

PATENT SPECIFICATION

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(54) PROCESS FOR THE PREPARATION OF THE O,O-DIMETHYL-O-(2,2-DICHLOROVINYL) ESTER AND THE O,O-DIETHYL-O-(2,2-DICHLOROVINYL) ESTER OF THIONOPHOSPHORIC ACID

(71) We, BAYER AKTIENGESSELLSCHAFT, 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:—

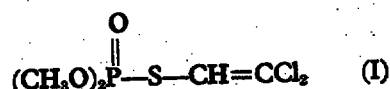
The present invention relates to a process for the preparation of the O,O - dimethyl - O - (2,2 - dichlorovinyl) ester or the O,O - diethyl - O - (2,2 - dichlorovinyl) ester of thionophosphoric acid, which esters are known as insecticides.

It has already been disclosed in the literature that the O,O - dimethyl - O - (2,2 - dichlorovinyl) ester of thionophosphoric acid can be obtained when the O - (2,2 - dichlorovinyl) ester of thionophosphoric acid dichloride is reacted with methanol. However, this process has a number of disadvantages. Thus, the O - (2,2 - dichlorovinyl) ester of thionophosphoric acid dichloride which is required as the starting material is obtained in poor yields (less than 30% of theory) from the corresponding oxygen compound by reaction with phosphorus pentasulphide only at very high temperatures (about 150°C). Moreover, the further reaction of the dichloride with methanol can be carried out only with a yield of 50% of theory, so that the total yield for both stages is about 15%. The usefulness of this process is therefore limited (see DT-OS (German Published Specification) 2,150,108).

It is also known that the compounds prepared according to the process of DT-AS (German Published Specification) 1,058,046 do not have the structure of O,O - dialkyl - O - (2,2 - dichlorovinyl) esters of thionophosphoric acid (see DT-OS (German Published Specification) 2,133,199).

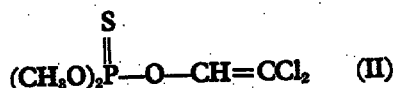
Moreover, it is stated in the literature that it is not possible to prepare the O,O - dimethyl - O - (2,2 - dichlorovinyl) ester of thionophosphoric acid starting from dimethyl

thiol-phosphite and chloral since the reaction takes another course (see Belgian Patent Specification 632,551 and Pelchowicz, J. Chem. Soc. 1961, page 241 *et seq.*). The isomeric compound of the formula



is obtained as the end product.

It is known, from DT-OS (German Published Specification) 2,150,108, pages 3 and 4, that the customary methods for obtaining vinyl phosphates and certain thiophosphates fail in the case of the preparation of the corresponding thiono compound of the formula



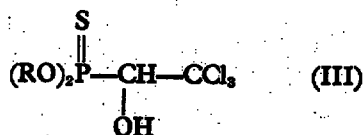
According to that specification, the classical Perkov reaction, which is employed for the preparation of vinyl phosphates, does not lead to the corresponding vinyl thiophosphates. When a trialkyl thiophosphite (trialkyl phosphorothioite) is reacted with chloral the product which results from this reaction is an O,S - dialkyl - O - halogeno - vinyl thiol-phosphate. Other customary processes are also stated to be unsuitable.

It is also known that the compound of the formula (II) is obtained, according to DT-OS (German Published Specification) 2,238,921, by allowing chloral and an alkali metal alcoholate to act on dimethyl thiophosphite in the presence of a base as the catalyst. This process also entails certain difficulties, since it is known that O,O - dialkyl esters of thiophosphorous acid form alkali metal salts in inert solvents, which salts are saponified by moisture or by treatment with water in a short time to give salts of O - monoalkyl esters of thiophosphorous acid. The alkali metal salts

also form in excess alcohol on the addition of alcoholate (see Houben Weyl, Volume XII/2, page 97).

