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(57) Abstract

Pesticidal compounds of formula (I), $R_ACR_3=CR_4CHDR_B$, in which formula R_A represents a group $ArCR_1R_2$ - in which Ar represents a phenyl or naphthyl group optionally substituted by one or more halogen, alkoxy, haloalkoxy, methylenedioxy, C_1-C_6 alkyl or haloalkyl groups; R_1 and R_2 together with the carbon to which they are attached represent a C_3-C_6 cycloalkyl group optionally substituted by one or more halogen atoms or C_1-C_6 alkyl groups. R_3 and R_4 which may be identical or differ, represent hydrogen halogen or C_1-C_6 alkyl groups and R_B represents the residue of an alcohol R_B CHDOH in which D is hydrogen or cyano and of which the [1R, *cis*]2,2-dimethyl-3-(2,2-dibromovinyl) cyclopropane carboxylic ester is significantly insecticidal, the configuration of R_A and $CHDR_B$ about the double bond being mutually *trans*, and processes for the production of compounds (I), intermediates, pesticidal compositions comprising (I), processes for the production thereof, methods for controlling pests, especially ricepests, in which such compounds are utilised and the use of compounds (I) for the manufacture of a pesticide.

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IMPROVEMENTS RELATING TO PESTICIDES

This invention relates to pesticides and in particular to pesticidal compounds, the production of such compounds, intermediates for use in their production, compositions containing such compounds and the use of such compounds and compositions for pest control.

Compounds have now been discovered formulations of which, whilst effective against a range of insect and other pests, are of particular interest for the control of infestation in rice crops.

Accordingly the present invention comprises a compound of formula I

$$R_ACR_3{=}CR_4CHDR_B$$

in which formula:

R_A represents a group $ArCR_1R_2$- in which Ar represents a phenyl or naphthyl group optionally substituted by one or more halogen, alkoxy, haloalkoxy, methylenedioxy, C_1-C_6 alkyl or haloalkyl groups;

R_1 and R_2 together with the carbon to which they are attached represent a C_3-C_6 cycloalkyl group optionally substituted by one or more halogen atoms or C_1-C_6 alkyl groups.

R_3 and R_4 which may be identical or differ, represent hydrogen, halogen or C_1-C_6 alkyl groups and

R_B represents the residue of an alcohol R_B CHDOH in which D is hydrogen or cyano and of which the [1R, *cis*]2,2-dimethyl-3-(2,2-dibromovinyl) cyclopropane carboxylic ester is significantly insecticidal,

the configuration of R_A and $CHDR_B$ about the double bond being mutually *trans*.

Although, desirably, methods for producing compounds I are such that the product is free from the structural isomer of formula II:

II $ArCR_1R_2CR_3HCR_4{=}CDR_B$

certain methods may give rise to a product contaminated with the isomer.

Although compound I is preferably substantially free from compound II, being contaminated by less than 10% and usually less than 1% thereof on a molar basis, higher levels of contamination may be tolerated, though it is unusual for more than 50% of compound II to be present.

Ar, is typically substituted phenyl and substitution is usually at the 3-(meta) and/or 4-(para)-position by fluorine, bromine, chlorine, a C_1-C_6 alkyl group e.g. methyl or tertbutyl, a C_1-C_6 alkoxy group e.g. methoxy, ethoxy, a halomethoxy or haloethoxy group, which may comprise one or more halogens, e.g. OCF_3, OCF_2H or halomethyl or haloethyl group e.g. CF_3. Ar generally carries no more than two substituents, and typically only one.

The substituents R_1 and R_2 , together with the carbon bearing them, typically represent a substituted or unsubstituted cyclopropyl group which, when substituted, preferably carries halogen and especially fluorine as in 2,2-difluorocyclopropyl.

When the compound of formula I is chiral (as in the immediately foregoing case) it can of course exist in different stereoisomeric forms. Both mixtures of stereoisomers and single stereoisomers are included within the scope of the present invention.

One or each of R_3 and R_4 typically represents hydrogen. When, however, one or both represent halogen, and in particular bromine chlorine or fluorine, fluorine is usually preferred.

R_BCHD may represent the residue of an alcohol of formula R_BCHDOH claimed or described in the specification for UK Patent No.1413491 which gives rise to significant insecticidal activity when esterified with [IR, cis]-2,2-dimethyl-3-(2,2-dibromovinyl) carboxylic acid. Potency towards houseflies is usually at least 5 relative to bioresmethrin = 100 and may be 10 or more.

Typically R_BCHD represents the residue of an alcohol R_BCHDOH which is a phenoxy, benzyl or benzoyl substituted benzyl alcohol. 3-Phenoxybenzyl and 4-fluoro-3-phenoxybenzyl residues are of particular interest.

The present invention includes within its scope a process for the production of a pesticide compound in which a compound comprising a moiety R_A and a compound comprising a moiety R_B are reacted together forming the link $-CR_3{=}CR_4CHD-$ between R_A and R_B in the product of formula I: $R_ACR_3{=}CR_4CHDR_B$. Typically the link is formed by a reaction of a known class.

Compounds of Formula I may be produced by a preferred process within the scope of the present invention, in which the product of a sterically hindered organoborane with a compound of formula $R_AC{\equiv}CH$ is catalytically coupled to a compound of formula R_BCHDX, the resultant reaction mixture being treated with an oxidising agent prior to isolation of the product of formula I. Typically, the organoborane is a sterically hindered mono or dialkyl borane e.g. disiamyl, dicyclohexyl, thexyl borane or is catechol borane, which is reacted with the ethynyl compound of formula $R_AC{\equiv}CH$ to give a product which is coupled to the compound of formula R_BCHDX (in which X represents halogen, e.g. bromine) in the presence of a palladium(0) catalyst e.g. trikis - or tetrakis(triphenylphosphine)-palladium(0).The oxidising agent added may be alkaline e.g. alkaline hydrogen peroxide. Palladium(0) catalysis is described in Tsuji,J., Organic Synthesis with Palladium Compounds, Pub. Springer-Verlag, Berlin, 1980 and this type of coupling reaction is described in Miyaura et al, Tetrahedron Letters Vol.21 pp.2865-2868. The production of sterically hindered boranes is described in Brown, H.C. Organic Syntheses via Boranes, J. Wiley & Sons, N.Y. 1975 Ch.III. Sterically hindered mono-and dialkyl boranes may be produced by reaction of a complex of borane and e.g. dimethyl sulphide, tetrahydrofuran or an amine for example a tertiary amine with a suitable alkene, such as in the case of disiamyl borane, 2-methyl-2-butene.

The procedure is shown in the following simplified scheme:-

$$ArCR_1CR_2CH_2OH \longrightarrow ArCR_1R_2CHO \longrightarrow ArCR_1R_2CH{=}CBr_2 \longrightarrow$$

$$ArCR_1R_2C{\equiv}CH \quad + R_BCHDX \longrightarrow ArCR_1R_2CH\overset{t}{=}CH.CHDR_B$$

Intermediates of formula $ArCR_1R_2C{\equiv}CH$ and complexes thereof with sterically hindered mono or dialkyl boranes or catechol borane and products of the compound R_BCHDX with a palladium(0) catalyst e.g. tetrakis(triphenylphosphine)palladium(0) are within the scope of the present invention.

In an alternative process within the scope of the present invention for producing a compound of formula I, a nucleophilic species of formula R_B^- is catalytically reacted with:-

(i) a compound of formula $R_ACR_3(CR_4{=}CH_2)OR$

or

(ii) a compound of formula $R_ACR_3\overset{t}{=}CR_4CHDQ$, in which formulae R_A R_3 and R_4 are as hereinbefore described, and

OR and Q represent good leaving groups.

