

1083.377



PATENT SPECIFICATION

NO DRAWINGS

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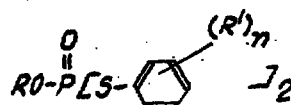
COMPLETE SPECIFICATION

Esters of Thiophosphorus Acids

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

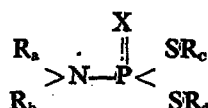
The present invention relates to dithiolphosphoric acid triesters having fungicidal properties, and to their preparation and use.

These triesters have the general formula:



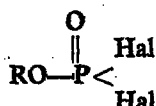
wherein R stands for an alkyl, alkenyl, alkynyl or alkyl haloalkyl halide radical, and R' stands for a halogen atom, a nitro radical or a lower alkyl or alkoxy radical containing 1—4 carbon atoms and n is 0, 1 or 2.

French Patent Specification No. 1,378,035 discloses (thiono) dithiolphosphoric acid diester monoamides of the general formula:

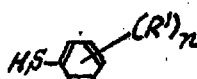


wherein R_a and R_b may signify hydrogen atoms or alkyl or aryl radicals and R_c or R_d stand for (*inter alia*) aryl radicals, while X is an oxygen or sulphur atom. According to the information given in the aforesaid French Patent Specification, these compounds are suitable for the control of plant pests and plant diseases.

We have found that S,S-diphenyldithiolphosphoric acid triesters of the general formula (I) are readily obtained in good yields and with considerable purity when phosphoric acid monoester dihalides of the general formula:



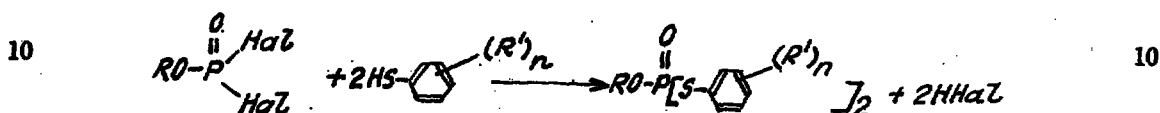
(wherein R has the same meaning as in formula (I) and Hal is a halogen atom) are reacted with thiophenols of the general formula:



(wherein R' and n have the same meaning as in formula (I)) in the form of their salts or in the presence of acid-binding agents.

We have also found that the S,S-diphenyldithiophosphoric acid triesters of the general formula (I) are distinguished by outstanding fungitoxic properties and, surprisingly, they are in this respect distinctly superior to the compounds of analogous constitution and the same direction of activity which are known from the aforesaid French Patent Specification.

The course of the reaction according to the invention is illustrated by the following equation:



(V)

wherein R, R', Hal and n have the same meaning as above.

In the above general formulae, R preferably stands for a straight or branched alkyl radical which has 1 to 6 carbon atoms and may, if desired, bear one or more halogen substituents, (for example, R may stand for a methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, iso-butyl, sec.-butyl, *n*-amyl, 2-chloroethyl or 2,2,2-trichloroethyl radical) or for an alkenyl or alkynyl radical with up to 4 carbon atoms (for example an allyl, crotonyl or propargyl radical); R' preferably stands for chlorine, bromine or fluorine, a nitro, methyl or methoxy radical; Hal preferably stands for a chlorine atom; and n is preferably 0 or 1.

As examples of the phosphoric acid monoester dihalides of general formula (III), there may be mentioned: O-ethyl-, O-*n*-propyl-, O-isopropyl-, O-*n*-butyl-, O-allyl-, O-crotonyl-, O-propargyl-, O-2-chloroethyl- and O-2,2,2-trichloroethyl- phosphoric acid monoester dichlorides. As examples of the thiophenols of general formula (IV), there may be mentioned: thiophenol, 2-, 3- and 4-chloro-, 4-isopropyl-, 4-methoxy- and 4-nitrothiophenol, 2-, 3- and 4-thiocresol, and 2-bromothiocresol.

The phosphoric acid monoester dihalides to be used as starting materials according to the present invention have already been described in the literature. They may be prepared according to known methods from the phosphorus oxyhalides by reaction with the corresponding alcohols, frequently without the concurrent use of acid acceptors. The crude products obtainable in this manner can in most cases be immediately further reacted for the purposes of the present invention without prior purification by distillation.

