

PATENT SPECIFICATION

(11) 1348 096

1348 096

- (21) Application No. 9992/72 (22) Filed 3 March 1972
 (31) Convention Application No. P21 11 156.8
 (32) Filed 9 March 1971 in
 (33) Germany (DT)
 (44) Complete Specification published 13 March 1974
 (51) International Classification C07C 131/00 A01N 9/20
 (52) Index at acceptance

C2C 200 20Y 220 222 227 22Y 30Y 313 314 31Y 338
 340 342 346 34Y 360 361 36Y 581 591 627
 62X 652 71Y 791 79Y KB KR

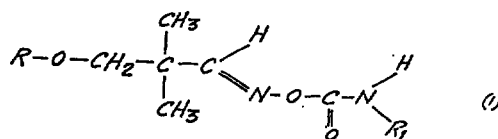


(54) INSECTICIDALLY ACTIVE
 3-SUBSTITUTED-2,2-DIMETHYLPROPANALDOXIME
 CARBAMATES

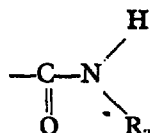
(71) We, FARBWERKE HOECHST AKTIENGESellschaft, vormals Meister Lucius & Brüning, a body corporate recognised under German law, of 6230 Frankfurt Main 80, Hoechst, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to propanalcarbamoyloximes, a process for their preparation and insecticidal compositions containing them.

The present invention provides compounds of the general formula

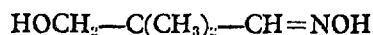


in which R represents a hydrogen atom or a radical of the formula



and R₁ and R₂, which may be the same or different, each represents an alkyl or alkenyl group having from 1 to 4 carbon atoms, or a phenyl or naphthyl radical in which one or more hydrogen atoms may be substituted by halogen atoms and/or alkyl groups having from 1 to 4 carbon atoms. Preferred halogen atoms are chlorine and/or bromine atoms, preferred alkyl groups are the methyl and/or ethyl group. Unsubstituted phenyl radicals, or phenyl radicals in which one or two hydrogen atoms are substituted as defined above are preferred.

The present invention also provides a process for the preparation of these compounds, which comprises reacting 3-hydroxy-2,2-dimethyl-propanaldoxime of the formula



II

with a substantially equimolar amount of an isocyanate of the formula R₁NCO, to obtain a compound of the formula 1 in which R is hydrogen and, if desired, reacting the product obtained with a substantially equimolar amount of an isocyanate of the formula R₂NCO and subsequently isolating the reaction product.

When R₁ is the same as R₂, the reaction is advantageously carried out in a single step using 2 moles of isocyanate per mole of oxime.

This reaction of the hydroxy-propanaldoxime with the isocyanate may be carried out in a known manner, for example, at a temperature of from 10° to 60°C, preferably from 30° to 50°C, in a solvent which is inert under the reaction conditions, for example, in benzene, toluene, hexane, methylene chloride, CCl₄, chloroform, or an ether, for example di-isopropyl ether, tetrahydrofuran or dioxan.

Inert solvents having a boiling point of less than 130°C are preferred.

After complete reaction, the solvent is distilled off and the reaction product is obtained either as a crystalline compound, or, often, as an oil.

Numerous compounds of the formula I can be obtained according to the process of the present invention, for example

