

PATENT SPECIFICATION

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- (72) Inventors VOLKER MUES, WOLFGANG BEHRENS, KLAUS
 DITGENS, and THOMAS SCHMIDT



(54) INSECTICIDAL AND ACARICIDAL AGENTS

(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 new arthropodicidal, especially insecticidal and acaricidal, synergistic combinations of certain benzodioxoles (some of which are known), and certain other, known, pesticidal active compounds.

It has already been disclosed that benzodioxole derivatives, for example α,α -dimethyl-(3,4-methylenedioxyphenyl)-acetonitrile and α,α -ethylene-(3,4-methylenedioxyphenyl)-acetonitrile, may be used as intermediates for the preparation of pharmaceuticals (see German Offenlegungsschrift (German Published Specification) 2,215,496 and J. of org. Chem. 1972, pages 977—982).

The following insecticidal active compounds or groups of active compounds have also been disclosed:

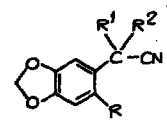
(A) carbamates, such as, for example, 2-isopropoxy-phenyl N-methyl-carbamate, 3,4,5-trimethyl-phenyl N-methyl-carbamate, 1-naphthyl N-methyl-carbamate, 2,3-dihydro-2,2-dimethyl-7-benzofuranyl N-methyl-carbamate, 2-[1,3-dioxolan-2-yl-phenyl] N-methyl-carbamate and 2,2-dimethyl-1,3-benzodioxol-4-yl N-methyl-carbamate,

(B) carboxylic acid esters, such as, for example, 2,3,4,5-tetrahydrophthalimido-methyl chrysanthemate and (5-benzyl-3-furyl)-methyl-2,2-dimethyl-3-(2-methylpropenyl)-cyclopropane-carboxylate, and

(C) phosphoric acid esters, such as, for example, O,O-dimethyl-O-(2,2-dichlorovinyl)-phosphoric acid esters.

Furthermore, synergistic mixtures of carbamates, for example 2-isopropoxy-phenyl-N-methylcarbamate, or of phosphoric acid esters, for example O,O-diethyl-O-(2-isopropyl-4-methylpyridine-dimethyl-[6]-phosphorothioate, or of natural or synthetic pyrethroids with piperonyl ethers, such as, for example, α -[2-(2-butoxy-ethoxy)-ethoxy]-4,5-methylenedioxy-2-propyl-toluene, are known (see Bull. Org. Health Org. 1966, 35, pages 691—708, Schrader, G.: Die Entwicklung neuer insektizider Phosphorsäureester (The Development of new Insecticidal Phosphoric Acid Esters), 1963, page 158; Perkov, W.: Die Insektizide (The Insecticides), 1966, pages 516—524). However, the activity of these synergistic active-compound combinations is not satisfactory. Hitherto, only α -[2-(2-butoxy-ethoxy)-ethoxy]-4,5-methylenedioxy-2-propyl-toluene has essentially achieved a certain practical importance.

The present invention now provides an arthropodicidal composition containing as active ingredients (1) a benzodioxole derivative of the general formula



(I)

in which

R represents hydrogen, alkyl, alkenyl, halogen or nitro,

R¹ represents alkyl or hydrogen, and

R² represents aralkyl, alkyl, alkenyl or cycloalkyl or may represent hydrogen, provided that R represents alkyl, alkenyl or nitro, or

R¹ and R² together represent an alkylene radical,

and (2) at least one compound selected from (A) carbamates, (B) carboxylic acid esters (including the natural and synthetic pyrethroids) and (C) phosphoric acid esters, alone or in admixture with a solid or liquid or liquefied gaseous diluent or carrier.

Surprisingly, the insecticidal and/or acaricidal action of the active-compound combinations according to the invention is substantially higher than the action of the individual components or the sum of the actions of the individual components. Furthermore, it is substantially higher than the action of the active-compound combination, which is already known, of 2-isopropoxy-phenyl N-methyl-carbamate and piperonyl butoxide. In addition, the benzodioxole derivatives exhibit excellent synergistic activity not only with one class of active compounds but with active compounds from the most diverse chemical groups of substances. Thus the synergistic mixtures, according to the invention, containing benzodioxole derivatives represent a valuable enrichment of the art.

The formula (I) provides a general definition of the benzodioxole derivatives to be used in the compositions according to the invention. Preferably, however, in the formula (I),

R represents hydrogen, chlorine, bromine, nitro or straight-chain or branched alkyl with 1 to 6 (especially 1 to 4) carbon atoms, or straight-chain or branched alkenyl with 2 to 6 carbon atoms (especially propenyl, allyl or isopropenyl),

R¹ represents hydrogen or straight-chain or branched alkyl with 1 to 3 carbon atoms (especially methyl),

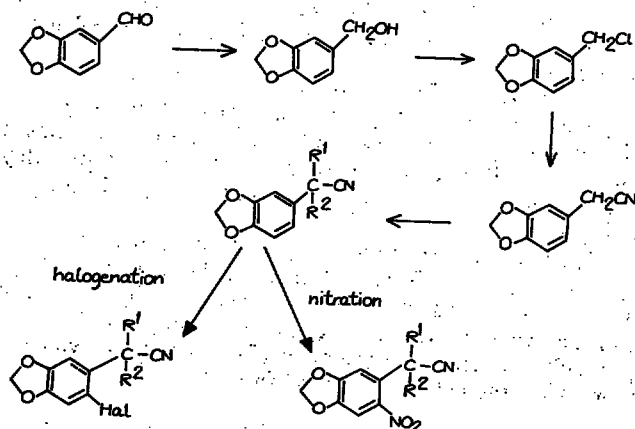
R² represents straight-chain or branched alkyl or alkenyl with up to 6 (especially with up to 4) carbon atoms, cycloalkyl with 3 to 8 (especially 4 to 6) carbon atoms or benzyl or may represent hydrogen, provided that R represents nitro, alkyl or alkenyl, or R¹ and R² together represent an alkylene radical with 2 to 8 (especially 2 to 5) carbon atoms.

Examples which may be mentioned of the benzodioxole derivatives of the formula (I) are: α -methyl-, α -ethyl-, α -n-propyl-, α -iso-propyl-, α -n-butyl-, α -iso-butyl-, α -sec-butyl-, α -tert-butyl-, α -allyl-, α -benzyl-, α,α -dimethyl-, α -methyl- α -ethyl-, α -methyl- α -n-propyl-, α -methyl- α -iso-propyl-, α,α -ethylene-, α,α -trimethylene-, α,α -tetramethylene-, α -cyclopropyl- and α -cyclohexyl-(3,4-methylenedioxyphenyl)-acetonitrile; the derivatives substituted, in each case, in the 6-position by chlorine, bromine, methyl, ethyl, n-propyl, isopropyl, tert-butyl, allyl, propenyl, iso-propenyl or nitro; and 6-nitro-, 6-methyl-, 6-ethyl-, 6-n-propyl-, 6-iso-propyl-, 6-tert-butyl-, 6-allyl-, 6-propenyl or 6-isopropenyl-(3,4-methylene-dioxyphenyl)-acetonitrile.

