

PATENT SPECIFICATION

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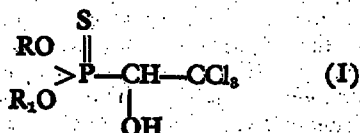
(54) NOVEL SUBSTITUTED THIONOPHOSPHONIC ACID DIALKYL ESTERS AND THEIR USE AS INSECTICIDES

(71) We, 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 certain new 1 - hydroxy - 2,2,2 - trichloroethane - thionophosphonic acid dialkyl esters, to a process for their preparation and to their use as arthropodicides, especially as insecticides.

It is already known that 1 - hydroxy - 2,2,2 - trichloroethane - phosphonic acid dialkyl esters, for example 1 - hydroxy - 2,2,2 - trichloroethane - phosphonic acid dimethyl esters, have a pesticidal, especially an insecticidal, action (see German Patent Specification 977,119).

The present invention provides, as new compounds, the 1 - hydroxy - 2,2,2 - trichloroethane - thionophosphonic acid dialkyl esters of the general formula



in which

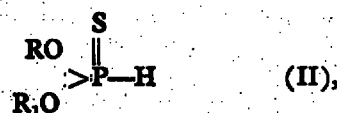
R and R₁, which may be identical or different, are each an alkyl radical with 1 to 4 carbon atoms.

The compounds of the formula (I) have been found to possess arthropodical, especially powerful insecticidal, properties.

Preferably, R and R₁ are each a straight or branched alkyl radical with 1 to 3 carbon atoms.

The present invention also provides a process for the preparation of a 1 - hydroxy - 2,2,2 - trichloroethane - thionophosphonic acid dialkyl ester of the formula (I), in which

a thionophosphorous acid dialkyl ester of the general formula



in which

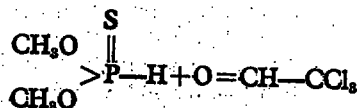
R and R₁ have the above-mentioned meanings, is reacted with chloral, of the formula



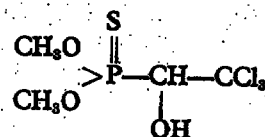
in the presence of a basic catalyst and optionally in the presence of an inert solvent.

Surprisingly, the 1 - hydroxy - 2,2,2 - trichloroethanethionophosphonic acid dialkyl esters according to the invention exhibit a substantially greater insecticidal action, coupled with very low toxicity to warm-blooded animals, than the 1-hydroxy-2,2,2-trichloroethane-phosphonic acid dialkyl esters of the same type of action, known from the state of the art. The compounds according to the invention thus represent an enrichment of the art.

If, for example, thionophosphorus acid dimethyl ester and chloral are used as starting materials, the course of the reaction can be represented by the following equation:



(basic catalyst) →



The thionophosphorus acid dialkyl esters (II) to be used as starting materials are known

and can be prepared in accordance with customary processes (see, for example, German Offenlegungsschrift (German Published Specification) 1,768,503).

- 5 The following may be mentioned as examples of such thionophosphorous acid dialkyl esters: thionophosphorous acid dimethyl ester, diethyl ester, dipropyl ester, diisopropyl ester and dibutyl ester, and also thionophosphorous acid methyl ethyl ester, methyl propyl ester, methyl isopropyl ester, methyl butyl ester, ethyl propyl ester, ethyl isopropyl ester, ethyl butyl ester and propyl butyl ester.

- 10 The process of preparation of the new compounds (I) is preferably carried out in the presence of a suitable solvent or diluent. Practically all inert organic solvents can be used for this purpose, especially aliphatic and aromatic, optionally chlorinated, hydrocarbons, such as benzene, toluene, xylene, benzene, methylene chloride, chloroform, carbon tetrachloride and chlorobenzene, ethers, for example diethyl ether, dibutyl ether and dioxan, and also nitriles, such as acetonitrile and propionitrile.

