

PATENT SPECIFICATION

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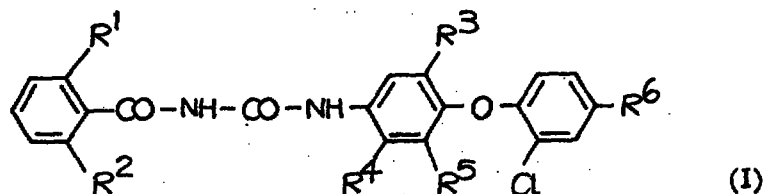
(54) BENZOYLUREIDO-DIPHENYL ETHERS AND THEIR USE AS INSECTICIDES

(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 certain new benzoylureido-diphenyl ethers, to a process for their preparation and to their use as insecticides.

It is already known that certain benzoylureas, such as, for example, N-(2,6-dichlorobenzoyl) - N' - (4 - chlorophenyl- and - 3,4 - dichlorophenyl) - urea, possess insecticidal properties (see German Offenlegungsschrift (German Published Specification) 2,123,236).

The present invention provides the benzoylureido-diphenyl ethers of the general formula



in which

- R¹ is fluorine, chlorine, bromine or methyl,
 R² is hydrogen, fluorine or chlorine,
 R³ is hydrogen or chlorine,
 R⁴ is hydrogen, chlorine or methyl,
 R⁵ is hydrogen or chlorine, and
 R⁶ is nitro or trifluoromethyl.

The compounds of the formula (I) have been found to possess powerful insecticidal properties.

A preferred class of benzoylureidodiphenyl ethers of the formula (I) are those in which R¹ is chlorine or fluorine, R² is hydrogen, chlorine or fluorine, R³, R⁴ and R⁵ are each hydrogen, and R⁶ represents trifluoromethyl.

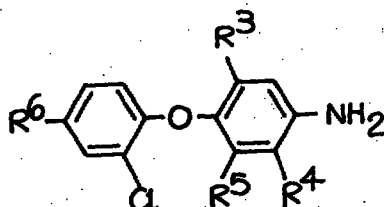
Another preferred class of benzoylureidodiphenyl ethers of the formula (I) are those in which R¹ is chlorine, fluorine or methyl, R² is hydrogen, chlorine or fluorine, R³ is hydrogen or chlorine, R⁴ is hydrogen, R⁵ is hydrogen or chlorine, and R⁶ is nitro.

A further preferred class of benzoylureidodiphenyl ethers of the formula (I) are those in which R¹ is chlorine, fluorine or bromine, R² is hydrogen or fluorine, R³ is

hydrogen, R⁴ is methyl or chlorine, R⁵ is hydrogen and R⁶ represents nitro.

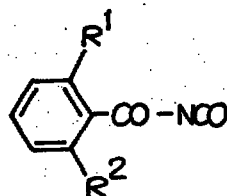
The present invention also provides a process for the preparation of a benzoylureidodiphenyl ether of the formula (I) in which

(a) a phenoxyaniline of the general formula



(II)

is reacted with a benzoylisocyanate of the general formula

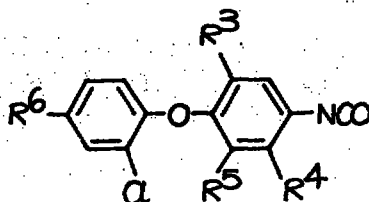


(III)

in which formulas

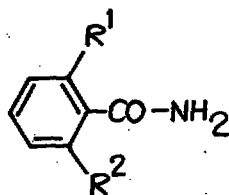
R¹ to R⁶ have the above-mentioned meanings, if appropriate in the presence of a diluent or solvent, or

(b) a 4-isocyanato-diphenyl ether of the general formula



(IV)

is reacted with a benzamide of the general formula



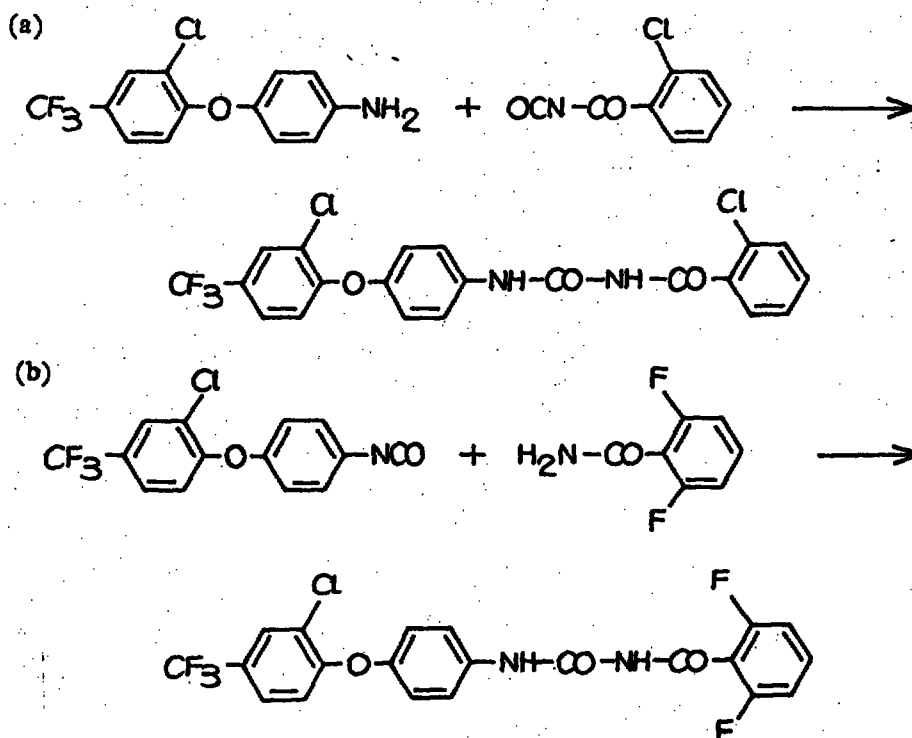
(V)

in which formulas

R¹ to R⁶ have the above-mentioned meanings, if appropriate in the presence of a diluent or solvent.

