

FORM 1

60 6971

SPRUSON & FERGUSON

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

Ciba-Geigy AG, incorporated in Switzerland, of Klybeckstrasse 141, 4002 Basle, SWITZERLAND, hereby apply for the grant of a standard patent for an invention entitled:

N-benzoyl-N'-2.5-dihalo-4-perfluoroalkoxyphenylureas, their Preparation and Use in the Control of Pests

which is described in the accompanying complete specification.

Details of basic application(s):-

<u>Basic Applic. No:</u>	<u>Country:</u>	<u>Application Date:</u>
2751/87-0	CH	21 July 1987
1920/88-9	CH	20 May 1988

The address for service is:-

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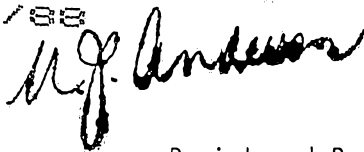
DATED this NINETEENTH day of JULY 1988

PRINT OF RECEIPT

001117 20/07/88

Ciba-Geigy AG

By:



Registered Patent Attorney

TO: THE COMMISSIONER OF PATENTS
OUR REF: 63942
S&F CODE: 52760

APPLICATION ACCEPTED AND AMENDMENTS

5845/2

ALLOWED 26.11.90

COMMONWEALTH OF AUSTRALIA

Patents Act 1952 - 1969

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

In support of the Convention Application made by CIBA-GEIGY AG for a patent for an invention entitled:

N-benzoyl-N'-2,5-dihalo-4-perfluoroalkoxyphenylureas, their preparation and use in the control of pests

I, Ernst Altherr of CIBA-GEIGY AG, Klybeckstrasse 141, 4002 Basle, Switzerland do solemnly and sincerely declare as follows:

1. I am authorised by the applicant for the patent to make this declaration on its behalf.
2. The basic application(s) as defined by Section 141 of the Act ~~was~~-(were) made in Switzerland on July 21, 1987 and on May 20, 1988

both by CIBA-GEIGY AG, 4002 Basle, Switzerland

3. Jozef Drabek, Benkenstrasse 12, 4104 Oberwil, Switzerland and Urs Siegrist, Rebenweg 32, 5268 Eiken, Switzerland

~~is~~ (are) the actual inventor(s) of the invention and the facts upon which the applicant is entitled to make the application are as follows: The said applicant is the assignee of the actual inventor(s).

4. The basic application(s) referred to in paragraph 2 of this Declaration ~~was~~-(were) the first application(s) made in a Convention country in respect of the inventionthe subject of the application.

DECLARED at Basle, Switzerland on
June 27, 1988

CIBA-GEIGY AG



Ernst Altherr
Single Signature, by special power

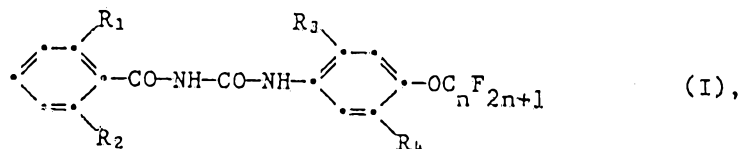
To: The Commissioner of Patents

(12) PATENT ABRIDGMENT (11) Document No. AU-B-19261/88
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 606971

- (54) Title
N-BENZOYL-N'-2,5-DIHALO-4-PERFLUOROALKOXYPHENYLUREAS, THEIR PREPARATION AND USE IN THE CONTROL OF PESTS
- International Patent Classification(s)
 (51)⁴ C07C 127/22 A01N 047/30 C07C 079/35 C07C 093/14
- (21) Application No. : 19261/88 (22) Application Date : 20.07.88
- (30) Priority Data
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- (43) Publication Date : 27.01.89
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 (56) Prior Art Documents
 AU 590911 69527/87 C07C 127/22
 AU 68094/87 C07C 127/22
 EP 179021

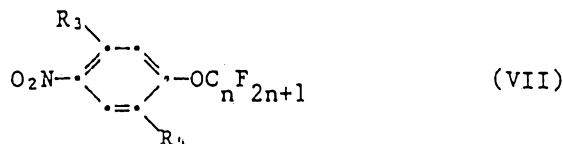
(57) Claim

1. Compounds of formula I



in which R₁ is hydrogen, fluorine, chlorine or bromine; R₂ is fluorine or chlorine; each of R₃ and R₄ is chlorine; and n is 2, 3, 4, 5, 6, 7 or 8.

13. Compounds of formula VII



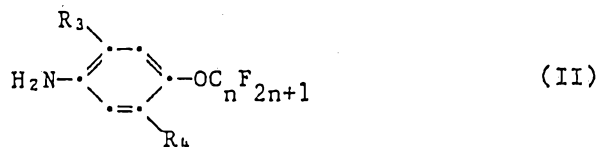
in which each of R₃ and R₄ is chlorine, and n is 2, 3, 4, 5, 6, 7 or 8

~~for the exclusive use~~ in the preparation of compounds of formula I according to claim 1.

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(10) 606971

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16. Compounds of formula II



in which each of R₃ and R₄ is chlorine, and n is 2, 3, 4, 5, 6, 7 or 8
when used
/ ~~for the exclusive use~~ in the preparation of compounds of formula I
according to claim 1.

S & F Ref: 63942

FORM 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

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COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE:

Class Int Class

Complete Specification Lodged:
Accepted:
Published:

Priority:

Related Art:

This document contains the amendments made under Section 49 and is correct for printing.

Name and Address
of Applicant:

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Complete Specification for the invention entitled:

N-benzoyl-N'-2,5-dihalo-4-perfluoroalkoxyphenylureas, their
Preparation and Use in the Control of Pests

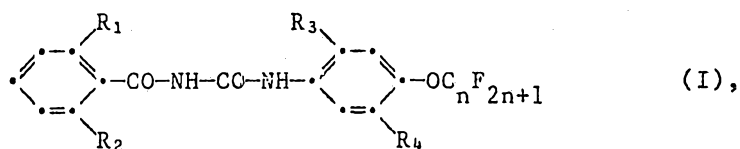
The following statement is a full description of this invention, including the best method of performing it known to me/us

5-16589/1+2/ZFO

N-benzoyl-N'-2,5-dihalo-4-perfluoroalkoxyphenylureas, their preparation and use in the control of pests

Abstract

Novel substituted N-benzoyl-N'-2,5-dihalo-4-perfluoroalkoxyphenylureas of formula I



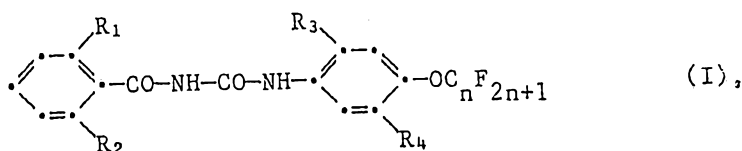
in which R₁ is hydrogen, fluorine, chlorine or bromine; R₂ is fluorine or chlorine; each of R₃ and R₄ is ^{chlorine;} ~~fluorine, chlorine or bromine;~~ and n is 2, 3, 4, 5, 6, 7 or 8, processes and intermediates for their preparation, their use in pest control, and pesticidal compositions that contain at least one compound of formula I as active ingredient, are disclosed. The preferred field of application is the control of pests in and on animals and plants.