The process of the present invention is preferably carried out in the presence of solvents or diluents. As such, practically all inert organic solvents are suitable. However, particularly good results have been obtained with aliphatic and aromatic hydrocarbons (optionally chlorinated), for example methylene chloride, di-, tri- and tetrachloroethylene, chloroform, carbon tetrachloride, benzene, chlorobenzene, toluene and xylene; ethers, for example diethyl and di-*n*-butyl ether, dioxan, tetrahydrofuran; aliphatic ketones and nitriles of low molecular weight, for example acetone, methylethyl ketone, methylisopropyl ketone, methylisobutyl ketone, acetonitrile and propionitrile; and low-boiling aliphatic alcohols, for example methanol, ethanol and isopropanol.

As mentioned above, the reaction of the invention may be carried out in the presence of acid-binding agents. The usual acid acceptors such as alkali metal hydroxides, carbonates and alcoholates, and also tertiary organic bases, for example triethylamine, dimethyl aniline and pyridine, may be used as acid-binding agents. Instead of working in the presence of acid-binding agents, the salts, preferably alkali metal or ammonium salts, of the thiophenols concerned may first be prepared and then reacted with the phosphoric acid monoester dihalides.

The process of the invention can be carried out successfully within a wide range of temperatures. It is generally performed between -20°C and the boiling point of the mixture, preferably at from 0° to 100°C.

The reaction is preferably carried out under normal atmospheric pressure, but it is also possible to work at increased or reduced pressure.

When carrying out the process of the invention, two mols of the thiophenol are generally used for each mol of the phosphoric acid monoester dihalide concerned; the thiophenol may, however, also be used in excess.

Moreover, the phosphoric acid monoester dihalide is expediently added dropwise,

at the above mentioned temperatures and with stirring, to the solution or suspension of the thoiphenol (or of the corresponding phenolate). External cooling of the mixture is often necessary, because the reaction generally proceeds with a more or less strong evolution of heat. Finally, it has proved expedient, after uniting the starting components, to stir the reaction mixture for an appreciable period (1 to 5 hours or overnight); optionally with moderate heating, in order to complete the reaction. In this case the process products are obtained in particularly good yields as well as with outstanding purity.

The working up of the reaction mixture may be effected according to methods which are known in principle by pouring the mixture into water, washing and drying the organic phase, distilling off the solvent and (as far as possible) fractional distillation of the residue under reduced pressure.

The dithiolphosphoric acid triesters obtainable by the process are obtained either in the form of crystalline compounds with a sharp melting point which can easily be further purified by recrystallisation from the customary solvents, or in the form of colourless to yellow oils some of which can be distilled under greatly reduced pressure without decomposition. If this is not possible, the compounds obtainable according to the invention may, for the purpose of purification, be "partially distilled," i.e. freed from the last volatile impurities by heating to slightly to moderately elevated temperatures for an appreciable period and under reduced pressure.

By means of the present process, *inter alia* the following compounds can be obtained: O-ethyl, O-*n*-propyl- and O-*n*-butyl-S,S-diphenyl-, O-ethyl-, O-*n*-propyl- and O-*n*-butyl-S,S-di(2- or 4-methylphenyl)-, O-ethyl-, O-isopropyl-S,S-di(4-chlorophenyl)-, O-ethyl-S,S-di(4-methoxyphenyl)-, O-allyl-S,S-diphenyl-, O-ethyl-S,S-di(2,4-dichlorophenyl)-, O-ethyl-S,S-di(4-nitrophenyl)-, O-isopropyl-S,S-diphenyl- and O-isopropyl-S,S-di(2-methylphenyl) dithiolphosphoric acid esters.

As already mentioned, the dithiolphosphoric acid triesters of the invention are strongly fungitoxic to a number of fungoid pathogenic agents. By reason of this fact, as well as in view of their low toxicity towards warm-blooded animals, they are particularly suitable for the control of undesirable plant growth, their good compatibility with higher plants particularly favouring their use against fungus diseases. The compounds of the invention can be used as fungitoxic agents in plant protection against fungi of the most widely varied classes, e.g. *Archimycetes*, *Phycomycetes*, *Ascomycetes*, *Basidiomycetes* and *Fungi imperfecti*.

However, the compounds of the invention have yielded particularly good results in the control of diseases of rice, since they possess an excellent protective and curative action against *Piricularia oryzae* in rice.

When used as fungitoxic agents, the active compounds of the invention can be used either individually or in combination with one another. Moreover, admixture with other plant protection agents, such as fungicides, herbicides, insecticides and bactericides, is possible.

