

PATENT SPECIFICATION

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(54) 2,3-DIHYDROBENZOFURANYL-7-N-METHYL-CARBAMATES, 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 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:—

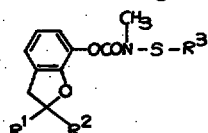
The present invention relates to N-sulphenylated 2,3-dihydrobenzofuranyl-7-N-methylcarbamates, to a process for their preparation and to their use as insecticides and acaricides.

It has already been disclosed that carbamates possess pesticidal properties. The best-known representatives of this class are the active compounds *o*-isopropoxyphenylcarbamate and α -naphthylcarbamate, which are used as commercial products. However, the activity of these compounds is not always satisfactory, especially if low concentrations are used.

Further, it has already been disclosed that trihalogenomethylsulphenylated N-methyl-carbamic acid aryl esters are very good insecticides and that they are superior compared to the unsubstituted carbamates because of the greater insecticidal activity and their lower toxicity to warm-blooded animals (see German Offenlegungsschrift (German Published Specification) 1,922,929).

However, the disadvantage of these compounds is that they frequently exhibit a skin-irritant action, which prevents their technical utilisation in many fields.

The present invention provides N-sulphenylated 2,3-dihydrobenzofuranyl-7-N-methylcarbamates of the general formula

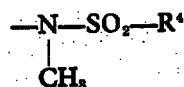


in which

R¹ is hydrogen or C₁—C₆ alkyl,

R² is C₁—C₆ alkyl and

R³ is phenyl substituted by trihalogenomethyl, or is methoxycarbonyl or the radical



wherein

R⁴ is alkylamino, dialkylamino or phenyl (which phenyl may optionally be substituted by halogen, C₁—C₆ alkyl or trihalogenomethyl),

or, provided that R¹ is hydrogen, R³ may be phenyl substituted by halogen or C₁—C₆ alkyl.

The compounds of the formula (I) have been found to possess strong insecticidal, including soil-insecticidal, and acaricidal properties.

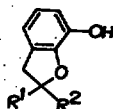
Preferably, R¹ is hydrogen or methyl, R² is methyl, and R³ is *m*-trifluoromethylphenyl, N,N',N' - trimethylsulphonyldiamide, N-methylbenzenesulphonamide, N - methyl - 3-trifluoromethylbenzenesulphonamide, N - methyl - 4 - chlorobenzenesulphonamide or N - methyl - 4 - toluenesulphonamide, or (provided R¹ is hydrogen) *p*-chlorophenyl, *p*-tolyl or 3,4-dichlorophenyl.

The present invention also provides a process for the preparation of a sulphenylated compound of the formula (I), in which (a) a sulphenylated carbamic acid fluoride of the general formula



in which

R³ has the above-mentioned meaning, is reacted in the presence of a diluent, with a compound of the general formula



(III),

in which

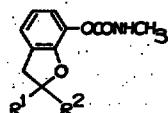
R¹ and R² have the above-mentioned meanings, the latter being used as such, in the presence of an acid-binding agent, or in the form of an alkali metal salt thereof, or (b) a compound of the general formula



(IV),

in which

R³ has the above-mentioned meaning, is reacted with a carbamate of the general formula



(V)

in which

R¹ and R² have the above-mentioned meanings, in the presence of a diluent and of an acid-binding agent.

It is distinctly surprising that the compounds according to the invention exhibit a greater insecticidal, acaricidal and soil-insecticidal action than the commercially available carbamates *o*-isopropoxyphenylcarbamate and α -naphthylcarbamate. It is also surprising that the compounds according to the invention are substantially better tolerated by the skin than the known trihalogenomethylsulphenylated carbamic acid esters. The compounds according to the invention thus represent a real enrichment of the art.

The sulphenylated carbamic acid fluorides of the formula (II) are, in a number of cases, known.

They can be prepared analogously to the process known from German Auslegeschrift (German Published Specification) DAS 1,297,095 from the corresponding sulphenic acid chlorides, which are known, by reaction with the corresponding known N-mono-substituted carbamic acid fluorides.

The 2,3 - dihydrobenzofuranyl - N-methylcarbamates to be used as starting products are known.