The present invention relates to novel substituted N-benzoyl-N'-2,5-dihalo-4-perfluoroalkoxyphenylureas, processes and intermediates for their preparation and their use in pest control.

The compounds according to the invention have the formula I

5



in which R_1 is hydrogen, fluorine, chlorine or bromine; R_2 is fluorine or chlorine; each of R_3 and R_4 is chlorine; and n is 2, 3, 4, 5, 6, 7 or 8.

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The perfluorinated C_2 - C_8 alkyl radicals suitable as substituents may be straight-chained or branched but are preferably unbranched.

Suitable examples of such substituents are, inter alia, CF_2CF_3 ,

$(CF_2)_2CF_3$, $(CF_2)_3CF_3$, $CF_2CF(CF_3)_2$ or the perfluoro-pentyl, -hexyl, -heptyl or -octyl radicals.

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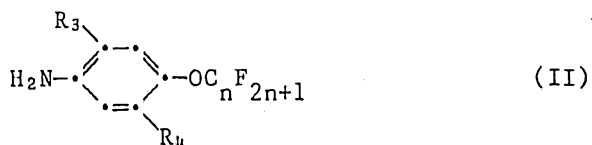
The compounds of formula I that should be given special emphasis are those in which R_1 is hydrogen, fluorine or chlorine; R_2 is fluorine or chlorine; R_3 is chlorine; R_4 is chlorine; and n is 2, 3, 4, 5, 6 or 7.



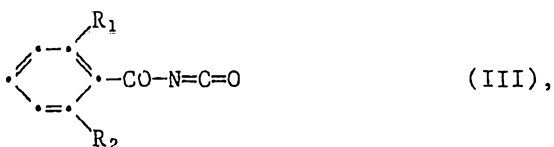
Compounds of formula I in which R₁ is hydrogen or fluorine; R₂ is fluorine or chlorine; each of R₃ and R₄ is chlorine; and n is 2, 3 or 4 are preferred.

The compounds according to the invention can be prepared according to processes that are known in principle. Such processes are described, inter alia, in DE-OS 21 23 236, 26 01 780 and 32 40 975. For example, the compounds of formula I can be obtained as follows:

a) an aniline of formula II

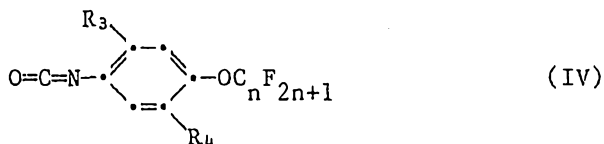


is reacted with a benzoyl isocyanate of formula III



or

b) an isocyanate of formula IV

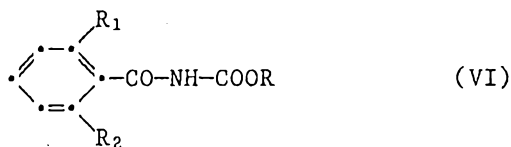


is reacted with a benzamide of formula V



or

c) an aniline of formula II is reacted with a urethane of formula VI

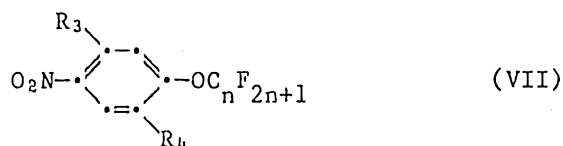


In the above formulae II to VI, the symbols R_1 , R_2 , R_3 , R_4 and n have the meanings given for formula I and R is a C_1 - C_8 alkyl radical that may be unsubstituted or may be substituted by halogen, preferably chlorine.

The mentioned processes a), b) and c) are preferably carried out under normal pressure and in the presence of an organic solvent or diluent. Suitable solvents and diluents are, for example, ethers and ethereal compounds, such as diethyl ether, dipropyl ether, dibutyl ether, dioxane, dimethoxyethane and tetrahydrofuran; N,N -dialkylated carboxylic acid amides; aliphatic, aromatic and halogenated hydrocarbons, especially benzene, toluene, xylene, chloroform, methylene chloride, carbon tetrachloride and chlorobenzene; nitriles, such as acetonitrile or propionitrile; dimethyl sulfoxide and ketones, for example acetone, methyl ethyl ketone, methyl isopropyl ketone and methyl isobutyl ketone. Process a) is generally carried out at a temperature of from -10 to $+200^\circ\text{C}$, preferably from 0 to $+100^\circ\text{C}$, for example at room temperature, in the absence or presence of an organic base, for example triethylamine. Process b) is carried out at a temperature of from 0 to $+150^\circ\text{C}$, preferably at the boiling point of the solvent used, and in the absence or presence of an organic base, such as pyridine, and/or with the addition of an alkali metal or an alkaline earth metal, preferably sodium. For process c), that is to say for the reaction of a urethane of formula VI with an aniline of formula II, temperatures of from approximately $+60^\circ\text{C}$ up to the boiling point of the reaction mixture are preferred, there being used as solvents especially aromatic hydrocarbons, such as toluene, xylenes, chlorobenzene, etc.

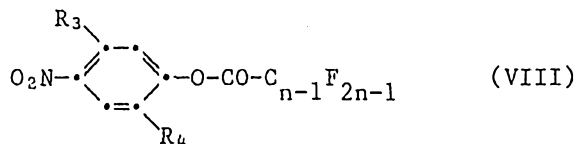
Some of the starting materials of formulae III, V and VI are known. Both the starting materials that are known and any that are novel can be prepared analogously to known processes.

The starting materials of formula II are novel compounds to which the present invention also relates. The compounds of formula II can be prepared in a manner known per se, for example by hydrogenating correspondingly substituted nitrobenzenes of formula VII



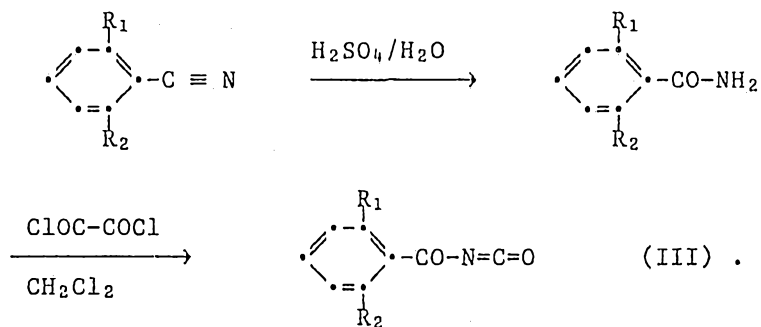
analogously to the process indicated in J. Org. Chem. 29 (1964), 1, (see also the literature cited in that reference). It is, however, also possible to obtain anilines of formula II by chemical reduction (for example by means of Sn(II) chloride/HCl) of the corresponding nitro compounds of formula VII (see Houben Weyl, "Methoden d. org. Chemie", 11/1, 422).