Depending on the purpose for which they are to be used, the active compounds of the invention can be converted into the usual preparations, such as solutions, emulsions, suspensions, powders, pastes and granulates. These may be produced in known manner, for example by dilution of the active compounds with solvents and/or carriers, optionally with the use of emulsifying agents and/or dispersing agents. Organic solvents may optionally be used as auxiliary solvents, for example in cases where water is employed as diluent (cf. Agricultural Chemicals, March 1960, Pages 35—38). As auxiliary substances, the following are preferable: solvents, such as aromatic hydrocarbons (for example xylene, benzene), chlorinated aromatic hydrocarbons (for example chlorobenzenes), paraffins (for example mineral oil fractions), alcohols (for example methanol, butanol), amines and amine derivatives (for example ethanolamine, dimethyl formamide), and water; carriers such as natural stone powders (for example kaolins, clays, talc, chalk) and synthetic stone powders (for example highly dispersed silicic acid, silicates); emulsifying agents, such as non-ionic and anionic emulsifiers (for example polyoxyethylene fatty acid esters, polyoxyethylene fatty alcohol ethers, alkyl sulphonates and aryl sulphonates) and dispersing agents, such as lignin sulphite waste liquors and methyl cellulose.

The active compounds according to the invention may be present in the preparations in admixture with known active compounds.

The preparations generally contain between 0.1 and 95%, preferably between 0.5 and 90%, by weight of active compound. The application of the active compounds or their preparations as fungitoxic agents may be effected in the usual manner, for example by sprinkling, dispersion, spraying or atomisation, the active compound

generally being used in a concentration of from 0.2 to 0.001%, depending on its purpose. This range of concentrations may, however, in special cases be exceeded or gone below.

The invention provides a method of combating fungus infestation wherein there is applied to a fungus habitat an active compound according to the invention, alone or in admixture with a solvent or carrier.

The outstanding fungitoxic action of the dithiolphosphoric acid triesters of the invention, as well as their distinct superiority compared with prior art products of analogous structure, can be seen from the following experimental results:

Example A

Piricularia test:	liquid preparation of active substance
Solvent:	1 part by weight actone
Dispersing agent:	0.05 part by weight sodium oleate
Other additives:	0.2 part by weight gelatin
Water:	98.75 parts by weight H ₂ O

The amount of active compound required for the desired concentration in the spray liquor is mixed with the stated amount of solvent and the concentrate obtained diluted with the stated amount of water containing the other additives and the dispersing agent.

Thirty rice plants, which are about 14 days old, are sprayed with the spray liquor until dripping wet. The plants remain in a greenhouse at a temperature of 22 to 24°C. and at a relative atmospheric humidity of about 70%, until dry. They are then inoculated with an aqueous suspension of 100,000 to 200,000 spores/ml. of *Piricularia oryzae* and placed in a chamber at 24—26°C. and at a relative atmospheric humidity of 100%.

Five days after inoculation, the degree of infestation of all the leaves of the treated plants which were present at the time of inoculation is determined as a percentage of the untreated but also inoculated control plants. 0% means that no infestation occurred and 100% that the infestation is exactly the same as that of the control plants.

Test for Curative Action.

In the test just described using a liquid preparation of the active compound, besides the protective action the curative action of the process products is also determined. The test for curative action varies in certain points from the test procedure described above which only yields an indication of the protective effect in so far as the active compounds are applied not before inoculation, but 16 hours after inoculation. Substances which exhibit an action when the test is carried out in this manner are capable of destroying the fungus after the infection and thereby exercising a curative action.

The active compounds, their concentrations and the results obtained can be seen from the following table:

TABLE
Piricularia Test
Liquid Preparation of the Active Compound

Infestation expressed as percentage of the infestation of the untreated control with an active compound concentration of (%)