The diluents which can be used are all inert organic solvents. These include ethers, such as diethyl ether, dioxane and tetrahydrofuran, hydrocarbons, such as benzene, and chlorinated hydrocarbons, such as chloroform and chlorobenzene.

To bind the hydrogen halide liberated in

the reaction, an acid-binding agent, preferably a tertiary organic base such as triethylamine, is added to the reaction mixture. It is optionally also possible to start directly from the alkali metal salts of the compounds of the formula (III).

The reaction temperatures can be varied over a fairly wide range; in general, the reaction is carried out at between 0° and 100° C., preferably at from 20° to 40° C.

In carrying out the process according to the invention, equimolar amounts of the reactants may be used in general. In many cases, however, it has proved advantageous in process variant (a) to use the compound of the formula (III) in a slight excess. Preferably, 1.2 moles of benzofuranol of the formula (III) are employed per mole of the carbamic acid fluoride of the formula (II).

As already mentioned, the N-sulphenylated 2,3 - dihydrobenzofuranyl - 7 - N - methylcarbamates of the present invention are distinguished by an outstanding insecticidal and acaricidal activity, especially against plant pests and pests harmful to health. They can also be used as fungicides. The compounds according to the invention are further distinguished by their low toxicity to warm-blooded animals, compared to the non-sulphenylated carbamates on which the compounds according to the invention are based.

The present compounds can therefore be employed particularly advantageously for combating sucking and biting insects, including pests harmful to health and pests of stored products, as well as soil insects and mites and phytopathogenic fungi. Furthermore, they possess a nematicidal and microbistatic action.

To the sucking insects there belong, in the main, aphids (*Aphididae*) such as green peach aphid (*Myzus persicae*), the bean aphid (*Doralis fabae*), the bird cherry aphid (*Rhopalosiphum padi*), the pea aphid (*Macrosiphum pisi*) and the potato aphid (*Macrosiphum solanifolii*), the currant gall aphid (*Cryptomyzus korschelti*), the rosy apple aphid (*Sappaphis mali*), the mealy plum aphid (*Hyalopterus arundinis*) and the cherry blackfly (*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 (*Rhodnius prolixus*) and Chagas' bug (*Triatoma infestans*) and, further, cicadas, such as *Euscelis bilobatus* and *Nephotettix bipunctatus*.

In the case of the biting insects, above all there should be mentioned butterfly or moth caterpillars (*Lepidoptera*) such as the diamond-back moth (*Plutella maculipennis*), the

the gipsy moth (*Lymantria dispar*), the brown-tail moth (*Euproctis chrysorrhoea*) and tent caterpillar (*Malacosoma neustria*); further the cabbage moth (*Mamestra 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 kuehniella*) and greater wax moth (*Galleria mellonella*).

With the mites (*Acarina*) there are classed, in particular, the spider mites (*Tetranychidae*) such as the two-spotted spider mite (*Tetranychus urticae*) and the European red mite (*Paratetranychus pilosus*=*Panonychus ulmi*), gall mites, for example the blackcurrant gall mite (*Eriophyes ribis*) and tarsonemids, for example the broad mite (*Hemitarsonemus latus*) and the cyclamen mite (*Tarsonemus pallidus*); finally, ticks, such as the relapsing fever tick (*Ornithodoros moubata*).

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

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

By liquefied gaseous diluents or carriers are meant liquids which would be gaseous at normal temperatures and pressures, for example aerosol propellants, such as halogenated

hydrocarbons, for example Freon (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 highly-dispersed silicic acid, alumina or silicates.

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

The active compounds according to the invention can be present in the formulations as a mixture with other active compounds.

In general, the formulations contain from 0.1 to 95 per cent by weight of active compound, preferably from 0.5 to 90 per cent.

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

The active-compound concentrations in the ready-to-use preparations can be varied within fairly wide ranges. In general, they are between 0.0001 and 10%, preferably between 0.01 and 1%, by weight.

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

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

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

The present invention further provides crops protected from damage by insects or acarids by being grown in areas in which immediately prior to and/or during the time of the growing a compound of the present invention was applied alone or in admixture

5 The pesticidal activity of the present compounds is illustrated by the following biotest Examples.

Example A.