- | | | |
|----|---|----|
| 5 | 3-hydroxy-2,2-dimethylpropanal-(O-methyl-carbamoyloxime), | 5 |
| | 3-hydroxy-2,2-dimethylpropanal-(O-ethyl-carbamoyloxime), | |
| | 3-hydroxy-2,2-dimethylpropanal-(O-n-propyl-carbamoyloxime), | |
| | 3-hydroxy-2,2-dimethylpropanal-(O-isopropyl-carbamoyloxime), | |
| 15 | 3-hydroxy-2,2-dimethylpropanal-(O-allyl-carbamoyloxime), | 15 |
| | 3-hydroxy-2,2-dimethylpropanal-(O-n-butyl-carbamoyloxime), | |
| | 3-hydroxy-2,2-dimethylpropanal-(O-isobutyl-carbamoyloxime), | |
| | 3-hydroxy-2,2-dimethylpropanal-(O- <i>o</i> -chlorophenyl-carbamoyloxime), | |
| | 3-hydroxy-2,2-dimethylpropanal-(O- <i>m</i> -chlorophenyl-carbamoyloxime), | |
| 20 | 3-hydroxy-2,2-dimethylpropanal-(O- <i>p</i> -chlorophenyl-carbamoyloxime), | 20 |
| | 3-hydroxy-2,2-dimethylpropanal-(O-3,4-dichlorophenyl-carbamoyloxime), | |
| | 3-hydroxy-2,2-dimethylpropanal-(O-2,4-dichlorophenyl-carbamoyloxime), | |
| | 3-hydroxy-2,2-dimethylpropanal-(O-4-bromophenyl-carbamoyloxime), | |
| | 3-hydroxy-2,2-dimethylpropanal-(O-2-methyl-5-chlorophenyl-carbamoyloxime), | |
| 25 | 3-hydroxy-2,2-dimethylpropanal-(O-2-chloro-5-methylcarbamoyloxime), | 25 |
| | 3-hydroxy-2,2-dimethylpropanal-(O- α -naphthyl-carbamoyloxime), | |
| | 3-hydroxy-2,2-dimethylpropanal-(O- β -naphthyl-carbamoyloxime), | |
| | 3-hydroxy-2,2-dimethylpropanal-(O- <i>o</i> -methylphenyl-carbamoyloxime), | |
| 30 | 3-hydroxy-2,2-dimethylpropanal-(O- <i>m</i> -methylphenyl-carbamoyloxime), | 30 |
| | 3-hydroxy-2,2-dimethylpropanal-(O- <i>p</i> -methylphenyl-carbamoyloxime), | |
| | 3-hydroxy-2,2-dimethylpropanal-(O- <i>o</i> -ethylphenyl-carbamoyloxime), | |
| | 3-hydroxy-2,2-dimethylpropanal-(O- <i>p</i> -ethylphenyl-carbamoyloxime), | |
| | 3-methyl-carbamoyloxy-2,2-dimethylpropanal-(O-methyl-carbamoyloxime), | |
| | 3-ethyl-carbamoyloxy-2,2-dimethylpropanal-(O-ethyl-carbamoyloxime), | |
| 35 | 3-propyl-carbamoyloxy-2,2-dimethylpropanal-(O-propyl-carbamoyloxime), | 35 |
| | 3-butyl-carbamoyloxy-2,2-dimethylpropanal-(O-n-butyl-carbamoyloxime), | |
| | 3-isobutyl-carbamoyloxy-2,2-dimethylpropanal-(O-isobutyl-carbamoyloxime), | |
| | 3- <i>p</i> -chlorophenyl-carbamoyloxy-2,2-dimethylpropanal-(O- <i>p</i> -chlorophenyl- | |
| 40 | carbamoyloxime), | 40 |
| | 3- <i>o</i> -chlorophenyl-carbamoyloxy-2,2-dimethylpropanal-(O- <i>o</i> -chlorophenyl- | |
| | carbamoyloxime), | |
| | 3- <i>m</i> -chlorophenyl-carbamoyloxy-2,2-dimethylpropanal-(O- <i>m</i> -chlorophenyl- | |
| | carbamoyloxime), | |
| 45 | 3-(3,4-dichlorophenyl-carbamoyloxy)-2,2-dimethylpropanal-(O-3,4-dichloro- | 45 |
| | phenyl-carbamoyloxime), | |
| | 3-(<i>p</i> -bromophenyl-carbamoyloxy)-2,2-dimethylpropanal-(O- <i>p</i> -bromophenyl- | |
| | carbamoyloxime), | |
| | 3- <i>p</i> -chlorophenyl-carbamoyloxy-2,2-dimethylpropanal-(O-methyl-carbamoyl- | |
| 50 | oxime), | 50 |
| | 3-(3,4-dichlorophenyl-carbamoyloxy)-2,2-dimethylpropanal-(O-methyl- | |
| | carbamoyloxime), | |
| | 3-ethyl-carbamoyloxy-2,2-dimethylpropanal-(O-methyl-carbamoyloxime), | |
| | 3-n-propyl-carbamoyloxy-2,2-dimethylpropanal-(O-methyl-carbamoyloxime), | |
| 55 | 3-allyl-carbamoyloxy-2,2-dimethylpropanal-(O-methyl-carbamoyloxime), | 55 |
| | 3-isobutyl-carbamoyloxy-2,2-dimethylpropanal-(O-methyl-carbamoyloxime), | |
| | 3-n-butyl-carbamoyloxy-2,2-dimethylpropanal-(O-methyl-carbamoyloxime), | |
| | 3-methyl-carbamoyloxy-2,2-dimethylpropanal-(O-n-butyl-carbamoyloxime), | |
| | 3-ethyl-carbamoyloxy-2,2-dimethylpropanal-(O-n-butyl-carbamoyloxime), | |
| 60 | 3-propyl-carbamoyloxy-2,2-dimethylpropanal-(O-n-butyl-carbamoyloxime), | 60 |
| | 3-allyl-carbamoyloxy-2,2-dimethylpropanal-(O-n-butyl-carbamoyloxime), | |
| | 3-isobutyl-carbamoyloxy-2,2-dimethylpropanal-(O-n-butyl-carbamoyloxime), | |
| | 3-(<i>p</i> -chlorophenyl-carbamoyloxy)-2,2-dimethylpropanal-(O-n-butyl-carbamoyl- | |
| 65 | oxime), | 65 |
| | 3-(3,4-dichlorophenyl-carbamoyloxy)-2,2-dimethylpropanal-(O-n-butyl- | |
| | carbamoyloxime), | |

