

PATENT SPECIFICATION

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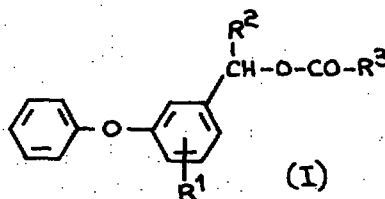
(54) NOVEL SUBSTITUTED PHENOXYBENZYLOXYCARBONYL DERIVATIVES AND THEIR USE AS INSECTICIDES AND ACARICIDES

(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 certain new substituted phenoxybenzyloxycarbonyl derivatives, to a process for their preparation and to their use as arthropodocides, especially insecticides and acaricides.

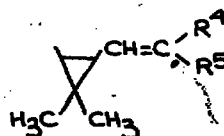
It is already known the phenoxybenzyl acetates or carboxylates, such as, for example, 3'-phenoxybenzyl - α - isopropyl - (3,4 - dimethoxyphenyl) - acetate and 3' - [2 - fluoro or 4 - fluoro - phenoxy] - α - cyanobenzyl [2,2 - dimethyl - 3 - (2,2 - dichlorovinyl) - cyclopropane] - carboxylate, possess insecticidal and acaricidal properties (see German Offenlegungsschriften (German Published Specifications) 2,335,347 and 2,547,534 and Belgian Patent Specification 801,946).

The present invention now provides, as new compounds, the substituted phenoxybenzyloxycarbonyl derivatives of the general formula



in which

- R¹ represents fluorine,
 R² represents hydrogen, cyano or ethynyl and
 R³ represents the radical



wherein

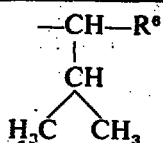
- R⁴ and R⁵ are identical and represent chlorine, bromine or methyl, or
 R³ represents the radical

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wherein

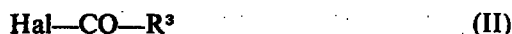
R⁶ represents a phenyl ring which optionally carries one or more substituents selected independently from halogen, alkyl with 1 to 4 carbon atoms, alkylthio with 1 to 4 carbon atoms, alkoxy with 1 to 4 carbon atoms, nitro and methylenedioxy.

The compounds of this invention are distinguished by a powerful insecticidal and acaricidal activity.

Preferably, R¹ represents fluorine, R² represents hydrogen or cyano and R³ represents a 2,2 - dimethyl - 3 - (2,2 - dichlorovinyl) - cyclopropane, 2,2 - dimethyl - 3 - (2,2 - dibromovinyl) - cyclopropane or 2,2 - dimethyl - 3 - (2,2 - dimethylvinyl) - cyclopropane radical or represents an α -isopropylbenzyl radical, the ring of which can optionally carry one or more substituents selected independently from fluorine, chlorine, bromine, methylenedioxy, methoxy, ethoxy, methylthio, ethylthio, straight-chain or branched alkyl with 1 to 3 carbon atoms and nitro.

The general formula (I) includes here the various possible stereoisomers, the optical isomers and mixtures of these components.

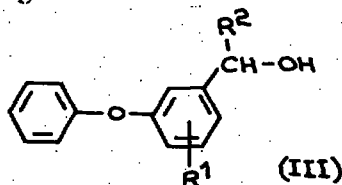
The invention also provides a process for the preparation of a substituted phenoxybenzyloxycarbonyl derivative of the formula (I), with a carbonyl halide of the general formula



in which

R³ has the meaning stated above and

Hal represents halogen, preferably chlorine, is reacted with a substituted phenoxybenzyl alcohol of the general formula

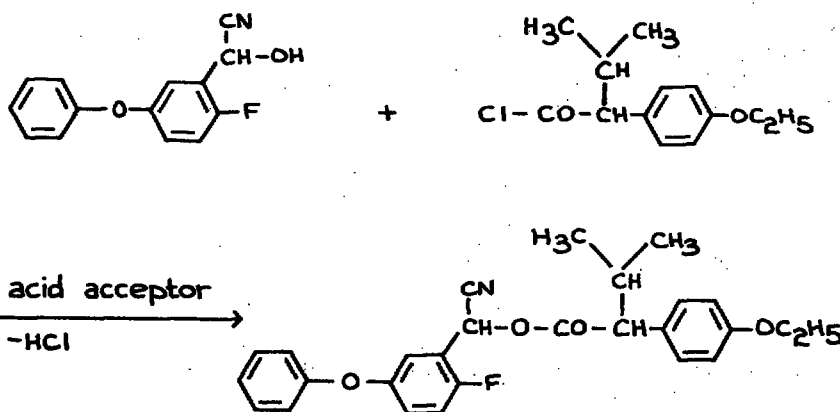


in which

R¹ and R² have the meanings stated above, optionally in the presence of an acid acceptor and optionally in the presence of a solvent or diluent.

Surprisingly, the substituted phenoxybenzyloxycarbonyl derivatives according to the invention exhibit a better insecticidal and acaricidal action than the corresponding previously known products of analogous structure and the same type of action. The products according to the present invention thus represent a true enrichment of the art.

