

PATENT SPECIFICATION

(11) 1 496 842

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(54) N-SULPHENYLATED ARYLCARBAMATES, PROCESSES FOR THEIR PREPARATION AND THEIR USE AS INSECTICIDES

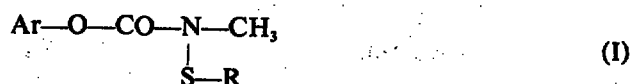
(71) We, BAYER AKTIENGESELLSCHAFT, a body corporate, organised under the laws of Germany, of Leverkusen, Germany, do hereby declare this invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to certain new N-sulphenylated arylcarbamates, to a process for their preparation and to their use as insecticides.

It has already been disclosed that N-methylcarbamates of benzo-1,3-dioxolan-4-ol and 2 (1,3-dioxolan-2-yl)-phenol exhibit an insecticidal action (compare published Netherlands Patent Applications 68 02492 and 65 13024).

However, a disadvantage of these compounds is their high toxicity to warm-blooded animals and the fact that their insecticidal action is not always satisfactory, especially if low concentrations are used.

The present invention provides N-sulphenylated arylcarbamates of the general formula



Ar represents 2,2-dimethyl benzo-1,3-dioxolan-4-yl and

R represents phenyl optionally monosubstituted or polysubstituted by halogen, nitro, alkyl or trifluoromethyl, or

Ar represents 1,3-dioxolan-2-yl-phenyl-(2) and

R represents phenyl optionally monosubstituted or polysubstituted by halogen, nitro or alkyl or, in the 2- and/or 4-position, by trifluoromethyl.

The compounds exhibit strong insecticidal, above all soil-insecticidal, properties.

The preferred compounds are those of formula (I) which are sulphenylated arylcarbamates in which Ar represents 2,2-dimethyl benzo-1,3-dioxolan-4-yl and R represents phenyl, tolyl, ethylphenyl, fluorophenyl, chlorophenyl, bromophenyl, nitrophenyl or trifluoromethylphenyl (especially trifluoromethylphenyl, chlorophenyl or phenyl), or arylcarbamates in which Ar represents 1,3-dioxolan-2-yl-phenyl-(2) and R represents phenyl, chlorophenyl, 2-trifluoromethylphenyl, 4-trifluoromethylphenyl, 2-trifluoromethyl-3-chlorophenyl, 2-trifluoromethyl-4-chlorophenyl, 4-trifluoromethyl-2-chlorophenyl, 4-trifluoromethyl-3-chlorophenyl, tolyl, ethylphenyl, fluorophenyl, bromophenyl or nitrophenyl.

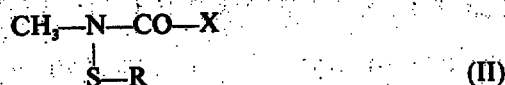
The invention also provides a process for the preparation of a N-sulphenylated arylcarbamate of the formula (I) in which

(a) a N-sulphenylated arylcarbamic acid halide of the general formula

(R)

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R has the abovementioned meaning and
X represents fluorine or chlorine
is reacted with a compound of the general formula



in which

Ar has the abovementioned meaning
optionally in the presence of a diluent and of an acid-binding agent, or
(b) a sulphenyl chloride of the general formula



in which

R has the abovementioned meaning
is reacted with a carbamate of the general formula

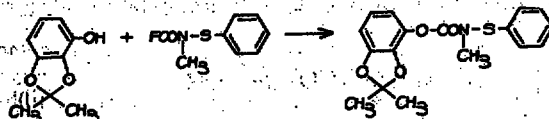


in which

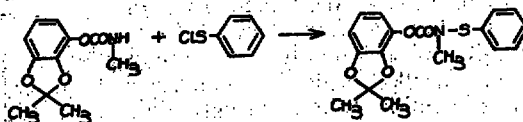
Ar has the abovementioned meaning,
optionally in the presence of a diluent and of an acid-binding agent.

