

PATENT SPECIFICATION

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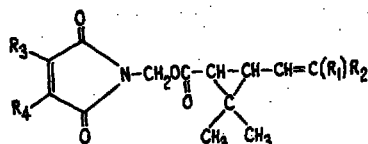
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(54) MALEIMIDOMETHYLCYCLOPROPANECARBOXYLATES, PROCESS FOR THEIR PRODUCTION AND PESTICIDAL COMPOSITIONS CONTAINING THEM

(71) We, SUMITOMO CHEMICAL COMPANY LIMITED, a corporation organized under the laws of Japan, of 15, Kitahama-5-chome, Higashi-ku, Osaka, Japan, 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 provides a cyclopropanecarboxylic acid ester of the general formula (I),



wherein R₁ is a hydrogen atom, a methyl group or a fluorine, chlorine or bromine atom, R₂ is a fluorine, chlorine or bromine atom, and each of R₃ and R₄ is independently a hydrogen atom, a C₁—C₈ alkyl, C₂—C₈ alkenyl or C₂—C₈ alkynyl group, an alkyl- or halogen-substituted aryl group, an unsubstituted aryl group or an aralkyl group.

Compounds within the present invention can be obtained at low cost and are useful as insecticides or acaricides, since they are of low toxicity to mammals but have a strong insecticidal activity and a rapid insecticidal effect. They can be used to protect agricultural or horticultural crops as well as to safeguard public health.

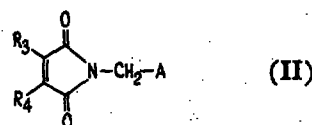
Among the known insecticides are pyrethrum extracts (containing pyrethrin) and synthetic allethrin which is a homologue of the active ingredient of these extracts. These have been widely used for the control of harmful insects because of their rapid effect upon insects and their low toxicity to mammals. However, the pyrethrum extracts tend to be limited in their

use owing to the relatively high cost, in spite of their excellent properties.

We have synthesized various cyclopropanecarboxylic acid esters and tested their biological activity. As a result, it was found that esters within the present invention, hereinafter called "the present esters" or "the present compounds" have an excellent knock-down effect and insecticidal activity against insani- tary insects, for example, houseflies, and particularly against insects harmful to agricultural crops, examples of which insects are green rice leaf-hoppers, diamond-back moths, army- worms and cutworms, and, in addition have a repellency effect on mites which are para- sitic on animals and plants. We have further found that the present esters are of low toxicity to mammals and can be prepared at a low cost.

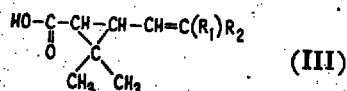
The present esters can be widely used to safeguard public health, and in addition, they have a strong insecticidal activity against insects harmful to stored cereals and agri- cultural or forest plants, and against mites which are parasitic on animals. Therefore they are very useful for controlling these insects. Particularly, they have such a low toxicity to mammals that they can be used for protecting agricultural crops before harvest, greenhouse cultivations, household horticultural plants and food-packaging.

A cyclopropanecarboxylic acid ester of the formula (I) can be obtained by reacting an alcohol, halide or arylsulfonate, of the general formula (II),



wherein R₃ and R₄ are as defined above, and A is a hydroxyl group, a halogen atom, or

an arylsulfoxy group with a cyclopropane-carboxylic acid of the general formula (III),



wherein R_1 and R_2 are as defined above, or a reactive derivative thereof, optionally in the presence of a suitable solvent, reaction assistant or catalyst.

The abovementioned reactive derivative of the cyclopropanecarboxylic acid may be an acid halide, acid anhydride, alkali metal salt thereof or an organic tertiary amine salt thereof.

The esters of the formula (I) have geometrical isomers due to the stereo structure of the carboxylic acid (III) and optical isomers due to the asymmetric carbon atoms of the carboxylic acid (III), and all of these isomers are within the scope of the present invention.

General methods embodying the invention for the preparation of the present compounds of the formula (I) will be illustrated in more detail below.

The first general method comprises reacting an alcohol of the formula (II) with a carboxylic acid of the formula (III) or an acid halide or acid anhydride thereof.

When the carboxylic acid itself is used, the reaction is preferably carried out under conditions which promote dehydration. Thus, the alcohol can be reacted with the carboxylic acid at room temperature or with heating, in a suitable inert solvent such as benzene or petroleum ether in the presence of a dehydrating agent such as dicyclohexylcarbodiimide.

When a carboxylic acid halide is used, the reaction can be sufficiently accomplished at room temperature by reacting the alcohol with the acid halide using as a hydrogen halide acceptor, for example, an organic tertiary base, e.g. pyridine or triethylamine. The acid halide used in this case may optionally be selected from any such halide, but is preferably an acid chloride. In this reaction, the presence of a solvent is desirable for smooth progress of the reaction and an inert solvent such as benzene, toluene or petroleum ether is usually used.

When the carboxylic acid anhydride is used, the reaction can be achieved by reacting the alcohol with the acid anhydride at room temperature and no particular reaction assistant is required. In this case, heating of the reaction system and the use of an inert solvent are desirable for smooth progress of the reaction, but they are not essential.

In the second general method for obtaining an ester of the formula (I) a compound which is obtained by substituting the hydroxyl group of the alcohol of formula (II) with a halogen

atom is used. The halogen atom is preferably a chlorine or bromine atom but alternatively, any other halogen atom can optionally be selected. The carboxylic acid of the formula (III) which is the other reactant can be used in the form of an alkali metal salt or an organic tertiary base salt. Alternatively, a base which can form one of these salts may be added to the reaction system together with the carboxylic acid. In this case, it is desirable for improved performance of the reaction to use a suitable inert solvent such as benzene or acetone and to heat the reaction system at the boiling point of the solvent used or at a temperature slightly below this.

In the third general method for obtaining an ester of the formula (I) a compound which is obtained by substituting the hydroxyl group of the alcohol of formula (II) with an arylsulfoxy group is used. The other reactant and the reaction conditions used herein are the same as those described in the second general method.

The previously mentioned halogen or sulfoxy compound of the formula (II) can easily be prepared by respectively halogenating the alcohol of formula (II), or by reacting the alcohol of formula (II) with p-toluenesulfonic acid chloride.

Methods for the production of compounds of the present invention will now be illustrated in more detail with reference to the procedures given below. Specific esters within the present invention were produced by one of these standard procedures each represented by A, B, C, D and E as follows. These esters are given in a subsequent Table.

Method A: The reaction between an alcohol of the formula (II) and a carboxylic acid halide.

An alcohol (0.05 mole) is dissolved in three times its volume of dry benzene and 0.075 mole of pyridine is added to the solution. Separately, 0.053 mole of a carboxylic acid chloride is dissolved in three times its volume of dry benzene and the resulting solution is added in portions to the former solution. The reaction proceeds with generation of heat. The reaction mixture is allowed to stand overnight in a tightly sealed vessel. Thereafter, a small amount of water is added thereto to dissolve the pyridine hydrochloride thus deposited and the aqueous layer is separated. The organic layer obtained is washed successively with a 5% by weight aqueous hydrochloric acid solution, an aqueous solution saturated with sodium hydrogen carbonate and then a saturated aqueous solution of sodium chloride. After drying over anhydrous sodium sulfate, the benzene is removed under reduced pressure and the residue obtained is purified by chromatography on silica gel to obtain the desired ester.

Method B: The dehydration reaction between an alcohol of the formula (II) and a carboxylic acid of the formula (III).

5 An alcohol (0.05 mole) and a carboxylic acid (0.05 mole) are dissolved in three times their volume of benzene. To the solution is added 0.08 mole of dicyclohexylcarbodiimide, and the mixture is allowed to stand overnight in a tightly sealed vessel, then refluxed for 10 two hours to complete the reaction and subjected to the same after-treatment as that described in the standard Method A to obtain the desired compound.

15 Method C: The reaction between an alcohol of the formula (II) and a carboxylic acid anhydride.

An alcohol (0.05 mole) is dissolved in three times its volume of toluene and 0.05 mole of a carboxylic acid anhydride (prepared from the carboxylic acid and acetic anhydride) is added thereto. The mixture is reacted at 20 100°C for 3 hours with heating and then cooled. The reaction mixture is neutralized with a 10% by weight aqueous solution of sodium hydroxide at a temperature lower 25 than 10°C and the carboxylic acid resulting from the reaction is recovered as the sodium salt thereof from the aqueous layer. The organic layer is treated in the same manner as 30 that described in the standard Method A to obtain the desired ester.