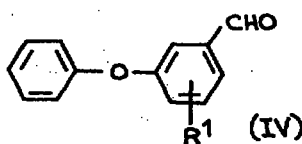
If, for example, 2 - fluoro - 5 - phenoxy - α - cyanobenzyl alcohol and α - isopropyl - 4 - ethoxyphenylacetyl chloride are used as the starting materials, the course of the reaction can be represented by the following equation:



The carbonyl halides of the general formula (II) to be used as starting materials are known and can be prepared by processes which are generally customary and are described in the literature (see, for example, German Offenlegungsschriften (German Published Specifications) 2,365,555; 1,926,433 and 2,231,312)

Examples of the compounds (II) which may be mentioned are: 2,2 - dimethyl - 3 - (2,2 - dichlorovinyl) - cyclopropanecarboxylic acid chloride, 2,2 - dimethyl - 3 - (2,2 - dibromovinyl) - cyclopropanecarboxylic acid chloride, 2,2 - dimethyl - 3 - (2,2 - dimethylvinyl) - cyclopropanecarboxylic acid chloride, α - isopropylphenylacetyl chloride, α - isopropyl - 4 - fluorophenylacetyl chloride, α - isopropyl - 4 - chlorophenylacetyl chloride, α - isopropyl - 4 - bromophenylacetyl chloride, α - isopropyl - 4 - methylphenylacetyl chloride, α - isopropyl - 4 - ethylphenylacetyl chloride, α - isopropyl - 4 - n - propylphenylacetyl chloride, α - isopropyl - 4 - iso - propylphenylacetyl chloride, α - isopropyl - 4 - methoxyphenylacetyl chloride, α - isopropyl - 4 - ethoxyphenylacetyl chloride, α - isopropyl - 4 - methylthiophenylacetyl chloride, α - isopropyl - 4 - ethylthiophenylacetyl chloride, α - isopropyl - 4 - nitrophenylacetyl chloride, α - isopropyl - 3 - fluorophenylacetyl chloride, α - isopropyl - 3 - bromophenylacetyl chloride, α - isopropyl - 3 - chlorophenylacetyl chloride, α - isopropyl - 3 - methylphenylacetyl chloride, α - isopropyl - 3 - ethylphenylacetyl chloride, α - isopropyl - 3 - methoxyphenylacetyl chloride, α - isopropyl - 3 - ethoxyphenylacetyl chloride, α - isopropyl - 3 - methylthiophenylacetyl chloride, α - isopropyl - 3 - ethylthiophenylacetyl chloride and α - isopropyl - 3,4 - methylenedioxyphenylacetyl chloride.

The phenoxybenzyl alcohols of the general formula (III) which are also to be used as starting compounds have not hitherto been described in the literature. However, they are the subject matter of U.K. Application 7912602. (Serial No. 1,565,933). They are obtained by the process in which phenoxybenzaldehydes of the general formula



in which

R^1 has the meaning stated above,

(a), in the case where R^2 represents hydrogen, are reduced with a complex metal hydride in an inert solvent,

(b), in the case where R^2 represents cyano, are reacted with an alkali metal cyanide, for example sodium cyanide or potassium cyanide, in the presence of an acid, optionally with the addition of a solvent, or

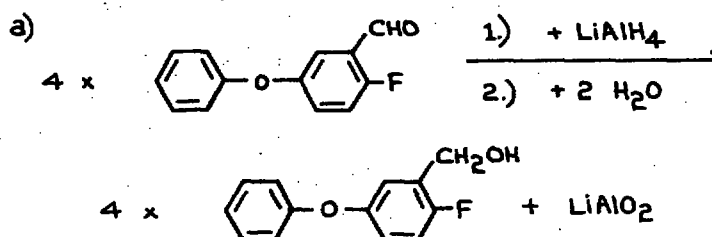
(c), in the case where R^2 represents ethynyl, are reacted with an ethynyl compound of the formula



in which

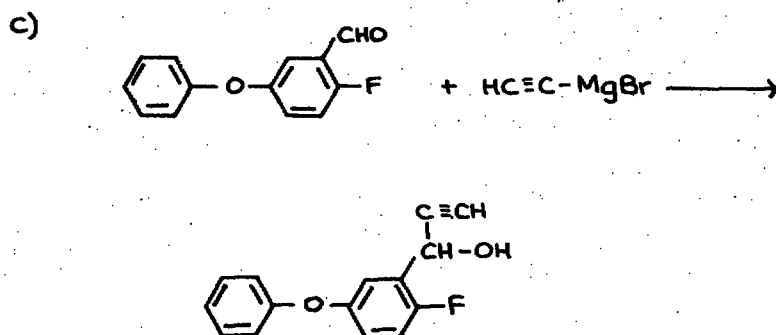
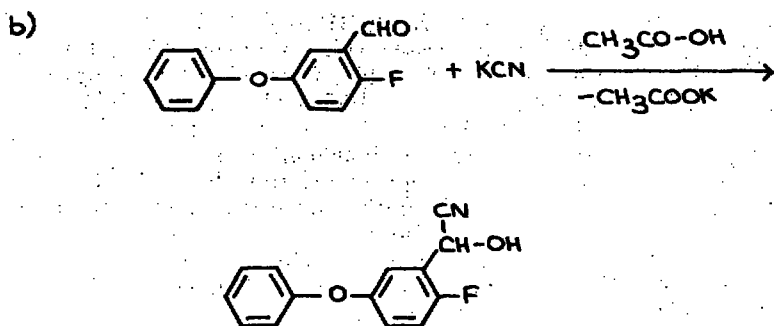
Hal' represents halogen, especially bromide, in a suitable solvent.

