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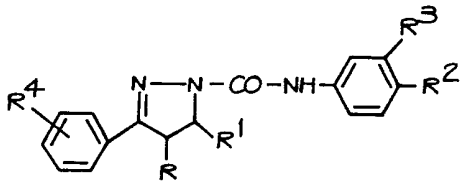
(54) NOVEL PHENYLCARBAMOYL-2-PYRAZOLINES AND THEIR USE AS INSECTICIDES

(71) We, BAYER AKTIENGESELLSCHAFT, a body corporate, organised under the laws of Germany, of Leverkusen, Federal Republic of 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 substituted phenylcarbamoyl-2-pyrazolines, to a process for their preparation and their use as arthropodicides, especially insecticides.

It is already known that chlorophenylcarbamoyl-2-pyrazolines, for example 1-(4-chlorophenylcarbamoyl)-3-(4-chlorophenyl)-5-methyl- or 1-(4-chlorophenylcarbamoyl)-3,5-bis-(4-chlorophenyl)pyrazoline, are distinguished by an insecticidal activity (see German Offenlegungsschriften (German Published Specifications) 2,304,584 and 2,529,689).

The present invention now provides, as new compounds, the substituted phenylcarbamoyl-2-pyrazolines of the general formula



(I)

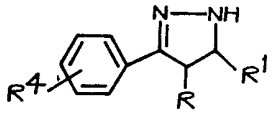
in which

R represents hydrogen or alkyl,
R^1 represents hydrogen or halogenophenyl,
R^2 represents hydrogen, halogenoalkoxy or halogenoalkylthio,
R^3 represents hydrogen, halogen, halogenoalkoxy or halogenoalkylthio and
R^4 represents halogen,

with the proviso that one of the radicals R^2 and R^3 must represent halogenoalkoxy or halogenoalkylthio.

Preferably, R represents hydrogen or straight-chain or branched alkyl with 1 to 3 carbon atoms (especially methyl), R^1 represents hydrogen or phenyl which carries one or more substituents selected independently from chlorine and bromine atoms, R^2 represents hydrogen or halogenoalkoxy or halogenoalkylthio with 1 to 3 carbon atoms (especially monofluoro-, difluoro-, trifluoro-, monochlorodifluoro-, dichloromonofluoro- and monochloromonofluoro-methoxy or methylthio, or 1,1,2,2-tetrafluoroethoxy or -ethylthio), R^3 represents hydrogen, chlorine, bromine or halogenoalkoxy or halogenoalkylthio with 1 to 3 carbon atoms and R^4 represents chlorine or bromine.

The invention also provides a process for the preparation of a substituted phenylcarbamoyl-2-pyrazoline of the formula (I) in which a 2-pyrazoline of the general formula

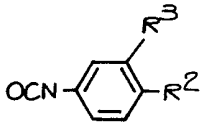


(II),

in which

R, R^1 and R^4 have the above-mentioned meanings,

is reacted with a phenyl isocyanate of the general formula



(III),

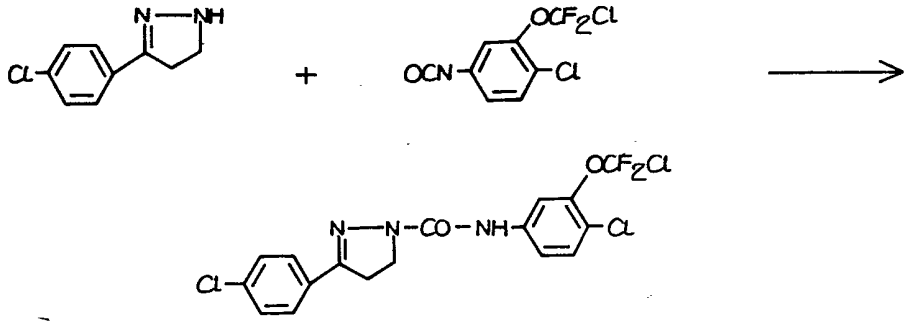
in which

R^2 and R^3 have the above-mentioned meanings,

if appropriate in the presence of a diluent or solvent.

