

PATENT SPECIFICATION

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 (72) Inventors WILHELM SIRRENBURG, JURGEN SCHRAMM,
 ERICH KLAUKE, INGEBORG HAMMANN, and
 WILHELM STENDEL



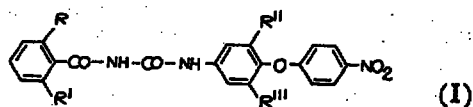
(54) BENZOYL-UREIDO-DIPHENYL ETHERS AND THEIR USE AS INSECTICIDES

(71) We, BAYER AKTIENGESSELLSCHAFT, 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-nitro-diphenyl ethers, to a process for their preparation and to their use as insecticides.

It has already been disclosed 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-nitro-diphenyl ethers of the general formula



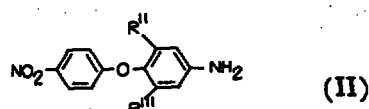
in which

R is chlorine, fluorine or methyl,
 R' is hydrogen, chlorine or fluorine, and
 R'' and R''' are identical and are each hydrogen or chlorine, but if R is chlorine and R' is hydrogen, R'' and R''' can only be hydrogen.

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

The present invention also provides a process for the preparation of a benzoylureido-nitro-diphenyl ether of the formula (I), in which

(a) a phenoxyaniline of the general formula



in which

R'' and R''' have the above-mentioned meanings

is reacted with a benzoylisocyanate of the general formula

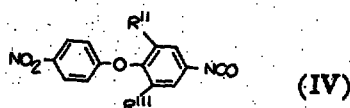


in which

R and R' have the above-mentioned meanings,

if appropriate in the presence of a diluent or solvent, or

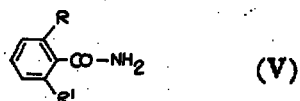
(b) a 4-isocyanato-diphenyl ether of the general formula



in which

R'' and R''' have the above-mentioned meanings,

is reacted with a benzamide of the general formula



in which

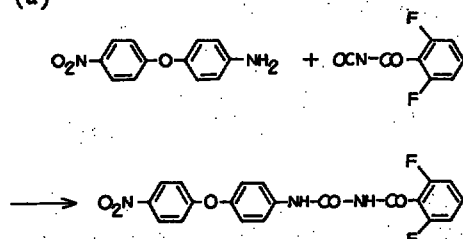
R and R' have the above-mentioned meanings,

if appropriate in the presence of a diluent or solvent.

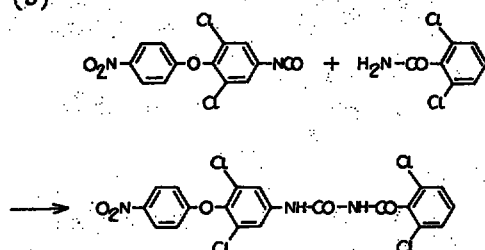
Surprisingly, the benzoylureido-nitro-diphenyl ethers according to the invention have a substantially better insecticidal action than the nearest compounds of analogous structure and of the same type of action previously known from the state of the art. The compounds according to the invention thus represent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

If, using process variant (a), 4-(4'-nitro-phenoxy)-aniline and 2,6-difluorobenzoylisocyanate are employed as starting materials and, using process variant (b), 3,5-dichloro-4-(4'-nitro-phenoxy)-phenylisocyanate and 2,6-dichlorobenzamide are employed as starting materials, the courses of the reactions can be represented by the following equations:

(a)



(b)



The benzoylisocyanates of the general formula (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 4 306—4 307 (1965)]. The benzamides of the general formula (V) are known from the literature and can be prepared according to known methods (see Beilsteins Handbuch der Organischen Chemie (Beilstein's Handbook of Organic Chemistry), volume 9, page 336). The phenoxy-anilines of the general formula (II) can be prepared according to generally customary processes, for example from alkali metal aminophenolates and aromatic nitrohalogen compounds in a solvent, for example dimethylsulphoxide (see Jürgen Schramm *et al.*, Justus Liebigs Annalen der Chemie 1970, 740, 169—179). The amino group can be converted to the isocyanate group in accordance with generally customary processes, for example by reaction

with phosgene, whereby the 4-isocyanato-diphenyl ethers of the general formula (IV) are obtained.

