United States Patent Office 2,978,479 Patented Apr. 4, 1961

2,978,479

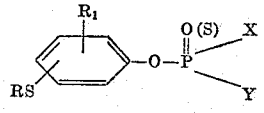
PEST CONTROL AGENTS

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No Drawing. Filed Mar. 4, 1959, Ser. No. 797,052

12 Claims. (Cl. 260—461)

The present invention relates to and has as its objects new and useful phosphoric acid ester amides or diamides and processes for obtaining the same. Generally the new compounds of the present invention may be represented by the following formula

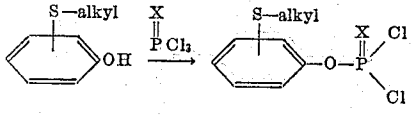


wherein R and R_1 stand for low molecular weight alkyl radicals such as methyl, ethyl, propyl, butyl and the like, and R_1 may also be hydrogen, X is NH_2 or the radical of any primary or secondary amine, and Y may be X or stands for any alkoxy group.

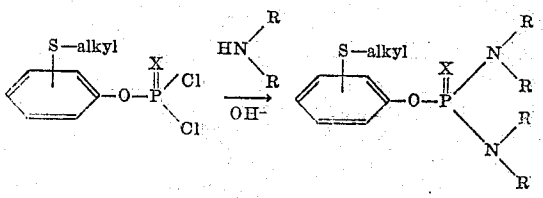
A great number of phenyl-phosphoric acid or phenyl-thionophosphoric acid ester amides or diamides have already been described in the literature. Their insecticidal action is likewise already known (see for instance U.S. Patents 2,552,541 and 2,811,480).

It has now been found that alkylmercapto-phenyl-phosphoric acid or -thionophosphoric acid ester amides or diamides are essentially more effective than the compounds described in literature and that they can be used as contact-insecticides and partially also as systemic agents.

The new alkylmercapto-phenyl-phosphoric acid or -thionophosphoric acid ester amides or diamides are obtainable by various ways. By reacting alkylmercapto phenols with phosphorus oxychloride or phosphorus sulfochloride, the corresponding alkylmercapto-phenyl-phosphoric acid or -thiophosphoric acid dichlorides are formed. This reaction may be shown by the following equation:

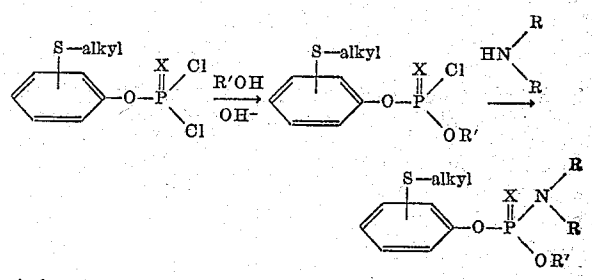


(wherein X stands for oxygen or sulfur). These dichlorides may then be reacted directly with ammonia, alkyl amines or dialkyl amines to form the desired amides as it is to be seen from the following formulae:

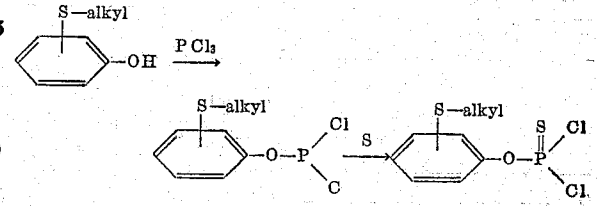


(wherein X stands for oxygen or sulfur, and R stands for hydrogen or amine-forming radicals). The said alkylmercapto-phenyl-phosphoric acid- or -thiophosphoric acid dichlorides may also first be reacted in the presence of an acid-binding agent with the equivalent amount of any

alcohol and subsequently converted into a mono-amide; this is to be seen from the following formulae:



(wherein X stands for oxygen or sulfur, R stands for hydrogen or amine-forming radicals, R' stands for ester-forming radicals). It is moreover possible to react alkylmercapto phenols with phosphorus trichloride to form the corresponding alkylmercapto-phenyl-phosphorous acid dichlorides and subsequently to convert the latter with sulfur into the corresponding alkylmercapto-phenyl-thionophosphoric acid dichlorides; this is to be seen from the following formulae:



The conversion of the alkylmercapto-phenyl-thiophosphoric acid dichlorides thus obtained into the corresponding ester amides or diamides is then effected in the manner described above.

In this way there are formed the compounds of the above mentioned general formula, more particularly the compounds obtainable according to the present invention are those in which the symbols shown in the above said general formula have the following meaning: R stands for a low molecular alkyl radical up to 4 carbon atoms, R_1 stands for hydrogen or R, X and Y stand for a group



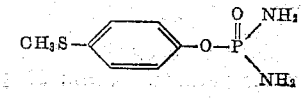
R_3 and R_4 being hydrogen or low molecular alkyl radicals up to 4 carbon atoms, and wherein Y may also stand for O—R_5, R_5 being a low molecular alkyl radical up to 4 carbon atoms.

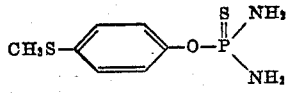
Some of the new compounds are crystalline substances which are distinguished by a sharp melting point, others are obtained in the form of barely water-soluble oils which are distillable under vacuum without decomposition.

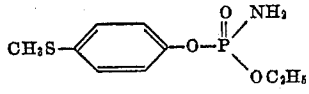
The new compounds according to the invention are used in the manner customary for other phosphoric acid ester insecticides. They are preferably applied in combination with solid or liquid extenders or diluents, talcum, chalk, bentonites, charcoal or similar compounds being chiefly used as solid extenders. As liquid preparations aqueous dilutions have proved to be particularly useful which are preferably obtained in combinaion with suitable emulsifiers and solvents.

As an example for the special utility of the inventive compounds the compounds of the following formulae

(I)



(II) 

(III) 

have been tested against spider mites and caterpillars.