Active Compound (Constitution)	0.05	0.025	0.01	0.005	0.001
$\begin{array}{c} \text{O} \\ \parallel \\ n\text{-C}_3\text{H}_7\text{O}-\text{P}(s\text{-C}_6\text{H}_5)_2 \end{array}$	pr. cur.	0 0	0 11	0	75
$\begin{array}{c} \text{O} \\ \parallel \\ n\text{-C}_4\text{H}_9\text{O}-\text{P}(s\text{-C}_6\text{H}_5)_2 \end{array}$	pr. cur.	0 0	5	14	
$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_2\text{H}_5\text{O}-\text{P}(s\text{-C}_6\text{H}_4\text{-CH}_3)_2 \end{array}$	pr.	0	2	83	
$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_2\text{H}_5\text{O}-\text{P}(s\text{-C}_6\text{H}_3(\text{CH}_3))_2 \end{array}$	pr. cur.	0 0	0	75	
$\begin{array}{c} \text{O} \\ \parallel \\ n\text{-C}_3\text{H}_7\text{O}-\text{P}(s\text{-C}_6\text{H}_3(\text{CH}_3))_2 \end{array}$	pr. cur.	0 25	0	15	

pr. = protective action
cur. = curative action

TABLE—Continued
Piricularia Test
(Liquid Preparation of the Active Compound)

Infestation expressed as percentage of the infestation of the untreated control with an active compound concentration of (%)

Active Compound (Constitution)	0.05	0.025	0.01	0.005	0.001
$\text{ISO}-\text{C}_3\text{H}_7\text{O}-\text{P}(=\text{O})(\text{S}-\text{C}_6\text{H}_4-\text{Cl})_2$	pr. 0	0	75		
$\text{C}_2\text{H}_5\text{O}-\text{P}(=\text{O})(\text{S}-\text{C}_6\text{H}_4)_2$	pr. 0	0	0	13	58
	cur. 0	3			
$n\text{-C}_4\text{H}_9\text{O}-\text{P}(=\text{O})(\text{S}-\text{C}_6\text{H}_4-\text{CH}_3)_2$	pr. 0	0	75		
$\text{ISO}-\text{C}_3\text{H}_7\text{O}-\text{P}(=\text{O})(\text{S}-\text{C}_6\text{H}_4)_2$	pr. 0	0	0	0	
	cur. 0	25			
$\text{C}_2\text{H}_5\text{O}-\text{P}(=\text{O})(\text{S}-\text{C}_6\text{H}_4-\text{OCH}_3)_2$	pr. 0	0	28	75	
	cur. 0				

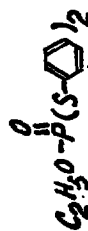
pr. = protective action
cur. = curative action

TABLE—Continued
Piricularia Test
Liquid Preparation of the Active Compound

Active Compound (Constitution)	Infestation expressed as percentage of the infestation of the untreated control with an active compound concentration of (%)				
	0.05	0.025	0.01	0.005	0.001
$(C_2H_5)_2N-P(=O)(S-C_6H_4-CH_3)_2$	pr. cur.	0 96	50		
(known comparative preparation)					

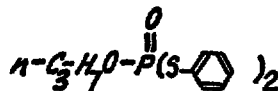
The following Examples further illustrate the present invention:

EXAMPLE 1.



- 5 110 grams (1 mol) of thiophenol are dissolved in 800 cc of benzene. To the solution is added, with stirring, a sodium methylate solution which contains 1 mol of sodium in solution. 82 grams (0.05 mol) of O-ethylphosphoric acid ester dichloride are then added dropwise to the reaction mixture at 5 to 10°C with further stirring. The reaction mixture is kept at the stated temperature for a further three hours, poured into 400 cc of ice water and then washed twice with 300 cc of water in each case. The benzene solution is then dried over anhydrous sodium sulphate. During the ensuing fractional distillation, after evaporation of the solvent, 108 grams (70% of the theoretical amount) of O-ethyl-S,S-diphenyl-dithiol-phosphoric acid ester with a boiling point of 154°C/0.01 mm.Hg. are obtained.
- 10

EXAMPLE 2.



5 a) A solution of 44 grams (0.4 mol) of thiophenol in 100 cc of benzene is
 5 neutralised with a sodium methylate solution containing 0.4 mol of sodium. After
 200 cc of benzene and to this suspension there are added dropwise, at 0 to 5°C,
 35.4 grams (0.2 mol) of O-*n*-propylphosphoric acid ester dichloride. The reaction
 10 mixture is then stirred for a further 3 hours at 50°C, washed with water after cooling
 to room temperature, and dried over anhydrous sodium sulphate. The solvent is
 10 evaporated under reduced pressure and, as residue, 28 grams (43.3% of the theoretical
 amount) of O-*n*-propyl-S,S-diphenyl-dithiolphosphoric acid ester are obtained.