Plutella test

10 Solvent: 3 parts by weight of dimethylformamide

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

15 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*). 20

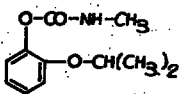
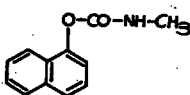
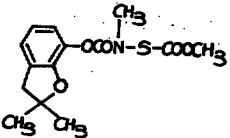
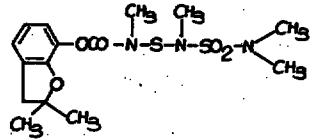
After the specified periods of time, the degree of destruction was determined as a percentage: 100% means that all the caterpillars were killed, whereas 0% means that none of the caterpillars were killed.

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

TABLE A

(Insects which damage plants).

Plutella test

Active compounds	Active compound concentration in %	Degree of destruction in % after 3 days
 (known)	0.1 0.01 0.001	100 90 0
 (known)	0.1 0.01 0.001	100 60 0
 (3)	0.1 0.01 0.001	100 100 65
 (4)	0.1 0.01 0.001	100 100 95

Example B.
Tetranychus test (resistant)

Solvent: 3 parts by weight of dimethylformamide

5 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.

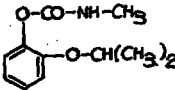
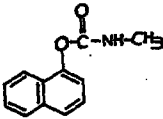
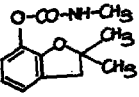
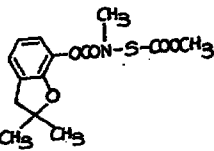
10 Bean plants (*Phaseolus vulgaris*), which had a height of approximately 10–30 cm, were sprayed with the preparation of the active

compound until dripping wet. These bean plants were heavily infested with the two-spotted spider mite (*Tetranychus urticae*) in all stages of development.

After the specified periods of time, the effectiveness of the preparation of active compound was determined by counting the dead mites. The degree of destruction thus obtained was expressed as a percentage: 100% means that all the spider mites were killed whereas 0% means that none of the spider mites were killed.

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

TABLE B
 (Mites which damage plants)

Active compounds	<i>Tetranychus</i> test	Active compound concentration in %	Degree of destruction in % after 2 days
	(known)	0.1	0
	(known)	0.1	0
	(known)	0.1	0
	(6)	0.1	85

Example C.

Critical concentration test/soil insects

35 Test insect: *Phorbia brassicae* grubs in the soil

Solvent: 3 parts by weight of acetone

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

40 To produce a suitable preparation of active compound, 1 part by weight of active com-

45 pound 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 the soil. The concentration of the active compound in the preparation was practically immaterial, the only decision factor

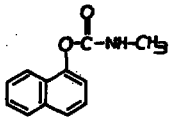
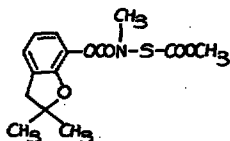
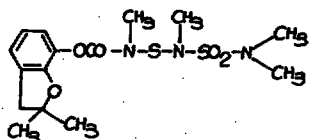
being the amount by weight of active compound per unit volume of soil, which is quoted in ppm. (for example mg/l). The soil was filled into pots and the pots were left to stand at room temperature. After 24 hours the test insects were introduced into the treated soil and after a further 48 hours the degree of effectiveness of the active com-

pound was determined in % by counting the dead and live test insects. The degree of effectiveness was 100% if all test insects had been killed and was 0% if exactly as many test insects were still alive as in the case of the control.

The active compounds, amounts used and results can be seen from the Table which follows:

TABLE C

Phorbia brassicae grubs in the soil

Active compound	Degree of destruction in % at an active-compound concentration in ppm of					
	20	10	5	2.5	1.25	0.625
 (known)	0					
 (6)	100	100	100	100	50	0
 (7)	100	100	100	50	0	

Example D.