Aqueous solutions of these compounds have been prepared by mixing the active ingredient with the same amount of dimethyl formamide as an auxiliary solvent adding thereto 20% by weight referred to active ingredient of a commercial emulsifier consisting of a benzyl hydroxy polyglycol ether containing about 10 to 15 glycol residues, and diluting at last this premixture with water to the desired concentration indicated in the following paragraphs.

The tests have been carried out as follows:

(*a*) Against spider mites: (contact-insecticidal action). Bean plants (*Phaseolus vulgaris*) of about 15 inches height are sprayed drip wet with solutions prepared as indicated above and in a concentration as shown below. The bean plants have been infested heavily with the two-spotted spider (species *Tetranychus telarius*). Evaluation has been carried out after 24 hours, 48 hours and 8 days. The following results have been obtained:

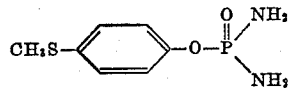
Compound	aqueous concentration (in percent active ingredient/water)	killing rate (in percent)
(I)	0.01	100
(II)	0.01	100
(III)	0.01	100

(*b*) Against caterpillars of the type diamond black moth (*Plutella maculipennis*): white cabbage has been sprayed drip wet with aqueous emulsions as prepared above in a concentration as shown below. Caterpillars (10 each) have been placed on the sprayed leaves of the white cabbage. The living status of the caterpillars has been determined after 24 hours and 48 hours. The following results have been obtained:

Compound	aqueous concentration (in percent active ingredient/water)	killing rate (in percent)
(I)	0.1	100
(II)	0.1	100
(III)	0.1	100

The following examples are given to illustrate the processes applied and the biological activity of the compounds thus obtained.

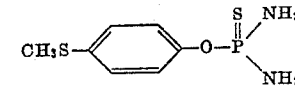
Example 1



Into a solution of 77 grams (0.3 mol) of 4-methyl-mercapto-phenyl-dichlorophosphate (B.P. 130–132° C./1.2 mm. Hg) in 600 ccm. of benzene, ammonia is introduced at 0–10° C. with stirring and cooling, until the reaction is alkaline. After the addition of 300 ccm. of petroleum ether, stirring is continued for another hour, the crystalline mixture is then filtered off with suction, washed with petroleum ether and dried. The ammonium chloride formed is removed by suspension in water, and the remaining diamido-4-methyl-mercapto-phenylphosphate is dried under vacuum. Yield: 53 grams corresponding to 82% of the theoretical. M.P. 184–185° C. LD_{95} on rats per os 100 mg./kg.

Spider mites are completely killed by 0.01% solutions. The compound has a marked systemic action. Eating insects such as caterpillars are likewise completely killed by 0.1% solutions.

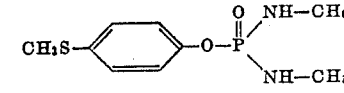
Example 2



Into a solution of 82 grams (0.3 mol) of 4-methyl-mercapto-phenyl-dichloro-thionophosphate (B.P. 105–110° C./0.05 mm. Hg) in 300 ccm. of benzene, ammonia is introduced in a rapid stream while stirring and cooling with ice and sodium chloride, the temperature of the reaction mixture rising thereby to 45° C. The mixture is then kept at 50–60° C. for another hour and ammonia is further introduced in a slow stream. After cooling, 300 ccm. of petroleum ether are added, the precipitate is filtered off with suction, washed with petroleum ether and dried. The ammonium chloride formed is removed by suspension in water. The remaining diamido-4-methylmercapto-phenyl-thionophosphate is re-crystallized from xylene. Yield: 58 grams, corresponding to 82.5% of the theoretical. M.P. 140–141° C.

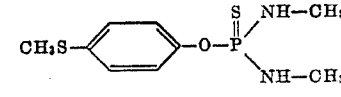
Spider mites are completely killed with 0.01% solutions. At a concentration of 0.1% the compound shows a 100% systemic action on aphids. Caterpillars are killed completely with 0.1% solutions.

Example 3



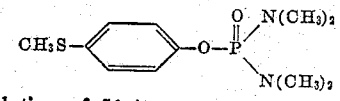
Into a solution of 51.4 grams (0.2 mol) of 4-methyl-mercapto-phenyl-dichloro-phosphate (B.P. 130–132° C./1.2 mm. Hg) in 400 ccm. of benzene methylamine is introduced, until the mixture which is stirred and kept at 0–10° C. by cooling, shows an alkaline reaction, 200 ccm. of petroleum ether are then added and the mixture is stirred for another hour. The precipitate is then filtered off with suction and the solution evaporated to dryness. The crystalline products are combined and suspended with water, in order to remove the methylamine hydrochloride, the residue is filtered off with suction, dried under vacuum and re-crystallized from carbon tetrachloride. Yield: 41 grams corresponding to 83.5% of the theoretical. M.P. 96–97° C. LD_{95} on rats per os 250 mg./kg.

Example 4



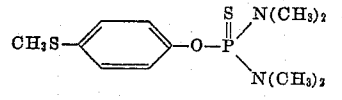
Into a solution of 82 grams (0.3 mol) of 4-methyl-mercapto-phenyl-dichloro-thionophosphate (B.P. 105–110° C./0.05 mm. Hg) in 600 ccm. of benzene, methylamine is introduced in a rapid stream with stirring and cooling, the temperature of the reaction mixture rising thereby to 45° C. After the reaction has subsided, the mixture is kept at 50–60° C. for another hour and methylamine is further introduced, now in a moderate stream. After cooling, the mixture is shaken out with water, until the reaction is neutral, dried over sodium sulfate and the benzene is distilled off under vacuum. When crystallization sets in, the distillation is interrupted, and complete precipitation is achieved by the addition of petroleum ether. Re-crystallization from benzene by the addition of petroleum ether. Yield: 64 grams corresponding to 81.5% of the theoretical. M.P. 63–64° C. LD_{95} on rats per os 250 mg./kg. With solution of 0.01% spider mites are killed to 90% and flies are killed completely.