Surprisingly, the benzoylureido-diphenyl ethers according to the invention have a substantially better insecticidal action than the nearest compounds of analogous structure and of the same type of action previously known from the state of the art. The compounds according to the invention thus represent a genuine enrichment of the art.

If, using process variant (a), 4 - (2' - chloro - 4' - trifluoromethylphenoxy)-aniline and 2 - chlorobenzoylisocyanate are used as starting materials and, using process variant (b), 4 - (2' - chloro - 4' - trifluoromethyl - phenoxy) - phenylisocyanate and 2,6 - difluorobenzamide are used as starting materials, the course of the reactions can be represented by the following equations:



The benzoylisocyanates (III) to be used as starting materials are known from the literature and can be prepared according to generally customary processes (see A. J. Speziale *et al.*, J. Org. Chem. 30 (12), pages 4306—4307 (1965)).

2,6-Difluorobenzamide and the other benzamides (V) are known and can be prepared according to generally customary processes (see Beilsteins Handbuch der organischen Chemie (Beilstein's Handbook of Organic Chemistry), volume 9, page 336). The phenoxyanilines (II) can be prepared according to generally customary processes, for example from alkali metal aminophenolates and 1,2-dichloro-4-trifluoromethylbenzene or aromatic nitrohalogeno compounds such as 1,2-dichloro-4-trifluoro- in a solvent, for example dimethylsulphoxide (see also Jürgen Schramm *et al.*, Justus Liebigs Annalen der Chemie 1970, 740, 169—179). The amino group can be converted into the isocyanate group in accordance with generally customary processes, for example by reaction with phosgene, whereby the 4-isocyanatodiphenyl ethers of the general formula (IV) are obtained.

The following may be mentioned as examples of the benzoylisocyanates (III) and benzamides (V) to be reacted in accordance with the process: 2-chloro-, 2-fluoro-, 2-bromo-, 2,6-dichloro- or 2,6-difluoro-benzoylisocyanate, and 2-chloro-, 2-fluoro-, 2-bromo-, 2,6-dichloro- or 2,6-difluoro-benzamide.

The following may be mentioned as examples of the phenoxyanilines (II) and 4-isocyanato-diphenyl ethers (IV) to be reacted in accordance with the process: 3-chloro-4-(2'-chloro-4'-nitro-phenoxy)-aniline, 3,5-dichloro-4-(2'-chloro-4'-nitro-phenoxy)-aniline and 4-(2'-chloro-4'-nitro-phenoxy)-aniline, and 2,6-dichloro-4-isocyanato-2'-chloro-4'-nitro-diphenyl ether, 2-chloro-4-isocyanato-2'-chloro-4'-nitro-diphenyl ether and 4-isocyanato-2'-chloro-4'-nitro-diphenyl ether.

The process for the preparation of the benzoylureidodiphenyl ethers according to the invention is preferably carried out in the presence of an inert organic solvent or diluent. Preferred inert organic solvents that can be used for this purpose are aliphatic and aromatic, optionally chlorinated hydrocarbons, such as benzene, toluene, xylene, benzine, methylene chloride, chloroform, carbon tetrachloride and chlorobenzene; ethers, for example diethyl ether, dibutyl ether and dioxane; ketones, for example acetone, methyl ethyl ketone, methyl isopropyl ketone and methyl isobutyl ketone; and nitriles such as acetonitrile and benzonitrile.

The reaction temperature can be varied within a fairly wide range. In general, the reaction is carried out at between 0° and 120°C, preferably at 70° to 85°C.

In general, the reaction is allowed to take place under normal pressure.

Preferably, the reactants are employed in equimolar amounts for carrying out the process. An excess of one or other component produces no significant advantages.

The 4-isocyanato-diphenyl ethers (IV) used in process variant (b) above can be employed as such or, without intermediate isolation, in the form of their reaction mixtures obtained from the reaction of amine with phosgene. This reaction mixture, in one of the above-mentioned solvents, is mixed with a benzamide, for example with 2,6-difluorobenzamide. The reaction is carried out under the desired conditions and the product which separates out is isolated in the usual manner by filtration, washing and, if appropriate, recrystallisation.

The compounds are obtained in a crystalline form of sharp melting point.

As has already been mentioned, the benzoylureidodiphenyl ethers according to the invention are distinguished by an excellent insecticidal activity; this is coupled with low toxicity to warm-blooded animals and good toleration by plants.

For this reason, the compounds according to the invention can be employed successfully in plant protection as pesticides against biting and sucking insects.

To the sucking insects there belong, in the main, aphids (*Aphididae*) such as the green peach aphid (*Myzus persicae*), the bean aphid (*Voridis 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 (*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 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 (*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 (*Ephesia kuehniella*) 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 obtectus*), 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 comprises essentially the flies, such as the vinegar fly (*Drosophila melanogaster*), the Mediterranean fruit fly (*Ceratitidis 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 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 can be converted to the customary formulations, such as solutions, emulsions, wettable powders, suspensions, powders, dusting agents, foams, pastes, soluble powders, granules, aerosols, suspension-emulsion concentrates, seed-treatment powders, natural and synthetic materials impregnated with active compound, very fine capsules in polymeric substances and in coating compositions, for use on seed, and formulations used with burning equipment, such as fumigating cartridges, fumigating cans or fumigating coils, as well as ULV (ultra-low-volume) cold mist and warm mist formulations.

These formulations are 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 (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.

The formulations in general 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 as the use forms prepared therefrom. 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% strength or even to use the active compound by itself.

The present invention also provides an insecticidal 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 which comprises applying to the insects or an insect habitat 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 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 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 insecticidal activity of the compounds of the present invention is illustrated by the following biotest Examples.

Example A.

Plutella test

Solvent: 3 parts by weight of dimethylformamide

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

5 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 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.