35 Method D: The reaction between a halogenated methyl compound of the formula (II) and the carboxylic acid of the formula (III).

A halogenated methyl compound (0.05 mole) and a carboxylic acid (0.06 mole) are dissolved in three times their volume of 40 acetone. The resulting solution is kept at 15° to 20°C, and a solution of 0.08 mole of tri-

ethylamine in three times its volume of acetone is gradually added dropwise to the solution with stirring. After the addition is complete, the solution is refluxed for 2 hours to complete the reaction and then cooled. The precipitated triethylamine hydrochloride is filtered off and the filtrate is distilled to remove the acetone under reduced pressure. To the residual solution is added three times its volume of benzene and the organic layer is 45 then treated using the same procedure as that described in the standard Method A to obtain the desired ester. 50

Method E: The reaction between an arylsulfonate of the alcohol of the formula (II) and a carboxylic acid salt of the formula (III). 55

An arylsulfonate (0.05 mole) is dissolved in three times its volume of acetone and 0.06 mole of a sodium carboxylate (which has been prepared by reacting equimolar amounts of the carboxylic acid and sodium hydroxide in water and distilling off the water to obtain a dry mass) is gradually added to the solution at room temperature with stirring. After the addition, the mixture is refluxed for 30 minutes to complete the reaction. After cooling, the deposited solid matter is filtered off and the filtrate is distilled to remove the acetone under reduced pressure. The residue is dissolved in 65 three times its volume of benzene and the same after-treatment as that described in the standard Method A is then carried out to obtain the desired compound. 70

Esters obtained using the abovementioned standard procedures are shown in the following Table together with the starting materials from which they were prepared. The symbols (C) and (F) in the elementary analysis column mean the calculated theoretical value and found measured value, respectively. 75 80

TABLE

Example No.	Starting Material		Reaction method	Cyclopropanecarboxylic acid ester obtained				
	Alcohol or derivative thereof	Cyclopropane-carboxylic acid or derivative thereof		Compound No.	Name	Yield (%)	Refractive index (n_D^{25})	Elemental analysis (%) C H N
1	2,3-Dimethylmaleimide-methyl alcohol	2,2-Dimethyl-3-(2,2-dichlorovinyl)-cyclopropane-carboxylic acid chloride	A	(1)	2,3-Dimethylmaleimide-methyl 2',2'-dimethyl-3'-(2,2-dichlorovinyl)-cyclopropane-carboxylate	95	1.5261	(F)52.38 4.71 4.29 (C)52.04 4.95 4.05 as $C_{13}H_{17}Cl_2NO_4$
2	2,3-Dimethylmaleimide-methyl alcohol	2,2-Dimethyl-3-(2-chlorovinyl)-cyclopropane-carboxylic acid chloride	A	(2)	2,3-Dimethylmaleimide-methyl 2',2'-dimethyl-3'-(2-chlorovinyl)-cyclopropane-carboxylate	92	1.5074	(F)57.51 5.99 4.52 (C)57.78 5.82 4.49 as $C_{13}H_{16}ClNO_4$
3	2-Methyl-3-ethylmaleimide-methyl alcohol	2,2-Dimethyl-3-(2,2-dichlorovinyl)-cyclopropane-carboxylic acid	B	(3)	2-Methyl-3-ethylmaleimide-methyl 2',2'-dimethyl-3'-(2,2-dichlorovinyl)-cyclopropane-carboxylate	71	1.5278	(F)53.73 5.08 4.01 (C)53.35 5.32 3.89 as $C_{16}H_{19}Cl_2NO_4$

TABLE (Continued)

Example No.	Starting Material		Reaction method	Cyclopropanecarboxylic acid ester obtained				
	Alcohol or derivative thereof	Cyclopropane-carboxylic acid or derivative thereof		Compound No.	Name	Yield (%)	Refractive index (n_D^{25})	Elemental analysis (%) C H N
4	2,3-Dimethylmaleimido-methyl tosylate	Sodium 2,2-dimethyl-3-(2-chloro-1-propenyl)-cyclopropane-carboxylate	E	(4)	2,3-Dimethylmaleimido-methyl 2',2'-dimethyl-3'-(2-chloro-1-propenyl)-cyclopropane-carboxylate	79	1.5162	(F)59.74 6.45 4.22 (C)59.82 6.20 4.10 as $C_{18}H_{20}ClNO_4$
5	2,3-Diethylmaleimidomethyl alcohol	2,2-Dimethyl-3-(2,2-difluorovinyl)-cyclopropane-carboxylic acid chloride	A	(5)	2,3-Diethylmaleimido-methyl 2',2'-dimethyl-3'-(2,2-difluorovinyl)-cyclopropane-carboxylate	90	1.5029	(F)59.74 6.45 4.22 (C)59.82 6.20 4.10 as $C_{17}H_{21}F_2NO_4$
6	2,3-Dimethylmaleimidomethyl chloride	2,2-Dimethyl-3-(2,2-dibromovinyl)-cyclopropane-carboxylic acid	D	(6)	2,3-Dimethylmaleimido-methyl 2',2'-dimethyl-3'-(2,2-dibromovinyl)-cyclopropane-carboxylate	89	1.5457	(F)41.62 4.07 3.44 (C)41.40 3.94 3.22 as $C_{15}H_{17}Br_2NO_4$

TABLE (Continued)

Example No.	Starting Material		Reaction method	Cyclopropanecarboxylic acid ester obtained				
	Alcohol or derivative thereof	Cyclopropane-carboxylic acid or derivative thereof		Compound No.	Name	Yield (%)	Refractive index (n_D^{25})	Elemental analysis (%) C H N
7	2-Methyl-3-n-propyl-maleimido-methyl alcohol	2,2-Dimethyl-3-(2,2-dichlorovinyl)-cyclopropane-carboxylic acid anhydride	C	(7)	2-Methyl-3-n-propyl-maleimido-methyl 2',2'-dimethyl-3'-(2,2-dichlorovinyl)-cyclopropane-carboxylate	86	1.5289	(F)54.31 5.89 3.87 (C)54.56 5.66 3.74 as $C_{17}H_{21}Cl_2NO_4$
		2,2-Dimethyl-3-(2,2-dichlorovinyl)-cyclopropane-carboxylic acid chloride						(F)60.41 5.60 3.46 (C)60.56 5.31 3.21 as $C_{22}H_{23}Cl_2NO_4$
8	2-Methyl-3-(o,p-di-methyl-phenyl)-maleimido-methyl alcohol	2,2-Dimethyl-3-(2,2-dichlorovinyl)-cyclopropane-carboxylic acid chloride	A	(8)	2-Methyl-3-(o,p-di-methyl-phenyl)-maleimido-methyl 2',2'-dimethyl-3'-(2,2-dichlorovinyl)-cyclopropane-carboxylate	89	1.5531	(F)59.97 6.78 4.39 (C)60.09 6.53 4.12 as $C_{17}H_{22}ClNO_4$
		2,2-Dimethyl-3-(2-chlorovinyl)-cyclopropane-carboxylic acid						
9	2-Methyl-3-isopropyl-maleimido-methyl alcohol	2,2-Dimethyl-3-(2-chlorovinyl)-cyclopropane-carboxylic acid	B	(9)	2-Methyl-3-isopropyl-maleimido-methyl 2',2'-dimethyl-3'-(2-chlorovinyl)-cyclopropane-carboxylate	71	1.5093	

TABLE (Continued)

Example No.	Starting Material		Reaction method	Cyclopropanecarboxylic acid ester obtained				
	Alcohol or derivative thereof	Cyclopropane-carboxylic acid or derivative thereof		Compound No.	Name	Yield (%)	Refractive index (n _D ²⁰)	Elemental analysis (%) C H N
10	2-Ethyl-3-n-propylmaleimide-methyl alcohol	2,2-Dimethyl-3-(2,2-dichlorovinyl)-cyclopropane-carboxylic acid anhydride	C	(10)	2-Ethyl-3-n-propylmaleimide-methyl-2',2'-dimethyl-3'-(2,2-dichlorovinyl)-cyclopropane-carboxylate	84	1.5294	(F)55.37 6.20 3.78 (C)55.68 5.97 3.61 as C ₁₈ H ₂₃ Cl ₂ NO ₄
11	2-Methyl-3-ethylmaleimide-methyl alcohol	2,2-Dimethyl-3-(2-bromovinyl)-cyclopropane-carboxylic acid chloride	A	(11)	2-Methyl-3-ethylmaleimide-methyl-2',2'-dimethyl-3'-(2-bromovinyl)-cyclopropane-carboxylate	87	1.5379	(F)51.77 5.64 3.99 (C)51.90 5.44 3.78 as C ₁₈ H ₂₀ BrNO ₄
12	2,2-Dimethylmaleimide-methyl alcohol	2,2-Dimethyl-3-(2-bromo-2-chlorovinyl)-cyclopropane-carboxylic acid	B	(12)	2,2-Dimethylmaleimide-methyl-2',2'-dimethyl-3'-(2-bromo-2-chlorovinyl)-cyclopropane-carboxylate	73	1.5396	(F)45.96 4.47 3.54 (C)46.12 4.39 3.59 as C ₁₈ H ₁₇ BrClNO ₄