3-(*p*-bromophenyl-carbamoyloxy)-2,2-dimethylpropanal-(*O*-*n*-butyl-carbamoyl-oxime).

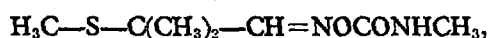
As insecticides, the compounds of the present invention have systemic and contact activity. They may be used as insecticides in the usual compositions, for example as dusting powders, granules, and, preferably, as spray liquors.

Accordingly the present invention also provides an insecticidal composition comprising as active ingredient a compound of the general formula I together with a suitable inert carrier.

Generally, the compositions will contain from 5 to 90% of the active ingredient, the remainder being conventional additives, for example, solid or liquid inert substances, wetting, adhesion or dispersing agents, or grinding auxiliaries.

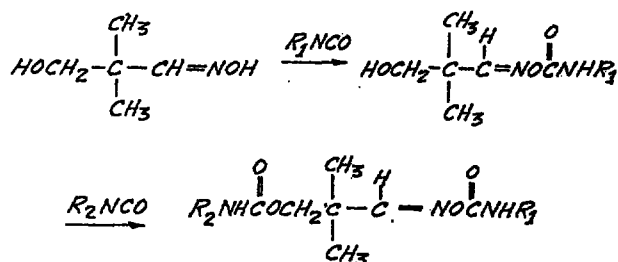
The present invention further provides a method of combating insects which comprises applying to their habitat a compound of the general formula I.