Some of these compounds are new, but they can be prepared in accordance with processes which are known from the literature [see, for example, German Offenlegungsschrift (German Published Specification) 2,215,496 and 2,335,347, British Patent Specification 1,109,527, J. Amer. Chem. Soc., 64 (1942), pages 2,486—2,487 and J. Org. Chem., 1972, pages 977—982].

The new compounds can be prepared, in the case where R is hydrogen, halogen or nitro, by reducing 3,4-methylenedioxy-benzaldehyde to piperonyl alcohol, converting this into the corresponding halide and reacting the halide with a cyanide to give 3,4-methylenedioxyphenylacetonitrile [see von Braun and Wirz, Ber. dt. Chem. Ges. 60, 110 (1927)]. This compound can then be alkylated to give the compounds of the formula (V) indicated below, in accordance with the customary processes which are known from the literature [see Dehmlow, New Synthetic Methods, Vol. 1, 19 (1975); Makosza *et al.*, Chimie et Industrie (Paris) 93, 537 (1965); Makosza, Pure Appl. Chem., 43, 439 (1975) and Makosza and Jonczyk, Org. Syn., 55, 91 (1976)]. The compounds of the formula (V) can then be halogenated, for example with sulphuryl chloride or bromine or nitrated, for example with a mixture of concentrated sulphuric acid and nitric acid.

The following equation illustrates the course of the reaction:



It is also possible to halogenate 3,4-methylenedioxy-benzaldehyde [see Dallacker, Liebigs Ann. Chem. 633, 14 (1960) and Weisse, Ber. dt. Chem. Ges. 43, 2605 (1910)] and then to proceed in the manner described. This method of sequence, however leads to poor yields.

The synthesis proceeds via the following stages when R stands for

(a) n-propyl: safrol → dihydrosafrol → 6-chloromethyldihydrosafrol → 6-cyanomethyldihydrosafrol → desired compound,

(b) allyl: safrol → 6-chloromethylsafrol → 6-cyanomethylsafrol → desired α-alkylacetonitriles,

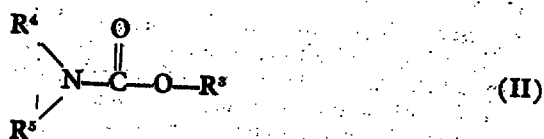
(c) propenyl: isosafrol → 6-chloromethylisosafrol → 6-cyanomethylsafrol → desired compound, the subsequent isomerisation of the alkyl compound indicated under (b) is more advantageous) and

(d) tert. - butyl: 4 - tert. - butylpyrocatechol → 3,4 - methylenedioxy - tert. - butylbenzene → 6 - chloromethyl - 3,4 - methylenedioxy - tert. - butylbenzene → 6-cyanomethyl - 3,4 - methylenedioxy - tert. - butylbenzene → desired compound.

The toluenes and ethylbenzenes according to the invention can be prepared analogously from 4-methyl- or 4-ethyl-pyrocatechol respectively (compare with the 6-chloromethyl compounds in U.S. Patent Specifications 2,485,600 and 2,485,680).

The individual stages of the synthesis paths given are known or are carried out in accordance with procedures which are in themselves known. For example, the 6-chloromethyl compounds serving, in each case, as intermediates can be prepared in accordance with the processes indicated in U.S. Patent Specifications 2,485,600 and 2,485,680.

Preferred carbamates (A) are those of the general formula



in which

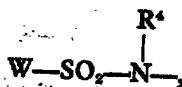
R³ represents aryl, a heterocyclic radical or an oxime radical,

R⁴ represents hydrogen or alkyl with 1-4 C atoms and

R⁵ represents alkyl or alkylcarbonyl with 1 to 6 C atoms in the alkyl radical [which can be optionally substituted by hydroxyl or methylthio] or the radical -S-Y,

wherein

Y represents an aliphatic radical with 1-4 C atoms [which is optionally substituted by halogen (especially Cl, and CF₃)], or an aryl radical (especially phenyl) [which is optionally (indeed preferably) substituted by CN, halogen (especially chlorine), methyl, trihalogenomethyl, trifluoromethylmercapto or No₂], or methoxycarbonyl or the radical



wherein

W represents alkyl, halogenoalkyl, alkylamino or dialkylamino or an aryl radical [which is optionally (indeed preferably) substituted by halogen, trihalogenomethyl, CN, methyl or nitro].

Particularly preferred carbamates (II) are those in which

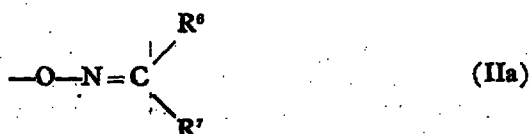
R³ represents phenyl or naphthyl [either of which is optionally substituted by alkyl, alkenyl, alkoxy or alkylmercapto with up to 5 C atoms in each case, dialkylamino or dialkenylamino with up to 3 C atoms per alkyl or alkenyl part, halogen (especially chlorine), dioxolanyl or the radical —N=CH—N—(C₁₋₄-alkyl)₂].

Other particularly preferred carbamates (II) are those in which

R³ represents 2,3-dihydrobenzofuranyl, benzodioxole, benzothienyl, pyrimidinyl or pyrazolyl [each of which is optionally substituted by C₁₋₄-alkyl (especially methyl) or dialkylamino with 1-4 C atoms per alkyl part].

Yet further particularly preferred carbamates (II) are those in which

R³ represents an oxime radical of the general formula

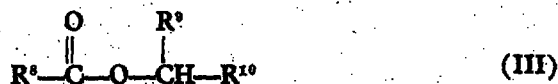


in which

R⁶ and R⁷, which may be identical or different, each represent alkyl, cycloalkyl, alkenyl, alkynyl, alkoxy, alkylmercapto, alkoxycarbonyl, carbonylamide or alkylmercaptoalkyl with up to 5 C atoms in each case, CN, aryl (especially phenyl), an optionally substituted heterocyclic radical or alkyl which is substituted by a heterocyclic radical, or

R⁶ and R⁷ together form a dioxolanyl or dithiolanyl radical which is optionally substituted by C₁₋₄-alkyl.

Preferred carboxylic acid esters (B) are those of the general formula



in which

R⁸ represents alkyl, aralkyl, aryl or cycloalkyl, each of which can be optionally substituted,

R⁹ represents hydrogen, alkyl, halogenoalkyl, alkenyl, alkynyl or CN, and

R¹⁰ represents aryl or a heterocyclic radical, or

R⁹ and R¹⁰ together form an optionally substituted cyclopentenone ring.

Particularly preferred carboxylic acid esters (III) are those in which

in which

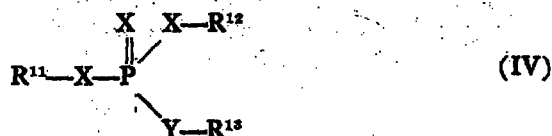
R⁸ represents alkyl with 1-6 C atoms [which is optionally substituted by optionally halogen-substituted phenyl], cyclopropyl [which is optionally substituted by alkyl, alkenyl, halogenoalkyl or halogenoalkenyl with up to 6 C atoms in each case] or phenyl which is optionally substituted by halogen, and/or

R⁹ represents hydrogen, alkyl with 1-6 C atoms, halogenoalkyl with 1-4 C atoms and up to 3 halogen atoms, CN or ethynyl, and/or

R¹⁰ represents phenyl [which is optionally substituted by C₁₋₄-alkyl, halogen (especially fluorine or chlorine), optionally halogen- or methyl-substituted phenoxy or optionally substituted benzyl], furanyl, tetrahydrophthalimido or benzodioxole [any of which is optionally substituted by halogen (especially chlorine), alkyl or alkenyl with up to 4 C atoms or benzyl] or cyclopentenone [which is optionally substituted by C₁₋₄-alkyl, furfuryl or C₂₋₅-alkenyl].