TABLE (Continued)

Example No.	Starting Material		Reaction method	Cyclopropanecarboxylic acid ester obtained				
	Alcohol or derivative thereof	Cyclopropane-carboxylic acid or derivative thereof		Compound No.	Name	Yield (%)	Refractive index (n_D^{25})	Elemental analysis (%) C H N
13	2-Methyl-3-ethylmaleimide alcohol	2,2-Dimethyl-3-(2-bromo-1-propenyl)-cyclopropane-carboxylic acid chloride	A	(13)	2-Methyl-3-ethylmaleimide 2',2'-dimethyl-3'-(2-bromo-1-propenyl)-cyclopropane-carboxylate	84	1.5432	(F)53.25 5.81 3.71 (C)53.13 5.77 3.65 as $C_{17}H_{22}BrNO_4$
14	2-Methyl-maleimide methyl tosylate	Sodium 2,2-dimethyl-3-(2,2-dichlorovinyl)-cyclopropane-carboxylate	E	(14)	2-Methyl-maleimide methyl 2',2'-dimethyl-3'-(2,2-dichlorovinyl)-cyclopropane-carboxylate	77	1.5247	(F)50.59 4.82 4.09 (C)50.62 4.55 4.22 as $C_{24}H_{15}Cl_2NO_4$
15	Maleimide-methyl alcohol	2,2-Dimethyl-3-(2,2-dibromovinyl)-cyclopropane-carboxylic acid anhydride	C	(15)	Maleimide-methyl 2',2'-dimethyl-3'-(2,2-dibromovinyl)-cyclopropane-carboxylate	87	1.5388	(F)38.55 3.49 3.48 (C)38.36 3.22 3.44 as $C_{15}H_{13}Br_2NO_4$

TABLE (Continued)

Example No.	Starting Material		Reaction method	Cyclopropanecarboxylic acid ester obtained				
	Alcohol or derivative thereof	Cyclopropane-carboxylic acid or derivative thereof		Compound No.	Name	Yield (%)	Refractive index (n_D^{25})	Elemental analysis (%) C H N
16	2,3-Dimethyl-3-(2,2-dimethyl-3-phenylmaleimido)cyclopropanecarboxylic acid chloride	2,3-Dimethyl-3-(2,2-dimethyl-3-phenylmaleimido)cyclopropanecarboxylic acid chloride	A	(16)	2,3-Dimethyl-3-(2,2-dimethyl-3-phenylmaleimido)cyclopropanecarboxylate	83	1.5004	(F)57.70 5.54 4.66 (C)57.50 5.47 4.47 as $C_{15}H_{17}F_2NO_4$
17	2-Methyl-3-allyl-3-phenylmaleimidoalcohol	2,2-Dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylic acid	B	(17)	2-Methyl-3-allyl-3-phenylmaleimidoalcohol	68	1.5748	(F)58.77 4.82 3.50 (C)58.84 4.69 3.43 as $C_{20}H_{19}Cl_2NO_4$
18	2-Methyl-3-allyl-3-phenylmaleimidoalcohol	2,2-Dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylic acid chloride	A	(18)	2-Methyl-3-allyl-3-phenylmaleimidoalcohol	86	1.5318	(F)54.79 5.23 3.98 (C)54.85 5.14 3.76 as $C_{17}H_{19}Cl_2NO_4$

TABLE (Continued)

Example No.	Starting Material		Reaction method	Cyclopropanecarboxylic acid ester obtained				
	Alcohol or derivative thereof	Cyclopropane-carboxylic acid or derivative thereof		Compound No.	Name	Yield (%)	Refractive index (n_D^{25})	Elemental analysis (%) C H N
22	2-Allyl-maleimido-methyl alcohol	2,2-Dimethyl-3-(2-chloro-1-propenyl)-cyclopropane-carboxylic acid chloride	A	(22)	2-Allyl-maleimido-methyl 2',2'-dimethyl-3'-(2-chloro-1-propenyl)-cyclopropane-carboxylate	84	1.5364	(F)60.18 6.04 4.33 (C)60.44 5.97 4.15 as $C_{17}H_{20}ClNO_4$
23	2-Methyl-3-(m-methyl-phenyl)-maleimido-methyl chloride	2,2-Dimethyl-3-(2,2-dichlorovinyl)-cyclopropane-carboxylic acid	D	(23)	2-Methyl-3-(m-methyl-phenyl)-maleimido-methyl 2',2'-dimethyl-3'-(2,2-dichlorovinyl)-cyclopropane-carboxylate	74	1.5712	(F)59.90 5.07 3.46 (C)59.72 5.01 3.32 as $C_{21}H_{21}Cl_2NO_4$
24	2-Methyl-3-(p-chloro-phenyl)-maleimido-methyl alcohol	2,2-Dimethyl-3-(2-bromo-1-propenyl)-cyclopropane-carboxylic acid	B	(24)	2-Methyl-3-(p-chloro-phenyl)-maleimido-methyl 2',2'-dimethyl-3'-(2-bromo-1-propenyl)-cyclopropane-carboxylate	79	1.5783	(F)54.25 4.66 2.87 (C)54.04 4.53 3.00 as $C_{21}H_{21}BrClNO_4$

TABLE (Continued)

Example No.	Starting Material		Reaction method	Cyclopropanecarboxylic acid ester obtained				
	Alcohol or derivative thereof	Cyclopropane-carboxylic acid or derivative thereof		Compound No.	Name	Yield (%)	Refractive index (n_D^{25})	Elemental analysis (%) C H N
25	2-Methyl-3-(p-ethyl-phenyl)-maleimido-methyl alcohol	2,2-Dimethyl-3-(2-chloro-vinyl)-cyclopropane-carboxylic acid chloride	A	(25)	2-Methyl-3-(p-ethyl-phenyl)-maleimido-methyl 2',2'-dimethyl-3'-(2-chloro-vinyl)-cyclopropane-carboxylate	92	1.5567	(F)65.73 6.31 3.53 (C)65.75 6.02 3.49 as $C_{22}H_{24}ClNO_4$
26	2-Methyl-3-(m-methyl-phenyl)-maleimido-methyl alcohol	2,2-Dimethyl-3-(2,2-di-fluorovinyl)-cyclopropane-carboxylic acid chloride	A	(26)	2-Methyl-3-(m-methyl-phenyl)-maleimido-methyl 2',2'-dimethyl-3'-(2,2-di-fluorovinyl)-cyclopropane-carboxylate	95	1.5474	(F)64.94 5.62 3.78 (C)64.77 5.44 3.60 as $C_{21}H_{21}F_2NO_4$
27	2-Methyl-3-(1-propenyl)-maleimido-methyl alcohol	2,2-Dimethyl-3-(2,2-di-bromovinyl)-cyclopropane-carboxylic acid chloride	A	(27)	2-Methyl-3-(1-propenyl)-maleimido-methyl 2',2'-dimethyl-3'-(2,2-di-bromovinyl)-cyclopropane-carboxylate	88	1.5499	(F)44.06 4.27 3.21 (C)44.27 4.15 3.04 as $C_{11}H_{19}Br_2NO_4$

TABLE (Continued)

Example No.	Starting Material		Reaction method	Cyclopropanecarboxylic acid ester obtained				
	Alcohol or derivative thereof	Cyclopropane-carboxylic acid or derivative thereof		Compound No.	Name	Yield (%)	Refractive index (n _D ²⁵)	Elemental analysis (%) C H N
28	2-Phenyl-maleimido-methyl alcohol	2,2-Dimethyl-3-(2,2-dichlorovinyl)-cyclopropane-carboxylic acid anhydride	C	(28)	2-Phenyl-maleimido-methyl 2',2'-dimethyl-3'-(2,2-dichlorovinyl)-cyclopropane-carboxylate	86	1.5727	(F)58.02 4.30 3.65 (C)57.88 4.35 3.55 as C ₁₉ H ₁₇ Cl ₂ NO ₄
29	2-Methyl-3-(m-chlorophenyl)-maleimido-methyl alcohol	2,2-Dimethyl-3-(2-chlorovinyl)-cyclopropane-carboxylic acid chloride	A	(29)	2-Methyl-3-(m-chlorophenyl)-maleimido-methyl 2',2'-dimethyl-3'-(2-chlorovinyl)-cyclopropane-carboxylate	93	1.5706	(F)58.69 4.80 3.59 (C)58.84 4.69 3.43 as C ₂₀ H ₁₉ Cl ₂ NO ₄

In order to demonstrate the excellent effects of the present compounds more clearly, experimental examples and their results will be shown below.