Typically, the reaction is carried out in the presence of a transition metal catalyst which is preferably a copper salt or a complex thereof with a lithium salt

The nucleophilic species R_B^- is generally present in the form of a Grignard reagent of formula R_BMgBr or an alkali metal compound e.g. R_BLi, and the leaving group is typically acyloxy e.g. acetoxy or tosyloxy especially when representing OR, in case (i) or halogen e.g. bromine or acyloxy particularly when representing Q in case (ii). The copper salt is usually cuprous and a halide e.g. a bromide or iodide or a cyanide, and the complex of formula $Li_2CuY_2Z_2$ wherein Y & Z represent chlorine, bromine, iodine or cyano. Transformations of type (ii) are described by E. Erdick in Tetrahedron, 1984, <u>40</u>, 641-657.

The following route illustrates a typical procedure, the transformation (b) of which is analagous to one described in Tetrahedron Letters 1982, 4669.

$$\mathrm{RCHO} \xrightarrow[(a)]{\mathrm{CH_2{=}CR_4MgBr}} \mathrm{R_ACR_3OH.CR_4{=}CH_2}$$

$$\mathrm{R_ACR_3OH.CR_4{=}CH_2} \xrightarrow[(b)]{\mathrm{aq.HCl\ or\ HBr}} \mathrm{R_ACR_3{=}CR_4CH_2Q(Q{=}Br\ or\ \ Cl)}$$

$$\mathrm{R_ACR_3{=}CR_4CH_2Q{+}}\underset{\mathrm{or\ R_BLi}}{\mathrm{R_BMgBr}} \xrightarrow[\mathrm{or\ Li_2CuCl_4}]{\mathrm{Cuhal(hal{=}halogen)\ or\ CuCN}} \mathrm{R_ACR_3{=}CR_4CH_2R_B}$$

or

$$\mathrm{R_ACR_3OH.CR_4{=}CH_2} \longrightarrow \mathrm{R_ACR_3OR.CR_4{=}CH_2}$$

$$\mathrm{R_ACR_3OR.CR_4{=}CH_2{+}}\ \underset{\mathrm{or\ R_BLi}}{\mathrm{R_BMgBr}} \xrightarrow[\mathrm{or\ Li_2Cu_2CN_2}]{\mathrm{Cuhal(hal{=}halogen)}} \mathrm{R_ACR_3{=}CR_4CH_2R_B}$$

In the foregoing reaction scheme R_A typically represents 4-chlorophenyl or 4-ethoxyphenyl, R_3 and R_4 hydrogen, Q bromine and R_B 3-phenoxyphenyl or 4-fluoro-3-phenoxyphenyl.

Intermediates of formula $R_ACR_3=CR_4CHDQ$, $R_ACR_3OR.CR_4=CH_2$ and $R_ACR_3OH.CR_4=CH_2$ are also within the scope of the present invention.

In a yet further process within the scope of the present invention for the production of a compound I, an alcohol of formula $R_ACR_3=CR_4CHOHR_B$ is reduced, typically with a mixture of a trialkylsilane, such as triethylsilane, with a complex of boron trifluoride such as boron trifluoride etherate (e.g. diethyl etherate). Separation from the contaminating isomer $R_ACR_3HCR_4=CDR_B$ may be desirable or requisite. Typically R_3 R_4 and D represent hydrogen.

Compounds of formula $R_ACR_3=CR_4CDOHR_B$ may be produced, in accordance with the further aspect of the present invention, by treatment of compounds of formula $R_ACR_3=CR_4COR_B$ with a mild reducing agent, typically a mild hydride reducing agent such as sodium borohydride.

Intermediates of formula $R_ACR_3=CR_4CDOHR_B$ are further included within the scope of the present invention, R_3, R_4 and D typically representing hydrogen.

Compounds of formula I can be used to combat pest infestation in the domestic, horticultural or agricultural or medical, including veterinary, areas.

The present invention also includes within its scope a process for the production of a pesticidal composition which comprises formulating a compound of formula I with an inert carrier or diluent and compositions thereby produced. The compound of formula I in the composition is normally contaminated by less than 50% on a molar basis of the isomer II $ArCR_1R_2CR_3HCR_4=CDR_B$ and is preferably substantially free therefrom.

Compositions may be in the form of dusts and granular solids, wettable powders, mosquito coils and other solid preparations or as emulsions, emulsifiable concentrates, sprays and aerosols and other liquid preparations after the addition of appropriate solvents, diluents and surface-active agents.

Agriculturally and horticulturally applicable compositions, which require the active ingredient to possess significant photostability are of particular interest and especially compositions which are acceptable for application to crops, such as rice, which are cultivated in environments in which fish are exposed to the compound I. It will be appreciated that fish safety is of great importance in such applications and that suitable compositions should contain no fish-toxic ingredients.

The pesticidal compositions of the invention normally contain from 0.001 to 25% by weight of the compound of formula I but the compositions can contain higher concentrations of active ingredient of formula I e.g. up to 95% in compositions to be sold as concentrates for dilution before use by the ultimate user.

The compositions of the invention can, depending on the intended application, include diluents such as hydrocarbon oils, e.g. xylene or other petroleum fractions, water, anionic, cationic or non-ionic surface-active agents, anti-oxidants and other stabilisers as well as perfumes and colouring matters. These inert ingredients may be of the type and in proportions such as are conventionally used in pesticidal compositions containing pyrethroid-like compounds.

In addition to these inactive ingredients, the compositions of the present invention may contain one or more further active ingredients which may be other pesticidal compounds of the pyrethroid type or of other types and the composition may also include synergists particularly those of a type known to be capable of synergising the activity of natural pyrethrin and pyrethroid-like insecticides. Synergists of this type include piperonyl butoxide, tropital and sesamex.

Compounds of formula I may be applied in such a manner that pest infestation is diminished or prevented or both.

In accordance with a further aspect of the present invention, a method of pest control comprises treating a pest or a surface or environment susceptible to pest infestation with an effective amount of a compound of formula I

I $R_ACR_3{=}CR_4CHDR_B$

in which formula:-

R_A represents a group of formula $ArCR_1R_2-$ in which Ar represents a phenyl or naphthyl group optionally substituted by one or more halogen, alkoxy, haloalkoxy, methylenedioxy, C_1-C_6 alkyl or haloalkyl groups.

R_1 and R_2 together with the carbon to which they are attached represent jointly a C_3-C_6 cycloalkyl group optionally substituted by one or more halogen atoms or C_1-C_6 alkyl groups

R_3 and R_4, which may be identical or differ, represent hydrogen, halogen or C_1-C_6 alkyl groups;

R_B represents the residue or an alcohol R_BCHDOH in which D is hydrogen or cyano and of which the [1R, *cis*] 2,2-dimethyl-3-(2,2-dibromovinyl) cyclopropane carboxylic ester is significantly insecticidal;

the configuration of R_A and $CHDR_B$ about the double bond being mutually *trans*.

The compounds or compositions of the invention can be used as insecticides or acaricides for example in a domestic environment in spraying rooms to combat infestation with houseflies or other insects, they can be used for treatment of stored crops or cereals to combat infestation by insects or other pests, they can be used to spray growing crops, e.g. cotton to combat infestation by common pests and they can be used in the medical or veterinary field, e.g. as a cattle spray to prevent or treat infestation by insects or other pests.

It is envisaged, however, that the compounds and compositions of the present invention will be of especial interest for application to crops which are cultivated in environments in which fish are exposed to pesticides.

The present invention is of particular interest for controlling rice pests, particularly *Chilo* species such as *Chilo suppressalis*, the rice stem borer, *Nilaparvata lugens*, the brown plant hopper, *Nephotettix cincticeps*, the green rice leaf hopper and *Lissorhoptrus oryzophilus*, the rice water weevil. Other particular pests against which it is envisaged that the compounds and compositions of the present invention will find application include *Blattella* species such as *Blatella germanica*, the German cockroach, *Anthonomus grandis*, the Boll weevil, and Lepidopteran pests, particularly Lepidopteran pests other than *Heliothis* species such as *Spodoptera* species and especially Spodoptera exigua, the beet army worm.