The nitro compounds of formula VII are also new and the present invention relates also to these. They can be prepared according to methods that are known in principle, for example by fluorination of compounds of formula VIII



by means of SF₄ and HF (see, for example, Organic Reactions Vol. 21, pp. 37-42, 1974; Vol. 34, p. 339, 1985). The compounds of formula VIII are known or can be prepared according to methods that are known in principle.

It is possible to obtain benzoyl isocyanates according to formula III, for example as follows (see J. Agr. Food Chem. 21, 348 and 993; 1973):



The 4-perfluoroalkoxyphenyl isocyanates of formula IV can be prepared, for example, by phosgenating the anilines of formula II by generally customary processes. The benzamides of formula V also to be used as starting materials are known (see, for example, Beilstein "Handbuch der organischen Chemie", Vol. 9, p. 336).

Urethanes of formula VI can be obtained according to methods that are known in principle by reacting a benzoyl isocyanate of formula III with a corresponding alcohol or by reacting a benzamide of formula V in the presence of a basic compound with a corresponding ester of the chloroformic acid Cl-COOR.

N-(2,6-dihalobenzoyl)-N'-(2,5-dichloro-4-haloalkoxyphenyl)-ureas having insecticidal action are known very generally from US Patent Specification 4,518,804. Perfluorinated alkoxy radicals, however, are not disclosed.

Surprisingly, it has been found that the compounds according to the invention are valuable active ingredients in pest control, while being well tolerated by warm-blooded animals and by plants. The compounds of formula I are suitable, for example, for controlling pests in and on animals and plants. Such pests belong mainly to the strain of the arthropods, such as, especially, insects of the order Lepidoptera, Coleoptera, Homoptera, Heteroptera, Diptera, Thysanoptera, Orthoptera, Anoplura, Siphonaptera, Mallophaga, Thysanura, Isoptera, Psocoptera or Hymenoptera and arachnids of the order Acarina, such as, for example, mites and ticks. It is possible to control every stage of development of

the pests, that is to say the adults, pupae and nymphs as well as, especially, the larvae and eggs. It is possible to control effectively especially the larvae and eggs of phytopathogenic insect and mite pests in ornamentals and useful plants, such as, for example, in fruit and vegetables, and especially in cotton. If the compounds of formula I are ingested by imagines, their action can manifest itself in the immediate death of the pests or in reduced oviposition and/or hatching rates. The latter phenomenon is to be observed especially in Coleoptera. In the control of pests that parasiticise animals, especially domestic animals and productive livestock, there come into consideration especially ectoparasites, such as, for example, mites and ticks and Diptera, such as, for example, *Lucilia sericata*. The compounds of formula I are also suitable for controlling snails in ornamentals and useful plants.

The good pesticidal activity of the compounds of formula I according to the invention corresponds to a mortality of at least from 50 to 60 % of the mentioned pests.

The activity of the compounds of the invention or the compositions containing them can be substantially broadened and adapted to prevailing circumstances by the addition of other insecticides and/or acaricides. Additives that come into consideration are, for example, representatives of the following classes of active ingredients: organophosphorus compounds, nitrophenols and derivatives thereof, formamidines, ureas, carbamates, pyrethroids, chlorinated hydrocarbons and *Bacillus thuringiensis* preparations.

The compounds of formula I are used in unmodified form or, preferably, together with the adjuvants conventionally employed in the art of formulation, and are therefore formulated in known manner e.g. into emulsifiable concentrates, directly sprayable or dilutable solutions, dilute emulsions, wettable powders, soluble powders, dusts, granulates, and also encapsulations in e.g. polymer substances. As with the nature of the compositions, the methods of application, such as spraying, atomising, dusting, scattering or pouring, are chosen in accordance with the intended objectives and the prevailing circumstances.

The formulations, i.e. the compositions, preparations or mixtures containing the compound (active ingredient) of formula I, or combinations thereof with other insecticides or acaricides, and, where appropriate, a solid or liquid adjuvant, are prepared in known manner, e.g. by homogeneously mixing and/or grinding the active ingredients with extenders, e.g. solvents, solid carriers and, where appropriate, surface-active compounds (surfactants).

Suitable solvents are: aromatic hydrocarbons, preferably the fractions containing 8 to 12 carbon atoms, e.g. xylene mixtures or substituted naphthalenes, phthalates such as dibutyl phthalate or dioctyl phthalate, aliphatic hydrocarbons such as cyclohexane or paraffins, alcohols and glycols and their ethers and esters, such as ethanol, ethylene glycol, ethylene glycol monomethyl or monoethyl ether, ketones such as cyclohexanone, strongly polar solvents such as N-methyl-2-pyrrolidone, dimethyl sulfoxide or dimethylformamide, as well as vegetable oils or epoxidised vegetable oils, such as epoxidised coconut oil or soybean oil, or water.

The solid carriers used e.g. for dusts and dispersible powders, are normally natural mineral fillers such as calcite, talcum, kaolin, montmorillonite or attapulgite. In order to improve the physical properties it is also possible to add highly dispersed silicic acids or highly dispersed absorbent polymers. Suitable granulated adsorptive carriers are porous types, for example pumice, broken brick, sepiolite or bentonite; and suitable nonsorbent carriers are, for example, calcite or sand. In addition, a great number of granulated materials of inorganic or organic nature can be used, e.g. especially dolomite or pulverised plant residues.

Depending on the nature of the compound of formula I to be formulated, or on the nature of the combinations thereof with other insecticides or acaricides, suitable surface-active compounds are non-ionic, cationic

and/or anionic surfactants having good emulsifying, dispersing and wetting properties. The term "surfactants" will also be understood as comprising mixtures of surfactants.

Both so-called water-soluble soaps and also water-soluble synthetic surface-active compounds are suitable anionic surfactants.

Suitable soaps are the alkali metal salts, alkaline earth metal salts or unsubstituted or substituted ammonium salts of higher fatty acids (C_{10} - C_{22}), e.g. the sodium or potassium salts of oleic or stearic acid, or of natural fatty acid mixtures which can be obtained e.g. from coconut oil or tall oil. Mention may also be made of fatty acid methylaurin salts and modified and unmodified phospholipids as surfactants.

More frequently, however, so-called synthetic surfactants are used, especially fatty sulfonates, fatty sulfates, sulfonated benzimidazole derivatives or alkylarylsulfonates.

The fatty sulfonates or sulfates are usually in the form of alkali metal salts, alkaline earth metal salts or unsubstituted or substituted ammonium salts and generally contain a C_8 - C_{22} alkyl radical which also includes the alkyl moiety of acyl radicals, e.g. the sodium or calcium salt of lignosulfonic acid, of dodecylsulfate or of a mixture of fatty alcohol sulfates obtained from natural fatty acids. These compounds also comprise the salts of sulfated and sulfonated fatty alcohol/ethylene oxide adducts. The sulfonated benzimidazole derivatives preferably contain 2 sulfonic acid groups and one fatty acid radical containing about 8 to 22 carbon atoms. Examples of alkylarylsulfonates are the sodium, calcium or triethanolamine salts of dodecylbenzenesulfonic acid, dibutyl-naphthalenesulfonic acid, or of a condensate of naphthalenesulfonic acid and formaldehyde.