Surprisingly, the substituted phenylcarbamoyl-2-pyrazolines according to the invention exhibit a better insecticidal action than the known chlorophenylcarbamoyl-2-pyrazolines of analogous structure and of the same type of action. The products according to the present invention thus represent a genuine enrichment of the art.

If, for example, 3-(4-chlorophenyl)-2-pyrazoline and 3-monochlorodifluoromethoxy-4-chlorophenyl isocyanate are used as starting materials, the course of the reaction can be represented by the following equation:



The 2-pyrazolines of the formula (II) to be used as starting materials are in some cases known; they can all be prepared in accordance with processes known from the literature (see, for example, German Offenlegungsschriften (German Published Specifications) 2,304,584 and 2,529,689).

The following may be mentioned as individual examples of suitable 2-pyrolazines of the formula (II): 3 - (4 - chlorophenyl) - 2 - pyrazoline, 3 - (4-bromophenyl) - 2 - pyrazoline, 3 - (3 - chlorophenyl) - 2 - pyrazoline, 3 - (3 - bromophenyl) - 2 - pyrazoline, 3 - (4 - chlorophenyl) - 4 - methyl - 2 - pyrazoline, 3 - (4-bromophenyl) - 4 - methyl - 2 - pyrazoline, 3 - (3 - chlorophenyl) - 4 - methyl - 2-pyrazoline, 3 - (3 - bromophenyl) - 4 - methyl - 2 - pyrazoline, 3,5 - bis - (4-chlorophenyl) - 2 - pyrazoline, 3,5 - bis - (4 - bromophenyl) - 2 - pyrazoline, 3,5-bis - (3 - chlorophenyl) - 2 - pyrazoline and 3,5 - bis - (3 - bromophenyl) - 2-pyrazoline.

The phenyl isocyanates of the formula (III) to be used as starting compounds are known or can be prepared in accordance with processes known from the literature, for example from the corresponding anilines, by means of phosgene (see Belgian Patent Specification 746,566).

The following may be mentioned as individual examples of suitable phenyl isocyanates of the formula (III): 3 - monofluoromethoxy - phenyl isocyanate, 3 - difluoromethoxy - phenyl isocyanate, 3 - trifluoromethoxy - phenyl isocyanate, 3 - monochloromonofluoromethoxy - phenyl isocyanate, 3 - dichloromonofluoromethoxy - phenyl isocyanate, 3 - monochlorodifluoromethoxy-phenyl isocyanate, 3 - (1,1,2,2 - tetrafluoroethoxy) - phenyl isocyanate, 3 - monofluoromethylthio - phenyl isocyanate, 3 - difluoromethylthio - phenyl isocyanate, 3 - trifluoromethylthiophenyl isocyanate, 3 - monochloromonofluoromethyl-