The spectrum of effectiveness of the compounds of formula I is demonstrated by activity against mosquito larvae, houseflies, black bean aphids, red spider mite, and Spodoptera littoralis, especially against adult caterpillars. Ovicidal activity, including activity towards eggs of the red spider mite and of Spodoptera littoralis is of particular significance.

The present invention further includes within its scope the use of a compound of formula I for the manufacture of a pesticide, typically an insecticide or acaricide and in particular a pesticide for use in controlling rice pests.

The compounds are additionally of interest for the control of pests such as the following:-

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

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

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

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

from the order of the Thysanura, for example lepisma saccharine;

from the order of the Collembola, for example Onychiurus armatus;

from the order of the Orthoptera, for example Blatta orientalis, Periplaneta americana, Leucophaea madarae, Acheta domesticus, Cryllotalpa spp., Locusta migratoria migratorioides, Melanoplus differentialis and Schistocerca gregaria;

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

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

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

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

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

from the order of the Heteroptera, for example Eurygaster spp., Dysdercus intermedius, Piesma quadrata, Cimex lectularius, Rhodnius prolius 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, Lecanium corni, Saissetia oleae, Laodelphax striatellus, Aondiiella 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, Laphygma exigua, Mamestra brassicae, Panolis flammea, Prodenia litura, Trichoplusia ni, Carpocapsa pomonella, Fieris spp.,

Pyrausta nubilalis, Ephestia kuehniella, Galleria mellonella, Cacoecia podana, Capua reticulana, Choristoneura fumiferana, Clysia ambiguella, Homona magnanima and Tortrix viridana;

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

from the order of the Hymenoptera, for example Diprion spp., Hoplacampa 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 invention is illustrated by the following Examples:

Temperatures are in ^{o}C and refractive indices are measured at 20^{o}C.

EXAMPLE 1

1-(4-chlorophenyl)-1-(E-3-(phenoxyphenyl)-prop-1-enyl)-cyclopropane

A. 1-(4-chlorophenyl)-1-cyclopropanemethanal

(Compound a)

A mixture of 1-(4-chlorophenyl)-1-cyclopropanemethanol (7 g) pyridinium dichromate (21.7 g) and dichloromethane (200 ml) is stirred overnight at room temperature. Petroleum ether b.p. 40-60^{o}C (200 ml) is added and stirring continued for another 30 minutes. The mixture is filtered through a pad of celite and charcoal and the solvent is evaporated off under reduced pressure. The residue is distilled at 0.3 mm Hg and the main fraction, bp 73-75^{o}C consists of the required aldehyde, yield 5.2 g, n_D1.5532.

B. 1-(4-chlorophenyl(-1-(2,2-dibromovinyl)-cyclopropane

(Compound b)

To a stirred solution of dry carbon tetrabromide (11 g) in dry dichloromethane (200 ml) under nitrogen is added triphenylphosphine (17.4g). After 15 minutes 1-(4-chlorophenyl)-1-cyclopropanemethanal (3 g) dissolved in dichloromethane (10 ml) is added. The mixture is stirred for 2 hours at room temperature, poured onto saturated ammonium chloride solution and extracted with petroleum ether b.p.60-80°C (x3). The combined extracts are washed with water, dried and the solvent evaporated off under reduced pressure to give the required compound, yield 5.1 g, n_D1.5976

c. 1-(4-chlorophenyl)-1-ethynylcyclopropane

(Compound c)

To a stirred solution of 1-(4-chlorophenyl)-1-(2,2-dibromovinyl)-cyclopropane (1 g) in dry ether (50 ml) under nitrogen and cooled to -78°C, is added 1.6 M n-butyllithium (3.7 ml) over 15 minutes whilst maintaining the temperature below -60°C. After stirring for a further 5 minutes, 2 N aqueous hydrochloride acid (40 ml) is added and the mixture is allowed to warm up to room temperature. The mixture is extracted with ether (x3) filtered, dried and the solvent evaporated off under reduced pressure to give the required compound, yield 0.5 g n_D1.5460.

D. 1-(4-chlorophenyl)-1-(E-3-(3-phenoxyphenyl)-prop-1-enyl-cyclopropane

(Compound 1)

To a stirred solution of 2-methyl-2-butene (0.5 ml) in dry ether (2 ml) under nitrogen at 0°C, is added borane-methyl sulphide complex (1.15 ml of 2 M solution in ether) and the mixture stirred for 1 hour. A solution of 1-(4-chlorophenyl)-1-ethynylcyclopropane (0.4 g) in ether (5 ml) is added in one portion, stirred for 10 minutes and then allowed to warm to room temperature over 1 hour. The ether is then evaporated off at reduced pressure and the residue dissolved in dry benzene (10 ml) and kept under nitrogen.

In another flask, tetrakis (triphenylphosphine)palladium(0) (0.1g) is stirred under nitrogen in dry benzene (10 ml) and a solution of 3-phenoxybenzyl bromide (0.6 g) in dry benzene (10 ml) added over 10 minutes. To this mixture is then added the reagent prepared above followed by 2 M aqueous sodium hydroxide (2.3 ml) and the mixture is refluxed for about two hours. After cooling 3Maq. sodium hydroxide (1 ml) is added followed by 30% H_2O_2 (1 ml). After cessation of the exothermic reaction, the reaction mixture is stirred at room temperature for half an hour, poured onto water, and extracted with ether (x3). The combined extracts are washed with water, dried and the solvent removed under reduced pressure. The product is isolated by thin layer chromatography on silica eluting with neat petroleum ether b.p 40-60°C to yield 0.41 g, n_D 1.5988.

EXAMPLES 2-11

The following aldehydes are prepared as described in Example 1(A:)-

d. 1-(3,4-methylenedioxyphenyl)-1-cyclopropane methanal, n_D^{20}1.5545

e. 1-(4-ethoxyphenyl)-2,2-difluoro-1-cyclopropane methanal, n_D^{20}1,5063

The precursor for compound e is prepared as follows:-

1-(4-ethoxyphenyl)-2,2-difluorocyclopropane-1-methanol

To 1.0g of lithium aluminium hydride in 120 ml of dry ether, at room temperature is added dropwise 5.4g (0.02 moles) of ethyl-1-(4-ethoxyphenyl)-2,2-difluorocyclopropane-1-carboxylate in 20 ml of ether. The reaction mixture is stirred for 1 hr after which 1.0 ml of water 1.0 ml of 15% NaOH, followed by 3.0 ml of water are added. The solid precipitate is filtered off, washed with ether and the combined filtrates dried and concentrated under reduced pressure to yield (4.2g) a colourless oil; n_D1.5129

1-(4-ethoxyphenyl-1-cyclopropanemethanal (Reference f) is prepared as follows;-

1-cyano-1-(4-ethoxyphenyl)cyclopropane

To 7.5 ml (0.012 mol) of 1.7 M n-butyllithium in hexane, at room temperature, under an atmosphere of nitrogen, is added rapidly 10 ml of anhydrous tetrahydrofuran, followed by a solution of 4-ethoxyphenyl acetonitrile (0.8 g 0.005 mol) in 4 ml of tetrahydrofuran, during 5 minutes. The reaction mixture is stirred magnetically for 1 hour then treated with 0.50 g (0.005 mol) of 1,2-dichloroethane in 10 ml of tetrahydrofuran, during a period of 40 minutes (slow addition is important). After 16 hours, the mixture is hydrolysed by 10 ml of 3 N HCl and then taken up in ether, washed with water, sodium bicarbonate, water and dried over anhydrous sodium sulphate. The solvent is removed under reduced pressure. Yield: 0.64 g of a viscous semi-crystalline oil.