In all cases part of the O,O - dialkyl ester of thiophosphorous acid is withdrawn from the actual reaction by this side reaction or alternative reaction. There is therefore great interest in a process which obviates the difficulties of the prior art.

The present invention provides a process for the preparation of the O,O - dimethyl - O - (2,2 - dichlorovinyl) ester or the O,O - diethyl - O - (2,2 - dichlorovinyl) ester of thiophosphoric acid, in which the O,O - dimethyl ester or the O,O - diethyl ester, respectively, of 1 - hydroxy - 2,2,2 - trichloroethane - thionophosphonic acid, of the general formula



in which

R is a methyl or ethyl radical, is reacted at from -20° to $+100^\circ\text{C}$ with (a) a solution of an equivalent amount of an alkali metal alcoholate in an inert organic solvent or (b) a solution in an alcohol of an alkali metal hydroxide or an alkali metal carbonate, if appropriate in the presence of water, and optionally in the presence of another inert organic solvent.

In process variant (b), the presence of water may be necessary in order to obtain a solution of the alkali metal carbonate, if such is used.

It is to be regarded as extremely surprising that the process according to the invention leads to the desired ester because, in view of the state of the art, a product corresponding to the formula (I), or its O,O - diethyl analogue, would have been expected.

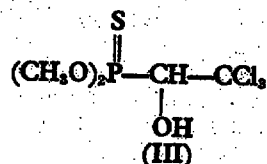
The process according to the invention has a number of advantages and represents a new route, which was not hitherto known and which also was not regarded as being capable of realisation, to the desired O,O - dimethyl - O(2,2 - dichloro - vinyl) ester and the O,O - diethyl - O - (2,2 - dichlorovinyl) ester of thiophosphoric acid. The new pro-

cess dispenses with the use of expensive crystalline (solid) sodium alcoholate (compare DT-OS (German Published Specification) 2,150,108, page 10). The O,O - dimethyl ester or O,O - diethyl ester of 1 - hydroxy - 2,2,2 - trichloroethane thionophosphonic acid, which is required as the starting material, can be prepared in a high yield in a technically simple manner, whereas the intermediate required according to DT-OS (German Published Specification) 2,150,108 is obtainable only in about 30% yield and by means of a process which industrially can be controlled only with difficulty. The accessibility of the intermediate used in the present invention is therefore much better than that of the intermediate required according to DT-OS (German Published Specification) 2,150,108.

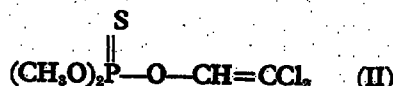
Moreover, the process according to this invention has the advantage that it is possible to dispense with the use of expensive solid sodium alcoholate and to use instead a solution of sodium methylate or sodium ethylate in methanol or ethanol, respectively. Moreover, 2 moles of sodium methylate are required per mole of the intermediate according to DT-OS (German Published Specification) 2,150,108, whereas only 1 mole of sodium alcoholate dissolved in methanol or ethanol is required according to the present invention, which signifies a considerable saving.

A further advantage of the process according to the invention is that, according to one variant, the use of sodium alcoholate is completely dispensed with and a solution of an alkali metal hydroxide or alkali metal carbonate in methanol or ethanol may be employed with equal success.

If the O,O - dimethyl ester of 1 - hydroxy - 2,2,2 - trichloro - ethane - thionophosphonic acid is used as the starting material and a solution of an alkali metal hydroxide or alkali metal carbonate in methanol is used, the course of reaction can be represented by the following equation:



alkali metal hydroxide or alkali metal carbonate in methanol



The O,O - dimethyl ester and O,O - diethyl ester of 1 - hydroxy - 2,2,2 - trichloroethane - thionophosphonic acid, which are to be used as the starting materials, have not yet been described hitherto in the literature but

can be obtained from dimethyl thiolphosphite or diethyl thiolphosphite, respectively, and chloral.