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

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10

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Table A

(insects which damage plants)

Plutella test

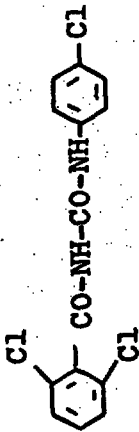
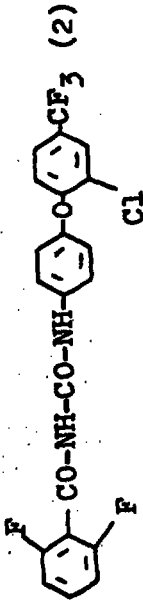
Active compound	Active compound concentration in %	Degree of destruction in % after 8 days
 (known)	0.1 0.01	65 0
 (known)	0.1 0.01 0.001	100 100 15
 (known)	0.1 0.01 0.001	100 100 90
 (2)	0.1 0.01 0.001	100 100 95

Table A (continued)
(insects which damage plants)

Plutella test

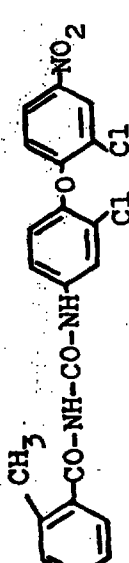
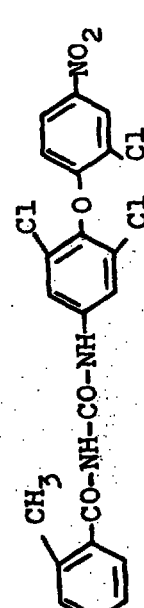
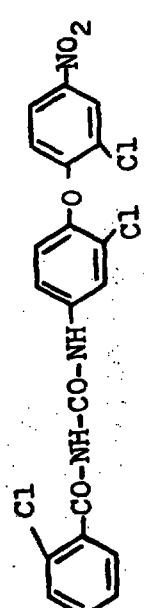
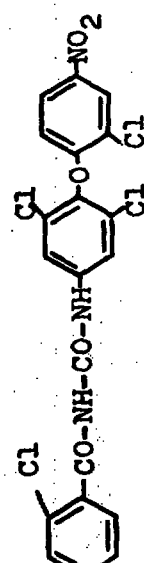
Active compound	Active compound concentration in %	Degree of destruction in % after 8 days
 (5)	0.1 0.01 0.001	100 100 100
 (12)	0.1 0.01 0.001	100 100 100
 (9)	0.1 0.01 0.001	100 100 100
 (4)	0.1 0.01 0.001	100 100 100

Table A (continued)

(insects which damage plants)

Plutella test

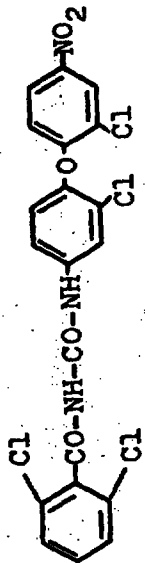
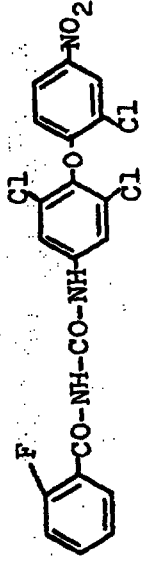
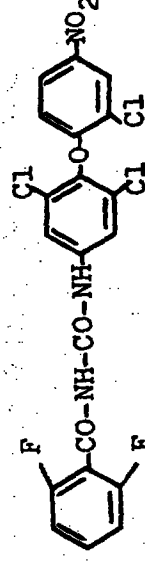
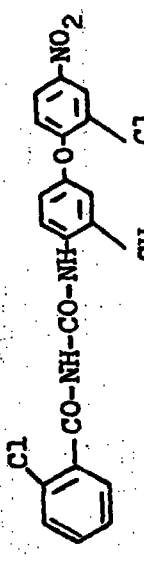
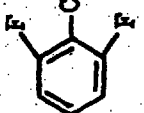
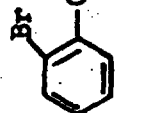
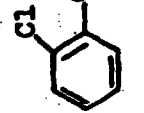
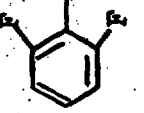
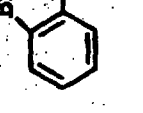
Active compound	Active compound concentration in %	Degree of destruction in % after 8 days
 (8)	0.1 0.01 0.001	100 100 100
 (10)	0.1 0.01 0.001	100 100 100
 (11)	0.1 0.01 0.001	100 100 100
 (17)	0.1 0.01 0.001	100 100 100

Table A (continued)
(insects which damage plants)

Plutella test

Active compound	Active compound concentration in %	Degree of destruction in % after 8 days
 (14)	0.1 0.01 0.001	100 100 100
 (18)	0.1 0.01 0.001	100 100 100
 (13)	0.1 0.01 0.001	100 100 100
 (15)	0.1 0.01 0.001	100 100 100
 (16)	0.1 0.01 0.001	100 100 100

Example B.

Laphygma test

Solvent: 3 parts by weight of dimethylformamide

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

5 To produce a suitable preparation of active compound, 1 part by weight of the active compound was mixed with the stated amount of solvent and the stated amount of emulsifier and the concentrate was diluted with water to the desired concentration. 5

10 Cotton leaves (*Gossypium hirsutum*) were sprayed with the preparation of the active compound until dew-moist and were then infested with caterpillars of the owlet moth (*Laphygma exigua*). 10

After the specified periods of time, the destruction in % was determined. 100% means that all the caterpillars had been killed, whereas 0% indicates that no caterpillars had been killed.