Also suitable are corresponding phosphates, e.g. salts of the phosphoric acid ester of an adduct of p-nonylphenol with 4 to 14 moles of ethylene oxide.

Non-ionic surfactants are preferably polyglycol ether derivatives of aliphatic or cycloaliphatic alcohols, saturated or unsaturated fatty acids and alkylphenols, said derivatives containing 3 to 30 glycol ether groups and 8 to 20 carbon atoms in the (aliphatic) hydrocarbon moiety and 6 to 18 carbon atoms in the alkyl moiety of the alkylphenols. Further suitable non-ionic surfactants are the water-soluble adducts of polyethylene oxide with polypropylene glycol, ethylenediaminopolypropylene glycol and alkylpolypropylene glycol containing 1 to 10 carbon atoms in the alkyl chain, which adducts contain 20 to 250 ethylene glycol ether groups and 10 to 100 propylene glycol ether groups. These compounds usually contain 1 to 5 ethylene glycol units per propylene glycol unit.

Representative examples of non-ionic surfactants are nonylphenolpolyethoxyethanols, castor oil polyglycol ethers, castor oil thioxilate, polypropylene/polyethylene oxide adducts, tributylphenoxypolyethoxyethanol, polyethylene glycol and octylphenoxypolyethoxyethanol. Fatty acid esters of polyoxyethylene sorbitan, e.g. polyoxyethylene sorbitan trioleate, are also suitable non-ionic surfactants.

Cationic surfactants are preferably quaternary ammonium salts which contain, as N-substituent, at least one C_8-C_{22} alkyl radical and, as further substituents, unsubstituted or halogenated lower alkyl, benzyl or hydroxy-lower alkyl radicals. The salts are preferably in the form of halides, methyl sulfates or ethyl sulfates, e.g. stearyltrimethylammonium chloride or benzyldi(2-chloroethyl)ethylammonium bromide.

The surfactants customarily employed in the art of formulation are described, inter alia, in the following publications:

"McCutcheon's Detergents and Emulsifiers Annual",
MC Publishing Corp., Ridgewood, New Jersey, 1979;
Dr. Helmut Stache, "Tensid-Taschenbuch",
Carl Hanser Verlag, Munich/Vienna 1981.

The pesticidal compositions usually contain 0.1 to 99 %, preferably 0.1 to 95 %, of a compound of formula I or combinations thereof with other insecticides or acaricides, 1 to 99.9 % of a solid or liquid adjuvant, and 0 to 25 %, preferably 0.1 to 20 %, of a surfactant. Whereas commercial products will preferably be formulated as concentrates, the end user will normally employ dilute formulations containing considerably lower concentrations of active ingredient.

The compositions may also contain further auxiliaries such as stabilisers, antifoams, viscosity regulators, binders and tackifiers as well as fertilisers or other active ingredients in order to obtain special effects.

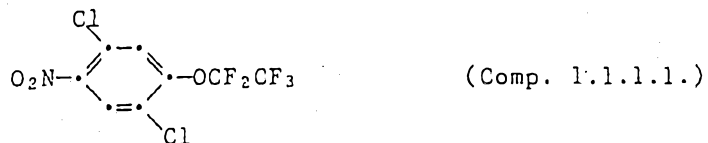
Example 1: Preparation

1.1. Intermediates

1.1.1. Nitrobenzenes

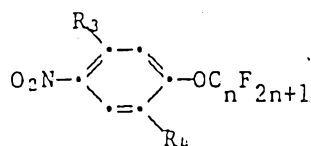
1.1.1.1. 2,5-dichloro-4-pentafluoroethoxynitrobenzene

An autoclave is charged with 20 g of 2,5-dichloro-4-nitrophenyl trifluoroacetate and evacuated. At from -10 to 0°C, first 60 g of hydrogen fluoride are added and then 14.3 g of sulfur tetrafluoride are introduced in portions with inert gas under pressure. The reaction mixture is then stirred for 15 hours at +50°C. The readily volatile portion is then distilled off at room temperature and the residue is taken up in methylene chloride and poured into ice-water. The organic phase is separated off and the aqueous phase is extracted twice with methylene chloride and, finally, the combined organic extracts are washed twice with water and twice with sodium carbonate and dried over sodium sulfate. The solvent is evaporated off and the residue is taken up in a hexane/ether mixture (30:1) and filtered over silica gel. After distilling off the solvent, the title compound of formula



is obtained in the form of a pale yellow oil; n_D^{22} : 1.4678;
b.p. 65-68°C/0.1 torr.

The following compounds are prepared in an analogous manner:

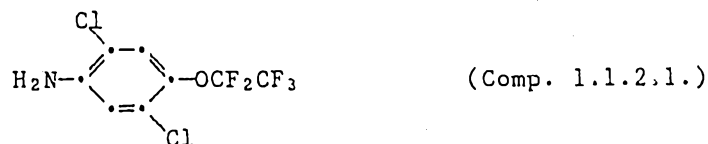


Comp. No.	R ₃	R ₄	C _n F _{2n+1}	phys. data
1.1.1.2.	Cl	Cl	(CF ₂) ₂ CF ₃	b.p. 74-77°C/0.15 torr
1.1.1.3.	Cl	Cl	(CF ₂) ₃ CF ₃	b.p. 76-82°C/0.05 torr

1.1.2. Anilines

1.1.2.1. 2,5-dichloro-4-pentafluoroethoxylaniline

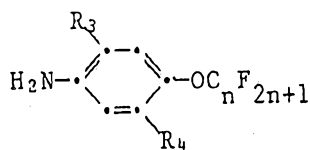
41 g of 2,5-dichloro-4-pentafluoroethoxynitrobenzene are dissolved in 410 ml of tetrahydrofuran and hydrogenated at room temperature for 32 hours in the presence of Raney nickel (H₂ absorption: 7.62 l). The reaction mixture is filtered and concentrated and the residue is distilled. The title compound of formula



is obtained in the form of a colourless liquid; b.p. 56-61°C/0.04 torr.