Example 5



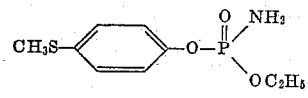
Into a solution of 51.4 grams (0.2 mol) of 4-methyl-mercapto-phenyl-dichloro-phosphate (B.P. 130–132° C./1.2 mm. Hg) in 400 ccm. of benzene dimethylamine is introduced with stirring and cooling, until the mixture shows an alkaline reaction. After prolonged standing, the reaction mixture is shaken out with water, then twice with a 5% sodium carbonate solution and again with water, until the reaction is neutral, then dried over sodium sulfate and the benzene is evaporated off under vacuum. The residue is not distillable without decomposition under high vacuum and is therefore rubbed with kieselguhr and filtered. A viscous slightly yellow liquid is thus obtained. Yield: 39 grams corresponding to 71% of the theoretical. n_D^{21}: 1.5462. LD_{95} on rats per os 50 mg./kg.

Example 6



Into a solution of 82 grams (0.3 mol) of 4-methyl-mercapto - phenyl - dichloro - thionophosphate (B.P. 105–110° C./0.05 mm. Hg) in 600 ccm. of benzene dimethylamine is introduced with stirring and cooling in a rapid stream, the temperature of the reaction mixture rising thereby to 45° C. After the reaction has subsided, the mixture is kept at 50–60° C. for another hour and dimethylamine is further introduced, now in a moderate stream. After cooling, the product is washed with water until the reaction is neutral, dried over sodium sulfate and the benzene is evaporated off under vacuum until crystallization sets in. For complete precipitation, petroleum ether is added. Re-crystallization from benzene by the addition of petroleum ether. Yield: 67 grams corresponding to 77% of the theoretical. M.P. 66–67° C. LD_{50} on rats per os 100 mg./kg. Flies are killed completely with solutions of 0.01%. The compound has a marked ovicidal action on spider mites.

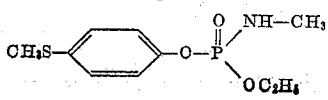
Example 7



Into a solution of 77 grams (0.3 mol) of 4-methyl-mercapto-phenyl-dichloro-phosphate (B.P. 130–132° C./1.2 mm. Hg), 13.8 grams (0.3 mol) of ethanol and 300 ccm. of benzene, ammonia is slowly introduced at 20–25° C. without external cooling so that the mixture is only slightly warmed. After showing an alkaline reaction, 250 ccm. of petroleum ether are added and the mixture is then kept at room temperature with stirring for 2 hours, the precipitate is then filtered off with suction and washed with petroleum ether and dried. The ammonium chloride formed is removed by suspension in water. After filtering off with suction and drying under vacuum, the product is re-crystallized from carbon tetrachloride. 61 grams of the new compound are thus obtained. Yield: 82.3% of the theoretical. M.P. 78–79° C. LD_{95} on rats per os 5 mg./kg.

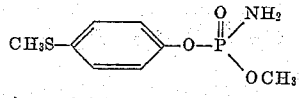
Aphids and spider mites are killed completely with 0.01% solutions. At a concentration of 0.1% the compound shows a systemic action. Eating insects such as caterpillars are likewise completely killed by 0.1% solutions.

Example 8



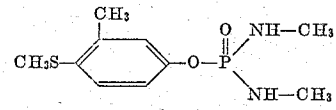
Into a solution of 51.4 grams (0.2 mol) of 4-methyl-mercapto-phenyl-dichloro-phosphate (B.P. 130–132° C./1.2 mm. Hg), 9.2 grams of ethanol (0.2 mol) and 300 ccm. of benzene methylamine is slowly introduced with stirring at 15–20° C., until the reaction is weakly alkaline, so that the mixture is only slightly warmed. After standing for several hours, the product is shaken out with water, a 5% sodium carbonate solution and again with water, dried over sodium sulfate and the benzene then evaporated under vacuum. Finally, the product is filtered after the addition of kieselguhr. 36 grams of a viscous yellowish liquor are thus obtained. Yield: 69% of the theoretical. LD_{50} on rats per os 1 mg./kg.

Example 9



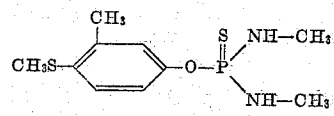
Into a solution of 77 grams (0.3 mol) of 4-methyl-mercapto-phenyl-dichloro-phosphate (B.P. 130–132° C./1.2 mm. Hg), 9.6 grams of methanol and 600 ccm. of benzene, ammonia is slowly introduced at 20–25° C., until the reaction is alkaline. 300 ccm. of petroleum ether are then added and the mixture is stirred for a further 2 hours. The precipitate is filtered off with suction, washed with petroleum ether and dried and the ammonium chloride is then removed by suspension with water. After filtering with suction and drying under vacuum, the remaining precipitate is re-crystallized from carbon tetrachloride. 53 grams of the new compound of M.P. 91° C. are thus obtained. Yield: 83% of the theoretical. LD_{50} on rats per os 10 mg./kg. Spider mites are killed completely with solutions of 0.001%. Caterpillars and aphids are killed completely with solutions of 0.1%. At a concentration of 0.1% the compound shows a 100% systemic action on aphids.