thio - phenyl isocyanate, 3 - dichloromonofluoromethylthio - phenyl isocyanate, 3 - monochlorodifluoromethylthio - phenyl isocyanate, 3 - (1,1,2,2 - tetrafluoroethylthio) - phenyl isocyanate, 4 - monofluoromethoxy - phenyl isocyanate, 4 - difluoromethoxy - phenyl isocyanate, 4 - trifluoromethoxy - phenyl isocyanate, 4-monochloromonofluoromethoxy - phenyl isocyanate, 4 - dichloromonofluoromethoxy - phenyl isocyanate, 4 - monochlorodifluoromethoxy - phenyl isocyanate, 4 - (1,1,2,2 - tetrafluoroethoxy) - phenyl isocyanate, 4 - monofluoromethylthio - phenyl isocyanate, 4 - difluoromethylthio - phenyl isocyanate, 4 - trifluoromethylthio - phenyl isocyanate, 4 - monochlorofluoromethylthio - phenyl isocyanate, 4 - dichloromonofluoromethylthio - phenyl isocyanate, 4 - monochlorodifluoromethylthio - phenyl isocyanate, 4 - (1,1,2,2 - tetrafluoroethylthio)-phenyl isocyanate, 3 - chloro - 4 - monofluoromethoxy - phenyl isocyanate, 3-chloro - 4 - difluoromethoxy - phenyl isocyanate, 3 - chloro - 4 - trifluoromethoxy-phenyl isocyanate, 3 - chloro - 4 - monochloromonofluoromethoxy - phenyl isocyanate, 3 - chloro - 4 - dichloromonofluoromethoxy - phenyl isocyanate, 3-chloro - 4 - monochlorodifluoromethoxy - phenyl isocyanate, 3 - chloro - 4-(1,1,2,2 - tetrafluoroethoxy) - phenyl isocyanate, 3 - bromo - 4 - monofluoromethoxy - phenyl isocyanate, 3 - bromo - 4 - difluoromethoxy - phenyl isocyanate, 3 - bromo - 4 - trifluoromethoxy - phenyl isocyanate, 3 - bromo - 4 - monochloromonofluoromethoxy - phenyl isocyanate, 3 - bromo - 4 - monochlorodifluoromethoxy - phenyl isocyanate, 3 - bromo - 4 - (1,1,2,2 - tetrafluoroethoxy)-phenyl isocyanate, 3 - chloro - 4 - monofluoromethylthio - phenyl isocyanate, 3-chloro - 4 - difluoromethylthiophenyl isocyanate, 3 - chloro - 4 - trifluoromethylthio - phenyl isocyanate, 3 - chloro - 4 - monochloromonofluoromethylthiophenyl isocyanate, 3 - chloro - 4 - dichloromonofluoromethylthio - phenyl isocyanate, 3 - chloro - 4 - monochlorodifluoromethylthio - phenyl isocyanate, 3-chloro - 4 - (1,1,2,2 - tetrafluoroethylthio) - phenyl isocyanate, 3 - bromo - 4-monofluoromethylthio - phenyl isocyanate, 3 - bromo - 4 - difluoromethylthiophenyl isocyanate, 3 - bromo - 4 - trifluoromethylthiophenyl isocyanate, 3 - bromo-4 - monochloromonofluoromethylthio - phenyl isocyanate, 3 - bromo - 4 - dichloromonofluoromethylthio - phenyl isocyanate, 3 - bromo - 4 - monochlorodifluoromethylthio - phenyl isocyanate and 3 - bromo - 4 - (1,1,2,2 - tetrafluoroethylthio) - phenyl isocyanate.

The process for the preparation of the compounds according to the invention is preferably carried out in the presence of a suitable solvent or diluent. Virtually all inert organic solvents can be used for this purpose, especially 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; ketones, for example acetone, methyl ethyl ketone, methyl isopropyl ketone and methyl isobutyl ketone; and nitriles, such as acetonitrile and propionitrile.

The reaction temperature can be varied within a substantial range. In general, the reaction is carried out at from 20° to 120°C, preferably at from 50° to 90°C.

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

To carry out the process, the starting components are in most cases employed in stoichiometric amounts. An excess of one or other reactant produces no significant advantages. In most cases, the reactants are brought together in one of the above-mentioned solvents and are stirred at an elevated temperature for one or more hours to complete the reaction, the reaction solution is cooled and the compound which precipitates is filtered off. The compounds are obtained in a crystalline form and are characterised by their melting point.

As already mentioned, the substituted phenylcarbamoyl-2-pyrazolines according to the invention are distinguished by an excellent insecticidal action. They are active against plant pests and, in the veterinary medicine field, against ectoparasites, such as parasitic fly larvae. Some of the compounds also exhibit fungicidal and bactericidal actions.