The following compounds are prepared in an analogous manner:

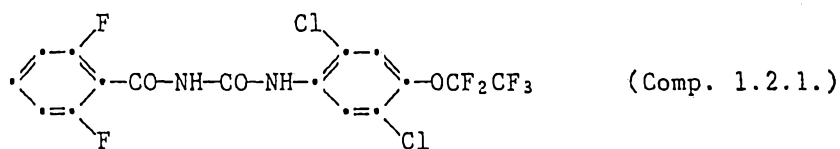


Comp. No.	R ₃	R ₄	C _n F _{2n+1}	phys. data
1.1.2.2.	Cl	Cl	(CF ₂) ₂ CF ₃	b.p. 110°C/0.04 torr
1.1.2.3.	Cl	Cl	(CF ₂) ₃ CF ₃	b.p. 140°C/0.08 torr

1.2. End products

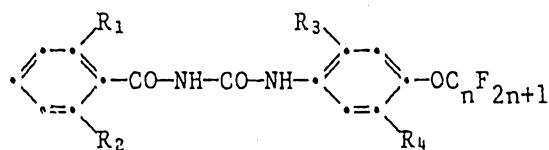
1.2.1. N-(2,6-difluorobenzoyl)-N'-(2,5-dichloro-4-pentafluoroethoxy-phenyl)-urea

3.4 g of 2,6-difluorobenzoyl isocyanate, dissolved in 10 ml of dry toluene, are added at room temperature and with the exclusion of moisture to 5.6 g of 2,5-dichloro-4-pentafluoroethoxyaniline dissolved in 40 ml of dry toluene, and the batch is stirred for 10 hours. Approximately 60 % of the solvent is then removed. The precipitate formed is filtered off with suction, washed with hexane and dried in vacuo. The title compound of formula



is obtained in the form of colourless crystals; m.p. 178-179°C.

The following compounds are prepared in an analogous manner:



Comp. No.	R ₁	R ₂	R ₃	R ₄	C _n F _{2n+1}	phys. data
1.2.2	F	F	Cl	Cl	(CF ₂) ₂ CF ₃	m.p. 176-178°C
1.2.3	F	F	Cl	Cl	(CF ₂) ₃ CF ₃	m.p. 171-173°C
1.2.4	H	F	Cl	Cl	CF ₂ CF ₃	m.p. 164-165°C
1.2.5	H	F	Cl	Cl	(CF ₂) ₃ CF ₃	m.p. 162-164°C
1.2.6	H	Cl	Cl	Cl	CF ₂ CF ₃	m.p. 177-179°C
1.2.7	H	Cl	Cl	Cl	(CF ₂) ₂ CF ₃	m.p. 178-179°C
1.2.8	H	Cl	Cl	Cl	(CF ₂) ₃ CF ₃	m.p. 166-168°C
1.2.9	F	F	Cl	Cl	(CF ₂) ₄ CF ₃	
1.2.10	F	F	Cl	Cl	(CF ₂) ₆ CF ₃	
1.2.11	F	F	Cl	Cl	(CF ₂) ₇ CF ₃	
1.2.12	H	Cl	Cl	Cl	(CF ₂) ₄ CF ₃	
1.2.13	H	Cl	Cl	Cl	(CF ₂) ₆ CF ₃	
1.2.14	H	Cl	Cl	Cl	(CF ₂) ₇ CF ₃	

Example 2: Formulations for compounds of formula I according to Preparation Example 1.2.

(throughout percentages are by weight)

2.1 Emulsifiable concentrates

compound according to

Preparation Example 1.2.

10%

castor oil polyethylene glycol ether

(36 moles of ethylene oxide)

25%

butanol

15%

ethyl acetate

50%



Emulsions of any desired concentration can be produced from such concentrates by dilution with water.

2.2. <u>Solutions</u>	a)	b)
compound according to Preparation Example 1.2.	10 %	5 %
polyethylene glycol (mol. wt. 400)	70 %	-
N-methyl-2-pyrrolidone	20 %	20 %
epoxidised coconut oil	-	1 %
petroleum fraction (boiling range 160-190°C)	-	74 %

These solutions are suitable for application in the form of microdrops.

2.3. <u>Granulates</u>	a)	b)
compound according to Preparation Example 1.2.	5 %	10 %
kaolin	94 %	-
highly dispersed silicic acid	1 %	-
attapulgate	-	90 %

The active ingredient is dissolved in methylene chloride, the solution is sprayed onto the carrier and the solvent is subsequently evaporated off in vacuo.

2.4. <u>Extruder granulate</u>	
compound according to Preparation Example 1.2.	10 %
sodium lignosulfonate	2 %
carboxymethylcellulose	1 %
kaolin	87 %

The active ingredient is mixed and ground with the adjuvants, and the mixture is moistened with water. The mixture is extruded and then dried in a stream of air.

2.5. Coated granulate

compound according to

Preparation Example 1.2.	3 %
polyethylene glycol (mol. wt. 200)	3 %
kaolin	94 %

The finely ground active ingredient is uniformly applied, in a mixer, to the kaolin moistened with polyethylene glycol. Non-dusty coated granulates are obtained in this manner.

2.6. Dusts

compound according to

	a)	b)	c)	d)
Preparation Example 1.2.	2 %	5 %	5 %	8 %
highly dispersed silicic acid	1 %	5 %	-	-
talcum	97 %	-	95 %	-
kaolin	-	90 %	-	92 %

Ready-for-use dusts are obtained by intimately mixing the carriers with the active ingredient and optionally grinding the mixture in a suitable mill.

2.7. Wettable powders

compound according to

	a)	b)	c)
Preparation Example 1.2.	20 %	50 %	75 %
sodium lignosulfonate	5 %	5 %	-
sodium lauryl sulfate	3 %	-	5 %
sodium diisobutyl naphthalene-sulfonate	-	6 %	10 %
octylphenol polyethylene glycol ether (7-8 moles of ethylene oxide)	-	2 %	-
highly dispersed silicic acid	5 %	10 %	10 %
kaolin	67 %	27 %	-

The active ingredient is thoroughly mixed with the adjuvants and the mixture is ground in a suitable mill, affording wetttable powders which can be diluted with water to give suspensions of any desired concentration.

2.8. Suspension concentrate

compound according to

Preparation Example 1.2.	40 %
ethylene glycol	10 %
nonylphenolpolyethylene glycol ether (15 moles of ethylene oxide)	6 %
sodium lignosulfonate	10 %
carboxymethylcellulose	1 %
37 % aqueous formaldehyde solution	0.2 %
silicone oil in the form of a 75 % aqueous emulsion	0.8 %
water	32 %

The finely ground active ingredient is intimately mixed with the adjuvants, giving a suspension concentrate from which suspensions of any desired concentration can be obtained by dilution with water.

Example 3: Biological tests

3.1. Action against Musca domestica

A sugar cube is so moistened with a solution of the test compound that the concentration of active ingredient in the cube after drying is 500 ppm. The treated cube is placed on a dish together with a wet cotton wool swab and covered with a beaker. 10 adult one-week-old, OP-resistant flies are placed under the beaker and kept at 25°C and 50 % humidity. The insecticidal action is determined after 24 hours by evaluating the mortality rate.

Compounds according to Example 1.2. exhibit good activity in the above test.

3.2. Action against *Lucilia sericata*

1 ml of an aqueous formulation containing 0.5 % of test compound is added at 50°C to 9 ml of a culture medium. Then about 30 freshly hatched *Lucilia sericata* larvae are added to the culture medium, and the insecticidal action is determined after 48 and 96 hours by evaluating the mortality rate.