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

The process variants (a) and (b) for the preparation of the compounds according to the invention are 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 dioxan; ketons, 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 from 70° to 85°C.

The reaction is allowed to take place under normal pressure.

To carry out the process, the reactants are preferably employed in equimolar amounts. An excess of one or other reactant produces no significant advantages.

The 4-isocyanato-nitro-diphenyl ethers (IV) to be employed in process variant (b) above can be employed as such or, without intermediate isolation, in the form of their reaction mixture which is obtained in the reaction with amine and phosgene. This reaction mixture, in one of the above-mentioned solvents, is treated with the appropriate benzamides. 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 already mentioned, the benzoylureido-nitro-diphenyl ethers according to the invention are distinguished by an excellent insecticidal activity. They are not only active against plant pests but also, in the veterinary medicine field, against animal parasites (ectoparasites), such as parasitic fly larvae. They possess favourable values for toxicity to warm-blooded animals and are well tolerated by plants.

For this reason, the compounds according to the invention can be employed successfully in plant production against biting and sucking insects. They can furthermore be employed in the veterinary field as pest control agents against animal parasites.

The active compounds according to the invention can be used for combating all or individual stages of development, including the pre-embryonic, normally sensitive and resistant, stages of development, of insects, where these are known as pests in agriculture, in forestry, in the protection of stored products and materials, and in hygiene.

The economically important insect pests in agriculture and forestry, as well as pests of stored products, pests destructive of materials and pests harmful to health include: from the order of the *Thysanura*, for example, *Lepisma saccharina*; from the order of the *Collembola* for example, *Onychiurus armatus*; from the order of the *Orthoptera*, for example, *Blatta orientalis*; *Periplaneta americana*, *Leucophaea maderae*, *Blattella germanica*, *Acheta domesticus*, *Gryllotalpa* spec., *Locusta migratoria migratorioides*, *Melanoplus differentialis* and *Schistocerca gregaria*; from the order of the *Dermoptera*, for example, *Forficula auricularia*; from the order of the *Isoptera*, for example, *Reticulitermes* spec.; from the order of the *Anoplura*, for example, *Phylloxera vastatrix*, *Pemphigus* spec. and *Pediculus humanus corporis*; from the order of the *Thysanoptera*, for example, *Hercinothrips femoralis* and *Thrips tabaci*; from the order of the *Heteroptera*, for example, *Eurygaster* spec., *Dysdercus intermedius*, *Piesma quadrata*, *Cimex lectularius*, *Rhodnius prolixus* and *Triatoma* spec.; from the order of the *Homoptera*, for example, *Aleurodes brassicae*, *Bemisia tabaci*, *Trialeurodes vaporariorum*, *Aphis gossypii*, *Brevicoryne brassicae*, *Cryptomyzus ribis*, *Doralis fabae*, *Doralis pomei*, *Eriosoma lanigerum*, *Hyalopterus arundinis*, *Macrosiphum avenae*, *Myzus cerasi*, *Myzus persicae*, *Phorodon humuli*, *Rhopalosiphum padi*, *Empoasca* spec., *Euscelis bilobatus*, *Nephotettix cincticeps*, *Lecanium corni*, *Saissetia oleae*, *Laodelphax striatellus*, *Nilaparvata lugens*, *Aonidiella aurantii*, *Aspidiotus hederiae*, *Pseudococcus* spec. and *Psylla* spec.; from the order of the *Lepidoptera*, for example, *Pectinophora gossypiella*, *Bupalus piniarius*, *Cheimatobia brumata*, *Lithocolletis blancardella*, *Hyponomeuta padella*, *Plutella maculipennis*, *Malacosoma neustria*, *Euproctis crysorrhoea*, *Lymantria* spec., *Bucculatrix thurberiella*, *Phyllocnistis citrella*, *Agrotis* spec., *Euxoa* spec., *Feltia* spec., *Earias insulana*, *Heliothis* spec., *Laphygma exigua*, *Mamestra brassicae*, *Panolis flammea*, *Prodenia litura*, *Spodoptera* spec., *Trichoplusia ni*, *Carpocapsa pomonella*, *Pieris* spec., *Chilo* spec., *Pyrausta nubilalis*, *Ephestia kuehniella*, *Galleria mellonella*, *Cacoecia podana*, *Capua reticulana*, *Choristoneura fumiferana*, *Clysis ambiguella*, *Homona magnanima* and *Tortrix viridana*; from the order of the *Coleoptera*, for example, *Anobium punctatum*, *Rhizopertha dominica*, *Bruchidius obtectus*, *Acanthoscelides obtectus*, *Hylotrupes bajulus*,