The active compounds are well tolerated by plants, have a favourable level of toxicity to warm-blooded animals, and can be used for combating arthropod pests, especially insects, which are encountered in agriculture, in forestry, in the protection of stored products and of materials, and in the hygiene field. They are active against normally sensitive and resistant species and against all or some stages of development. The abovementioned pests include:

from the class of the *Isopoda*, for example *Oniscus asellus, Armadillidium vulgare* and *Porcellio scaber*;

from the class of the *Diplopoda*, for example *Blaniulus guttulatus*;

from the class of the *Chilopoda*, for example *Geophilus carpophagus* and *Scutigera* spec.;

from the class of the *Symphyla*, for example *Scutigerella immaculata*;

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, Achete domesticus, Gryllotalpa* spp., *Locusta migrazoria migratorioides, Melanoplus differentialis* and *Schistocerca gregaria*;

from the order of the *Dermaptera*, for example *Forficula auricularia*;

from the order of the *Isoptera*, for example *Reticulitermes* spp.;

from the order of the *Anoplura*, for example *Phylloxera vastatrix, Pemphigus* spp., *Pediculus humanus corporis, Haematopinus* spp. and *Linognathus* spp.;

from the order of the *Mallophaga*, for example *Trichodectes* spp. and *Damalinea* spp.;

from the order of the *Thysanoptera*, for example *Hercinothrips femoralis* and *Thrips tabaci*;

from the order of the *Heteroptera*, for example *Eurygaster* spp., *Dysdercus intermedius, Piesma quadrata, Cimex lectularius, Rhodnius prolixus* and *Triatoma* spp.;

from the order of the *Homoptera*, for example *Aleurodes brassicae, Bemisia tabaci, Trialeurodes vaporariorum, Aphis gossypii, Brevicoryne brassicae, Cryptomyzus ribis, Doralis fabae, Doralis pomi, Eriosoma lanigerum, Hyalopterus arundinis, Macrosiphum avenae, Myzus* spp., *Phorodon humuli, Rhopalosiphum padi, Empoasca* spp., *Euscelis bilobatus, Nephotettix cincticeps, Lecanium corni, Saissetia oleae, Laodelphax striatellus, Nilaparvata lugens, Aonidiella aurantii, Aspidiotus hederae, Pseudococcus* spp. and *Psylla* spp.;

from the order of the *Lepidoptera, for example Pectinophora gossypiella, Bupalus piniarius, Cheimatobia brumata, Lithocolletis blancardella, Hyponomeuta padella, Plutella maculipennis, Malacosoma neustria, Euproctis chrysorrhoea, Lymantria* spp., *Buccalatrix thurberiella, Phyllocnistis citrella, Agrotis* spp., *Euxoa* spp., *Feltia* spp., *Earias insulana, Heliothis* spp., *Laphygma exigua, Mamestra brassicae, Panolis flammea, Prodenia litura, Spodoptera* spp., *Trichoplusia ni, Carpocapsa pomonella, Pieris* spp., *Chilo* spp., *Pyrausta nubilalis, Ephestia kuehniella, Galleria mellonella, Cacoecia podana, Capua reticulana, Choristoneura fumiferana, Clysia ambiguella, Homona magnanima* and *Tortrix viridana*;

from the order of the *Coleoptera*, for example *Anobium punctatum, Rhizopertha dominica, Bruchidius obtectus, Acanthoscelides obtectus, Hylotruptes bajulus, Agelastica alni, Leptinotarsa decemlineata, Phaedon cochleariae, Diabrotica* spp., *Psylliodes chrysocephala, Epilachna varivestis, Atomaria* spp., *Oryzaephilus surinamensis, Anthonomus* spp., *Sitophilus* spp., *Otiorrhynchus sulcatus, Cosmopolites sordidus, Ceuthorrhynchus assimilis, Hypera postica, Dermestes* spp., *Trogoderma* spp., *Anthrenus* spp., *Attagenus* spp., *Lyctus* spp., *Meligethes aeneus, Ptinus* spp., *Niptus hololeucus, Gibbium psylloides, Tribolium* spp., *Tenebrio molitor, Agriotes* spp., *Conoderus* spp., *Melolontha melolontha, Amphimallon solstitialis* and *Costelytra zealandica*;

from the order of the *Hymenoptera*, for example *Diprion* spp., *Hoplocampa* spp., *Lasius* spp., *Monomorium pharaonis* and *Vespa* spp.;