In this test, compounds according to Example 1.2. exhibit good activity against *Lucilia sericata*.

3.3. Action against *Aedes aegypti*

A concentration of 12.5 ppm is obtained by pipetting a specific amount of a 0.1 % solution of the test compound in acetone onto the surface of 150 ml of water in a container. After the acetone has evaporated, 30 to 40 two-day-old *Aedes* larvae are put into the container. Mortality counts are made after 2 and 7 days.

Compounds according to Example 1.2. exhibit good activity in this test.

3.4. Insecticidal stomach poison action

Cotton plants (about 20 cm high) are sprayed with an aqueous emulsion (obtained from a 10 % emulsifiable concentrate) that contains the test compound in a concentration of 100 ppm.

After the coating has dried, each of the cotton plants is populated with *Spodoptera littoralis* and *Heliothis virescens* larvae in the L₃ stage. The test is carried out at 24°C and 60 % relative humidity. The mortality and defects in the development and sloughing of the larvae are determined at 24-hour intervals.

Compounds according to Example 1.2. exhibit good activity in this test.

3.5. Action against Spodoptera littoralis and Heliothis virescens (larvae and eggs)

Three cotton plants about 15-20 cm high grown in pots are treated with a sprayable liquid formulation of the test compound. After the spray-coating has dried, the potted plants are placed in a sheet-metal container that has a capacity of about 20 litres and is covered with a glass plate. The humidity inside the covered container is so regulated that no condensation water is formed. No direct light is allowed to fall on the plants. The three plants are then infested with a total of:

- a) 50 larvae of Spodoptera littoralis or Heliothis virescens in the L₁ stage;
- b) 20 larvae of Spodoptera littoralis or Heliothis virescens in the L₃ stage;
- c) two egg deposits of Spodoptera littoralis or Heliothis virescens (for that purpose, in each case 2 leaves of a plant are enclosed in a plexi-glass cylinder closed at both ends with gauze); two egg deposits of Spodoptera or a portion of a cotton leaf on which eggs of Heliothis have been deposited are(is) added to the enclosed leaves.

After 4 and 5 days, an evaluation is made in comparison with untreated controls taking into account the following criteria:

- a) number of surviving larvae,
- b) inhibition of larval development and sloughing,
- c) feeding damage (skeletonising damage and pitting damage),
- d) hatching rate (number of larvae that have hatched from the eggs).

Compounds according to Example 1.2., in a concentration of 400 ppm, exhibit good overall activity in the above test.

3.6. Ovicidal action against Spodoptera littoralis

Eggs of *Spodoptera littoralis* deposited on filter paper are cut out of the paper and immersed in a 0.05 % by weight solution of the test compound in a mixture of acetone and water (1:1). The treated egg deposits are then removed from the mixture and stored at 28°C and 60 % relative humidity in plastic dishes.

After 5 days, the hatching rate, that is to say the number of larvae that have developed from the treated eggs, is determined.

Compounds according to Example 1.2. exhibit good activity in the above test.

3.7. Action against Laspeyresia pomonella (eggs)

Egg deposits of *Laspeyresia pomonella* not more than 24 hours old are immersed for 1 minute, on filter paper, in an aqueous acetic solution containing 400 ppm of the test compound. When the filter paper has dried it is placed, with the eggs, in a petri dish and left at a temperature of 28°C. After 6 days the percentage hatching rate from the treated eggs is evaluated.

Compounds according to Example 1.2. exhibit good activity in the above test.

3.8. Influence on the reproduction of Anthonomus grandis

Anthonomus grandis adults which are not more than 24 hours old after hatching are transferred in groups of 25 beetles to barred cages. The cages populated with the beetles are then immersed for 5 to 10 seconds in an acetic solution containing 0.1 % by weight of the test compound. When the beetles are dry again they are placed in covered dishes containing feed and are left for copulation and oviposition. Egg deposits are flushed out with running water twice to three times weekly, counted, disinfected by putting them for 2 to 3 hours in an aqueous disinfectant, and then placed in dishes containing a suitable larval diet. A count is made after 7 days to determine whether larvae have developed from the deposited eggs.

In order to determine the duration of the reproduction-influencing effect of the test compounds, the egg deposits of the beetles are monitored over a period of about four weeks. Evaluation is made by assessing the reduction in the number of deposited eggs and larvae hatched from them in comparison with untreated controls.

Compounds according to Example 1.2. exhibit a good reproduction-reducing activity in the above test.

3.9. Action against Anthonomus grandis (adults)

Two cotton plants in the 6-leaf stage, in pots, are each sprayed with wettable aqueous emulsion formulations containing 100 ppm of the test compound. After the spray-coating has dried (about 1.5 hours) each plant is populated with 10 adult beetles (*Anthonomus grandis*). Plastic cylinders, covered at the top with gauze, are then slipped over the treated plants populated with the test insects to prevent the beetles from migrating from the plants. The treated plants are kept at 25°C and about 60 % relative humidity. Evaluation is made after 2, 3, 4 and 5 days to determine the percentage mortality of the beetles (percentage in dorsal position) and the anti-feeding action as compared with untreated controls.

Compounds according to Example 1.2. exhibit good activity in this test.

3.10. Action against Epilachna varivestis

Phaseolus vulgaris plants (dwarf beans) about 15-20 cm in height are sprayed with aqueous emulsion formulations of the test compound in a concentration of 800 ppm. After the spray-coating has dried, each plant is populated with 5 larvae of *Epilachna varivestis* (Mexican bean beetle) in the L₄ stage. A plastic cylinder is slipped over the infested plants and covered with a copper gauze top. The test is carried out at 28°C and 60 % relative humidity.

The percentage mortality is determined after 2 and 3 days. Evaluation of any feeding damage (anti-feeding effect), and of defects in development and sloughing, is made by observing the test insects for a further 3 days.

Compounds according to Example 1.2. exhibit good activity in the above test.

3.11. Ovicidal action against *Heliothis virescens* and *Spodoptera littoralis*

Corresponding amounts of a wettable powder formulation containing 25 % by weight of the test compound are mixed with sufficient water to produce an aqueous emulsion with an active ingredient concentration of 400 ppm.

One-day-old egg deposits of *Heliothis* on cellophane and of *Spodoptera* on paper are immersed in these emulsions for 3 minutes and then collected by suction on round filters. The treated deposits are placed in petri dishes and kept in the dark at 28°C and 60 % relative humidity. The hatching rate, i.e. the number of larvae which have developed from the treated eggs, in comparison with untreated controls, is determined after 5 to 8 days.

In the above test, compounds according to Example 1.2. exhibit an 80 to 100 % ovicidal action (mortality) against *Heliothis virescens* and *Spodoptera littoralis*.