If, for example, 5-phenoxy-2-fluoro-benzaldehyde and lithium aluminium hydride are used as starting materials according to process variant (a), 5-phenoxy-2-fluorobenzaldehyde and potassium cyanide are used as starting materials according to process variant (b) and 5-phenoxy-2-fluorobenzaldehyde and ethynylmagnesium bromide are used as starting materials according to process variant (c), the course of the reactions can be represented by the following equations:



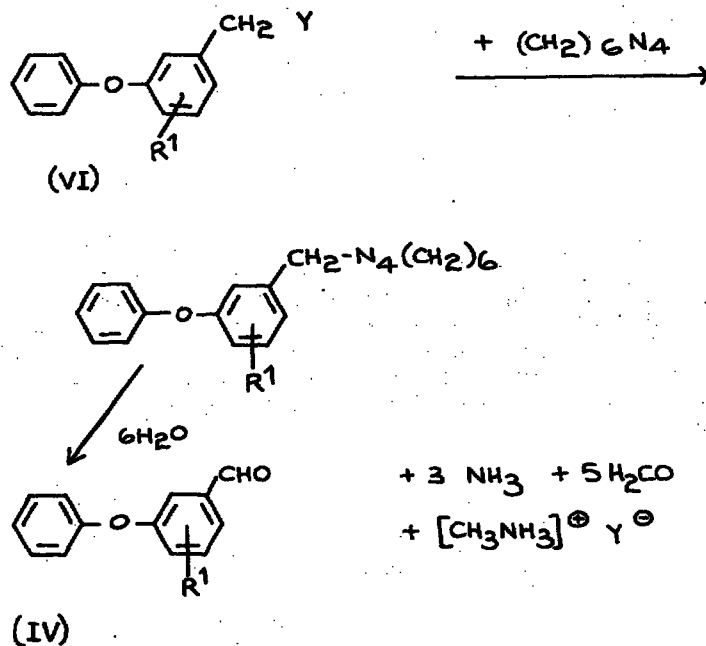
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The ethynyl compounds of the formula (V) are described in the literature, as are the alkali metal cyanides and complex metal hydrides.

The phenoxy-benzaldehydes of the formula (IV) can be prepared by generally customary processes, and in particular, for example, by reacting the corresponding phenoxybenzyl halides of the general formula (VI) below, which are prepared from the corresponding phenoxytoluenes by customary methods, with hexamethylenetetramine according to the following scheme:



wherein

R¹ has the meaning stated above and Y represents halogen.

Examples which may be mentioned of the phenoxybenzaldehydes to be reacted according to the process are: 3 - phenoxy - 4 - fluoro - benzaldehyde, 5 - phenoxy - 2 - fluoro - benzaldehyde and 3 - fluoro - 5 - phenoxy - benzaldehyde.

Variants (a) to (c) for the preparation of the phenoxybenzyl alcohols of the general formula (III) are preferably carried out using suitable solvents or diluents at the same time.

Preferred solvents or diluents for carrying out process variant (a) are ethers, such as diethyl ether, tetrahydrofuran and dioxan, as well as hydrocarbons, such as toluene and benzene. When sodium borohydride is used as the reducing agent, water alcohols, such as methanol or ethanol, or nitriles, such as acetonitrile or propionitrile, can additionally be used. Preferred solvents or diluents for carrying out process variant (b) are water, alcohols, such as methanol or ethanol, ethers, such as diethyl ether or tetrahydrofuran, or nitriles, such as acetonitrile. Preferred solvents or diluents for process variant (c) are ethers, such as diethyl ether, tetrahydrofuran and dioxan.

Complex metal hydrides which may be mentioned as preferred for process variant (a) are lithium aluminium hydride and sodium borohydride.

Acids which can be used in process variant (b) are inorganic acids, for example hydrochloric acid or sulphuric acid, or organic acids, for example acetic acid or formic acid.

In all process variants, the reaction temperature can be varied within a relatively wide range. In general, the reaction is carried out at from -10° to 110°C ; in variant (a) it is preferably carried out at 0° to 60°C , in variant (b) it is preferably carried out at from -5° to 20°C and in variant (c) it is preferably carried out at from 0° to 80°C .

In general, the reactions are allowed to proceed under normal pressure.

In carrying out variant (a), the reactants are preferably employed in equimolar amounts. An excess of one or other component provides no advantage. In variant (b) the cyanide is preferably employed in 100—150% excess. The reaction is preferably carried out in one of the solvents or diluents indicated above at the temperatures indicated, whilst stirring. After a reaction time of one or more hours, usually at elevated temperature, the reaction mixture is worked up by methods which are generally customary.

The new compounds (III) are obtained in the form of oils, which either can be distilled or are freed from the last volatile constituents by so-called "incipient distillation", that is to say by prolonged heating to moderately elevated temperatures under reduced pressure, and are purified in this manner. The refractive index or the boiling point is used for their characterisation.

Examples which may be mentioned of the new phenoxybenzyl alcohols of the general formula (III) which can be used for the preparation of the phenoxybenzyloxycarbonyl derivatives of the general formula (I) are: 3 - phenoxy - 4 - fluorobenzyl alcohol, 5 - phenoxy - 2 - fluoro - benzyl alcohol, 3 - fluoro - 5 - phenoxy - benzyl alcohol, 3 - phenoxy - 4 - fluoro - α - cyanobenzyl alcohol, 5 - phenoxy - 2 - fluoro - α - cyanobenzyl alcohol, 3 - fluoro - 5 - phenoxy - α - cyanobenzyl alcohol, 3 - phenoxy - 4 - fluoro - α - ethynyl - benzyl alcohol, 5 - phenoxy - 2 - fluoro - α - ethynylbenzyl alcohol and 3 - fluoro - 5 - phenoxy - α - ethynylbenzyl alcohol.