- 20 Mosquito larvae test
 Test insects: *Aedes aegypti* (4th Larval stage)
 Solvent: 99 parts by weight of acetone
 Emulsifier: 1 part by weight of benzylhydroxy-diphenylpolyglycol ether
- 25 To produce a suitable preparation of active compound, 2 parts by weight of the active compound were dissolved in 1,000 parts by volume of the solvent containing the amount of emulsifier stated above. The solution thus obtained was diluted with water to the desired lower concentrations.
- 30

The aqueous preparations of the active compounds were placed in glass vessels and about 25 mosquito larvae were then placed in each glass vessel.

After 24 hours, the degree of destruction was determined as a percentage. 100% means that all the larvae were killed. 0% means that no larvae at all were killed.

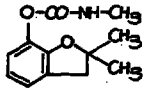
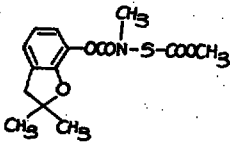
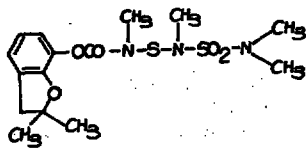
The active compounds, the concentrations of the active compounds, the test insects and the results can be seen from the following Table:

35

40

TABLE D

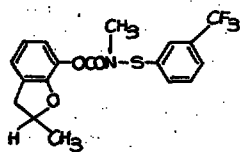
Mosquito larvae test

Active compound	Active-compound concentration of the solution in ppm	Degree of destruction in %
	10 1 0.1	100 100 0
(known)		
	(3) 10 1 0.1	100 100 90
	(4) 10 1 0.1	100 100 50

The process of the present invention is illustrated by the following preparative Examples.

5

Example 1.



(1)

Process (a): 0.05 moles of 2 - methylbenzofuranol - (7) and 0.05 mole of N - methyl-N - phenylsulphenylcarbamic acid fluoride were dissolved in 200 ml of toluene. 6 g of triethylamine were then slowly added dropwise. After stirring for two hours at room temperature, the salt was filtered off, the filtrate was repeatedly washed with water and dried and the solvent was distilled off. The residue had a refractive index n_D^{25} of 1.5382. Process (b): 0.1 mole of 2 - methyl - benzofuranyl - (7) - N - methylcarbamate were suspended in 300 ml of toluene, and thereafter 14.5 g (0.1 mole) of phenylsulphene chloride were added. 11 g of triethylamine were slowly added dropwise whilst stirring vigorously. The mixture was then stirred for a further 2 hours at 30° C. The salt was

then filtered off, the filtrate was twice washed with water and dried with Na_2SO_4 and the solvent was distilled off in order to obtain the product.

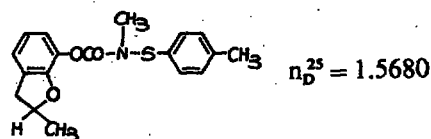
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Examples 2 and 3.

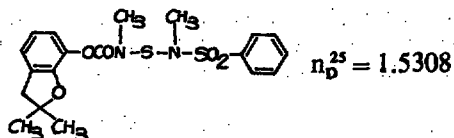
The following were obtained by processes analogous to those described above:

30

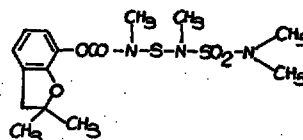
(2)



(3)



Example 4.



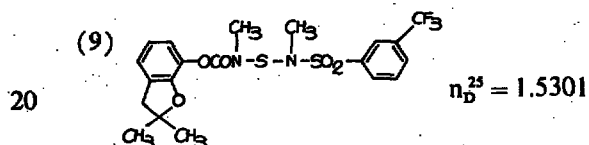
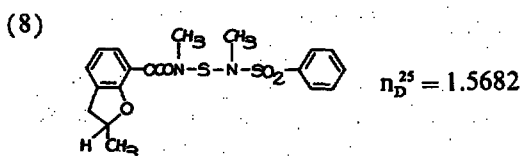
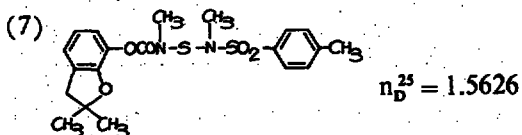
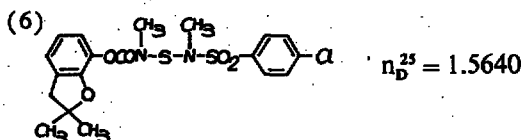
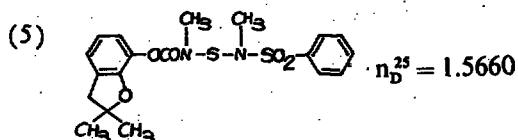
(4) 35