As compared with the known commercial product Aldicarb (2 - methyl - 2 - (methylthio) - propionaldehyde - *O* - (methyl - carbamoyl) - oxime) of the formula



which, on account of its high toxicity and volatility, must be employed in the form of granules and must be worked into the soil, the compounds of the present invention must be used in a 2 to 2.5 fold amount in order to achieve the same results; however, they have a far lower toxicity (1/12 to 1/15, as compared with Aldicarb) which ensures easier application. When worked into the soil as granules, their effect is of about equal duration to that of Aldicarb, but their special advantage resides in the fact that they can be employed as spray liquors, especially as aqueous emulsions, which allows them to be used successfully and simply to combat pests everywhere and in every stage of growth. Their capability of decomposition (see Example 21 below), permits spray treatment even just before the harvesting, especially in order to combat the very resistant fruit fly. The poor volatility of the compounds according to the present invention (see Example 22 below) allows their application in closed rooms, such as greenhouses.

The starting material for the preparation of the compounds of the present invention, namely 3 - hydroxy - 2,2 - dimethyl - propanaloxime (ω - hydroxy - pivalinaldoxime) of the formula II (melting point 29.5°C, boiling point 118°—120°C at 12 mm Hg) is described in German Patent No. 726,387 (1939) and can be prepared according to Wessely, Monatshefte 21 (1901), 230. By reacting it with 1 or 2 moles of an isocyanate (in the first step, oxime carbamates are obtained) according to the following equation



the compounds of the invention are obtained in practically quantitative yields.

The following Examples illustrate the invention.

Examples of Preparation

Example 1

3-hydroxy-2,2-dimethylpropanal-(*O*-methylcarbamoyloxime)

30 g (0.35 mole) of II were dissolved in 100 ml of chloroform, and 16.2 g (0.352 mole) of methyl isocyanate were added. The temperature of the mixture rose to 50°C, and, after complete reaction, agitation was continued for a further 3 hours at 40°C. After elimination of the solvent in a water jet vacuum, the residue solidified, and, after redissolution in benzene, a product having a melting point of 109°C was obtained. The yield was 46 g.

Analysis:

	$\text{C}_7\text{H}_{14}\text{N}_2\text{O}_3$	(MW 174)
calculated	C 48.2%	found 48.1%
	H 8.0%	8.0%
	N 16.1%	16.4%

The proton resonance spectrum proved a substitution of O-carbamoyl at the oxime radical.

In the analogy to Example 1, there were prepared from II:
using n-propyl-isocyanate

- 5 (2) 3-hydroxy-2,2-dimethylpropanal-(O-n-propyl-carbamoyloxime) 5
colorless oil, n_D^{20} 1.4736
using n-butyl-isocyanate
(3) 3-hydroxy-2,2-dimethylpropanal-(O-n-butyl-carbamoyloxime)
oil, n_D^{20} 1.4520
10 using isobutyl-isocyanate 10
(3a) 3-hydroxy-2,2-dimethylpropanal-(O-isobutyl-carbamoyloxime)
oil, n_D^{20} 1.4708

Example 4

- 15 3-methylcarbamoyloxy-2,2-dimethylpropanal-(O-methylcarbamoyloxime) 15
35.1 g (0.3 mole) of II were dissolved in 100 ml of chloroform. With cooling by ice, 34.2 g (0.6 mole) of methyl isocyanate were added dropwise. Subsequently, the solution was agitated for a further 5 hours at 40°C, and the chloroform was eliminated in a water jet vacuum. 69 g of a viscous oil remained as residue, having a refractive index of 1.4636.

- 20 Analysis: 20
calculated $C_9H_{17}N_3O_4$ (MW 231)
found N 18.2% N 18.0%

According to Example 4, there were prepared:
using ethyl-isocyanate

- 25 (5) 3-ethylcarbamoyloxy-2,2-dimethylpropanal-(O-ethylcarbamoyloxime) 25
viscous oil, n_D^{20} 1.4756
using n-propyl-isocyanate
(6) 3-propylcarbamoyloxy-2,2-dimethylpropanal-(O-propyl-carbamoyloxime)
viscous oil, n_D^{20} 1.4747
30 using n-butyl-isocyanate 30
(7) 3-n-butylcarbamoyloxy-2,2-dimethylpropanal-(O-n-butylcarbamoyloxime)
oil, n_D^{20} 1.4763
using isobutyl-isocyanate
(7a) 3-isobutylcarbamoyloxy-2,2-dimethylpropanal-(O-isobutylcarbamoyloxime)
35 viscous oil, n_D^{20} 1.4793 35
using p-chlorophenyl-isocyanate
(8) 3-p-chlorophenylcarbamoyloxy-2,2-dimethylpropanal-(O-p-chlorophenyl-
carbamoyloxime)
crystals, m.p. 115—116°C (decomposition)

Example 9

3-p-chlorophenylcarbamoyloxy-2,2-dimethylpropanal-(O-methylcarbamoyloxime)
To 17.4 g (0.1 mole) of the product of Example 1, dissolved in 100 ml of chloroform, 15.3 g (0.1 mole) of p-chlorophenyl-isocyanate were added. The mixture was heated for 10 hours to 50°C; the solvent was then eliminated in a water

jet vacuum. 32 g of a crystalline product remained, which was recrystallized from chloroform/petroleum ether (60—90), and which had a melting point of 156°C (decomposition).

Analysis:

5		$C_{14}H_{18}ClN_2O_4$	(MW 327,5)	5
	calculated	N 12.8%	found N 12.5%	

According to Example 9, there were prepared:
using ethyl-isocyanate

(10) 3-ethylcarbamoyloxy-2,2-dimethylpropanal-(O-methylcarbamoyloxime)

10	viscous oil; n_D^{20} 1.4540	10
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(11) 3-n-propylcarbamoyloxy-2,2-dimethylpropanal-(O-methylcarbamoyloxime)

oil; n_D^{20} 1.4548
using allyl-isocyanate

15	(12) 3-allylcarbamoyloxy-2,2-dimethylpropanal-(O-methylcarbamoyloxime)	15
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oil; n_D^{20} 1.4637
using isobutyl-isocyanate

(13) 3-isobutylcarbamoyloxy-2,2-dimethylpropanal-(O-methylcarbamoyloxime)

oil; n_D^{20} 1.4548

20	From the product of Example 3, according to Example 9, there was prepared using methylisocyanate:	20
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(14) 3-methylcarbamoyloxy-2,2-dimethylpropanal-(O-n-butylcarbamoyloxime)

oil; n_D^{20} 1.4536

Examples of Application

25	Example 15	25
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Horse beans (*Vicia faba*) infested with bean aphids (*Doralis fabae*) were sprayed with a suspension containing the compound 3 - hydroxy - 2,2 - dimethylpropanal - (O-methylcarbamoyloxime) of Example 1 in a concentration of 0.06%, until the liquid began to drip off. The plants were then stored in a greenhouse at 20°C. When the effect was investigated after 24 hours, all aphids were killed.

30		30
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When the compounds of Examples 2 or 4 were analogously employed, the same results were obtained.

Example 16

35	Milkweed bugs (<i>Oncopeltus fasciatus</i>) on potted cotton plants were sprayed, until the liquid began to drip off, with an aqueous dilution of an emulsifiable concentrate, in which 0.125% of 3 - methylcarbamoyloxy - 2,2 - dimethylpropanal - (O-methylcarbamoyloxime) of Example 4 was contained.	35
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The plants with the bugs were stored in cylindrical gauze cages at 25°C. 24 hours after the spray treatment, all bugs were killed.

40	The same results were obtained using the agents of Example 5, 6, 7 and 8 in an analogous manner.	40
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Example 17

3-methylcarbamoyloxy-2,2-dimethylpropanal-(O-methylcarbamoyloxime)

45	In order to prove systemic properties, 0.25 mg of the agent of Example 4 was homogenously spread in the area of a root ball of horse beans (<i>Vicia faba</i>) wrapped in a sheet, which beans were infested with bean aphids, by completely moistening the earth with an aqueous dilution of an emulsifiable concentrate.	45
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The agent penetrates the roots and is rapidly conducted into the upper parts of the plant, where all aphids were killed within 24 hours after the application of the agent.