Analysis:

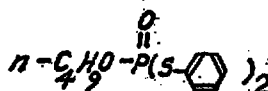
calculated:	P: 9.58%:	S: 19.76%:
found :	P: 9.35%:	S: 19.70%:

15 b) 220 grams (2.0 mol) of thiophenol are converted into the corresponding
 15 sodium thiophenolate in the manner described in Example 2a). The dry salt is
 suspended in 500 cc of acetonitrile, and to this suspension 177 grams (1.0 mol) of
 O-*n*-propylphosphoric acid ester dichloride are added dropwise at 0 to 10°C. The
 20 reaction proceeds with evolution of heat. The reaction mixture is further stirred for
 some time at room temperature and then poured into water. The oil which is separated
 20 is dissolved in benzene and the benzene solution is washed with water and dried over
 anhydrous sodium sulphate. The solvent is then distilled off under reduced pressure.
 The last volatile portions are removed at a bath temperature of 100°C and 1.5 mm.Hg.,
 25 and the O-*n*-propyl-S,S-diphenyl-dithiol-phosphoric acid ester is obtained in the form
 of a yellow oil. The yield is 221 grams (68% of the theoretical amount).

Analysis:

calculated:	P: 9.58%:	S: 19.76%
found :	P: 9.70%:	S: 19.90%

EXAMPLE 3.



30 110 grams (1.0 mol) of thiophenol are converted in the usual manner into the
 sodium salt. The dry thiophenolate is suspended in 500 cc of acetonitrile and the
 suspension is reacted with 95.5 grams of O-*n*-butylphosphoric acid ester dichloride
 35 in the manner described in Example 2b). The reaction mixture is then stirred over-
 night at room temperature, the separated oil is dissolved in benzene after the mixture
 has been poured into water, and the benzene solution is washed with water until there
 is a neutral reaction and then it is dried. After evaporation of the solvent and removal
 of all volatile portions at a bath temperature of 150°C and a pressure of 1 mm.Hg.,
 40 120.5 grams (71.3% of the theoretical amount) of O-*n*-butyl-S,S-diphenyldithiol-
 phosphoric acid ester are obtained as a pale yellow oil with a refractive index n_D^{25}
 of 1.5965.

Analysis:

calculated:	P: 9.18%:	S: 18.94%
found :	P: 9.30%:	S: 19.30%

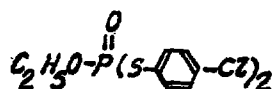
45 The following compounds can be prepared by methods analogous to the method
 described above:

45

Constitution	Yield (% of the theory)	Physical Properties	
		(Refractive Index or Melting Point)	
$\text{C}_2\text{H}_5\text{O}-\overset{\text{O}}{\parallel}\text{P}(\text{S}-\text{C}_6\text{H}_4-\text{CH}_3)_2$	67	n_D^{26}	1,6067
$\text{C}_2\text{H}_5\text{O}-\overset{\text{O}}{\parallel}\text{P}(\text{S}-\text{C}_6\text{H}_3(\text{CH}_3)-)_2$	58	n_D^{26}	1,6078
$n\text{-C}_3\text{H}_7\text{O}-\overset{\text{O}}{\parallel}\text{P}(\text{S}-\text{C}_6\text{H}_3(\text{CH}_3)-)_2$	67	n_D^{26}	1,5993
$n\text{-C}_4\text{H}_9\text{O}-\overset{\text{O}}{\parallel}\text{P}(\text{S}-\text{C}_6\text{H}_3(\text{CH}_3)-)_2$	71	n_D^{26}	1,5860
$\text{C}_2\text{H}_5\text{O}-\overset{\text{O}}{\parallel}\text{P}(\text{S}-\text{C}_6\text{H}_4-\text{OCH}_3)_2$	68.2	n_D^{26}	1,6152
$n\text{-C}_3\text{H}_7\text{O}-\overset{\text{O}}{\parallel}\text{P}(\text{S}-\text{C}_6\text{H}_4-\text{OCH}_3)_2$	73.0	n_D^{26}	1,6088
$\text{iso-C}_3\text{H}_7\text{O}-\overset{\text{O}}{\parallel}\text{P}(\text{S}-\text{C}_6\text{H}_3(\text{CH}_3)-)_2$	79.6	n_D^{26}	1,5946
$\text{iso-C}_3\text{H}_7\text{O}-\overset{\text{O}}{\parallel}\text{P}(\text{S}-\text{C}_6\text{H}_4)_2$	69.2	n_D^{26}	1,6178
$\text{Cl-CH}_2\text{-CH}_2\text{-O}-\overset{\text{O}}{\parallel}\text{P}(\text{S}-\text{C}_6\text{H}_4)_2$	71.9	n_D^{26}	1,6281

