

PATENT SPECIFICATION

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- (21) Application No. 23536/78 (22) Filed 26 May 1978
 (31) Convention Application No. 52/073 721
 (32) Filed 20 June 1977 in
 (33) Japan (JP)
 (44) Complete Specification published 10 Dec. 1980
 (51) INT CL³ C07D 233/72
 (52) Index at acceptance

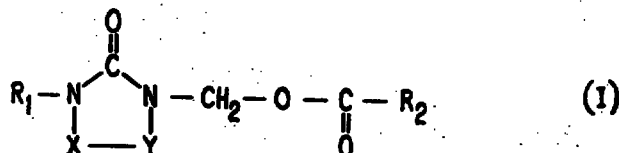
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 628 635 658 65X 662 668 695 697 701 719 761 764
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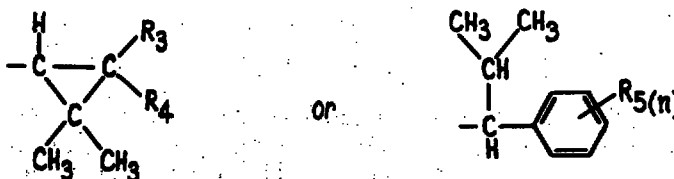
(54) HYDANTOIN N-METHYL ESTERS HAVING PESTICIDAL PROPERTIES

(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 relates to carboxylic acid esters and provides a carboxylic acid ester of the formula (I),



wherein one of X and Y is a carbonyl group and the other is a methylene group in which one of the hydrogen atoms is optionally replaced by a methyl or ethyl group; R₁ is a C₂₋₃ alkyl, C₂₋₃ alkenyl or C₂₋₃ alkynyl group; R₂ is a group of the formula,



in which R₃ is a hydrogen atom or a methyl group and (i) when R₃ is a hydrogen atom, R₄ is a methoxyiminomethyl or 2,2-disubstituted vinyl group in which the substituents are, independently of one another, each methyl, vinyl fluorine, chlorine or bromine, or the substituents together form a tetramethylene chain, (ii) when R₃ is a methyl group, R₄ is a methyl group; R₄ is a methyl group; R₅ is a methyl, methoxy, fluorine, chlorine, bromine or 3,4-methylenedioxy group; and n is 1 or 2.

The invention additionally provides a process for producing such compounds, and an insecticidal and/or acaricidal composition containing such a compound as active ingredient and an inert carrier.

Various insecticides of the cyclopropanecarboxylic acid ester series are well known and some of them are present in pyrethrum extracts.

Among many insecticides now in practical use, these pyrethrum extracts have been widely used for controlling harmful insanitary insects and insects harmful to agricultural crops and household horticultural plants. This is because they are very superior as insecticides in that they have a strong insecticidal activity, low toxicity to mammals and rapid effect against harmful insects, and moreover harmful insects

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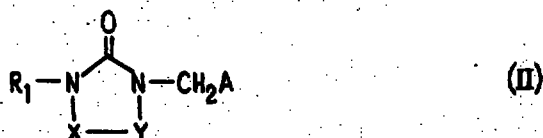
have difficulty in acquiring a resistance to these pesticides. On the other hand, there are drawbacks in applying them; for example, they are high in cost so that their application range is limited from the economical point of view. Accordingly, many homologues have been synthesized by many investigators, but there are very few which are superior to natural pyrethrin or allethrin in terms of wide applicability and relation between effect of cost.

The most important property of insecticides is that they can rapidly knock down and kill harmful insects thereby preventing the harm which the insects would otherwise cause.

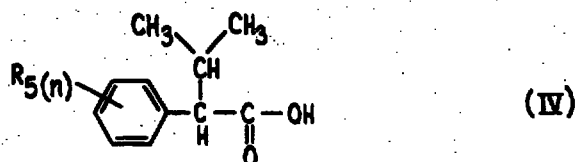
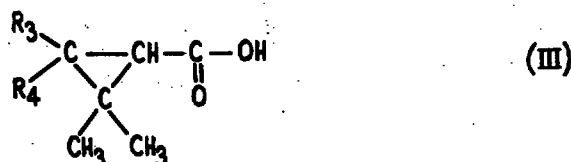
We have extensively searched for insecticides having the abovementioned desirable characteristics, and have found that carboxylic acid esters within the formula (I) were superior to known insecticides in their knockdown effect and insecticidal and/or acaricidal activity on harmful insanitary insects or acarids and moreover were easily synthesized.

Processes embodying the invention for synthesizing esters within the formula (I) will now be explained.

An ester of the formula (I) can be obtained by reacting an alcohol or halide of the formula (II),



wherein R_1 , X and Y are as defined above and A is respectively, a hydroxyl group or a halogen atom, for example chlorine or bromine, with preferably an approximately equimolar amount of, a carboxylic acid of the formula (III) or (IV).



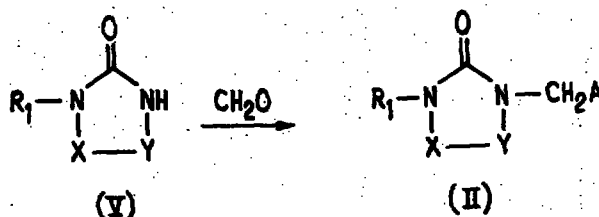
wherein R_3 , R_4 , R_5 and n are as defined above, or a reactive derivative thereof optionally in the presence of a suitable reaction assistant. The reactive derivative can be an acid halide, (optionally mixed) acid anhydride, alkali metal salt or an organic tertiary base salt. When an alcohol of the formula (II), (i.e. A is hydroxyl) and a carboxylic acid of the formula (III) or (IV) are used, the reaction is preferably conducted under conditions which promote dehydration. That is, the alcohol is reacted with the carboxylic acid in the presence of more than 1 mole of dehydrating agent, for example, dicyclohexylcarbodiimide, in a suitable solvent, for example, benzene, toluene or diethyl ether, at a temperature between 10°C and the boiling point of the solvent used, and the reaction is continued for a period of 30 minutes to 1 day. When the alcohol of the formula (II) (i.e. A is hydroxyl) and an acid halide, preferably the chloride or the bromide, of the formula (III) or (IV) are used, the reaction is preferably conducted in a suitable solvent, for example, benzene, toluene or diethyl ether, at a temperature between 0°C and the boiling point of the solvent used, and in the presence of more than 1 mole of an acid acceptor, for example, an organic tertiary amine, e.g. pyridine or triethylamine. The reaction is accomplished soon after mixing the reactants.

When an acid anhydride (optionally a mixed acid anhydride) is used in place of the acid halide, the reaction is preferably conducted in the same manner, except that the reaction is achieved more slowly and is favourably conducted at an elevated temperature.

When a halide of the formula (II) (i.e. A is chlorine or bromine) is used, the carboxylic acid of the formula (III) or (IV), is preferably used in the form of its alkali metal salt or organic tertiary base salt, or may be added to the reaction system as the free acid together with the corresponding base.

In this process, it is desirable to use a solvent for example, benzene or acetone and to heat the reaction system at the boiling point or below of the solvent.

The alcohol of the formula (II) (i.e. A is hydroxyl) can be readily obtained by reaction of the appropriate hydantoin of the formula (V) with formaldehyde or an equivalent thereof, e.g. paraformaldehyde, (an analogous reaction is shown in Beil, 21, 475).



Typical examples of hydantoin N-methylols of the formula (II) (i.e. A is hydroxyl) which are used in processes embodying the present invention are as shown below.

The halide of the formula (II) (i.e. A is a halogen atom, e.g. chlorine or bromine) can be readily obtained by reaction of an alcohol of the formula (II) with a halogenating agent, e.g. phosphorus oxychloride, phosphorus trichloride, phosphorus tribromide, hydrochloric acid, hydrobromic acid, thionyl chloride, (an analogous reaction is shown in Beil. 21, 476).