50		50
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During the test time, the plants were stored in a greenhouse at 20°C.

Example 18

Relapsing fever ticks (*Ornithodoros moubata*) were put into Petri dishes, the cover plate and bottom of which had been uniformly covered with 1 cc. each of a 0.0125% acetic solution of 3 - methylcarbamoyloxy - 2,2 - dimethylpropanal - (O-methylcarbamoyloxime) of Example 4.

24 hours after having put in the test animals, all ticks were killed.

The same results were obtained using the compounds of Example 5 and 6 in an analogous manner.

Example 19

Potted cinerariae infested with Green peach aphid (*Myzodes persicae*) were sprayed, until the liquid began to drip off, with an aqueous dilution of an emulsifiable concentrate containing 0.006% of the agent of Example 10. The sprayed plants were stored in a climatic test cabinet at 25°C and a relative atmospheric moisture of 60%.

After 24 hours, all pests were found killed.

The same results were obtained when the compounds of Examples 13, 9, 11, 12 and 14 were used in an analogous manner.

Example 20

Half-ripe bananas were sprayed, until the liquid began to drip off, with the aqueous dilution of an emulsifiable concentrate containing 0.006% of the compound of Example 4. After the sprayed layer had superficially dried, the treated bananas were suspended in glass jars, in which adults of the Mediterranean fruit fly (*Ceratitis capitata*) were present.

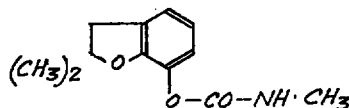
The flies repeatedly settled down on the treated bananas and thus were killed within 2 hours after the start of the contact in a 100% rate.

Example 21

Series of horse beans (*Vicia faba*) were simultaneously sprayed, until the liquid began to drip off, with the aqueous dilution of an emulsifiable concentrate containing 0.025% of the agent of Example 4, and, after a superficial drying, infected with bean aphids (*Doralis fabae*) in different time intervals. In this test it was proved that the activity of the sprayed layer is still unchanged after 8 days, that after 10 days only 70% of the original efficiency is remaining, which efficiency is completely lost after 14 days.

Thus it was also proved that the plants, 14 days after the spray treatment, were freed from the layer of insecticide activity.

In comparison to this test, the agent 2,3 - dihydro - 2,2 - dimethyl - benzo-furan - 7 - yl - methylcarbamate of the following formula



carbofuran applied in the same manner, was active even 4 weeks after the spray treatment.

Example 22

In glass jars which contained plants (*Vicia faba*) infested with bean aphids (*Doralis fabae*), filters were suspended to which the agent of Example 4 in an acetic solution was applied in such a manner that 0.25 mg/l of air was vaporized. After 48 hours, there was no effect (temperature: 20°C; relative atmospheric moisture: 45%). As compared with this result, the agent Dichlorvos (O,O - dimethyl - O - 2,2 - dichlorovinyl-phosphate) applied in the same manner, was still active in as low a concentration as 0.005 mg/l of air. The low gas phase concentration which results from this test allows the application of the preparation also under glass (greenhouses) in order to combat pests.

Example 23

An emulsion concentrate containing
15% of agent
65% of cyclohexanone or dimethylformamide
20% of oxyethylated nonylphenol (10 EO).