Example 10



Into a solution of 81 grams (0.3 mol) of (3-methyl-4-methylmercapto-phenyl)-dichloro-phosphate (B.P. 135–138° C./1 mm. Hg) in 300 ccm. of benzene, methylamine is introduced at 0–10° C. with stirring and cooling, until the reaction is alkaline, 300 ccm. of petroleum ether are then added and the reaction mixture is kept at room temperature with stirring for a further hour. The precipitate is filtered off with suction, washed with petroleum ether and dried and then suspended with water, in order to remove the methylamine hydrochloride formed, then filtered off with suction, well washed and dried under vacuum. The product is re-crystallized from benzene, and petroleum ether is added for complete precipitation. 70 grams of the new product of M.P. 92–94° C. are thus obtained. Yield: 89.5% of the theoretical. LD_{50} on rats per os 250 mg./kg. 0.1%. Solutions kill spider mites to 90%. At a concentration of 0.1% the compound shows a 100% systemic action on aphids.

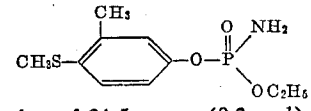
Example 11



Into a solution of 87 grams (0.3 mol) of (3-methyl-4-methylmercapto-phenyl)-dichloro-thionophosphate (B.P. 115–120° C./0.05 mm. Hg) in 300 ccm. of benzene, methylamine is introduced in a rapid stream while stirring and cooling with ice and sodium chloride, the mixture thus being warmed to 50° C. After the reaction has subsided, the mixture is kept at 50–60° C. for another hour and more methylamine is introduced. After cool-

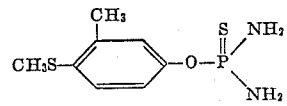
ing, the product is washed with water until the reaction is neutral and dried over sodium sulfate. After distilling off the benzene, a liquid remains behind which does not crystallize. It is taken up with chloroform, again washed with water, dried and the bulk of the chloroform is evaporated under vacuum. After prolonged standing, crystals begin to separate out from the concentrate. Complete precipitation is achieved by the addition of petroleum ether. Re-crystallization from benzene by the addition of petroleum ether. Yield: 68 grams corresponding to 82% of the theoretical; M.P. 51–52° C. LD_{50} on rats per os 500 mg./kg.

Example 12



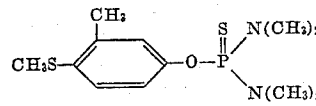
Into a solution of 81.5 grams (0.3 mol) of (3-methyl-4-methylmercapto-phenyl)-dichloro-phosphate (B.P. 135–138° C./1 mm. Hg), 13.8 grams (0.3 mol) of ethanol and 300 ccm. of benzene, ammonia is introduced in a very slow stream at 20–25° C., until the mixture shows a weakly alkaline reaction, 300 ccm. of petroleum ether are then added and the mixture is stirred for another hour. The precipitate is filtered off with suction, washed with petroleum ether, dried and suspended with water, in order to remove the ammonium chloride. The product is filtered off with suction, washed with water dried under vacuum and then recrystallized from carbon tetrachloride. 65 grams of the new compound of M.P. 73–75° C. are thus obtained. Yield: 87.5% of the theoretical. LD_{50} on rats per os 5 mg./kg. Solutions of 0.001% kill spider mites to 90% (ovicidal action). Caterpillars are killed completely with 0.1% solutions. At a concentration of 0.1% the compound shows a 100% systemic action on aphids.

Example 13



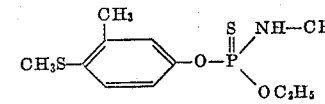
Into a solution of 87 grams (0.3 mol) of (3-methyl-4-methylmercapto - phenyl) - dichloro - thionophosphate (B.P. 115–120° C./0.05 mm. Hg) in 300 ccm. of benzene, ammonia is introduced in a rapid stream while stirring and cooling with ice and sodium chloride, the temperature of the mixture rising thereby to about 50° C. After the reaction has subsided, the mixture is kept at 50–60° C. for another hour, and ammonia is further introduced in a moderate stream. After cooling, 300 ccm. of petroleum ether are added, the precipitate is filtered off with suction, washed with petroleum ether and dried. The ammonium chloride formed is removed by suspension with water. The residue is dried under vacuum and then re-crystallized from xylene. Yield: 62 grams corresponding to 82.5% of the theoretical. M.P. 112–113° C. LD_{50} on rats per os 1000 mg./kg. 0.01% solutions kill spider mites completely (ovicidal action). The compound shows 100% systemic action on aphids.

Example 14



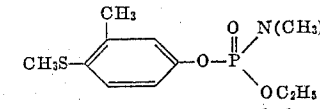
Into a solution of 87 grams (0.3 mol) of (3-methyl-4-methylmercapto - phenyl) - dichloro - thionophosphate (B.P. 115–120° C./0.05 mm. Hg) in 300 ccm. of benzene, dimethylamine is introduced with stirring and cooling with ice and sodium chloride, the temperature of the mixture rising thereby to about 45° C. After the reaction has subsided, the temperature is maintained at 50–60° C. and the introduction of dimethylamine is continued. At the end of the reaction, the mixture shows an alkaline reaction. After cooling the product is washed until the reaction is neutral, dried over sodium sulfate and the benzene is removed under vacuum, until crystallization sets in. The precipitation is completed by the addition of petroleum ether. The product is then re-crystallized from benzene by the addition of petroleum ether. 76 grams of the new compound of M.P. 60–61° C. are thus obtained. Yield: 83.5% of the theoretical. LD_{50} on rats per os 250 mg./kg.

Example 15



Into a solution of 89 grams (0.3 mol) of O-ethyl-(3-methyl - 4 - methylmercapto-phenyl)-chloro-thionophosphate in 300 ccm. of benzene methylamine is introduced with stirring, the reaction mixture being thereby warmed to 40–50° C. After the reaction has subsided, the mixture is kept at 50° C. for another hour, and the introduction of methylamine is continued. The mixture shows finally an alkaline reaction. After cooling, the product is washed with water until the reaction is neutral, dried over sodium sulfate and then fractionally distilled, the main runnings going over under a high vacuum of 0.01 mm. Hg. at 123–125° C. LD_{95} on rats per os 10 mg./kg. Aphids are killed completely with 0.01% solutions. At a concentration of 0.1% the compound shows a 100% systemic action on aphids. Spider mites are killed completely with solutions of 0.001%, ovicidal action. Caterpillars are killed completely with 0.1% solutions.