Constitution	Yield (% of the theory)	Physical Properties	
		(Refractive Index or Melting Point)	
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{O}-\overset{\text{O}}{\underset{\text{CH}_3}{\text{P}}}(\text{S}-\text{C}_6\text{H}_4)_2$	42.9	n_D^{25}	1,6160
$\text{Cl}_3\text{C}-\text{CH}_2-\text{O}-\overset{\text{O}}{\underset{\text{CH}_3}{\text{P}}}(\text{S}-\text{C}_6\text{H}_4)_2$	56.2	Melting point: 90 to 92°C.	

EXAMPLE 4.



5 145 grams (1 mol) of 4-chlorothiophenol are dissolved in 400 cc of benzene. To
this solution is added, with stirring, a sodium ethylate solution which contains 1 mol
of sodium. Then, with further stirring, 82 grams (0.5 mol) of O-ethylphosphoric acid
ester dichloride are added dropwise to the reaction mixture at 10 to 15°C. The
10 reaction mixture is stirred for a further 2 hours at the temperature stated and then
poured into 300 cc of ice water. The benzene solution is washed once more with
water and dried over anhydrous sodium sulphate. After the solvent has been distilled
off, an oily, crude product is obtained as residue which solidifies very rapidly in
crystalline form. 105 grams (55% of the theoretical amount) of O-ethyl-S,S-bis(4-
chloro-phenyl)-dithiolphosphoric acid ester with a melting point of 71°C are isolated.

EXAMPLE 5.



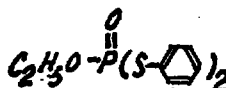
15 To a solution of 145 grams (1 mol) of 4-chlorothiophenol in 600 cc of benzene
is added 1 mol of sodium methylate. 89 grams of O-isopropylphosphoric acid ester
dichloride are then added dropwise at 15 to 20°C, with stirring, after which the
20 reaction mixture is stirred for a further 2 hours at the temperature stated and then
poured into 400 cc of ice water. After the benzene solution has been washed several
times with water it is dried over anhydrous sodium sulphate and, finally, the solvent
is distilled off. 123 grams (63% of the theoretical amount) of O-iso-propyl-S,S-bis-
(4-chlorophenyl) dithiolphosphoric acid ester with a melting point of 52°C are
obtained.

EXAMPLE 6.



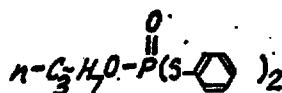
180 grams (1 mol) of 4-nitrothiophenol-sodium are dissolved in 400 cc of acetonitrile. To this solution are added 82 grams (0.5 mol) of O-ethylphosphoric acid ester dichloride at 20°C, with stirring, and the reaction mixture is then stirred for a further 2 hours at room temperature, after which it is worked up in the manner which has already been described several times. 155 grams (77% of the theoretical amount) of O-ethyl-S,S-bis(4-nitrophenyl) dithiol-phosphoric acid ester with a melting point of 106°C are obtained.

EXAMPLE 7.



To a solution of 55 grams (0.5 mol) of thiophenol in 400 cc of ethanol which contains 0.5 mol of sodium are added dropwise 40.75 grams (0.25 mol) of O-ethylphosphoric acid ester dichloride at 0 to 10°C., and the mixture is then stirred overnight at room temperature. The reaction mixture is then poured into water, the separated oil is dissolved in benzene, the benzene solution is washed with water until there is a neutral reaction, and the organic phase is then dried over anhydrous sodium sulphate. After evaporation of the solvent there remain 51.5 grams (60.9% of the theoretical amount) of O-ethyl-S,S-diphenyl-dithiolphosphoric acid ester which is identical to the compound of the same constitution which is obtainable according to Example 1.

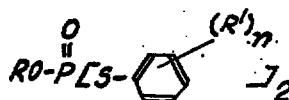
EXAMPLE 8.