In addition, naturally occurring pyrethroids are particularly preferred.

Preferred phosphoric acid esters (C) are those of the general formula



in which

each X, independently of one another, represents O or S,

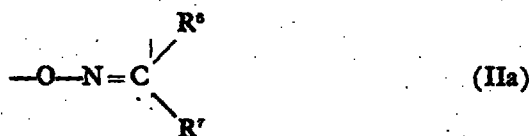
Y represents O, S, —NH— or a direct bond between the central P atom and the radical R^{13} ,

R^{11} and R^{12} , which may be identical or different, each represent alkyl or aryl and R^{13} represents alkyl, aryl, heteroaryl, aralkyl, alkenyl, dioxanyl or an oxime radical, or represents a radical identical to that to which it is bonded.

Particularly preferred phosphoric acid esters (IV) are those in which

R^{11} and R^{12} , which may be identical or different, each represents C_{1-4} -alkyl or phenyl, and

R^{13} represents alkyl with 1—4 C atoms [which is optionally substituted by halogen, OH, CN, optionally halogen-substituted phenyl, carbonylamide, sulphonylalkyl, sulphonylalkyl, carbonylalkyl, alkoxy, alkylmercapto or alkoxy-carbonyl], alkenyl with up to 4 C atoms [which is optionally substituted by halogen, optionally halogen-substituted phenyl or alkoxy-carbonyl] or an oxime radical of the general formula



wherein

R^6 and R^7 have the meanings stated above (especially cyano or phenyl), or

R^{13} represents dioxanyl which is substituted by a radical identical to that to which R^{13} is bonded, or R^6 represents a radical identical to that to which it is bonded, or

R^{13} represents phenyl [which is optionally substituted by methyl, nitro, CN, halogen or methylmercapto], or R^{13} represents hetero-aromatic structures (such as pyridine, quinoline, quinoxaline, pyrimidine, diazine or benzo-1,2,4-triazine) optionally substituted by C_{1-4} -alkyl or halogen.

Preferred compositions of this invention are those in which the component (2) is a compound selected from

(A) carbamates of the general formula (II)

in which

R^8 represents an aryl or a heterocyclic radical,

R^4 represents alkyl with 1—4 carbon atoms, and

R^5 represents acetyl, —SCCl₂ or —SCF₃,

(B) carboxylic acid esters of the general formula (III)

in which

R^8 represents alkyl or an alkyl-substituted or alkenyl substituted cyclopropyl ring,

R^9 represents hydrogen or halogenoalkyl, and

R^{10} represents aryl (optionally substituted by halogen) or a heterocyclic radical,

and (C) phosphoric acid esters of the formula (IV)

in which

X and Y each represent oxygen,

R^{11} and R^{12} each represent alkyl with 1—4 C atoms and

R^{13} represents —CH=CHal, wherein

Hal is a halogen atom.

The carbamates (group A) of the formula (II) which may be used as components of the mixture include: 2-methylphenyl, 2-ethylphenyl, 2-n-propylphenyl, 2-methoxyphenyl, 2-ethoxyphenyl, 2-iso-propoxyphenyl, 4-methylphenyl, 4-ethylphenyl, 4-n-propylphenyl, 4-methoxyphenyl, 4-ethoxyphenyl, 4-n-propoxyphenyl, 3,4,5-trimethylphenyl, 1-naphthyl, 2,3-dihydro-2,2-dimethyl-7-benzofuranyl, 2-[1,3-dioxolan-2-yl-phenyl] and 2,2-dimethyl-1,3-benzodioxol-4-yl N-methyl-carbamate and the corresponding N-methyl-N-acetyl-, N-methyl-N-trifluoromethylthio-, N-methyl-N-dichloromonofluoromethylthio- and N-methyl-N-dimethylaminothio-carbamate.

These compounds, their preparation and their use are known (see, for example, U.S. Patent Specifications 3,009,855; 2,903,478 and 3,111,539).

The carboxylic acid esters (group B) of the formula (III) which may be used as components of the mixture include: acetic acid 1-(3,4-dichlorophenyl)-2,2,2-trichloroethyl ester, 2,3,4,5-tetrahydrophthalimidomethyl chrysanthemate and (5-benzyl-3-furyl)-methyl-2,2-dimethyl-3-(2-methylpropenyl)-cyclopropanecarboxylate.

The compounds listed are known and in many cases are generally known commercial products [see R. Wegler "Chemie der Pflanzenschutz- und Schädlingsbekämp-

fungsmittel" ("Chemistry of Plant Protection Agents and Agents for Combating Pests"), Volume 1, pages 87—118, Heidelberg (1970)].

The phosphoric acid esters of the formula (IV) which may be used as components of the mixture include: O,O-dimethyl- and O,O-diethyl-O-(2,2-dichloro- or 2,2-dibromo-vinyl)-phosphoric acid esters.

The compounds of the formula (IV) are known and are easily accessible by processes which are known from the literature (see, for example, U.S. Patent Specification 2,956,073, German Auslegeschrift (German Published Specification) 1,167,324 and Belgian Patent Specification 633,478).

The weight ratios of the groups of active compounds can vary within relatively wide limits. In general, the benzodioxole derivative component (1) is employed with the remaining active compound(s) (2) in a weight ratio of from 0.1:10 to 10:0.1. However, a weight ratio of from 0.5:1 to 3:1 has proved particularly suitable.

The active compound combinations according to the invention not only produce a rapid knock-down action but also bring about the lasting destruction of all or some stages of development of animal pests, especially insects. The pests include those which occur in agriculture, forestry, the protection of stored products and the protection of materials, as well as in the hygiene field. They 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 *Scutigera 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 *Dermoptera*, 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., *Buscelis 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 blandcardella*, *Hyponomeuta padella*, *Plutella maculipennis*, *Malacosoma neustria*, *Euproctis chrysorrhoea*, *Lymantria* spp., *Bucculatrix thurberiella*, *Phyllocnistis citrella*, *Agrotis* spp., *Buxoa* spp., *Feltia* spp., *Baries insulana*, *Heliothis* spp., *Laphygma exigua*, *Mamestra brassicae*, *Panolis flammea*, *Prodenia litura*, *Spodoptera* spp., *Trichoplusia ni*, *Carpocapsa pomonella*, *Pieris* spp., *Chilo* spp., *Pyrausta nubilalis*, *Ephesttia 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*, *Hylotrupes bajulus*, *Agelastica alni*, *Leptinotarsa decemlineata*, *Phaedon cochleariae*, *Diabrotica* spp., *Psylliodes chrysocephala*, *Epilachna varivestis*, *Atomaria* spp., *Oryzaephilus surinamensis*, *Anthonomus* spp., *Sitophilus* spp., *Otiotrhynchus sulcatus*, *Cosmopolites sordidus*, *Ceuthorrhynchus assimilis*, *Hypera postica*, *Dermestes* spp., *Trogoderma* spp., *Anthrenus* spp., *Attagenus* spp., *Lycius* spp., *Meligethes aeneus*, *Ptinus* spp., *Niptus hololeucus*, *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., *Hopllocampa* 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 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 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 dichlorodifluoromethane or trichlorofluoromethane.