- 25 A whole range of basic compounds can be used as catalysts for carrying out the reaction. Aliphatic, aromatic and heterocyclic amines, for example triethylamine, dimethylaniline, dimethylbenzylamine and pyridine, have proved particularly suitable, as have inorganic basic compounds such as alkali metal hydroxides and alkali metal carbonates.

- 30 The reaction temperatures can be varied within a fairly wide range. In general, the reaction is carried out at between -20° and $+80^{\circ}\text{C}$, preferably at from 0° to 30°C .

- 35 The reaction is in general carried out under normal pressure.

- 40 To carry out the process, the thionophosphorous acid dialkyl ester and chloral are preferably employed in equimolar amounts, whilst the basic catalyst is preferably added in an amount which can be between 2 and 10 mole per cent.

- 45 The reaction is preferably carried out in the presence of one of the above-mentioned solvents, at the stated temperatures. After stirring for a little while, the reaction mixture is repeatedly washed with water, dried and freed from the solvent under reduced pressure. The compounds according to the invention are obtained in the form of oils and can be distilled. They are characterised by their boiling point and refractive index.

- 50 The new 1 - hydroxy - 2,2,2 - trichloroethane - thionophosphonic acid dialkyl esters are distinguished by an activity against arthropods, especially by an excellent insecticidal activity, and a favourable level of toxicity to warm-blooded animals. In part, they also exhibit a herbicidal action.

The compounds according to the invention can be employed successfully as pesticides in

the hygiene field and against ectoparasites in the veterinary field.

The active compounds according to the invention are well tolerated by plants and can be used for combating all or individual stages of development, including the preembryonic, normally sensitive and resistant, stages of development of arthropods where these are known as pests in agriculture, in forestry, in the protection of stored products and materials, and in hygiene.

The economically important pests in agriculture and forestry, as well as pests of stored products, pests destructive of materials and pests harmful to health, include: from the class of the *Isopoda*, for example, *Oniscus asellus*, *Armadillidium vulgare* and *Porcellio scaber*; from the class of the *Diplopoda*, for example, *Blaniulus guttulatus*; from the class of the *Chilopoda*, for example, *Geophilus carpophagus* and *Scutigera spec.*; from the class of the *Symphyla*, for example, *Scutigera immaculata*; from the class of the *Arachnida*, for example, *Scorpio maurus* and *Latrodectus mactans*; from the order of the *Acarina*, for example, *Acarus siro*, *Argas reflexus*, *Ornithodoros moubata*, *Dermanyssus gallinae*, *Eriophyes ribis*, *Phyllocoptura oleivora*, *Boophilus microplus*, *Rhipicephalus evertsi*, *Sarcoptes scabiei*, *Tarsonemus spec.*, *Bryobia praetiosa*, *Panonychus citri*, *Panonychus ulmi*, *Tetranychus tumidus* and *Tetranychus urticae*; from the order of the *Thysanura*, for example, *Lepisma saccharina*; from the order of the *Collembola*, for example, *Onychiurus armatus*; from the order of the *Orthoptera*, for example, *Blatta orientalis*, *Periplaneta americana*, *Leucophaea maderae*, *Blattella germanica*, *Acheta domesticus*, *Grylotalpha spec.*, *Locusta migratoria migratorioides*, *Melanoplus differentialis* and *Schistocerca gregaria*; from the order of the *Dermaptera*, for example, *Forficula auricularia*; from the order of the *Isoptera*, for example, *Reticulitermes spec.*; from the order of the *Anoplura* for example, *Phylloxera vastatrix*, *Pemphigus spec.*, and *Pediculus humanus corporis*; from the order of the *Thysanoptera*, for example, *Hercinothrips femoralis* and *Thrips tabaci*; from the order of the *Heteroptera*, for example, *Eurygaster spec.*, *Dysdercus intermedius*, *Piesma quadrata*, *Cimex lectularius*, *Rhodnius prolixus* and *Triatoma spec.*; from the order of the *Homoptera*, for example, *Aleurodes brassicae*, *Bemisia tabaci*, *Trialeurodes vaporariorum*, *Aphis gossypii*, *Brevicoryne brassicae*, *Cryptomyzus ribis*, *Doralis fabae*, *Doralis pomi*, *Eriosoma lanigerum*, *Hyalopteris arundinis*, *Macrosiphum avenae*, *Myzus cerasi*, *Myzus persicae*, *Phorodon humuli*, *Rhopalosiphum padi*, *Empoasca spec.*, *Euscelis bilobatus*, *Nephotettix cincticeps*, *Lecanium corni*, *Saissetia oleae*, *Laodelphax striatellus*, *Nila-*