55 grams (0.5 mol) of thiophenol are dissolved together with 56 grams (0.55 mol) of anhydrous triethylamine in 400 cc of benzene. 44 grams (0.25 mol) of O-n-propylphosphoric acid ester dichloride are added dropwise to this solution at 0 to 10°C. The ensuing reaction proceeds exothermically. After the mixture has been stirred for a short time at room temperature, the precipitated triethylammonium hydrochloride is filtered off, the filtrate is washed with water, and the organic phase is dried and concentrated by evaporation. There remain as residue 56 grams (65.9% of the theoretical amount) of O-n-propyl-S,S-diphenyldithiolphosphoric acid ester. The compound is identical to that obtainable according to Example 2.

WHAT WE CLAIM IS:—

1. Dithiolphosphoric acid triesters of the general formula



wherein

R is an alkyl, alkenyl, alkynyl or haloalkyl radical, and
R' is a halogen atom, a nitro radical or an alkyl or alkoxy radical containing 1—4 carbon atoms and

n is 0, 1 or 2.

2. Compounds according to Claim 1 wherein R is a straight or branched alkyl radical which has 1 to 6 carbon atoms and may bear one or more halogen substituents.

3. Compounds according to Claim 2 wherein R is a methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, sec.-butyl, n-amyl, 2-chloroethyl or 2,2,2-trichloroethyl radical.

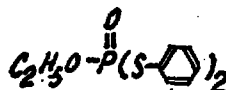
4. Compounds according to Claim 1 wherein R is an alkenyl or alkynyl radical which has up to 4 carbon atoms.

5. Compounds according to Claim 4 wherein R is an allyl, crotonyl or propargyl radical.

6. Compounds according to any of Claims 1 to 5 wherein R' is a chlorine, bromine or fluorine atom, a nitro radical, or a methyl or methoxy radical.

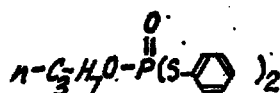
180 grams (1 mol) of 4-nitrothiophenol-sodium are dissolved in 400 cc of acetonitrile. To this solution are added 82 grams (0.5 mol) of O-ethylphosphoric acid ester dichloride at 20°C, with stirring, and the reaction mixture is then stirred for a further 2 hours at room temperature, after which it is worked up in the manner which has already been described several times. 155 grams (77% of the theoretical amount) of O-ethyl-S,S-bis(4-nitrophenyl) dithiol-phosphoric acid ester with a melting point of 106°C are obtained.

EXAMPLE 7.



To a solution of 55 grams (0.5 mol) of thiophenol in 400 cc of ethanol which contains 0.5 mol of sodium are added dropwise 40.75 grams (0.25 mol) of O-ethylphosphoric acid ester dichloride at 0 to 10°C., and the mixture is then stirred overnight at room temperature. The reaction mixture is then poured into water, the separated oil is dissolved in benzene, the benzene solution is washed with water until there is a neutral reaction, and the organic phase is then dried over anhydrous sodium sulphate. After evaporation of the solvent there remain 51.5 grams (60.9% of the theoretical amount) of O-ethyl-S,S-diphenyl-dithiolphosphoric acid ester which is identical to the compound of the same constitution which is obtainable according to Example 1.

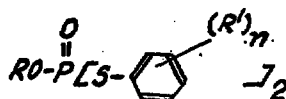
EXAMPLE 8.



55 grams (0.5 mol) of thiophenol are dissolved together with 56 grams (0.55 mol) of anhydrous triethylamine in 400 cc of benzene. 44 grams (0.25 mol) of O-n-propylphosphoric acid ester dichloride are added dropwise to this solution at 0 to 10°C. The ensuing reaction proceeds exothermically. After the mixture has been stirred for a short time at room temperature, the precipitated triethylammonium hydrochloride is filtered off, the filtrate is washed with water, and the organic phase is dried and concentrated by evaporation. There remain as residue 56 grams (65.9% of the theoretical amount) of O-n-propyl-S,S-diphenyldithiolphosphoric acid ester. The compound is identical to that obtainable according to Example 2.

WHAT WE CLAIM IS:—

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wherein

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R' is a halogen atom, a nitro radical or an alkyl or alkoxy radical containing 1—4 carbon atoms and

n is 0, 1 or 2.

2. Compounds according to Claim 1 wherein R is a straight or branched alkyl radical which has 1 to 6 carbon atoms and may bear one or more halogen substituents.

3. Compounds according to Claim 2 wherein R is a methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, sec.-butyl, n-amyl, 2-chloroethyl or 2,2,2-trichloroethyl radical.