The process variant (b) according to the invention can be carried out without or with

the use of additional solvents. Solvents which can be used are all inert organic solvents, especially hydrocarbons, such as benzene, benzene and toluene; ethers, such as diethyl ether and dioxane; chlorinated hydrocarbons, such as methylene chloride and ethylene chloride; ketones, such as acetone and butanone; and nitriles, such as acetonitrile and benzonitrile.

It may be possible to effect process variant (a) in any of these solvents, as well as in alcohols such as propanol and butanol, provided that the solvent does not react with the alcoholate; however, preference is given to methanol or ethanol since, in this way, trans-esterifications can be excluded. Methanol and ethanol are the preferred alcohols in variant (b), for the same reason.

The reaction is preferably carried out at a temperature between $+10^{\circ}$ and $+20^{\circ}\text{C}$; it is also generally effected under normal pressure.

When carrying out the process according to the invention, 1 mole of alkali metal hydroxide or $1/2$ mole of alkali metal carbonate is preferably employed per mole of the O,O-dimethyl ester or O,O - diethyl ester of 1-hydroxy - 2,2,2 - trichloroethane - thionophosphonic acid. Relatively large deviations from this ratio result in an impure product and a high loss in yield.

The compounds of the formula (III) and their preparation are disclosed and claimed in U.K. Patent Application 11165/76 (Serial No. 1,488,334).

As already mentioned, the O,O - dimethyl - O - (2,2 - dichlorovinyl) ester and O,O - diethyl - O - (2,2 - dichlorovinyl) ester of thionophosphoric acid may be used as pest control agents, above all as insecticides, especially for plant protection and in the field of hygiene and the protection of stored products.

To the sucking insects there belong, in the main, aphids (*Aphididae*) such as the green peach aphid (*Myzus persicae*), the bean aphid (*Doralis fabae*), the bird cherry aphid (*Rhopalosiphum padi*), the pea aphid (*Macrosiphum pisi*) and the potato aphid (*Macrosiphum solanifolii*), the currant gall aphid (*Cryptomyzus korschelti*), the rosy apple aphid (*Sappaphis mali*), the mealy plum aphid (*Hyalopterus arundinis*) and the cherry black-fly (*Myzus cerasi*); in addition, scales and mealybugs (*Coccinea*), for example the oleander scale (*Aspidiotus hederæ*) and the soft scale (*Lecanium hesperidum*) as well as the grape mealybug (*Pseudococcus maritimus*); thrips (*Thysanoptera*), such as *Hercinothrips femoralis*, and bugs, for example the beet bug (*Piesma quadrata*), the red cotton bug (*Dysdercus intermedius*), the bed bug (*Cimex lectularius*), the assassin bug (*Rhodnius prolixus*) and Chagas' bug (*Triatoma infestans*) and, further cicadas, such as *Euscelis bilobatus* and *Nephotettix bipunctatus*.

In the case of the biting insects, above all there should be mentioned butterfly caterpillars (*Lepidoptera*) such as the diamond-back moth (*Plutella maculipennis*), the gipsy moth (*Lymantria dispar*), the brown-tail moth (*Euproctis chrysorrhoea*) and tent caterpillar (*Malacosoma neustria*); further, the cabbage moth (*Manestra brassicae*) and the cut-worm (*Agrotis segetum*), the large white butterfly (*Pieris brassicae*), the small winter moth (*Cheimatobia brumata*), the green oak tortrix moth (*Tortrix viridana*), the fall armyworm (*Laphygma frugiperda*) and cotton worm (*Prodenia litura*), the ermine moth (*Hyponomeuta padella*), the Mediterranean flour moth (*Ephestia kuehniella*) and greater wax moth (*Galleria mellonella*).

The active compounds prepared according to the present invention can be converted into the usual formulations, such as solutions, emulsions, suspensions, powders, pastes and granulates. These 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 benzenes, 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

(B)

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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.