Surprisingly, the N-sulphenylated arylcarbamates according to the invention exhibit a substantially better insecticidal, and above all soil-insecticidal, action than the known benzo-1,3-dioxolan-4-ol N-methylcarbamate. Further, the N-sulphenylated arylcarbamates according to the invention are substantially less toxic to warm-blooded animals than the corresponding non-sulphenylated carbamates. The compounds according to the invention thus represent a genuine enrichment of the art.

If 2,2-dimethyl benzo-1,3-dioxolan-4-ol and N-methyl-N-phenylmercapto-carbamic acid fluoride are used, the course of the reaction can be represented by the following equation:



If 2,2-dimethyl benzo-1,3-dioxolan-4-ol N-methylcarbamate and phenylsulphenyl chloride are used, the course of the reaction can be represented by the following equation:



The arylcarbamic acid halides of the general formula (II) used as starting materials are known (compare German Auslegeschrift (German Published Specification) 1,297,095). The phenols of the formula (III) and the carbamates of the formula (V) may be prepared in accordance with processes analogous to those described in published Netherlands Patent Applications 65 13042 and 68 02492.

Diluents which can be used in the reaction according to the invention are all inert organic solvents. These include ethers such as diethyl ether, dioxan and tetrahydrofuran, hydrocarbons such as benzene and toluene, and chlorinated hydrocarbons such as chloroform and chlorobenzene.

To bind hydrogen halide liberated in the reaction, an acid-binding agent, preferably a tertiary organic base such as triethylamine, is preferably added to the reaction mixture.

If desired, the compounds of the formula (II) may be used in the form of alkali metal salts.

The reaction temperatures can be varied within a substantial range; in general, the reaction is carried out at 0 to 100°C, preferably at 20 to 40°C.

As previously mentioned, the new N-substituted carbamates are distinguished by an excellent insecticidal, above all soil-insecticidal, action. Furthermore, the compounds according to the invention are distinguished by their low toxicity to warm-blooded animals, compared with the unsubstituted carbamates on which they are based.

The compounds can therefore be employed particularly advantageously for combating sucking and biting insects, including hygiene pests and pests of stored products, as well as soil insects. They furthermore possess a soil-fungicidal and microbistatic action.

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

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

Also to be classed with the biting insects are beetles (*Coleoptera*), for example the granary weevil (*Sitophilus granarius* = *Calandra granaria*), the Colorado beetle (*Leptinotarsa decemlineata*), the dock beetle (*Gastrophysa viridula*), the mustard beetle (*Phaedon cochleariae*), the blossom beetle (*Meligethes aeneus*), the raspberry beetle (*Byturus tomentosus*), the bean weevil (*Bruchidius* = *Acanthoscelides obiectus*), the leather beetle (*Dermestes frischii*), the khapra beetle (*Trogoderma granarium*), the flour beetle (*Tribolium castaneum*), the northern corn billbug (*Calandra* or *Sitophilus zeamais*), the drugstore beetle (*Stegobium paniceum*), the yellow mealworm (*Tenebrio molitor*) and the saw-toothed grain beetle (*Oryzaephilus surinamensis*), but also species living in the soil, for example wireworms (*Agriotes* spec.) and larvae of the cockchafer (*Melolontha melolontha*); cockroaches, such as the German cockroach (*Blattella germanica*), American cockroach (*Periplaneta americana*), Madeira cockroach (*Leucophaea* or *Rhyparobia maderae*), oriental cockroach (*Blatta orientalis*), the giant cockroach (*Blaberus giganteus*) and the black giant cockroach (*Blaberus fuscus*) as well as *Henschoutedenia flexivitta*; further, *Orthoptera*, for example the house cricket (*Gryllus domesticus*); termites such as the eastern subterranean termite (*Reticulitermes flavipes*) and *Hymenoptera* such as ants, for example the garden ant (*Lasius niger*).

The *Diptera* comprise essentially the flies, such as the vinegar fly (*Drosophila melanogaster*), the Mediterranean fruit fly (*Ceratitis capitata*), the house fly (*Musca domestica*), the little house fly (*Fannia canicularis*), the black blow fly (*Phormia regina*) and bluebottle fly (*Calliphora erythrocephala*) as well as the stable fly (*Stomoxys calcitrans*); further, gnats, for example mosquitoes such as the yellow fever mosquito (*Aedes aegypti*), the northern house mosquito (*Culex pipiens*) and the malaria mosquito (*Anopheles stephensi*).