12.5 g (0.05 mole) of trimethylsulphonyl-

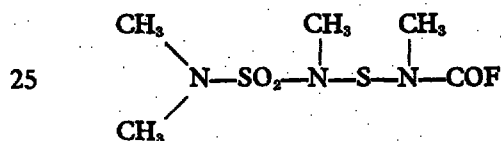
5 diamido - N - sulphenyl - N - methylcarbam-
amic acid fluoride and 8.2 g (0.05 mole) of
2,2 - dimethylbenzofuranol - (7) were dis-
solved in 200 ml of toluene and 6 g of tri-
ethylamine were then slowly added dropwise.
After stirring for two hours at 30° C., the
salt was filtered off and the filtrate was twice
washed with water. After drying with Na₂SO₄
and evaporating off the solvent, a yellow oil
10 remained. $n_D^{25} = 1.5355$.

Examples 5-9.

15 The following compounds could be prepared
by processes analogous to that described above,
starting from known sulphenylated carbamic
acid fluorides.



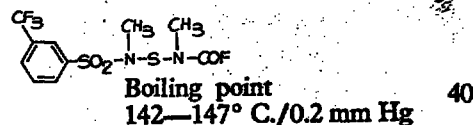
Trimethylsulphonylamido - N - sulphenyl-
N - methyl - carbamic acid fluoride, which
has not been described previously in the litera-
ture, can be prepared as follows:



30 20.4 g (0.1 mole) of N,N,N' - trimethyl-
sulphonyldiamido - N' - sulphenyl chloride
and 7.7 g (0.1 mole) of N-methylcarbam-
ic acid fluoride were dissolved in 200 ml of
absolute toluene. 10 g of triethylamine were

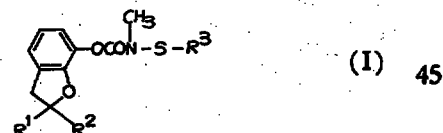
added dropwise, whilst stirring (the tempera-
ture not exceeding 40° C.). The mixture was
stirred for a further 2 hours at room tem-
perature, the salt was filtered off and the
filtrate was extracted by shaking with ice 35
water, dried and distilled *in vacuo*. Boiling
point = 137° C./0.2 mm Hg.

The following compound could be prepared
analogously:



WHAT WE CLAIM IS:-

1. N - Sulphenylated 2,3 - dihydrobenzo-
furan-7-methylcarbamates of the general
formula

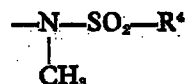


in which

R¹ is hydrogen or C₁-C₆ alkyl,

R² is C₁-C₆ alkyl, and

R³ is phenyl substituted by trihalogeno-
methyl, or is methoxycarbonyl or the 50
radical



wherein

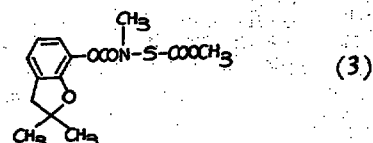
R₄ is alkylamino, dialkylamino or phenyl
(which phenyl may optionally be substi- 55
tuted by halogen, C₁-C₆ alkyl or tri-
halogenomethyl)-,

or, provided that R¹ is hydrogen, R³ may be
phenyl substituted by halogen or C₁-C₆ 60
alkyl.

2. Compounds according to claim 1, in
which R¹ is hydrogen or methyl, R²
is methyl, and R³ is *m* - trifluoromethyl-
phenyl, N,N',N'-trimethylsulphonylamide, N-
methylbenzenesulphonamide, N - methyl - 3-
trifluoromethylbenzenesulphonamide, N-
methyl - 4 - chlorobenzenesulphonamide or
N - methyl - 4 - toluenesulphonamide. 65

3. Compounds according to claim 1, in
which R¹ is hydrogen, R² is methyl and R³ 70
is *p*-chlorophenyl, *p*-tolyl or 3,4-dichloro-
phenyl.