3 *parvata lugens*, *Aonidiella aurantii*, *Aspidiotus hederæ*, *Pseudococcus* spec., and *Psylla* spec.; from the order of the *Lepidoptera*, for example, *Pectinophora gossypiella*, *Bupalus piniarius*, *Cheimatobia brumata*, *Lithocolletis blancardella*, *Hyponomeuta padella*, *Plutella maculipennis*, *Malacosoma neustria*, *Euproctis chrysorrhoea*, *Lymantria* spec., *Bucculatrix thurberiella*, *Phyllocnistis citrella*, *Agrotis* spec., *Euxoa* spec., *Feltia* spec., *Earias insulana*, *Heliothis* spec., *Laphygma exigua*, *Mamestra brassicae*, *Panolis flammea*, *Prodenia litura*, *Spodoptera* spec., *Trichoplusia ni*, *Carpocapsa pomonella*, *Pieris* spec., *Chilo* spec., *Pyrausta nubilalis*, *Ephestia kühniella*, *Galleria mellonella*, *Cacoecia podana*, *Capua reticulana*, *Choristoneura fumiferana*, *Clysia ambiguella*, *Homona magnanima* and *Tortrix viridana*; from the order of the *Coleoptera*, for example, *Anobium punctatum*, *Rhizophtha dominica*, *Bruchidius obtectus*, *Hylotrupes bajulus*, *Agelastica alni*, *Leptinotarsa decemlineata*, *Phaedon cochleariae*, *Diabrotica* spec., *Psylliodes chrysocephala*, *Epilachna varivestis*, *Atomaria* spec., *Oryzaephilus surinamensis*, *Anthonomus* spec., *Sitophilus* spec., *Otiorrhynchus sulcatus*, *Cosmopolites sordidus*, *Ceuthorrhynchus assimilis*, *Hypera postica*, *Dermestes* spec., *Trogoderma* spec., *Anthrenus* spec., *Attagenus* spec., *Lyctus* spec., *Meligethes aeneus*, *Ptinus* spec., *Niptus hololeucus*, *Gibbium psyllodes*, *Tribolium* spec., *Tenebrio molitor*, *Agriotes* spec., *Conoderus* spec., *Melolontha melolontha*, *Amphimallus solstitialis* and *Costelytra zealandica*; from the order of the *Hymenoptera*, for example, *Diprion* spec., *Hoplocampa* spec., *Lasius* spec., *Monomorium pharaonis* and *Vespa* spec.; from the order of the *Diptera*, for example, *Aedes* spec., *Anopheles* spec., *Culex* spec., *Drosophila melanogaster*, *Musca domestica*, *Fannia* spec., *Stomoxys calcitrans*, *Hypoderma* spec., *Bibio hortulanus*, *Oscinella frit*, *Phorbia* spec., *Pegomyia hyoscyami*, *Calliphora erythrocephala*, *Lucilia* spec., *Chrysomya* spec., *Ceratitis capitata*, *Dacus oleae* and *Tipula paludosa*; and from the order of the *Siphonaptera*, for example *Xenopsylla cheopis*.
 The active compounds can be converted to the customary formulations, such as solutions, emulsions, wettable powders, suspensions, powders, dusting agents, foams, pastes, soluble powders, granules, aerosols, suspension-emulsion concentrates, seed-treatment powders, natural and synthetic materials impregnated with active compound, very fine capsules in polymeric substances and in coating compositions, for use on seed, and formulations used with burning equipment, such as fumigating cartridges, fumigating cans and fumigating coils, as well as ULV (ultra-low-volume) cold mist and warm mist formulations.
 These formulations may be produced in known manner, for example by mixing the