As solid carriers there are preferably used ground natural minerals, such as kaolins, clays, talc, chalk, quartz, attapulgit, 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 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.

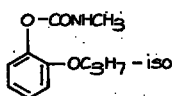
When used against pests harmful to health and pests of stored products, the active compounds are distinguished by an excellent residual activity on wood and clay as well as a good stability to alkali on limed substrates.

The present invention also provides a method of combating arthropods, especially insects, which comprises applying to the arthropods, or to a habitat thereof, a composition according to the present invention.

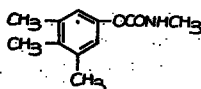
The present invention also provides crops protected from damage by arthropods by being grown in areas in which immediately prior to and/or during the time of the growing a composition according to the present invention was applied.

The Examples which follow show the synergistic properties of the benzodioxole derivatives which can be used according to the invention, in connection with the following known active compounds:

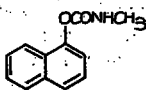
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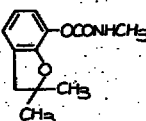
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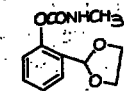
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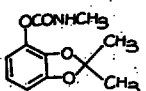
(D)



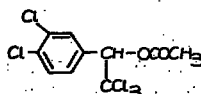
(E)



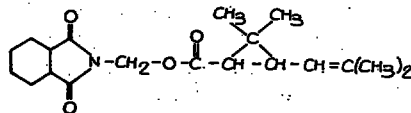
(F)



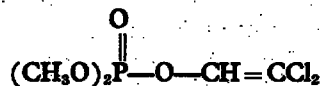
(G)



(H)



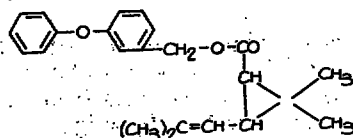
(I)



(J)

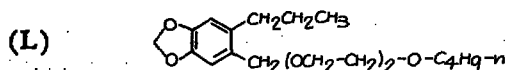
Pyrethrins as a 25% strength pyrethrum extract

(K)



12

For comparative purposes, the known piperonyl-butoxide, also employed as a synergistic agent, was additionally used



In the tables of the Examples which follow, the known active compounds and the known synergistic agent have been characterised by the capital letters given above, whilst each synergistic agent of the formula (I) is identified by the number of the corresponding preparative Example, given later in the text.

Example A.

LT₁₀₀ test

Test animals: Female *Musca domestica*, Weymann's strain, which are resistant to phosphoric acid esters

Solvent: acetone

Solutions of the active compounds, synergistic agents and mixtures of active compounds and synergistic agents were prepared and 2.5 ml thereof were pipetted onto filterpaper discs of 9.5 cm diameter in Petri dishes. The filterpaper absorbed the solutions. The Petri dishes were left standing open until the solvent had completely evaporated. 25 test animals were then placed in each Petri dish, and the dishes were covered with a glass lid.

The condition of the test animals was checked continuously for up to 6 hours. The time required for a 100% knock-down action was determined. If the LT₁₀₀ was not reached after 6 hours, the % of test animals which had been knocked down was ascertained.

The concentrations of the active compounds, synergistic agents and mixtures, and their actions, can be seen from the table which follows:

TABLE A

LT₁₀₀ test with female *Musca domestica* (Weymann's strain) which are resistant to phosphoric acid esters

Active compounds/ synergistic agents	Concentrations in %	LT ₁₀₀ in minutes
A	1.0	360 = 0%
B	1.0	360 = 0%
C	1.0	360 = 0%
D	1.0	360 = 20%
E	1.0	360 = 10%
F	1.0	360 = 30%
G	1.0	360 = 20%
H	0.04	260 = 95%
J	0.04	360 = 90%
K	0.04	120 ^a
L	1.0	360 = 0%
1	0.2	210 ^a
2	1.0	360 = 95%
3	1.0	360 = 80%

TABLE A (continued)

LT₁₀₀ test with female *Musca domestica* (Weymanns strain) which are resistant to phosphoric acid esters

Active compounds/ synergistic agents	Concentrations in %	LT ₁₀₀ in minutes
4	1.0	360 - 90%
35	0.2	360
37	1.0	360
38	1.0	360 - 80%
39	1.0	360 - 0%
40	1.0	360 - 0%
45	1.0	360 - 25%
46	1.0	360 - 20%
A + L	0.2 + 0.2	360 - 85%
A + 4	0.008 + 0.008	360
A + 40	0.04 + 0.04	240
A + 2	0.04 + 0.04	150
A + 3	0.04 + 0.04	150
A + 38	0.008 + 0.008	360 - 90%
A + 1	0.008 + 0.008	240
A + 45	0.008 + 0.008	360
B + L	1.0 + 1.0	360 - 90%
B + 4	0.04 + 0.04	360 - 90%
B + 2	0.2 + 0.2	240
B + 3	0.2 + 0.2	360
B + 38	0.04 + 0.04	360 - 85%
B + 1	0.2 + 0.2	240
B + 37	0.04 + 0.04	360
B + 39	0.04 + 0.04	360 - 90%
B + 46	0.2 + 0.2	240
B + 45	0.04 + 0.04	360
C + L	1.0 + 1.0	360 - 40%
C + 38	0.2 + 0.2	6 hrs - 90%
C + 1	0.2 + 0.2	180
C + 46	1.0 + 1.0	360

TABLE A (continued)

LT₁₀₀ test with female *Musca domestica* (Weymanns strain) which are resistant to phosphoric acid esters

Active compounds/ synergistic agents	Concentrations in %	LT ₁₀₀ in minutes
C + 45	0.2 + 0.2	360 = 95%
D + L	0.2 + 0.2	360 = 75%
D + 4	0.008 + 0.008	360
D + 2	0.008 + 0.008	240
D + 35	0.008 + 0.008	180
D + 3	0.04 + 0.04	180
D + 38	0.008 + 0.008	240
D + 1	0.008 + 0.008	150
D + 37	0.008 + 0.008	210
D + 39	0.008 + 0.008	240
D + 46	0.008 + 0.008	360
D + 45	0.008 + 0.008	210
E + L	0.2 + 0.2	360
E + 4	0.2 + 0.2	240
E + 2	0.2 + 0.2	360
E + 35	0.04 + 0.04	360
E + 3	0.2 + 0.2	210
E + 38	0.04 + 0.04	360 = 95%
E + 1	0.2 + 0.2	150
E + 37	0.04 + 0.04	360 = 90%
E + 46	0.2 + 0.2	240
F + L	0.2 + 0.2	360 = 70%
F + 4	0.008 + 0.008	360
F + 2	0.008 + 0.008	360
F + 35	0.008 + 0.008	210
F + 3	0.04 + 0.04	180
F + 38	0.008 + 0.008	180
F + 1	0.008 + 0.008	360
F + 37	0.008 + 0.008	180
F + 46	0.008 + 0.008	360

TABLE A (continued)

LT₁₀₀ test with female *Musca domestica* (Weymanns strain) which are resistant to phosphoric acid esters