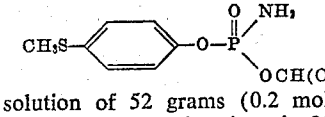
Example 16



51.4 grams (0.2 mol) of 4-methylmercapto-phenyl-dichloro-phosphate are dissolved in 200 ccm. of benzene. A mixture of 9.2 grams of anhydrous alcohol, 24 grams of anhydrous pyridine and 200 ccm. of petroleum ether is added dropwise with stirring. The reaction product is then heated under reflux for 30 minutes. It is then cooled to room temperature and the pyridine hydrochloride formed is filtered off with suction. Gaseous dimethylamine is then introduced into the filtrate with stirring, until the reaction becomes just alkaline. The reaction product is then washed twice with 50 ccm. portions of water. The water is separated off. The organic layer is dried over sodium sulfate. The solvents are evaporated under vacuum. The residue is kept at a bath temperature of 50° C. under a pressure of 0.01 mm. for 2 hours. The still warm residue is rubbed with a small amount of kieselguhr and then filtered. 43 grams of the new ester are thus obtained as a viscous, water-insoluble liquid. Yield: 78% of the theoretical.

Mean toxicity on rats per os 10 mg./kg. Aphids are killed completely by 0.1% solutions. Caterpillars are likewise completely destroyed by 0.1% solutions. Spider mites are still killed to 90% by 0.01% concentrations. The ester shows, moreover, a marked ovicidal action on the eggs of red spiders.

Example 17

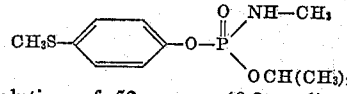


To a solution of 52 grams (0.2 mol) of 4-methyl-mercapto-phenyl-dichloro-phosphate in 200 ccm. of benzene there is added with external cooling and stirring a mixture of 12 grams of anhydrous isopropyl-alcohol, 32 grams of anhydrous pyridine and 200 ccm. of petroleum ether. The reaction product is then heated under reflux for 30 minutes. After cooling to room temperature, the pyridine hydrochloride formed is filtered off with suction.

Anhydrous ammonia is then introduced with external cooling and simultaneous stirring into the filtrate until the reaction just becomes alkaline. 200 ccm. of petroleum ether are added in order to facilitate stirring of the product. After the introduction of ammonia, the mixture is stirred for a further hour. The salt thus formed which contains besides ammonium chloride the new ester is then filtered off with suction. The precipitate is washed with petroleum ether and the precipitate is then suspended in water, in order to remove the ammonium chloride. The residue thus obtained is filtered off with suction and washed with water. After re-crystallization from carbon tetrachloride, 38 grams of the new ester are obtained as colorless needles showing a melting point of 75° C. Yield: 73% of the theoretical. The new ester is barely water-soluble. The ester shows on rats per os a mean toxicity of 2.5 mg./kg.

Aphids are completely killed with 0.01% solutions. Spider mites are still killed to 50% by 0.001% solutions. When applied at a concentration of 0.1%, the preparation has a marked systemic action on aphids.

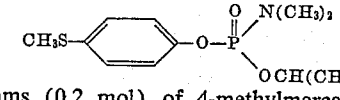
Example 18



To a solution of 52 grams (0.2 mol) of 4-methylmercapto-phenyl-dichloro-phosphate in 200 ccm. of benzene, there is added with external cooling and stirring a mixture of 12 grams of anhydrous isopropyl alcohol, 32 grams of anhydrous pyridine and 200 ccm. of petroleum ether. The reaction mixture is then heated under reflux for 30 minutes. After cooling to room temperature, the pyridine hydrochloride formed is filtered off with suction. Gaseous anhydrous methylamine is introduced with further stirring and external cooling into the filtrate until the reaction becomes just alkaline. The reaction product is stirred at room temperature for a further hour, then washed twice with 50 ccm. portions of water, and the organic layer is dried over sodium sulfate. After evaporation of the solvent, a viscous pale yellow oil remains behind which is kept at a bath temperature of 60° C. under a pressure of 0.01 mm. Hg for 2 hours. The still warm product is rubbed with a small amount of kieselguhr and then filtered. 42 grams of the new ester are thus obtained as a viscous barely water-soluble liquid. Yield: 77% of the theoretical.

The ester shows on rats per os a mean toxicity of 5 mg./kg. Aphids are killed completely with 0.01% solutions. Spider mites are still safely killed with 0.001% solutions. The preparation has a marked ovicidal action on the eggs of red spiders.

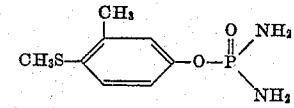
Example 19



52 grams (0.2 mol) of 4-methylmercapto-phenyl-dichlorophosphate are dissolved in 200 ccm. of benzene. A mixture of 12 grams of anhydrous isopropyl-alcohol, 32 grams of anhydrous pyridine and 200 ccm. of petroleum ether is added with stirring and external cooling. The reaction product is heated under reflux for 30 minutes. The mixture is then cooled to room temperature and the pyridine hydrochloride formed is filtered off with suction. Gaseous anhydrous dimethylamine is introduced with stirring and external cooling into the filtrate until a weakly alkaline reaction sets in. The reaction product is stirred at room temperature for a further hour and then shaken out twice with 50 ccm.-portions of water. The organic layer is dried over sodium sulfate. The solvent is then removed under vacuum. The residue thus obtained is kept at a bath temperature of 60° C. under a vacuum of 0.01 mm. Hg for 2 hours. The still warm viscous reaction product is rubbed with a little kieselguhr and filtered. 44 grams of the new ester are thus obtained as a thickly liquid water-insoluble oil. Yield: 76% of the theoretical.