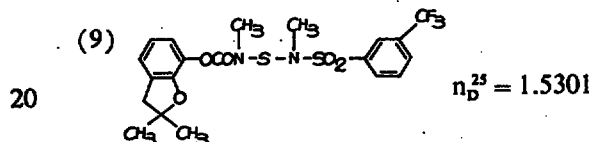
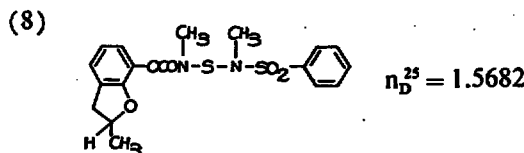
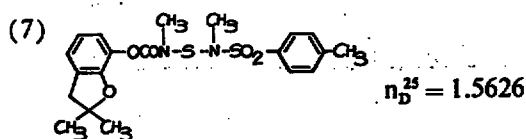
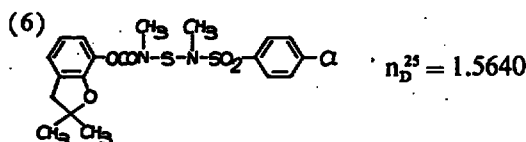
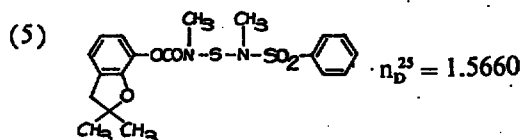
4. The compound of the formula



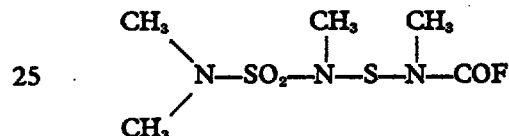
- 5 diamido - N - sulphenyl - N : methylcarbam-
amic acid fluoride and 8.2 g (0.05 mole) of
2,2 - dimethylbenzofuranol - (7) were dis-
solved in 200 ml of toluene and 6 g of tri-
ethylamine were then slowly added dropwise.
After stirring for two hours at 30° C., the
salt was filtered off and the filtrate was twice
washed with water. After drying with Na₂SO₄
and evaporating off the solvent, a yellow oil
10 remained. $n_D^{25} = 1.5355$.

Examples 5—9.

- 15 The following compounds could be prepared
by processes analogous to that described above,
starting from known sulphenylated carbamic
acid fluorides.



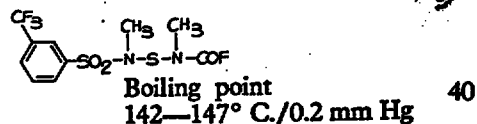
Trimethylsulphonylamido - N - sulphenyl-
N - methyl - carbamic acid fluoride, which
has not been described previously in the litera-
ture, can be prepared as follows:



- 30 20.4 g (0.1 mole) of N,N,N' - trimethyl-
sulphonyldiamido - N' - sulphenyl chloride
and 7.7 g (0.1 mole) of N-methylcarbam-
ic acid fluoride were dissolved in 200 ml of
absolute toluene. 10 g of triethylamine were

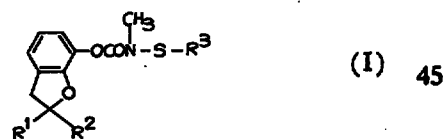
added dropwise, whilst stirring (the tempera-
ture not exceeding 40° C.). The mixture was
stirred for a further 2 hours at room tem-
perature, the salt was filtered off and the
filtrate was extracted by shaking with ice
water, dried and distilled *in vacuo*. Boiling
point = 137° C./0.2 mm Hg.