$ \begin{array}{c} \text{O} \\ \parallel \\ \text{R}_1-\text{N}-\text{C}-\text{N}-\text{CH}_2\text{OH} \\ \quad \\ \text{X} \quad \text{Y} \end{array} $			
R ₁	X	Y	n _D ²⁵
HC ≡ C - CH ₂ -	-CH ₂ -	-C(=O)-	1.5230
HC ≡ C - CH ₂ -	-C(=O)-	-CH ₂ -	1.5250
HC ≡ C - CH ₂ -	$ \begin{array}{c} \text{CH}_3 \\ \\ -\text{C}- \\ \\ \text{H} \end{array} $	-C(=O)-	1.5107
H ₂ C = CH - CH ₂ -	-CH ₂ -	-C(=O)-	1.5102
H ₂ C = CH - CH ₂ -	-C(=O)-	-CH ₂ -	1.5107
H ₃ C - CH ₂ - CH ₂ -	-CH ₂ -	-C(=O)-	1.5092
HC ≡ C - CH ₂ -	$ \begin{array}{c} \text{C}_2\text{H}_5 \\ \\ -\text{C}- \\ \\ \text{H} \end{array} $	-C(=O)-	1.5070

Examples of processes embodying the invention will now be explained in more detail with reference to standard procedures.

A. Reaction between an alcohol and a carboxylic acid halide

0.05 Mole of the alcohol is dissolved in three times its volume of dry benzene and 0.075 mole of pyridine is added thereto. Separately from this, 0.053 mole of the carboxylic acid chloride is dissolved in three times its volume of dry benzene, and the solution is added, portions at a time, to the former solution when an exothermic reaction begins. After allowing to stand overnight in an air-tight condition, a small amount of water is added to dissolve the precipitated pyridine hydrochloride, and the aqueous layer is separated. The organic layer is washed progressively with a 5% aqueous hydrochloric acid, and aqueous solution saturated with sodium hydrogen carbonate and an aqueous solution saturated with sodium chloride, and is then dried over anhydrous sodium sulfate. The benzene solution is concentrated and purified by chromatography on silica gel to obtain the desired ester.

B. Dehydration reaction between an alcohol and a carboxylic acid

0.05 Mole of the alcohol and 0.05 mole of the carboxylic acid are mixed by dissolving them in three times their total volumes of dry benzene, 0.08 mole of dicyclohexylcarbodiimide is added thereto, and the mixture is allowed to stand overnight in an air-tight condition. Next day, the reaction solution is heated under reflux for 2 hours to complete the reaction, cooled and filtered to remove the precipitated dicyclohexylurea. Thereafter, the aftertreatment is carried out in the same manner as that described in the standard procedure A to obtain the desired compound.

C. Reaction between an alcohol and a carboxylic acid anhydride

0.05 Mole of the alcohol is dissolved in three times its volume of toluene, and 0.05 mole of the carboxylic acid anhydride (synthesized from the carboxylic acid and acetic anhydride) is added thereto. The reaction solution is heated under reflux for 3 hours, and then the solution is distilled under reduced pressure or neutralized with a 5% sodium hydroxide to recover the carboxylic acid produced as a by-product. Thereafter, the aftertreatment is carried out in the same manner as that described in the standard procedure A to obtain the desired compound.

D. Reaction between an alcohol halide and a carboxylic acid salt

0.05 Mole of the halide and 0.06 mole of the carboxylic acid are dissolved in three times their total volume of acetone, and a solution of 0.08 mole of triethylamine in three times its volume of acetone is gradually added dropwise thereto at 15° to 20°C with stirring. After the addition is complete, the reaction solution is refluxed for 2 hours to complete the reaction. After cooling, the precipitated triethylamine hydrochloride is filtered off and the filtrate is freed from acetone under reduced pressure.

Three times its volume of benzene is added to the residual liquor, and the aftertreatment is carried out in the same manner as that described in the standard procedure A to obtain the desired ester.

Typical processes embodying the invention carried out using the above mentioned standard procedures will now be explained hereinafter with reference to the following Preparative Examples.

Preparative Example 1

(Example of the standard procedure A)

8.4 g of 1-propargyl-3-hydrantoinylmethyl alcohol was dissolved in a mixture of 26 ml of benzene and 6 g of pyridine, and a solution of 12.0 g of dl-cis, trans-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylic acid chloride in 36 ml of benzene was added dropwise thereto with stirring. After allowing the mixture to stand overnight, a small amount of water was added to dissolve the precipitated pyridine hydrochloride and the resulting two layers were separated from each

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other. The organic layer was washed progressively with a 5% aqueous hydrochloric acid, an aqueous sodium hydrogen carbonate solution and an aqueous solution saturated with sodium chloride, and then dried over anhydrous sodium sulfate. The benzene solution was concentrated and purified by chromatography on silica gel.

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Yield was 16.7 g (93.0%)

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$n_D^{20.5}$ 1.5341

Elemental analysis:

	C(%)	H(%)	N(%)	
Found	50.41	4.32	7.62	
10 Calculated	50.15	4.49	7.80	10

Preparative Example 2

(Example of the standard procedure B)

8.4 g of 1-propargyl-3-hydantoinylmethyl alcohol and 9.0 g of dl-trans-2,2-dimethyl-3-(2-methylbutadienyl)-cyclopropanecarboxylic acid were dissolved in 52 ml of benzene, 16.5 g of dicyclohexylcarbodiimide was added thereto with stirring, and the mixture was allowed to stand overnight. Next day, the reaction solution was heated under reflux for a further 2 hours and cooled. The precipitated dicyclohexylurea was removed by filtration and the solvent was concentrated. Thereafter, purification was carried out in the same manner as that described in preparative Example 1.

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Yield 11.1 g (67.3%)

$n_D^{20.6}$ 1.5373

Elemental analysis:

	C(%)	H(%)	N(%)	
25 Found	65.19	6.78	8.40	25
Calculated	65.43	6.71	8.48	

Preparative Example 3

(Example of the standard procedure C)

8.5 g of 1-allyl-3-hydantoinylmethyl alcohol was dissolved in a mixture of 26 ml of toluene and 6 g of pyridine, and 20.4 g of α -(4-chlorophenyl)isovaleric anhydride was added thereto, followed by heating under reflux for 3 hours. After cooling, the toluene solution obtained was extracted with 5% sodium hydroxide to remove the carboxylic acid produced as a by-product, followed by washing with an aqueous solution saturated with sodium chloride. The toluene solution was then concentrated and then purification was carried out in the same manner as that described in Preparative Example 1.

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Yield 13.0 g (71.0%)

n_D^{23} 1.5357

Elemental analysis:

	C(%)	H(%)	N(%)	
40 Found	58.92	5.77	7.49	40
Calculated	59.26	5.80	7.68	

Preparative Example 4

(Example of the standard procedure D)

9.3g of 1-propargyl-3-hydantoinylmethyl chloride and 11.7 g of dl-trans-2,2-dimethyl-3-cyclopentylidenemethyl-cyclopropanecarboxylic acid were dissolved in 63 ml of acetone, and a solution of 8.1 g of triethylamine in 15 ml of acetone was added dropwise thereto. The reaction mixture was gradually heated and refluxed for 2 hours. After cooling, triethylamine hydrochloride was removed by filtration, and water and benzene were added to the filtrate which was then shaken and separated into two layers. The organic layer was progressively washed with a 5% aqueous sodium hydroxide solution and an aqueous solution saturated with sodium chloride, and the solvent was then concentrated. Thereafter, purification was carried out in the same manner as that described in Preparative Example 1.

Yield was 10.7 g (62.1%)

 $n_D^{25.5}$ 1.5172

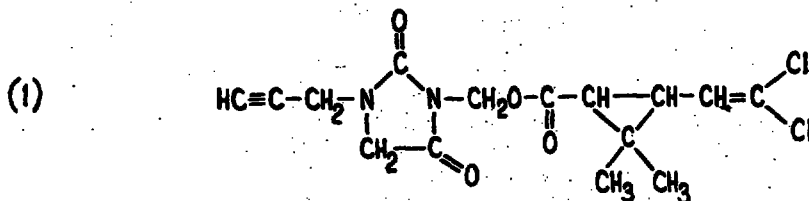
Elemental analysis:

	C(%)	H(%)	N(%)
Found	66.30	7.08	8.39
Calculated	66.26	7.02	8.13

Carboxylic acid esters embodying the present invention and within the formula (I) do not appear to have been previously disclosed in the literature. Typical examples of such compounds are given below.