All the customary acid-binding agents can be used as acid acceptors in the preparation of the phenoxybenzyloxycarbonyl derivatives according to the invention. Alkali metal carbonates and alcoholates, such as sodium carbonate and potassium carbonate, sodium methylate and ethylate and potassium methylate and ethylate, and furthermore aliphatic, aromatic or heterocyclic amines, for example triethylamine, trimethylamine, dimethylaniline, dimethylbenzylamine and pyridine, have proved particularly suitable.

The reaction temperature can be varied within a relatively wide range. In general, the reaction is carried out at from 0° to 100°C , preferably at from 15° to 40°C .

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

The process for the preparation of the compounds of the formula (I) according to the invention is preferably carried out using a suitable solvent or diluent. Possible solvents are virtually all the inert organic solvents, especially aliphatic and aromatic, optionally chlorinated hydrocarbons, such as benzene, toluene, xylene, benzene, methylene chloride, chloroform, carbon tetrachloride and chlorobenzene; ethers, for example diethyl ether, dibutyl ether and dioxan; ketones, for example

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acetone, methyl ethyl ketone, methyl isopropyl ketone and methyl isobutyl ketone; and nitriles, such as acetonitrile and propionitrile.

In carrying out the process, the starting materials are preferably employed in equimolar amounts. An excess of one or other reactant provides no substantial advantages. In general, the reactants are brought together in one of the solvents indicated and the mixture is stirred for one or more hours, usually at elevated temperature, in order to bring the reaction to completion. The reaction mixture is then poured into water and the organic phase is separated off and rinsed with water. After drying, the solvent is distilled off *in vacuo*.

The compounds of the formula (I) are obtained in the form of oils, some of which cannot be distilled without decomposition, but are freed from the last volatile constituents by so-called "incipient distillation", that is to say by prolonged heating to moderately elevated temperatures under reduced pressure, and are purified in this manner. The refractive index is used for their characterisation.

As already mentioned, the substituted phenoxybenzyloxycarbonyl derivatives according to the invention are distinguished by an outstanding insecticidal and acaricidal activity.

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 and acarids, 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 carpohagus* and *Scutigera spec.*;

from the class of the *Symphyla*, for example *Scutigrella 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*, *Acheta domesticus*, *Gryllotalpa* spp., *Locusta migratoria migratorioides*, *Melanoplus differentialis* and *Schistocerca gregaria*;

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

from the order of the *Isotera*, 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., *Bucculatrix 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 recticulana*, *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* spp., *Psylliodes*

chrysocephala, *Epilachna varivestis*, *Atomaria* spp., *Oryzaephilus surinamensis*, *Anihonomus* 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 holoeucus*, *Gibbium psyllodes*, *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., *Chrysomya* spp., *Cuterebra* spp., *Gastrophilus* spp., *Hyppobosca* spp., *Stomoxys* spp., *Oestrus* spp., *Hypoderma* spp., *Tabanus* 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*, *Phyllocoptura 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 compounds according to the invention exhibit powerful ectoparasiticidal and tickicidal properties, especially against ticks which, as animal ectoparasites, attack domesticated animals, such as, for example, cattle and sheep. However, as mentioned above, the active compounds according to the invention have a favourable level of toxicity towards warm-blooded animals. They are therefore very suitable for combating animal ectoparasites, especially ticks.

As economically important ectoparasites of this type, which play a major role especially in tropical and sub-tropical countries, there may be mentioned, for example, the Australian and South American single-host cattle tick *Boophilus microplus*, the South African cattle tick *Boophilus decoloratus*, both from the family of the *Ixodidae*, the African multi-host cattle ticks and sheep ticks, such as, for example, *Rhipicephalus appendiculatus*, *Rhipicephalus evertsi*, *Amblyomma hebraeum* and *Hyalomma aruncatum* and the South American multi-host cattle ticks such as, for example, *Amblyomma cajennense* and *Amblyomma americanum*.

In the course of time such ticks have, in numerous areas, become resistant to the phosphoric acid esters and carbamates hitherto used as combating agents, so that the success of combating them has in many areas become increasingly dubious. To ensure economical stock raising in the infected areas, there is an urgent need for agents by means of which all stages of development, that is to say larvae, metalarvae, nymphs, metanymphs and adults, even of resistant strains, for example of the genus *Boophilus*, can be combated reliably. For example, in Australia the Mackay strain, the Mount Alfort strain and the Biarra strain of *Boophilus microplus* are highly resistant to the phosphoric acid ester agents used hitherto.

The active compounds according to the invention are equally effective against both the normally sensitive strains and the resistant strains, for example of *Boophilus*. When applied in the usual manner to the host animal, they have a direct destructive effect on all forms parasitic on the animal, so that the development cycle of the ticks is interrupted in the parasitic phase on the animal.

The laying of fertile eggs and hence the development and slipping of the larvae is inhibited.

The compounds are used, for example, in a dip or bath, in which case the active compounds in the dirtied aqueous dip liquor, which is exposed to microbial attack, must remain stable for 6 months or longer. Other methods of application include spraying and pouring.

In all use forms, the compounds according to the invention are completely stable, that is to say no decrease in action is detectable after 6 months.

The active compounds can be converted into 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, 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 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 liquefied gaseous or solid diluents or carriers, optionally with the use of surface-active agents, that is to say emulsifying agents and/or dispersing agents and/or foam-forming agents. In the case of the use of water as an extender, organic solvents can, for example, also be used as auxiliary solvents.

As liquid solvents diluents or carriers, especially solvents, there are suitable in the main, aromatic hydrocarbons, such as xylene, toluene or alkyl naphthalenes, 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 halogenated hydrocarbons as well as butane, propane, nitrogen and carbon dioxide.