from the order of the *Diptera*, for example *Aedes* spp., *Anopheles* spp., *Culex* spp., *Drosophila melanogaster, Musca* spp., *Fannia* spp., *Calliphora erythrocephala, Lucilia* spp., *Chrysomyia* spp., *Cuterebra* spp., *Gastrophilus* spp., *Hyppobosca* spp., *Stomoxys* spp., *Oestrus* spp., *Hypoderma* spp., *Tabanus* spp., *Tannia* spp., *Bibio hortulanus, Oscinella frit, Phorbia* spp., *Pegomyia hyoscyami, Ceratitis capitata, Dacus oleae* and *Tipula paludosa*;

from the order of the *Siphonaptera*, for example *Xenopsylla cheopis* and *Ceratophyllus* spp;

from the class of the *Arachnida*, for example *Scorpio maurus* and *Latrodectus mactans*;

from the order of the *Acarina*, for example *Acarus siro, Argas* spp., *Ornithodoros* spp., *Dermanyssus gallinae, Eriophyes ribis, Phyllocoptruta oleivora, Boophilus* spp., *Rhipicephalus* spp., *Amblyomma* spp., *Hyalomma* spp., *Ixodes* spp., *Psoroptes* spp., *Chorioptes* spp., *Sarcoptes* spp., *Tarsonemus* spp., *Bryobia praetiosa, Panonychus* spp. and *Tetranychus* spp.

The plant-parasitic nematodes include *Pratylenchus* spp., *Radopholus similis, Ditylenchus dipsaci, Tylenchulus semipenetrans, Heterodera* spp., *Meloidogyne* spp.,

Aphelenchoides spp., *Longidorus* spp., *Xiphinema* spp., and *Trichodorus* spp.

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 may be produced in known manner, for example by mixing the active compounds with extenders, that is to say, liquid or solid or liquefied gaseous diluents or carriers, optionally with the use of surface-active agents, that is to say, emulsifying agents and/or dispersing agents and/or foaming 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, especially solvents, there are suitable in the main, aromatic hydrocarbons, such as xylene, toluene, benzene or alkylnaphthalenes, chlorinated aromatic or chlorinated 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 dimethylformamide and dimethylsulphoxide, as well as water.

By liquefied gaseous diluents or carriers are meant liquids which would be gaseous at normal temperature and under normal pressure, for example aerosol propellants, such as dichlorodifluoromethane or trichlorofluoromethane.

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

Preferred examples of emulsifying and foam-forming agents include nonionic 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 hydrolysis products; and preferred examples of dispersing agents include lignin sulphite waste liquors and methylcellulose.

Adhesives such as carboxymethylcellulose and natural and synthetic polymers in the form of powders, granules or latices, such as gum arabic, polyvinyl alcohol and polyvinyl acetate, can be used in the formulations.

It is possible to use colorants such as inorganic pigments, for example iron oxide, titanium oxide and Prussian Blue, and organic dyestuffs, such as alizarin dyestuffs, azo dyestufs or metal phthalocyanine dyestuffs, and trace nutrients, such as salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc.

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 by weight.

The active compounds according to the invention may be used in the form of their formulations of the types that are commercially available or in the use forms prepared from these formulations.

The active compound content of the use forms prepared from the formulations of the types that are commercially available can vary within wide ranges. The active compound concentration of the use forms can be from 0.0000001 to 100% by weight of active compound, preferably from 0.01 to 10% by weight.

The compounds may be employed in a customary manner appropriate for the particular use forms.

In the veterinary field, the active compounds according to the invention may be used in a known manner, such as orally in the form of, for example, tablets, capsules, drenches and granules; dermally by means of, for example, dipping, spraying, pouring-on, spotting-on and powdering; and parenterally, for example by means of injections.

The present invention also provides an arthropodicidal 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 arthropods,

especially insects, which comprises applying to the arthropods, or to a habitat thereof, a compound of the present invention alone or in the form of a composition containing as active ingredient a compound of the present invention in admixture with a diluent or carrier.

