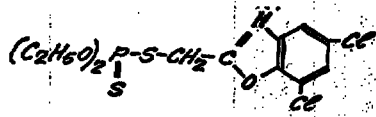
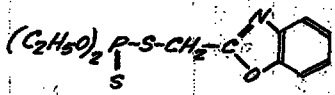
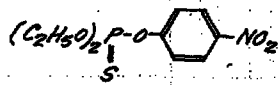
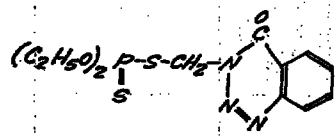
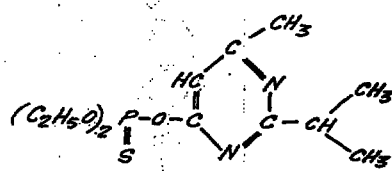
The following compound was used as active ingredient: 2-O,O-diethyldithiophosphorylmethyl-5,7-dichlorobenzoxazole. All lice were killed.

#### EXAMPLE 5

A plate with cockroaches of the types *Phyllodromia germanica* and *Periplaneta americana* was treated with 2—3 grams of a dusting powder containing as active ingredient 2% of 2-O,O-diethyldithiophosphorylmethyl-6-chlorobenzoxazole and talcum and bleaching earth as diluents. The cockroaches died within 2 hours.

## EXAMPLE 6

The following comparative Table illustrates some of the advantages of the 5,7-dichloro compound in a formation analogous to that of the preceding example over known compounds as regards their effect on larvae of Mexican bean beetles (*Epilachna varivertus*):

| Active Ingredient                                                                                             | Concentration    | Destruction |
|---------------------------------------------------------------------------------------------------------------|------------------|-------------|
| <br>(according to invention) | 0.001%<br>0.002% | 90%<br>100% |
| <br>(known)                  | 0.002%           | 40%         |
| <br>(commercial)             | 0.002%           | 60%         |
| <br>(commercial)           | 0.002%           | 70%         |
| <br>(commercial)           | 0.002%           | 20%         |

## EXAMPLE 7

Stored grain infested with grain weevils was mixed in a ratio of 1000:1 by weight with a dusting powder of the following composition:

1% of 2-O,O-diethyldithiophosphorylmethyl-6-chlorobenzoxazole  
 3% of bleaching earth  
 96% of talcum  
 All of the grain weevils were killed.

With the same concentration of O,O-diethyldithiophosphorylmethylbenzoxazole only 40% of the parasites were destroyed.

# EXAMPLES 8 and 9

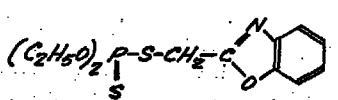
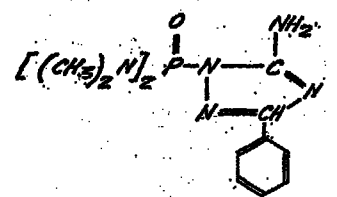
In order to establish the fungicidal effect of the compounds according to the invention cultured plants were treated five days after having been infested with fungi, with an aqueous suspension prepared from a wettable powder of the following composition:

|    |                                                       |    |
|----|-------------------------------------------------------|----|
| 5  | 10% of effective ingredient (cf. the following Table) | 5  |
|    | 20% of amorphous preparation of silicic acid          |    |
| 10 | 56.5% of sodium sulphate                              | 10 |
|    | 10% of calcium lignin sulphonate                      |    |
|    | 2% of alkylphenylpolyglycol ether                     |    |
|    | 1.5% of stearyl alcohol.                              |    |

The following Table shows the superiority of the compounds according to the invention over the known 2-O,O-diethyldithiophosphorylmethylbenzoxazole and the commercial 5-amino-1-[bis(dimethyl-amidophosphoryl-3-phenyl-1,2,4-triazole)].

|                                                                                                                                       | Concentration of spray liquor (with 10% active ingredient) | Diminution of infestation about 2 weeks after treatment compared with untreated specimen |                        |                                   | Toxicity to warm-blooded animals LD <sub>50</sub> in mg/kg of rat |
|---------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------|------------------------------------------------------------------------------------------|------------------------|-----------------------------------|-------------------------------------------------------------------|
|                                                                                                                                       |                                                            | <i>Erysiphe graminis</i>                                                                 | <i>Phaseolis spec.</i> | <i>Erysiphe dichloriaceaureum</i> |                                                                   |
| $(C_2H_5O)_2P(S)-S-CH_2-C \begin{array}{c} \diagup N \\ \diagdown O \end{array} \text{C}_6H_4-Cl$ <p>(according to the invention)</p> | 0.03%<br>0.06%                                             | 95%<br>100%                                                                              |                        |                                   | 110                                                               |
| $(C_2H_5O)_2P(S)-S-CH_2-C \begin{array}{c} \diagup N \\ \diagdown O \end{array} \text{C}_6H_3Cl_2$ <p>(according to invention)</p>    | 0.012%                                                     |                                                                                          | 100%                   |                                   | 105                                                               |