As solid carriers there may be 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. As solid carriers for granules there may be used crushed and fractionated natural rocks such as calcite, marble, pumice, sepiolite and dolomite, as well as synthetic granules of inorganic and organic metals, and granules of organic material such as sawdust, coconut shells, maize cobs and tobacco stalks.

As emulsifying and/or foam-forming agents there may be used non-ionic and anionic emulsifiers, such as polyoxyethylene-fatty acid esters, polyoxyethylene-fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkyl sulphonates, alkyl sulphates, aryl sulphonates as well as albumin hydrolysis products. Dispersing agents include, for example, 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 dyestuffs 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.

When used against pests harmful to health and pests of stored products, the active compounds are distinguished by an excellent residual activity on wood and clay as well as a good stability to alkali on limed substrates.

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 or acarids) 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 or acarids (especially ticks) which comprises externally 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.

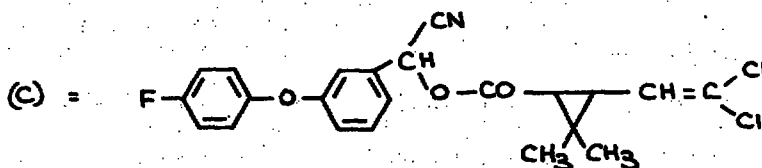
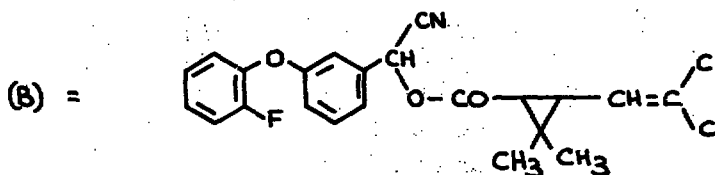
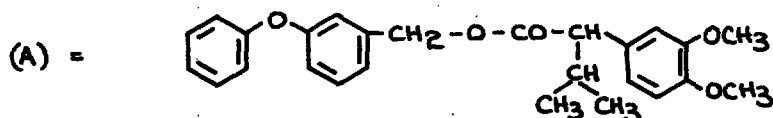
It will be seen that the usual methods of providing a harvested crop may be improved by the present invention.

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

The insecticidal and acaricidal 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:



Example A

Phaedon Larvae Test

Solvent: 3 parts by weight dimethylformamide

Emulsifier: 1 part by weight 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

5	Active compounds (A)	Active compound concentration in %	Degree of destruction in % after 3 days	10
		0.1	100	
		0.01	90	
10		0.001	0	10
	(B)	0.1	100	
		0.01	100	
		0.001	100	
		0.0001	0	
15	(7)	0.1	100	15
		0.01	100	
		0.001	100	
		0.0001	100	
20	(6)	0.1	100	20
		0.01	100	
		0.001	100	
		0.0001	100	
25	(8)	0.1	100	25
		0.01	100	
		0.001	100	
		0.0001	90	
30	(2)	0.1	100	30
		0.01	100	
		0.001	100	
		0.0001	100	

Example B

Tetranychus Test (Resistant)

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.

Bean plants (*Phaseolus vulgaris*) which were heavily infested with the two-spotted spider mite (*Tetranychus urticae*) in all stages of development were sprayed with the preparation of the active compound until dripping wet.

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

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

TABLE B
(Mites which Damage Plants)
Tetranychus Test

50	Active compounds (A)	Active compound concentration in %	Degree of destruction in % after 2 days	50
	(A)	0.1	20	
55	(2)	0.1	100	55
	(3)	0.1	100	
	(8)	0.1	100	

Example C

LT₁₀₀ Test for *Diptera*

Test animals: *Aedes aegypti*

Solvent: Acetone

The active compound was dissolved in the solvent at a rate of 2 g per litre. The solution so obtained was diluted with further solvent to the desired lower concentrations.

2.5 ml of the solution of active compound were pipetted into a Petri dish. On the bottom of the Petri dish there was a filter paper with a diameter of about 9.5 cm. The Petri dish remained uncovered until the solvent had completely evaporated. The amount of active compound per square metre of filter paper varied with the concentration of the solution of active compound. About 25 test animals were then placed in the Petri dish and it was covered with a glass lid.

The condition of the test animals was continuously observed. The time which was necessary for 100% destruction was determined.

The active compounds, the concentrations of the active compounds and the times at which there was 100% destruction can be seen from the following table:

TABLE C
(LT₁₀₀ Test for *Diptera*)

Aedes Aegypti

Active compounds (C) (2)	Active compound concentration of the solution	
	in %	LT ₁₀₀
	0.0002	3 hrs=0%
	0.0002	3 hrs=100%

Example D

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 in question 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*) 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% meant that none of the larvae had been killed.

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

TABLE D
(Test with Parasitic Fly Larvae)

Lucilia Cuprina (Resistant)

Active compound (6) (7)	Active compound concentration	
	in ppm	Destructive action in %
	1,000	100
	300	100
	100	100
	1,000	100
	300	100
	100	100

Example E

Tick Test

Solvent: 35 parts by weight of ethylene glycol monomethyl ether

Emulsifier: 35 parts by weight of nonylphenol polyglycol ether

To prepare a suitable formulation, three parts by weight of active compound

were mixed with seven parts of the above-mentioned solvent/emulsifier mixture and the emulsion concentrate thus obtained was diluted with water to the particular concentration desired.