The present invention also provides a method of freeing or protecting domesticated animals from ectoparasitical insects which comprises applying to said animals a compound according to the present invention, in admixture with a diluent or carrier.

The present invention further provides crops protected from damage by arthropods 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.

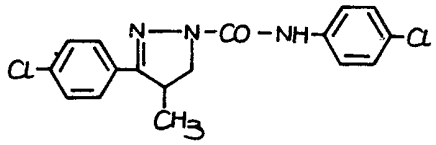
The present invention further provides domesticated animals whenever freed or protected from ectoparasitical insects by the application to said animals of a compound according to the present invention, in admixture with a diluent or carrier.

The insecticidal activity of the compounds of this invention is illustrated by the following biotest Examples.

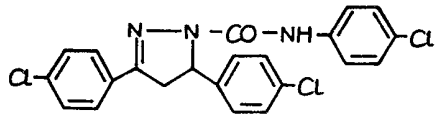
In these Examples, the compounds according to the present invention are each identified by the number (given in brackets) of the corresponding preparative Example, which will be found later in this specification.

The known comparison compounds are identified as follows:

(A) =



(B) =



Example A.
Phaedon larvae test

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

To produce a suitable preparation of active compound, 1 part by weight of 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 dripping wet and were then infested with mustard beetle larvae (*Phaedon cochleariae*).

After the specified periods of time, the degree of destruction was determined in %: 100% meant that all of the beetle larvae had been killed whereas 0% meant 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:

TABLE A

(Insects which damage plants)

Phaedon larvae test

Active compounds	Active compound concentration in %	Degree of destruction in % after 4 days
(A)	0.01	100
	0.001	0
(B)	0.01	100
	0.001	0
(13)	0.01	100
	0.001	100
(17)	0.01	100
	0.001	100
(11)	0.01	100
	0.001	100
(2)	0.01	100
	0.001	95

Example B.
Laphygma 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 and the stated amount of emulsifier and the concentrate was diluted with water to the desired concentration.

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*).

After the specified periods of time, the destruction in % was determined. 100% meant that all of the caterpillars had been killed whereas 0% indicated that none of the caterpillars 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:

TABLE B

(Insects which damage plants)

Laphygma test

Active compounds	Active compound concentration in %	Degree of destruction in % after 4 days
(B)	0.1	100
	0.01	80
	0.001	0
(20)	0.1	100
	0.01	100
	0.001	100
(22)	0.1	100
	0.01	100
	0.001	70
(24)	0.1	100
	0.01	100
	0.001	100
(21)	0.1	100
	0.01	100
	0.001	100
(29)	0.1	100
	0.01	100
	0.001	80
(25)	0.1	100
	0.01	100
	0.001	100

Example C.
Test with parasitic fly larvae

Emulsifier: 80 parts by weight of castor oil polyglycol ether

To produce a suitable preparation of active compound, 20 parts by weight of the active compound were mixed with the stated amount of the emulsifier and the mixture thus obtained was diluted with water to the desired concentration.

About 20 fly larvae (*Lucilia cuprina,* resistant) were introduced into a test tube which contained about 3 ml of a 20% strength suspension of egg-yolk-powder in water, and which was fitted with cottonwool plugs of appropriate size. 0.5 ml of the active compound preparation was placed on this egg-yolk-powder suspension. After 24 hours, the degree of destruction in % was determined. 100% meant that all of the larvae had been killed and 0% that none of the larvae had been killed.

The active compounds, active compound concentrations and results can be seen from the table which follows:

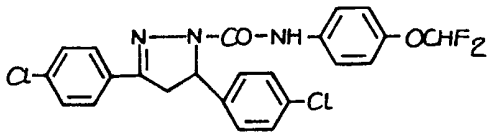
TABLE C

Test with parasitic fly larvae

Active compound	Active compound concentration in ppm	Destructive action in %
(13)	1,000	100
	300	100
	100	100
(16)	1,000	100
	300	100
	100	100
(25)	1,000	100
	100	100
(20)	1,000	100
	300	100
	100	100

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

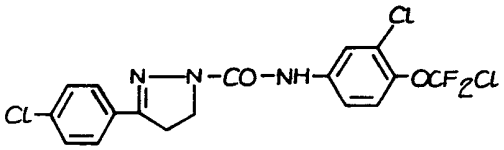
Example 1.