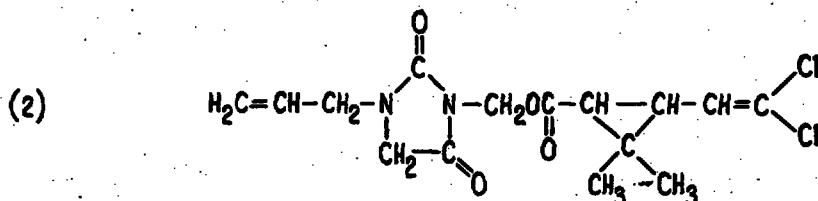
Esters within the formula (I) have steric isomers due to the steric configuration of the carboxylic acid and optical isomers due to the asymmetric carbon atom of the acid. All these isomeric esters are within the scope of the present invention.

Compound Number



1-Propargyl-3-hydantoinylmethyl 2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylate

(dl-Cis, trans ester: $n_D^{25.5}$ 1.5341, process A)
(d-Trans ester: $n_D^{22.5}$ 1.5328, process A)

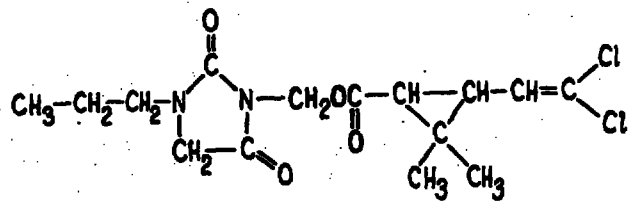


1-Allyl-3-hydantoinylmethyl 2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylate

(dl-Cis, trans ester: n_D^{18} 1.5303, process A)

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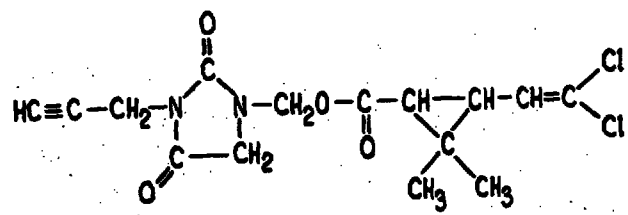
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1-Propyl-3-hydantoinylmethyl 2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylate
(dl-Cis, trans ester: n_D^{19} 1.5288, process A)

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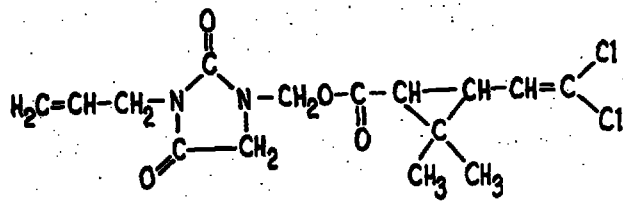
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3-Propargyl-1-hydantoinylmethyl 2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylate
(dl-Cis, trans ester: n_D^{20} 1.5365, process A)

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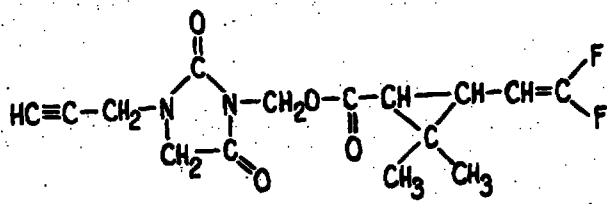


3-Allyl-1-hydantoinylmethyl 2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylate
(dl-Cis, trans ester: $n_D^{17.5}$ 1.5290, process A)

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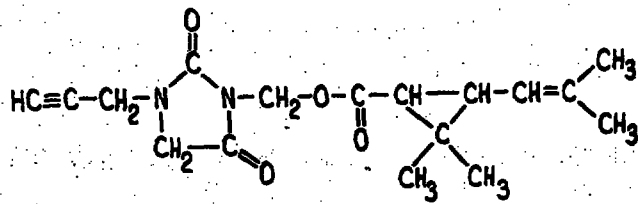


1-Propargyl-3-hydantoinylmethyl 2,2-dimethyl-3-(2,2-difluoromethyl)cyclopropanecarboxylate
(d-Trans ester: n_D^{20} 1.4925, process A)

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1-Propargyl-3-hydantoinylmethyl chrysanthemate
(d-Trans ester: $n_D^{19.5}$ 1.5135, process D)

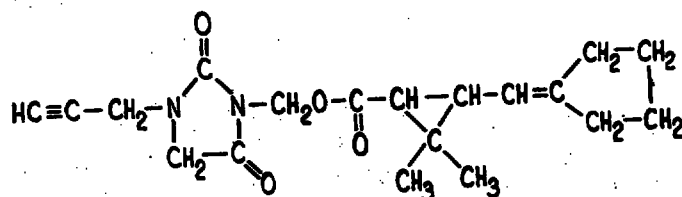
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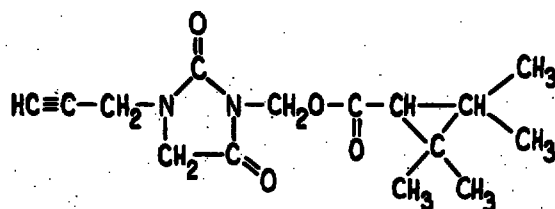
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(8)



1-Propargyl-3-hydantoinylmethyl 2,2-dimethyl-3-cyclopentylidenemethylcyclopropanecarboxylate
(dl-Trans ester: $n_D^{25.5}$ 1.5172, process D)

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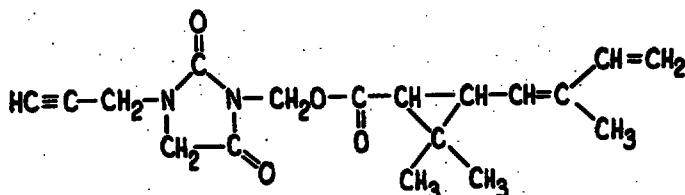


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1-Propargyl-3-hydantoinylmethyl 2,2,3,3-tetramethylcyclopropanecarboxylate

(m.p. 86–93°C, process C)

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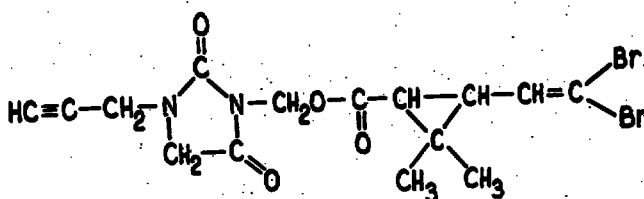


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1-Propargyl-3-hydantoinylmethyl 2,2-dimethyl-3-(2-methylbutadienyl)cyclopropanecarboxylate
(dl-Trans ester: $n_D^{25.5}$ 1.5373, process B)

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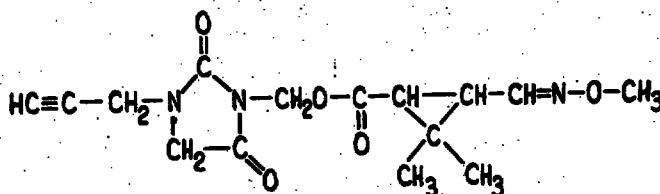
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1-Propargyl-3-hydantoinylmethyl 2,2-dimethyl-3-(2,2-dibromovinyl)cyclopropanecarboxylate
d-Trans ester: n_D^{25} 1.5925, process A)

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(d-Cis ester: n_D^{25} 1.5921, process A)

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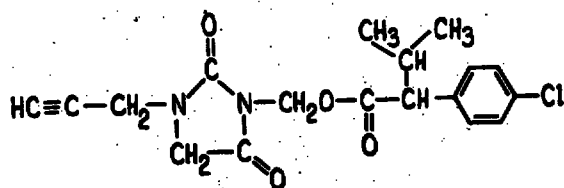