Agelastica alni, *Leptinotarsa decemlineata*, *Phaedon cochleariae*, *Diabrotica* spec., *Psylliodes chrysocephala*, *Epilachna varivestis*, *Atomaria* spec., *Oryzaephilus surinamensis*, *Anthonomus* spec., *Sitophilus* spec., *Otiorynchus sulcatus*, *Cosmopolites sordidus*, *Ceuthorrhynchus assimilis*, *Hypera postica*, *Dermestes* spec., *Trogoderma* spec., *Anthrenus* spec., *Attagenus* spec., *Lyctus* spec., *Meligethes aeneus*, *Ptinus* spec., *Niptus hololeucus*, *Gibbium psyllodes*, *Tribolium* spec., *Tenebrio molitor*, *Agriotes* spec., *Conoderus* spec., *Melolontha melolontha*, *Amphimallus solstitialis* and *Costelytra zealandica*; from the order of the *Hymenoptera*, for example, *Diprion* spec., *Hoplocampa* spec., *Lasium* spec., *Monomorium pharaonis* and *Vespa* spec.; from the order of the *Diptera*, for example, *aedes* spec., *Anopheles* spec., *Culex* spec., *Drosophila melanogaster*, *Musca domestica*, *Fannia* spec., *Stomoxys calcitrans*, *Hypoderma* spec., *Bibio hortulanus*, *Oscinella frit*, *Phorbia* spec., *Pegomya hyoscyami*, *Calliphora erythrocephala*, *Lucilia* spec., *Chrysomya* spec., *Ceratitis capitata*, *Dacus oleae* and *Tipula paludosa*; and from the order of the *Siphonoptera*, for example, *Xenopsylla cheopis*.

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 and 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 dispensing 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 from 0.0001 to 10%, preferably from 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% active compound 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 present compounds 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

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*).

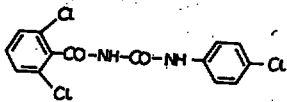
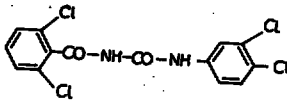
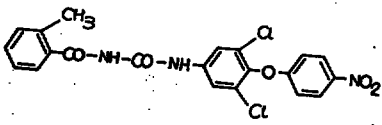
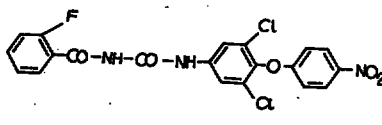
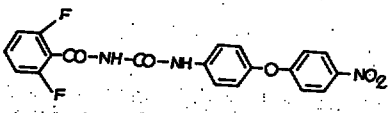
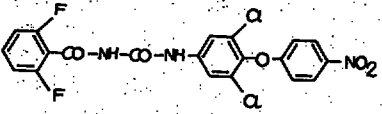
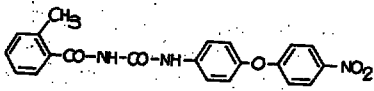
After the specified periods of time, the degree of destruction was determined as a percentage: 100% means that all the caterpillars were killed whereas 0% means that none of the caterpillars were killed.