1-(4-ethoxyphenyl)-1-cyclopropane methanal

(Compound f)

To 0.625 g (0.0033 M) of 1-cyano-1-(4-ethoxyphenyl)cyclopropane in dry benzene (25 ml) and dry heptane (10 ml) at 0°C under an atmosphere of nitrogen, di-isobutylaluminium hydride in hexane (3.4 ml of 1M., 0.0033 mol) is added dropwise via a hypodermic syringe The mixture is stirred at 0°C for 3 hours, then allowed to warm to room temperature, poured onto saturated ammonium chloride and ice and is acidified with dil. H_2SO_4 then extracted with ether. The ethereal layer is washed with saturated sodium bicarbonate, saturated sodium chloride, and dried. The solvent is removed under reduced pressure and the aldehyde is purified by column chromatography on florisil with petroleum ether (b.p.60-80°C.) as eluant.

Yield: 0.42 g (n_D: 1.5342).

The above aldehydes are coverted to the corresponding dibromovinyl compounds by following the method of Example 1(B) to give:-

Compound

g 1-(2,2-dibromovinyl)-1-(4-ethoxyphenyl)cyclopropane, n_D^{20}1.5976

h 1-(2,2-dibromovinyl)-1-(3,4-methylenedioxyphenyl)cyclopropane, n_D^{20}1.5970

i 1-(2,2-dibromovinyl)-1-(4-ethoxyphenyl)-2,2-difluorocyclopropane, n_D^{20}1.5433

The following acetylenes are prepared by following the method of Example 1(C):-

Compound

j 1-(4-ethoxyphenyl)-1-ethynylcyclopropane,n_D^{20}1.5325

k 1-(3,4-methylenedioxyphenyl)-1-ethynylcyclopropane, n_D^{20}1.5569

kk 1-(4-ethoxyphenyl)-1-ethynyl-2,2-difluorocyclopropane, n_D^{20}1.5170

The following olefins are prepared by following the method of Example 1(D):-

Compound

2. 1-(4-chlorophenyl)-1-(E-3-(4-fluoro-3-phenoxyphenyl)-

prop-1-enyl)-cyclopropane, n_D^{20} 1.5805

3. 1-(4-ethoxyphenyl)-1-(E-3-phenoxyphenyl)-prop-1-enyl)-cyclopropane, n_D^{20} 1.5837
4. 1-(4-ethoxyphenyl)-1-(E-3-(4-fluoro-3-phenoxyphenyl)-prop-1-enyl)-cyclopropane, n_D^{20} 1.5799
5. 1-(3,4-methylenedioxyphenyl)-1-(E-3-(3-phenoxyphenyl)-prop-1-enyl)-cyclopropane, n_D^{20} 1,5969
6. 1-(3,4-methylenedioxyphenyl)-1-(E-3-(4-fluoro-3-phenoxyphenyl)-prop-1(E)-enyl)-cyclopropane n_D^{20} 1.5886
7. 1-(4-ethoxyphenyl)-1-(E-3-(3-phenoxyphenyl)-prop-1-enyl-2,2-difluorocyclopropane, n_D^{20} 1.5763
8. 1-(4-ethoxyphenyl)-1-(E-3-(4-fluoro-3-phenoxyphenyl)-prop-1-enyl)-2,2-difluorocyclopropane, n_D^{20} 1.5689

For production of compounds 7 and 8 the method of Example 1(D) is modified by diminishing the time the reaction mixture is exposed to alkaline hydrogen peroxide to five minutes.

EXAMPLE 9

A. 1-(4-chlorophenyl)-1-(E-3-(3-phenoxyphenyl)-prop-1-en-3-onyl)-cyclopropane

(Compound m)

A mixture of 1-(4-chlorophenyl)-1-cyclopropane methanal 1.80 g (0.01 M), 3-phenoxy-acetophenone 2.12 g (0.01M), and 3.0 g of potassium hydroxide in 25 ml of ethanol is stirred at room temperature for 2 hours. The reaction mixture is poured into 200 ml of water and extracted with ether. The ether extract is washed with water, dried and the solvent is removed under reduced pressure to give 4.1 g of crude 1-(4-chlorophenyl)-1-(E-3-(3-phenoxyphenyl)-prop-1-en-3-onyl)cyclopropane, which is purified by column chromatography on 100 g of florisil (eluant: petroleum ether (b.p.60-80°C) and ethyl acetate: 9/1) to give 3.04 g of the pure product, n_D 1.5943

B. 1-(4-chlorophenyl)-1-(E-3-(3-phenoxyphenyl)-prop-1-enyl)-cyclopropane and 1-(4-chlorophenyl)-1-(E-3-(3-phenoxyphenyl) prop-2-enyl)-cyclopropane

To 1.87 g (0.005 M) of 1-(4-chlorophenyl)-1-(E-3-(3-phenoxy phenyl)-1-prop-1-en-3-onyl)-cyclopropane in 30ml of ethanol is added 0.28 g (0.0075 mol, 1.5 mol eq.) of sodium borohydride and the mixture is stirred at room temperature for 3 hours. Water (20 ml) is then added, followed by dil HCl (25 ml) and the mixture is taken up in ether (150 ml). The ethereal layer is washed with sodium bicarbonate (x2) water (x3) and dried. The solvent is removed under reduced pressure to give the crude intermediate alcohol (1.88g.)

The alcohol (1.88g, 0.005 mol) and triethylsilane (0.87 g, 0.0075 mol, 1.5 mol eq) in 50 ml of dry dichloromethane are cooled using an acetone/solid carbon dioxide bath under an atmosphere of nitrogen. Dropwise addition of boron trifluoride etherate (0.77 g, 0.0055 mol.) gives a solution which is stirred until thin layer chromatography indicates that no alcohol is present and is then quenched by addition of ca. 15 ml of aqueous sodium bicarbonate. The cooling bath is removed and the solution allowed to warm to room temperature with vigorous stirring. The mixture is transferred to a separating funnel, ether (100 ml) is added and the whole washed with bicarbonate (50 ml) and water (x2). Drying and removal of the solvents affords an oil. Purification by column chromatography on florisil using petroleum ether (b.p 60-80°C) as eluant yields 1.02 g of an oil, a 3:7 mixture of the two olefins. They are separated using petroleum ether (b.p. 40-60°C) as eluant by thin layer chromatography on silica, the plate being developed three times. 1-(4-chlorophenyl)-1-(E-3-(3-phenoxy-phenyl) prop-1-enyl)-cylopropane (n_D: 1.5988, yield; 0.18 g,rf: 0.36) (Compound 1) and 1-(4-chlorophenyl)-1-(E-3-(3-phenoxyphenyl)-prop-2-enyl)-cyclopropane (n_D: 1.5686, yield:: 0.53 g,rf: 0.4) are both colourless viscous oils.

EXAMPLE 10

A. 1-(4-chlorophenyl)-1-(1-hydroxyprop-2-enyl)cyclopropane (compound n)

To a stirred solution of 1-(4-chlorophenyl)-1-cyclopropane-methanol (1.8 g) in dry tetrahydrofuran (60 ml) at -78°C is added IM vinylmagnesium bromide (12 ml) in tetrahydrofuran over 10 mins. The mixture is then allowed to warm to -20°C and saturated aqueous ammonium chloride added (30 ml). The mixture is concentrated under reduced pressure, and extracted with ether (x3). The combined extracts are dried and the solvent evaporated under reduced pressure to the required compound, 3 g, n_D 1.5523.