15 The active compounds, the concentrations of the active compound, the evaluation times and the results can be seen from the following table: 15

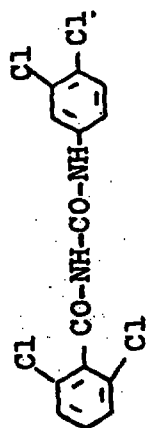
Table B
(insects which damage plants)

Laphygma test

Degree of destruction
in % after 8 days

Active compound
concentration in %

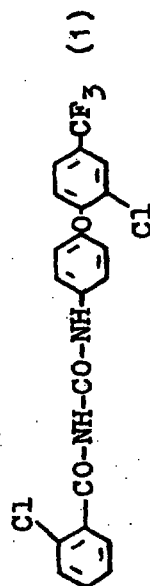
Active compounds



(known)

100
50
0

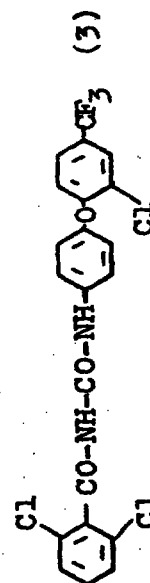
0.001
0.0001
0.00001



(1)

100
100
100

0.001
0.0001
0.00001

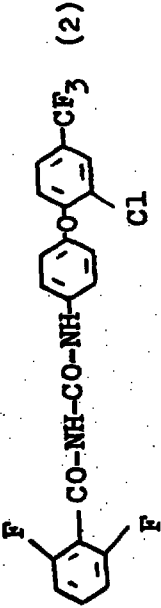
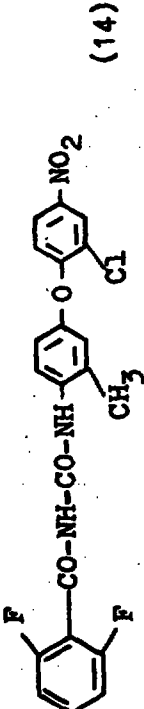
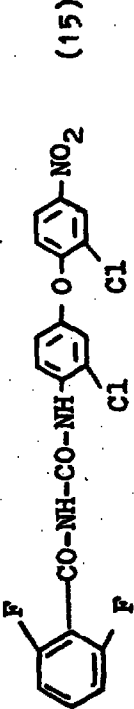


(3)

100
80
60

0.001
0.0001
0.00001

Table B (continued)
(insects which damage plants)
Laphygma test

Active compound	Active compound concentration in %	Degree of destruction in % after 8 days
 (2)	0.001 0.0001 0.00001	100 100 95
 (14)	0.001 0.0001 0.00001	100 100 70
 (15)	0.001 0.0001 0.00001	100 100 50

Example C.

Phaedon larvae test

Solvent: 3 parts by weight of dimethylformamide

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

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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.

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Cabbage plants (*Brassica oleracea*) were sprayed with the preparation of the active compound until dripping wet and were then infested with mustard beetle larvae (*Phaedon cochleariae*).

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After the specified periods of time, the degree of destruction was determined in %: 100% means that all beetle larvae had been killed, whereas 0% means that none of the beetle larvae had been killed.

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

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Table C
(insects which damage plants)

Phaedon larvae test

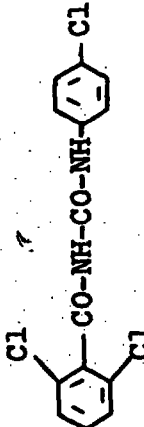
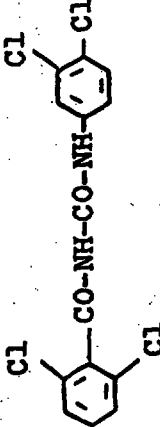
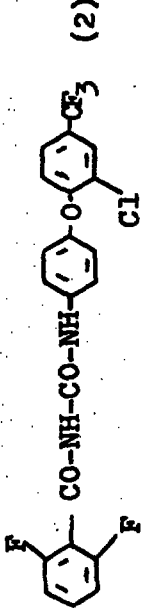
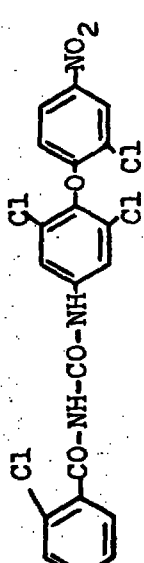
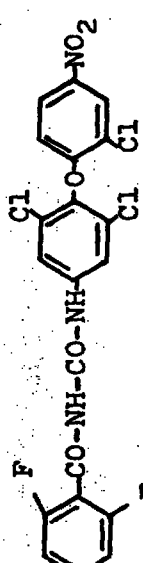
Active compounds	Active compound concentration in %	Degree of destruction in % after 3 days
 (known)	0.1 0.01 0.001	100 55 0
 (known)	0.1 0.01 0.001	100 15 0
 (2)	0.1 0.01 0.001	100 100 80

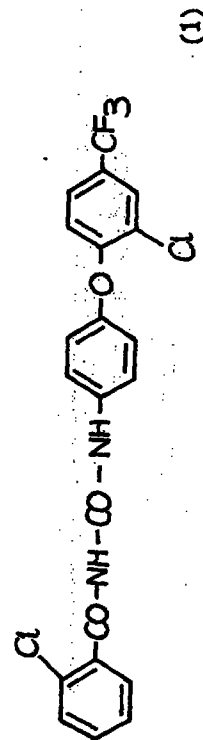
Table C (continued)
(insects which damage plants)

Phaedon larvae test

Active compounds	Active compound concentration in %	Degree of destruction in % after 3 days
 (4)	0.1	100
	0.01	100
	0.001	50
 (11)	0.1	100
	0.01	100
	0.001	80

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

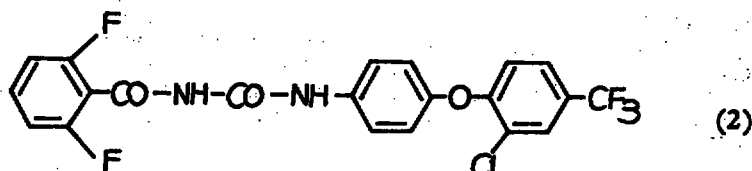
Example 1.



A solution of 3.7 g (0.02 mole) of 2-chlorobenzoylisocyanate in 20 ml of toluene was added dropwise at 80°C to 5.8 g (0.02 mole) of 4-(2'-chloro-4'-trifluoromethylphenoxy)-aniline in 100 ml of toluene. The batch was stirred for 1 hour at 80°C.