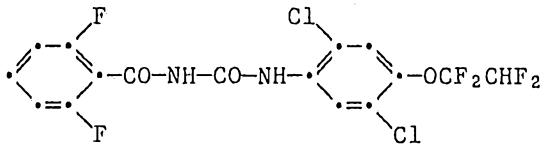
3.12. Stomach-poison action against *Heliothis virescens* larvae (L₁)

Potted soybean plants in the 4- to 5-leaf stage are sprayed with an aqueous emulsion (obtained from a 10 % emulsifiable concentrate) containing the test compound in a concentration of 0.8 ppm.

After the spray-coating has dried, each soybean plant is populated with 20 *Heliothis virescens* larvae in the L₁ stage. The test is carried out at 26°C and about 55 % relative humidity. An assessment is made 6 days after populating the plants, the mortality of the larvae being determined as a percentage.

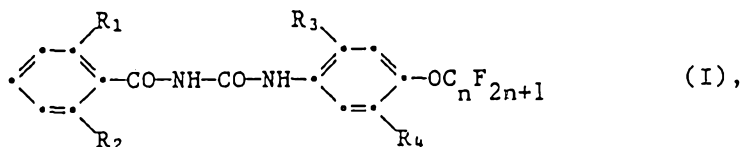
Compounds		Percentage mortality at 0.8 ppm
1.	Comp. No. 1.2.1.	70
2.	Comp. No. 1.2.2.	85
3.	Comp. No. 1.2.3.	100
4.	Comp. Example 1B US 4,518,804*	25

*



The claims defining the invention are as follows:

1. Compounds of formula I

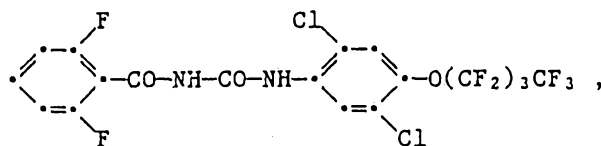
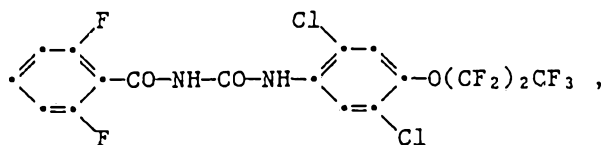
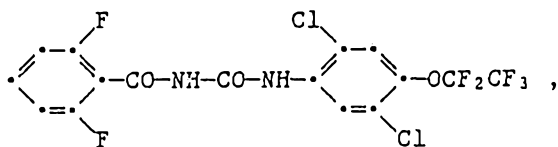


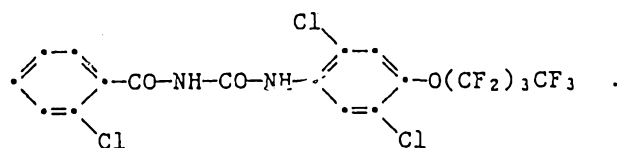
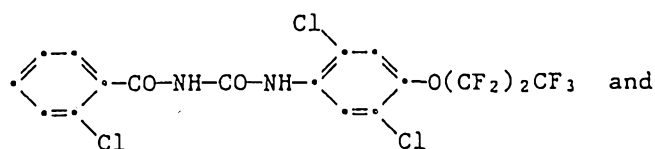
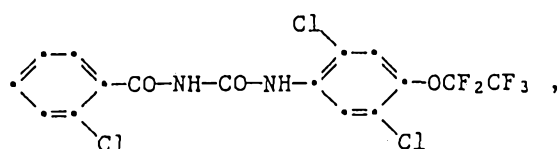
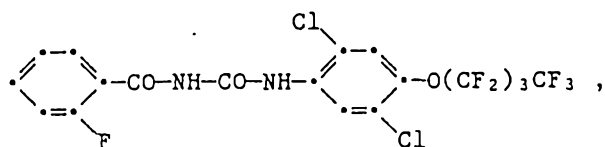
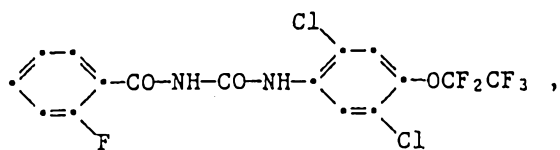
in which R₁ is hydrogen, fluorine, chlorine or bromine; R₂ is fluorine or chlorine; each of R₃ and R₄ is chlorine; and n is 2, 3, 4, 5, 6, 7 or 8.

2. Compounds of formula I according to claim 1, in which R₁ is hydrogen, fluorine or chlorine; R₂ is fluorine or chlorine; R₃ and R₄ are chlorine; and n is 2, 3, 4, 5, 6 or 7.

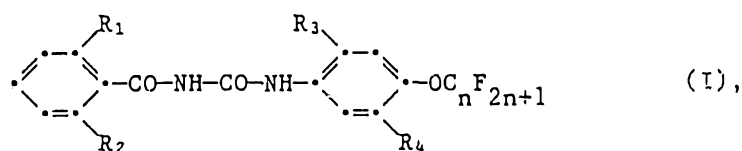
3. Compounds of formula I according to claim 2, in which R₁ is hydrogen or fluorine; R₂ is fluorine or chlorine; each of R₃ and R₄ is chlorine; and n is 2, 3 or 4.

4. The compounds according to claim 3 of the formulae



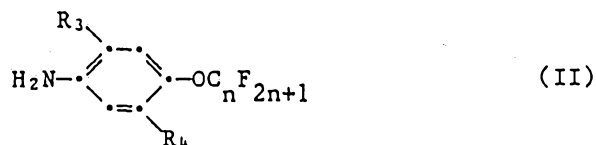


5. A process for the preparation of a compound of formula I

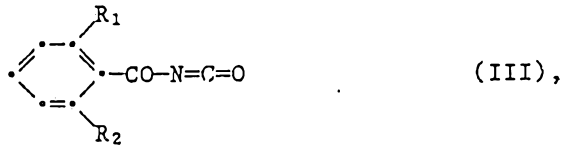


in which R_1 is hydrogen, fluorine, chlorine or bromine; R_2 is fluorine or chlorine; each of R_3 and R_4 is chlorine; and n is 2, 3, 4, 5, 6, 7 or 8, which comprises

a) reacting an aniline of formula II

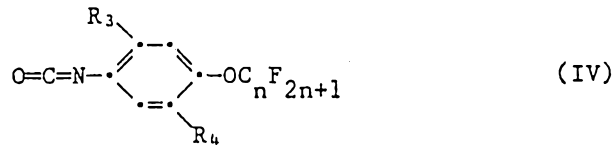


with a benzoyl isocyanate of formula III

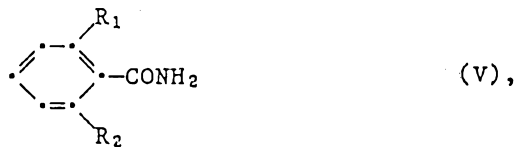


or

b) reacting an isocyanate of formula IV

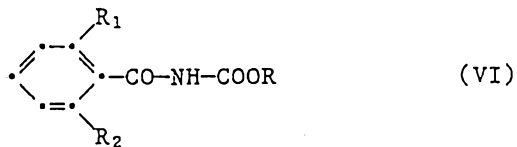


with a benzamide of formula V



or

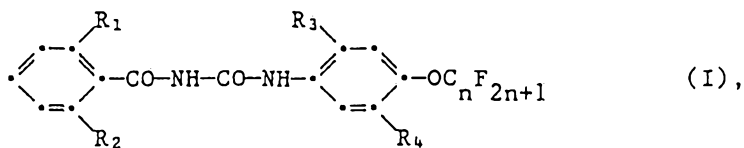
c) reacting an aniline of formula II with a urethane of formula VI



the symbols R_1 , R_2 , R_3 , R_4 and n in formulae II to VI having the meanings indicated and R being a C_1 - C_8 alkyl radical that is unsubstituted or is halogenated.