B <u>1-(4-chlorophenyl)-1-(E-3-bromoprop-1-enyl)cyclopropane</u> (Compound 0)

To a stirred solution of 1-(4-chlorophenyl)-1-(1-hydroxyprop-2-enyl)cyclopropane (2 g) in petroleum ether b.pt 60-80°C(100ml) is added 48% aqueous hydrobromic acid (30 ml) whilst maintaining the temperature between - 20°C and - 10°C. After ½h, water (100 ml) is added and the mixture extracted with petroleum ether b.p.60-80°C (x3). The combined extracts are washed with water, saturated sodium bicarbonate, dried and the solvent evaporated off under reduced pressure to give the required compound, 2.8g, n_D 1.5678.

C <u>1-(4-chlorophenyl)-1-(E-3-(3-phenoxyphenyl)-prop-1-enyl)-cyclopropane</u>

A Grignard reagent is prepared at 20°C by reacting 3-phenoxyphenyl bromide (0.3 g) and dry magnesium turnings (0.26g) in dry ether (4 ml) and cooled to -78°C. Cuprous bromide (0.03g) is added followed by a solution of 1-(4-chlorophenyl)-1-(E-3-bromoprop-1-enyl) cyclopropane (0.28g) in dry tetrahydrofuran (4 ml) added over 3 min. The mixture is stirred at -78°C for 5 min and then allowed to warm to room temperature over 15h. Saturated aqueous ammonium chloride solution (10 ml) is added and the mixture extracted with ether (x3), washed with water, dried and the solvent evaporated under reduced pressure. The residue is purified by thin layer chromatography, eluting with petroleum ether b.p. 60-80°C. Yield 0.3g.

Pesticidal activity is assessed against houseflies and mustard beetles by using the following techniques:-

Houseflies (Musca domestica)

Female flies are treated on the thorax with a one microlitre drop of insecticide dissolved in acetone. Two replicates of 15 flies are used at each dose rate and 6 dose rates are used per compound under test. After treatment, the flies are maintained at a temperature of $20^{o} \pm 1^{o}$ and kill is assessed 24 and 48 hours after treatment. LD_{50} values are calculated in micrograms of insecticide per fly and relative toxicities are calculated from the inverse ratios of the LD_{50} values (see Sawicki et al, Bulletin of the World Health Organisation, 35, 893, (1966) and Sawicki et al, Entomologia and Exp. Appli. 10 253, (1967)).

Mustard beetles (Phaedon cochleariae Fab)

Acetone solutions of the test compound are applied ventrally to adult mustard beetles using a micro drop applicator. The treated insects are maintained for 48 hours after which time kill is assessed. Two replicates of 40 to 50 mustard beetles are used at each dose level and 5 dose levels are used for each compound. LD_{50} values and thence relative potencies are calculated as for houseflies.

For both insect species relative potencies are calculated by comparison with 5-benzyl-3-furylmethyl (IR)-trans-chrysanthemate (Bioresmethrin) which is one of the more toxic chrysanthemate esters known to houseflies and mustard beetle, its toxicity being about 24 times that of allethrin to houseflies and 65 times that of allethrin to mustard beetles.

Results

Relative potencies to Houseflies and Mustard Beetles (Bioresmethrin = 100) are given under HF and MB respectively in the Table.

TABLE

Compounds of formula $ArCR_1R_2CR_3=CR_4CHDR_B$(3 POB=3-phenoxybenzyl; 4F3POB=4-Fluoro-3-phenoxybenzyl

Compound	Ar	CR_1R_2	R_3	R_4	Configuration about double bond	$-CHDR_B$	Bioassay Results HF	Bioassay Results MB
1	4-chlorophenyl	cyclopropyl	H	H	E	3POB	53	12
2	"	"	H	H	E	4F3POB	70	79
3	4-ethoxyphenyl	cyclopropyl	H	H	E	3POB	52	58
4	"	"	H	H	E	4F3POB	100	160
5	3,4-methylene dioxyphenyl	cyclopropyl	H	H	E	3POB	34	15
6	"	"	H	H	E	4F3POB	77	42
7	4-ethoxyphenyl	2,2-difluoro cyclopropyl	H	H	E	3POB	-	42
8	"	"	H	H	E	4F3POB		130

CLAIMS

1. A compound of formula I

I: $R_ACR_3=CR_4CHDR_B$

in which formula:

R_A represents a group $ArCR_1R_2$ - in which Ar represents a phenyl or naphthyl group optionally substituted by one or more halogen, alkoxy, haloalkoxy, methylenedioxy, C_1-C_6 alkyl or haloalkyl groups;

R_1 and R_2 together with the carbon to which they are attached represent a C_3-C_6 cycloalkyl group optionally substituted by one or more halogen atoms or C_1-C_6 alkyl groups.

R_3 and R_4 which may be identical or differ, represent hydrogen halogen or C_1-C_6 alkyl groups and

R_B represents the residue of an alcohol R_B CHDOH in which D is hydrogen or cyano and of which the [1R, cis]2,2-dimethyl-3-(2,2-dibromovinyl) cyclopropane carboxylic ester is significantly insecticidal,

The configuration of R_A and $CHDR_B$ about the double bond being mutually trans.

2. A compound according to Claim 1, which is substantially free from the isomer of formula II: $ArCR_1R_2CR_3HCR_4=CDR_B$

3. A compound according to Claim 1 or 2, in which Ar represents phenyl substituted at the 3-position or 4-position or at both the 3-and 4-positions.

4. A compound according to any of Claims 1 to 3, in which Ar is substituted by one or more C_1-C_6 alkoxy or C_1-C_6 alkyl groups or halogen or by a methylenedioxyphenyl group.

5. A compound according to any of Claims 1 to 4, in which Ar represents phenyl carrying no more than two substituents.

6. A compound according to Claim 5, in which Ar represents 4-chlorophenyl or 4-ethoxyphenyl.

7. A compound according to any of Claims 1 to 6, in which the cycloalkyl group is substituted or unsubstituted cyclopropyl.

8. A compound according to any of Claims 1 to 7, in which R_3 and R_4 each represent hydrogen.

9. A compound according to any of Claims 1 to 8, in which $ArCR_1R_2$ represents 4-chlorophenylcyclopropyl or 4-ethoxyphenylcyclopropyl.

10. A compound according to any of Claims 1 to 9, in which D represents hydrogen.

11. A compound according to any of Claims 1 to 10, in which R_BCHD represents the residue of a phenoxy, benzyl or benzoyl substituted benzyl alcohol.

12. A compound according to Claim 11, in which R_BCHD represents the residue of 3-phenoxybenzyl or 4-fluorophenoxybenzyl alcohol.

13. A compound according to any of Claims 1 to 12 which is 1-(4-chlorophenyl)-1-(E-3-(4-fluoro-3-phenoxyphenyl)-prop-1-enyl)-cyclopropane.

14. A compound according to any of Claims 1 to 12 which is 1-(4-ethoxyphenyl)-1-(E-3-(4-fluoro-3-phenoxyphenyl)-prop-1-enyl)-cyclopropane.

15. A compound according to any of Claims 1 to 12 which is 1-(4-chlorophenyl)-1-(E-3-(3-phenoxyphenyl)-prop-1-enyl-cyclopropane, 1-(4-ethoxyphenyl)-1-(E-3-phenoxyphenyl)-prop-1-enyl)-cyclopropane, 1-(3,4-methylenedioxyphenyl)-1-(E-3-(3-phenoxyphenyl)-prop-1-enyl)-cyclopropane, 1-(3,4-methylenedioxyphenyl)-1-(E-3-(4-fluoro-3-phenoxyphenyl)-prop-1(E)-enyl)-cyclopropane, 1-(4-ethoxyphenyl)-1-(E-3-(3-phenoxyphenyl)-prop-1-enyl-2,2-difluorocyclopropane, or 1-(4-ethoxyphenyl)-1-(E-3-(4-fluoro-3-phenoxyphenyl)-prop-1-enyl)-2,2-difluorocyclopropane.