The active compounds, the concentration 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 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
 (4)	0.1 0.01 0.001	100 100 100
 (3)	0.1 0.01 0.001	100 100 100
 (2)	0.1 0.01 0.001	100 100 100
 (1)	0.1 0.01 0.001	100 100 100
 (7)	0.1 0.01 0.001	100 100 100

EXAMPLE B.*Phaedon* larvae test.

Solvent: 3 parts by weight of dimethylformamide

- 5 Emulsifier: 1 part by weight of alkylaryl polyglycol ether

- 10 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 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*). 15

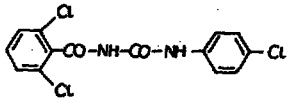
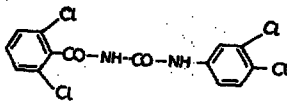
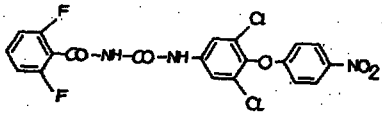
After the specified periods of time, the degree of destruction was determined in %: 100% means that all of the beetle larvae had been killed whereas 0% means that none of the beetle larvae have been killed. 20

The active compounds, the concentrations of the active compounds, the evaluation times and the results can be seen from the following table: 25

TABLE B

(Insects which damage plants)

Phaedon larvae test

Active compounds	Active compound concentration in %	Degree of destruction in % after 3 days
	0.1 0.01 0.001	100 55 0
(known)		
	0.1 0.01 0.001	100 15 0
(known)		
	0.1 0.01 0.001	100 100 80
(1)		

EXAMPLE C.

Test with parasitic fly larvae.

- 30 Solvent: 35 parts by weight of ethylene polyglycol monomethyl ether
35 parts by weight of nonylphenol polyglycol ether

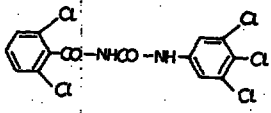
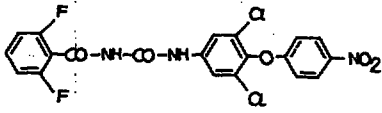
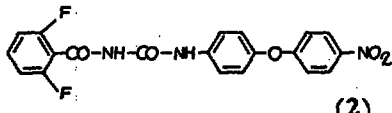
- 35 To produce a suitable preparation of active compound, 30 parts by weight of the active substance in question were mixed with the stated amount of solvent which contained the above-mentioned proportion of emulsifier and the concentrate thus obtained was diluted with water to the desired concentration.

About 20 fly larvae (*Lucilia cuprina*) were introduced into a test tube which contained approx. 2 cm³ of horse muscle. 0.5 ml of the preparation of the active compound was applied to this horse meat. After 24 hours, the degree of destruction in % was determined. 100% means that all larvae had been killed and 0% means that no larvae had been killed. 45

The active compounds investigated, the concentrations of the active compounds used and the results obtained can be seen from the table which follows: 50

TABLE C

(Test with parasitic fly larvae/*Lucilia cuprina*/resistant)

Active compound	Active compound concentration in ppm	Degree of destruction in %
 (known)	1000	0
 (1)	1000 100	100 100
 (2)	1000 300	100 100

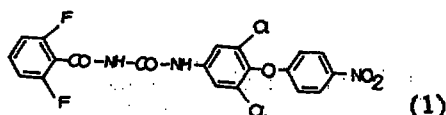
The process according to this invention is illustrated by the following preparative Examples.

Example 2:

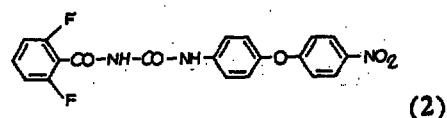
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5

Example 1:



10 A solution of 3.7 g (0.02 mole) of 2,6-difluorobenzoyl-isocyanate in 20 ml of toluene was added dropwise, at 80°C, to 6 g (0.02 mole) of 3,5-dichloro-4-(4'-nitrophenoxy)-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, 8 g (83% of theory) of analytically pure 4-nitro-2',6'-dichloro-4'-[N-(N'-2,6-difluorobenzoyl)-ureido]-diphenyl ether of melting point 226° were obtained.