(1)

5.55 g (0.03 mol) of 4-difluoromethoxy-phenyl isocyanate in 20 ml of toluene were added, at 50°C, to a solution of 8.74 g (0.03 mol) of 3-(4-chlorophenyl)-5-(4-chlorophenyl)-2-pyrazoline in 100 ml of toluene and the batch was stirred for 2 hours at 80°C. After it had cooled, the product which had precipitated was isolated by filtration. 5 g (35% of theory) of 1-(4-difluoromethoxyphenylcarbamoyl)-3-(4-chlorophenyl)-5-(4-chlorophenyl)-2-pyrazoline of melting point 174°C were obtained.

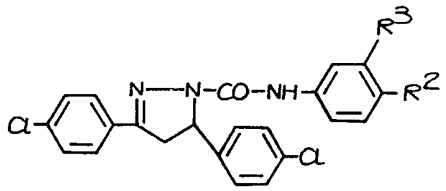
Example 2.



(2)

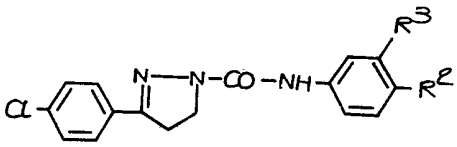
12.7 g (0.05 mol) of 3-chloro-4-monochlorodifluoromethoxy-phenyl isocyanate in 20 ml of toluene were added, at 60°C, to a solution of 9 g (0.05 mol) of 3-(4-chlorophenyl)-2-pyrazoline in 60 ml of toluene. The batch was stirred for 2 hours at 80°C. On cooling to room temperature, the product precipitated and was filtered off. 8.5 g (39% of theory) of 1-[3-chloro-4-monochlorodifluoromethoxy-phenyl)-carbamoyl]-3-(4-chlorophenyl)-2-pyrazoline with a melting point of 161°C were obtained.

The following compounds were synthesised analogously to Example 1 or 2. The yields were not optimised:



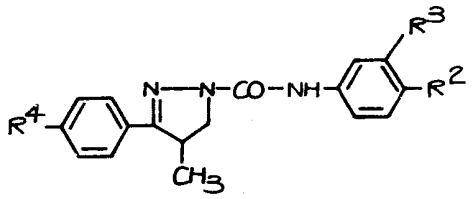
(Ia)

Example No.	R^2	R^3	Melting point °C
3	OCF_2Cl	Cl	161
4	SCF_2Cl	Cl	165
5	OCF_3	Cl	173
6	H	SCF_3	173
7	H	OCF_3	177
8	SCF_3	H	160
9	SCF_3	Cl	193
10	OCF_3	H	180



(Ib)

Example No.	R^2	R^3	Melting point °C
11	$OCHF_2$	H	150.5
12	SCF_2Cl	Cl	180
13	OCF_3	H	127
14	H	OCF_3	128
15	H	SCF_3	155
16	SCF_3	H	155
17	OCF_3	Cl	176
18	SCF_3	Cl	178
19	$OCHF_2$	Cl	174
20	OCF_2–CHF_2	H	134

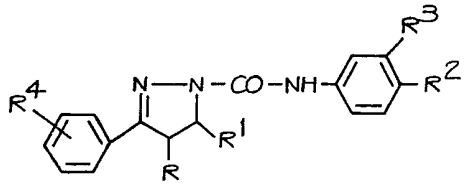


(Ic)