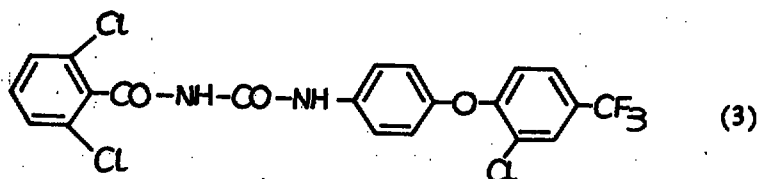
After cooling, the product which had precipitated was filtered off and washed first with toluene and then with petroleum ether. After drying, 6.6 g (70% of theory) of analytically pure 2-chloro-4-trifluoromethyl-4'-[N-(N'-(o-chlorobenzoyl))-ureido]-diphenyl ether of melting point 182°C were obtained.

Example 2.



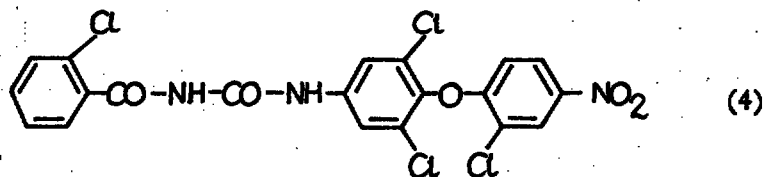
A solution of 3.7 g (0.02 mole) of 2,6-difluorobenzoylisocyanate in 20 ml of toluene was added dropwise at 80°C to a solution of 5.8 g (0.02 mole) of 4-(2'-chloro-4'-trifluoromethylphenoxy)-aniline in 100 ml of toluene. The batch was stirred for 1 hour at 80°C. The substance which separated out was filtered off after cooling the reaction mixture to 20°C and was washed with toluene and petroleum ether. After drying, 8 g (95% of theory) of 2-chloro-4-trifluoromethyl-4'-[N-(N'-(2,6-difluorobenzoyl))-ureido]-diphenyl ether of melting point 187°C were obtained.

Example 3.



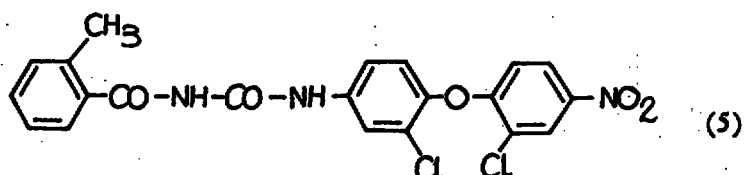
Using an analogous procedure to that described under Examples 1 and 2, 2-chloro-4-trifluoromethyl-4'-[N-(N'-(2,6-dichlorobenzoyl))-ureido]-diphenyl ether was obtained in a yield of 89% of theory, and with a melting point of 177°C.

Example 4.



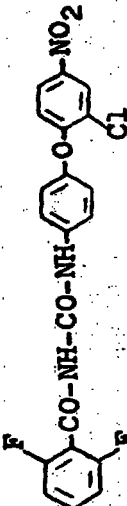
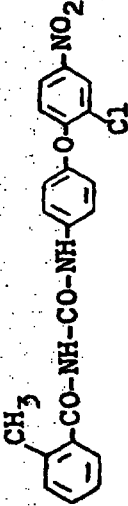
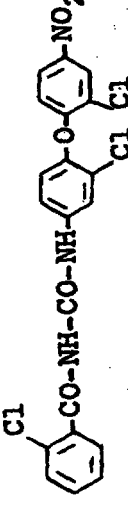
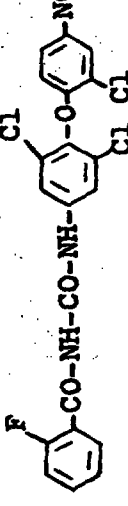
A solution of 2.8 g (0.015 mole) of 2-chlorobenzoylisocyanate in 10 ml of toluene was added dropwise at 80°C to 5 g (0.015 mole) of 3,5-dichloro-4-(2'-chloro-4'-nitrophenoxy)-aniline in 50 ml of toluene. The batch was stirred for 1 hour at 80°C. After cooling, the product which had precipitated was filtered off and was washed first with toluene and then with petroleum ether. After drying, 6.5 g (84% of theory) of analytically pure 2-chloro-4-nitro-2',6'-dichloro-4'-[N-(N'-(o-chlorobenzoyl))-ureido]-diphenyl ether of melting point 221°C were obtained.

Example 5.

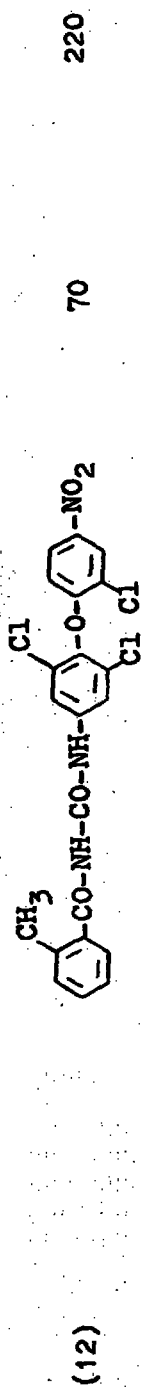
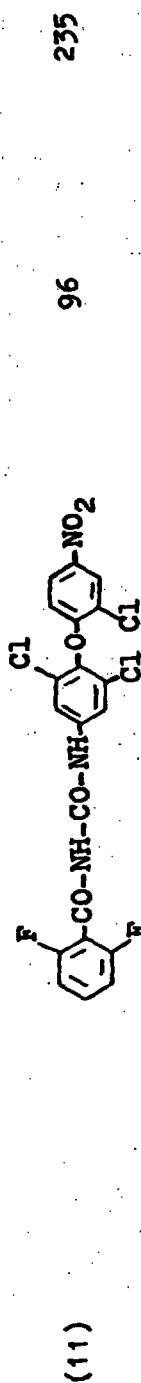


5 A solution of 3.25 g (0.02 mole) of 2 - methyl - benzoylisocyanate in 20 ml of
toluene was added dropwise at 80°C to a solution of 6.0 g (0.02 mole) of 3 - chloro-
4 - (2' - chloro - 4' - nitrophenoxy) - aniline in 80 ml of toluene. The batch was
stirred for 1 hour at 80°C. The substance which separated out was filtered off after
cooling the reaction mixture to 20°C and was washed with toluene and petroleum
ether. After drying, 8 g (87% of theory) of 2 - chloro - 4 - nitro - 2' - chloro - 4'-
[N - (N' - (o - methylbenzoyl)) - ureido] - diphenyl ether of melting point 220°C
were obtained.