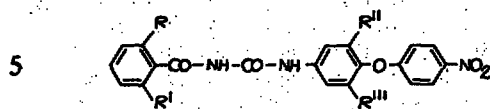
25 A solution of 9.2 g (0.05 mole) of 2,6-difluorobenzoyl-isocyanate in 20 ml of toluene was added dropwise, at 80°C, to a solution of 11.5 g (0.05 mole) of 4-(4'-nitrophenoxy)-aniline in 100 ml of toluene and 30 ml of acetonitrile. The batch was stirred for 1 hour at 80°C. The substance which separated out was filtered off after cooling the reaction mixture to 20°C, and was washed with toluene and petroleum ether. After drying, 18 g (87% of theory) of 4-nitro-4'-[N-(N'-2,6-difluorobenzoyl)-ureido]-diphenyl ether of melting point 240°C were obtained.

35 The following compounds were prepared by methods analogous to those of Examples 1 and 2:

Example No.	Formula	Yield (% of theory)	Physical data (melting point, °C)
3		88	207
4		76	201
5		84	239
6		75	215
7		61	193

WHAT WE CLAIM IS:—

1. Benzoylureido-nitro-diphenyl ethers of the general formula (I)

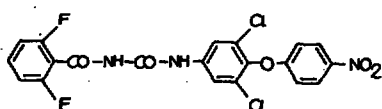


(I)

in which

R is chlorine, fluorine or methyl, R' is hydrogen, chlorine or fluorine, and R'' and R''' are identical and are each hydrogen or chlorine, but if R is chlorine and R' is hydrogen, R'' and R''' can only be hydrogen.

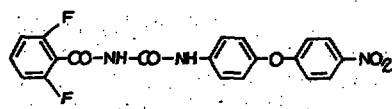
2. The compound of the formula



(1)

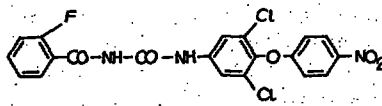
3. The compound of the formula

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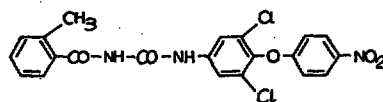
(2)

4. The compound of the formula



(3)

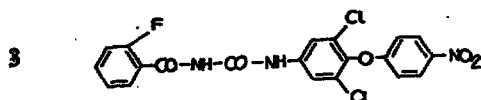
5. The compound of the formula



(4)

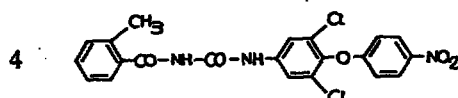
20

Example No.	Formula	Yield (% of theory)	Physical data (melting point, °C)
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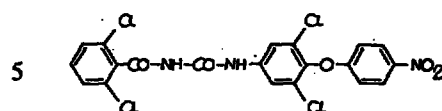
88

207



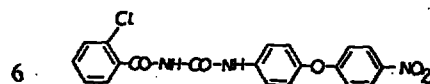
76

201



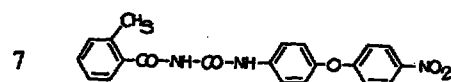
84

239



75

215

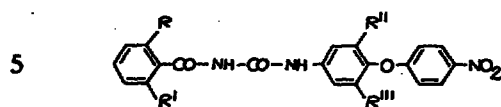


61

193

WHAT WE CLAIM IS:—

1. Benzoylureido-nitro-diphenyl ethers of the general formula (I)



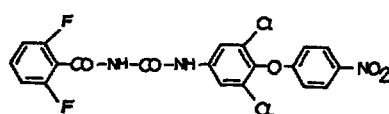
(I)

in which

R is chlorine, fluorine or methyl, R' is hydrogen, chlorine or fluorine, and R'' and R''' are identical and are each hydrogen or chlorine, but if R is chlorine and R' is hydrogen, R'' and R''' can only be hydrogen.