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1-Propargyl-3-hydantoinylmethyl 2,2-dimethyl-3-methoxyiminomethylcyclopropanecarboxylate
(d-Trans ester: n_D^{20} 1.5175, process D)

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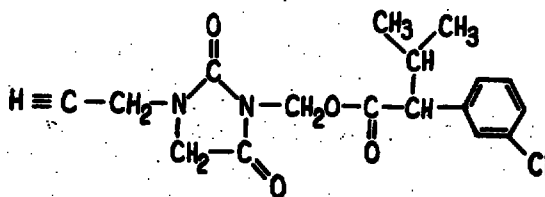
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1-Propargyl-3-hydantoinylmethyl α -(4-chlorophenyl)-isovalerate

($n_D^{22.5}$ 1.5377, process C)

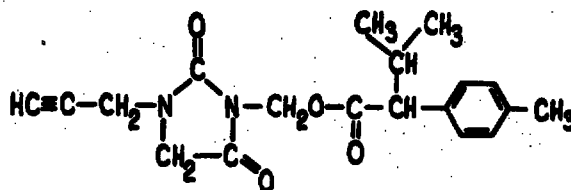
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1-Propargyl-3-hydantoinylmethyl α -(3-chlorophenyl)-isovalerate

(n_D^{24} 1.5391, process C)

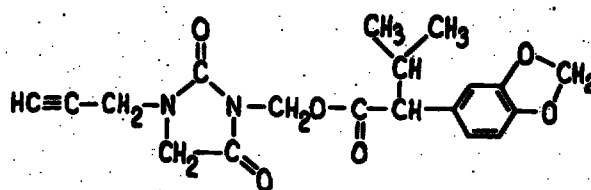
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1-Propargyl-3-hydantoinylmethyl α -(4-methylphenyl)-isovalerate

($n_D^{20.0}$ 1.5257, process C)

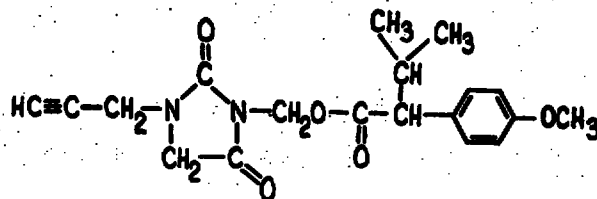
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1-Propargyl-3-hydantoinylmethyl α -(3,4-methylenedioxyphenyl)-isovalerate

($n_D^{21.5}$ 1.5371, process C)

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1-Propargyl-3-hydantoinylmethyl α -(4-methoxyphenyl)-isovalerate

(n_D^{22} 1.5290, process A)

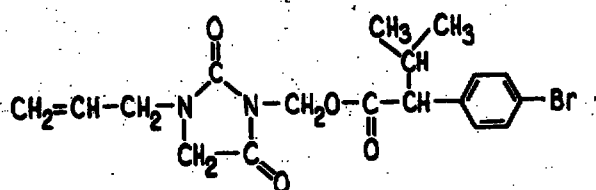
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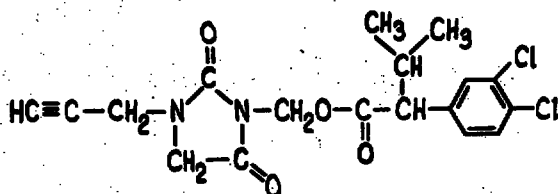
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1-Allyl-3-hydantoinylmethyl α -(4-bromophenyl)isovalerate(n_D²⁴ 1.5423, process A)

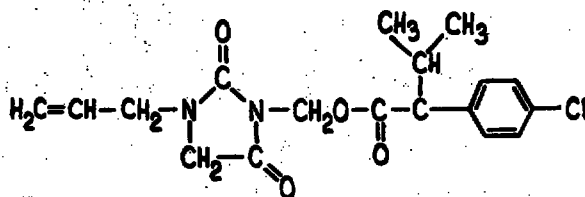
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1-Propargyl-3-hydantoinylmethyl α -(3,4-dichlorophenyl)-isovalerate(n_D²³ 1.5403, process A)

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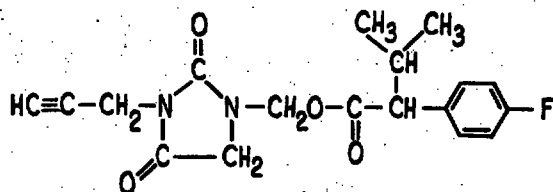
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1-Allyl-3-hydantoinylmethyl α -(4-chlorophenyl)isovalerate(n_D²³ 1.5357, process C)

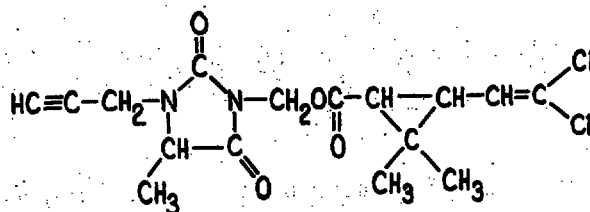
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3-Propargyl-1-hydantoinylmethyl α -(4-fluorophenyl)isovalerate(n_D²² 1.4478, process A)

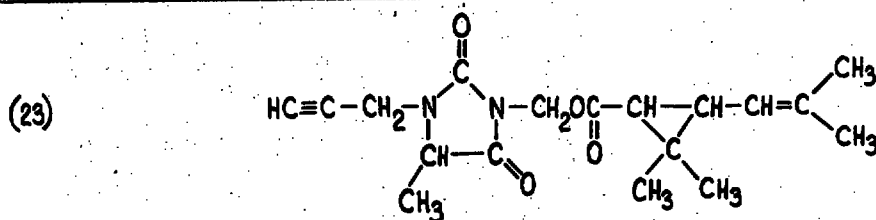
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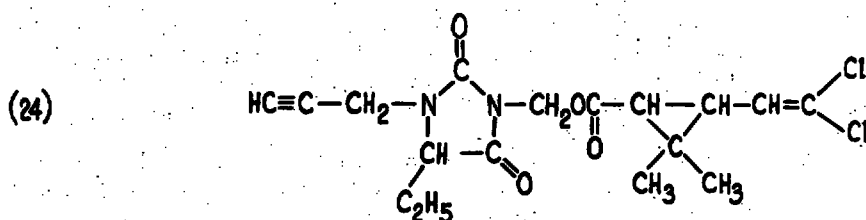
1-Propargyl-5-methyl-3-hydantoinylmethyl 2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylate

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1-Propargyl-5-methyl-3-hydantoinylmethyl chrysanthemate



1-Propargyl-5-ethyl-3-hydantoinylmethyl 2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylate

Compounds embodying the present invention and within the formula (I) exert a very rapid effect on harmful insanitary insects and acarids such as houseflies, (*Musca domestica*), mosquitoes (*Culex spp.*, *Aedes spp.* and *Anopheles spp.*) and cockroaches (*Blattella spp.* and *Periplaneta spp.*). Also, the compounds are very effective for controlling not only insects harmful to agricultural crops such as planthoppers (*Laodelphax striatellus*, *Sogatella furcifera* and *Nilaparvata lugens*), leafhoppers (*Nephotettix spp.*), cutworms (*Spodoptera spp.*) diamondback moths (*Plutella xylostella*), tortorixes (Tortricidae), aphids (Aphididae), stem-borers (*Chilo spp.* and *Tryporyza spp.*), and acarids (*Tetranychus spp.*, *Panonychus spp.* and *Oligonychus spp.*), but also insects and acarid harmful to stored cereals such as grain mite (*Tyrophagus dimidiatus*), Indian meal moth (*Plodia interpunctella*) and rice weevil (*Sitophilus zeamais*) and animal-parasitic lyce (*Anoplura*) and ticks (*Ixodidae*). The compounds are also effective to control other harmful insect and acarids such as *Onychiurus yagii*, *Ctenolepisma villosa*, *Conocephalus spp.*, *Teleogryllus spp.*, *Gryllotalpa africana*, *Locusta migratoria*, *Oxya spp.*, *Coptotermes formosanus*, *Menopon gallinae*, *Damalinea spp.*, *Pediculus humanus*, *Thripidae*, *Eurydema rugosa*, *Eysarcoris spp.*, *Halyomorpha mista*, *Lagymotomus elongatus*, *Nezara spp.*, *Cletus spp.*, *Lygaeidae*, *Dysdercus spp.*, *Stephanitis spp.*, *Psyllidae*, *Aleyrodidae*, *Pseudococcidae*, *Coccidae*, *Diaspididae*, *Hepialidae*, *Tinea spp.*, *Psychidae*, *Lyonetidae*, *Gracilariidae*, *Yponomeutidae*, *Aegeriidae*, *Cnaphalocrois medinalis*, *Galleria mellonella*, *Ostrinia spp.*, *Heterogeneidae*, *Geometridae*, *Lasiocampidae*, *Lymantriidae*, *Notodontidae*, *Adris spp.*, *Agrotis spp.*, *Apatele spp.*, *Heliothis spp.*, *Leucania spp.*, *Mamestra spp.*, *Oraesia spp.*, *Plusia spp.*, *Sesamia spp.*, *Arctiidae*, *Sphingidae*, *Parnara guttata*, *Papilio spp.*, *Pieris spp.*, *Lampides boeticus*, *Elateridae*, *Buprestidae*, *Dermestes spp.*, *Lyctus spp.*, *Anobiidae*, *Bostrychidae*, *Epilachna spp.*, *Tenebrio spp.*, *Cerambycidae*, *Chrysomelidae*, *Bruchidae*, *Curculionidae*, *Attelabidae*, *Scolytidae*, *Scarabaeidae*, *Tenthredinidae*, *Cynipidae*, *Simuliidae*, *Calliphoridae*, *Hypoderma spp.*, *Gasterophilis spp.*, *Trypetidae*, *Drosophilidae*, *Agromyzidae*, *Pulicidae* and so on. Further, not only do compounds within the present invention cause harmful insects and acarids to be knocked down and to die, but they additionally exhibit repellency and flushing effects.

Compounds within the formula (I), hereinafter called "the present compounds" can, for practical use as insecticides or acaricides be optionally made up into those formulations adopted for conventional pyrethroids, using the common auxiliary diluents for insecticides and acaricides and using well known formulating methods. Examples of such formulations are oil sprays, emulsifiable concentrates, dusts, aerosols, wettable powders, coarse or fine granulates, fumigants effective without heating or upon heating (for example mosquito coils) and powdery or solid baits containing attractants.

By combined use of two or more of the present compounds, a stronger insecticidal and/or acaricidal activity can be developed. Further, the insecticidal

and/or acaricidal effect of the present compounds can be increased by combination with the well-known synergists for pyrethroids such as α - [2 - (butoxyethoxy)ethoxyl - 4,5 - methylenedioxy - 2 - propyltoluene (hereinafter referred to as piperonylbutoxide), 1,2 - methylenedioxy - 4 - [2 - (octylsulfanyl)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]hepta - 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), or with the well-known synergists for allethrin or pyrethrin.

In general, the carboxylic acid esters tend to be inferior in their resistances to light, heat and oxidation. Accordingly, compositions having a more stable effect can, if necessary, be obtained by adding suitable amounts of stabilizing agents, for example, antioxidants or UV absorbers such as phenol derivatives (e.g. 2,6-di-tert-butyl-4-methyl phenol), bisphenol derivatives, arylamines (e.g. phenyl- α -naphthylamine, phenyl- β -naphthylamine, condensation products of phenetidine and acetone) and benzophenone compounds.

Additionally, the present compounds can be formulated into multipurpose compositions having a 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 (hereinafter referred to as phenothrin), 5-propargylfurfuryl chrysanthemate and 2-methyl-5-propargyl-3-furylmethyl chrysanthemate; d-trans- or d-cis,trans-chrysanthemic acid esters thereof; pyrethrum extracts; d-trans- or d-cis,trans-chrysanthemic acid esters of d-allethrolone; 3-phenoxybenzyl 2,2-dimethyl-3-(2,2-dichlorovinyl)-cyclopropanecarboxylate, α -cyano-3-phenoxybenzyl 2',2'-dimethyl-3'-(2,2-dichlorovinyl)cyclopropanecarboxylate, α -cyano-3-phenoxybenzyl 2',2',3',3'-tetramethylcyclopropanecarboxylate, α -cyano-3-phenoxybenzyl 2-(4-chlorophenyl)isovalerate and other well-known cyclopropanecarboxylic acid esters; organophosphorus type insecticides, for example, 0,0-dimethyl-0-(3-methyl-4-nitrophenyl)-phosphorothioate (hereinafter referred to as Fenitrothion), 0,0-dimethyl-0-4-cyanophenylphosphorothioate (hereinafter referred to as cyanphos), 0,0-dimethyl-0-(2,2-dichlorovinyl)-phosphate, Fenthion, Phenthoate, Malathion, Salithion, Dipterex and diazinon; carbamate type insecticides, for example, 1-naphthyl-N-methylcarbamate, 3,4-dimethylphenyl-N-methylcarbamate, 3-methylphenyl-N-methylcarbamate, 2-isopropoxyphenyl-N-methylcarbamate and S-methyl-N-(methylcarbamoyloxy)-thioacetimidate; N'-(2-methyl-4-chlorophenyl)-N,N-dimethylformamidine (hereinafter referred to as chlorodimeform); 1,3-bis(carbamoylthio)-2-(N,N-dimethylamino)propane hydrochloride; other insecticides, fungicides, nematocides, acaricides, plant growth regulators, microbial insecticides, insect hormone analogues, herbicides, fertilizers or other chemicals used in agriculture. Further, a synergistic effect due to the combination can also be expected.

The preparation of insecticidal and acaricidal compositions containing the present compounds will now be illustrated with reference to the following Formulation Examples.

An insecticidal and/or acaricidal composition embodying invention preferably contains from 0.001 to 80.0%, more preferably 0.01 to 50% by weight of active ingredient.

Formulation Example 1

0.2 Part of one of each of the present compounds (1) to (24) is dissolved in respective portions of kerosene and each portion is made up to 100 parts with kerosene. Thus, an oil spray of each respective compound is obtained.

Formulation Example 2

0.05 Part of the present compound (7) and 0.25 part of piperonylbutoxide are mixed, dissolved in kerosene and made up to 100 parts with kerosene. Thus, an oil spray of the compound is obtained.

Formulation Example 3

To 20 parts of one of each of the present compounds (1) to (24) are added respective 15 parts of a mixture of nonionic surfactant and anionic surfactant and 65 parts of xylene, and each mixture is well stirred to make a solution of each

respective compound. Thus, an emulsifiable concentrate of each compound is obtained.

Formulation Example 4

To 10 parts of one of each of the present compounds (2), (4), (7), (8), (9), (12), (13), (16) and (20) are added respective 20 parts of S-421, 15 parts of a mixture of nonionic surfactant and anionic surfactant and 55 parts of xylene. Each mixture is well stirred to make a solution. Thus, an emulsifiable concentrate of each compound is obtained.

Formulation Example 5

0.1 Part of the present compound (13), 0.2 part of tetramethrin, 7 parts of xylene and 7.7 parts of deodorized kerosene are well mixed to make a solution. The solution is poured into an aerosol container. After attaching a valve portion to the container, 85 parts of a propellant (liquefied petroleum gas) is introduced into the container under pressure through the valve. Thus, an aerosol of the compound is obtained.