When applied against hygiene pests and pests of stored products, particularly flies and mosquitoes, the compounds are also distinguished by an outstanding residual activity on wood and clay, as well as a good stability to alkali on limed substrates.

The active compounds according to the present invention can be converted into the usual formulations, such as solutions, emulsions, suspensions, powders,

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

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

By liquefied gaseous diluents or carriers are meant liquids which would be gaseous at normal temperatures and pressures, e.g. aerosol propellants, such as halogenated hydrocarbons, e.g. Freon. "Freon" is a Registered Trade Mark.

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

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

The active compounds according to the invention can be used as a mixture with other active compounds.

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

The active compounds can be used as such or in the form of their formulations or the use forms prepared therefrom, such as ready-to-use solutions, emulsions, foams, suspensions, powders, pastes, soluble powders, dusting agents and granules. They may be applied in the customary manner, for example by squirting, spraying, atomising, dusting, scattering, fumigating, gassing, watering, dressing or encrusting.

The compositions may be diluted for actual application, and the active compound concentrations in the ready-to-use preparations can be varied within substantial ranges. In general, they are 0.0001 to 10%, preferably 0.01 to 1%, by weight.

The active compounds can also be used with good success in the ultra-low volume (ULV) method, where it is possible to apply formulations of up to 95% strength or even the 100% strength active compound by itself.

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

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

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

The compounds according to the invention, and the preparation and use of the compounds according to the invention, are illustrated by the following Examples. In Examples A and B, the active compounds according to the invention are identified by numbers which are those of the corresponding preparative Examples.

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Example A.

Plutella Test.

Solvent: 3 parts by weight of dimethylformamide
Emulsifier: 1 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of the active compound was mixed with the stated amount of solvent containing the stated amount of emulsifier and the concentrate was diluted with water to the desired concentration.

Cabbage leaves (*Brassica oleracea*) were sprayed with the preparation of the active compound until dew moist and were then infested with caterpillars of the diamond-back moth (*Plutella maculipennis*).

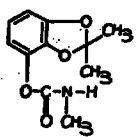
After the specified periods of time, the degree of destruction was determined as a percentage: 100% means that all the caterpillars were killed whereas 0% means that none of the caterpillars were killed.

The active compounds, the concentrations of the active compounds, the evaluation times and the results can be seen from the following Table A.

TABLE A

(Insects which damage plants)

Plutella test

Active compounds	Active compound concentration in % by weight	Degree of destruction in % after 3 days
	0.01 0.001	100 0
(known)		
(1)	0.01 0.001	100 100
(2)	0.01 0.001	100 75
(3)	0.01 0.001	100 85

Example B.

Critical concentration test/soil insects.

Test insect: *Phorbia antiqua*—grubs
Solvent: 3 parts by weight of acetone
Emulsifier: 1 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound was mixed with the stated amount of solvent, the stated amount of emulsifier was added and the concentrate was diluted with water to the desired concentration.

The preparation of active compound was intimately mixed with soil. The concentration of the active compound in the preparation was of practically no importance; only the amount by weight of active compound per unit volume of soil, which is given in ppm (= mg/l) was decisive. The soil was filled into pots and the pots were left to stand at room temperature.