Experimental Example 1.

Each of the present compounds (1) to (29) and pyrethrin was respectively formulated into a 0.1% by weight oil spray using deodorized kerosene.

Groups of insects, each group containing

either twenty adult Northern house mosquitoes (*Culex pipiens pallens*) or twenty adult house-flies (*Musca domestica*) were introduced into respective (70 cm)³ glass chambers. A 0.7 ml volume of one of each of the oil sprays obtained above was sprayed under a pressure of 20 lb/inch² onto a respective group of insects and the knock-down ratio after 5 minutes was determined. The results are shown in Table 1.

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5

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TABLE 1

Test Compound (0.1 % oil spray)	Knock-down ratio (%) after 5 minutes	
	Adult Northern house mosquitoes	Adult House-flies
Present compound (1)	100	100
" (2)	100	100
" (3)	100	100
" (4)	100	100
" (5)	100	95
" (6)	100	100
" (7)	95	90
" (8)	80	80
" (9)	90	90
" (10)	100	95
" (11)	95	95
" (12)	100	100
" (13)	90	90
" (14)	80	75
" (15)	75	80
" (16)	100	100
" (17)	80	75
" (18)	90	90
" (19)	100	100
" (20)	80	80
" (21)	75	70
" (22)	75	70
" (23)	80	75
" (24)	85	85
" (25)	70	70
" (26)	90	95
" (27)	80	75
" (28)	70	70

TABLE 1 (Continued)

Test Compound (0.1 % oil spray)	Knock-down ratio (%) after 5 minutes	
	Adult Northern house mosquitoes	Adult House-flies
Present compound (29)	75	70
Pyrethrin (control)	60	45

Experimental Example 2.

The following compounds were each formulated into a respective 0.3% by weight mosquito coil: —

the racemic form of the present compounds (1), (2), (3), (6), (12), (19) and (28), the dl-trans acid isomer of the compounds (4), (16) and (23), and various control compounds given in Table 2.

Groups of insects, each group containing twenty adult Northern house mosquitoes (*Culex pipiens pallens*) or twenty adult

house-flies (*Musca domestica*) were introduced into respective (70 cm)³ glass chambers. A one gram amount of one of each of the mosquito coils obtained above was ignited at both ends and placed at the centre of a respective chamber. The number of knocked down insects with lapse of time was counted. This test was repeated several times and the values of KT₅₀ (Time required for 50% knock-down) were obtained from the test results. The results are shown in Table 2.

TABLE 2

Test Compound (0.3 % mosquito coil)	KT ₅₀ (min. sec.)	
	Adult Northern house mosquitoes	Adult house-flies
Present compound (1)	9' 30"	12' 15"
" (2)	11' 07"	16' 21"
" (3)	10' 05"	13' 00"
dl-trans acid isomer of Present compound (4)	12' 36"	18' 25"
Present compound (6)	10' 10"	13' 14"
" (12)	10' 40"	13' 22"
dl-trans acid isomer of Present compound (16)	11' 06"	16' 40"
Present compound (19)	12' 13"	13' 57"
dl-trans acid isomer of Present compound (23)	13' 00"	19' 18"
Present compound (28)	12' 39"	18' 33"
Control (allethrin) **	14' 00"	>24'

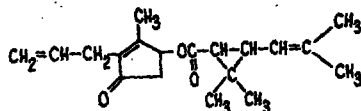
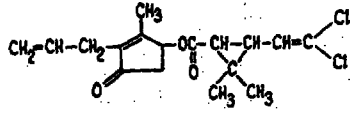
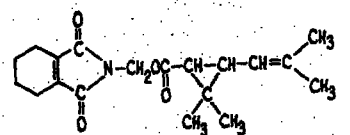
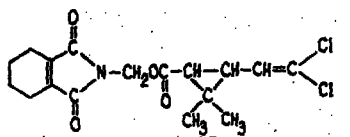
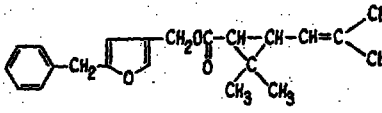
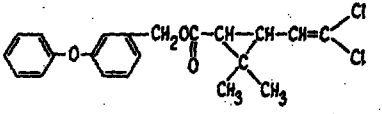


TABLE 2 (Continued)

Test Compound (0.3% mosquito coil)	KT ₅₀ (min. sec.)	
	Adult Northern house mosquitoes	Adult house-flies
Control *	13' 20"	22' 00"
	15' 12"	21' 06"
Control (tetramethrin) **	14' 18"	20' 09"
	17' 05"	21' 33"
Control *	18' 30"	> 24'
		
Control *		
		
Control *		
		

Note: * Compounds described in U.K. Patent Specification No. 1413491

** Commercially available compounds

Experimental Example 3.

Each of the present compounds (1), (2), (4), (6), (11), (12), (13), (16), (19), (23), (26) and (28), in racemic form, the d-trans acid isomer of the compound (1), and various control compounds given in Table 3 was formulated into a respective 0.1% by weight oil spray using deodorized kerosene.

10 The value of KT₅₀ (Time required for

50% knock-down) of each oil spray on the Northern house mosquitoes were obtained in the same manner as that described in Experimental Example 1. Further, the knocked down insects were collected and transferred into another chamber, and the % mortality after 24 hours was then checked. The results are shown in Table 3.

TABLE 3

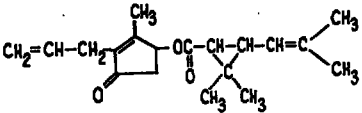
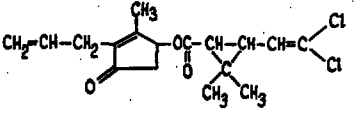
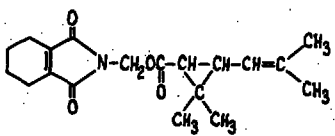
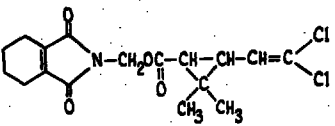
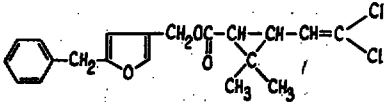
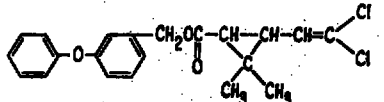
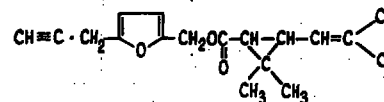
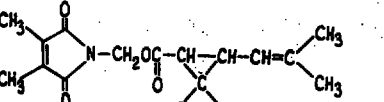
Test Compound (0.1 % oil spray)	Northern house mosquito	
	KT ₅₀ (sec.)	Mortality after 24 hours (%)
Present compound (1)	53"	100
" (2)	70"	100
" (4)	75"	100
" (6)	74"	100
" (11)	78"	100
" (12)	67"	100
" (13)	82"	100
" (16)	72"	100
" (19)	79"	100
" (23)	105"	100
" (26)	103"	95.0
" (28)	126"	95.0
d-trans acid isomer of Present compound (1)	30"	100
Control (allethrin) ***	324"	65.0
		
Control *	295"	80.0
		
Control (tetramethrin) ***	135"	80.0
		
Control *	130"	84.2
		

TABLE 3 (Continued)

Test Compound (0.1 % oil spray)	Northern house mosquito	
	KT ₅₀ (sec.)	Mortality after 24 hours (%)
Control * 	256"	94.7
Control * 	328"	93.3
Control * 	145"	90.0
Control ** 	141"	77.8
Control (pyrethrin) ***	150"	89.5

Note: * Compounds described in U.K. Patent Specification No. 1413491.