Formulation Example 6

0.3 Part of the present compound (9), 0.1 part of 3-phenoxybenzyl d-cis,trans-chrysanthemate, 7 parts of xylene and 7.6 parts of deodorized kerosene are well mixed to make a first solution. Additionally, 0.3 part of d-trans acid isomer of the present compound (6), 0.1 part of tetramethrin, 7 parts of xylene and 7.6 parts of deodorized kerosene are well mixed to make a second solution. Each solution is poured into a respective aerosol container and treated in the same manner as that described in Formulation Example 5. Thus, an aerosol of each compound is obtained.

Formulation Example 7

0.2 Part of the present compound (8), 0.1 part of the d-trans-chrysanthemic acid ester of allethrin, 7 parts of xylene and 7.7 parts of deodorized kerosene are well mixed to make a first solution. Additionally, 0.2 part of the d-trans acid isomer of the present compound (11), 0.2 part of Resmethrin, 7 parts of xylene and 7.6 parts of deodorized kerosene are well mixed to make a second solution. Each solution is poured into a respective aerosol container and treated in the same manner as that described in Formulation Example 5. Thus, an aerosol of each compound is obtained.

Formulation Example 8

To 0.6 g of the d-trans acid isomer of each of the present compounds (1) and (11) is added respectively, 0.4 g of BHT, and each mixture is dissolved in 20 ml of methanol. Each solution is uniformly mixed with 99 g of a mosquito coil carrier containing Tabu powder (the powder of *Machilus thunbergii*), Pyrethrum marc and wood powder in a ratio of 3:5:1, and the methanol is then evaporated. To each residue is added 150 ml of water and the mixture is kneaded thoroughly, shaped into a mosquito coil and dried. Thus, a mosquito coil of each compound is obtained.

Formulation Example 9

To 0.15 g of one of each of the present compounds (3), (5), (6), (9), (12) and (16) is added, respectively, 0.2 g of the d-trans-chrysanthemic acid ester of allethrin, and each mixture is dissolved in 20 ml of methanol. Each solution is uniformly mixed with 99.65 g of a mosquito coil carrier (the same as above), and the methanol is then evaporated. To each residue is added 150 ml of water and the mixture is well kneaded, shaped into a mosquito coil and dried. Thus, a mosquito coil of each compound is obtained.

Formulation Example 10

To 0.1 g of one of each of the present compounds (6) and (14) is added a respective mixture of 0.1 g of BHT and 0.1 g of piperonylbutoxide, and each resultant admixture is dissolved in a suitable amount of chloroform. Each solution is allowed to uniformly adsorb into a filter paper of 3.5cm x 1.5 cm x 0.3 cm (thick).

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

carrier, those having the same effect as pulp plate (e.g. filter paper), for example asbestos may be used.

Formulation Example 11

To 0.02 g of the d-trans acid isomer of the present compound (1) are added 0.05 g of 5-propargylfurfuryl dl-acid, trans-chrysanthemate and 0.1 g of BHT, and the mixture is dissolved in a suitable amount of chloroform. The solution is then allowed to uniformly adsorb into a filter paper of 3.5 cm x 1.5 cm x 0.3 cm (thick).

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

Formulation Example 12

To 20 parts of one of each of the present compounds (3), (5), (7), (9), (12), (16), (17), (19) and (20) is added a respective mixture of 10 parts of Fenitrothion and 5 parts of a mixture of nonionic and anionic surfactant, followed by thorough mixing. Each resultant admixture is then well mixed with 65 parts of 300 mesh diatomaceous earth by being well stirred in a mortar. Thus, a wettable powder of each compound is obtained.

Formulation Example 13

To 1 part of one of each of the present compounds (5), (7) and (13) is added a respective mixture of 2 parts of 3-methylphenyl-N-methylcarbamate, and the resultant admixture is dissolved in 20 parts of acetone. Each solution is then well mixed with 97 parts of 300 mesh talc by being well stirred in a mortar, and the acetone is then removed by evaporation. Thus, a dust of each compound is obtained.

Formulation Example 14

To 3 parts of one of each of the present compounds (2), (8), (11), (15) and (18) are added a respective mixture of 5 parts of lignin sulfonate derivative and 92 parts of clay, and each resultant admixture is well mixed by being stirred in a mortar.

Each mixture is then well mixed with 10% by weight of water based on the weight of the mixture, granulated by means of a granulator and air-dried. Thus, a granule of each compound is obtained.

Formulation Example 15

To 2 parts of one of each of the present compounds (4), (5), (7), (13) and (20) is added a respective mixture of 2 parts of Cyanophos, 5 parts of lignin sulfonate derivative and 91 parts of clay, and each resultant admixture is well mixed by being stirred in a mortar.

Each admixture is well mixed with 10% by weight of water based on the weight of the admixture, granulated by means of a granulator and air-dried. Thus, a fine granulate of each compound is obtained.

Formulation Example 16

0.1 Part of the d-trans acid isomer of the present compound (1), 0.2 part of the d-trans acid isomer of allethrin, 11.7 parts of deodorized kerosene and 1 part of an emulsifying agent, namely, a surfactant (glycerides of fatty acid), are well mixed and emulsified with addition of 50 parts of pure water. The emulsion is then poured into an aerosol container together with 35 parts of a 3:1 mixture of deodorized butane to deodorized propane. Thus, a water-based aerosol is obtained.

The application of the present compounds and their insecticidal and acaricidal activities will now be illustrated in more detail with reference to the following Application Examples.

Application Example 1

Ten percent emulsifiable concentrates were prepared as described in Formulation Example 3.

At the bottom of each of a number of polyethylene cups each of 5.5 cm in diameter was placed a filter paper of the same size, 0.75 ML of a 200-fold aqueous dilute solution of one of each of the emulsifiable concentrates (corresponding to 500 ppm) was dropped onto the filter paper, and 30 mg of sucrose as a food was uniformly placed over this. Ten female adult houseflies (*Musca domestica*) were introduced into each cup which was then covered with a lid. After 48 hours, the numbers of dead and alive were counted to obtain the % mortality (4 replications).

Test Compound	Mortality (%)
Present compound (1) (dl-cis, trans isomer)	100
Present compound (1) (d-trans isomer)	100
„ (2)	100
„ (4)	100
„ (5)	100
„ (6)	100
„ (7)	100
„ (8)	100
„ (9)	100
„ (10)	95
„ (11)	100
(d-trans isomer)	
„ (11)	100
(d-cis isomer)	
„ (13)	100
„ (14)	100
„ (15)	90
„ (16)	90
„ (17)	95
„ (18)	100
„ (21)	90

Application Example 2

0.1 Part of one of each of the present compounds was dissolved in kerosene and each solution was made up to 100 parts with kerosene. Thus, an oil spray of each compound was obtained. A group of insects consisting of ten adult females of the northern house mosquito (*Culex pipiens pallens*) and 10 adult houseflies (*Musca domestica*) was introduced into each of a number of (70 cm)³ glass chambers. 0.7 ml of one of each of the oil sprays was applied to a respective chamber and the number of knocked down insects was counted with lapse of time. The value of KT_{50} was obtained from the mean knock-down ratio of three applications according to Finney's graphic method. After 10 minutes, the knocked down insects were collected and transferred to a recovery container and fed with a 5% sugar solution. After 24 hours, the numbers of dead and alive were counted.

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Test compound	Adult female northern house mosquito		Adult housefly	
	KT ₅₀ (sec)	Mortality (%)	KT ₅₀ (sec)	Mortality (%)
Present compound (1) (dl-cis, trans acid ester)	69"	90	96"	60
Present compound (1) (d-trans acid ester)	30"	100	60"	80
Present compound (6)	19"	100	46"	70
Present compound (8)	75"	95	150"	25
Present compound (9)	35"	95	150"	20
Present compound (17)	140"	75	280"	35
Present compound (4)	50"	85	280"	30
Present compound (7)	30"	100	72"	10
Present compound (11) (d-trans acid ester)	35"	85	78"	30
Present compound (11) (d-cis acid ester)	38"	95	96"	10
Present compound (22)	75"	85	114"	20
Tetramethrin	162"	45	372"	20
Pyrethrins	320"	50	> 600"	0

Application Example 3

"P groups each of adult females of the northern house mosquito (*Culex pipiens pallens*) were each introduced into a respective (70 cm)³ glass chamber. 0.7 Ml of one of each of the oil sprays formulated by the method of Formulation Example 1 was sprayed and the number of knocked down mosquitoes was counted 10 minutes after spraying.