16. A process for the production of a pesticidal compound in which a compound comprising a moiety R_A and a compound comprising a moiety R_B are reacted together forming the link $-CR_3=CR_4CHD-$between R_A and R_B in the product of formula I: $R_ACR_3=CR_4CHDR_B$ in which formula;

R_A represents a group $ArCR_1R_2$ - in which Ar represents a phenyl or naphthyl group optionally substituted by one or more halogen, alkoxy, haloalkoxy, methylenedioxy, C_1-C_6 alkyl or haloalkyl groups;

R_1 and R_2 together with the carbon to which they are attached represent a C_3-C_6 cycloalkyl group optionally substituted by one or more halogen atoms or C_1-C_6 alkyl groups;

R_3 and R_4 which may be identical or differ, represent hydrogen, halogen or C_1-C_6 alkyl groups and

R_B represents the residue of an alcohol R_B CHDOH in which D is hydrogen or cyano and of which the [1R, cis]2,2-dimethyl-3-(2,2-dibromovinyl) cyclopropane carboxylic ester is significantly insecticidal,

the configuration of R_A and $CHDR_B$ about the double bond being mutually trans.

17. A process according to Claim 16 in which the link is formed by a reaction of a known class.

18. A process according to Claim 16 in which the product from reacting a sterically hindered organoborane with a compound of formula $R_AC{\equiv}CH$ is catalytically coupled to a compound of formula R_BCHDX, the resultant reaction mixture being treated with an oxidising agent prior to isolation of the product of formula 1, X representing halogen.

19. A process according to Claim 18 in which the organoborane is a sterically hindered mono or dialkyl borane or catechol borane.

20. A process according to Claim 19 in which the organoborane is disiamyl, dicyclohexyl, or thexyl borane.

21. A process according to Claim 18, in which the Catalyst is a palladium(0) catalyst.

22. A process according to Claim 21 in which the catalyst is trikis - or tetrakis(triphenylphosphine)palladium(0).

23. A process according to Claim 16 for producing a compound of formula I in which a nucleophilic species of formula R_B^- is catalytically reacted with:-

(i) a compound of formula $R_ACR_3(CR_4{=}CH_2)OR$

or

(ii) a compound of formula $R_ACR_3\overset{t}{=}CR_4CHDQ$

in which formulae R_AR_3 and R_4 are as hereinbefore described,

and

OR and Q represent good leaving groups.

24. A process according to Claim 23 in which the catalyst is a transition metal catalyst.

25. A process according to Claim 24 in which the transition metal catalyst is a copper salt or a complex thereof with a lithium salt.

26. A process according to Claim 23, in which the nucleophilic species is provided by a Grignard reagent or an alkali metal compound.

27. A process according to Claim 23 in which the leaving group of formula OR is acyloxy or Q represents halogen or acyloxy.

28. A process according to Claim 23, in which the catalyst is a cuprous halide or cyanide or the catalyst is a complex of formula $Li_2CuY_2Z_2$ wherein Y & Z represent chlorine, bromine, iodine or cyano.

29. A process according to any of Claims 16 to 28, in which Ar represents phenyl substituted at the 3-position or 4-position or at both the 3-and 4-positions.

30. A process according to any of Claims 16 to 29 in which Ar is substituted by one or more C_1-C_6 alkoxy or C_1-C_6 alkyl groups or halogen or by a methylenedioxyphenyl group.

31. A process according to Claim 30, in which Ar represents phenyl carrying no more than two substituents.

32. A process according to Claim 31, in which Ar represents 4-chlorophenyl or 4-ethoxyphenyl.

33. A process according to any of Claims 16 to 32, in which the cycloalkyl group is substituted or unsubstituted cyclopropyl.

34. A process according to any of Claims 16 to 33, in which R_3 and R_4 each represent hydrogen.

35. A process according to any of Claims 16 to 34, in which Ar CR_1R_2 represents 4-chlorophenylcyclopropyl or 4-ethoxyphenylcyclopropyl.

36. A process according to any of Claims 16 to 35, in which D represents hydrogen.

37. A process according to any of Claims 16 to 36, in which R_BCHD represents the residue of a phenoxy, benzyl or benzoyl substituted benzyl alcohol.

38. A process according to Claim 37 in which R_BCHD represents the residue of 3-phenoxybenzyl or 4-fluorophenoxybenzyl alcohol.

39. A process according to any of Claims 16 to 38 in which 1-(4-chlorophenyl)-1-(E-3-(4-fluoro-3-phenoxyphenyl)-prop-1-enyl)-cyclopropane is produced.

40. A process according to any of Claims 16 to 38, in which 1-(4-ethoxyphenyl)-(E-3-(4-fluoro-3-phenoxyphenyl)-prop-1-enyl)-cyclopropane is produced.

41. A process according to any of Claims 16 to 38, in which 1-(4-chlorophenyl)-1-(E-3-(3-phenoxyphenyl)-prop-1-enyl-cyclopropane, 1-(4-ethoxyphenyl)-1-(E-3-phenoxyphenyl)-prop-1-enyl)-cyclopropane, 1-(3.4-methylenedioxyphenyl)-1-(E-3-(3-phenoxyphenyl)-prop-1-enyl)-cyclopropane, 1-(3,4-methylenedioxy-phenyl)-1-(E-3-(4-fluoro-3-phenoxyphenyl)-prop-1(E)-enyl-cyclopropane, 1-(4-ethoxyphenyl)-1-(E-3-(3-phenoxyphenyl)-prop-1-enyl-2,2-difluorocyclopropane, or 1-(4-ethoxyphenyl)-1-(E-3-(4-fluoro-3-phenoxyphenyl)-prop-1-enyl)-2,2-difluorocyclopropane. is produced.

42. An intermediate of formula $ArCR_1R_2C{\equiv}CH$ or a product from reaction thereof with a sterically hindered mono or dialkyl boranes or catechol borane, in which formula Ar represents a phenyl or naphthyl group optionally substituted by one or more halogen, alkoxy, haloalkoxy, methylenedioxy, C_1-C_6 alkyl or haloalkyl groups and R_1 and R_2 together with the carbon to which they are attached represent a C_3-C_6 cycloalkyl group optionally substituted by one or more halogen atoms or C_1-C_6 alkyl groups,

43. An intermediate according to Claim 42, in which Ar represents phenyl substituted at the 3-position or 4-position or at both the 3- and 4-positions.

44. An intermediate according to Claim 43, in which Ar is substituted by one or more C_1-C_6 alkoxy or C_1-C_6 alkyl groups or halogen or by a methylenedioxyphenyl group.

45. An intermediate according to Claim 44, in which Ar represents phenyl carrying no more than two substituents.

46. An intermediate according to Claim 45, in which Ar represents 4-chlorophenyl or 4-ethoxyphenyl.

47. An intermediate according to Claim 42, in which the cycloalkyl group is substituted or unsubstituted cyclopropyl.

48. An intermediate according to Claim 42, in which Ar CR_1R_2 represents 4-chlorophenylcyclopropyl or 4-ethoxyphenylcyclopropyl

49. An intermediate according to Claim 42, in which D represents hydrogen.

50. An intermediate produced by a reaction of a compound of formula R_BCHDX with a palladium(0) catalyst, wherein R_B represents the residue of an alcohol R_B CHDOH in which D is hydrogen or cyano and of which the [1R, cis]2,2-dimethyl-3-(2,2-dibromovinyl) cyclopropane carboxylic ester is significantly insecticidal.

51. An intermediate according to Claim 50, in which the palladium(0) catalyst is tetrakis(triphenyl phosphine)palladium(0).