active compounds with extenders, that is, liquid or solid or liquefied gaseous diluents or carriers, optionally with the use of surface-active agents, that is, emulsifying agents and/or dispersing agents and/or foam-forming agents. In the case of the use of water as an extender, organic solvents can, for example, also be used as auxiliary solvents.

As liquid diluents or carriers, there are preferably used aromatic hydrocarbons, such as xylenes, toluene, benzene or alkyl naphthalenes, chlorinated aromatic or aliphatic hydrocarbons, such as chlorobenzenes, chloroethylenes or methylene chloride, aliphatic hydrocarbons, such as cyclohexane or paraffins, for example mineral oil fractions, alcohols, such as butanol or glycol as well as their ethers and esters, ketones, such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, or strongly polar solvents, such as dimethyl formamide, dimethyl sulphoxide or acetonitrile, as well as water.

By liquefied gaseous diluents or carriers are meant liquids which would be gaseous at normal temperatures and pressures, for example aerosol propellants, such as halogenated hydrocarbons, for example Freon (trade mark).

As solid diluents or carriers, there are preferably used ground natural minerals, such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, or ground synthetic minerals, such as highly-dispersed silicic acid, alumina or silicates.

Preferred examples of emulsifying and foam-forming agents include non-ionic and anionic emulsifiers, such as polyoxyethylene-fatty acid esters, polyoxyethylene-fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkyl sulphonates, alkyl sulphates and aryl sulphonates as well as albumin hydrolyzation products; and preferred examples of dispersing agents include lignin sulphite waste liquors and methyl cellulose.

The active compounds according to the invention can be present in the formulations as a mixture with other active compounds.

The formulations in general contain from 0.1 to 95 per cent by weight of active compound, preferably from 0.5 to 90 per cent.

The active compounds can be employed as such, in the form of their formulations or as the use forms prepared therefrom. They may be used in the customary manner, for example by squirting, spraying, atomising, dusting, scattering, fumigating, gassing, watering, dressing or encrusting.

The active compound concentrations in the ready-to-use preparations can be varied within fairly wide ranges. In general they are from 0.0001 to 10%, preferably from 0.01 to 1%, by weight.

The active compounds can also be used with good success in the ULV method, where

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it is possible to apply formulations of up to 95% strength or even to apply the active compound by itself.

When used against pests harmful to health and pests of stored products, the active compounds are distinguished by an excellent residual action on wood and clay, as well as a good stability to alkali on limed substrates.

The present invention also provides an arthropodicidal composition containing as active ingredient a compound of the present invention in admixture with a solid or liquefied gaseous diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.

The present invention also provides a method of combating arthropods which comprises applying to the arthropods (especially insects) or an arthropod habitat (especially an insect habitat) a compound of the present invention alone or in the form of a composition containing as active ingredient a compound of the present invention in admixture with a diluent or carrier.

The present invention further provides crops protected from damage by arthropods by being grown in areas in which immediately prior to and/or during the time of the growing a compound of the present invention was applied alone or in admixture with a diluent or carrier. It will be seen that the usual methods of providing a harvested crop may be improved by the present invention.

The pesticidal activity of the compounds

of this invention is illustrated by the following biotest Examples.

Example A.

LD₁₀₀ test

Test insects: *Sitophilus granarius*

Solvent: Acetone

2 parts by weight of the active compound were taken up in 1,000 parts by volume of the solvent. The solution so obtained was diluted with further solvent to the desired concentrations.