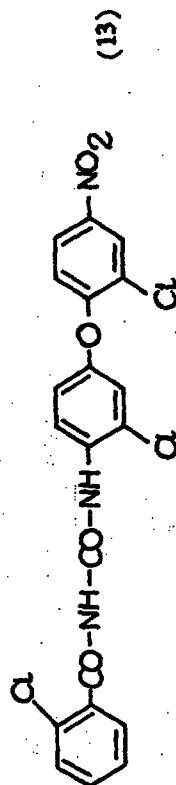
10 The following compounds were obtained by methods analogous to those described
above.

Example No.	Formula	Yield (%) of theory	Physical data (melting point, °C)
(6)		94	223
(7)		82	208
(8)		87	227
(9)		83	201
(10)		87	206

Example No.	Formula	Yield (% of theory)	Physical data (melting point, °C)
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Example 13.

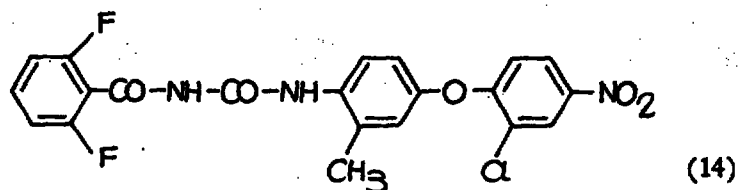


A solution of 3.7 g (0.02 mole) of 2-chlorobenzoylisocyanate in 20 ml of toluene was added dropwise at 30°C to 6.0 g (0.02 mole) of 4-(2'-chloro-4'-nitro-phenoxy)-2-chloroaniline in 100 ml of toluene. The batch was stirred for 1 hour at 50°C. After cooling, the product which had precipitated was filtered off and was washed first with toluene and then with petroleum ether. After drying, 6.0 g (62% of theory) of analytically pure 2,3'-dichloro-4-nitro-4'-[N-(2'-chloro-benzoyl)]-ureido-2-chlorobenzamide of melting point 193°C were obtained.

5

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Example 14.



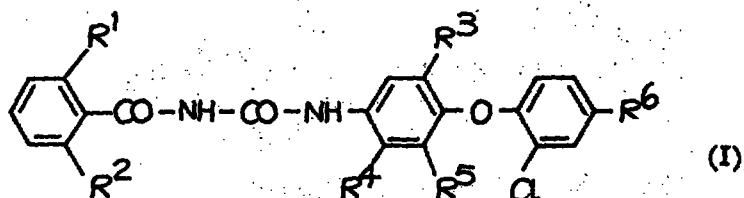
A solution of 3.7 g (0.02 mole) of 2,6 - difluorobenzoylisocyanate in 20 ml of toluene was added dropwise at 50°C to a solution of 5.6 g (0.02 mole) of 4 - (2'-chloro - 4' - nitrophenoxy) - 2 - methylaniline in 100 ml of toluene. The batch was stirred for 1 hour at 60°C. The substance which separated out was filtered off after cooling the reaction mixture to 20°C and was washed with toluene and petroleum ether. After drying, 7 g (75% of theory) of 2 - chloro - 4 - nitro - 3' - methyl - 4' - [N - (N' - 2,6 - difluorobenzoyl)) - ureido] - diphenyl ether of melting point 190°C were obtained.

The following compounds were obtained by using an analogous procedure to that described in Example 13 or 14:

Example No.	Formula	Physical data (melting point, °C)	Yield (%) of theory
(15)		200	93
(16)		193	82
(17)		197	65
(18)		200	86

WHAT WE CLAIM IS:—

1. Benzoylureido-diphenyl ethers of the general formula



in which

R¹ is fluorine, chlorine, bromine or methyl,

R² is hydrogen, fluorine or chlorine,

R³ is hydrogen or chlorine,

R⁴ is hydrogen or chlorine or methyl,

R⁵ is hydrogen or chlorine and

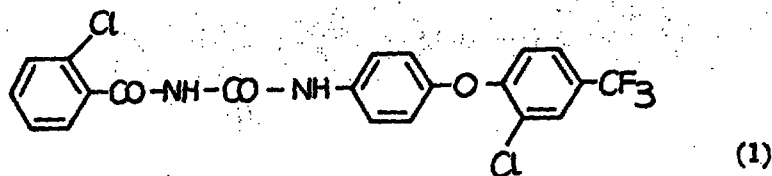
R⁶ is nitro or trifluoromethyl.

2. Benzoylureido-diphenyl ethers according to claim 1, in which R¹ is chlorine or fluorine, R² is hydrogen, chlorine or fluorine, R³, R⁴ and R⁵ are each hydrogen, and R⁶ represents trifluoromethyl.

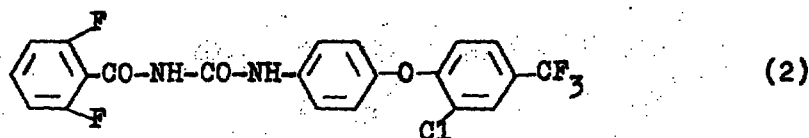
3. Benzoylureido-diphenyl ethers according to claim 1, in which R¹ is chlorine, fluorine or methyl, R² is hydrogen, chlorine or fluorine, R³ is hydrogen or chlorine, R⁴ is hydrogen, R⁵ is hydrogen or chlorine, and R⁶ is nitro.

4. Benzoylureido-diphenyl ethers according to claim 1, in which R¹ is chlorine, fluorine or bromine, R² is hydrogen or fluorine, R³ is hydrogen, R⁴ is methyl or chlorine, R⁵ is hydrogen and R⁶ is nitro.