52. An intermediate of formula $R_ACR_3\overset{t}{=}CR_4CHDQ$, $R_ACR_3OR.CR_4{=}CH_2$ or $R_ACR_3OH.CR_4{=}CH_2$ in which R_A represents a group $ArCR_1R_2$ - in which Ar represents a phenyl or naphthyl group optionally substituted by one or more halogen, alkoxy, haloalkoxy, methylenedioxy, C_1-C_6 alkyl or haloalkyl groups;

R_1 and R_2 together with the carbon to which they are attached represent a C_3-C_6 cycloalkyl group optionally substituted by one or more halogen atoms or C_1-C_6 alkyl groups,

R_3 and R_4 which may be identical or differ, represent hydrogen halogen or C_1-C_6 alkyl groups and D represents hydrogen or cyano and OR and Q represent good leaving groups.

53. An intermediate according to Claim 52, in which Q represents halogen, or acyloxy.

54. An intermediate according to Claim 52, in which OR represents acyloxy.

55. An intermediate according to Claim 52, in which Ar represent phenyl substituted at the 3-position or at both the 3-and 4-positions.

56. An intermediate according to Claim 52, in which Ar is substituted by one or more C_1-C_6 alkoxy or C_1-C_6 alkyl groups or halogen or by a methylenedioxyphenyl group.

57. An intermediate according to Claim 52, in which Ar represents phenyl carrying no more than two substituents.

58. An intermediate according to Claim 57, in which Ar represents 4-chlorophenyl or 4-ethoxyphenyl.

59. An intermediate according to Claim 52, in which the cycloalkyl group is substituted or unsubstituted cyclopropyl.

60. An intermediate according to Claim 52, in which R_3 and R_4 each represent hydrogen.

61. An intermediate according to Claim 52, in which Ar CR_1R_2 represents 4-chlorophenylcyclopropyl or 4-ethoxyphenylcyclopropyl.

62. An intermediate according to Claim 52, in which D represents hydrogen.

63. A process for the production of a compound I in which an alcohol of formula $R_ACR_3\overset{t}{=}CR_4CDOHR_B$ is reduced, R_A representing a group $ArCR_1R_2$ - in which Ar is a phenyl or naphthyl group optionally substituted by one or more halogen, alkoxy, haloalkoxy, methylenedioxy, C_1-C_6 alkyl or haloalkyl groups;

R_1 and R_2 together with the carbon to which they are attached representing a C_3-C_6 cycloalkyl group optionally substituted by one or more halogen atoms or C_1-C_6 alkyl groups;

R_3 and R_4 which may be identical or differ, representing hydrogen halogen or C_1-C_6 alkyl groups and

R_B represents the residue of an alcohol R_B CHDOH in which D is hydrogen or cyano and of which the [1R, cis]2,2-dimethyl-3-(2,2-dibromovinyl) cyclopropane carboxylic ester is significantly insecticidal,

64. A process according to Claim 63, in which reduction is effected by a mixture of a trialkylsilane with a complex of boron trifluoride.

65. A process according to Claim 63, in which Ar represents phenyl substituted at the 3-position or 4-position or at both the 3-and 4-positions.

66 A process according to Claim 63, in which Ar is substituted by one or more C_1-C_6 alkoxy or C_1-C_6 alkyl groups or halogen or by a methylenedioxyphenyl group.

67. A process according to Claim 63, in which Ar represents phenyl carrying no more than two substituents.

68. A process according to Claim 67, in which Ar represents 4-chlorophenyl or 4-ethoxyphenyl.

69. A process according to Claim 63, in which the cycloalkyl group is substituted or unsubstituted cyclopropyl.

70. A process according to Claim 63, in which R_3 and R_4 each represent hydrogen.

71. A process according to Claim 63, in which $ArCR_1R_2$ represents 4-chlorophenylcyclopropyl or 4-ethoxyphenylcyclopropyl

72. A process according to Claim 63, in which D represents hydrogen.

73. A process according to Claim 63, in which R_BCD represents the residue of a phenoxy, benzyl or benzoyl substituted benzyl alcohol.

74. A process according to Claim 63, in which R_BCD represents the residue of 3-phenoxybenzyl or 4-fluorophenoxybenzyl alcohol.

75. A process according to Claim 63, for the production of 1-(4-chlorophenyl)-1-(E-3-(4-fluoro-3-phenoxyphenyl)-prop-1-enyl)-cyclopropane.

76. A process according to Claim 63, for the production of 1-(4-ethoxyphenyl)-1-(E-3-(4-fluoro-3-phenoxyphenyl)-prop-1-enyl)-cyclopropane.

77. An intermediate of formula $R_ACR_3{=}CR_4CDOHR_B$, in which formula $R_AR_3R_4D$ & R_B are as defined in any of Claims 63 to 76.

78. A process for the production of a pesticidal composition which comprises formulating a compound of formula I: $R_ACR_3{=}CR_4CHDR_B$ with an inert carrier or diluent, in which formula

R_A represents a group $ArCR_1R_2$ - in which Ar represents a phenyl or naphthyl group optionally substituted by one or more halogen, alkoxy, haloalkoxy, methylenedioxy, C_1-C_6 alkyl or haloalkyl groups;

R_1 and R_2 together with the carbon to which they are attached represent a C_3-C_6 cycloalkyl group optionally substituted by one or more halogen atoms or C_1-C_6 alkyl groups;

R_3 and R_4 which may be identical or differ, represent hydrogen halogen or C_1-C_6 alkyl groups and

R_B represents the residue of an alcohol R_B CHDOH in which D is hydrogen or cyano and of which the [1R, *cis*]2,2-dimethyl-3-(2,2-dibromovinyl) cyclopropane carboxylic ester is significantly insecticidal, the configuration of R_A and $CHDR_B$ about the double bond being mutually trans.

79. A process according to Claim 78, in which the compound of formula I is substantially free from the isomer of formula II:

$ArCR_1R_2CR_3HCR_4=CDR_B$

80. A process according to Claim 78 or 79, in which Ar represents phenyl substituted at the 3-position or 4-position or at both the 3-and 4-positions in the compound of formula I

81. A process according to any of Claims 78 to 80, in which Ar is substituted by one or more C_1-C_6 alkoxy or C_1-C_6 alkyl groups or halogen or by a methylenedioxyphenyl group in the compound of formula I

82. A process according to any of Claims 78 to 81, in which Ar represents phenyl carrying not more than two substituents in the compound of formula I

83. A process according to any of Claims 78 to 82, in which Ar represents 4-chlorophenyl or 4-ethoxyphenyl in the compound of formula I

84. A process according to any of Claims 78 to 83, in which the cycloalkyl group is substituted or unsubstituted cyclopropyl in the compound of formula I

85. A process according to any of Claims 78 to 84, in which R_3 and R_4 each represent hydrogen in the compound of formula I

86. A process according to any of Claims 78 to 85, in which Ar CR_1R_2 represents 4-chlorophenylcyclopropyl or 4-ethoxyphenylcyclopropyl in the compound of formula I.

87. A process according to any of Claims 78 to 86, in which D represents hydrogen in the compound of formula I.

88. A process according to any of Claims 78 to 87, in which R_BCHD represents the residue of a phenoxy, benzyl or benzoyl substituted benzyl alcohol in the compound of formula I

89. A process according to Claim 88, in which R_BCHD represents the residue of 3-phenoxybenzyl or 4-fluorophenoxybenzyl alcohol in the compound of formula I.

90. A process according to any of Claims 78 to 89, in which the compound of formula I is 1-(4-chlorophenyl)-1-(E-3-(4-fluoro-3-phenoxyphenyl)-prop-1-enyl)-cyclopropane.