2.5 ml of the solution of the active compound were pipetted into a Petri dish. On the bottom of the Petri dish there was a filter paper with a diameter of about 9.5 cm. The Petri dish remained uncovered until the solvent had completely evaporated. The amount of active compound per m² of filter paper varied with the concentration of the solution of active compound. About 25 test insects were then placed in the Petri dish and it was covered with a glass lid.

The condition of the test insects was observed 3 days after the commencement of the experiments. The destruction, in %, was determined. 100% denotes that all of the test insects had been killed; 0% denotes that no test insects had been killed.

The active compounds, the concentrations of the active compounds, the test insects and the results can be seen from the following table:

TABLE A

(LD₁₀₀ Test/*Sitophilus granarius*)

Active compound	Active compound concentration in the solution, in %	Degree of destruction in %
$\begin{array}{c} \text{O} \\ \parallel \\ (\text{CH}_3\text{O})_2\text{P}-\text{CH}-\text{CCl}_3 \\ \\ \text{OH} \end{array}$	0.2 0.02	100 15
(known)		
$\begin{array}{c} \text{S} \\ \parallel \\ (\text{CH}_3\text{O})_2\text{P}-\text{CH}-\text{CCl}_3 \\ \\ \text{OH} \end{array}$	0.2 0.02 0.002	100 100 50

(1)

Example B.

Residual Test

Test insects: *Musca domestica* and *Aedes aegypti*

Wettable powder base consisting of:
3% of sodium diisobutylphthalene-1-sulphonate
6% of sulphite waste liquor, partially condensed with aniline
40% of highly dispersed silicic acid, containing CaO
51% of colloidal kaolin

To produce a suitable preparation of the active compound, 1 part by weight of the active compound was intimately mixed with 9 parts by weight of the wettable powder base. The spray powder thus obtained was suspended in 90 parts of water.

The suspension of the active compound was sprayed, in an amount of, for example, 1

g of the active compound per m², onto substrates consisting of different materials.

The sprayed coatings were, at specific intervals of time, tested for their biological activity.

For this purpose, the test insects were placed on the treated substrates. There was put over the test insects a squat cylinder which was closed at its upper end with a wire mesh in order to prevent the insects from escaping. After the insects had spent 8 hours on the substrate, the destruction of the test insects was determined in %. 100% denotes that all test insects had been killed; 0% denotes that none of the test insects had been killed.

The active compounds, their amounts, the nature of the substrates and the results can be seen from the following table:

TABLE B

(Residual Test / *Musca domestica* and *Aedes aegypti*)

Active compound	Test substrates	Test insects	Destruction of the test insects in % after hours (hrs)					
			1	2	4	6	10	12 weeks
$\begin{array}{c} \text{O} \\ \parallel \\ (\text{CH}_3\text{O})_2\text{P}-\text{CH}-\text{CCl}_3 \\ \\ \text{OH} \end{array}$ (known)	Plywood	<i>Aedes aegypti</i>						8 hrs=40
	Clay	<i>Aedes aegypti</i>				8 hrs=0		
	Clay + Lime	<i>Musca domestica</i>	5½ hrs=100					
$\begin{array}{c} \text{S} \\ \parallel \\ (\text{CH}_3\text{O})_2\text{P}-\text{CH}-\text{CCl}_3 \\ \\ \text{OH} \end{array}$ (I)	Plywood	<i>Aedes aegypti</i>						6 hrs=100
	Clay	<i>Aedes aegypti</i>				7½ hrs=100		
	Clay + Lime	<i>Musca domestica</i>	1½ hrs=100					

(14)

Example C.

Test with parasitic fly larvae

Solvent: 35 parts by weight of ethylene polyglycol monomethyl ether

5 Emulsifier: 35 parts by weight of nonyl-phenol polyglycol ether

10 To produce a suitable preparation of active compound, 30 parts by weight of the active substance in question were mixed with the stated amount of solvent which contained the above-mentioned proportion of emulsifier and the concentrate thus obtained was diluted with water to the desired concentration.