In general, the formulations 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 in the use forms prepared therefrom, such as ready-to-use solutions, emulsions, foams, suspensions, powders, pastes, soluble powders, dusting agents and granules. 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 between 0.0001 and 10%, preferably between 0.01 and 1% by weight.

The active compounds can also be used with good success in the ultra-low-volume (ULV) method where it is possible to apply formulations of up to 95% by weight active compound or even to use the active compound by itself.

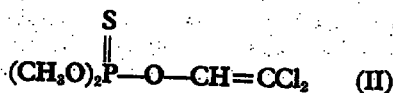
The present invention therefore also provides an insecticidal composition containing as active ingredient a compound whenever prepared according to the present invention in admixture with a solid or liquefied gaseous diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.

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

The present invention further provides crops protected from damage by insects by being grown in areas in which immediately prior to and/or during the time of the growing a compound whenever prepared according to 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.

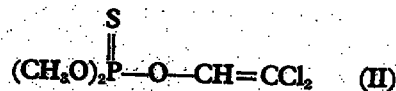
The examples which follow illustrate the process according to the present invention.

Example 1



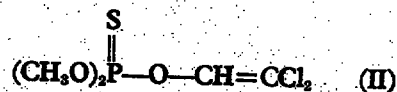
2.3 g of sodium dissolved in methanol were added dropwise at 10° to 20°C to a solution of 27.3 g (0.1 mole) of the O,O - dimethyl ester of 1 - hydroxy - 2,2,2 - trichloroethane - thionophosphonic acid in 50 ml of methanol. The batch was stirred for 15 minutes at 30°C, cooled and stirred in ice water. The aqueous solution was extracted twice with methylene chloride and the combined methylene chloride extracts were washed once with water and then dried. After distilling off the solvent under reduced pressure, 23.5 g of an oil, which, according to gas chromatographic determination, contained 92.4% of the O,O - dimethyl - O - (2,2-dichlorovinyl) ester of thiophosphoric acid, were obtained. The crude product could be distilled. It boiled at 76 to 80°C under a pressure of 2 mm Hg; the refractive index n_D^{22} was 1.4964. The structure of the compound was verified by NMR spectroscopy.

Example 2



A solution consisting of 6.9 g of potassium carbonate, 20 ml of methanol and 20 ml of water was added dropwise at 30°C to a solution of 27.3 g (0.1 mole) of the O,O - dimethyl ester of 1 - hydroxy - 2,2,2 - trichloroethane - thionophosphonic acid in 30 ml of methanol. The further procedure was then as described in Example 1. 23.6 g of an oil, which, according to gas chromatographic determination, contained 58% of theory of the O,O - dimethyl - O - (2,2 - dichlorovinyl) ester of thiophosphoric acid, were obtained.

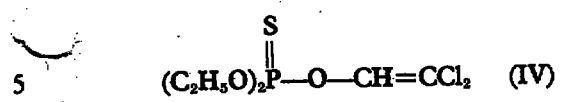
Example 3



A solution of 21.6 g (0.54 mole) of sodium hydroxide in 100 g of methanol was added dropwise, whilst stirring and with external cooling, in the course of 20 minutes to a mixture of 137.0 g (0.5 mole) of O,O - dimethyl 1 - hydroxy - 2,2,2 - trichloroethane - thionophosphate and 200 ml of toluene, the internal temperature being kept at between 15° and 20°C. After stirring for 1 hour at 20°C, the reaction mixture was extracted by shaking with four to five times 200 to 250 ml of water and the organic phase was then dried with 25 g of sodium sulphate and freed from solvent in a rotary evaporator under reduced pressure. On fractional distillation the residue gave 95.5 g (80.5% of theory) of the O,O - dimethyl O - (2,2 - dichlorovinyl) ester of thiophosphoric acid as a colourless liquid

with a boiling point of 78°C/2 mm Hg. The refractive index n_D^{19} was 1.4990. Content according to gas chromatogram: 99.2%.