91. A process according to any of Claims 78 to 89, in which the compound of formula I is 1-(4-ethoxyphenyl)-1-(E-3-(4-fluoro-3-phenoxyphenyl)-prop-1-enyl)-cyclopropane.

92. A process according to any of Claims 78 to 89, in which the compound of formula I is 1-(4-chlorophenyl)-1-(E-3-(3-phenoxyphenyl)-prop-1-enyl-cyclpropane, 1-(4-ethoxyphenyl)-1-(E-3-(3-phenoxyphenyl)-prop-1-enyl)-cyclopropane, 1-(3,4-methylenedioxyphenyl)-1-(E-3-(3-phenoxyphenyl)-prop-1-enyl)-cyclopropane, 1-(3,4-methylene-dioxy-phenyl)-1-(E-3-(4-fluoro-3-phenoxyphenyl)-prop-1(E)-enyl)-cyclopropane, 1-(4-ethoxyphenyl)-1-(E-3-(3-phenoxyphenyl)-prop-1-enyl-2,2-difluorocyclopropane or 1-(4-ethoxyphenyl)-1-(E-3-(4-fluoro-3-phenoxyphenyl)-prop-1-enyl)-2,2-difluorocyclopropane.

93. A composition produced by formulating a compound of formula I with an inert carrier or diluent in accordance with any of Claims 78 to 92.

94. A composition according to Claim 93, which is substantially free from the isomer II: $ArCR_1R_2CR_3HCR_4{=}CDR_B$

95. A composition according to Claim 94, in the form of a dust, granular solid, wettable powder, mosquito coil, emulsion, emulsifiable concentrate, spray or aerosol.

96. A composition according to Claim 95 containing from 0.001 to 25% by weight of the compound of formula I.

97. A method of pest control which comprises treating a pest or a surface or environment susceptible to pest infestation with an effective amount of a compound of formula I

I $R_ACR_3{=}CR_4CHDR_B$

in which formula:-

R_A represents a group of formula $ArCR_1R_2$ - in which Ar represents a phenyl or naphthyl group otpionally substituted by one or more halogen, alkoxy, haloalkoxy, methylenedioxy, C_1-C_6 alkyl or haloalkyl groups.

R_1 and R_2 together with the carbon to which they are attached represent jointly a C_3-C_6 cycloalkyl group optionally substituted by one or more halogen atoms or C_1-C_6 alkyl groups.

R_2 and R_4, which may be identical or differ, represent hydrogen, halogen or C_1-C_6 alkyl groups;

R_B represents the residue or an alcohol R_BCHDOH in which D is hydrogen or cyano and of which the [1R, cis]2,2-dimethyl-3-(2,2-dibromovinyl)cyclopropane carboxylic ester is significantly insecticidal;

the configuration of R_A and $CHDR_B$ about the double bond being mutually trans.

98. A method according to Claim 97, in which the pest is a rice pest.

99. A method according to Claim 97 or 98 in which the compound of formula I is;

1-(4-chlorophenyl)-1-(E-3-(4-fluoro-3-phenoxyphenyl)-prop-1-enyl)-cyclopropane

or

1-(4-ethoxyphenyl)-1-(E-3-(4-fluoro-3-phenoxyphenyl)-prop-1-enyl)-cyclopropane.

100. A method according to Claim 97 or 98 in which the compound of formula I is 1-(4-chlorophenyl)-1-(E-3-(3-phenoxyphenyl)-prop-1-enyl-cyclopropane, 1-(4-ethoxyphenyl)-1-(E-3-(3-phenoxyphenyl)-prop-1-enyl)-cyclopropane, 1-(3,4-methylenedioxyphenyl)-1-(E-3-(3-phenoxyphenyl)-prop-1-enyl)-cyclopropane, 1-(3,4-methylenedioxyphenyl)-1-(E-3-(4-fluoro-3-phenoxyphenyl)-prop-1(E)-enyl)-cyclopropane, 1-(4-ethoxyphenyl)-1-(E-3-(3-phenoxyphenyl)-prop-1-enyl-2,2-difluorocyclopropane or 1-(4-ethoxyphenyl)-1-(E-3-(4-fluoro-3-phenoxyphenyl)-prop-1-enyl)-2,2-difluorocyclopropane.

101. The use of a compound of formula I for the manufacture of a pesticide.

102. The use of 1-(4-chlorophenyl)-1-(E-3-(4-fluoro-3-phenoxyphenyl)-prop-1-enyl)-cyclopropane for the manufacture of a pesticide.

103. The use of 1-(4-ethoxyphenyl)-1-(E-3-(4-fluoro-3-phenoxyphenyl)-prop-1-enyl)-cyclopropane for the manufacture of a pesticide.

104. The use of a compound according to any of Claims 101 to 103 for the manufacture of a pesticide effective against a rice pest.

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 85/00146

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC^4: C 07 C 43/29; C 07 C 43/285; C 07 D 317/50; C 07 C 25/24
C 07 C 43/215; C 07 C 43/295; C 07 C 33/50; A 01 N 31/14 ./.

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC^4	C 07 C 25/00 C 07 C 33/00 C 07 C 43/00; C 07 D 317/00

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	EP, A, 0094085 (SUMITOMO CHEMICAL) 16 November 1983, see claims --	1-15,97-104
A	EP, A, 0104908 (COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION) 4 April 1984, see claims --	1-15,97-104
P,A	EP, A, 0125204 (CIBA-GEIGY) 14 November 1984, see claims --	1-15,97-104
P,A	WO, A, 84/04298 (CHEMINOVA) 8 November 1984, see claims --	1-15,97-104
A	Chemical Abstracts, volume 80, nr. 13, 1 April 1974, (Columbus, Ohio, US) R.R. Kostikov et al.:"Reactions of carbenes with conjugated di- and polyene compounds. VI. Reaction of dichlorocarbene with 2-aryl- 1,3- butadienes and 2-aryl-1-butenes"; & Zh. Org. Khim. 1973, 9(12), 2451-9 --	1-9
A	Tetrahedron Letters, volume 22, nr. 22, 1981,	

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report 26 AOUT 1985
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer G.L.M. Kruydenberg

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 85/00146

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC^4: A 01 N 43/30

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC^4	

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
	(Pergamon Press Ltd, GB) J.W. Blunt et al.: "Cyclopropane derivatives from the lithium aluminium hydride reduction of methoxyalkynols", pages 2143-2144	1,2
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* Special categories of cited documents: [10]

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 30th July 1985	Date of Mailing of this International Search Report
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer G.L.M. Kruydenberg

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V.☒ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [1]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1.☐ Claim numbers ...., because they relate to subject matter not required to be searched by this Authority, namely:

2.☒ Claim numbers °°)........., because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

°°) searched incompletely: 1-10,16-36,63-72,77-87,93-98; The definition of R_B in claim 1 is unclear without reference to GB 1413491 cited on page 2 of the application (PCT Art. 6 and Rule 6.2a)

not searched : 50,51; The nature of the intermediates claimed in claims 50 and 51 is also unclear.

3.☐ Claim numbers.........., because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI.☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [2]

This International Searching Authority found multiple inventions in this international application as follows:

1.☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2.☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3.☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4.☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/GB 85/00146 (SA 9441)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 13/08/85

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0094085	16/11/83	JP-A- 58198430	18/11/83
		JP-A- 59108733	23/06/84
EP-A- 0104908	04/04/84	WO-A- 8401147	29/03/84
		EP-A- 0120037	03/10/84
EP-A- 0125204	14/11/84	AU-A- 2674584	18/10/84
		JP-A- 59196836	08/11/84
WO-A- 8404298	08/11/84	AU-A- 2827884	19/11/84
		EP-A- 0143806	12/06/85

For more details about this annex :
see Official Journal of the European Patent Office, No. 12/82