** Compounds described in French Patent No. 1434956

*** Commercially available compounds

Experimental Example 4.

Each of the present compounds (1), (2), (3), (5), (7), (8), (10), (12), (14), (18), (24) and (27), in racemic form, and various control compounds as shown in Table 4 formulated into a respective 0.025% by weight oil spray using deodorized kerosene.

Ten cockroaches were released into a plastic cup (9.5 cm in diameter and 4 cm in height) and covered with a 16-mesh nylon net, and the cup was then placed at the bottom of a glass cylinder of 10 cm diameter and 37 cm height. 0.5 Ml of one of the above oil spray

formulations was sprayed into the glass cylinder through an atomizer at a pressure of 0.6 kg/cm². The glass cylinder was then immediately covered with a glass lid. The number of knocked down insects with the lapse of time was observed. This test was repeated for each of the other oil spray formulations given above, and for each oil spray formulation, was also repeated several times and the values of KT₅₀ (Time required for 50% knock-down) were obtained from the test results. The results are shown in Table 4.

TABLE 4

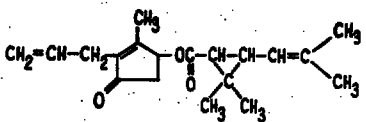
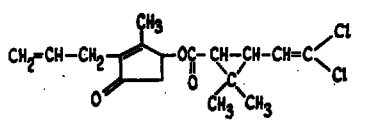
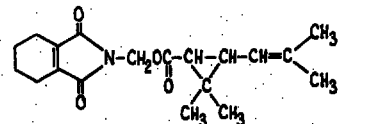
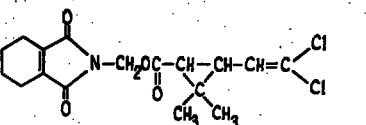
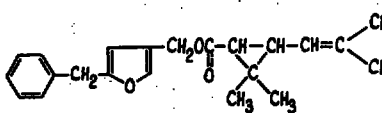
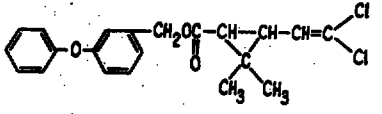
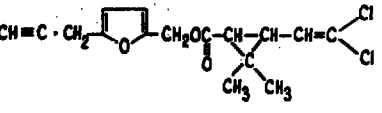
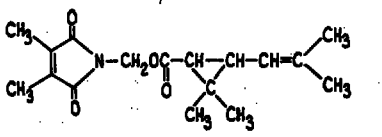
Test Compound (0.025 % oil spray)		German cockroach
		KT ₅₀ (min. sec.)
Present Compound	(1)	3' 30"
"	(2)	4' 40"
"	(3)	4' 00"
"	(5)	5' 10"
"	(7)	6' 30"
"	(8)	7' 20"
"	(10)	5' 00"
"	(12)	4' 20"
"	(14)	7' 50"
"	(18)	6' 40"
"	(24)	7' 00"
"	(27)	8' 00"
Control (allethrin) ***		> 20'
		
Control *		20' 00"
		
Control (tetramethrin) ***		13' 10"
		
Control *		10' 20"
		
Control *		> 20'

TABLE 4 (Continued)

Test Compound (0.025 % oil spray)	German cockroach
	KT ₅₀ (min. sec.)
 Control *	> 20'
 Control *	17' 40"
 Control **	15' 20"
 Control (pyrethrin) ***	10' 30"

Note:

* Compounds described in U.K. Patent Specification No. 1413491.

** Compounds described in French Patent No. 1434956

*** Commercially available compounds

These experiments show that the present compounds are superior to control compounds such as allethrin and pyrethrin. Further, because of their properties mentioned above, they can be widely used for knocking down or killing insects harmful to public health, examples of which insects are houseflies, mosquitoes and cockroaches, and insects harmful to stored cereals, examples of which insects are the grain mite, indian meal moth and rice weevils. Moreover, the present compounds are extremely effective for knocking down and killing insects harmful to agricultural, horticultural and forest plants, examples of which insects are planthoppers, leafhoppers, army worms and cut worms, diamond-back moth, tortorixes, aphids, stem-borers, mites and the Japanese giant silk moth; and animal-parasitic

lice and mites. The present compounds can also be used for controlling a wide range of other harmful insects.

The present compounds can cause the harmful insects to be knocked down and to die, and in addition, they exhibit repellency (the effect of keeping harmful insects away from their host plant). In particular, they are also particularly useful in that they can be used freely, due to their low toxicity and harmlessness to mammals, for protecting agricultural crops before harvest, household horticultural plants, greenhouse cultivations and food-packaging.

In practice the present compounds may be applied alone or in combination with a carrier for the convenience of use as a pesticide. The present compounds can be formulated into

optional preparation forms without any special treatment using known formulations of common pesticides. That is, such a compound can be formulated into, for example, an emulsifiable concentrate, wettable powder, dust, fine or coarse granulate, oil spray, aerosol, fumigant effective on heating, (for example a mosquito coil or electrically heated mosquito killer mat), thermal fogging agent, a fumigant effective without heating or a bait by well known methods, and can be used in any form, (and optionally in combination with a carrier) suitable for the particular application of the insecticide.

Furthermore, the insecticidal activity of the present compounds can be increased by combination thereof with known synergists for pyrethroid such as α - [2 - (2 - butoxyethoxy) - ethoxy] - 4,5 - methylenedioxy - 2 - propyltoluene (hereinafter referred to as piperonylbutoxide), 1,2 - methylenedioxy - 4 - [2 - (octylsulfinyl) - propyl] - benzene (hereinafter referred to as sulfoxide), 4 - (3,4-methylenedioxyphenyl) - 5 - methyl - 1,3-dioxane (hereinafter referred to as sulfoxane), N - (2 - ethylhexyl) - bicyclo[2,2,1]hept-5 - ene - 2,3 - dicarboximide (hereinafter referred to as MGK-264), octachlorodipropyl ether (hereinafter referred to as S-421), and isobornylthiocyano acetate (hereinafter referred to as Thanite); and with known synergists for allethrin or pyrethrin.

In general, the chrysanthemate type compounds tend to be inferior in the resistance to light, heat and oxidation. Accordingly, compositions having a more stable activity can be prepared by adding a suitable amount of a stabilizing agent, for example, an antioxidant or U.V. absorber such as a phenol derivative e.g. BHT or BHA, a bisphenol derivative, arylamine derivative e.g. phenyl- α -naphthylamine or phenyl- β -naphthylamine and a condensation product of phenetidine and acetone, or a benzophenone compound.

Additionally, the present compounds can be formulated into multipurpose compositions having superior activity in combination with other active ingredients such as allethrin, N-(chrysanthemoxymethyl) - 3,4,5,6 - tetrahydrophthalimide (hereinafter referred to as tetramethrin), 5 - benzyl - 3 - furylmethyl chrysanthemate (hereinafter referred to as resmethrin), 3-phenoxybenzyl chrysanthemate, 5-propargylfurfuryl chrysanthemate and 2-methyl - 5 - propargyl - 3 - furylmethyl chrysanthemate; isomers thereof, for example, d-trans-, and di-cis,trans-chrysanthemic acid esters thereof; pyrethrum extracts; d-trans-, or d-cis,trans-chrysanthemic acid esters of d-allethrolone; other well-known cyclopropane-carboxylic acid esters; organochlorine type insecticides, for example DDT, BHC and methoxychlor; organophosphorus type insecticides, for example, O,O-dimethyl - O - (3-methyl - 4 - nitrophenyl) - phosphorothioate

(hereinafter referred to as Sumithion (a registered trademark)), O,O - dimethyl - O - 4-cyanophenyl - phosphorothioate (hereinafter referred to as Cyanox (a registered trademark) and O,O - dimethyl - O - (2,2-dichlorovinyl) - phosphate (hereinafter referred to as DDVP); carbamate type insecticides, for example, 1 - naphthyl - N - methylcarbamate and 3,5 - dimethylphenyl - N-methylcarbamate (hereinafter referred to as Meobal (a registered trademark)); other insecticides, fungicides, nematocides, acaricides, herbicides, plant growth regulators, fertilizers, microbial insecticides e.g. B.t. and B.m.; insect hormone compounds; or other chemicals used in agriculture. Furthermore a synergistic effect due to this combination can be expected.