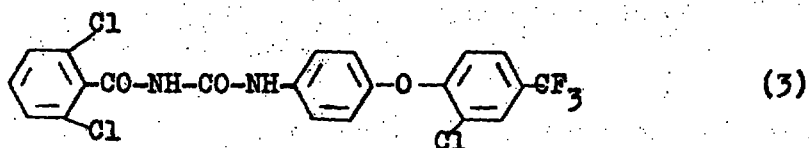
5. The compounds of the formula



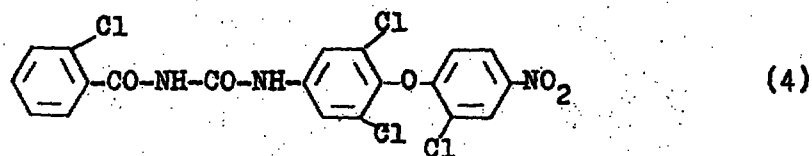
6. The compound of the formula



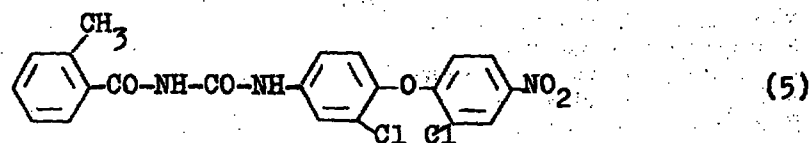
7. The compound of the formula



8. The compound of the formula



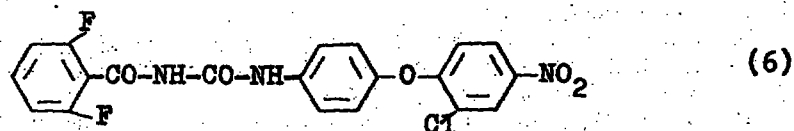
9. The compound of the formula



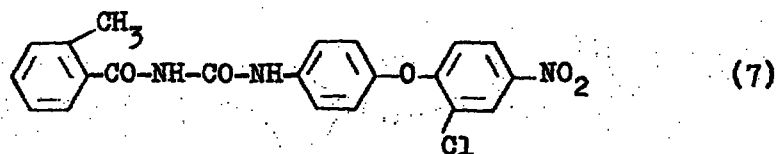
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10. The compound of the formula

5

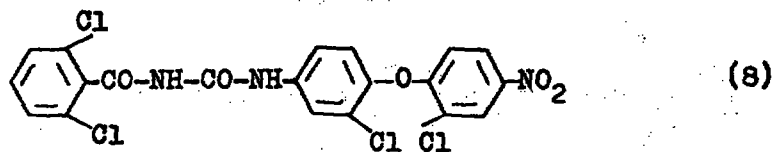


11. The compound of the formula



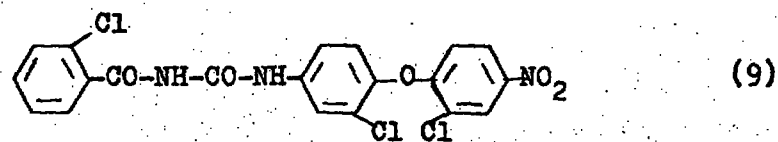
12. The compound of the formula

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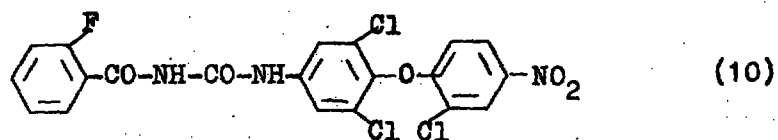


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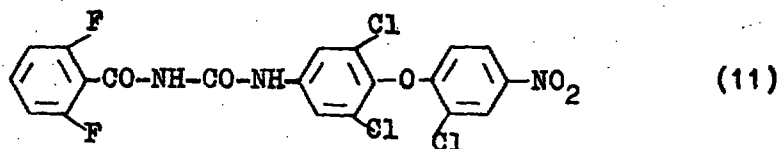
13. The compound of the formula



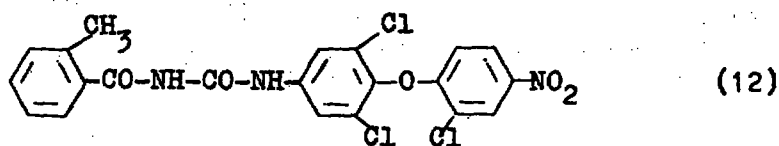
14. The compound of the formula



15. The compound of the formula

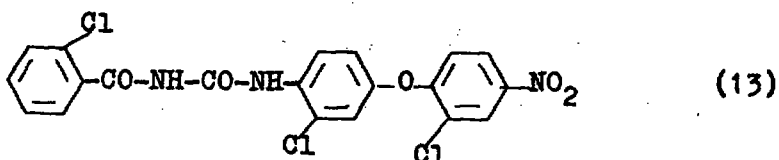


16. The compound of the formula



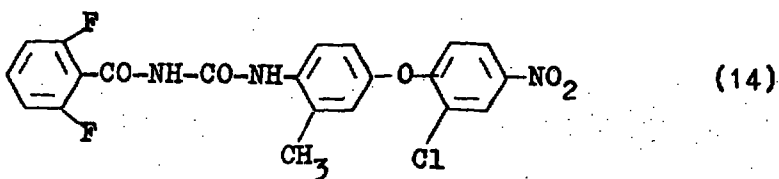
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17. The compound of the formula

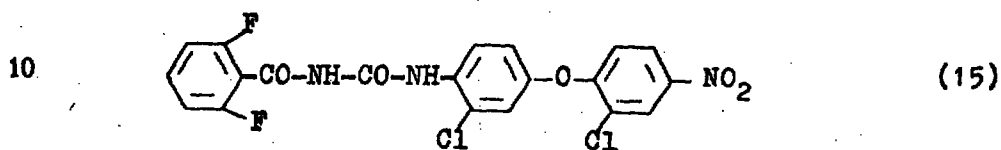


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18. The compound of the formula