10

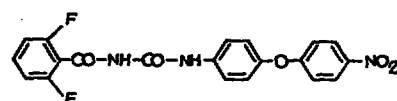
2. The compound of the formula



(1)

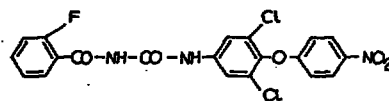
3. The compound of the formula

15



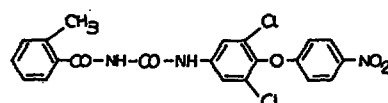
(2)

4. The compound of the formula



(3)

5. The compound of the formula

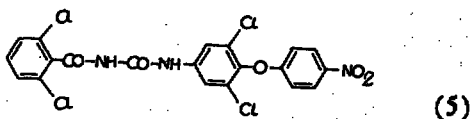


(4)

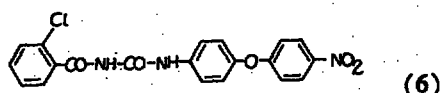
20



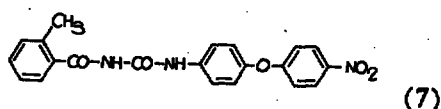
6. The compound of the formula



7. The compound of the formula

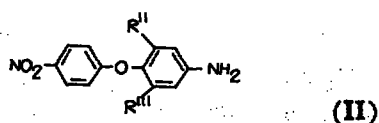


8. The compound of the formula



9. A process for the preparation of a benzoylureido-nitro-diphenyl ether according to claim 1, in which

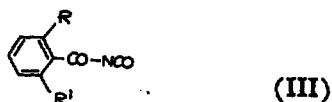
10 (a) a phenoxyaniline of the general formula



in which

R'' and R''' have the meanings stated in claim 1,

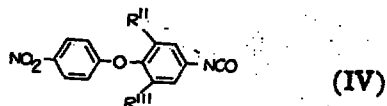
15 is reacted with a benzoylisocyanate of the general formula



in which

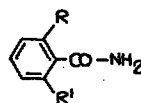
R and R' have the meanings stated in claim 1,

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



in which

25 R'' and R''' have the meanings stated in claim 1, is reacted with a benzamide of the general formula



in which

R and R' have the meanings stated in claim 1.

10. process according to claim 9, in which the reaction is effected in the presence of an inert organic diluent or solvent.

11. A process according to claim 9 or 10, in which the reaction is effected at between 0° and 120°C.

12. A process according to claim 11, in which the reaction is effected at from 70° to 85°C.

13. A process according to any of claims 9 to 12, in which the reactants are used in substantially equimolar amounts.

14. A process for the preparation of a compound according to claim 1, substantially as hereinbefore described in Example 1 or 2.

15. A compound according to claim 1, whenever prepared by a process according to any of claims 9 to 14.

16. An insecticidal composition containing as active ingredient a compound according to any of claims 1 to 8 and 15 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.

17. A composition according to claim 16 containing from 0.1 to 95% of the active compound, by weight.

18. A composition according to claim 17 containing from 0.5 to 90% of the active compound, by weight.

19. A method of combating insects which comprises applying to the insects or an insect habitat a compound according to any of claims 1 to 8 and 15 alone or in the form of a composition containing as active ingredient a compound according to any of claims 1 to 18 and 15 in admixture with a diluent or carrier.

20. A method according to claim 19, in which a composition is used containing from 0.0001 to 10% of the active compound, by weight.

21. A method according to claim 20, in which a composition is used containing from 0.01 to 1% of the active compound, by weight.

22. 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 one of claims 1 to 8 and 15 was applied alone or in admixture with a diluent or carrier.



For the Applicants,
CARPMAELS & RANSFORD,
Chartered Patent Agents,
43, Bloomsbury Square,
London, W.C.1.

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