About 20 fly larvae (*Lucilia cuprina*) were introduced into a test tube which contained approx. 2 cm³ of horse muscle. 0.5 ml of the preparation of active compound was applied to this horse meat. After 24 hours, the degree of destruction in % was determined. 100% means that all the larvae had been killed and 0% means that no larvae had been killed.

The active compounds investigated, the concentrations of the active compounds used and the results obtained can be seen from the table which follows:

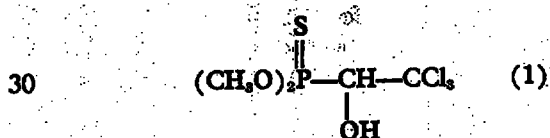
TABLE C

(Test with parasitic fly larvae/*Lucilia cuprina* res.)

Active compound	Active compound concentration in ppm	Degree of destruction in %
S	100	100
	30	100
(CH ₃ O) ₂ P-CH-CCl ₃	10	100
	3	0
OH		
(1)		

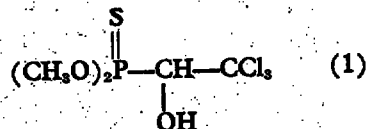
The process of this invention is illustrated by the following preparative Examples.

Example 1.



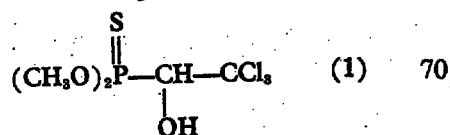
750 g (5.07 moles) of chloral were allowed to run into a mixture of 631 g (5 moles) of thionophosphorus acid dimethyl ester, 2 l of toluene and 10 g of triethylamine over the course of 25 to 30 minutes whilst stirring and applying external cooling, the internal temperature being 15–20°C. After stirring for a further hour at 20°C, the mixture was washed once with very dilute hydrochloric acid and then repeatedly with water, until the wash water reacted neutral. The organic phase was dried over sodium sulphate, treated with a little active charcoal and then freed from the solvent under reduced pressure. 1,330.5 g (97.4% of theory) of 1-hydroxy-2,2,2-trichloroethane-thionophosphonic acid dimethyl ester remained as a colourless oil of refractive index n_D^{20} : 1.5338. The product could be distilled *in vacuo* and had a boiling point of 116°C/2 mm Hg.

Example 2.



0.33 g of potassium hydroxide powder (86% strength) was added to a mixture of 12.6 g (0.1 mole) of thionophosphorus acid dimethyl ester and 100 ml of toluene at 10°C. After 5 minutes, 14.8 g (0.1 mole) of chloral, dissolved in 50 ml of toluene, were added dropwise whilst stirring and applying external cooling, the internal temperature being 10° to 15°C. The reaction mixture was stirred for a further hour at 50°C. After adding 3 g of kieselguhr, the solid products were filtered off at the pump. The filtrate, after washing with water and evaporating the solvent under reduced pressure, gave 24.2 g (89% of theory) of 1-hydroxy-2,2,2-trichloroethane-thionophosphonic acid dimethyl ester.

Example 3.

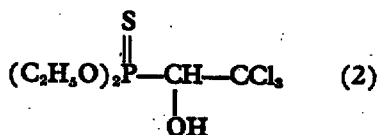


The same procedure as in Example 2 gave 24.3 g (89% of theory) of 1-hydroxy-2,2,2-

trichloroethane - thionophosphonic acid dimethyl ester when 0.7 g of potassium carbonate powder was used in place of the potassium hydroxide.

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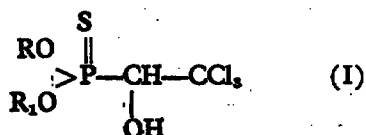
Example 4.