Adult, fully bloated ticks of the species *Boophilus microplus* (resistant) were dipped for one minute into these active compound preparations, 10 female specimens being used to each test. The specimens were then transferred into Petri dishes, the bottom of each of which was lined with a filter disc of corresponding size.

After 10 days, the activity of the active compound preparation was determined by examining the inhibition of the laying of eggs, as compared to untreated control ticks. The action was expressed as a percentage, with 100% denoting that eggs were no longer laid on 0% denoting that the ticks laid normal amounts of eggs.

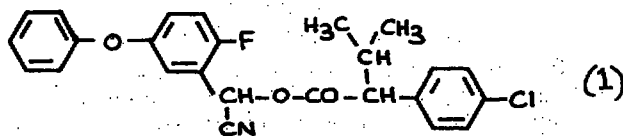
The active compound examined, the concentration tested, the parasites tested and the findings obtained can be seen from the table which follows.

TABLE E
Tick Test/*Boophilus Microplus* Resist.

Active compound (7)	Active compound concentration in ppm	Destructive action in %
	10,000	100
	1,000	100
(6)	10,000	100
	1,000	100

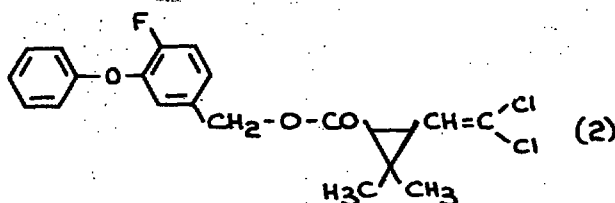
Preparative Examples

Example 1



8 g (0.033 mol) of 2 - fluoro - 5 - phenoxy - α - cyanobenzyl alcohol and 7.6 g (0.033 mol) of α - isopropyl - 4 - chlorophenylacetyl chloride was dissolved in 150 ml of anhydrous toluene and 2.64 g (0.033 mol) of pyridine dissolved in 50 ml of toluene were added dropwise at 25–30°C, whilst stirring. The mixture was then stirred for a further 3 hours at 25°C. The reaction mixture was poured into 150 ml of water and the organic phase was separated off and washed again with 100 ml of water. The toluene phase was then dried over sodium sulphate and the solvent was distilled off under a water pump vacuum. The last residues of solvent were removed by brief incipient distillation at a bath temperature of 60°C and under a pressure of 1 mm Hg. This gave 11.0 g (76.2% of theory) of 2' - fluoro - 5' - phenoxy - α' - cyanobenzyl α - isopropyl - 4 - chlorophenyl acetate as a yellow oil having a refractive index n_D^{25} of 1.5473.

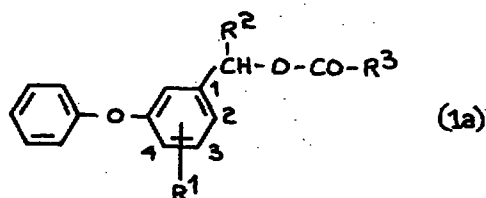
Example 2



2.18 g (0.01 mol) of 3 - phenoxy - 4 - fluoro - benzyl alcohol and 2.28 g (0.01 mol) of 2,2 - dimethyl - 3 - (2,2 - dichlorovinyl) - cyclopropanecarboxylic acid chloride were dissolved in 100 ml of anhydrous toluene, and 0.8 g (0.01 mol) of pyridine dissolved in 50 ml of toluene was added dropwise at 25–30°C, whilst stirring. The mixture was then stirred for a further 3 hours at 25°C. The reaction mixture was then poured into 150 ml of water and the toluene phase was separated off and washed again with 100 ml of water. The organic phase was dried over

sodium sulphate and the toluene was then distilled off under a water pump vacuum. The last residues of solvent were removed by incipient distillation at a bath temperature of 60°C and under a pressure of 1 mm Hg. This gave 3.5 g (85.6% of theory) of 3' - phenoxy - 4' - fluoro - benzyl 2,2 - dimethyl - 3 - (2,2 - dichlorovinyl) - cyclopropane carboxylate as a yellow oil having a refractive index n_D^{25} of 1.5548.

The compounds of the formula



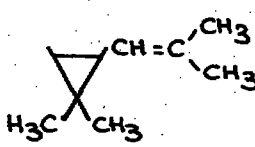
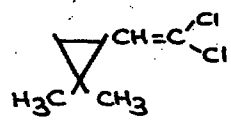
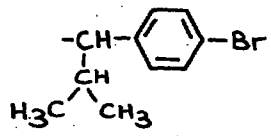
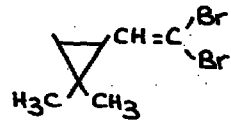
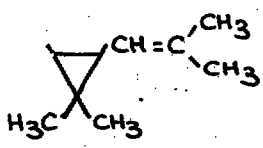
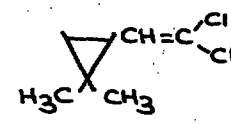
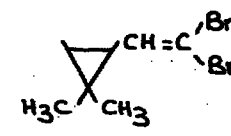
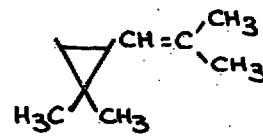
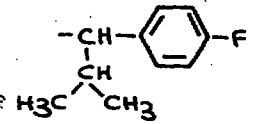
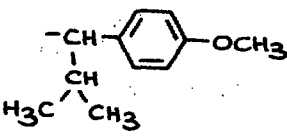
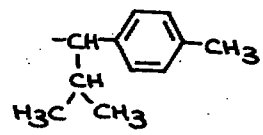
10		could be prepared analogously to either Example 1 or 2:				10	
Example No.	R ¹	R ²	R ³	Refractive index	Yield (% of theory)		
3	2-F	CN		$n_D^{26}: 1.5435$	71		
4	2-F	H		$n_D^{25}: 1.5555$	68		
5	4-F	H		$n_D^{25}: 1.5601$	72	15	
6	4-F	CN		$n_D^{25}: 1.5511$	82		
7	4-F	CN		$n_D^{23}: 1.5581$			
8	4-F	CN		$n_D^{25}: 1.5684$	82		
9	4-F	H		$n_D^{25}: 1.5723$			
10	4-F	CN		$n_D^{25}: 1.5684$	76		