The ester shows on rats per os a LD_{95} of 25 mg./kg. Spider mites are still safely killed by 0.01% solutions.

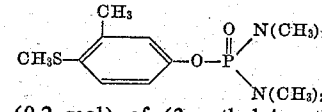
Example 20



54 grams (0.2 mol) of (3-methyl-4-methylmercapto-phenyl)-dichloro-phosphate are dissolved in 300 ccm. of anhydrous ether. Ammonia is introduced with stirring and external cooling at 10–20° C. until the reaction becomes just alkaline. 300 ccm. of petroleum ether are in order to facilitate stirring of the reaction product, and the precipitate formed is then filtered off with suction. The precipitate is washed with a little petroleum ether. The suction-filtered product is then freed from the ammonium chloride formed by suspension in water. The residue thus obtained is dissolved in methylethylketone. By the careful addition of petroleum ether the new ester is obtained in a crystalline form. 37 grams of the new ester are thus obtained. M.P. 137–138° C. Yield: 80% of the theoretical.

The new ester shows on rats per os a mean toxicity of 500 mg./kg. Spider mites are still safely killed by 0.001% solutions. Aphids are completely killed by 0.1% solutions. Caterpillars are also killed completely by application of 0.1% concentrations.

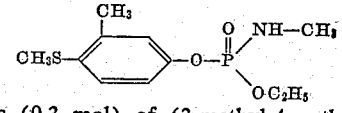
Example 21



54 grams (0.2 mol) of (3-methyl-4-methylmercapto-phenyl)-dichloro-phosphate are dissolved in 400 ccm. of benzene. Anhydrous dimethylamine is added at 10–20° C. with external cooling and stirring, until the reaction becomes just alkaline. The reaction product is then stirred for a further half hour at room temperature. The reaction product is then shaken out twice with 50 ccm.-portions of water. After working up as usual 52 grams of the new ester are obtained as a pale yellow water-insoluble liquid. Yield: 88% of the theoretical.

The new ester shows a LD_{95} on rats per os of 250 mg./kg.

Example 22

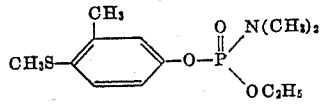


81 grams (0.3 mol) of (3-methyl-4-methylmercapto-phenyl)-dichloro-phosphate are dissolved in 200 ccm. of benzene. A mixture of 13.8 grams of anhydrous alcohol, 48 grams of anhydrous pyridine and 100 ccm. of petroleum ether is added with stirring and external cooling. The reaction product is then heated under reflux for a further half hour. After cooling to room temperature, the pyridine hydrochloride formed is filtered off with suction. Gaseous methylamine is introduced into the filtrate, until the reaction becomes alkaline. The reaction product is after-stirred for several hours and then washed with 50 ccm. of dilute hydrochloric acid and subsequently with a 5% sodium carbonate solution, in order to remove the last traces of acid. After drying the organic layer over sodium sulfate, the solvent is evaporated off under vacuum. The residue thus obtained is kept at a bath temperature of 80–90° C. under a pressure of 0.001 mm. Hg for 2 hours; 63 grams of the new ester are thus obtained as a viscous water-insoluble pale yellow liquid. Yield: 76% of the theoretical. The new ester shows on rats per os a mean toxicity of 2.5 mg./kg.

Spider mites are still completely killed by 0.001% solu-

tions. The preparation has a marked ovicidal action on the eggs of red spiders. Caterpillars are likewise completely killed by 0.1% solutions.

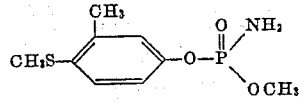
Example 23



To 81 grams (0.3 mol) of (3-methyl-4-methylmercaptophenyl)-dichloro-phosphate there is added with stirring and external cooling a mixture of 13.8 grams of anhydrous alcohol, 48 grams of anhydrous pyridine and 100 ccm. of petroleum ether. The reaction product is heated under reflux for 30 minutes, then cooled to room temperature and the pyridine hydrochloride formed is filtered off with suction. Dimethylamine is introduced with external cooling into the filtrate until the reaction becomes alkaline. After working up similarly to the preceding example, 65 grams of the new ester are obtained as a pale yellow water-insoluble oil. Yield: 75% of the theoretical.

The new ester shows on rats per os a LD_{95} of 25 mg./kg. Aphids are killed completely with 0.1% solutions. 0.01% solutions kill spider mites completely.

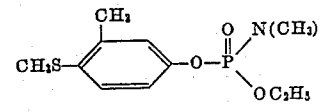
Example 24



54 grams (0.2 mol) of (3-methyl-4-methylmercaptophenyl)-dichloro-phosphate are dissolved in 200 ccm. of benzene. 6.4 grams of anhydrous methyl alcohol dissolved in 200 ccm. of benzene are added thereto. Ammonia is slowly introduced with external cooling, until the reaction becomes just alkaline. A thick pulp is formed which is just capable of being stirred. 400 ccm. of petroleum ether are added and the mixture is after-stirred for an hour. The precipitate formed is then filtered off with suction, washed with water and dissolved in methylethylketone. By careful addition of petroleum ether the new ester is obtained in a crystalline form. Yield: 41 grams, i.e. 83% of the theoretical, M.P. 80–81° C. The new ester shows a mean toxicity on rats per os of 10 mg./kg.

Spider mites are still destroyed to 80% by 0.001% solutions. Caterpillars are completely killed by 0.1% solutions. 0.1% preparations have a marked systemic action on aphids.