After 24 hours, the test animals were introduced into the treated soil and after a further 2 to 7 days the degree of effectiveness of the active compound was determined in % by counting the dead and live test insects. The degree of

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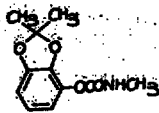
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destruction is 100% if all test insects had been killed and is 0% if just as many test insects were still alive as in the case of the control.
The active compounds, the amounts used and the results can be seen from Table B which follows:

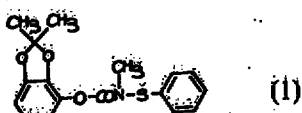
TABLE B

Soil insecticides

Phorbia antiqua grubs in the soil

Active compound (structure)	Active compound concentration in ppm	Degree of destruction in %
	10	0
(known)		
(2)	10	100
(1)	10	100
(3)	10	100

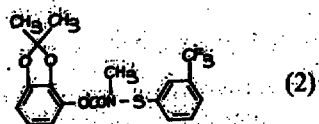
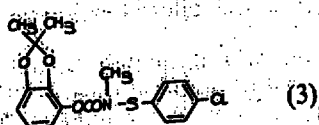
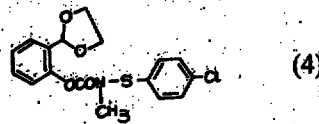
Example 1.



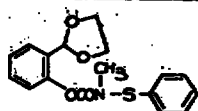
16.6 g (0.1 mol) of benzo-1,3-dioxolan-4-ol and 18.6 g (0.1 mol) of N-methyl-N-phenylmercaptocarbamic acid fluoride were dissolved in 250 ml of absolute toluene at room temperature and 11 g (0.11 mol) of triethylamine were added. In the course thereof, the temperature did not rise above 40°C. After stirring for a further two hours, water was added to the cold mixture and the organic phase was separated off, washed with water and dried. After evaporating off the solvent, an oil of refractive index $n_D^{25} = 1.5626$ remained. Yield 28 g.

Examples 2—5.

The following were prepared analogously to Example 1.

 $n_D^{25} = 1.5290$  $n_D^{25} = 1.5735$ 

Melting point 134°C

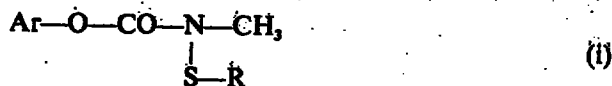


(5)

Melting point 85°C

WHAT WE CLAIM IS:—

1. N-sulphenylated arylcarbamates of the general formula



in which

Ar represents 2,2-dimethyl benzo-1,3-dioxolan-4-yl and

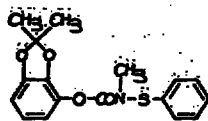
R represents phenyl optionally monosubstituted or polysubstituted by halogen, nitro, alkyl or trifluoromethyl, or

Ar represents 1,3-dioxolan-2-yl-phenyl-(2) and

R represents phenyl optionally monosubstituted or polysubstituted by halogen, nitro or alkyl or, in the 2- and/or 4-position, by trifluoromethyl.

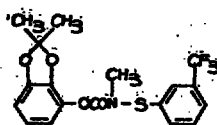
2. Compounds according to claim 1 in which Ar represents 2,2-dimethyl benzo-1,3-dioxolan-4-yl and R represents phenyl, tolyl, ethylphenyl, fluorophenyl, chlorophenyl, bromophenyl, nitrophenyl or trifluoromethylphenyl, or in which Ar represents 1,3-dioxolan-2-yl-phenyl-(2) and R represents phenyl, chlorophenyl, 2-trifluoromethylphenyl, 4-trifluoromethylphenyl, 2-trifluoromethyl-3-chlorophenyl, 2-trifluoromethyl-4-chlorophenyl, 4-trifluoromethyl-2-chlorophenyl, 4-trifluoromethyl-3-chlorophenyl, tolyl, ethylphenyl, fluorophenyl, bromophenyl or nitrophenyl.

3. The compound of the formula



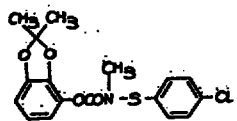
(1)

4. The compound of the formula



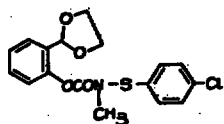
(2)

5. The compound of the formula



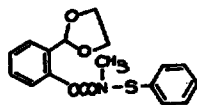
(3)

6. The compound of the formula



(4)

7. The compound of the formula

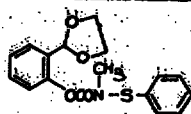


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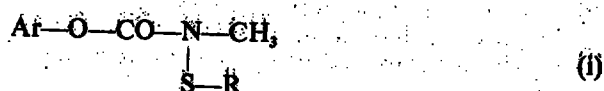