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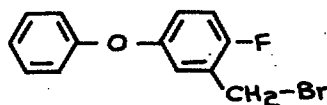
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Example No.	R ¹	R ²	R ³	Refractive index	Yield (% of theory)
11	4-F	CN		n _D ²⁵ : 1.5381	82
12	4-F	C≡CH			5
13	2-F	CN			
14	2-F	H			
15	4-F	H			
16	2-F	C≡CH			
17	4-F	C≡CH			10
18	2-F	CN			
19	4-F	CN			
20	4-F	CN			
21	4-F	CN			

Example No.	R ¹	R ²	R ³	Refractive index	Yield (% of theory)
22	4-F	CN			
23	3-F	H			5
24	3-F	CN			
25	3-F	CN			

The phenoxybenzyl alcohols required as starting compounds can be prepared, for example, as described in the following text:

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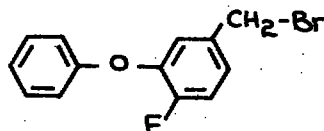
90 g (0.445 mol) of 2 - fluoro - 5 - phenoxy - toluene were dissolved in 300 ml of anhydrous carbon tetrachloride and the solution was heated under reflux, together with 79.3 g of N-bromosuccinimide. After a temperature of 70°C had been reached, 5 g of azodiisobutyronitrile were added and after about 10—20 minutes, the reaction began, with the evolution of heat. After the exothermic reaction had subsided, the mixture was heated under reflux for a further 4 hours. The reaction mixture was then cooled to 10°C, the succinimide was filtered off and the carbon tetrachloride was distilled off *in vacuo*. The oil which remained was distilled at 142—148°C/2 mm Hg. This gave 2 - fluoro - 5 - phenoxy - benzyl bromide in a yield of 56%.

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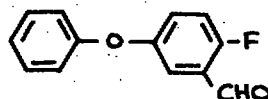
The compound of the formula



Boiling point 140—146°C/1 mm Hg
Yield: 58% of theory

could be prepared analogously.

(b)



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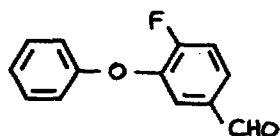
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48 g (0.17 mol) of 2 - fluoro - 5 - phenoxy - benzyl bromide and 47.8 g of hexamethylenetetramine in 250 ml of methylene chloride were heated under reflux for 3 hours, the mixture was then cooled to 5—10°C and the precipitate which had formed was filtered off. This precipitate was washed with 100 ml of methylene chloride, sucked dry and then heated under reflux for 5 hours in 100 ml of 50% strength aqueous acetic acid. Thereafter, 25 ml of concentrated hydrochloric acid were added and the mixture was again heated under reflux for 30 minutes and then

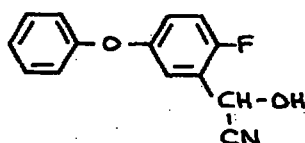
cooled to 10–20°C. 200 ml of water were added to the reaction mixture and this was extracted twice with 150 ml of ether each time and the combined ether phases were then washed with sodium bicarbonate solution and dried over sodium sulphate. The ether was distilled off *in vacuo*. This gave 2 - fluoro - 5 - phenoxy - benzaldehyde with a boiling point of 130–138°C/1 mm Hg in a yield of 42%.

The compound of the formula



Boiling point 132–135°C/2 mm Hg
Yield: 62% of theory

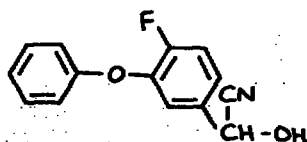
could be prepared analogously.



(c₁)

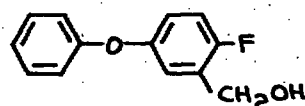
21.6 g (0.1 mol) of 2 - fluoro - 5 - phenoxy - benzaldehyde were dissolved in 25 ml of glacial acetic acid and 10.2 g of sodium cyanide dissolved in 25 ml of water were added dropwise at 15°C, whilst stirring. The reaction mixture was then stirred for 8 hours at 20°C, poured into 100 ml of water and extracted with 200 ml of ether and the ether phase was separated off. In order to remove the glacial acetic acid, the ether phase was washed with dilute sodium bicarbonate solution and then dried over sodium sulphate. After distilling off the ether *in vacuo*, 2 - fluoro - 5 - phenoxy - α - cyanobenzyl alcohol having a refractive index n_D^{25} of 1.5657 was obtained in a yield of 85%.

The compound of the formula



Refractive index: n_D^{25} : 1.5589
Yield: 87% of theory

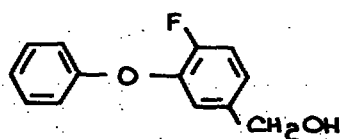
could be prepared analogously.