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Test compound	KD %
(2)	100
(3)	100
(5)	100
(10)	90
(12)	100
(13)	90
(14)	85
(15)	90
(16)	100
(18)	90
(19)	85
(20)	85
(21)	90
(23)	100
(24)	85
Pyrethrins	80
Resmethrin	50

Application Example 4

5 Five milliliters of one of each of the oil sprays formulated by the method of Formulation Example 2 were sprayed, according to the Campbells's turn table method [Soap and Sanitary Chemicals, Vol. 14, No. 6, 119 (1938)], onto a respective group of about 100 adult houseflies (*Musca domestica*) per group. The adult houseflies were exposed to the descending mist for 10 minutes. The number of knocked down insects was counted 10 minutes after spraying and mortality count was made after 24 hours.

Test compound	KD (%) at 10 minutes	Mortality (%)
(7) + piperonylbutoxide	100	95

Application Example 5

15 Each of the emulsifiable concentrates formulated by the method of Formulation Example 3 was diluted 100,000 times with water. Two hundred milliliters of one of each test solution so prepared was placed in a respective 300-ml glass beaker and 30 full grown larvae of the northern house mosquito (*Culex pipiens pallens*) were introduced into each beaker. By the next day, more than 90% of the larvae were killed in each case.

Application Example 6

The insecticidal activity on adult houseflies (*Musca domestica*) of each aerosol formulated by the methods of Formulation Examples 5, 6, 7 and 16 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 all aerosols, more than 80% of the flies were knocked down 15 minutes after spraying and more than 70% of the flies were killed by the next day.

Application Example 7

Groups each of about 50 adult females of the northern house mosquito (*Culex pipiens pallens*) were each introduced into a respective (70 cm)³ glass chamber in which a battery-type small electric fan (having a wing diameter of 13 cm) was placed and driven.

A 0.1 g portion of one of each of the mosquito coils formulated by the methods of Formulation Examples 8 and 9 was ignited at one end and placed at the centre of the bottom of a respective chamber. With all mosquito coils, more than 90% of the adults were knocked down within 20 minutes and more than 80% of the adults were killed by the next day.

Application Example 8

Ten adult German cockroaches (*Blattella germanica*) were introduced into a plywood-made trigonal prism-like shelter with diet and water. The shelter containing the cockroaches was made to stand so as to open upwards into a glass chamber (70 cm)³, and 0.7 ml of a 0.1% oil spray of one of the compounds shown in the following Table was applied to the chamber. The number of flushed out insects was counted with the lapse of time. The experiment was then repeated for each of the other compounds shown in the Table.

Test compound	Flushing out (%)				
	38"	75"	150"	300"	600"
(1) (dl-cis, trans acid ester)	35	65	75	85	95
(3)	30	45	45	50	65
(6)	47	74	79	79	100
(9)	15	55	60	70	80
Pyrethrins	15	20	35	40	50
Propoxur	0	0	0	0	5
Untreated	0	0	0	0	0

Application Example 9

Groups of about 50 adult houseflies (*Musca domestica*) were each introduced into a respective (70 cm)³ glass chamber in which a battery-type small electric fan (having a wing diameter of 13 cm) was placed and driven.

One of each of the fumigants formulated by the methods of Formulation Examples 10 and 11 was placed on a hot plate in a respective chamber and fumigated. More than 90% of the houseflies were knocked down within 20 minutes with all fumigants.

Application Example 10

About 20 rice seedlings were grown up to the 3 to 4-leaved stage in each of a number of flower pots each of 10 cm in diameter, and one of each of the dusts formulated by the method of Formulation Example 13 was dusted onto a respective

pot at a rate of 3 kg/10 are by means of a Bell jar duster. After dusting, each pot was covered with a wire net, and 20 to 30 adult green rice leafhoppers (*Nephotettix cincticeps*) were introduced. 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 11

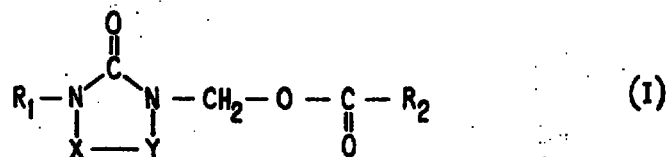
Ten litres of water were placed in each of a number of 14-litre polypropylene buckets and 1 g of one of each of the granular preparations formulated by the method of Formulation Example 14 was added to a respective bucket. After one day, about 100 full grown northern house mosquito larvae (*Culex pipiens pallens*) were immersed in the water in each bucket. The numbers of dead and alive were counted, and it was found that more than 90% of the larvae were killed within 24 hours in each case.

Application Example 12

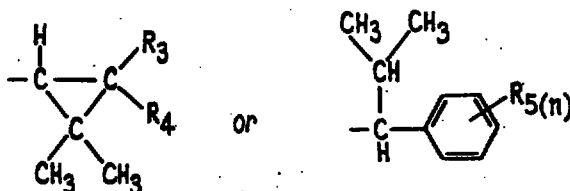
Adult female carmine mites (*Tetranychus cinnabarinus*) were made parasitic on leaves of the potted kidney bean (primordial leaf stage) which had elapsed 9 days after sowing, at a rate of 10—15/leaf, and bred at 27°C for a week in a constant temperature room. After this period, numerous carmine mites were found to be bred to various growth stages. At this time, a 200-fold aqueous dilute solution of one of each of the emulsifiable concentrates formulated from the present compounds (2), (6), (8), (9) and (13) by the method of Formulation Example 3 was sprayed at a rate of 10 ml/pot by means of a turn table. After 10 days, damage to the kidney bean by the mites was observed, but hardly any damage was observed in each case.

WHAT WE CLAIM IS:—

1. A hydantoin N-methyl ester of the formula,

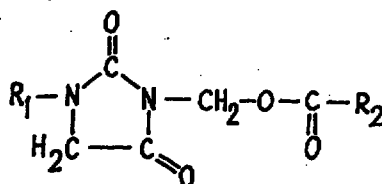


wherein one of X and Y is a carbonyl group and the other is a methylene group in which one of the hydrogen atoms is optionally replaced by a methyl or ethyl group; R₁ is a C₁₋₃ alkyl, C₂₋₃ alkenyl or C₂₋₃ alkynyl group; R₂ is a group of the formula,



in which R₃ is a hydrogen atom or a methyl group and (i) when R₃ is a hydrogen atom, R₄ is a methoxyiminomethyl or 2,2-disubstituted vinyl group in which the substituents are, independently of one another, each methyl, vinyl fluoride, chlorine or bromine, or the substituents together form a tetramethylene chain, (ii) when R₃ is a methyl group, R₄ is a methyl group; R₅ is a methyl, methoxy, fluorine, chlorine, bromine or a 3,4-methylenedioxy group; and n is 1 or 2.

2. A hydantoin N-methyl ester according to claim 1 which is specifically of the formula.



wherein R₁ and R₂ are as defined in Claim 1.



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pot at a rate of 3 kg/10 are by means of a Bell jar duster. After dusting, each pot was covered with a wire net, and 20 to 30 adult green rice leafhoppers (*Nephotettix cincticeps*) were introduced. The numbers of dead and alive after 24 hours were counted, and a mortality of more than 80% was obtained in each case.

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Application Example 11

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Ten litres of water were placed in each of a number of 14-litre polypropylene buckets and 1 g of one of each of the granular preparations formulated by the method of Formulation Example 14 was added to a respective bucket. After one day, about 100 full grown northern house mosquito larvae (*Culex pipiens pallens*) were immersed in the water in each bucket. The numbers of dead and alive were counted, and it was found that more than 90% of the larvae were killed within 24 hours in each case.