Example 4

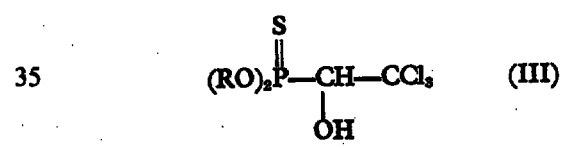


An ethanolic solution containing 5 moles of sodium ethylate was allowed to flow, in the course of one hour, into a solution of 1,508 g (5 moles) of O,O - diethyl 1 - hydroxy-2,2,2 - trichloroethane - thionophosphonate in 2 l of toluene, whilst stirring and with external cooling, at an internal temperature of 15° to 20°C. After stirring the mixture for 1 hour, it was washed with water and dried and the solvent was stripped off under reduced pressure. 994.1 g (75.0% of theory) of the O,O - diethyl - O - S 2,2 - dichlorovinyl) ester of thionophosphoric acid remain as a pale yellowish coloured liquid with a boiling point of 89°C/2 mm Hg and a refractive index n_D^{18} of 1.4875.

Having regard to the provisions of Section 9 of the Patents Act, 1949, attention is hereby directed to the claims of U.K. Patent Specification No. 1,341,506.

WHAT WE CLAIM IS:—

1. A process for the preparation of the O,O - dimethyl - O - (2,2 - dichlorovinyl) ester or O,O - diethyl - O - (2,2 - dichlorovinyl) ester of thionophosphoric acid, in which the O,O - dimethyl ester or the O,O - diethyl ester, respectively, of 1 - hydroxy-2,2,2 - trichloroethane - thionophosphonic acid, of the general formula



in which

R is a methyl or ethyl radical, is reacted at -20° to 100°C with (a) a solution of an equivalent amount of an alkali metal alcoholate in an inert organic solvent or (b) a solution in an alcohol of an alkali metal hydroxide or alkali metal carbonate, if appropriate in the presence of water, and optionally in the presence of another inert organic solvent.

2. A process according to claim 1(b), in which methanol is used as the alcohol.

3. A process according to claim 1(b), in which ethanol is used as the alcohol.

4. A process according to claim 1(b), 2 or 3 in which 1 mole of alkali metal hydroxide or 1/2 mole of alkali metal carbonate is employed per mole of the O,O - dimethyl ester or O,O - diethyl ester of 1 - hydroxy-2,2,2-trichloroethane - thionophosphonic acid.

5. A process according to claim 1(a), in which the ester (III) is treated with a solution of sodium methylate or sodium ethylate in methanol or ethanol, respectively.

6. A process according to any of claims 1 to 5, in which the reaction is carried out at temperatures between +10° and +20°C.

7. A process for the preparation of the O,O - dimethyl - O - (2,2 - dichlorovinyl) ester or O,O - diethyl - O - (2,2 - dichlorovinyl) ester of thionophosphoric acid, being a process substantially as herein described in any one of Examples 1 to 4.

8. The O,O - dimethyl - O - (2,2 - dichlorovinyl) ester or O,O - diethyl - O - (2,2 - dichlorovinyl) ester of thionophosphoric acid whenever prepared by a process according to any of claims 1 to 7.

9. An insecticidal composition containing as active ingredient a compound according to claim 8 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.

10. A composition according to claim 9 containing from 0.1 to 95% of the active compound, by weight.

11. A composition according to claim 10 containing from 0.5 to 90% of the active compound, by weight.

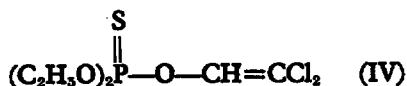
12. A method of combating insects which comprises applying to the insects or an insect habitat a compound according to claim 8 alone or in the form of a composition containing as active ingredient a compound according to claim 8 in admixture with a diluent or carrier.

13. Crops protected from damage by insects by being grown in areas in which immediately prior to and/or during the time of the growing a compound according to claim 8 was applied alone or in admixture with a diluent or carrier.