(5)

Melting point 85°C

WHAT WE CLAIM IS:—

1. N-sulphenylated arylcarbamates of the general formula



in which

Ar represents 2,2-dimethyl benzo-1,3-dioxolan-4-yl and

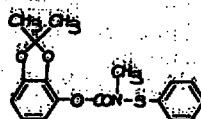
R represents phenyl optionally monosubstituted or polysubstituted by halogen, nitro, alkyl or trifluoromethyl, or

Ar represents 1,3-dioxolan-2-yl-phenyl-(2) and

R represents phenyl optionally monosubstituted or polysubstituted by halogen, nitro or alkyl or, in the 2- and/or 4-position, by trifluoromethyl.

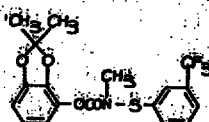
2. Compounds according to claim 1 in which Ar represents 2,2-dimethyl benzo-1,3-dioxolan-4-yl and R represents phenyl, tolyl, ethylphenyl, fluorophenyl, chlorophenyl, bromophenyl, nitrophenyl or trifluoromethylphenyl, or in which Ar represents 1,3-dioxolan-2-yl-phenyl-(2) and R represents phenyl, chlorophenyl, 2-trifluoromethylphenyl, 4-trifluoromethylphenyl, 2-trifluoromethyl-3-chlorophenyl, 2-trifluoromethyl-4-chlorophenyl, 4-trifluoromethyl-2-chlorophenyl, 4-trifluoromethyl-3-chlorophenyl, tolyl, ethylphenyl, fluorophenyl, bromophenyl or nitrophenyl.

3. The compound of the formula



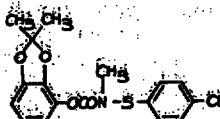
(1)

4. The compound of the formula



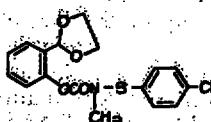
(2)

5. The compound of the formula



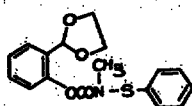
(3)

6. The compound of the formula



(4)

7. The compound of the formula



(5)

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8. A process for the preparation of a compound according to any of claims 1—7 in which

(a) a N-sulphenylated arylcarbamic acid halide of the general formula



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in which

R has the meaning given in claim 1 and

X represents fluorine or chlorine.

is reacted with a compound of the general formula

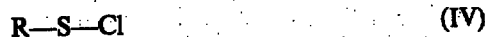


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in which

Ar has the meaning given in claim 1 optionally in the presence of a diluent and of an acid-binding agent, or

(b) a sulphenyl chloride of the general formula

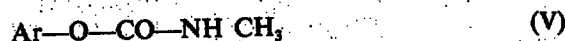


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in which

R has the meaning given in claim 1

is reacted with a carbamate of the general formula



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in which

Ar has the meaning given in claim 1, optionally in the presence of a diluent and of an acid-binding agent.

9. A process according to claim 8 in which the compound of formula (III) is used in the form of an alkali metal salt.

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10. A process according to claim 8 or 9 in which the reaction is carried out at 20—40°C.

11. A process according to claim 8 substantially as hereinbefore described in any of Examples 1—5.

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12. Compounds according to claim 1 whenever prepared by a process according to any of claims 8—11.

13. An insecticidal composition containing as active ingredient a compound according to any of claims 1—7 or 12 in admixture with a solid or liquefied gaseous diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.

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

15. A method of combating insect pests which comprises applying to the pests or a habitat thereof a compound according to any of claims 1—7 or 12 alone or in the form of a composition containing as active ingredient a compound according to any of claims 1—7 or 12 in admixture with a diluent or carrier.

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16. A method according to claim 15 in which a composition is used containing from 0.0001 to 10% of the active compound, by weight.

17. Crops protected from damage by insects by being grown in areas in which, immediately prior to and/or during the time of the growing, a compound according to any of claims 1—7 or 12 was applied alone or in admixture with a diluent or carrier.

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