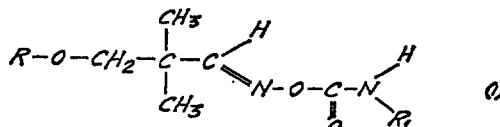
Example 24

Preparation of a dusting powder

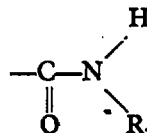
	20 g of agent are ground with	
5	5 g of finely dispersed silicic acid, and subsequently blended in a mixer with a mixture of	5
	11.5 g of finely dispersed silicic acid	
	3.5 g. of polypropyleneglycol (polymerization degree 750)	
	10.0 g of sodium lignin sulfonate	
	1.0 g of sodium oleic acid methyl tauride	
10	49.0 g of magnesium/aluminium silicate	10
	100.0 g	

WHAT WE CLAIM IS:—

1. A compound of the formula



15 in which R represents a hydrogen atom or a radical of the formula 15



20 and R₁ and R₂, which may be the same or different, each represents an alkyl or alkenyl group having from 1 to 4 carbon atoms, or a phenyl or naphthyl radical in which one or more hydrogen atoms may be substituted by halogen atoms and/or alkyl groups having from 1 to 4 carbon atoms. 20

2. A compound as claimed in claim 1 specifically mentioned herein.

3. A process for the preparation of a compound as claimed in claim 1, which comprises reacting 3 - hydroxy - 2,2 - dimethyl - propanaldoxime of the formula



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25 with a substantially equimolar amount of an isocyanate of the formula R₁NCO to obtain a compound in which R is hydrogen, and, if desired, reacting the product obtained with a substantially equimolar amount of an isocyanate of the formula R₂NCO. 25

30 4. A process as claimed in claim 3 substantially as described in any one of Examples 1 to 14 herein. 30

5. A compound as claimed in claim 1 prepared by a process as claimed in claim 3 or claim 4.

6. An insecticidal composition, comprising as active ingredient a compound as claimed in claim 1, together with a solid or liquid carrier.

35 7. An insecticidal composition as claimed in claim 6, substantially as described in Example 23 or Example 24 herein. 35

8. A method of combating insects which comprises applying to their habitat a compound as claimed in claim 1.

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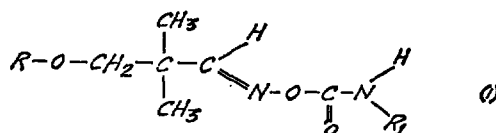
Example 24

Preparation of a dusting powder

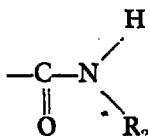
	20 g of agent are ground with	
5	5 g of finely dispersed silicic acid, and subsequently blended in a mixer with a mixture of	5
	11.5 g of finely dispersed silicic acid	
	3.5 g. of polypropyleneglycol (polymerization degree 750)	
	10.0 g of sodium lignin sulfonate	
10	1.0 g of sodium oleic acid methyl tauride	10
	49.0 g of magnesium/aluminium silicate	
	100.0 g	

WHAT WE CLAIM IS:—

1. A compound of the formula



15 in which R represents a hydrogen atom or a radical of the formula



20 and R_1 and R_2 , which may be the same or different, each represents an alkyl or alkenyl group having from 1 to 4 carbon atoms, or a phenyl or naphthyl radical in which one or more hydrogen atoms may be substituted by halogen atoms and/or alkyl groups having from 1 to 4 carbon atoms.

2. A compound as claimed in claim 1 specifically mentioned herein.

3. A process for the preparation of a compound as claimed in claim 1, which comprises reacting 3 - hydroxy - 2,2 - dimethyl - propanaloxime of the formula



II

25 with a substantially equimolar amount of an isocyanate of the formula R_1NCO to obtain a compound in which R is hydrogen, and, if desired, reacting the product obtained with a substantially equimolar amount of an isocyanate of the formula R_2NCO .

4. A process as claimed in claim 3 substantially as described in any one of Examples 1 to 14 herein.

5. A compound as claimed in claim 1 prepared by a process as claimed in claim 3 or claim 4.

6. An insecticidal composition, comprising as active ingredient a compound as claimed in claim 1, together with a solid or liquid carrier.

7. An insecticidal composition as claimed in claim 6, substantially as described in Example 23 or Example 24 herein.

8. A method of combating insects which comprises applying to their habitat a compound as claimed in claim 1.

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