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with a boiling point of 78°C/2 mm Hg. The refractive index n_D^{19} was 1.4990. Content according to gas chromatogram: 99.2%.

Example 4

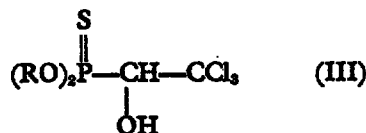


An ethanolic solution containing 5 moles of sodium ethylate was allowed to flow, in the course of one hour, into a solution of 1,508 g (5 moles) of O,O - diethyl 1 - hydroxy-2,2,2 - trichloroethane - thionophosphonate in 2 l of toluene, whilst stirring and with external cooling, at an internal temperature of 15° to 20°C. After stirring the mixture for 1 hour, it was washed with water and dried and the solvent was stripped off under reduced pressure. 994.1 g (75.0% of theory) of the O,O - diethyl - O - S 2,2 - dichlorovinyl ester of thionophosphoric acid remain as a pale yellowish coloured liquid with a boiling point of 89°C/2 mm Hg and a refractive index n_D^{18} of 1.4875.

Having regard to the provisions of Section 9 of the Patents Act, 1949, attention is hereby directed to the claims of U.K. Patent Specification No. 1,341,506.

WHAT WE CLAIM IS:—

1. A process for the preparation of the O,O - dimethyl - O - (2,2 - dichlorovinyl) ester or O,O - diethyl - O - (2,2 - dichlorovinyl) ester of thionophosphoric acid, in which the O,O - dimethyl ester or the O,O - diethyl ester, respectively, of 1 - hydroxy-2,2,2 - trichloroethane - thionophosphonic acid, of the general formula



in which

R is a methyl or ethyl radical, is reacted at -20° to 100°C with (a) a solution of an equivalent amount of an alkali metal alcoholate in an inert organic solvent or (b) a solution in an alcohol of an alkali metal hydroxide or alkali metal carbonate, if appropriate in the presence of water, and optionally in the presence of another inert organic solvent.

2. A process according to claim 1(b), in which methanol is used as the alcohol.

3. A process according to claim 1(b), in which ethanol is used as the alcohol.

4. A process according to claim 1(b), 2 or 3 in which 1 mole of alkali metal hydroxide or 1/2 mole of alkali metal carbonate is employed per mole of the O,O - dimethyl ester or O,O - diethyl ester of 1 - hydroxy - 2,2,2-trichloroethane - thionophosphonic acid.

5. A process according to claim 1(a), in which the ester (III) is treated with a solution of sodium methylate or sodium ethylate in methanol or ethanol, respectively.

6. A process according to any of claims 1 to 5, in which the reaction is carried out at temperatures between +10° and +20°C.

7. A process for the preparation of the O,O - dimethyl - O - (2,2 - dichlorovinyl) ester or O,O - diethyl - O - (2,2 - dichlorovinyl) ester of thionophosphoric acid, being a process substantially as herein described in any one of Examples 1 to 4.

8. The O,O - dimethyl - O - (2,2 - dichlorovinyl) ester or O,O - diethyl - O - (2,2 - dichlorovinyl) ester of thionophosphoric acid whenever prepared by a process according to any of claims 1 to 7.

9. An insecticidal composition containing as active ingredient a compound according to claim 8 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.

10. A composition according to claim 9 containing from 0.1 to 95% of the active compound, by weight.

11. A composition according to claim 10 containing from 0.5 to 90% of the active compound, by weight.

12. A method of combating insects which comprises applying to the insects or an insect habitat a compound according to claim 8 alone or in the form of a composition containing as active ingredient a compound according to claim 8 in admixture with a diluent or carrier.

13. Crops protected from damage by insects by being grown in areas in which immediately prior to and/or during the time of the growing a compound according to claim 8 was applied alone or in admixture with a diluent or carrier.

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