Preparation of insecticides and acaricides within the present invention, and their lethal effects will now be illustrated with reference to the following Preparation Examples and Application Examples.

Preparation Example 1.

0.2 part of one of each of the present compounds (1), (2), (6), (12) and (19) is respectively dissolved in kerosene to make the total weight up to 100 parts. Thus, an oil spray of each compound is obtained.

Preparation Example 2.

0.5 part of one of each of the present compounds (1), (2), (4), (6), (10), (11), (12), (16) and (23) is respectively dissolved in kerosene to make the total weight up to 100 parts. Thus, an oil spray of each compound is obtained. In the same manner, 0.5 part of di-trans acid isomer of one of each of the present compounds (3), (8), (13), (17) and (26) is formulated into a respective oil spray.

Preparation Example 3.

To 0.1 part of one of each of the present compounds (1), (2), (6) and (12) is added 0.5 part of piperonylbutoxide and each respective mixture is dissolved in kerosene to make the total weight up to 100 parts. Thus, an oil spray of each mixture is obtained. In the same manner 0.1 part of the di-trans acid isomer of the present compound (19) is formulated into an oil spray.

Preparation Example 4.

To 10 parts of one of each of the present compounds (1) to (29) are added 20 parts of S-421, 15 parts of Sorpol SH-200 (a registered trade mark) and 55 parts of xylene. Each mixture is thoroughly mixed to make a respective solution. Thus emulsifiable concentrates of one of each mixture are obtained.

Preparation Example 5.

To 20 parts of one of each of the present compounds (1), (4), (12), (16), (23) and

(27) are added 15 parts of Sorpol SM—200 (the same as above) and 65 parts of xylene. Each mixture is thoroughly mixed to make a respective solution. Thus emulsifiable concentrates, one of each mixture, are obtained. In the same manner, 20 parts of dl-trans acid isomer of one of each of the present compounds (6), (18) and (26) is formulated into a respective emulsifiable concentrate.

10 Preparation Example 6.

To 0.1 part of one of each of the present compounds (1), (6) and (12) are respectively added and mixed 0.2 part of resmethrin, 7 parts of xylene and 7.7 parts of deodorized kerosene to make a respective solution. The solutions are each introduced into a respective aerosol container. After attaching a valve portion to each container, 85 parts of a propellant (e.g. liquefied petroleum gas) is charged into it under pressure through the valve. Respective aerosols are thus obtained.

Preparation Example 7.

To 0.3 part of one of each of the present compounds (2) and (16) are respectively added and mixed 0.1 part of the d-trans acid isomer of resmethrin, 7 parts of xylene and 7.6 parts of deodorized kerosene to make a respective solution. The solutions are each introduced into a respective aerosol container. After attaching a valve portion to each container, 85 parts of a propellant (e.g. liquefied petroleum gas) is charged into it under pressure through the valve. Respective aerosols are thus obtained. In the same manner, 0.3 part of the dl-trans acid isomer of the compound (23) is formulated into an aerosol.

Preparation Example 8.

0.1 Part of the present compound (1), 0.2 part of the d-trans acid isomer of resmethrin, 11.7 parts of deodorized kerosene and 1 part of Atmos 300 (a registered trademark) are thoroughly mixed and emulsified by addition of 50 parts of pure water. An aerosol container is then filled with the resulting emulsion and 35 parts of a 3:1 mixture of deodorized butane to deodorized propane. A water-based aerosol is thus obtained.

Preparation Example 9.

To 0.2 part of the d-trans acid isomer of one of each of the present compounds (4), (6), (12), (16), (19) and (27) are respectively added and mixed 0.1 part of resmethrin, 7 parts of xylene and 7.7 parts of deodorized kerosene to make a respective solution. The solutions are each introduced into a respective aerosol container. After attaching a valve portion to each container, 85 parts of a propellant (e.g. liquefied petroleum gas) is charged into it under pressure through the valve. Respective aerosols are thus obtained.

Preparation Example 10.

To 0.3 g of the d-trans acid isomer of one of each of the present compounds (2), (5), (14), (22) and (26) are respectively added 0.3 g of allethrin and 0.6 g of BHT and each mixture is respectively dissolved in 20 ml of methanol. Each respective solution is uniformly mixed with 98.8 g of a mosquito coil carrier containing Tabu powder. Pyrethrum marc and wood powder in a ratio of 3:5:1, and the methanol is then evaporated. To each residue obtained is added 150 ml of water and the mixture is kneaded thoroughly, shaped into a mosquito coil and dried. Thus, respective mosquito coils are obtained.

Preparation Example 11.

A 0.5 g amount of one of each of the present compounds (1), (6) and (19) is respectively dissolved in 20 ml of methanol. Each respective solution is uniformly mixed with 99.5 g of a mosquito coil carrier (the same as above) and the methanol is then evaporated. To each residue obtained is added 150 ml of water and the mixture is kneaded thoroughly, shaped into a mosquito coil and dried. Thus, respective mosquito coils are obtained.

Preparation Example 12.

0.1 Gram of the dl-trans acid isomer of the present compound (6), 0.1 g of BHT and 0.1 g of piperonylbutoxide are dissolved in a suitable amount of chloroform. A filter paper of 3.5 cm x 1.5 cm in area and 0.3 cm thickness is uniformly impregnated with the solution.

Thus a fibrous fumigant for heating on a hot plate is obtained. Materials having an effect equivalent to the filter paper or other pulp plate, for example asbestos, may alternatively be used as the fibrous carrier.

Preparation Example 13.

0.02 Gram of the present compound (1), 0.05 g of 5-propargylfurfuryl dl-cis,trans-chrysanthemate and 0.1 g of BHT are dissolved in a suitable amount of chloroform. The solution is adsorbed uniformly on to a filter paper of 3.5 cm x 1.5 cm in area and 0.3 cm thickness.

Thus, a fibrous fumigant for heating on a hot plate is obtained.

Preparation Example 14.

A 20 part amount of one of each of the present compounds (3), (6), (12), (20) and (29) is respectively mixed thoroughly with 10 parts of Sumithion and 5 parts of Sorpol SM—200. Each mixture is respectively mixed with 65 parts of 300 mesh talc in a mortar while thoroughly stirring. Thus, respective wettable powder are obtained. In the same manner, 20 parts of the dl-trans acid isomer

of one of each of the present compounds (10), (16) and (24) is formulated into a respective wettable powder.

Preparation Example 15.

To 1 part of one of each of the present compounds (1), (2), (6), (8), (10), (16), (18), (23) and (25) is respectively added 2 parts of 1 - naphthyl - N - methylcarbamate and the mixture is dissolved in 20 parts of acetone, and then 97 parts of 300 mesh diatomaceous earth added thereto. After thoroughly mixing in a mortar while stirring, the acetone is removed by evaporation. Thus respective dusts are obtained.

Preparation Example 16.

A 3 part amount of one of each of the present compounds (1), (6), (10), (12), (20) and (26) is respectively thoroughly mixed in a mortar together with 5 parts of Toyolignin CT (a registered trademark) and 92 parts of GSM Clay (a registered trademark).

Then each respective mixture is mixed with water in a 10% amount based on the weight of the mixture, granulated by means of a granulator and air-dried. Thus respective granular preparations are obtained. In the same manner, 3 parts each of the dl-trans acid isomer of one of each of the present compounds (7) and (19) is formulated into a respective granular preparation.

Preparation Example 17.

A 4 part amount of one of each of the present compounds (1), (4), (9), (15), (17), (21), (24) and (28) is respectively thoroughly mixed in a mortar together with 2 parts of Cyanox (the same as above), 5 parts of Toyolignin CT (a registered trademark) and 89 parts of GSM Clay (a registered trademark).

Each respective mixture is then mixed with 10% by weight of water based on the weight of the mixture, granulated by means of a granulator and air-dried. Thus, respective fine granular preparations are obtained.

The insecticidal and acaricidal activities of the present compositions thus obtained are illustrated as follows.

Application Example 1.

A 5 ml aliquot of one of each of the oil sprays formulated by Preparation Examples 1, 2 and 3 was respectively sprayed, using the Campbell's turn table method [Soap and Sanitary Chemicals, Vol. 14, No. 6, 119 (1938)]. Groups each of 100 adult houseflies (*Musca domestica*) were exposed to the descending mist for 10 minutes. By the next day, more than 80% of the flies were dead in each case.

Application Example 2.