74.2 g (0.5 mole) of chloral were added dropwise over the course of 10 to 15 minutes to a mixture of 77.1 g (0.5 mole) of thionophosphorous acid diethyl ester, 200 ml of toluene and 1 g of triethylamine whilst stirring and applying external cooling, the internal temperature being 15° to 20°C, and the reaction mixture was then stirred for 30 minutes at 25°C. After working up, which took place as in Example 1, 143.4 g (95% of theory) of 1-hydroxy-2,2,2-trichloroethane-thionophosphonic acid diethyl ester were obtained in the form of a colourless oil which had a boiling point of 104°C/0.4 mm Hg and a refractive index n_D^{21} of 1.5104.

WHAT WE CLAIM IS:—

1. 1 - Hydroxy - 2,2,2 - trichloroethane-thionophosphonic acid dialkyl esters of the general formula

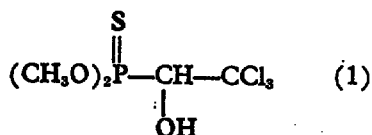


in which

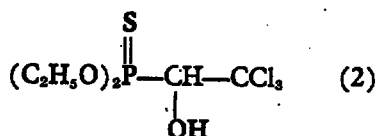
R and R_1 , which may be identical or different, are each an alkyl radical with 1 to 4 carbon atoms.

2. Compounds according to claim 1, in which R and R_1 are each a straight or branched alkyl radical with 1 to 3 carbon atoms.

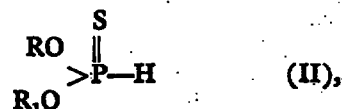
3. The compound of the formula



4. The compound of the formula



5. A process for the preparation of a 1-hydroxy - 2,2,2 - trichloroethane - thionophosphonic acid dialkyl ester according to any of claims 1 to 4, in which a thionophosphorus acid dialkyl ester of the general formula



in which

R and R_1 have the meanings stated in claim 1, is reacted with chloral, of the formula



in the presence of a basic catalyst.

6. A process according to claim 5, in which the reaction is effected in the presence of an inert solvent.

7. A process according to claim 5 or 6, in which the basic catalyst is an aliphatic, aromatic or heterocyclic amine, or an alkali metal hydroxide or carbonate.

8. A process according to claim 6, 7 or 8, in which the reaction is effected at between -20° and +80°C.

9. A process according to claim 8, in which the reaction is effected at from 0° to 30°C.

10. A process according to any of claims 5 to 9, in which the dialkyl ester (II) and the chloral (III) are employed in equimolar amounts, the basic catalyst being employed in an amount of 2 to 10 mole per cent.

11. A process for the preparation of a 1-hydroxy - 2,2,2 - trichloroethane - thionophosphonic acid dialkyl ester, substantially as described in any one of Examples 1 to 4.

12. A compound according to claim 1, whenever prepared by a process according to any of claims 5 to 11.

13. An arthropodicidal composition containing as active ingredient a compound according to any of claims 1 to 4 and 12 in admixture with a solid or liquefied gaseous diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.

14. A composition according to claim 13 containing from 0.1 to 95% of the active compound, by weight.

15. A composition according to claim 14 containing from 0.5 to 90% of the active compound, by weight.

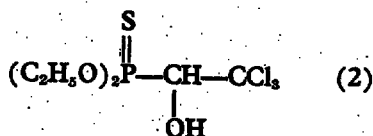
16. A method of combating arthropods which comprises applying to the arthropods or an arthropod habitat a compound according to any of claims 1 to 4 and 12 alone or in the form of a composition containing as active ingredient a compound according to any of claims 1 to 4 and 12 in admixture with a diluent or carrier.



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trichloroethane - thionophosphonic acid dimethyl ester when 0.7 g of potassium carbonate powder was used in place of the potassium hydroxide.

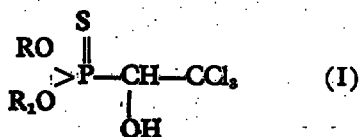
Example 4.



74.2 g (0.5 mole) of chloral were added dropwise over the course of 10 to 15 minutes to a mixture of 77.1 g (0.5 mole) of thionophosphorous acid diethyl ester, 200 ml of toluene and 1 g of triethylamine whilst stirring and applying external cooling, the internal temperature being 15° to 20°C, and the reaction mixture was then stirred for 30 minutes at 25°C. After working up, which took place as in Example 1, 143.4 g (95% of theory) of 1-hydroxy-2,2,2-trichloroethane-thionophosphonic acid diethyl ester were obtained in the form of a colourless oil which had a boiling point of 104°C/0.4 mm Hg and a refractive index n_D^{21} of 1.5104.

WHAT WE CLAIM IS:—

1. 1 - Hydroxy - 2,2,2 - trichloroethane-thionophosphonic acid dialkyl esters of the general formula

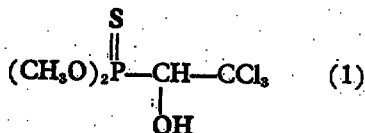


in which

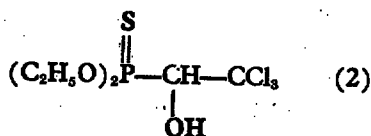
R and R_1 , which may be identical or different, are each an alkyl radical with 1 to 4 carbon atoms.

2. Compounds according to claim 1, in which R and R_1 are each a straight or branched alkyl radical with 1 to 3 carbon atoms.

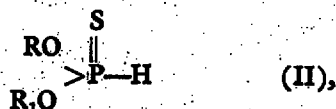
3. The compound of the formula



4. The compound of the formula



5. A process for the preparation of a 1-hydroxy - 2,2,2 - trichloroethane - thionophosphonic acid dialkyl ester according to any of claims 1 to 4, in which a thionophosphorus acid dialkyl ester of the general formula



in which

R and R_1 have the meanings stated in claim

1, is reacted with chloral, of the formula



in the presence of a basic catalyst.

6. A process according to claim 5, in which the reaction is effected in the presence of an inert solvent.

7. A process according to claim 5 or 6, in which the basic catalyst is an aliphatic, aromatic or heterocyclic amine, or an alkali metal hydroxide or carbonate.

8. A process according to claim 6, 7 or 8, in which the reaction is effected at between -20° and +80°C.

9. A process according to claim 8, in which the reaction is effected at from 0° to 30°C.

10. A process according to any of claims 5 to 9, in which the dialkyl ester (II) and the chloral (III) are employed in equimolar amounts, the basic catalyst being employed in an amount of 2 to 10 mole per cent.

11. A process for the preparation of a 1-hydroxy - 2,2,2 - trichloroethane - thionophosphonic acid dialkyl ester, substantially as described in any one of Examples 1 to 4.

12. A compound according to claim 1, whenever prepared by a process according to any of claims 5 to 11.

13. An arthropodicidal composition containing as active ingredient a compound according to any of claims 1 to 4 and 12 in admixture with a solid or liquefied gaseous diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.

14. A composition according to claim 13 containing from 0.1 to 95% of the active compound, by weight.

15. A composition according to claim 14 containing from 0.5 to 90% of the active compound, by weight.

16. A method of combating arthropods which comprises applying to the arthropods or an arthropod habitat a compound according to any of claims 1 to 4 and 12 alone or in the form of a composition containing as active ingredient a compound according to any of claims 1 to 4 and 12 in admixture with a diluent or carrier.



17. A method according to claim 16 in which a composition is used containing from 0.0001 to 10% of the active compound, by weight.
- 5 18. A method according to claim 17 in which a composition is used containing from 0.01 to 1% of the active compound, by weight.
- 10 19. A method according to claim 16, 17 or 18 in which the active compound is applied to insects or an insect habitat.
20. Crops protected from damage by

arthropods by being grown in areas in which immediately prior to and/or during the time of the growing a compound according to any of claims 1 to 4 and 12 was applied alone or in admixture with a diluent or carrier.

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