Active compounds/ synergistic agents	Concentrations in %	LT ₁₀₀ in minutes
F + 45	0.008 + 0.008	240
G + L	1.0 + 1.0	360 = 70%
G + 4	0.04 + 0.04	360 = 85%
G + 2	0.04 + 0.04	360
G + 35	0.04 + 0.04	360 = 95%
G + 3	0.2 + 0.2	360
G + 38	0.2 + 0.2	360 = 90%
G + 1	0.04 + 0.04	360
G + 46	0.2 + 0.2	360
G + 45	0.04 + 0.04	360
H + 4	0.04 + 0.04	90
H + 35	0.04 + 0.04	105
H + 38	0.04 + 0.04	105
H + 37	0.04 + 0.04	180
H + 39	0.04 + 0.04	150
J + 4	0.04 + 0.04	105
J + 35	0.04 + 0.04	180
J + 38	0.04 + 0.04	240
J + 39	0.04 + 0.04	150
J + 37	0.04 + 0.04	180
K + L	0.04 + 0.04	90
K + 4	0.04 + 0.04	45
K + 38	0.04 + 0.04	60
K + 37	0.04 + 0.04	60
K + 39	0.04 + 0.04	60

Example B.

	LT ₁₀₀ test	
	Test animals: <i>Blattella germanica</i> female (normally sensitive)	
	<i>Blattella germanica</i> female (resistant)	
5	<i>Tribolium confusum</i>	5
	<i>Dermestes peruvianus</i>	
	<i>Attagenus piceus</i> larvae	
	<i>Ornithodoros moubata</i> larvae	
	Solvent: Acetone	
10	Solutions of the active compounds, synergistic agents and mixtures of active compounds and synergistic agents were prepared and 2.5 ml thereof were pipetted onto filter paper of 9.5 cm diameter in Petri dishes. The filterpaper absorbed the solution. The Petri dishes were left standing open until the solvent had completely evaporated. 25 test animals were then placed in each Petri dish, and the dishes were covered with a glass lid.	10
15	The condition of the animals was checked continuously for up to 6 hours and thereafter also checked after 24, 28 and 72 hours. The time required for a 100% knock-down action was determined. If the LT ₁₀₀ was not reached after 72 hours, the % of test animals which had been knocked down was ascertained.	15
20	The concentrations of the active compounds, synergistic agents and mixtures, and their actions, can be seen from the table which follows:	20

TABLE B

LT₁₀₀ Test with various pests

Active compound	Synergistic agent	Pest	Concentrations in % Active compound	Synergistic agent	LT ₁₀₀ in minutes (') or hours (hrs)
A		<i>Blattella germ. female</i> (normally sensitive)	0.008		24 hrs = 80%
A		<i>Blattella germ. female</i> (resistant)	0.008		24 hrs = 60%
	4	<i>Blattella germ. female</i> (normally sensitive)		1.0	24 hrs = 0%
A +	4	<i>Blattella germ. female</i> (normally sensitive)	0.008 +	0.008	60'
A +	4	<i>Blattella germ. female</i> (resistant)	0.008 +	0.04	6 hrs
A		<i>Tribolium conf.</i>	0.2		72 hrs = 50%
	4	<i>Tribolium conf.</i>		0.2	72 hrs = 0%
A	4	<i>Tribolium conf.</i>	0.04 +	0.04	72 hrs = 90%
A		<i>Dermeestes peruvian.</i>	0.04		72 hrs = 0%
	4	<i>Dermeestes peruvian.</i>		0.2	72 hrs = 0%
	L	<i>Dermeestes peruvian.</i>		0.2	72 hrs = 0%
A +	L	<i>Dermeestes peruvian.</i>	0.04 +	0.04	72 hrs = 20%
A +	4	<i>Dermeestes peruvian.</i>	0.04 +	0.04	24 hrs
A		<i>Attagenus piceus</i> larvae	0.2		72 hrs = 0%

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TABLE B (continued)

LT₁₀₀ Test with various pests

Active compound	Synergistic agent	Pest	Active compound	Concentration in % Synergistic agent	L.T ₁₀₀ in minutes (') or hours (hrs)
	4	<i>Attagenus piceus</i> larvae		0.2	72 hrs = 0%
	L	<i>Attagenus piceus</i> larvae		0.2	72 hrs = 0%
A +	L	<i>Attagenus piceus</i> larvae	0.2 +	0.2	72 hrs = 0%
A +	4	<i>Attagenus piceus</i> larvae	0.2 +	0.2	24 hrs
A		<i>Ornithodoros moubata</i> larvae	0.008		72 hrs = 80%
	L	<i>Ornithodoros moubata</i> larvae		1.0	72 hrs = 0%
A +	L	<i>Ornithodoros moubata</i> larvae	0.008 +	0.008	72 hrs
	2	<i>Ornithodoros moubata</i> larvae		1.0	72 hrs = 0%
A +	2	<i>Ornithodoros moubata</i> larvae	0.008 +	0.008	24 hrs
	3	<i>Ornithodoros moubata</i> larvae		1.0	72 hrs = 80%
A +	3	<i>Ornithodoros moubata</i> larvae	0.008 +	0.008	24 hrs
	38	<i>Ornithodoros moubata</i> larvae		1.0	72 hrs = 0%
A +	38	<i>Ornithodoros moubata</i> larvae	0.008 +	0.008	120'
	1	<i>Ornithodoros moubata</i> larvae		1.0	72 hrs = 0%
A +	1	<i>Ornithodoros moubata</i> larvae	0.008 +	0.008	150
	45	<i>Ornithodoros moubata</i> larvae		1.0	72 hrs = 0%
A +	45	<i>Ornithodoros moubata</i> larvae	0.008 +	0.008	105'

Example C.

Aerosol Test

Test animals: Male and female *Musca domestica*, Weymann's strain, which are resistant to phosphoric acid esters

Solvent: Acetone

To produce a suitable preparation of active compound, the active compounds were dissolved in the solvent.

A wire cage containing about 25 test animals was suspended in the middle of a gas-tight glass chamber of size 1 m³. When the chamber had again been closed, 2 ml of the active compound preparation were atomised therein. The condition of the test animals was constantly checked from outside, through the glass walls, and the time required for a 100% knock-down action on the animals was determined. After 60 minutes, the test animals were taken from the test chambers, transferred to an atmosphere free from the active compound, and again checked after 24 hours.

The active compounds, amounts of active compounds and times at which a 100% knock-down action was achieved, and the percentage of the animals which were dead after 24 hours, can be seen from the table which follows:

TABLE C

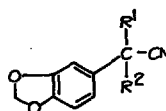
Aerosol test with female *Musca Domestica* (Weymann's strain) which are resistant to phosphoric acid esters

Active compound	Synergistic agent	Concentration in mg/m ³ of air		LT ₁₀₀ in minutes	% of dead animals after 24 hours	
Active compound	Synergistic agent	Active compound	Synergistic agent			
I		5		60 = 32%	40	
K		5		42' 13"	65	
	L		10	60 = 0%	0	
	37		10	60 = 0%	0	
I	L	5	5	60 = 0%	5	
I	37	5	5	60 = 68%	90	
K	37	5	5	33' 10"	100	
A		10		60 = 0%	0	
	L		10	60 = 0%	0	
	4		10	60 = 0%	0	
	3		10	60 = 0%	0	
	1		10	60 = 0%	0	
	37		10	60 = 0%	0	
A	L	10	+	10	60 = 0%	0
A	3	10	+	10	60 = 33%	90
A	1	5	+	5	60 = 93%	70
A	1	10	+	2.5	45' 23"	100
A	37	10	+	10	60 = 70%	100
A	37	10	+	2.5	60 = 63%	90
A	4	10	+	10	60 = 73%	10

Preparative Examples.