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Application Example 12

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Adult female carmine mites (*Tetranychus cinnabarinus*) were made parasitic on leaves of the potted kidney bean (primordial leaf stage) which had elapsed 9 days after sowing, at a rate of 10—15/leaf, and bred at 27°C for a week in a constant temperature room. After this period, numerous carmine mites were found to be bred to various growth stages. At this time, a 200-fold aqueous dilute solution of one of each of the emulsifiable concentrates formulated from the present compounds (2), (6), (8), (9) and (13) by the method of Formulation Example 3 was sprayed at a rate of 10 ml/pot by means of a turn table. After 10 days, damage to the kidney bean by the mites was observed, but hardly any damage was observed in each case.

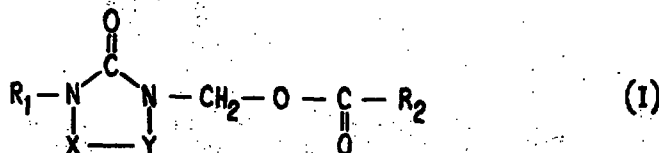
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WHAT WE CLAIM IS:—

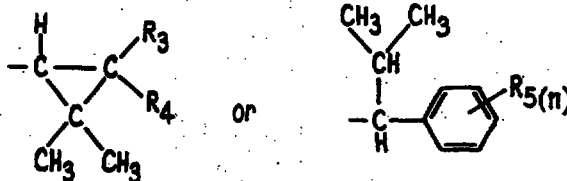
1. A hydantoin N-methyl ester of the formula,

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wherein one of X and Y is a carbonyl group and the other is a methylene group in which one of the hydrogen atoms is optionally replaced by a methyl or ethyl group; R₁ is a C₁₋₃ alkyl, C₂₋₃ alkenyl or C₂₋₃ alkynyl group; R₂ is a group of the formula,

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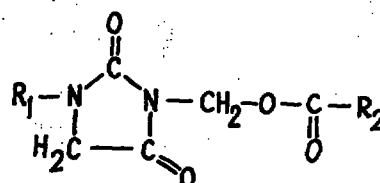
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in which R₃ is a hydrogen atom or a methyl group and (i) when R₃ is a hydrogen atom, R₄ is a methoxyiminomethyl or 2,2-disubstituted vinyl group in which the substituents are, independently of one another, each methyl, vinyl fluoride, chlorine or bromine, or the substituents together form a tetramethylene chain, (ii) when R₃ is a methyl group, R₄ is a methyl group; R₅ is a methyl, methoxy, fluorine, chlorine, bromine or a 3,4-methylenedioxy group; and n is 1 or 2.

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2. A hydantoin N-methyl ester according to claim 1 which is specifically of the formula.



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wherein R₁ and R₂ are as defined in Claim 1.

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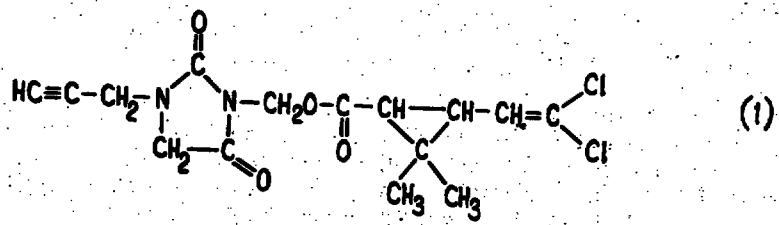


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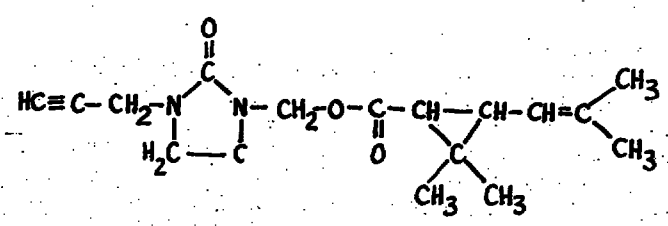
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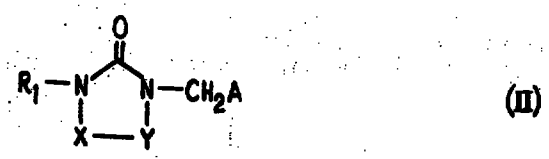
3. The hydantoin N-methyl ester according to Claim 2 which is specifically of the formula,



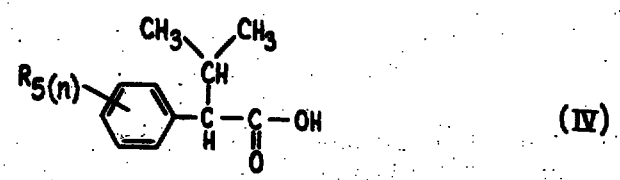
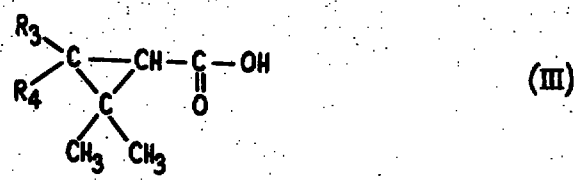
4. The hydantoin N-methyl ester according to Claim 2 which is specifically of the formula,



5. A process for producing a compound of the formula (I), given and defined in Claim 1, which comprises reacting an alcohol or halide of the formula,

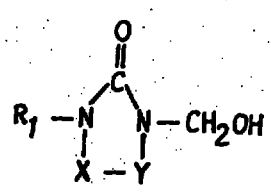


wherein R_1 , X and Y are as defined in Claim 1 and A is a hydroxyl group or a halogen atom respectively, with a carboxylic acid of the formula,



wherein R_3 , R_4 , R_5 and n are as defined in Claim 1, or with a reactive derivative of the carboxylic acid.

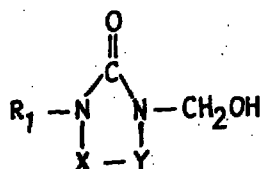
6. A process according to Claim 5, which comprises reacting the alcohol of the formula,





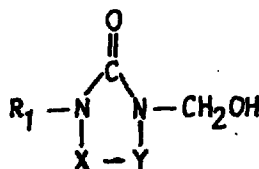
wherein R_1 , X and Y are as defined in Claim 5, with a halide of the said carboxylic acid, in an organic solvent in the presence of an acid acceptor.

7. A process according to Claim 5, which comprises reacting an alcohol of the formula,



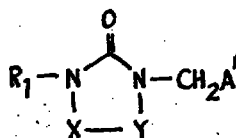
wherein R_1 , X and Y are as defined in Claim 5, with the said carboxylic acid, in an organic solvent in the presence of a dehydrating agent.

8. A process according to Claim 5, which comprises reacting the alcohol of the formula,



wherein R_1 , X and Y are as defined in Claim 5, with an anhydride of the said carboxylic acid.

9. A process according to Claim 5, which comprises reacting the halide of the formula,



wherein R_1 , X and Y are as defined in Claim 5 and A' is a halogen atom, with an alkali metal salt or organic tertiary base salt of the said carboxylic acid.

10. An insecticidal and/or acaricidal composition comprising an inert carrier and, as active ingredient, a compound of the formula (I) given and defined in Claim 1.

11. An insecticidal and/or acaricidal composition according to Claim 10, wherein the composition is in the form of an oil spray, emulsifiable concentrate, dust, aerosol, wettable powder, coarse or fine granulate, mosquito coil, fumigant effective with or without heating, bait or thermal fogging agent.

12. A process for controlling an insect and/or acarid, which comprises contacting the insect and/or acarid with a compound of the formula (I), given and defined in claim 1.

13. The hydantoin N-methyl esters of the formula given and defined in claim 1 other than those specifically claimed in claims 3 and 4 which are specifically disclosed herein.

14. Processes according to any one of claims 5 to 9 for producing a hydantoin N-methyl ester, which processes are substantially as herein described and exemplified.

15. Hydantoin N-methyl esters whenever produced by a process according to any one of claims 5 to 9 and 14.

16. Insecticidal and/or acaricidal compositions according to claim 10 or claim 11 substantially as herein described and exemplified.

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