The following compound could be prepared
analogously:



WHAT WE CLAIM IS:—

1. N - Sulphenylated 2,3 - dihydrobenzo-
furanyl-7-methylcarbamates of the general
formula



in which

R¹ is hydrogen or C₁—C₆ alkyl,

R² is C₁—C₆ alkyl, and

R³ is phenyl substituted by trihalogeno-
methyl, or is methoxycarbonyl or the 50
radical



wherein

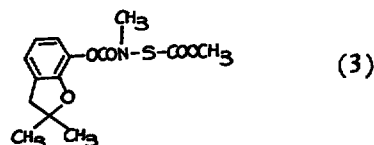
R₄ is alkylamino, dialkylamino or phenyl
(which phenyl may optionally be substi-
tuted by halogen, C₁—C₆ alkyl or tri-
halogenomethyl), 55

or, provided that R¹ is hydrogen, R³ may be
phenyl substituted by halogen or C₁—C₆
alkyl. 60

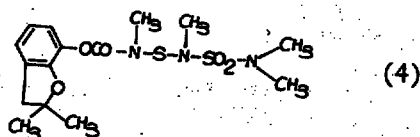
2. Compounds according to claim 1, in
which R¹ is hydrogen or methyl, R²
is methyl, and R³ is *m* - trifluoromethyl-
phenyl, N,N',N'-trimethylsulphonylamide, N-
methylbenzenesulphonylamide, N - methyl - 3-
trifluoromethylbenzenesulphonylamide, N-
methyl - 4 - chlorobenzenesulphonylamide or
N - methyl - 4 - toluenesulphonylamide. 65

3. Compounds according to claim 1, in
which R¹ is hydrogen, R² is methyl and R³
is *p*-chlorophenyl, *p*-tolyl or 3,4-dichloro-
phenyl. 70

4. The compound of the formula



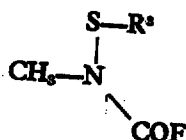
5. The compound of the formula



6. The compounds that are disclosed in Examples 1, 2 and 5 to 9.

7. A process for the preparation of an N-sulphenylated 2,3-dihydrobenzofuranyl-7-N-methylcarbamate according to claim 1, in which

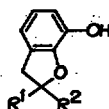
10 (a) a substituted carbamic acid fluoride of the general formula



in which

R^a has the meaning stated in claim 1, is reacted, in the presence of a diluent, with

15 a compound of the general formula



in which

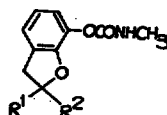
R₁ and R₂ have the meanings stated in claim 1,

20 the latter being reacted as such in the presence of an acid-binding agent or in the form of an alkali metal salt thereof, or (b) a sulphene-chloride of the general formula



25 in which

R^a has the meaning stated in claim 1, is reacted with a carbamate of the general formula



30 in which

R¹ and R² have the meanings stated in claim 1, in the presence of a diluent and of an acid-binding agent.

8. A process according to claim 7, in which the reaction is effected in the presence of 35 an inert organic solvent.

9. A process according to claim 7 or 8 in which the reaction is effected in the presence, as an acid-binding agent, of a 40 tertiary organic base.

10. A process according to claim 7, 8 or 9, in which the reaction is effected at between 0° and 100° C.

11. A process according to claim 10, in which the reaction is effected at from 20° to 45 40° C.

12. A process for the preparation of a compound according to claim 1, substantially as described in Example 1 or 4.

13. Compounds according to claim 1, 50 whenever prepared by a process according to any one of claims 7 to 12.

14. An insecticidal or acaricidal composition containing as active ingredient a compound according to any of claims 1 to 6 55 and 13 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.

15. A composition according to claim 14 60 containing from 0.1 to 95% of the active compound, by weight.

16. A composition according to claim 15 containing from 0.5 to 90% of the active 65 compound, by weight.

17. A method of combating insects or acarids which comprises applying to the insects or acarids or to a habitat thereof a compound according to any of claims 1 to 6 70 and 13 alone or in the form of a composition containing as active ingredient a compound according to any of claims 1 to 6 and 13 in admixture with a diluent or carrier.

18. A method according to claim 17 in which a composition is used containing from 75 0.0001 to 10% of the active compound, by weight.

19. A method according to claim 18 in which a composition is used containing from 80 0.01 to 1% of the active compound, by weight.

20. A method according to any of claims 17 to 19, in which the active compound is one of those hereinbefore mentioned in any of Examples A to E.

21. Crops protected from damage by insects or acarids by being grown in areas in which immediately prior to and/or during the 85 time of the growing a compound according to any of claims 1 to 6 and 13 was applied alone or in admixture with a diluent or 90 carrier.



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* C L M S *