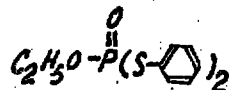
4. Compounds according to Claim 1 wherein R is an alkenyl or alkynyl radical which has up to 4 carbon atoms.

5. Compounds according to Claim 4 wherein R is an allyl, crotonyl or propargyl radical.

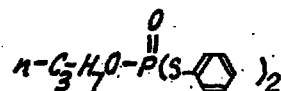
6. Compounds according to any of Claims 1 to 5 wherein R' is a chlorine, bromine or fluorine atom, a nitro radical, or a methyl or methoxy radical.



7. The compound of the formula

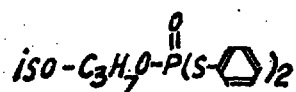


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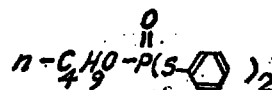


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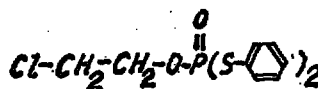
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10. The compound of the formula

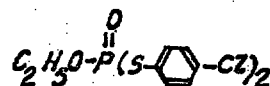


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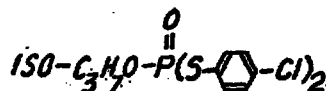


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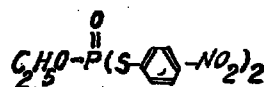


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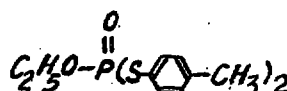


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14. The compound of the formula



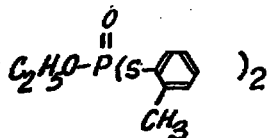
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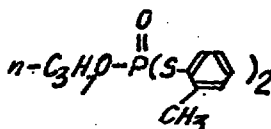
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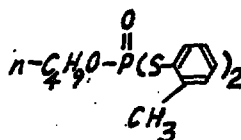
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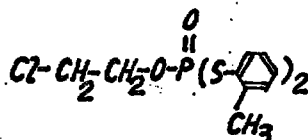
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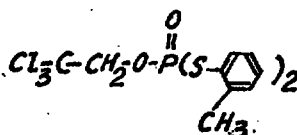
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19. The compound of the formula



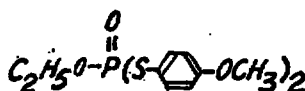
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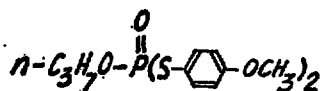
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21. The compound of the formula



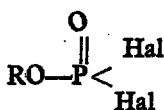
22. The compound of the formula



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23. A process for the production of compounds according to any of Claims 1 to 6 wherein a phosphoric acid monoester dihalide is reacted with a thiophenol in the form of a salt or in the presence of an acid-binding agent, the phosphoric acid monoester dihalide having the general formula

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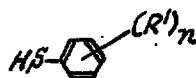


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and the thiophenol having the general formula

20





wherein R, R' and n have the meaning indicated in the relevant claim of Claims 1 to 6 and Hal is a halogen atom.

- 5 24. A process according to Claim 23 wherein Hal is a chlorine atom. 5
25. A process according to Claim 23 or 24 wherein the stated reaction is carried out in the presence of a solvent or diluent.
26. A process according to Claim 25 wherein the solvent is one of those hereinbefore specifically named for that purpose.
- 10 27. A process according to any of Claims 23 to 26 wherein the stated reaction is carried out at a temperature of 0° to 100°C. 10
28. A process according to any of Claims 23 to 27 wherein substantially two mols of the thiophenol are used for each mol of the phosphoric acid monoester dihalide.
- 15 29. A process according to any of Claims 23 to 28 wherein the phosphoric acid monoester dihalide is added dropwise with stirring to a solution or suspension of the thiophenol (or salt thereof) and the reaction mixture is stirred for a sufficient period to complete the reaction. 15
30. A process for the preparation of compounds according to Claim 1, substantially as hereinbefore described in Examples 1 to 8.
- 20 31. Compounds according to Claim 1, whenever prepared by a process according to any of Claims 23 to 30. 20
32. Fungicidal compositions containing, as active ingredient, a compound according to Claim 1 in admixture with a solvent or carrier.
- 25 33. A method of combating fungous infestation wherein there is applied to a fungus habitat a compound according to any of Claims 1 to 22, alone or in admixture with a solvent or carrier. 25

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