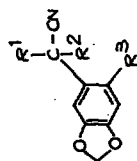
Alkylation of 3,4-methylenedioxyphenylacetonitrile:

1(a) 1.0 mole of 3,4-methylenedioxyphenylacetonitrile or 3,4-methylenedioxyphenyl- α -alkylacetonitrile was added dropwise to a suspension of 1.1 moles of potassium tert.-butylate in 1,500 ml of toluene at 25–30°C, whilst cooling slightly. The mixture was stirred for 30 minutes at 40–50°C and 1.1 moles of an alkyl halide were then added dropwise at 50°C, whilst cooling. The mixture was stirred for 3 hours under reflux and cooled, water was added, the organic phase was washed until neutral and dried over sodium sulphate. The solvent was stripped off and the residue was distilled *in vacuo*.



Example No.	Starting halide	R ¹	R ²	Yield (% of theory)	Boiling point °C/mm Hg
(1)	CH ₃ I	H	CH ₃	66	138/3
(2)	C ₂ H ₅ -Br	H	C ₂ H ₅	76	147–149/4
(3)	n-C ₃ H ₇ -Br	H	n-C ₃ H ₇	75	156/3
(4)	iso-C ₃ H ₇ -Br	H	iso-C ₃ H ₇	78	133/2–3
(5)	CH ₂ =CH-CH ₂ Br	H	-CH ₂ -CH=CH ₂	76	146/3
(6)		H	-CH ₂ -	73	206/3
(7)		H		46	134/1–2
(8)	2 CH ₃ I	CH ₃	CH ₃	85	134/4
(9)	C ₂ H ₅ -Br+CH ₃ I	CH ₃	C ₂ H ₅	70	138/3

The alkylation of the 6-alkyl-3,4-methylenedioxyphenylacetonitriles was carried out by methods analogous to that of 1(a)



Example No.	Starting halide	R ¹	R ²	R ³	Yield (%) of theory	Boiling point °C/mm Hg
10)	CH ₃ I	H	CH ₃	n-C ₃ H ₇	71	125/0.01
11)	C ₂ H ₅ Br	H	C ₂ H ₅	n-C ₃ H ₇	65	132/0.01
12)	n-C ₃ H ₇ Br	H	n-C ₃ H ₇	n-C ₃ H ₇	68	168/3
13)	iso-C ₃ H ₇ Br	H	iso-C ₃ H ₇	n-C ₃ H ₇	50	162/3
14)	CH ₂ =CH-CH ₂ Br	H	CH ₂ =CH-CH ₂	n-C ₃ H ₇	74	160/3
15)	-	H	H	tert.-C ₄ H ₉	68	138/0.01
16)	CH ₃ I	H	CH ₃	tert.-C ₄ H ₉	46	104
17)	C ₂ H ₅ Br	H	C ₂ H ₅	tert.-C ₄ H ₉	52	94
18)	n-C ₃ H ₇ Br	H	n-C ₃ H ₇	tert.-C ₄ H ₉	49	106
19)	iso-C ₃ H ₇ Br	H	iso-C ₃ H ₇	tert.-C ₄ H ₉	49	132/0.01
20)	-	H	H	CH ₃	62	145/3
21)	CH ₃ I	H	CH ₃	CH ₃	74	143/3
22)	C ₂ H ₅ Br	H	C ₂ H ₅	CH ₃	79	138/1
23)	n-C ₃ H ₇ Br	H	n-C ₃ H ₇	CH ₃	69	150/2
24)	iso-C ₃ H ₇ Br	H	iso-C ₃ H ₇	CH ₃	71	143/2
25)	-	H	H	CH ₃ -CH-CH ₃	61	110-112/0.1
26)	CH ₃ I	H	CH ₃	CH ₃ -CH-CH ₃	63	125/0.1

Example No.	Starting halide	R ¹	R ²	R ³	Yield (%) of theory	Boiling point °C/mm Hg
27)	C ₃ H ₇ Br	H	C ₂ H ₅	CH ₂ -CH=CH ₂	76	124/0.2
28)	n-C ₃ H ₇ Br	H	n-C ₃ H ₇	CH ₂ -CH=CH ₂	51	124/0.15
29)	iso-C ₃ H ₇ Br	H	iso-C ₃ H ₇	CH ₂ -CH=CH ₂	33	120/0.2
Example No.	Starting halide	R ¹	R ²	R ³	Yield (%) of theory	Boiling point °C/mm Hg melting-point °C
30)	-	H	H	-CH=CH-CH ₃	73	134/0.1 89
31)	CH ₃ I	H	CH ₃	-CH=CH-CH ₃	69	125/0.1
32)	C ₂ H ₅ Br	H	C ₂ H ₅	-CH=CH-CH ₃	64	141/0.7
33)	n-C ₃ H ₇ Br	H	n-C ₃ H ₇	-CH=CH-CH ₃	66	149/0.7
34)	iso-C ₃ H ₇ Br	H	iso-C ₃ H ₇	-CH=CH-CH ₃	67	129/0.1

1(b) By the phase-transfer catalyst method

- 5 1.0 mole of a dihalogenoalkane or alkyl halide or a dialkyl sulphate was added dropwise to a mixture of 1,000 ml of 50% strength sodium hydroxide solution, 1.0 mol of 3,4-methylenedioxyphenylacetonitrile and 10 g of a phase transfer catalyst (for example triethylbenzylammonium chloride) at 40-50°C. The mixture was stirred for 2 hours at 90°C, cooled, poured into 1,500 ml of ice-water and extracted with methylene chloride. The methylene chloride solution was washed until neutral and dried, the solvent was stripped off and the residue was distilled.
- 10

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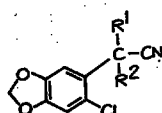
10

Example No.	Alkylating agent	Yield (%) of theory	Boiling point °C/mm Hg
35	Br-CH ₂ -CH ₂ -Br	19	130/3
36	Cl-CH ₂ -CH ₂ -CH ₂ -CH ₂ -Cl	58	155/3
37	(C ₂ H ₅ O) ₂ SO ₂	34	148/4

Halogenation of the 3,4-methylenedioxyphenyl- α -alkyl-acetonitriles

2(a) Chlorination with sulphuryl chloride

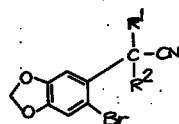
0.11 mole of sulphuryl chloride was added dropwise to 0.1 mole of a 3,4-methylenedioxyphenyl- α -alkylacetonitrile, dissolved in 100 ml of methylene chloride, at room temperature. The mixture was then stirred for 2 hours under reflux, cooled, washed with water, sodium bicarbonate solution and then with water until neutral and dried over calcium chloride. The solvent was stripped off and the residue was distilled or slightly distilled or recrystallised.