Each of the emulsifiable concentrates formu-

lated by Preparation Example 4 was respectively diluted 10,000 times with water. Two litres of each test emulsion so prepared were poured into a respective polystyrene case of 23 cm x 30 cm in area and 6 cm depth, and about 100 full grown larvae of the Northern house mosquito (*Culex pipiens pallens*) were introduced into each respective case. By the next day, more than 90% of the larvae were dead in each case.

Application Example 3.

In a 1/50,000 Wagner's pot, rice plants which had been allowed to grow for 45 days after sowing. Each of the emulsifiable concentrates formulated by Preparation Example 4 was respectively diluted 200 times with water. Each test solution so prepared was individually sprayed onto the rice plants in an amount ratio of 10 ml per respective pot. Each pot was covered with wire net and about 30 adult green rice leafhoppers (*Nephotettix cincticeps*) were introduced into each pot. After one day, more than 90% of the leafhoppers were dead in each case.

Application Example 4.

Each of the emulsifiable concentrates formulated by Preparation Example 4 was diluted 200 times with water. About 10 larvae of the tobacco cut worm (*Spodoptera litura*) in the third to fourth instar stage were introduced into each of a number of glass Petri dishes each having a 14 cm inside diameter, and 1 ml of each of the dilute solutions was sprayed into a respective dish. Thereafter, the larvae were transferred to another dish in which food had previously been placed. After two days, more than 90% of the larvae were dead in each case.

Application Example 5.

The insecticidal activity on adult houseflies (*Musca domestica*) of each aerosol formulated by Preparation Examples 6, 7, 8 and 9 was tested by the aerosol test method (Soap and Chemical Specialities, Blue Book, 1965) using a (6 ft)³ Peet Grady's chamber. Thus, with each aerosol, more than 80% of the flies were knocked down 15 minutes after spraying and more than 70% of the flies were dead by the next day.

Application Example 6.

About 50 adult Northern house mosquitoes (*Culex pipiens pallens*) were introduced into each of a number of (70 cm)³ glass chambers in each of which a battery-driven small electric fan (having a wing diameter of 13 cm) was located. A 0.1 g amount of one of each of the mosquito coils formulated by Preparation Examples 10 and 11 was ignited at one end and placed at the centre of the bottom of a respective chamber. With each mosquito coil, more than 90% of the adults were

knocked down within 20 minutes and more than 80% of the adults were dead by the next day.

Application Example 7.

- 5 About 50 adult house-flies (*Musca domestica*) were introduced into each of a number of (70 cm)³ glass chambers in each of which a battery small electric fan (having a wing diameter of 13 cm) was located. Each of the
- 10 fumigants formulated by Preparation Examples 12 and 13 was placed on a hot plate in a respective chamber and fumigated. More than 90% of the house-flies were knocked down within 20 minutes with each fumigant.

Application Example 8.

- 15 About 20 rice plants were grown up to a 3 to 4-leaved stage in each of a number of flower pots of 10 cm diameter, and a 200-fold aqueous dilute solution of one of each
- 20 wettable powder formulated by the Preparation Example 14 was then poured on to each respective pot by means of a turn table. After air-drying, each pot was covered with a wire cage and 20 to 30 adult smaller brown plant-
- 25 hoppers (*Laodelphax striatellus*) were introduced into each pot. The numbers of dead and alive after 24 hours were counted and a % mortality of more than 80% was obtained in each case.

Application Example 9.

- 30 Glass Petri dishes each having a 14 cm diameter were coated on the inside wall with butter, leaving at the lower part an uncoated portion 1 cm in width. Onto the bottom of
- 35 each dish, one of each of the dusts formulated by Preparation Example 15 was uniformly dusted respectively in a proportion of 2 g/m².

- 40 Subsequently, 10 adult German cockroaches (*Blattella germanica*) were introduced into each respective dish and were contacted with the dust for 30 minutes. After three days, more than 90% of the knocked down cockroaches were dead in each case.

Application Example 10.

- 45 Ten litres of water were introduced into each of a number of 14 litre polypropylene buckets, and 1 g of one of each of the granular preparations formulated by Preparation
- 50 Examples 16 and 17 was added to each respective bucket. After one day, about 100 full grown Northern house mosquito larvae (*Culex pipiens pallens*) were immersed in the water. The dead and alive were counted and more than 90% of the larvae were dead within
- 55 24 hours in each case.

Application Example 11.

- 60 Rice plants were grown up to the tillering stage in a number of 1/100,000 Wagner's pots and the water depth was kept at 5 cm. Each of the granular preparations formulated by

the Preparation Example 16 was placed in each respective pot in a ratio of 10 kg/10 ares. Thereafter, each pot was covered with a wire cage and adult smaller brown plant-hoppers (*Laodelphax striatellus*) were introduced into each pot. After 24 hours, more than 90% of the adults were dead in each case. 65

Application Example 12.

- 70 Three grams of one of each of the oil sprays formulated by Preparation Example 1 was fogged, by means of an insect fogger (Burgess (Vibrocrafter INC., America), into a respective Peet Grady's chamber (the same as in Example 5) into which about 500 adult house-flies (*Musca domestica*) had previously been introduced. After 30 minutes, more than 90% of the adults were knocked down in each case. 75

Application Example 13.

- 80 Leaves of the potted kidney bean (2-leaved stage) which had been allowed to grow in a number of pots for 9 days after sowing were infested with adult female carmine mites (*Tetranychus cinnabarinus*), in a proportion of 10-15/leaf, and bred at 27°C for a week in a constant temperature room, after which numerous carmine mites were found to be bred at various growth stages. At this time, a 200-fold aqueous dilute solution of one of each of the emulsifiable concentrates formulated by Preparation Example 5 was sprayed on to each respective pot in a ratio of 10 ml/pot by means of a turn table. After 10 days, the damage of the kidney bean by the mites was observed. 85 90 95

As a result, no increase in the damage was observed in each case.

Application Example 14.

- 100 Tea branches were placed in water in a number of Erlenmeyer flasks and a 200-fold aqueous dilute solution of one of each of the emulsifiable concentrates formulated by Preparation Example 5 was sprayed on to each respective flask in a ratio of 10 ml/branch by means of a turn table. The branches were then infested with larvae of the tea leaf roller (*Caloptilia theivora*) in a ratio of 10 larvae/branch and after 3 days, the number of rolled leaves was counted. 105 110

As a result, no rolled leaves were found in each case.

Application Example 15.

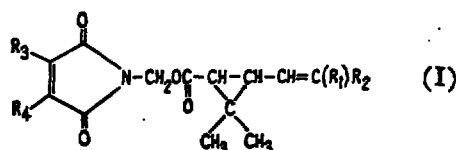
- Engorged female adults of the bull tick (*Boophilus microplus*), an animal-parasitic mite, were immersed in a 400-fold aqueous dilute solution of one of each of the emulsifiable concentrates formulated by Preparation Example 5 and the oviposition of the immersed adults was then observed. 115 120

As a result, the suppression percentage of

the oviposition of the treated adults was more than 80% in each case when the suppression percentage of the oviposition of untreated adults was taken as 0%.

5 WHAT WE CLAIM IS:—

1. A cyclopropanecarboxylic acid ester of the general formula (I),



10 wherein R_1 is a hydrogen atom, a methyl group or a fluorine, chlorine or bromine atom, R_2 is a fluorine, chlorine or bromine atom, and each of R_3 and R_4 is independently a hydrogen atom, a C_1-C_3 alkyl, C_2-C_3 alkenyl or C_2-C_3 alkynyl group, an alkyl- or halogen-substituted aryl group, an unsubstituted aryl group or an aralkyl group.

15 2. The compound 2,3 - dimethylmaleimidomethyl 2',2' - dimethyl - 3' - (2,2-dichlorovinyl) - cyclopropanecarboxylate.

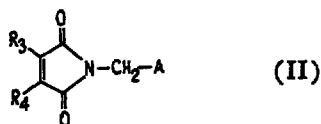
20 3. The compound 2 - methyl - 3 - ethylmaleimidomethyl 2',2' - dimethyl - 3' - (2,2-dichlorovinyl) - cyclopropanecarboxylate.

25 4. The compound 2,3 - diethylmaleimidomethyl 2',2' - dimethyl - 3' - (2,2 - difluorovinyl) - cyclopropanecarboxylate.

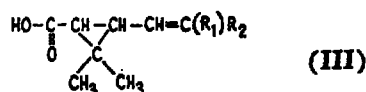
5. The compound 2,3 - dimethylmaleimidomethyl 2',2' - dimethyl - 3' - (2,2 - dibromovinyl) - cyclopropanecarboxylate.