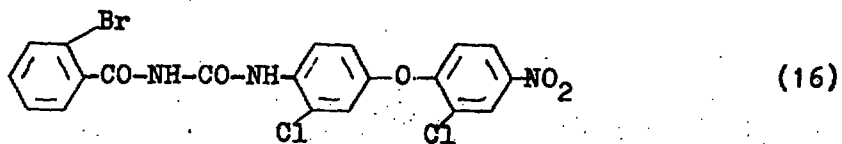


19. The compound of the formula

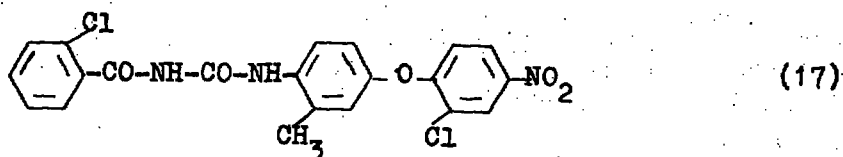


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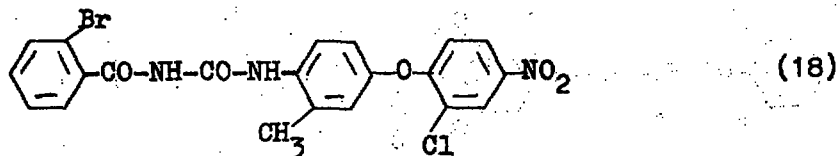
20. The compound of the formula



21. The compound of the formula

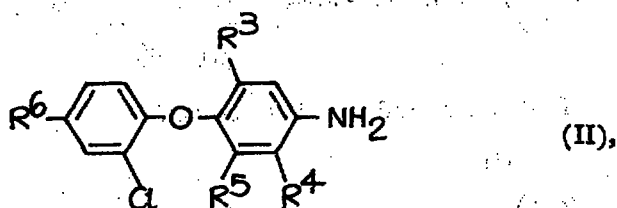


22. The compound of the formula

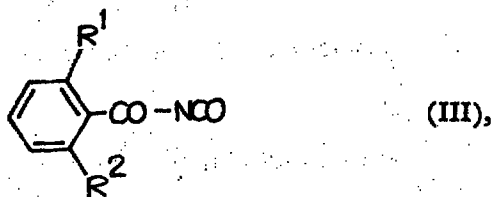


23. A process for the preparation of a benzoylureidodiphenyl ether according to claim 1, in which

(a) a phenoxyaniline of the general formula

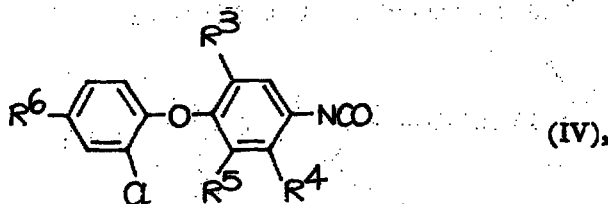


is reacted with a benzoylisocyanate of the general formula

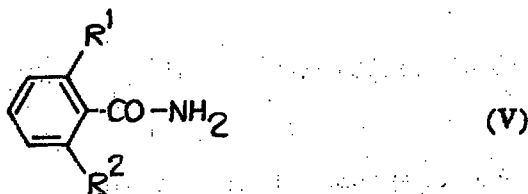


in which formulas

R¹ to R⁶ have the meanings stated in claim 1, or (b) a 4 - isocyanato - diphenyl ether of the general formula



is reacted with benzamides of the general formula



in which formulas

R¹ to R⁶ have the meanings stated in claim 1.

24. A process according to claim 23, in which the reaction is effected in the presence of an inert organic diluent or solvent.

25. A process according to claim 23 or 24, in which the reaction is effected at between 0° and 120°C.

26. A process according to claim 25, in which the reaction is effected at from 70° to 85°C.



27. A process according to any of claims 23 to 26, in which the reagents are used in substantially equimolar amounts.
28. A process according to any of claims 23 to 27 in which the substituents R¹ to R⁶ have the meanings stated in claim 2.
29. A process according to any of claims 23 to 27 in which the substituents R¹ to R⁶ have the meanings stated in claim 3.
30. A process according to any of claims 23 to 27 in which the substituents R¹ to R⁶ have the meanings stated in claim 4.
31. A process for the preparation of a compound according to claim 2, substantially as hereinbefore described in Example 1, 2 or 3.
32. A process for the preparation of a compound according to claim 3, substantially as hereinbefore described in Example 4 or 5.
33. A process for the preparation of a compound according to claim 4, substantially as hereinbefore described in Example 13 or 14.
34. Benzoylureido-diphenyl ethers, whenever prepared by a process according to any of claims 23 to 27.
35. Benzoylureido-diphenyl ethers, whenever prepared by a process according to claim 28 or 31.
36. Benzoylureido-diphenyl ethers, whenever prepared by a process according to claim 29 or 32.
37. Benzoylureido-diphenyl ethers, whenever prepared by a process according to claim 30 or 33.
38. An insecticidal composition containing as active ingredient a compound according to claim 1 or 34 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.
39. A composition according to claim 38 containing from 0.1 to 95% of the active compound, by weight.
40. A composition according to claim 38 or 39, in which the active compound is according to any of claims 2, 5 to 7 and 35.
41. A composition according to claim 38 or 39, in which the active compound is according to any of claims 3, 8 to 16 and 36.
42. A composition according to claim 38 or 39, in which the active compound is according to any of claims 4, 17 to 22 and 37.
43. A method of combating insects which comprises applying to the insects or an insect habitat a compound according to claim 1 or 34 alone or in the form of a composition containing as active ingredient a compound according to claim 1 or 34 in admixture with a diluent or carrier.
44. A method according to claim 43 in which a composition is used containing from 0.0001 to 10% of the active compound, by weight.
45. A method according to claim 44 in which a composition is used containing from 0.01 to 1% of the active compound, by weight.
46. A method according to claim 43, 44 or 45 in which the active compound is according to any of claims 2, 5 to 7 and 35.
47. A method according to claim 43, 44 or 45 in which the active compound is according to any of claims 3, 8 to 16 and 36.
48. A method according to claim 43, 44 or 45 in which the active compound is according to any of claims 4, 17 to 22 and 37.
49. 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 to 22 and 34 to 37 was applied alone or in admixture with a diluent or carrier.

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