Example No.	R ¹	R ²	Yield (% of theory)	Boiling point °C/mm Hg melting point °C
37)	H	CH ₃	61	152/4
38)	H	C ₂ H ₅	91	158/4
39)	H	n-C ₃ H ₇	74	165/4
40)	H	iso-C ₃ H ₇	81	163/4
41)	CH ₃	CH ₃	83	162-165/4
42)	-CH ₂ -CH ₂ -CH ₂ -CH ₂ -		70	83
43)	H	CH ₂ -C ₆ H ₅	87	84
44)	CH ₃	C ₂ H ₅	72	150/4

(b) Bromination

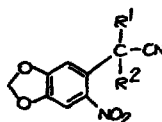
A solution of 0.105 mole of bromine in 10 ml of glacial acetic acid was added dropwise to a solution of 0.1 mole of a 3,4-methylenedioxyphenyl- α -alkylacetonitrile in 150 ml of glacial acetic acid at room temperature. The mixture was stirred for 4 hours at room temperature, poured into water and extracted with methylene chloride. The methylene chloride solution was washed with sodium bicarbonate solution and then with water until neutral and dried over calcium chloride. The solvent was stripped off and the solid residue was distilled or recrystallised.



Example No.	R ¹	R ²	Yield (% of theory)	Boiling point °C/mm Hg
45	H	CH ₃	55	158/4
46	H	C ₂ H ₅	54	158-160/3
47	H	n-C ₃ H ₇	45	160-164/4
48	H	iso-C ₃ H ₇	71	160/4
49	CH ₃	CH ₃	58	156/4

(3) Nitration

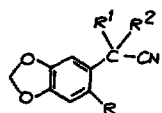
A mixture of 12 ml of concentrated sulphuric acid and 10 ml of nitric acid was added dropwise to 0.1 mole of a 3,4-methylenedioxyphenyl- α -alkyl-acetonitrile in 100 ml of glacial acetic acid at 20–30°C, whilst cooling slightly, and the mixture was stirred for 3 hours at room temperature and poured into ice-water. The working-up could be carried out by (a) filtering off the precipitate which had separated out, washing it until neutral and drying it, or (b) taking it up in methylene chloride, washing the methylene chloride solution with sodium bicarbonate solution and then with water until neutral and drying it, then stripping off the solvent and slightly distilling the remaining oil or triturating it with petroleum ether and filtering off and drying the solid yellow precipitate.



Example No.	R¹	R²	Physical data (melting point °C; refractive index; boiling point °C/mm Hg)	Yield (% of theory)
50)	H	CH₃	n _D ²⁰ : 1.5890	68
51)	H	H	114	85
52)	H	C₂H₅	n _D ²⁰ : 1.5757	60
53)	H	n-C₃H₇	196/4	81
54)	H	iso-C₃H₇	72	77
55)	CH₃	CH₃	126	74
56)	-CH₂-CH₂-CH₂-CH₂-		81	96
57)	H	-CH₂- 	161	87
58)	H	-CH₂-CH=CH₂	104	54

WHAT WE CLAIM IS:—

1. An arthropodocidal composition containing, as active compounds (1) a benzo-dioxole derivative of the general formula



(I)

in which

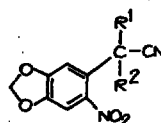
- R represents hydrogen, alkyl, alkenyl, halogen or nitro,
 R¹ represents alkyl or hydrogen, and
 R² represents aralkyl, alkyl, alkenyl or cycloalkyl or may represent hydrogen provided that R represents alkyl, alkenyl or nitro, or
 R¹ and R² together represent an alkylene radical,
 and (2) at least one compound selected from (A) carbamates, (B) carboxylic acid esters, including the natural and synthetic pyrethroids, and (C) phosphoric acid esters, alone or in admixture with a solid or liquid or liquefied gaseous diluent or carrier.



* C L M S *

(3) Nitration

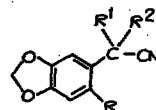
A mixture of 12 ml of concentrated sulphuric acid and 10 ml of nitric acid was added dropwise to 0.1 mole of a 3,4-methylenedioxyphenyl- α -alkyl-acetonitrile in 100 ml of glacial acetic acid at 20–30°C, whilst cooling slightly, and the mixture was stirred for 3 hours at room temperature and poured into ice-water. The working-up could be carried out by (a) filtering off the precipitate which had separated out, washing it until neutral and drying it, or (b) taking it up in methylene chloride, washing the methylene chloride solution with sodium bicarbonate solution and then with water until neutral and drying it, then stripping off the solvent and slightly distilling the remaining oil or triturating it with petroleum ether and filtering off and drying the solid yellow precipitate.



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55)	CH ₃	CH ₃	126	74
56)	-CH ₂ -CH ₂ -CH ₂ -CH ₂ -		81	96
57)	H	-CH ₂ -	161	87
58)	H	-CH ₂ -CH=CH ₂	104	54

WHAT WE CLAIM IS:—

1. An arthropodocidal composition containing, as active compounds (1) a benzo-dioxole derivative of the general formula



(I)

in which

R represents hydrogen, alkyl, alkenyl, halogen or nitro,

R¹ represents alkyl or hydrogen, andR² represents aralkyl, alkyl, alkenyl or cycloalkyl or may represent hydrogen provided that R represents alkyl, alkenyl or nitro, orR¹ and R² together represent an alkylene radical,

and (2) at least one compound selected from (A) carbamates, (B) carboxylic acid esters, including the natural and synthetic pyrethroids, and (C) phosphoric acid esters, alone or in admixture with a solid or liquid or liquefied gaseous diluent or carrier.

2. A composition according to claim 1, which contains a benzodioxole derivative of the formula (I)

in which

R represents hydrogen, chlorine, bromine, nitro or straight-chain or branched alkyl with 1 to 6 carbon atoms, or straight-chain or branched alkenyl with 2 to 6 carbon atoms,

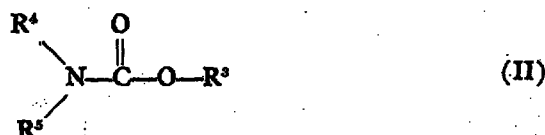
R¹ represents hydrogen or straight-chain or branched alkyl with 1 to 3 carbon atoms,

R² represents straight-chain or branched alkyl or alkenyl with up to 6 carbon atoms, cycloalkyl with 3 to 8 carbon atoms or benzyl or may represent hydrogen, provided that R represents nitro, alkyl or alkenyl, or

R¹ and R² together represent an alkylene radical with 2 to 8 carbon atoms.