30 6. The compound 2 - methyl - 3 - isopropylmaleimidomethyl 2',2' - dimethyl - 3' - (2 - chlorovinyl) - cyclopropanecarboxylate.

35 7. A process for producing a cyclopropanecarboxylic acid ester of the general formula (I), given and defined in claim 1, which includes reacting an alcohol, halide or arylsulfonate compound of the general formula (II),

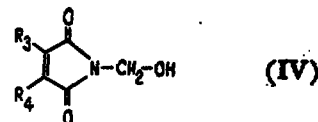


40 wherein R_3 and R_4 are as defined in claim 1 and A is a hydroxyl group, a halogen atom or an arylsulfoxy group, with a cyclopropanecarboxylic acid of the general formula (III),

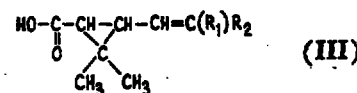


45 wherein R_1 and R_2 are as defined in claim 1, or a reactive derivative thereof.

8. A process according to claim 7, wherein the reaction is conducted by contacting an alcohol compound of the general formula (IV),



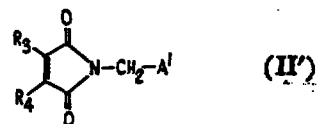
50 wherein R_3 and R_4 are as defined in Claim 1, with a cyclopropanecarboxylic acid of the general formula (III),



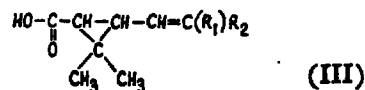
55 wherein R_1 and R_2 are as defined in Claim 1 under conditions which promote dehydration, or with an acid halide of the said acid in the presence of a hydrogen halide acceptor, or with an acid anhydride of the said acid.

60 9. A process according to Claim 8, wherein the said reaction is conducted in the presence of a suitable inert solvent.

10. A process according to claim 7, wherein the said esterification reaction is conducted by contacting a halide or arylsulfonate compound of the general formula (II'),



70 wherein R_3 and R_4 are as defined in claim 1 and A' is a halogen atom or an arylsulfoxy group, with an alkali metal salt or an organic tertiary amine salt of the cyclopropanecarboxylic acid of the general formula (III),



75 wherein R_1 and R_2 are as defined in claim 1, or with the said acid of the formula (III) itself in the presence of a base capable of forming a said salt of the acid.

11. A process according to claim 10, wherein the said reaction is conducted in the presence of a suitable inert solvent.

80 12. An insecticidal composition containing an inert carrier and, as active ingredient, a cyclopropanecarboxylic acid ester of the general formula (I), given and defined in claim 1.

85 13. A composition according to claim 12, wherein the said composition is in the form of an emulsifiable concentrate, wettable powder, dust, coarse or fine granulate, oil spray, aerosol, fumigant effective on heating, thermal fogging agent, fumigant effective without heating or a bait.

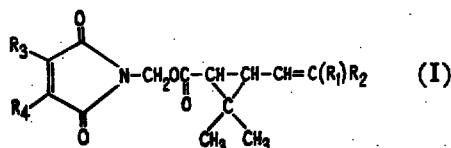
90 14. A composition according to claim 13 in the form of a fumigant effective on heating, which fumigant is a mosquito coil or electrically heated mat.



the oviposition of the treated adults was more than 80% in each case when the suppression percentage of the oviposition of untreated adults was taken as 0%.

WHAT WE CLAIM IS:—

1. A cyclopropanecarboxylic acid ester of the general formula (I),



wherein R_1 is a hydrogen atom, a methyl group or a fluorine, chlorine or bromine atom, R_2 is a fluorine, chlorine or bromine atom, and each of R_3 and R_4 is independently a hydrogen atom, a C_1-C_3 alkyl, C_2-C_3 alkenyl or C_2-C_3 alkynyl group, an alkyl- or halogen-substituted aryl group, an unsubstituted aryl group or an aralkyl group.

2. The compound 2,3 - dimethylmaleimidomethyl 2',2' - dimethyl - 3' - (2,2-dichlorovinyl) - cyclopropanecarboxylate.

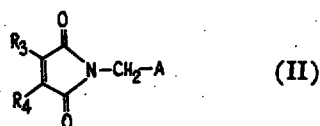
3. The compound 2 - methyl - 3 - ethylmaleimidomethyl 2',2' - dimethyl - 3' - (2,2-dichlorovinyl) - cyclopropanecarboxylate.

4. The compound 2,3 - diethylmaleimidomethyl 2',2' - dimethyl - 3' - (2,2 - difluorovinyl) - cyclopropanecarboxylate.

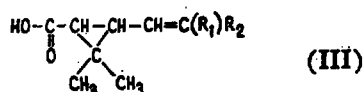
5. The compound 2,3 - dimethylmaleimidomethyl 2',2' - dimethyl - 3' - (2,2 - dibromovinyl) - cyclopropanecarboxylate.

6. The compound 2 - methyl - 3 - isopropylmaleimidomethyl 2',2' - dimethyl - 3' - (2 - chlorovinyl) - cyclopropanecarboxylate.

7. A process for producing a cyclopropanecarboxylic acid ester of the general formula (I), given and defined in claim 1, which includes reacting an alcohol, halide or arylsulfonate compound of the general formula (II),

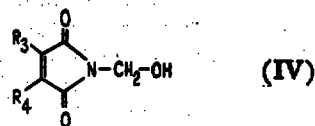


wherein R_3 and R_4 are as defined in claim 1 and A is a hydroxyl group, a halogen atom or an arylsulfoxy group, with a cyclopropanecarboxylic acid of the general formula (III),

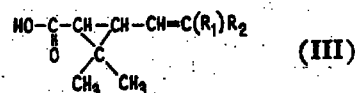


wherein R_1 and R_2 are as defined in claim 1, or a reactive derivative thereof.

8. A process according to claim 7, wherein the reaction is conducted by contacting an alcohol compound of the general formula (IV),



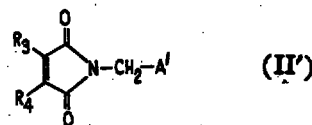
wherein R_3 and R_4 are as defined in Claim 1, with a cyclopropanecarboxylic acid of the general formula (III),



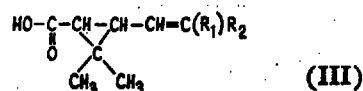
wherein R_1 and R_2 are as defined in Claim 1 under conditions which promote dehydration, or with an acid halide of the said acid in the presence of a hydrogen halide acceptor, or with an acid anhydride of the said acid.

9. A process according to Claim 8, wherein the said reaction is conducted in the presence of a suitable inert solvent.

10. A process according to claim 7, wherein the said esterification reaction is conducted by contacting a halide or arylsulfonate compound of the general formula (II'),



wherein R_3 and R_4 are as defined in claim 1 and A' is a halogen atom or an arylsulfoxy group, with an alkali metal salt or an organic tertiary amine salt of the cyclopropanecarboxylic acid of the general formula (III),



wherein R_1 and R_2 are as defined in claim 1, or with the said acid of the formula (III) itself in the presence of a base capable of forming a said salt of the acid.

11. A process according to claim 10, wherein the said reaction is conducted in the presence of a suitable inert solvent.

12. An insecticidal composition containing an inert carrier and, as active ingredient, a cyclopropanecarboxylic acid ester of the general formula (I), given and defined in claim 1.

13. A composition according to claim 12, wherein the said composition is in the form of an emulsifiable concentrate, wettable powder, dust, coarse or fine granulate, oil spray, aerosol, fumigant effective on heating, thermal fogging agent, fumigant effective without heating or a bait.

14. A composition according to claim 13 in the form of a fumigant effective on heating, which fumigant is a mosquito coil or electrically heated mat.



15. A method of killing insects or acarids, which comprises contacting the insects or acarids with a compound of the formula (I), given and defined in claim 1 or with a composition containing the said compound.
- 5 16. Cyclopropanecarboxylates of the formula (I), given and defined in claim 1, and other than those specifically claimed in claims 2 to 6, which are specifically disclosed herein.
- 10 17. Processes for producing cyclopropanecarboxylates of the formula (I), given and defined in claim 1, substantially as herein described and exemplified.
18. A cyclopropanecarboxylate whenever prepared by a process according to any one of claims 7 to 11 and 17.
19. Compositions according to claim 12 substantially as herein described and exemplified.

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