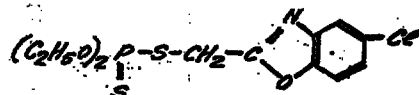
|                                                                                                       | Concentration of<br>spray liquor<br>(with 10% active<br>ingredient) | Diminution of infestation about 2 weeks after<br>treatment compared with untreated specimen |                            |                                       | Toxicity to<br>warm-blooded<br>animals<br>LD <sub>50</sub> in<br>mg/kg of rat |
|-------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------|---------------------------------------------------------------------------------------------|----------------------------|---------------------------------------|-------------------------------------------------------------------------------|
|                                                                                                       |                                                                     | <i>Erysiphe<br/>graminus</i>                                                                | <i>Phaseolis<br/>spec.</i> | <i>Erysiphe di-<br/>chloriacearum</i> |                                                                               |
| <br>(known compound) | 0.012%<br>0.025%<br>0.03%<br>0.05%<br>0.06%                         | <br><br><br>60%<br><br>95%                                                                  | <br><br>50%<br>90%         | <br><br><br><br>90%                   | <br><br><br><br>30                                                            |
| <br>(commercial)    | <br>0.025%<br>0.05%                                                 |                                                                                             | <br>80%                    | <br><br><br>40%                       | <br><br><br>10 — 20                                                           |

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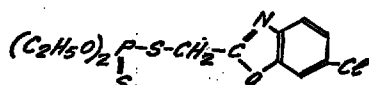


## WHAT WE CLAIM IS:—

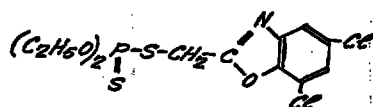
1. The compound of the formula



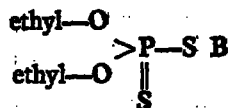
2. The compound of the formula



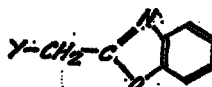
3. The compound of the formula



4. A process for the manufacture of 2-O,O-diethyldithiophosphorylmethyl-5-chlorobenzoxazole, 2-O,O-diethyldithiophosphorylmethyl-6-chlorobenzoxazole and 2-O,O-diethyldithiophosphorylmethyl-5,7-dichlorobenzoxazole wherein a salt of O,O-diethyl-dithiophosphoric acid of the formula



is reacted with the corresponding chlorobenzoxazole carrying the chlorine substituents in the benzene nucleus and having the general formula



in which formulae B represents an alkali metal, alkaline earth metal or ammonium cation or a cation of an organic base, Y stands for a halogen atom or a reactive acid radical, and in which the benzene nucleus of the benzoxazole compound is substituted in the 5- or 6-position or in the 5,7-position by chlorine atoms.

5. A process as claimed in claim 4, wherein the reaction is carried out in an organic solvent that is inert to the reactants.

6. A process as claimed in claim 4 or 5, wherein the reaction is carried out at a temperature within the range of from 20 to 100°C.

7. A process according to claim 4, and conducted substantially as described in any one of Examples 1 to 3 herein.

8. A pesticidal preparation comprising as active ingredient a compound as claimed in claim 1, 2 or 3, together with a solid or liquid carrier material and a solvent, an adhesive, wetting, dispersing or grinding auxiliary.

9. A preparation as claimed in claim 8, in the form of a wettable powder.

10. A preparation as claimed in claim 8, in the form of a solution or emulsion concentrate.

11. A preparation as claimed in claim 8, in the form of granules.

12. A preparation according to claim 8, and substantially as described in any one of Examples 4 to 9 herein.

13. A pesticidal preparation comprising as active ingredient 2-O,O-diethyldithiophosphorylmethyl-5,7-dichlorobenzoxazole together with a carrier material.

14. A pesticidal preparation comprising as active ingredient 2-O,O-diethyldithiophosphorylmethyl-5,7-dichlorobenzoxazole together with a solid or liquid carrier material and a solvent, an adhesive, wetting, dispersing or grinding auxiliary.

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