6. A pesticidal composition containing as active component at least one compound of formula I



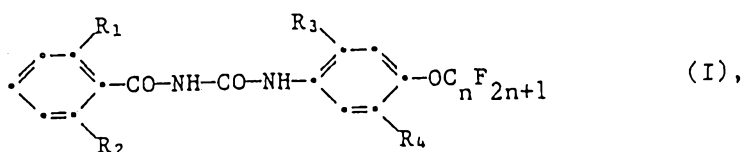


in which R_1 is hydrogen, fluorine, chlorine or bromine; R_2 is fluorine or chlorine; each of R_3 and R_4 is chlorine; and n is 2, 3, 4, 5, 6, 7 or 8, together with suitable carriers and/or adjuvants.

7. A pesticidal composition according to claim 6, containing as active component at least one compound of formula I in which R_1 is hydrogen, fluorine or chlorine; R_2 is fluorine or chlorine; R_3 is chlorine; R_4 is chlorine; and n is 2, 3, 4, 5, 6 or 7.

8. A pesticidal composition according to claim 7, containing as active component at least one compound of formula I in which R_1 is hydrogen or fluorine; R_2 is fluorine or chlorine; each of R_3 and R_4 is chlorine; and n is 2, 3 or 4.

9. The use of a compound of formula I

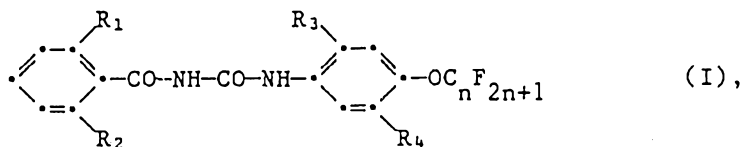


in which R_1 is hydrogen, fluorine, chlorine or bromine; R_2 is fluorine or chlorine; each of R_3 and R_4 is chlorine; and n is 2, 3, 4, 5, 6, 7 or 8, for controlling pests in and on animals and plants.

10. The use according to claim 9 of a compound of formula I for controlling insects and arachnids.

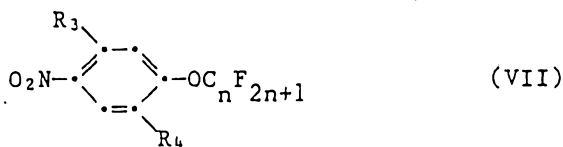
11. The use according to claim 10 of a compound of formula I for controlling larval stages of plant-destructive insects.

12. A method of controlling pests on animals and plants, which comprises bringing the pests, in their various stages of development, into contact with a compound of formula I



in which R_1 is hydrogen, fluorine, chlorine or bromine; R_2 is fluorine or chlorine; each of R_3 and R_4 is chlorine; and n is 2, 3, 4, 5, 6, 7 or 8.

13. Compounds of formula VII

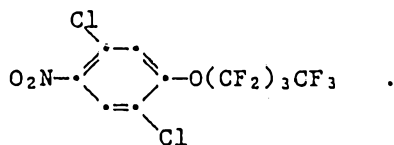
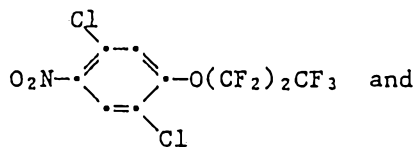
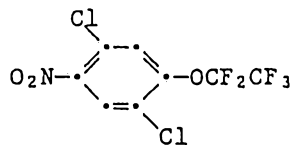


in which each of R_3 and R_4 is chlorine, and n is 2, 3, 4, 5, 6, 7 or 8

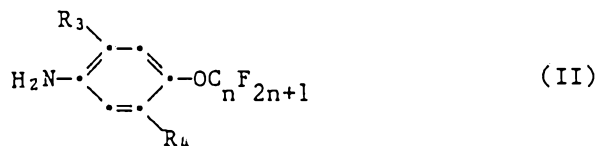
^{when used}
~~for the exclusive use~~ in the preparation of compounds of formula I according to claim 1.

14. Compounds of formula VII according to claim 13, in which each of R_3 and R_4 is chlorine and n is 2, 3 or 4.

15. The compounds according to claim 14 of formulae



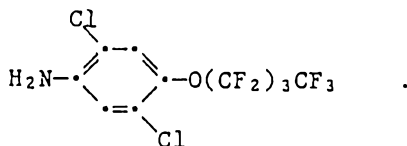
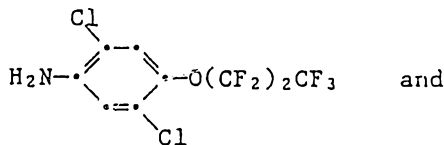
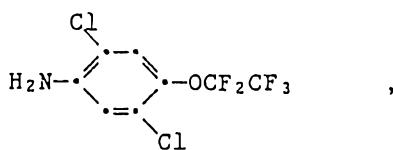
16. Compounds of formula II



in which each of R_3 and R_4 is chlorine, and n is 2, 3, 4, 5, 6, 7 or 8
~~for the exclusive use~~ when used in the preparation of compounds of formula I according to claim 1.

17. Compounds of formula II according to claim 16, in which each of R_3 and R_4 is chlorine, and n is 2, 3 or 4.

18. The compounds according to claim 17 of formulae



19. Substituted N-benzoyl-N'-2,5-dihalo-4-perfluoroalkoxyphenylureas, substantially as hereinbefore described with reference to Examples 1.2.1 to 1.2.14.

20. A process for the preparation of a substituted N-benzoyl-N'-2,5-dihalo-4-perfluoroalkoxyphenylureas, substantially as hereinbefore described with reference to Example 1.2.1.

21. A pesticidal composition, substantially as hereinbefore described with reference to any one of Examples 2.1 to 2.8.

22. A method of controlling pests on animals and plants, which comprises bringing the pests in their various stages of development into contact with a compound according to claim 19 or a composition according to claim 21.



23. Substituted N-benzoyl-N'-2,5-dihalo-4-perfluoroalkoxyphenylureas
whenever produced by the process of claim 5 or claim 20.

DATED this NINETEENTH day of OCTOBER 1990
Ciba-Geigy AG

Patent Attorneys for the Applicant
SPRUSON & FERGUSON



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