3. A composition according to claim 1 or 2 which contains one or more compounds selected from

(A) carbamates of the general formula



in which

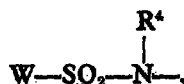
R³ represents aryl, a heterocyclic radical or an oxime radical,

R⁴ represents hydrogen or alkyl with 1-4 C atoms and

R⁵ represents alkyl or alkylcarbonyl with 1 to 6 C atoms in the alkyl radical [which can be optionally substituted by hydroxyl or methylthio] or the radical -S-Y,

wherein

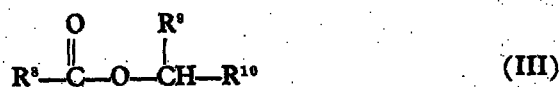
Y represents an aliphatic radical with 1-4 C atoms [which is optionally substituted by halogen], an aryl radical [which is optionally substituted by CN, halogen, methyl, trihalogenomethyl, trifluoromethylmercapto or NO₂], or methoxycarbonyl or the radical



wherein

W represents alkyl, halogenoalkyl, alkylamino or dialkylamino or an aryl radical [which is optionally substituted by halogen, trihalogenomethyl, CN, methyl or nitro],

(B) naturally occurring pyrethroids and carboxylic acid esters of the general formula



in which

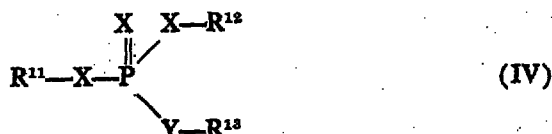
R⁸ represents alkyl, aralkyl, aryl or cycloalkyl, each of which can be optionally substituted,

R⁹ represents hydrogen, alkyl, halogenoalkyl, alkenyl, alkynyl or CN, and

R¹⁰ represents aryl or a heterocyclic radical, or

R⁹ and R¹⁰ together form an optionally substituted cyclopentenone ring,

and (C) phosphoric acid esters of the general formula



in which

each X, independently of one another, represents O or S,

Y represents O, S, -NH- or a direct bond between the central P atom and the radical R¹³,

R¹¹ and R¹², which may be identical or different, each represent alkyl or aryl and

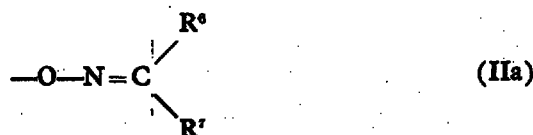
R¹³ represents alkyl, aryl, heteroaryl, aralkyl, alkenyl, dioxanyl or an oxime radical, or represents a radical identical to that to which it is bonded.



4. A composition according to claim 3 which contains one or more compounds selected from

(A) carbamates of the formula (II) in which

R^5 represents phenyl or naphthyl [either of which is optionally substituted by alkyl, alkenyl, alkoxy or alkylmercapto with up to 5 C atoms in each case, dialkylamino or dialkenylamino with up to 3 C atoms per alkyl or alkenyl part, halogen, dioxolanyl or the radical $-N=CH-N(C_{1-4}\text{-alkyl})_2$, or R^5 represents 2,3-dihydrobenzofuranyl, benzodioxole, benzothienyl, pyrimidinyl or pyrazolyl [each of which is optionally substituted by C_{1-4} -alkyl or dialkylamino with 1-4 C atoms per alkyl part], or R^5 represents an oxime radical of the general formula



in which

R^6 and R^7 , which may be identical or different, each represent alkyl, cycloalkyl, alkenyl, alkynyl, alkoxy, alkylmercapto, alkoxycarbonyl, carbonylamide or alkylmercaptoalkyl with up to 5 C atoms in each case, CN, aryl, an optionally substituted heterocyclic radical or alkyl which is substituted by a heterocyclic radical, or

R^6 and R^7 together form a dioxolanyl or dithiolanyl radical which is optionally substituted by C_{1-4} alkyl,

(B) carboxylic acid esters of the formula (III) in which

R^8 represents alkyl with 1-6 C atoms [which is optionally substituted by optionally halogen-substituted phenyl], cyclopropyl [which is optionally substituted by alkyl, alkenyl, halogenoalkyl or halogenoalkenyl with up to 6 C atoms in each case] or phenyl which is optionally substituted by halogen,

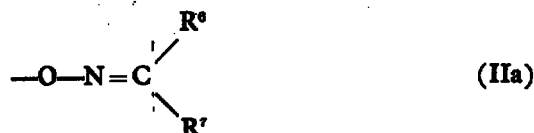
R^9 represents hydrogen, alkyl with 1-6 C atoms, halogenoalkyl with 1-4 C atoms and up to 3 halogen atoms, CN or ethynyl, and

R^{10} represents phenyl [which is optionally substituted by C_{1-4} -alkyl, halogen, optionally halogen- or methyl-substituted phenoxy or optionally substituted benzyl], furanyl, tetrahydrophthalimido or benzodioxole [any of which is optionally substituted by halogen, alkyl or alkenyl with up to 4 C atoms or benzyl] or cyclopentenone [which is optionally substituted by C_{1-4} -alkyl, furfuryl or C_{2-5} -alkenyl],

and (C) phosphoric acid esters of the formula (IV) in which

in which R^{11} and R^{12} , which may be identical or different, each represent C_{1-4} -alkyl or phenyl, and

R^{13} represents alkyl with 1-4 C atoms [which is optionally substituted by halogen, OH, CN, optionally halogen-substituted phenyl, carbonylamide, sulphonyl-alkyl, sulphoxyalkyl, carbonylalkyl, alkoxy, alkylmercapto or alkoxycarbonyl], alkenyl with up to 4 C atoms [which is optionally substituted by halogen, optionally halogen-substituted phenyl or alkoxycarbonyl] or an oxime radical of the general formula



wherein

R^6 and R^7 have the meanings stated above, or

R^{13} represents dioxanyl which is substituted by a radical identical to that to which R^{13} is bonded, or R^{13} represents a radical identical to that to which it is bonded, or R^{13} represents phenyl [which is optionally substituted by methyl, nitro, CN, halogen or methylmercapto], or R^{13} represents a hetero-aromatic structure that is optionally substituted by C_{1-4} -alkyl or halogen.

5. A composition according to claim 3, in which the component (2) is a compound selected from

(A) carbamates of the general formula (II)

in which

R³ represents an aryl or a heterocyclic radical,

R⁴ represents alkyl with 1—4 carbon atoms, and

R⁵ represents acetyl, —SCCl₂ or —SCF₃,

(B) carboxylic acid esters of the general formula (III)

in which

R⁸ represents alkyl or an alkyl-substituted or alkenyl substituted cyclopropyl ring,

R⁹ represents hydrogen or halogenoalkyl, and

R¹⁰ represents aryl (optionally substituted by halogen) or a heterocyclic radical,

and (C) phosphoric acid esters of the formula (IV)

in which

X and Y each represent oxygen,

R¹¹ and R¹² each represent alkyl with 1—4 C atoms and

R¹³ represents —CH=CHal, wherein Hal is a halogen atom.

6. A composition according to claim 1, in which the components (1) and (2) are selected from the compounds that are hereinbefore specifically mentioned.

7. A composition according to any of claims 1 to 6, in which the weight ratio of component (1) to component (2) is from 0.1:10 to 10:0.1.

8. A composition according to claim 7, in which the said weight ratio is from 0.5:1 to 3:1.

9. A composition according to any of claims 1 to 8 containing from 0.1 to 95% of the total active compounds, by weight.

10. A composition according to claim 1, substantially as described in any one of Examples A to C.

11. A method of combating arthropods which comprises applying to the arthropods, or to a habitat thereof, a composition according to any of claims 1 to 10.

12. A method according to claim 11 in which a composition is used containing from 0.0000001 to 100% of the total active compounds, by weight.

13. A method according to claim 12 in which a composition is used containing from 0.01 to 10% of the total active compounds, by weight.

14. A method according to claim 11, 12 or 13 in which the arthropods are insects or acarids.

15. 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 composition according to any of claims 1 to 10 was applied.

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

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* C L H S *