Example No.	R^2	R^3	R^4	Melting point °C
21	OCF_2Cl	Cl	Cl	127
22	$OCHF_2$	H	Cl	130–131
23	SCF_2Cl	Cl	Cl	158
24	$OCHF_2$	H	Br	137–138
25	OCF_3	H	Br	159
26	H	SCF_3	Br	140–141
27	SCF_2Cl	Cl	Br	173.5
28	OCF_2–CF_2H	H	Br	187.5
29	SCF_3	Cl	Br	151.5
30	$OCHF_2$	Cl	Br	150

WHAT WE CLAIM IS:—

1. Phenylcarbamoyl-2-pyrazolines of the general formula



(I)

in which

R represents hydrogen or alkyl,

R^1 represents hydrogen or halogenophenyl,

R^2 represents hydrogen, halogenoalkoxy or halogenoalkylthio,

R^3 represents hydrogen, halogen, halogenoalkoxy or halogenoalkylthio and

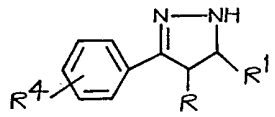
R^4 represents halogen,

with the proviso that one of the radicals R^2 and R^3 must represent halogenoalkoxy or halogenoalkylthio.

2. Compounds according to claim 1, in which R represents hydrogen or straight-chain or branched alkyl with 1 to 3 carbon atoms, R^1 represents hydrogen or phenyl which carries one or more substituents selected independently from chlorine and bromine atoms, R^2 represents hydrogen or halogenoalkoxy or halogenoalkylthio with 1 to 3 carbon atoms, R^3 represents hydrogen, chlorine, bromine or halogenoalkoxy or halogenoalkylthio with 1 to 3 carbon atoms and R^4 represents chlorine or bromine.

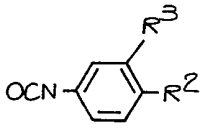
3. The compound according to claim 1 that is disclosed in any one of Examples 1 to 30.

4. A process for the preparation of a phenylcarbamoyl-2-pyrazoline according to claim 1, in which a 2-pyrazoline of the general formula



(II)

in which
R, R^1 and R^4 have the meanings stated in claim 1,
is reacted with a phenyl isocyanate of the general formula



(III)

in which
R^2 and R^3 have the meanings stated in claim 1,
if appropriate in the presence of a diluent or solvent.

5. A process according to claim 4, in which the reaction is effected in an inert organic solvent.

6. A process according to claim 4 or 5, in which the reaction is effected at from 20° to 120°C.

7. A process according to claim 6, in which the reaction is effected at from 50° to 90°C.

8. A process according to any of claims 4 to 7, in which the reactants (II) and (III) are employed in stoichiometric amounts.

9. A process according to any of claims 4 to 8, in which the reactants (II) and (III) are each one of those hereinbefore specifically mentioned.

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

11. Compounds according to claim 1 whenever prepared by a process according to any of claims 4 to 10.

12. An arthropodicidal composition containing as active ingredient a compound according to any of claims 1 to 3 and 11 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.

13. A composition according to claim 12 containing from 0.1 to 95% of the active compound, by weight.

14. A method of combating arthropods which comprises applying to the arthropods, or to a habitat thereof, a compound according to any of claims 1 to 3 and 11 alone or in the form of a composition containing as active ingredient a compound according to any of claims 1 to 3 and 11, in admixture with a diluent or carrier.

15. A method of freeing or protecting domesticated animals from ectoparasitical insects which comprises applying to said animals a compound according to any of claims 1 to 3 and 11, in admixture with a diluent or carrier.

16. A method according to claim 14 in which a composition is used containing from 0.0000001 to 100% of the active compound, by weight.

17. A method according to claim 16 in which a composition is used containing from 0.01 to 10% of the active compound, by weight.

18. A method according to claim 14, 16 or 17 in which the arthropods are insects.

19. Crops protected from damage by arthropods 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 3 and 11 was applied alone or in admixture with a diluent or carrier.

20. Domesticated animals whenever freed or protected from ectoparasitical insects by the application to said animals of a compound according to any of claims 1 to 3 and 11, in admixture with a diluent or carrier.

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