(c₂)

54 g (0.25 mol) of 2 - fluoro - 5 - phenoxy - benzaldehyde dissolved in 50 ml of dry ether were added dropwise, at the boil, to 3.8 g of lithium aluminium hydride in 100 ml of anhydrous ether, whilst stirring well. The reaction mixture was subsequently stirred for a further 10 hours at 22°C and then cooled to 0°C, and ice-water was added dropwise, whilst stirring, until no further evolution of hydrogen could be observed. The precipitate which had formed was dissolved by adding 10% sulphuric acid and the reaction mixture was then extracted twice with 100 ml of ether each time. The ether phases were separated off, washed with saturated sodium chloride solution and dried over sodium sulphate. After distilling off the ether *in vacuo*, 2 - fluoro - 5 - phenoxybenzyl alcohol with a boiling point of 161–165°C/4 mm Hg was obtained in a yield of 90%.

The compound of the formula



melting point: 43°C
Yield: 92% of theory

could be prepared analogously.



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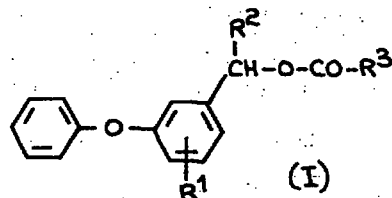
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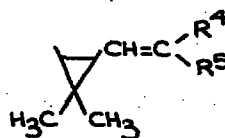
WHAT WE CLAIM IS:—

1. Substituted phenoxybenzyloxycarbonyl derivatives of the general formula



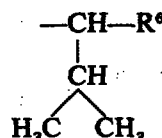
in which

R¹ represents fluorine,
R² represents hydrogen, cyano or ethynyl and
R³ represents the radical



wherein

R⁴ and R⁵ are identical and represent chlorine, bromine or methyl, or
R⁵ represents the radical



wherein

R⁶ represents a phenyl ring which optionally carries one or more substituents selected independently from halogen, alkyl with 1 to 4 carbon atoms, alkylthio with 1 to 4 carbon atoms, alkoxy with 1 to 4 carbon atoms, nitro and methylenedioxy.

2. Compounds according to claim 1, in which R¹ represents fluorine, R² represents hydrogen or cyano and R³ represents a 2,2-dimethyl-3-(2,2-dichlorovinyl)-cyclopropane, 2,2 - dimethyl - 3 - (2,2 - dibromovinyl) - cyclopropane or 2,2 - dimethyl - 3 - (2,2 - dimethylvinyl) - cyclopropane radical or represents an α -isopropylbenzyl radical, the ring of which can optionally carry one or more substituents selected independently from fluorine, chlorine, bromine, methylenedioxy, methoxy, ethoxy, methylthio, ethylthio, straight-chain or branched alkyl with 1 to 3 carbon atoms and nitro.

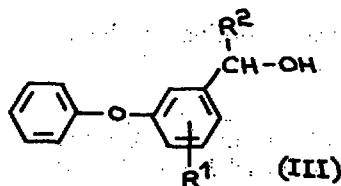
3. The compound according to claim 1 that is disclosed in any one of Examples 1 to 24.

4. A process for the preparation of a substituted phenoxybenzyloxycarbonyl derivative according to claim 1, in which a carbonyl halide of the general formula



in which

R³ has the meaning stated in claim 1 and
Hal represents halogen, is reacted with a substituted phenoxybenzyl alcohol of the general formula



in which

R¹ and R² have the meanings stated in claim 1, optionally in the presence of an acid acceptor and optionally in the presence of a solvent or diluent.

5. A process according to claim 4, in which Hal represents chlorine.



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

7. A process according to claim 4, 5 or 6, in which the reaction is effected in the presence, as an acid-binding agent, of an alkali metal carbonate, an alkali metal alcoholate or an aliphatic, aromatic or heterocyclic amine.

8. A process according to any of claims 4 to 7, in which the reaction is effected at from 0° to 100°C.

9. A process according to claim 8, in which the reaction is effected at from 15° to 40°C.

10. A process according to any of claims 4 to 9, in which the compound (III) is one that is hereinbefore specifically mentioned.

11. A process according to any of claims 4 to 10, in which the reactants are employed in equimolar amounts.

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

13. Compounds according to claim 1 whenever prepared by a process according to any of claims 4 to 12.

14. An arthropodicidal composition containing as active ingredient a compound according to any of claims 1 to 3 and 13 in admixture with a solid or liquefied gaseous diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.

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

16. 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 13 alone or in the form of a composition containing as active ingredient a compound according to any of claims 1 to 3 and 13, in admixture with a diluent or carrier.

17. A method of freeing or protecting domesticated animals from ectoparasitical insects or acarids, comprises externally applying to said animals a compound according to any of claims 1 to 3 and 13, in admixture with a diluent or carrier.

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

19. A method according to claim 18 in which a composition is used containing from 0.01 to 10% of the active compound, by weight.

20. A method according to claim 16, 18 or 19 in which the arthropods are acarids or insects.

21. A method according to claim 17 in which the ectoparasites are ticks.

22. 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 13 was applied alone or in admixture with a diluent or carrier.

23. Domesticated animals whenever freed or protected from ectoparasitical insects or acarids by the external application to said animals of a compound according to any of claims 1 to 3 and 13, in admixture with a diluent or carrier.

24. The compound disclosed in Example 25.

25. A composition according to claim 14 or 15 in which the active ingredient is the compound according to claim 24.

26. A method according to any of claims 16 to 21, in which the active compound is the compound according to claim 24.

27. Crops according to claim 22, protected by the application of the compound according to claim 24.

28. Domesticated animals according to claim 23, to which the compound according to claim 24 has been applied.

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