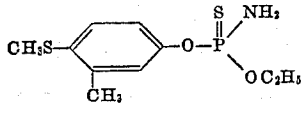
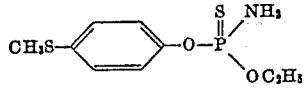
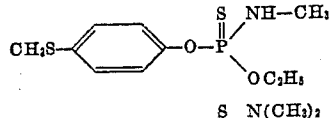
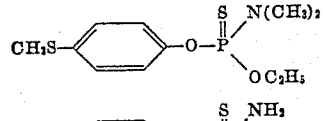
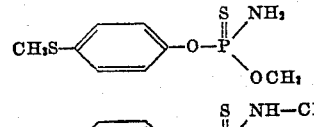
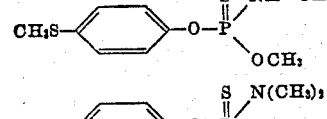
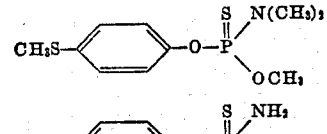
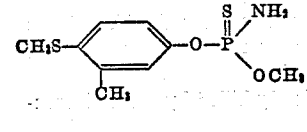
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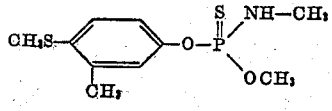
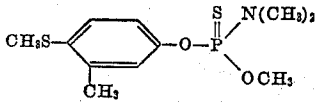
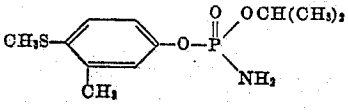
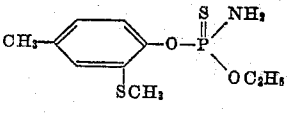
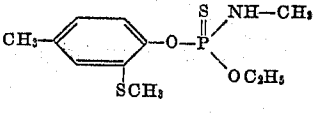
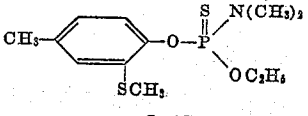
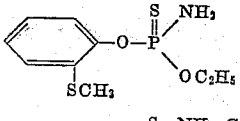
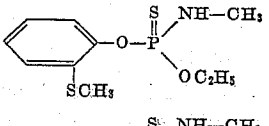
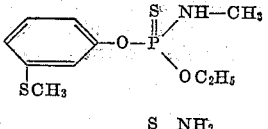
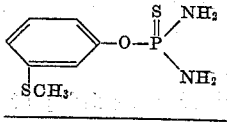


89 grams (0.3 mol) of ethyl-(3-methyl-4-methylmercapto-phenyl)-chloro-thionophosphate are dissolved in 300 ccm. of benzene. A slow stream of dimethylamine is introduced with stirring and external cooling. The temperature rises to 40–50° C. Dimethylamine is further passed through the reaction product at 50° C., the reaction product is then cooled to room temperature and washed with 50 ccm.-portions of water (twice). The organic layer is separated out and dried over sodium sulfate. After evaporation of the solvent, there remains a pale yellow residue which can be fractionated under high vacuum. Under a pressure of 0.01 mm. Hg the new ester goes over at 113° C. 47 grams of a pale yellow water-insoluble oil are thus obtained. Yield: 51% of the theoretical.

The new ester shows on rats per os a LD_{95} of 50 mg./kg. Spider mites are completely killed by 0.01% solutions.

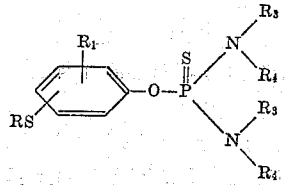
By the same way there may be obtained the compounds of the following formulae:

Compound		Yield, percent	Toxicity on rats per os	biological activity
	M.P., 39°--	63	LD_{95}, 25 mg./kg	spider mites—0.001%—100%.
	M.P., 139–140°	77	LD_{50}, 1,000 mg./kg	spider mites—0.01%—100%.
	B.P.$_{0.01}$, 140–143°	59	LD_{50}, 2.5 mg./kg	spider mites—0.001%—100%.
	B.P.$_{0.01}$, 120–123°	72	LD_{50}, 10 mg./kg	spider mites—0.01%—100%.
	M.P., 147–150°	81	LD_{95}, 500 mg./kg.	Do.
		87	LD_{50}, 2.5 mg./kg	aphids—0.001%—100%. spider mites—0.001%—100%.
	B.P.$_{0.01}$, 136°	89	LD_{50}, 25 mg./kg	spider mites—0.01%—100%.
	M.P., 88–90°	78	LD_{50}, 100 mg./kg.	aphids—0.01%—100%.

Compound		Yield, percent	Toxicity on rats per os	biological activity
		86	LD_{50}, 10 mg./kg.	aphids—0.01%—100%.
		83	LD_{50}, 100 mg./kg.	spider mites—0.1%—100%.
	M.P., 91°	74	LD_{50}, 5 mg./kg.	spider mites—0.01%—100%.
	M.P., 70–72°	94	LD_{50}, 1,000 mg./kg.	aphids—0.1%—100%.
		91	LD_{50}, 500 mg./kg.	
		93	LD_{95}, 500 mg./kg.	
	M.P., 50–51°	93	symptoms, 1,000 mg./kg.	spider mites—0.01%—100%.
		89	LD_{50}, 500 mg./kg.	spider mites—0.01%—60%.
	B.P.$_{0.01}$, 106–111°	79	LD_{50}, 100 mg./kg.	aphids—0.0001%—100%. spider mites—0.0001%—80%.
	M.P., 99–101°	63	LD_{50}, 250 mg./kg.	spider mites—0.01%—100%. caterpillars—0.1%—100%.

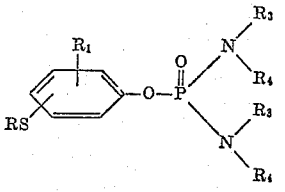
We claim:

1. A phosphoric acid amide of the following formula



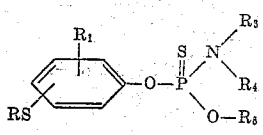
wherein R stands for a low molecular alkyl radical up to 4 carbon atoms, R_1 stands for a member selected from the group consisting of hydrogen and a low molecular alkyl radical up to 4 carbon atoms, R_3 and R_4 stand for a member selected from the group consisting of hydrogen and low molecular alkyl radicals up to 4 carbon atoms.

2. A phosphoric acid amide of the following formula



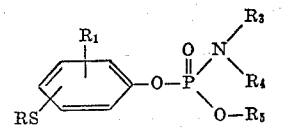
wherein R stands for a low molecular alkyl radical up to 4 carbon atoms, R_1 stands for a member selected from the group consisting of hydrogen and a low molecular alkyl radical up to 4 carbon atoms, R_3 and R_4 stand for a member selected from the group consisting of hydrogen and low molecular alkyl radicals up to 4 carbon atoms.

3. A phosphoric acid amide of the following formula



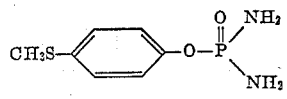
wherein R stands for a low molecular alkyl radical up to 4 carbon atoms, R_1 stands for a member selected from the group consisting of hydrogen and a low molecular alkyl radical up to 4 carbon atoms, R_3 and R_4 stand for a member selected from the group consisting of hydrogen and low molecular alkyl radicals up to 4 carbon atoms, R_5 stands for a low molecular alkyl radical up to 4 carbon atoms.

4. A phosphoric acid amide of the following formula

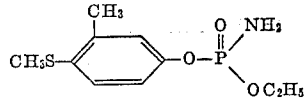


wherein R stands for a low molecular alkyl radical up to 4 carbon atoms, R_1 stands for a member selected from the group consisting of hydrogen and a low molecular alkyl radical up to 4 carbon atoms, R_3 and R_4 stand for a member selected from the group consisting of hydrogen and low molecular alkyl radicals up to 4 carbon atoms, R_5 stands for a low molecular alkyl radical up to 4 carbon atoms.

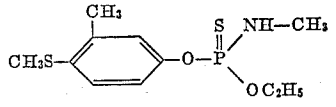
5. A phosphoric acid amide of the following formula



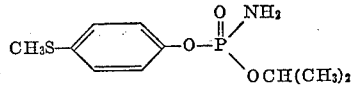
6. The phosphoric acid amide of the following formula



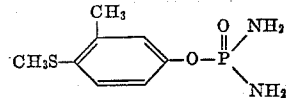
7. The phosphoric acid amide of the following formula



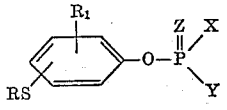
8. The phosphoric acid amide of the following formula



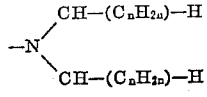
9. The phosphoric acid amide of the following formula



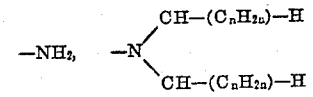
10. A phosphoric acid amide of the following formula



wherein R stands for an alkyl radical having up to four carbon atoms; R_1 stands for a member selected from the group consisting of hydrogen and an alkyl radical having up to four carbon atoms; Z is a chalcogen having an atomic weight from 16 to 33; X is a member selected from the group consisting of $—NH_2$ and

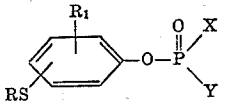


Y is a member selected from the group consisting of

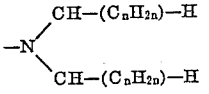


and O—CH—(C_nH_{2n})—H; and n is an integer from 0 to 3.

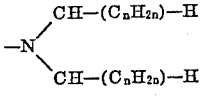
11. A phosphoric acid amide of the following formula



wherein R stands for an alkyl radical having up to four carbon atoms; R_1 stands for a member selected from the group consisting of hydrogen and an alkyl radical having up to four carbon atoms; X is a member selected from the group consisting of $—NH_2$ and

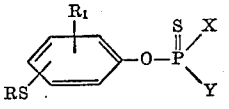


Y is a member selected from the group consisting of $—NH_2$

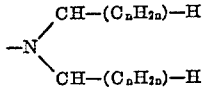


and O—CH—(C_nH_{2n})—H; and n is an integer from 0 to 3.

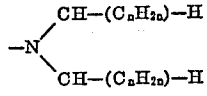
12. A phosphoric acid amide of the following formula



wherein R stands for an alkyl radical having up to four carbon atoms; R_1 stands for a member selected from the group consisting of hydrogen and an alkyl radical having up to four carbon atoms; X is a member selected from the group consisting of $—NH_2$ and



Y is a member selected from the group consisting of $—NH_2$



and O—CH—(C_nH_{2n})—H; and n is an integer from 0 to 3.

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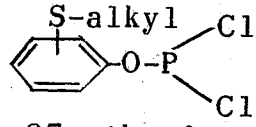
UNITED STATES PATENT OFFICE
CERTIFICATION OF CORRECTION

Patent No. 2,978,479 April 4, 1961

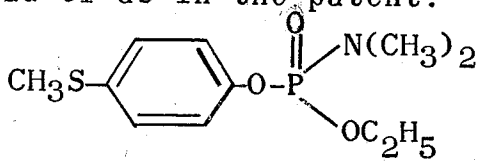
Heinrich Kayser et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

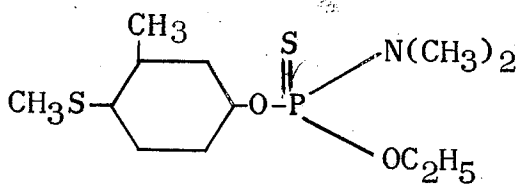
Column 2, lines 28 to 32, the first structural formula should appear as shown below instead of as in the patent:



column 8, lines 34 to 37, the formula should appear as shown below instead of as in the patent:



column 12, lines 15 to 18, the formula should appear as shown below instead of as in the patent:



Signed and sealed this 14th day of November 1961.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents