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SPRUSON & FERGUSON

AUSTRALIA

PATENTS ACT 1990

PATENT REQUEST: STANDARD PATENT

I/We, the Applicant(s)/Nominated Person(s) specified below, request I/We be granted a patent for the invention disclosed in the accompanying standard complete specification.

[70,71] Applicant(s)/Nominated Person(s):

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[54] Invention Title:

Dioxolane Derivatives

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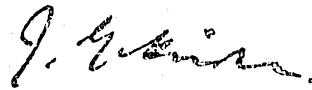
[32] Application Date:

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Ciba-Geigy AG

By:



Registered Patent Attorney

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Australia

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NOTICE OF ENTITLEMENT

I, John David O'Connor, of 31 Market Street, Sydney, New South Wales, 2000, Australia,
patent attorney for the Applicant/Nominated Person in respect of an application entitled

Dioxolane Derivatives

state the following:-

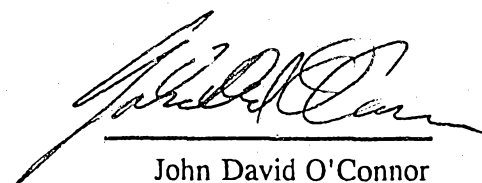
The Applicant/Nominated Person has entitlement from the actual inventor as follows:-

The Applicant/Nominated Person is the assignee of the actual inventor.

The Applicant/Nominated Person is the applicant of the basic application listed on the Patent Request.

The basic application listed on the Patent Request is the application first made in a Convention Country in respect of the invention.

Dated 26 February 1993



John David O'Connor



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(54) Title
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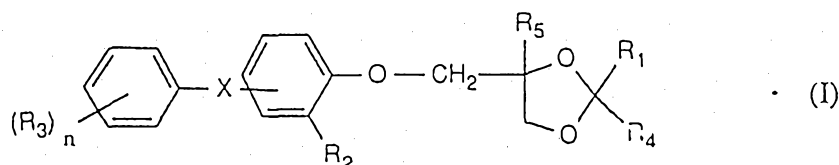
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(56) Prior Art Documents
US 4971981

(57) Claim

1. A compound of the formula



in which:

n is 0, 1 or 2, and, if n is 2, the two radicals R₃ are identical or different;

either R₁ is C₁-C₆alkyl, halo-C₁-C₃alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₃alkoxy or C₃-C₆cycloalkyl and R₄ is hydrogen or C₁-C₃alkyl, or R₁ and R₄ together with the carbon atom to which R₁ and R₄ are bonded are a ring having 4, 5 or 6 ring members, and the ring skeleton, which may contain a carbon-carbon double bond, is composed either only of carbon atoms or of 1 oxygen atom and 3, 4 or 5 carbon atoms, and the ring is unsubstituted or mono- or disubstituted by identical or different C₁-C₃alkyl radicals;

R₂ is C₁-C₃alkyl, halo-C₁-C₃alkyl, C₁-C₃alkoxy, halo-C₁-C₃alkoxy, fluorine, chlorine or bromine;

R₃ is C₁-C₃alkyl, halo-C₁-C₃alkyl, C₁-C₃alkoxy, halo-C₁-C₃alkoxy, fluorine, chlorine or bromine;

R₅ is hydrogen or C₁-C₃alkyl and

X is methylene, O, S or C(=O).

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15. A pesticide, which comprises at least one compound according to claim 1 as active ingredient and at least one adjuvant.

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COMPLETE SPECIFICATION

FOR A STANDARD PATENT

ORIGINAL

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Invention Title:

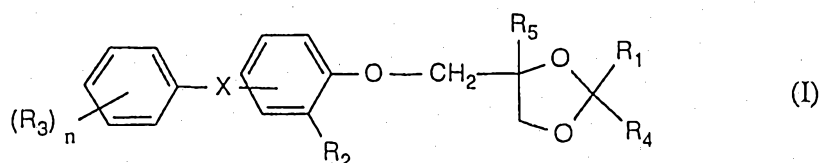
Dioxolane Derivatives

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

PI/5-19006/A

Dioxolane derivatives

The invention relates to compounds of the formula



in which:

- 5 n is 0, 1 or 2, and, if n is 2, the two radicals R_3 are identical or different;
either R_1 is C_1 - C_6 alkyl, halo- C_1 - C_3 alkyl, C_2 - C_4 alkenyl, C_2 - C_4 alkynyl, C_1 - C_3 alkoxy or C_3 - C_6 cycloalkyl and R_4 is hydrogen or C_1 - C_3 alkyl, or R_1 and R_4 together with the carbon atom to which R_1 and R_4 are bonded are a ring having 4, 5 or 6 ring members, and the ring skeleton, which may contain a carbon-carbon double bond, is composed either only of 10 carbon atoms or of 1 oxygen atom and 3, 4 or 5 carbon atoms, and the ring is unsubstituted or mono- or disubstituted by identical or different C_1 - C_3 alkyl radicals;
 R_2 is C_1 - C_3 alkyl, halo- C_1 - C_3 alkyl, C_1 - C_3 alkoxy, halo- C_1 - C_3 alkoxy, fluorine, chlorine or bromine;
 R_3 is C_1 - C_3 alkyl, halo- C_1 - C_3 alkyl, C_1 - C_3 alkoxy, halo- C_1 - C_3 alkoxy, fluorine, chlorine or 15 bromine;
 R_5 is hydrogen or C_1 - C_3 alkyl and
 X is methylene, O, S or $C(=O)$,
to a process for the preparation and to the use of these compounds, to pesticides whose active ingredient is selected from these compounds, to a process for the preparation and to 20 the use of these compositions and to intermediates for the preparation of the compounds of the formula I.

Unless otherwise defined, the general terms used hereinbefore and hereinafter are as defined below.

The halogen atoms which are suitable as substituents of haloalkyl and haloalkoxy are

fluorine and chlorine as well as bromine and iodine, with fluorine, chlorine and bromine being preferred.

Carbon-containing groups and compounds contain, unless otherwise defined, in each case preferably 1 up to and including 4, in particular 1 or 2, carbon atoms.

5 C₃-C₆Cycloalkyl is cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl.

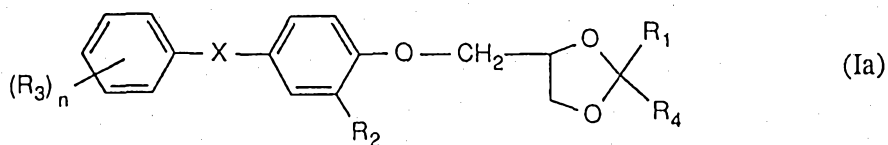
Alkyl - as a group per se and as a structural element of other groups and compounds such as alkoxy, haloalkyl and haloalkoxy - is, in each case with due consideration of the specific number of carbon atoms in the respective group or compound, either straight-chain or branched and methyl, ethyl, propyl, isopropyl, butyl, isobutyl, 10 sec-butyl or tert-butyl, or pentyl, hexyl, octyl or in each case one of their isomers. Preferred alkyl groups R₁ are C₁-C₃alkyl groups, in particular C₂-C₃alkyl groups.

Alkenyl and alkynyl contain one or more, preferably not more than two, unsaturated carbon-carbon bonds. Examples which may be mentioned are vinyl, allyl, methallyl, prop-1-en-1-yl, 2-methyl-prop-1-en-1-yl, but-2-en-1-yl, ethynyl, propargyl, prop-1-yn-1-yl 15 and but-1-yn-1-yl.

Halogen-substituted groups, i.e. haloalkyl and haloalkoxy, can be part-halogenated or perhalogenated. Examples of haloalkyl - as a group per se and as a structural element of other groups and compounds such as haloalkoxy - are methyl which is monosubstituted to trisubstituted by fluorine, chlorine and/or bromine, such as CHF₂ or CF₃; ethyl which is 20 monosubstituted to pentasubstituted by fluorine, chlorine and/or bromine, such as CH₂CF₃, CF₂CF₃, CF₂CCl₃, CF₂CHCl₂, CF₂CHF₂, CF₂CFCl₂, CF₂CHBr₂, CF₂CHClF, CF₂CHBrF or CClFCHClF; and propyl or isopropyl, each of which is monosubstituted to heptasubstituted by fluorine, chlorine and/or bromine, such as CH₂CHBrCH₂Br, CF₂CHFCF₃, CH₂CF₂CF₃ or CH(CF₃)₂.

25 The following are preferred within the scope of the invention:

(1) Compounds of the formula



in which:

n is 0, 1 or 2, and, if n is 2, the two radicals R_3 are identical or different;

R_1 is C_1 - C_4 alkyl, vinyl or cyclopropyl;

5 R_2 is methyl or chlorine;

R_3 is methyl, fluorine or chlorine;

R_4 is hydrogen or methyl and

X is oxygen or methylene;

(2) Compounds of the formula Ia in which X is oxygen, in particular those in which X is oxygen and R_2 is chlorine, very particularly those in which X is oxygen, R_2 is chlorine and R_4 is hydrogen, especially those in which X is oxygen, R_2 is chlorine, R_4 is hydrogen and R_1 is C_1 - C_4 alkyl;

(3) Compounds of the formula Ia in which R_2 is chlorine;

(4) Compounds of the formula Ia in which R_4 is hydrogen, in particular those in which R_4 is hydrogen and X is oxygen;

(5) Compounds of the formula Ia in which R_1 is C_1 - C_4 alkyl, in particular those in which R_1 is C_1 - C_4 alkyl and X is oxygen, especially those in which R_1 is C_1 - C_4 alkyl, X is oxygen and R_2 is chlorine;

(6) Compounds of the formula Ia according to the above-defined groups (1) to (5) in which n is 0, 1 or 2 and R_3 is fluorine or chlorine, in particular those in which n is 1 or 2 and R_3 is fluorine or chlorine, especially those in which n is 1 and R_3 is fluorine or chlorine;

(7) Compounds of the formula Ia according to the above-defined groups (1) to (6) in which n is 1 and the radical R_3 is bonded in the 3- or 4-position, or n is 2 and the radicals R_3 are bonded in the 2,4-, 3,4- or 3,5-position, in particular those in which n is 1 and the radical R_3 is bonded in the 3-position, or n is 2 and one of the radicals R_3 is bonded in the

3-position, especially those in which n is 1 and the radical R₃ is bonded in the 3-position, or n is 2 and the radicals R₃ are bonded in the 3,4- or 3,5-position;

(8) Compounds of the formula Ia in which X is methylene, R₂ is chlorine and R₄ is hydrogen, in particular those in which X is methylene, R₂ is chlorine, R₄ is hydrogen and
5 R₁ is C₁-C₄alkyl;

(9) Compounds of the formula Ia according to the above-defined group (8) in which n and R₃ are as defined in the above-defined groups (6) and (7);

(10) Compounds of the formula I in which R₅ is hydrogen;

(11) Compounds of the formula I in which the (R₃)_nC₆H_{5-n}X group is bonded in the
10 para-position relative to R₂ or to the dioxolanylmethoxy group, in particular in the para-position relative to the dioxolanylmethoxy group;

(12) Compounds of the formula I in which the two radicals R₁ and R₄ are not linked to one another.

Particularly preferred within the scope of the invention are the compounds of the formula I
15 which are mentioned in Examples H3 and H4.

Individually preferred within the scope of the invention are the following compounds of the formula I:

4-(2-chloro-4-phenoxyphenoxymethyl)-2-ethyl-1,3-dioxolane;

4-(2-chloro-4-phenoxyphenoxymethyl)-2-propyl-1,3-dioxolane;

20 4-(2-chloro-4-phenoxyphenoxymethyl)-2-isopropyl-1,3-dioxolane;

4-(2-chloro-4-phenoxyphenoxymethyl)-2-cyclopropyl-1,3-dioxolane;

4-[2-chloro-4-(3-fluorophenoxy)phenoxymethyl]-2-ethyl-1,3-dioxolane;

4-[2-chloro-4-(3-fluorophenoxy)phenoxymethyl]-2-propyl-1,3-dioxolane;

4-[2-chloro-4-(3-fluorophenoxy)phenoxymethyl]-2-isopropyl-1,3-dioxolane;

25 4-[2-chloro-4-(3-fluorophenoxy)phenoxymethyl]-2-cyclopropyl-1,3-dioxolane;

4-[2-chloro-4-(3-chlorophenoxy)phenoxymethyl]-2-ethyl-1,3-dioxolane;

4-[2-chloro-4-(3-chlorophenoxy)phenoxymethyl]-2-propyl-1,3-dioxolane;

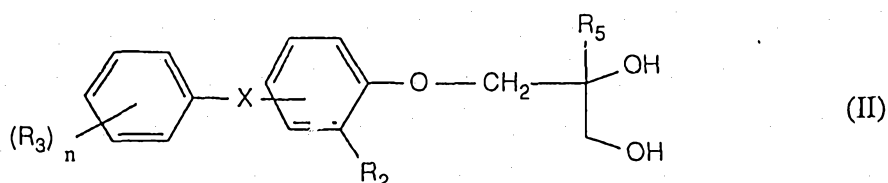
4-[2-chloro-4-(3-chlorophenoxy)phenoxymethyl]-2-isopropyl-1,3-dioxolane;

4-[2-chloro-4-(3,5-difluorophenoxy)phenoxymethyl]-2-ethyl-1,3-dioxolane;

- 4-[2-chloro-4-(3,5-difluorophenoxy)phenoxyethyl]-2-propyl-1,3-dioxolane;
 4-[2-chloro-4-(3,5-difluorophenoxy)phenoxyethyl]-2-isopropyl-1,3-dioxolane;
 4-[2-chloro-4-(3,4-dichlorophenoxy)phenoxyethyl]-2-ethyl-1,3-dioxolane;
 4-[2-chloro-4-(3-chloro-4-fluorophenoxy)phenoxyethyl]-2-ethyl-1,3-dioxolane;
 5 4-(2-chloro-4-benzylphenoxyethyl)-2-ethyl-1,3-dioxolane;
 4-(2-chloro-4-benzylphenoxyethyl)-2-propyl-1,3-dioxolane;
 4-(2-chloro-4-benzylphenoxyethyl)-2-isopropyl-1,3-dioxolane;
 4-(2-chloro-4-benzylphenoxyethyl)-2-cyclopropyl-1,3-dioxolane;
 4-[2-chloro-4-(3-fluorobenzyl)phenoxyethyl]-2-ethyl-1,3-dioxolane;
 10 4-[2-chloro-4-(3-fluorobenzyl)phenoxyethyl]-2-propyl-1,3-dioxolane;
 4-[2-chloro-4-(3,5-difluorobenzyl)phenoxyethyl]-2-ethyl-1,3-dioxolane and
 4-[2-chloro-4-(3,4-dichlorobenzyl)phenoxyethyl]-2-ethyl-1,3-dioxolane.

The invention also relates to the process for the preparation of the compounds of the formula I which comprises, for example,

- 15 a) reacting a compound of the formula

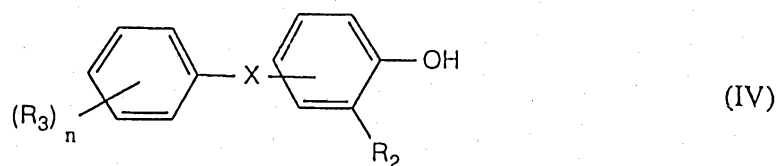


with a compound of the formula



preferably in the presence of an acidic catalyst, or

- 20 b) reacting a compound of the formula



with a compound of the formula



preferably in the presence of a base, or

5 c) reacting a compound of the formula II with a compound of the formula



preferably in the presence of an acidic catalyst, where n, R₁, R₂, R₃, R₄, R₅ and X are in each case as defined for formula I, R₆ and R₇ either independently of one another are C₁-C₈alkyl or together are -(CH₂)₂- or -(CH₂)₃- and Z is chlorine, bromine, iodine, methanesulfonyloxy or p-toluenesulfonyloxy and, if desired, in each case a mixture of isomers which can be obtained according to the process is separated and the desired isomer is isolated.

The reactions described hereinbefore and hereinafter are carried out in a manner known per se, for example in the absence or, as a rule, in the presence of a suitable solvent or diluent or a mixture of these, the process being carried out, as required, with cooling, at room temperature or with heating, for example in a temperature range from approx. -80°C to the boiling point of the reaction medium, preferably from approx. -20°C to approx. +150°C, for example at the reflux temperature of the reaction mixture and, if necessary, in a sealed vessel, under pressure, in an inert gas atmosphere and/or under anhydrous conditions. Particularly advantageous reaction conditions can be seen from the examples.

The starting material described hereinbefore and hereinafter, which is used for the preparation of the compounds I, is known or can be prepared by methods known per se, for example following the information given hereinafter.

Variant a):

- 5 Suitable acidic catalysts are, for example, sulfonic acids such as methane- or p-toluenesulfonic acid, including the acidic ion-exchanger resins having sulfo groups, Lewis acids such as boron trifluoride/diethyl ether complexes or boron trifluoride/dimethyl ether complexes, as well as mineral acids such as sulfuric acid or phosphoric acid.
- 10 The reactants can be reacted with each other as such, i.e. without an addition of a solvent or diluent, for example in the melt. However, in most cases it is advantageous to add an inert solvent or diluent or a mixture of these. Examples of such solvents or diluents which may be mentioned are: aromatic, aliphatic and alicyclic hydrocarbons and
- 15 petroleum ether, hexane, cyclohexane, dichloromethane, trichloromethane, dichloroethane or trichloroethene; ethers such as diethyl ether, tert-butyl methyl ether, tetrahydrofuran or dioxane; ketones such as acetone or methyl ethyl ketone; amides such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methylpyrrolidone or hexamethylphosphoric triamide; nitriles such as acetonitrile; and sulfoxides such as
- 20 dimethyl sulfoxide.

The reaction is carried out advantageously in a temperature range from approx. 0°C to approx. +180°C, preferably from approx. +20°C to approx. +130°C, in many cases at the reflux temperature of the solvent used.

- In a preferred embodiment of variant a), a compound II is reacted with a compound III at
- 25 reflux temperature, in an aromatic hydrocarbon, preferably in toluene, and in the presence of a sulfonic acid as catalyst, preferably in the presence of p-toluenesulfonic acid.

The compounds II are known or can be prepared in analogy to known compounds, for example by reacting a compound of the formula IV with 2-R₅-2,3-epoxypropan-1-ol, the process being carried out in a manner known per se, advantageously in an inert solvent or

30 diluent, for example of the abovementioned type, for example in an aromatic hydrocarbon such as toluene or xylene, in the presence of a catalyst, for example a quaternary

ammonium salt, such as in the presence of tetramethylammonium chloride, and at room temperature or increased temperature, for example in a temperature range from approx. 20°C to approx. 200°C, preferably from approx. 50°C to approx. 150°C.

The compounds of the formula III are known or can be prepared in analogy to known compounds.

The compounds IV are known or can be prepared in analogy to known compounds.

Variant b):

Bases which are suitable for facilitating the elimination of HZ are, for example, hydroxides, hydrides, amides, alkanolates, carbonates, dialkylamides or alkylsilylamides of alkali metals or alkaline earth metals, or alkylamines, alkylenediamines, free or N-alkylated saturated or unsaturated cycloalkylamines, basic heterocycles, ammonium hydroxides and carbocyclic amines. Examples which may be mentioned are sodium hydroxide, sodium hydride, sodium amide, sodium methanolate, sodium carbonate, potassium tert-butanolate, potassium carbonate, lithium diisopropylamide, potassium bis(trimethylsilyl)amide, calcium hydride, triethylamine, triethylenediamine, cyclohexylamine, N-cyclohexyl-N,N-dimethylamine, N,N-diethylaniline, pyridine, 4-(N,N-dimethylamino)pyridine, N-methylmorpholine, benzyltrimethylammonium hydroxide as well as 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU).

The reaction is carried out advantageously in an inert solvent or diluent, for example of the type mentioned under variant a), and in a temperature range from approx. -80°C to approx. +200°C, for example from approx. -20°C to approx. +100°C.

The compounds of the formula V are known or can be prepared in analogy to known compounds.

Variant c):

Suitable acidic catalysts are, for example, of the type mentioned under variant a) for the reaction of compounds II and III.

The reaction is carried out advantageously in an inert solvent or diluent, for example of the type mentioned under variant a), and in a temperature range from approx. 0°C to approx. +180°C, preferably from approx. +20°C to approx. +130°C, frequently at the

reflux temperature of the solvent used.

The compounds of the formula VI are known or can be prepared in analogy to known compounds.

The compounds I can exist in the form of one of the possible isomers or as a mixture of
5 these, for example as pure isomers, such as antipodes and/or diastereomers, or as isomer mixtures, such as enantiomer mixtures, for example racemates, diastereomer mixtures or racemate mixtures, depending on the number and the absolute and relative configuration of the asymmetric carbon atoms; the invention relates to the pure isomers and to all possible isomer mixtures and is to be understood correspondingly in each case
10 hereinbefore and hereinafter even when stereochemical details are not mentioned specifically in each case.

Diastereomer mixtures and racemate mixtures of compounds I which can be obtained according to the process - depending on the choice of starting materials and the procedures - or by other routes can be resolved in a known manner on the basis of the
15 physicochemical differences of the components to give the pure diastereomers or racemates, for example by fractional crystallisation, distillation and/or chromatography.

Enantiomer mixtures which can be obtained accordingly, such as racemates, can be resolved by known methods to give the optical antipodes, for example by recrystallisation from an optically active solvent, by chromatography on chiral adsorbents, for example
20 high-pressure liquid chromatography (HPLC) on acetylcellulose, with the aid of suitable microorganisms, by cleavage with specific, immobilised enzymes, via the formation of inclusion compounds, for example using chiral crown ethers, where only one enantiomer is complexed.

Pure diastereomers or enantiomers can be obtained according to the invention not only by
25 separating corresponding isomer mixtures but also by generally known methods of diastereoselective or enantioselective synthesis, for example by carrying out the process according to the invention with educts whose stereochemistry is suitable.

It is advantageous to isolate or synthesise in each case the biologically more active isomer, for example enantiomer, or isomer mixture, for example enantiomer mixture, if the
30 individual components differ in their biological activity.

The compounds I can also be obtained in the form of their hydrates and/or include other solvents, for example those which may have been used for the crystallisation of compounds in solid form.

The invention relates to all those embodiments of the process which start from a compound which can be obtained in any desired step of the process as starting material or intermediate and in which all or some of the missing steps are carried out, or in which a starting material in the form of a derivative or salt and/or racemates or antipodes thereof are used or, in particular, formed under the reaction conditions.

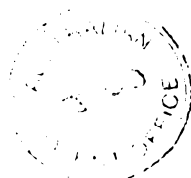
The process of the present invention preferably uses those starting materials and intermediates which lead to the compounds I which have been described at the outset as being particularly valuable.

In particular, the invention relates to the preparation processes described in Examples H1 to H5.

The invention also describes starting materials and intermediates which are used according to the invention for the preparation of the compounds I and which are novel, and to their use and to processes for their preparation.

Dioxolanes which are substituted in the 4-position and which have a similar structure have already been disclosed, for example in the European patent application with the Publication Number 0 411 676. The compounds I of the present invention differ from these known compounds in structural terms in a characteristic manner in that they are substituted in the 2-position of the phenyl ring of the phenoxymethyl group shown in formula I by C_1-C_3 alkyl, halo- C_1-C_3 alkyl, C_1-C_3 alkoxy, halo- C_1-C_3 alkoxy, fluorine, chlorine or bromine (R_2); moreover, the compounds I of the present invention have an activity in the field of pest control which is increased to a surprising extent.

The compounds I of the present invention are oils, resins or solids which are stable at room temperature. While having a favourable tolerability for warm-blooded species, fish



and plants, they are valuable active ingredients in the field of pest control. The active ingredients according to the invention are particularly active against insects and arachnids, as they can be found on useful plants and ornamentals in agriculture and horticulture, in particular in rice, cotton, vegetable and fruit crops, and in forests. The compounds I are particularly suitable for controlling insects in crops of rice, fruit and vegetables, in particular for controlling plant-injurious insects such as *Nilaparvata lugens* and *Heliothis virescens*. Other fields in which the active ingredients according to the invention can be applied are the protection of stored goods and of materials, and in the hygiene sector, in particular the protection of domestic animals and productive livestock. The compounds I are active against all or individual development stages of normally-sensitive, but also resistant pests species. Their action may become apparent for example by destruction of the pests, either immediately or only after some time has elapsed, for example during moulting, or by reduced oviposition and/or hatching rate.

The abovementioned pests include:

- from the order of the Lepidoptera, for example *Acleris* spp., *Adoxophyes* spp., *Aegeria* spp., *Agrotis* spp., *Alabama argillaceae*, *Amorpha* spp., *Anticarsia gemmatilis*, *Archips* spp., *Argyrotaenia* spp., *Autographa* spp., *Busseola fusca*, *Cadra cautella*, *Carpocapsa nipponensis*, *Chilo* spp., *Choristoneura* spp., *Clysia ambiguella*, *Cnaphalocrocis* spp., *Cnephasia* spp., *Cochylis* spp., *Coleophora* spp., *Crocidolomia binotalis*, *Cryptophlebia leucotreta*, *Cydia* spp., *Diatraea* spp., *Diparopsis castanea*, *Earias* spp., *Ephestia* spp., *Eucosma* spp., *Eupoecilia ambiguella*, *Euproctis* spp., *Euxoa* spp., *Grapholita* spp., *Hedya nubiferana*, *Heliothis* spp., *Hellula undalis*, *Hyphantria cunea*, *Keiferia lycopersicella*, *Leucoptera scitella*, *Lithocollethis* spp., *Lobesia botrana*, *Lymantria* spp., *Lyonetia* spp., *Malacosoma* spp., *Mamestra brassicae*, *Manduca sexta*, *Operophtera* spp., *Ostrinia nubilalis*, *Pammene* spp., *Pandemis* spp., *Panolis flammea*, *Pectinophora gossypiella*, *Phthorimaea operculella*, *Pieris rapae*, *Pieris* spp., *Plutella xylostella*, *Prays* spp., *Scirpophaga* spp., *Sesamia* spp., *Sparganothis* spp., *Spodoptera* spp., *Synanthedon* spp., *Thaumetopoea* spp., *Tortrix* spp., *Trichoplusia ni* and *Yponomeuta* spp.;
- from the order of the Coleoptera, for example *Agriotes* spp., *Anthonomus* spp., *Atomaria linearis*, *Chaetocnema tibialis*, *Cosmopolites* spp., *Curculio* spp., *Dermestes* spp., *Diabrotica* spp., *Epilachna* spp., *Eremnus* spp., *Leptinotarsa decemlineata*, *Lissorhoptrus* spp., *Melolontha* spp., *Oryzaephilus* spp., *Otiorynchus* spp., *Phlyctinus* spp., *Popillia* spp., *Psylliodes* spp., *Rhizopertha* spp., *Scarabeidae*, *Sitophilus* spp., *Sitotroga* spp., *Tenebrio* spp., *Tribolium* spp. and *Trogoderma* spp.;
- from the order of the Orthoptera, for example *Blatta* spp., *Blattella* spp., *Gryllotalpa* spp.,

Leucophaea maderae, *Locusta* spp., *Periplaneta* spp. and *Schistocerca* spp.;

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

from the order of the Psocoptera, for example *Liposcelis* spp.;

from the order of the Anoplura, for example *Haematopinus* spp., *Linognathus* spp.,

5 *Pediculus* spp., *Pemphigus* spp. and *Phylloxera* spp.;

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

from the order of the Thysanoptera, for example *Frankliniella* spp., *Hercinothrips* spp.,

Taeniothrips spp., *Thrips palmi*, *Thrips tabaci* and *Scirtothrips aurantii*;

from the order of the Heteroptera, for example *Cimex* spp., *Distantiella theobroma*,

10 *Dysdercus* spp., *Euchistus* spp., *Eurygaster* spp., *Leptocoris* spp., *Nezara* spp., *Piesma*

spp., *Rhodnius* spp., *Sahlbergella singularis*, *Scotinophara* spp. and *Triatoma* spp.;

from the order of the Homoptera, for example *Aleurothrixus floccosus*, *Aleyrodes*

brassicae, *Aonidiella* spp., *Aphididae*, *Aphis* spp., *Aspidiotus* spp., *Bemisia tabaci*,

Ceroplaster spp., *Chrysomphalus aonidium*, *Chrysomphalus dictyospermi*, *Coccus*

15 *hesperidum*, *Empoasca* spp., *Eriosoma larigerum*, *Erythroneura* spp., *Gascardia* spp.,

Laodelphax spp., *Lecanium corni*, *Lepidosaphes* spp., *Macrosiphus* spp., *Myzus* spp.,

Nephotettix spp., *Nilaparvata* spp., *Paratoria* spp., *Pemphigus* spp., *Planococcus* spp.,

Pseudaulacaspis spp., *Pseudococcus* spp., *Psylla* spp., *Pulvinaria aethiopica*,

Quadraspidiotus spp., *Rhopalosiphum* spp., *Saissetia* spp., *Scaphoideus* spp., *Schizaphis*

20 spp., *Sitobion* spp., *Trialeurodes vaporariorum*, *Trioza erytrae* and *Unaspis citri*;

from the order of the Hymenoptera, for example *Acromyrmex*, *Atta* spp., *Cephus* spp.,

Diprion spp., *Diprionidae*, *Gilpinia polytoma*, *Hoplocampa* spp., *Lasius* spp.,

Monomorium pharaonis, *Neodiprion* spp., *Solenopsis* spp. and *Vespa* spp.;

from the order of the Diptera, for example *Aedes* spp., *Antherigona soccata*, *Bibio*

25 *hortulanus*, *Calliphora erythrocephala*, *Ceratitis* spp., *Chrysomyia* spp., *Culex* spp.,

Cuterebra spp., *Dacus* spp., *Drosophila melanogaster*, *Fannia* spp., *Gastrophilus* spp.,

Glossina spp., *Hypoderma* spp., *Hyppobosca* spp., *Liriomyza* spp., *Lucilia* spp.,

Melanagromyza spp., *Musca* spp., *Oestrus* spp., *Orseolia* spp., *Oscinella frit*, *Pegomyia*

hyoscyami, *Phorbia* spp., *Rhagoletis pomonella*, *Sciara* spp., *Stomoxys* spp., *Tabanus* spp.,

30 *Tannia* spp. and *Tipula* spp.;

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

from the order of the Thysanura, for example *Lepisma saccharina* and

from the order of the Acarina, for example *Acarus siro*, *Aceria sheldoni*, *Aculus*

35 *schlechtendali*, *Amblyomma* spp., *Argas* spp., *Boophilus* spp., *Brevipalpus* spp., *Bryobia*

praetiosa, *Calipitimerus* spp., *Choriopetes* spp., *Dermanyssus gallinae*, *Eotetranychus*

carpini, Eriophyes spp., Hyalomma spp., Ixodes spp., Olygonychus pratensis, Ornithodoros spp., Panonychus spp., Phyllocoptruta oleivora, Polyphagotarsonemus latus, Psoroptes spp., Rhipicephalus spp., Rhizoglyphus spp., Sarcoptes spp., Tarsonemus spp. and Tetranychus spp..

5 The good pesticidal activity of the compounds I according to the invention is reflected in a destruction rate (mortality) of at least 50-60% of the abovementioned pests.

The activity of the compounds I according to the invention and the compositions comprising them can be broadened substantially and adapted to prevailing circumstances by adding other insecticides and/or acaricides. Suitable additions are, for example,
10 representatives of the following classes of active ingredients: organophosphorus compounds, nitrophenols and derivatives, formamidines, ureas, carbamates, pyrethroids, chlorinated hydrocarbons and Bacillus thuringiensis preparations.

The compounds I are employed as pure active ingredients or, preferably, together with the auxiliaries conventionally used in the art of formulation, and they can therefore be
15 processed in a known manner to give, for example, emulsifiable concentrates, directly sprayable or dilutable solutions, dilute emulsions, wettable powders, soluble powders, dusts and granules, and also encapsulations in polymeric substances. The application methods such as spraying, atomising, dusting, scattering or pouring, as well as the compositions are selected to suit the intended aims and the prevailing circumstances. The
20 compounds I are furthermore suitable for use in the treatment of seed. The seed can be treated or dressed with the active ingredient, or a formulation comprising the active ingredient, before sowing, or the active ingredient can be applied to the seed furrow during sowing.

The formulations, i.e. the compositions, preparations or combinations comprising the
25 active ingredient of the formula I, or a combination of this active ingredient with other insecticides and/or acaricides, and, if desired, solid or liquid adjuvants, are prepared in a known manner, for example by intimately mixing and/or grinding the active ingredient with the adjuvants such as extenders, for example solvents or solid carriers, or such as surface-active compounds (surfactants).

30 The following are suitable as solvents: aromatic hydrocarbons, preferably the fractions C₈ to C₁₂ of alkylbenzenes such as xylene mixtures or alkylated naphthalenes, aliphatic or

cycloaliphatic hydrocarbons such as cyclohexane, paraffins or tetrahydronaphthalene, alcohols such as ethanol, propanol or butanol, glycols as well as their ethers and esters such as propylene glycol, dipropylene glycol ether, ethylene glycol, ethylene glycol monomethyl ether or ethylene glycol monoethyl ether, ketones such as cyclohexanone, isophorone or diacetone alcohol, strongly polar solvents such as N-methyl-2-pyrrolidone, dimethyl sulfoxide or N,N-dimethylformamide, water and epoxidised or unepoxidised vegetable oils such as epoxidised or unepoxidised rapeseed oil, castor oil, coconut oil or soya oil; silicone oils may also be used.

Solid carriers which are suitable, for example for dusts and dispersible powders, are, as a rule, ground natural minerals, such as calcite, talc, kaolin, montmorillonite or attapulgite. To improve the physical properties, it is also possible to add highly-disperse silicas or highly-disperse absorptive polymers. Possible particulate, adsorptive carriers for granules are either porous types such as pumice, crushed brick, sepiolite or bentonite, or non-sorptive carrier materials, such as calcite or sand. Moreover, a large number of granulated materials of inorganic or organic nature can be used, in particular dolomite or comminuted plant residues.

Suitable surface-active compounds are non-ionic, cationic and/or anionic surfactants which have good emulsifying, dispersing and wetting properties, depending on the nature of the active ingredient I to be formulated or of the combination of this active ingredient with other insecticides and/or acaricides. Surfactants are also to be understood as meaning mixtures of surfactants.

Suitable non-ionic surfactants are mainly polyglycol ether derivatives of aliphatic or cycloaliphatic alcohols, saturated or unsaturated fatty acids and alkylphenols which can contain 3 to 30 glycol ether groups and 8 to 20 carbon atoms in the (aliphatic) hydrocarbon radical and 6 to 18 carbon atoms in the alkyl radical of the alkylphenols. Also suitable are the water-soluble polyethylene oxide adducts with polypropylene glycol, ethylenediaminopolypropylene glycol and alkyl polypropylene glycol which have 1 to 10 carbon atoms in the alkyl chain and contain 20 to 250 ethylene glycol ether groups and 10 to 100 propylene glycol ether groups. As a rule, the compounds mentioned contain 1 to 5 ethylene glycol units per propylene glycol unit. Examples of non-ionic surfactants which may be mentioned are nonylphenolpolyethoxyethanols, castor oil polyglycol ethers, polypropylene/polyethylene oxide adducts, tributylphenoxypolyethoxyethanol, polyethylene glycol and octylphenoxypolyethoxyethanol. Other suitable substances are

fatty acid esters of polyoxyethylene sorbitan, such as polyoxyethylene sorbitan trioleate.

The cationic surfactants are mainly quaternary ammonium salts which contain at least one alkyl radical having 8 to 22 C atoms as N substituents and which have lower halogenated or free alkyl, benzyl or lower hydroxyalkyl radicals as further substituents. The salts are preferably in the form of halides, methyl sulfates or ethyl sulfates, for example stearyltrimethylammonium chloride or benzyldi(2-chloroethyl)ethylammonium bromide.

Suitable anionic surfactants can be either so-called water-soluble soaps or water-soluble synthetic surface-active compounds. Soaps which are suitable are the alkali metal salts, alkaline earth metal salts or substituted or unsubstituted ammonium salts of higher fatty acids ($C_{10}-C_{22}$) such as the sodium salts or potassium salts of oleic or stearic acid, or of natural mixtures of fatty acids which can be obtained, for example, from coconut oil or tall oil; mention must also be made of the fatty acid methyltaurates. However, so-called synthetic surfactants are used more frequently, in particular fatty sulfonates, fatty sulfates, sulfonated benzimidazole derivatives or alkylarylsulfonates. The fatty sulfonates or fatty sulfates are, as a rule, in the form of alkali metal salts, alkaline earth metal salts or substituted or unsubstituted ammonium salts and have, as a rule, an alkyl radical having 8 to 22 C atoms, alkyl also including the alkyl moiety of acyl radicals; examples which may be mentioned are the sodium salt or calcium salt of ligninsulfonic acid, of dodecylsulfuric ester or of a fatty alcohol sulfate mixture prepared from natural fatty acids. This group also includes the salts of the sulfuric esters and sulfonic acids of fatty alcohol/ethylene oxide adducts. The sulfonated benzimidazole derivatives preferably contain 2 sulfo groups and a fatty acid radical having approx. 8-22 C atoms. Examples of alkylarylsulfonates are the sodium, calcium or triethanolammonium salts of dodecylbenzenesulfonic acid, of dibutyl-naphthalenesulfonic acid or of a naphthalenesulfonic acid/formaldehyde condensation product. Other suitable compounds are the corresponding phosphates, such as salts of the phosphoric ester of a p-nonylphenol/(4-14)-ethylene oxide adduct, or phospholipids.

The abovementioned surfactants are only to be understood as being examples; a large number of further surfactants which are conventionally used in the art of formulation and which are suitable according to the invention are described in the specialist literature.

As a rule, the pesticidal compositions comprise 0.1 to 99%, in particular 0.1 to 95%, of active ingredient I or of the combination of this active ingredient with other insecticides

and/or acaricides and 1 to 99.9%, in particular 5 to 99.9%, of a solid or liquid adjuvant, and, as a rule, 0 to 25%, in particular 0.1 to 20%, of the preparations can be composed of surfactants (% is in each case to be understood as meaning percent by weight). While concentrated compositions are more preferred as commercial goods, the end user usually uses dilute compositions with much lower concentrations of active ingredient. Typical use concentrations are between 0.1 and 1000 ppm, preferably between 0.1 and 500 ppm. As a rule, the application rates per hectare are 1 to 1000 g of active ingredient per hectare, preferably 25 to 500 g/ha.

Preferred formulations have, in particular, the following composition (% = percent by weight):

Emulsifiable concentrates:

Active ingredient:	1 to 90%, preferably 5 to 20%
Surfactant:	1 to 30%, preferably 10 to 20%
Liquid carrier:	5 to 94%, preferably 70 to 85%

Dusts:

Active ingredient:	0.1 to 10%, preferably 0.1 to 1%
Solid carrier:	99.9 to 90%, preferably 99.9 to 99%

Suspension concentrates:

Active ingredient:	5 to 75%, preferably 10 to 50%
Water:	94 to 24%, preferably 88 to 30%
Surfactant:	1 to 40%, preferably 2 to 30%

Wettable powders:

Active ingredient:	0.5 to 90%, preferably 1 to 80%
Surfactant:	0.5 to 20%, preferably 1 to 15%
Solid carrier:	5 to 95%, preferably 15 to 90%

Granules:

Active ingredient:	0.5 to 30%, preferably 3 to 15%
Solid carrier:	99.5 to 70%, preferably 97 to 85%

The preparations can also comprise further adjuvants such as stabilisers, for example

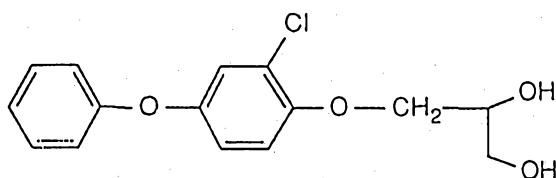
epoxidised or unepoxidised vegetable oils (for example epoxidised coconut oil, rapeseed oil or soya oil), defoamers, for example silicone oil, preservatives, viscosity regulators, binders and/or tackifiers, as well as fertilisers or other active ingredients for achieving specific effects.

5 The invention also embraces a method of controlling the abovementioned pests, which is distinguished by applying an active ingredient of the formula I, or a composition according to the invention which comprises an active ingredient of the formula I, to the pests or the various development stages of the pests, or to their locus.

The examples which follow illustrate the above-described invention without imposing any
10 limitation to its scope. " n_D^T " is the refractive index at a temperature of $T^\circ\text{C}$.
Temperatures are given in degrees Celsius. "m.p." is the melting point; "%" is percent by weight, unless otherwise indicated. Compounds I in which R_1 and R_4 are different can form diastereomers; "A" and "B" are in each case the two separated diastereomer components of such mixtures; if, however, no symbols "A" and "B" are given, the product
15 is a diastereomer mixture.

Preparation Examples

Example H1: 3-(2-Chloro-4-phenoxyphenoxy)-1,2-dihydroxypropane



0.2 g of tetramethylammonium chloride is added to a solution of 22.1 g (0.1 mol) of
20 2-chloro-4-phenoxyphenol in 20 ml of xylene, the mixture is heated at 60°C , and 8.1 g of 2,3-epoxypropan-1-ol are added dropwise with stirring in the course of 20 minutes.
Stirring of the reaction mixture is then continued for 8 hours at 90°C , 60 ml of hexane are added with stirring at 60°C in the course of 5 minutes, the mixture is cooled to 0°C , and the solid which has precipitated is filtered off. The crude product obtained is recrystallised
25 in isopropanol/hexane. Colourless crystals of the title compound with a melting point of $87-88^\circ\text{C}$ (Compound No. 1.13) are obtained.

Example H2: The other compounds of the formula II which are listed in Table 1 can also be prepared analogously to the procedure given in Example H1, if desired after additional purification by chromatography [$\text{CH}_2\text{Cl}_2/(\text{C}_2\text{H}_5)_2\text{O} = 3:2$].

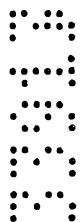
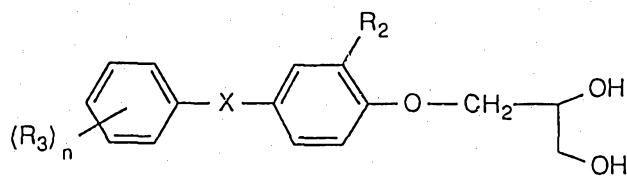


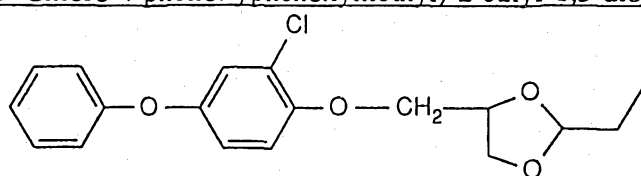
Table 1



Comp. No.	R ₂	(R ₃) _n	X	Physical Data
1.1	Cl	3-F	O	n _D ²⁰ = 1.5782
5 1.2	Cl	3-Cl	O	n _D ²⁰ = 1.5940
1.3	Cl	3-F,5-F	O	m.p. = 52-53°
1.4	Cl	3-Cl,4-F	O	n _D ²⁰ = 1.5706
1.5	Cl	3-Cl,4-Cl	O	m.p. = 61-62°
1.6	Cl	3-Cl,5-Cl	O	
10 1.7	Cl	4-F	O	n _D ²⁰ = 1.5762
1.8	Cl	4-Cl	O	n _D ²⁰ = 1.5920
1.9	Cl	3-CH ₃	O	n _D ²⁰ = 1.5671
1.10	Cl	2-F,4-F	O	
1.11	CH ₃	n = 0	O	n _D ²⁰ = 1.5724
15 1.12	CH ₃	3-F	O	n _D ²⁰ = 1.5621
1.13	Cl	n = 0	O	m.p. = 87-88°
1.14	CH ₃	3-F,5-F	O	n _D ²⁰ = 1.5702
1.15	CH ₃	3-Cl	O	n _D ²⁰ = 1.5794
1.16	CH ₃	3-Cl,4-Cl	O	m.p. = 42-43°
20 1.17	CH ₃	3-Cl,4-F	O	
1.18	Cl	n = 0	CH ₂	m.p. = 75-77°
1.19	CH ₃	n = 0	CH ₂	m.p. = 73-74°
1.20	Cl	3-F	CH ₂	m.p. = 80-81°
1.21	CH ₃	3-F	CH ₃	n _D ²⁰ = 1.5621
25 1.22	Cl	3-F,5-F	CH ₂	m.p. = 89-90°
1.23	Cl	3-Cl,4-Cl	CH ₂	m.p. = 97-98°
1.24	Br	n = 0	O	m.p. = 79-80°
1.25	Br	3-F	O	n _D ²⁰ = 1.5869
1.26	Br	n = 0	CH ₂	m.p. = 89-90°
30 1.27	Cl	n = 0	C=O	n _D ²⁰ = 1.6139
1.28	Cl	4-Cl	C=O	m.p. = 112-113°
1.29	F	n = 0	O	m.p. = 74-75°

Comp. No.	R ₂	(R ₃) _n	X	Physical Data
1.30	F	3-Cl	O	n _D ²⁰ = 1.5671
1.31	F	3-F	O	n _D ²⁰ = 1.5529
1.32	Br	3-Cl,4-Cl	CH ₂	
5 1.33	F	3-F	CH ₂	

Example H3: 4-(2-Chloro-4-phenoxyphenoxy)-2-ethyl-1,3-dioxolane

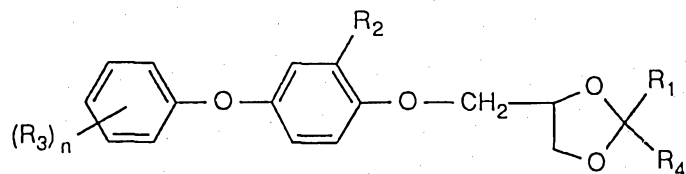


1.6 g (0.028 mol) of freshly distilled propanal are added dropwise with stirring at reflux temperature to a solution of 5.9 g (0.02 mol) of

10 3-(2-chloro-4-phenoxyphenoxy)-1,2-dihydroxypropane and 20 mg of 4-toluenesulfonic acid in 40 ml of toluene. Stirring of the mixture is continued for 6 hours at reflux temperature, and the mixture is then washed repeatedly with 10% sodium carbonate solution and then with water. The toluene phase is dried over sodium sulfate and freed from solvent in vacuo. Chromatographic purification of the crude product on silica gel 15 [hexane:diethyl ether (15:1)] gives the title compound in the form of two separate diastereomers [diastereomer A (Compound No. 2.3.1): n_D²⁰ = 1.5591; diastereomer B (Compound No. 2.3.2): n_D²⁰ = 1.5611].

Example H4: The other compounds of the formula I which are listed in Tables 2 to 8 can also be prepared analogously to the procedure given in Example H3.

Table 2



Comp. No.	R ₁	R ₂	(R ₃) _n	R ₄	Physical Data
5 2.1	CH ₃	Cl	n = 0	CH ₃	n _D ²⁰ = 1.5564
2.2	CH ₃	Cl	n = 0	H	
2.3	C ₂ H ₅	Cl	n = 0	H	
2.3.1	C ₂ H ₅	Cl	n = 0	H	A; n _D ²⁰ = 1.5591
2.3.2	C ₂ H ₅	Cl	n = 0	H	B; n _D ²⁰ = 1.5611
10 2.4	C ₃ H ₇	Cl	n = 0	H	
2.4.1	C ₃ H ₇	Cl	n = 0	H	A; n _D ²⁰ = 1.5539
2.4.2	C ₃ H ₇	Cl	n = 0	H	B; n _D ²⁰ = 1.5552
2.5	i-C ₃ H ₇	Cl	n = 0	H	n _D ²⁰ = 1.5524
2.6	i-C ₄ H ₉	Cl	n = 0	H	
15 2.7	s-C ₄ H ₉	Cl	n = 0	H	
2.8	cyclo-C ₃ H ₅	Cl	n = 0	H	
2.8.1	cyclo-C ₃ H ₅	Cl	n = 0	H	A; n _D ²⁰ = 1.5693
2.8.2	cyclo-C ₃ H ₅	Cl	n = 0	H	B; n _D ²⁰ = 1.5702
2.9	C ₂ H ₅	CH ₃	n = 0	H	
20 2.9.1	C ₂ H ₅	CH ₃	n = 0	H	A; n _D ²⁰ = 1.5463
2.9.2	C ₂ H ₅	CH ₃	n = 0	H	B; n _D ²⁰ = 1.5481
2.10	C ₃ H ₇	CH ₃	n = 0	H	
2.10.1	C ₃ H ₇	CH ₃	n = 0	H	A; n _D ²⁰ = 1.5408
2.10.2	C ₃ H ₇	CH ₃	n = 0	H	B; n _D ²⁰ = 1.5421
25 2.11	i-C ₃ H ₇	CH ₃	n = 0	H	
2.12	cyclo-C ₃ H ₅	CH ₃	n = 0	CH ₃	
2.13	CH ₃	Cl	3-F	CH ₃	
2.14	CH ₃	Cl	3-F	H	
2.14.1	CH ₃	Cl	3-F	H	A; n _D ²⁰ = 1.5529
30 2.14.2	CH ₃	Cl	3-F	H	B; n _D ²⁰ = 1.5541
2.15	C ₂ H ₅	Cl	3-F	H	

Comp. No.	R ₁	R ₂	(R ₃) _n	R ₄	Physical Data
2.15.1	C ₂ H ₅	Cl	3-F	H	A; n _D ²⁰ = 1.5481
2.15.2	C ₂ H ₅	Cl	3-F	H	B; n _D ²⁰ = 1.5501
5 2.16	C ₃ H ₇	Cl	3-F	H	
2.16.1	C ₃ H ₇	Cl	3-F	H	A; n _D ²⁰ = 1.5432
2.16.2	C ₃ H ₇	Cl	3-F	H	B; n _D ²⁰ = 1.5456
2.17	i-C ₃ H ₇	Cl	3-F	H	
2.17.1	i-C ₃ H ₇	Cl	3-F	H	A; n _D ²⁰ = 1.5422
10 2.17.2	i-C ₃ H ₇	Cl	3-F	H	B; n _D ²⁰ = 1.5431
2.18	s-C ₄ H ₉	Cl	3-F	H	
2.19	i-C ₄ H ₉	Cl	3-F	H	
2.19.1	i-C ₄ H ₉	Cl	3-F	H	A; n _D ²⁰ = 1.5382
2.19.2	i-C ₄ H ₉	Cl	3-F	H	B; n _D ²⁰ = 1.5392
15 2.20	cyclo-C ₃ H ₅	Cl	3-F	H	
2.20.1	cyclo-C ₃ H ₅	Cl	3-F	H	A; n _D ²⁰ = 1.5592
2.20.2	cyclo-C ₃ H ₅	Cl	3-F	H	B; n _D ²⁰ = 1.5612
2.21	C ₂ H ₅	CH ₃	3-F	H	n _D ²⁰ = 1.5371
2.22	C ₃ H ₇	CH ₃	3-F	H	n _D ²⁰ = 1.5332
20 2.23	i-C ₃ H ₇	CH ₃	3-F	H	
2.24	CH ₃	Cl	3-F,5-F	CH ₃	
2.25	CH ₃	Cl	3-F,5-F	H	
2.26	C ₂ H ₅	Cl	3-F,5-F	H	
2.26.1	C ₂ H ₅	Cl	3-F,5-F	H	A; n _D ²⁰ = 1.5369
25 2.26.2	C ₂ H ₅	Cl	3-F,5-F	H	B; n _D ²⁰ = 1.5379
2.27	C ₃ H ₇	Cl	3-F,5-F	H	
2.27.1	C ₃ H ₇	Cl	3-F,5-F	H	A; n _D ²⁰ = 1.5330
2.27.2	C ₃ H ₇	Cl	3-F,5-F	H	B; n _D ²⁰ = 1.5339
2.28	i-C ₃ H ₇	Cl	3-F,5-F	H	
30 2.28.1	i-C ₃ H ₇	Cl	3-F,5-F	H	A; n _D ²⁰ = 1.5325
2.28.2	i-C ₃ H ₇	Cl	3-F,5-F	H	B; n _D ²⁰ = 1.5331
2.29	i-C ₄ H ₉	Cl	3-F,5-F	H	
2.30	C ₄ H ₉	Cl	3-F,5-F	H	
2.31	s-C ₄ H ₉	Cl	3-F,5-F	H	
35 2.32	cyclo-C ₃ H ₅	Cl	3-F,5-F	H	

Comp. No.	R ₁	R ₂	(R ₃) _n	R ₄	Physical Data
2.32.1	cyclo-C ₃ H ₅	Cl	3-F,5-F	H	A; n _D ²⁰ = 1.5461
2.32.2	cyclo-C ₃ H ₅	Cl	3-F,5-F	H	B; n _D ²⁰ = 1.5470
5 2.33	C ₂ H ₅	CH ₃	3-F,5-F H		
2.34	C ₃ H ₇	CH ₃	3-F,5-F	H	
2.35	i-C ₃ H ₇	CH ₃	3-F,5-F	H	
2.36	cyclo-C ₃ H ₅	CH ₃	3-F,5-F	CH ₃	
2.37	CH ₃	Cl	3-Cl	CH ₃	
10 2.38	C ₂ H ₅	Cl	3-Cl	H	
2.38.1	C ₂ H ₅	Cl	3-Cl	H	A; n _D ²⁰ = 1.5662
2.38.2	C ₂ H ₅	Cl	3-Cl	H	B; n _D ²⁰ = 1.5679
2.39	C ₃ H ₇	Cl	3-Cl	H	
2.39.1	C ₃ H ₇	Cl	3-Cl	H	A; n _D ²⁰ = 1.5604
15 2.39.2	C ₃ H ₇	Cl	3-Cl	H	B; n _D ²⁰ = 1.5624
2.40	i-C ₃ H ₇	Cl	3-Cl	H	
2.41	cyclo-C ₃ H ₅	Cl	3-Cl	H	
2.42	C ₂ H ₅	CH ₃	3-Cl	H	n _D ²⁰ = 1.5561
2.43	CH ₃	Cl	4-F	CH ₃	
20 2.44	C ₂ H ₅	Cl	4-F	H	
2.45	C ₃ H ₇	Cl	4-F	H	
2.46	i-C ₃ H ₇	Cl	4-F	H	
2.47	cyclo-C ₃ H ₅	Cl	4-F	H	
2.48	CH ₃	Cl	4-Cl	H	
25 2.49	C ₂ H ₅	Cl	4-Cl	H	
2.50	C ₃ H ₇	Cl	4-Cl	H	
2.51	i-C ₃ H ₇	Cl	4-Cl	H	
2.52	cyclo-C ₃ H ₅	Cl	4-Cl	H	
2.53	CH ₃	Cl	3-CH ₃	CH ₃	
30 2.54	CH ₃	Cl	3-CH ₃	H	
2.55	C ₂ H ₅	Cl	3-CH ₃	H	
2.56	C ₃ H ₇	Cl	3-CH ₃	H	
2.57	i-C ₃ H ₇	Cl	3-CH ₃	H	
2.58	cyclo-C ₃ H ₅	Cl	3-CH ₃	H	
35 2.59	CH ₃	Cl	3-Cl,4-Cl	CH ₃	

Comp. No.	R ₁	R ₂	(R ₃) _n	R ₄	Physical Data
2.60	CH ₃	Cl	3-Cl,4-Cl	H	
2.61	C ₂ H ₅	Cl	3-Cl,4-Cl	H	
5 2.61.1	C ₂ H ₅	Cl	3-Cl,4-Cl	H	A; n _D ²⁰ = 1.5749
2.61.2	C ₂ H ₅	Cl	3-Cl,4-Cl	H	B; n _D ²⁰ = 1.5758
2.62	C ₃ H ₇	Cl	3-Cl,4-Cl	H	
2.62.1	C ₃ H ₇	Cl	3-Cl,4-Cl	H	A; n _D ²⁰ = 1.5691
2.62.2	C ₃ H ₇	Cl	3-Cl,4-Cl	H	B; n _D ²⁰ = 1.5705
10 2.63	i-C ₃ H ₇	Cl	3-Cl,4-Cl	H	
2.64	i-C ₄ H ₉	Cl	3-Cl,4-Cl	H	
2.65	cyclo-C ₃ H ₅	Cl	3-Cl,4-Cl	H	
2.65.1	cyclo-C ₃ H ₅	Cl	3-Cl,4-Cl	H	A; n _D ²⁰ = 1.5798
2.65.2	cyclo-C ₃ H ₅	Cl	3-Cl,4-Cl	H	B; n _D ²⁰ = 1.5815
15 2.66	cyclo-C ₃ H ₅	Cl	3-Cl,4-Cl	CH ₃	
2.67	C ₂ H ₅	CH ₃	3-Cl,4-Cl	H	
2.68	C ₃ H ₇	CH ₃	3-Cl,4-Cl	H	
2.69	CH ₃	Cl	3-Cl,4-F	CH ₃	
2.70	CH ₃	Cl	3-Cl,4-F	H	
20 2.71	C ₂ H ₅	Cl	3-Cl,4-F	H	
2.71.1	C ₂ H ₅	Cl	3-Cl,4-F	H	A; n _D ²⁰ = 1.5561
2.71.2	C ₂ H ₅	Cl	3-Cl,4-F	H	B; n _D ²⁰ = 1.5572
2.72	C ₃ H ₇	Cl	3-Cl,4-F	H	
2.73	i-C ₃ H ₇	Cl	3-Cl,4-F	H	
25 2.74	cyclo-C ₃ H ₅	Cl	3-Cl,4-F	H	
2.75	cyclo-C ₃ H ₅	Cl	3-Cl,4-F	CH ₃	
2.76	C ₂ H ₅	CH ₃	3-Cl,4-F	H	
2.77	CH ₃	Cl	2-F,4-F	CH ₃	
2.78	CH ₃	Cl	2-F,4-F	H	
30 2.79	C ₂ H ₅	Cl	2-F,4-F	H	
2.80	C ₃ H ₇	Cl	2-F,4-F	H	
2.81	i-C ₃ H ₇	Cl	2-F,4-F	H	
2.82	cyclo-C ₃ H ₅	Cl	2-F,4-F	H	
2.83	i-C ₄ H ₉	Cl	3-Cl	H	

Comp. No.	R ₁	R ₂	(R ₃) _n	R ₄	Physical Data
2.83.1	i-C ₄ H ₉	Cl	3-Cl	H	A; n _D ²⁰ = 1.5541
2.83.2	i-C ₄ H ₉	Cl	3-Cl	H	B; n _D ²⁰ = 1.5552
5 2.84	C ₂ H ₅	Br	H	H	
2.84.1	C ₂ H ₅	Br	H	H	A; n _D ²⁰ = 1.5738
2.84.2	C ₂ H ₅	Br	H	H	B; n _D ²⁰ = 1.5754
2.85	R ₁ +R ₄ : -(CH ₂) ₃ -	Cl	3-F		n _D ²⁰ = 1.5586
2.86	C ₂ H ₅	Br	3-F	H	
10 2.86.1	C ₂ H ₅	Br	3-F	H	A; n _D ²⁰ = 1.5584
2.86.2	C ₂ H ₅	Br	3-F	H	B; n _D ²⁰ = 1.5611
2.87	C ₃ H ₇	Br	3-F	H	
2.87.1	C ₃ H ₇	Br	3-F	H	A; n _D ²⁰ = 1.5529
2.87.2	C ₃ H ₇	Br	3-F	H	B; n _D ²⁰ = 1.5561
15 2.88	CH ₃	Cl	3-Cl	H	
2.88.1	CH ₃	Cl	3-Cl	H	A; n _D ²⁰ = 1.5701
2.88.2	CH ₃	Cl	3-Cl	H	B; n _D ²⁰ = 1.5705
2.89	R ₁ +R ₄ : -(CH ₂) ₅ -	Cl	3-Cl		n _D ²⁰ = 1.5631
2.90	R ₁ +R ₄ : -(CH ₂) ₄ -	Cl	3-Cl		n _D ²⁰ = 1.5721
20 2.91	R ₁ +R ₄ : -(CH ₂) ₄ -	Cl	3-F		n _D ²⁰ = 1.5539
2.92	R ₁ +R ₄ : -(CH ₂) ₅ -	Cl	3-F		n _D ²⁰ = 1.5558
2.93	OCH ₃	Cl	H	H	
2.93.1	OCH ₃	Cl	H	H	A; n _D ²⁰ = 1.5646
2.93.2	OCH ₃	Cl	H	H	B; n _D ²⁰ = 1.5650
25 2.94	OCH ₃	Cl	3-Cl	H	
2.94.1	OCH ₃	Cl	3-Cl	H	A; n _D ²⁰ = 1.5700
2.94.2	OCH ₃	Cl	3-Cl	H	B; n _D ²⁰ = 1.5706
2.95	OCH ₃	Cl	3-F	H	
2.95.1	OCH ₃	Cl	3-F	H	A; n _D ²⁰ = 1.5530
30 2.95.2	OCH ₃	Cl	3-F	H	B; n _D ²⁰ = 1.5536
2.96	-CH=CH ₂	Cl	3-F	H	
2.96.1	-CH=CH ₂	Cl	3-F	H	A; n _D ²⁰ = 1.5572
2.96.2	-CH=CH ₂	Cl	3-F	H	B; n _D ²⁰ = 1.5579
2.97	-CH=CH ₂	Cl	H	H	
35 2.97.1	-CH=CH ₂	Cl	H	H	A; n _D ²⁰ = 1.5681

Comp. No.	R ₁	R ₂	(R ₃) _n	R ₄	Physical Data
2.97.2	-CH=CH ₂	Cl	H	H	B; n _D ²⁰ = 1.5698
2.98	Ethynyl	Cl	3-Cl	H	n _D ²⁰ = 1.5798
5 2.99	C ₃ H ₇	CH ₃	3-Cl	H	n _D ²⁰ = 1.5511
2.100	C ₃ H ₇	F	H	H	
2.100.1	C ₃ H ₇	F	H	H	A; n _D ²⁰ = 1.5355
2.100.2	C ₃ H ₇	F	H	H	B; n _D ²⁰ = 1.5369
2.101	C ₂ H ₅	F	3-Cl	H	
10 2.101.1	C ₂ H ₅	F	3-Cl	H	A; n _D ²⁰ = 1.5481
2.101.2	C ₂ H ₅	F	3-Cl	H	B; n _D ²⁰ = 1.5491
2.102	C ₃ H ₇	F	3-Cl	H	
2.102.1	C ₃ H ₇	F	3-Cl	H	A; n _D ²⁰ = 1.5431
2.102.2	C ₃ H ₇	F	3-Cl	H	B; n _D ²⁰ = 1.5448
15 2.103	C ₂ H ₅	F	3-F	H	
2.103.1	C ₂ H ₅	F	3-F	H	A; n _D ²⁰ = 1.5291
2.103.2	C ₂ H ₅	F	3-F	H	B; n _D ²⁰ = 1.5306
2.104	C ₃ H ₇	F	3-F	H	
2.104.1	C ₃ H ₇	F	3-F	H	A; n _D ²⁰ = 1.5248
20 2.104.2	C ₃ H ₇	F	3-F	H	B; n _D ²⁰ = 1.5262
2.105	C ₆ H ₁₃	Cl	n = 0	H	
2.106	C ₅ H ₁₁	Cl	3-Cl	H	
2.107	s-C ₄ H ₉	Cl	3-Cl	H	
2.108	C ₂ H ₅	Cl	3-F	CH ₃	
25 2.109	cyclo-C ₃ H ₅	Cl	3-Cl	CH ₃	
2.110	C ₂ H ₅	Cl	3-Cl	CH ₃	
2.111	-CH ₂ CH ₂ F	Cl	n = 0	H	
2.112	-CH ₂ CH ₂ F	Cl	3-Cl	H	
2.113	-CH ₂ CH ₂ F	Cl	3-F	H	
30 2.114	-CH ₂ CH ₂ F	Cl	3-F,5-F	H	
2.115	-CH ₂ CH ₂ F	F	3-F	H	
2.116	-CH ₂ CH ₂ F	CH ₃	3-Cl	H	
2.117	-CH ₂ CH ₂ F	F	3-Cl	H	
2.118	-CH ₂ CH ₂ F	F	n = 0	H	
35 2.119	-CH ₂ CH ₂ Cl	Cl	n = 0	H	

Comp. No.	R ₁	R ₂	(R ₃) _n	R ₄	Physical Data
2.120	-CH ₂ CH ₂ Cl	Cl	3-F	H	
2.121	-CH ₂ CH ₂ Cl	Cl	3-Cl	H	
5 2.122	-CH=CH ₂	Cl	3-Cl	H	
2.123	-CH=CH ₂	Cl	3-F,5-F	H	
2.124	-CH=CHCH ₃ (E)	Cl	3-Cl	H	
2.125	-CH=CHCH ₃ (Z)	Cl	3-Cl	H	
2.126	-CH=CHCH ₃ (E/Z)	F	3-Cl	H	
10 2.127	-CH=C(CH ₃) ₂	Cl	n = 0	H	
2.128	-CH=C(CH ₃) ₂	Cl	3-Cl	H	
2.129	-CH=C(CH ₃) ₂	Cl	3-F	H	
2.130	i-C ₄ H ₉	F	n = 0	H	
2.131	i-C ₄ H ₉	F	3-Cl	H	
15 2.132	i-C ₄ H ₉	CH ₃	n = 0	H	
2.133	i-C ₄ H ₉	CH ₃	3-Cl	H	
2.134	i-C ₄ H ₉	CH ₃	3-F	H	
2.135	-CHFCH ₃	Cl	n = 0	H	
2.136	-CHFCH ₃	Cl	3-Cl	H	
20 2.137	-CHFCH ₃	Cl	3-F	H	
2.138	prop-1-yn-1-yl	Cl	n = 0	H	
2.139	prop-1-yn-1-yl	Cl	3-F	H	
2.140	prop-1-yn-1-yl	Cl	3-Cl	H	
2.141	prop-1-yn-1-yl	CH ₃	n = 0	H	
25 2.142	prop-1-yn-1-yl	CH ₃	3-F	H	
2.143	but-1-yn-1-yl	Cl	n = 0	H	
2.144	but-1-yn-1-yl	CH ₃	n = 0	H	
2.145	but-1-yn-1-yl	F	3-Cl	H	
2.146	OC ₂ H ₅	Cl	n = 0	H	
30 2.147	OC ₂ H ₅	Cl	3-Cl	H	
2.148	OC ₂ H ₅	Cl	3-F	H	
2.149	OC ₂ H ₅	CH ₃	3-Cl	H	
2.150	cyclo-C ₃ H ₅	F	n = 0	H	
2.151	cyclo-C ₃ H ₅	F	3-Cl	H	
35 2.152	cyclo-C ₃ H ₅	F	3-F	H	

Comp. No.	R ₁	R ₂	(R ₃) _n	R ₄	Physical Data
2.153	cyclo-C ₃ H ₅	CH ₃	n = 0	H	
2.154	cyclo-C ₃ H ₅	CH ₃	3-Cl	H	
5 2.155	cyclo-C ₃ H ₅	CH ₃	3-F	H	
2.156	cyclo-C ₃ H ₅	CH ₃	3-F,5-F	H	
2.157	OC ₃ H ₇	Cl	n = 0	H	
2.158	OC ₃ H ₇	Cl	3-Cl	H	
2.159	OC ₃ H ₇	Cl	3-F	H	
10 2.160	OC ₃ H ₇ -i	Cl	n = 0	H	
2.161	OC ₃ H ₇ -i	Cl	3-Cl	H	
2.162	OC ₃ H ₇ -i	Cl	3-F	H	
2.163	cyclo-C ₄ H ₇	Cl	n = 0	H	
2.164	cyclo-C ₄ H ₇	Cl	3-Cl	H	
15 2.165	cyclo-C ₄ H ₇	F	n = 0	H	
2.166	cyclo-C ₄ H ₇	F	3-Cl	H	
2.167	cyclo-C ₅ H ₉	Cl	n = 0	H	
2.168	cyclo-C ₅ H ₉	Cl	3-Cl	H	
2.169	cyclo-C ₅ H ₉	Cl	3-F	H	
20 2.170	cyclo-C ₅ H ₉	F	n = 0	H	
2.171	cyclo-C ₅ H ₉	F	3-Cl	H	
2.172	cyclo-C ₅ H ₉	F	3-F	H	
2.173	cyclo-C ₆ H ₁₁	Cl	n = 0	H	
2.174	cyclo-C ₆ H ₁₁	Cl	3-Cl	H	
25 2.175	cyclo-C ₆ H ₁₁	Cl	3-F	H	
2.176	C ₂ H ₅	Cl	n = 0	C ₂ H ₅	
2.177	C ₂ H ₅	F	n = 0	C ₂ H ₅	
2.178	C ₂ H ₅	Br	n = 0	C ₂ H ₅	
2.179	C ₂ H ₅	Cl	3-Cl	C ₂ H ₅	
30 2.180	C ₂ H ₅	Cl	3-F	C ₂ H ₅	
2.181	C ₂ H ₅	Cl	n = 0	CH ₃	
2.182	C ₃ H ₇	Br	3-F,5-F	H	
2.183	C ₃ H ₇	Br	3-Cl	H	
2.184	R ₁ +R ₄ : -(CH ₂) ₃ -	Cl	n = 0		
35 2.185	R ₁ +R ₄ : -(CH ₂) ₃ -	Cl	3-Cl		

Comp. No.	R ₁	R ₂	(R ₃) _n	R ₄	Physical Data
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2.186	R ₁ +R ₄ : -(CH ₂) ₃ -	F	n = 0		
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2.187	R ₁ +R ₄ : -(CH ₂) ₃ -	F	3-Cl		
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5 2.188	R ₁ +R ₄ : -(CH ₂) ₃ -	F	3-F		
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2.189	R ₁ +R ₄ : -(CH ₂) ₃ -	CH ₃	n = 0		
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2.190	R ₁ +R ₄ : -(CH ₂) ₃ -	CH ₃	3-Cl		
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2.191	R ₁ +R ₄ : -(CH ₂) ₃ -	CH ₃	3-F		
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2.192	R ₁ +R ₄ : -(CH ₂) ₄ -	Cl	n = 0		
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10 2.193	R ₁ +R ₄ : -(CH ₂) ₄ -	F	n = 0		
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2.194	R ₁ +R ₄ : -(CH ₂) ₄ -	Br	n = 0		
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2.195	R ₁ +R ₄ : -(CH ₂) ₄ -	CH ₃	n = 0		
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2.196	R ₁ +R ₄ : -(CH ₂) ₄ -	CH ₃	3-Cl		
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2.197	C ₃ H ₇	Br	n = 0	H	
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15 2.198	R ₁ +R ₄ : -(CH ₂) ₅ -	Cl	n = 0		
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2.199	R ₁ +R ₄ : -(CH ₂) ₅ -	CH ₃	n = 0		
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2.200	R ₁ +R ₄ : -(CH ₂) ₅ -	F	n = 0		
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2.201	R ₁ +R ₄ : -(CH ₂) ₅ -	F	3-Cl		
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2.202	R ₁ +R ₄ :	Cl	n = 0		
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	-CH ₂ CH ₂ CH=CH-				
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20 2.203	R ₁ +R ₄ :	Cl	3-F		
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	-CH ₂ CH ₂ CH=CH-				
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2.204	R ₁ +R ₄ :	Cl	3-Cl		
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	-CH ₂ CH ₂ CH=CH-				
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2.205	R ₁ +R ₄ :	Cl	n = 0		
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25	-CH ₂ OCH ₂ -				
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2.206	R ₁ +R ₄ :	Cl	3-F		
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	-CH ₂ OCH ₂ -				
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2.207	R ₁ +R ₄ :	Cl	3-Cl		
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	-CH ₂ OCH ₂ -				
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30 2.208	R ₁ +R ₄ :	F	n = 0		
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	-CH ₂ OCH ₂ -				
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2.209	R ₁ +R ₄ :	F	3-Cl		
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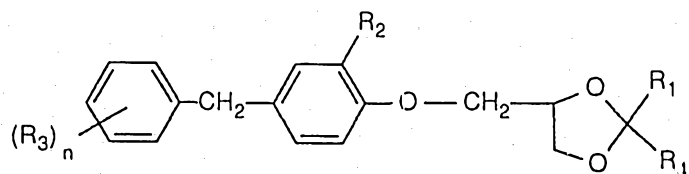
	-CH ₂ OCH ₂ -				
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Comp. No.	R ₁	R ₂	(R ₃) _n	R ₄	Physical Data
2.210	R ₁ +R ₄ : -CH ₂ CH ₂ OCH ₂ CH ₂ -	Cl	n = 0		
5 2.211	R ₁ +R ₄ : -CH ₂ CH ₂ OCH ₂ CH ₂ -	Cl	3-Cl		
2.212	R ₁ +R ₄ : -CH ₂ CH ₂ OCH ₂ CH ₂ -	Cl	3-F		
10 2.213	R ₁ +R ₄ : -CH ₂ CH(CH ₃)OCH ₂ CH ₂ -	Cl	n = 0		
2.214	R ₁ +R ₄ : -CH ₂ CH(CH ₃)OCH ₂ CH ₂ -	Cl	3-Cl		
2.215	C ₂ H ₅	C ₂ H ₅	n = 0	H	
2.216	C ₂ H ₅	C ₂ H ₅	3-Cl	H	
15 2.217	C ₂ H ₅	C ₂ H ₅	3-F	H	
2.218	C ₂ H ₅	C ₂ H ₅	3-F,5-F	H	
2.219	C ₂ H ₅	C ₃ H ₇	n = 0	H	
2.220	C ₂ H ₅	C ₃ H ₇	3-Cl	H	
2.221	C ₂ H ₅	C ₃ H ₇	3-F	H	
20 2.222	C ₂ H ₅	i-C ₃ H ₇	n = 0	H	
2.223	C ₂ H ₅	i-C ₃ H ₇	3-Cl	H	
2.224	C ₂ H ₅	i-C ₃ H ₇	3-F	H	
2.225	C ₃ H ₇	i-C ₃ H ₇	n = 0	H	
2.226	C ₃ H ₇	i-C ₃ H ₇	3-Cl	H	
25 2.227	C ₂ H ₅	CF ₃	n = 0	H	
2.228	C ₂ H ₅	CF ₃	3-Cl	H	
2.229	C ₂ H ₅	CF ₃	3-F	H	
2.230	C ₃ H ₇	CF ₃	n = 0	H	
2.231	C ₃ H ₇	CF ₃	3-Cl	H	
30 2.232	C ₃ H ₇	CF ₃	3-F	H	
2.233	CH ₃	OCH ₃	n = 0	H	
2.234	CH ₃	OCH ₃	3-Cl	H	
2.235	C ₂ H ₅	OCH ₃	n = 0	H	
2.236	C ₂ H ₅	OCH ₃	3-Cl	H	

Comp. No.	R ₁	R ₂	(R ₃) _n	R ₄	Physical Data
2.237	C ₂ H ₅	OCH ₃	3-F	H	
2.238	C ₃ H ₇	OCH ₃	n = 0	H	
5 2.239	C ₃ H ₇	OCH ₃	3-Cl	H	
2.240	C ₃ H ₇	OCH ₃	3-F,5-F	H	
2.241	ethynyl	Cl	n = 0	H	
2.242	ethynyl	Cl	3-F	H	
2.243	ethynyl	Cl	3-F,5-F	H	
10 2.244	C ₂ H ₅	Br	3-F,5-F	H	
2.245	CH ₃	OCF ₃	n = 0	CH ₃	
2.246	CH ₃	OCF ₃	n = 0	H	
2.247	CH ₃	OCF ₃	3-Cl	H	
2.248	C ₂ H ₅	OCF ₃	n = 0	H	
15 2.249	C ₂ H ₅	OCF ₃	3-Cl	H	
2.250	C ₂ H ₅	OCF ₃	3-F	H	
2.251	C ₂ H ₅	OCF ₃	3-F,5-F	H	
2.252	C ₃ H ₇	OCF ₃	n = 0	H	
2.253	C ₃ H ₇	OCF ₃	3-Cl	H	
20 2.254	C ₃ H ₇	OCF ₃	3-F	H	
2.255	CH ₃	F	n = 0	CH ₃	
2.256	CH ₃	F	n = 0	H	
2.257	CH ₃	F	3-F	H	
2.258	CH ₃	F	3-Cl	H	
25 2.259	C ₂ H ₅	F	3-F,5-F	H	
2.260	C ₂ H ₅	F	3-CH ₃	H	
2.261	C ₂ H ₅	F	4-CH ₃	H	
2.262	C ₂ H ₅	F	n = 0	H	
2.263	C ₃ H ₇	F	3-F,5-F	H	
30 2.264	C ₃ H ₇	F	3-CH ₃	H	
2.265	C ₃ H ₇	F	4-CH ₃	H	
2.266	C ₂ H ₅	Br	3-Cl	H	
2.267	CH ₃	Br	n = 0	CH ₃	
2.268	CH ₃	Br	n = 0	H	
35 2.269	CH ₃	Br	3-Cl	H	

Comp. No.	R ₁	R ₂	(R ₃) _n	R ₄	Physical Data
2.270	CH ₃	Br	3-F	H	
2.271	-CH=CHCH ₃ (E/Z)	F	n = 0	H	

Table 3



Comp. No. R₁ R₂ (R₃)_n R₄ Physical Data

5	3.1	CH ₃	Cl	n = 0	CH ₃	n _D ²⁰ = 1.5554
	3.2	CH ₃	Cl	n = 0	H	
	3.3	C ₂ H ₅	Cl	n = 0	H	
	3.3.1	C ₂ H ₅	Cl	n = 0	H	A; n _D ²⁰ = 1.5573
	3.3.2	C ₂ H ₅	Cl	n = 0	H	B; n _D ²⁰ = 1.5587
10	3.4	C ₃ H ₇	Cl	n = 0	H	
	3.4.1	C ₃ H ₇	Cl	n = 0	H	A; n _D ²⁰ = 1.5524
	3.4.2	C ₃ H ₇	Cl	n = 0	H	B; n _D ²⁰ = 1.5533
	3.5	i-C ₃ H ₇	Cl	n = 0	H	
	3.5.1	i-C ₃ H ₇	Cl	n = 0	H	A; n _D ²⁰ = 1.5512
15	3.5.2	i-C ₃ H ₇	Cl	n = 0	H	B; n _D ²⁰ = 1.5522
	3.6	cyclo-C ₃ H ₅	Cl	n = 0	H	
	3.6.1	cyclo-C ₃ H ₅	Cl	n = 0	H	A; n _D ²⁰ = 1.5670
	3.6.2	cyclo-C ₃ H ₅	Cl	n = 0	H	B; n _D ²⁰ = 1.5682
	3.7	i-C ₄ H ₉	Cl	n = 0	H	
20	3.8	C ₂ H ₅	CH ₃	n = 0	H	
	3.9	i-C ₃ H ₇	CH ₃	n = 0	H	
	3.10	cyclo-C ₃ H ₅	CH ₃	n = 0	H	
	3.11	CH ₃	Cl	3-F	CH ₃	
	3.12	CH ₃	Cl	3-F	H	
25	3.12.1	CH ₃	Cl	3-F	H	A; n _D ²⁰ = 1.5530
	3.12.2	CH ₃	Cl	3-F	H	B; n _D ²⁰ = 1.5549
	3.13	C ₂ H ₅	Cl	3-F	H	
	3.13.1	C ₂ H ₅	Cl	3-F	H	A; n _D ²⁰ = 1.5481
	3.13.2	C ₂ H ₅	Cl	3-F	H	B; n _D ²⁰ = 1.5490
30	3.14	C ₃ H ₇	Cl	3-F	H	
	3.14.1	C ₃ H ₇	Cl	3-F	H	A; n _D ²⁰ = 1.5439
	3.14.2	C ₃ H ₇	Cl	3-F	H	B; n _D ²⁰ = 1.5452

Comp. No.	R ₁	R ₂	(R ₃) _n	R ₄	Physical Data
3.15	i-C ₃ H ₇	Cl	3-F	H	
3.16	cyclo-C ₃ H ₅	Cl	3-F	H	
5 3.17	i-C ₄ H ₉	Cl	3-F	H	
3.18	C ₄ H ₉	CH ₃	3-F	H	
3.19	CH ₃	Cl	3-F,5-F	CH ₃	
3.20	CH ₃	Cl	3-F,5-F	H	
3.21	C ₂ H ₅	Cl	3-F,5-F	H	
10 3.21.1	C ₂ H ₅	Cl	3-F,5-F	H	A; n _D ²⁰ = 1.5401
3.21.2	C ₂ H ₅	Cl	3-F,5-F	H	B; n _D ²⁰ = 1.5409
3.22	C ₃ H ₇	Cl	3-F,5-F	H	
3.23	i-C ₃ H ₇	Cl	3-F,5-F	H	
3.24	cyclo-C ₃ H ₅	Cl	3-F,5-F	H	
15 3.25	i-C ₄ H ₉	Cl	3-F,5-F	H	
3.26	C ₂ H ₅	Cl	3-Cl,4-Cl	H	
3.26.1	C ₂ H ₅	Cl	3-Cl,4-Cl	H	A; m.p. = 86-87°
3.26.2	C ₂ H ₅	Cl	3-Cl,4-Cl	H	B; m.p. = 66-67°
3.27	C ₃ H ₇	Cl	3-Cl,4-Cl	H	
20 3.27.1	C ₃ H ₇	Cl	3-Cl,4-Cl	H	A; m.p. = 52-53°
3.27.2	C ₃ H ₇	Cl	3-Cl,4-Cl	H	B; m.p. = 58-59°
3.28	cyclo-C ₃ H ₅	Cl	3-Cl,4-Cl	H	
3.28.1	cyclo-C ₃ H ₅	Cl	3-Cl,4-Cl	H	A; n _D ²⁰ = 1.5808
3.28.2	cyclo-C ₃ H ₅	Cl	3-Cl,4-Cl	H	B; n _D ²⁰ = 1.5820
25 3.29	C ₂ H ₅	Br	3-Cl,4-Cl	H	m.p. = 70-72°
3.30	C ₂ H ₅	Br	n = 0	H	
3.30.1	C ₂ H ₅	Br	n = 0	H	A; n _D ²⁰ = 1.5701
3.30.2	C ₂ H ₅	Br	n = 0	H	B; n _D ²⁰ = 1.5718
3.31	i-C ₃ H ₇	Br	n = 0	H	
30 3.31.1	i-C ₃ H ₇	Br	n = 0	H	A; n _D ²⁰ = 1.5630
3.31.2	i-C ₃ H ₇	Br	n = 0	H	B; n _D ²⁰ = 1.5641
3.32	C ₂ H ₅	F	3-F	H	
3.32.1	C ₂ H ₅	F	3-F	H	A; n _D ²⁰ = 1.5304
3.32.2	C ₂ H ₅	F	3-F	H	B; n _D ²⁰ = 1.5311
35 3.33	C ₃ H ₇	F	3-F	H	

Comp. No.	R ₁	R ₂	(R ₃) _n	R ₄	Physical Data
3.33.1	C ₃ H ₇	F	3-F	H	A; m.p. = 47-48°
3.33.2	C ₃ H ₇	F	3-F	H	B; n _D ²⁰ = 1.5269
5 3.34	ethynyl	Cl	n = 0	H	n _D ²⁰ = 1.5695
3.35	CH ₃	Cl	3-CF ₃	CH ₃	
3.36	CH ₃	Cl	3-Cl	H	
3.37	CH ₃	Cl	3-CH ₃	H	
3.38	C ₂ H ₅	Cl	3-F,4-Cl	H	
10 3.39	C ₂ H ₅	Cl	3-Cl	H	
3.40	C ₂ H ₅	Cl	3-CH ₃	H	
3.41	C ₂ H ₅	Cl	3-OCH ₃	H	
3.42	C ₂ H ₅	Cl	3-CF ₃	H	
3.43	C ₂ H ₅	Cl	3-OCF ₃	H	
15 3.44	C ₂ H ₅	Cl	4-F	H	
3.45	C ₂ H ₅	Cl	3-Cl,5-Cl	H	
3.46	C ₃ H ₇	Cl	3-Cl	H	
3.47	C ₃ H ₇	Cl	3-CH ₃	H	
3.48	C ₃ H ₇	Cl	3-C ₂ H ₅	H	
20 3.49	C ₃ H ₇	Cl	3-OCH ₃	H	
3.50	C ₃ H ₇	Cl	3-CF ₃	H	
3.51	C ₃ H ₇	Cl	3-OCF ₃	H	
3.52	C ₃ H ₇	Cl	4-F	H	
3.53	i-C ₃ H ₇	Cl	3-Cl	H	
25 3.54	i-C ₃ H ₇	Cl	3-CH ₃	H	
3.55	i-C ₃ H ₇	Cl	3-C ₂ H ₅	H	
3.56	C ₂ H ₅	F	n = 0	H	
3.57	C ₂ H ₅	F	3-Cl	H	
3.58	C ₂ H ₅	F	3-F,5-F	H	
30 3.59	C ₃ H ₇	F	n = 0	H	
3.60	C ₃ H ₇	F	3-Cl	H	
3.61	cyclo-C ₃ H ₅	Cl	3-Cl	H	
3.62	cyclo-C ₃ H ₅	Cl	3-CH ₃	H	
3.63	i-C ₄ H ₉	Cl	3-Cl	H	
35 3.64	i-C ₄ H ₉	Cl	3-CH ₃	H	

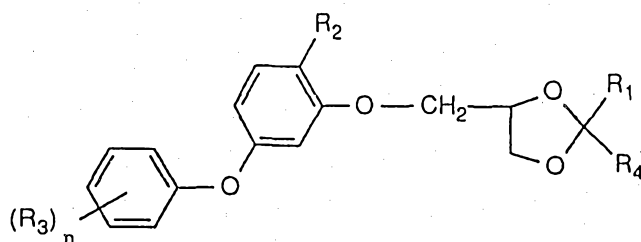
Comp. No.	R ₁	R ₂	(R ₃) _n	R ₄	Physical Data
3.65	C ₆ H ₁₃	Cl	n = 0	H	
3.66	C ₆ H ₁₃	Cl	3-Cl	H	
5 3.67	-CH=CH ₂	Cl	n = 0	H	
3.68	-CH=CH ₂	Cl	3-Cl	H	
3.69	-CH=CH ₂	Cl	3-F	H	
3.70	-CH=CH ₂	Cl	3-F,5-F	H	
3.71	ethynyl	Cl	3-Cl	H	
10 3.72	ethynyl	Cl	3-F	H	
3.73	ethynyl	Cl	3-F,5-F	H	
3.74	prop-1-yn-1-yl	Cl	n = 0	H	
3.75	prop-1-yn-1-yl	Cl	3-Cl	H	
3.76	prop-1-yn-1-yl	Cl	3-F	H	
15 3.77	prop-1-en-1-yl	Cl	n = 0	H	
3.78	prop-1-en-1-yl	Cl	3-Cl	H	
3.79	prop-1-en-1-yl	Cl	3-F	H	
3.80	-CH=C(CH ₃) ₂	Cl	n = 0	H	
3.81	-CH=C(CH ₃) ₂	Cl	3-Cl	H	
20 3.82	-CH=C(CH ₃) ₂	Cl	3-F	H	
3.83	CH ₃	CH ₃	n = 0	CH ₃	
3.84	CH ₃	CH ₃	3-Cl	CH ₃	
3.85	CH ₃	CH ₃	n = 0	H	
3.86	CH ₃	CH ₃	3-Cl	H	
25 3.87	CH ₃	CH ₃	3-F	H	
3.88	C ₂ H ₅	CH ₃	3-Cl	H	
3.89	C ₂ H ₅	CH ₃	3-F	H	
3.90	C ₂ H ₅	CH ₃	3-F,5-F	H	
3.91	C ₂ H ₅	CH ₃	3-C ₂ H ₅	H	
30 3.92	C ₃ H ₇	CH ₃	n = 0	H	
3.93	C ₃ H ₇	CH ₃	3-Cl	H	
3.94	C ₃ H ₇	CH ₃	3-F	H	
3.95	C ₃ H ₇	CH ₃	3-F,5-F	H	
3.96	C ₃ H ₇	CH ₃	3-CH ₃	H	
35 3.97	i-C ₃ H ₇	CH ₃	3-Cl	H	

Comp. No.	R ₁	R ₂	(R ₃) _n	R ₄	Physical Data
3.98	i-C ₃ H ₇	CH ₃	3-F	H	
3.99	cyclo-C ₃ H ₅	CH ₃	3-Cl	H	
5 3.100	cyclo-C ₃ H ₅	CH ₃	3-F	H	
3.101	-CH=CH ₂	CH ₃	n = 0	H	
3.102	-CH=CH ₂	CH ₃	3-Cl	H	
3.103	-CH=CH ₂	CH ₃	3-F	H	
3.104	ethynyl	CH ₃	n = 0	H	
10 3.105	ethynyl	CH ₃	3-Cl	H	
3.106	ethynyl	CH ₃	3-F	H	
3.107	R ₁ +R ₄ : -(CH ₂) ₃ -	Cl	n = 0		
3.108	R ₁ +R ₄ : -(CH ₂) ₃ -	Cl	3-F		
3.109	R ₁ +R ₄ : -(CH ₂) ₃ -	Cl	3-Cl		
15 3.110	R ₁ +R ₄ : -(CH ₂) ₄ -	Cl	n = 0		
3.111	R ₁ +R ₄ : -(CH ₂) ₄ -	Cl	3-F		
3.112	R ₁ +R ₄ : -(CH ₂) ₄ -	Cl	3-Cl		
3.113	R ₁ +R ₄ : -(CH ₂) ₅ -	Cl	n = 0		
3.114	R ₁ +R ₄ : -(CH ₂) ₅ -	Cl	3-F		
20 3.115	R ₁ +R ₄ : -(CH ₂) ₅ -	Cl	3-CH ₃		
3.116	R ₁ +R ₄ : -CH ₂ OCH ₂ CH ₂ CH ₂ -	Cl	n = 0		
3.117	R ₁ +R ₄ : -CH ₂ OCH ₂ CH ₂ CH ₂ -	Cl	3-F		
25 3.118	R ₁ +R ₄ : -CH ₂ OCH ₂ CH ₂ CH ₂ -	Cl	3-Cl		
3.119	C ₂ H ₅	CF ₃	n = 0	H	
3.120	C ₂ H ₅	CF ₃	3-Cl	H	
3.121	C ₂ H ₅	CF ₃	3-F	H	
30 3.122	C ₃ H ₇	CF ₃	n = 0	H	
3.123	C ₃ H ₇	CF ₃	3-Cl	H	
3.124	C ₃ H ₇	CF ₃	3-F	H	
3.125	C ₂ H ₅	OCH ₃	n = 0	H	
3.126	C ₂ H ₅	OCH ₃	3-Cl	H	
35 3.127	C ₂ H ₅	OCH ₃	3-F	H	

Comp. No.	R ₁	R ₂	(R ₃) _n	R ₄	Physical Data
3.128	OCH ₃	Cl	n = 0	CH ₃	
3.129	OCH ₃	Cl	3-Cl	CH ₃	
5 3.130	OCH ₃	Cl	3-F	CH ₃	
3.131	OCH ₃	Cl	3-F,5-F	H	
3.132	OC ₂ H ₅	Cl	n = 0	H	
3.133	OC ₂ H ₅	Cl	3-Cl	H	
3.134	OC ₂ H ₅	Cl	3-F	H	
10 3.135	OC ₂ H ₅	Cl	3-F,5-F	H	
3.136	OC ₂ H ₅	Cl	3-CH ₃	H	
3.137	OCH(CH ₃) ₂	Cl	n = 0	H	
3.138	OCH(CH ₃) ₂	Cl	3-Cl	H	
3.139	OCH(CH ₃) ₂	Cl	3-F	H	
15 3.140	OCH ₂ CH ₂ CH ₃	Cl	n = 0	H	
3.141	OCH ₂ CH ₂ CH ₃	Cl	3-Cl	H	
3.142	OCH ₂ CH ₂ CH ₃	Cl	3-F	H	
3.143	OCH ₃	Br	n = 0	H	
3.144	OCH ₃	Br	3-Cl	H	
20 3.145	OCH ₃	Br	3-F	H	
3.146	OC ₂ H ₅	Br	n = 0	H	
3.147	OC ₂ H ₅	Br	3-Cl	H	
3.148	OC ₂ H ₅	Br	3-Br	H	
3.149	OCH ₃	F	n = 0	H	
25 3.150	OCH ₃	F	3-Cl	H	
3.151	OCH ₃	F	3-F	H	
3.152	OC ₂ H ₅	F	n = 0	H	
3.153	OC ₂ H ₅	F	3-Cl	H	
3.154	OC ₂ H ₅	F	3-Br	H	
30 3.155	OCH ₃	CH ₃	n = 0	H	
3.156	OCH ₃	CH ₃	3-Cl	H	
3.157	OCH ₃	CH ₃	3-Br	H	
3.158	OCH ₃	CH ₃	3-F	H	
3.159	OC ₂ H ₅	CH ₃	n = 0	H	
35 3.160	OC ₂ H ₅	CH ₃	3-Cl	H	

Comp. No.	R ₁	R ₂	(R ₃) _n	R ₄	Physical Data
3.161	OC ₂ H ₅	CH ₃	3-F	H	

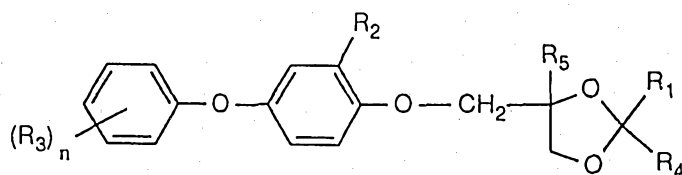
Table 4



Comp. No.	R ₁	R ₂	(R ₃) _n	R ₄	Physical data
5 4.1	C ₂ H ₅	Cl	3-Cl	H	n _D ²⁰ = 1.5662
4.2	C ₃ H ₇	Cl	3-Cl	H	n _D ²⁰ = 1.5609
4.3	CH ₃	Cl	n = 0	CH ₃	
4.4	CH ₃	Cl	n = 0	H	
4.5	CH ₃	Cl	3-Cl	H	
10 4.6	CH ₃	Cl	3-F	H	
4.7	C ₂ H ₅	Cl	n = 0	H	
4.8	C ₂ H ₅	Cl	3-F	H	
4.9	C ₂ H ₅	Cl	3-F,5-F	H	
4.10	C ₂ H ₅	Cl	3-CH ₃	H	
15 4.11	C ₃ H ₇	Cl	n = 0	H	
4.12	C ₃ H ₇	Cl	3-F	H	
4.13	C ₃ H ₇	Cl	3-F,5-F	H	
4.14	i-C ₃ H ₇	Cl	n = 0	H	
4.15	i-C ₃ H ₇	Cl	3-Cl	H	
20 4.16	i-C ₃ H ₇	Cl	3-F	H	
4.17	cyclo-C ₃ H ₅	Cl	n = 0	H	
4.18	cyclo-C ₃ H ₅	Cl	3-F	H	
4.19	cyclo-C ₃ H ₅	Cl	3-Cl	H	
4.20	cyclo-C ₃ H ₅	Cl	3-F,5-F	H	
25 4.21	C ₂ H ₅	Br	n = 0	H	
4.22	C ₂ H ₅	Br	3-Cl	H	
4.23	C ₂ H ₅	Br	3-F	H	
4.24	C ₃ H ₇	Br	n = 0	H	
4.25	C ₃ H ₇	Br	3-Cl	H	
30 4.26	C ₃ H ₇	Br	3-F	H	

Comp. No.	R ₁	R ₂	(R ₃) _n	R ₄	Physical data
4.27	C ₂ H ₅	CH ₃	n = 0	H	
4.28	C ₂ H ₅	CH ₃	3-Cl	H	
4.29	C ₂ H ₅	CH ₃	3-F	H	
5 4.30	C ₂ H ₅	CH ₃	3-F,5-F	H	
4.31	C ₃ H ₇	CH ₃	n = 0	H	
4.32	C ₃ H ₇	CH ₃	3-Cl	H	
4.33		CH ₃	3-F	H	

Table 5

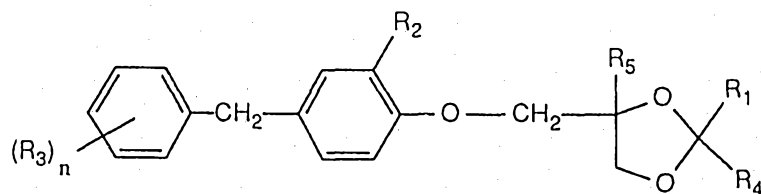


Comp. No. R₁ R₂ (R₃)_n R₄ R₅ Physical Data

5	5.1	C ₂ H ₅	Cl	3-F	H	CH ₃
	5.2	CH ₃	Cl	n = 0	H	CH ₃
	5.3	CH ₃	Cl	n = 0	CH ₃	CH ₃
	5.4	CH ₃	Cl	3-Cl	H	CH ₃
	5.5	CH ₃	Cl	3-F	H	CH ₃
10	5.6	C ₂ H ₅	Cl	n = 0	H	CH ₃
	5.7	C ₂ H ₅	Cl	3-Cl	H	CH ₃
	5.8	C ₂ H ₅	Cl	3-F,5-F	H	CH ₃
	5.9	C ₃ H ₇	Cl	n = 0	H	CH ₃
	5.10	C ₃ H ₇	Cl	3-Cl	H	CH ₃
15	5.11	C ₃ H ₇	Cl	3-F	H	CH ₃
	5.12	C ₃ H ₇	Cl	3-F,5-F	H	CH ₃
	5.13	cyclo-C ₃ H ₅	Cl	n = 0	H	CH ₃
	5.14	cyclo-C ₃ H ₅	Cl	3-Cl	H	CH ₃
	5.15	cyclo-C ₃ H ₅	Cl	3-F	H	CH ₃
20	5.16	i-C ₃ H ₇	Cl	n = 0	H	CH ₃
	5.17	i-C ₃ H ₇	Cl	3-Cl	H	CH ₃
	5.18	i-C ₃ H ₇	Cl	3-F	H	CH ₃
	5.19	C ₂ H ₅	F	n = 0	H	CH ₃
	5.20	C ₂ H ₅	F	3-Cl	H	CH ₃
25	5.21	C ₂ H ₅	F	3-F	H	CH ₃
	5.22	C ₂ H ₅	F	3-F,5-F	H	CH ₃
	5.23	C ₃ H ₇	F	n = 0	H	CH ₃
	5.24	C ₃ H ₇	F	3-Cl	H	CH ₃
	5.25	C ₃ H ₇	F	3-F	H	CH ₃
30	5.26	i-C ₄ H ₉	F	n = 0	H	CH ₃
	5.27	i-C ₄ H ₉	F	3-Cl	H	CH ₃
	5.28	C ₂ H ₅	CH ₃	n = 0	H	CH ₃

Comp. No.	R ₁	R ₂	(R ₃) _n	R ₄	R ₅	Physical Data
5.29	C ₂ H ₅	CH ₃	3-Cl	H	CH ₃	
5.30	C ₂ H ₅	CH ₃	3-F	H	CH ₃	
5 5.31	C ₂ H ₅	CH ₃	3-F,5-F	H	CH ₃	
5.32	C ₃ H ₇	CH ₃	n = 0	H	CH ₃	
5.33	C ₃ H ₇	CH ₃	3-Cl	H	CH ₃	
5.34	C ₃ H ₇	CH ₃	3-F	H	CH ₃	
5.35	C ₃ H ₇	CH ₃	3-F,5-F	H	CH ₃	
10 5.36	C ₂ H ₅	Cl	n = 0	H	C ₂ H ₅	
5.37	C ₂ H ₅	Cl	3-Cl	H	C ₂ H ₅	
5.38	C ₂ H ₅	Cl	3-F	H	C ₂ H ₅	
5.39	C ₂ H ₅	Cl	n = 0	H	C ₃ H ₇	
5.40	C ₂ H ₅	Cl	3-Cl	H	C ₃ H ₇	
15 5.41	C ₂ H ₅	Cl	3-F	H	C ₃ H ₇	

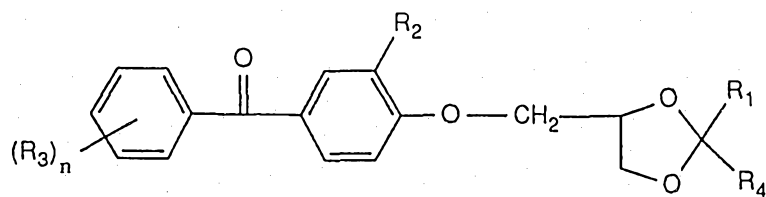
Table 6



Comp. R₁ R₂ (R₃)_n R₄ R₅ Physical Data
No.

5	6.1	C ₃ H ₇	CH ₃	3-F	H	CH ₃
	6.2	C ₃ H ₇	CH ₃	3-Cl	H	CH ₃
	6.3	CH ₃	Cl	n = 0	CH ₃	CH ₃
	6.4	CH ₃	Cl	n = 0	H	CH ₃
	6.5	C ₂ H ₅	Cl	n = 0	H	CH ₃
10	6.6	C ₂ H ₅	Cl	3-Cl	H	CH ₃
	6.7	C ₂ H ₅	Cl	3-F	H	CH ₃
	6.8	C ₂ H ₅	Cl	3-F,5-F	H	CH ₃
	6.9	C ₂ H ₅	CH ₃	n = 0	H	CH ₃
	6.10	C ₂ H ₅	CH ₃	3-Cl	H	CH ₃
15	6.11	C ₂ H ₅	CH ₃	3-F	H	CH ₃
	6.12	C ₂ H ₅	Br	n = 0	H	CH ₃
	6.13	C ₂ H ₅	Br	3-Cl	H	CH ₃
	6.14	C ₂ H ₅	Br	3-F	H	CH ₃
	6.15	C ₂ H ₅	F	n = 0	H	CH ₃
20	6.16	C ₂ H ₅	F	3-Cl	H	CH ₃
	6.17	C ₂ H ₅	F	3-F	H	CH ₃
	6.18	C ₂ H ₅	F	4-F	H	CH ₃
	6.19	C ₂ H ₅	F	3-F,5-F	H	CH ₃
	6.20	C ₃ H ₇	Cl	n = 0	H	CH ₃
25	6.21	C ₃ H ₇	Cl	3-Cl	H	CH ₃
	6.22	C ₃ H ₇	Cl	3-F	H	CH ₃
	6.23	C ₃ H ₇	Cl	3-F,5-F	H	CH ₃
	6.24	C ₃ H ₇	CH ₃	n = 0	H	CH ₃

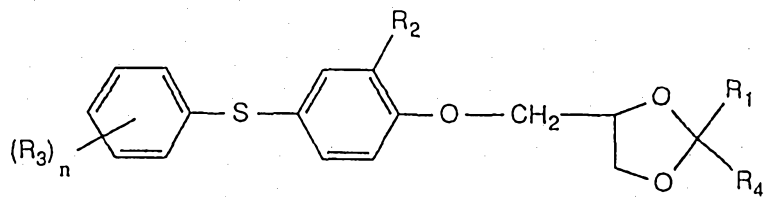
Table 7



Comp. No.	R ₁	R ₂	(R ₃) _n	R ₄	Physical Data
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5	7.1	cyclo-C ₃ H ₅	Cl	n = 0	H	
	7.1.1	cyclo-C ₃ H ₅	Cl	n = 0	H	A; n _D ²⁰ = 1.5825
	7.1.2	cyclo-C ₃ H ₅	Cl	n = 0	H	B; n _D ²⁰ = 1.5859
	7.2	C ₂ H ₅	Cl	n = 0	H	n _D ²⁰ = 1.5811
	7.3	C ₃ H ₇	Cl	4-Cl	H	
10	7.3.1	C ₃ H ₇	Cl	4-Cl	H	A; m.p. = 74-75°
	7.3.2	C ₃ H ₇	Cl	4-Cl	H	B; m.p. = 83-84°
	7.4	C ₂ H ₅	Cl	4-Cl	H	
	7.4.1	C ₂ H ₅	Cl	4-Cl	H	A; m.p. = 100-101°
	7.4.2	C ₂ H ₅	Cl	4-Cl	H	B; m.p. = 101-102°
15	7.5	CH ₃	Cl	n = 0	CH ₃	
	7.6	CH ₃	Cl	n = 0	H	
	7.7	CH ₃	Cl	3-Cl	H	
	7.8	CH ₃	Cl	3-F	H	
	7.9	C ₂ H ₅	Cl	3-Cl	H	
20	7.10	C ₂ H ₅	Cl	3-F	H	
	7.11	C ₃ H ₇	Cl	3-Cl	H	
	7.12	C ₃ H ₇	Cl	3-F	H	
	7.13	C ₂ H ₅	Br	n = 0	H	
	7.14	C ₂ H ₅	Br	3-Cl	H	
25	7.15	C ₂ H ₅	Br	3-F	H	

Table 8



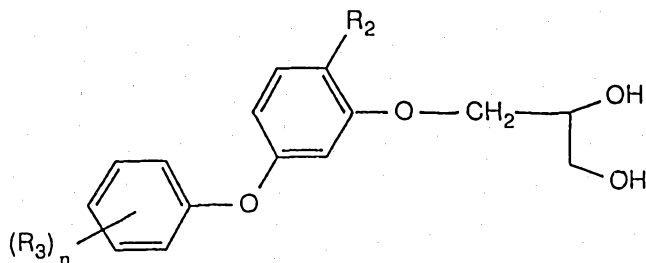
Comp. No. R₁ R₂ (R₃)_n R₄ Physical Data

5	8.1	CH ₃	Cl	n = 0	CH ₃
	8.2	CH ₃	Cl	3-Cl	CH ₃
	8.3	CH ₃	Cl	3-F	CH ₃
	8.4	CH ₃	Cl	n = 0	H
	8.5	CH ₃	Cl	3-Cl	H
10	8.6	CH ₃	Cl	3-F	H
	8.7	CH ₃	Cl	3-F,5-F	H
	8.8	C ₂ H ₅	Cl	n = 0	H
	8.9	C ₂ H ₅	Cl	3-CF ₃	H
	8.10	C ₂ H ₅	Cl	3-Cl	H
15	8.11	C ₂ H ₅	Cl	3-F	H
	8.12	C ₂ H ₅	Cl	3-F,5-F	H
	8.13	C ₃ H ₇	Cl	n = 0	H
	8.14	C ₃ H ₇	Cl	3-Cl	H
	8.15	C ₃ H ₇	Cl	3-F	H
20	8.16	cyclo-C ₃ H ₅	Cl	n = 0	H
	8.17	cyclo-C ₃ H ₅	Cl	3-Cl	H
	8.18	cyclo-C ₃ H ₅	Cl	3-F	H
	8.19	i-C ₃ H ₇	Cl	n = 0	H
	8.20	i-C ₃ H ₇	Cl	3-Cl	H
25	8.21	i-C ₃ H ₇	Cl	3-F	H
	8.22	i-C ₄ H ₉	Cl	n = 0	H
	8.23	i-C ₄ H ₉	Cl	3-Cl	H
	8.24	i-C ₄ H ₉	Cl	3-F	H
	8.25	C ₂ H ₅	Br	n = 0	H
30	8.26	C ₂ H ₅	Br	3-Cl	H
	8.27	C ₂ H ₅	Br	3-F	H

Comp. No.	R ₁	R ₂	(R ₃) _n	R ₄	Physical Data
8.28	C ₃ H ₇	Br	n = 0	H	
8.29	C ₃ H ₇	Br	3-Cl	H	
5 8.30	C ₃ H ₇	Br	3-F	H	

Example H5: The compound of the formula II which is listed in Table 9 can also be prepared analogously to the procedure described in Example H1, if desired after additional purification by chromatography [$\text{CH}_2\text{Cl}_2/(\text{C}_2\text{H}_5)_2\text{O} = 3:2$].

Table 9



Comp. No.	R_2	$(\text{R}_3)_n$	Physical Data
9.1	Cl	3-Cl	$n_D^{20} = 1.5909$

Formulation Examples

Example F1: Emulsion concentrates

	a)	b)	c)
Active ingredient according to Preparation Examples	25 %	40 %	50 %
Calcium dodecylbenzenesulfonate	5 %	8 %	6 %
Castor oil polyethylene glycol ether (36 mol EO)	5 %	-	-
Tributylphenol polyethylene glycol ether (30 mol EO)	-	12 %	4 %
Cyclohexanone	-	15 %	20 %
Xylene mixture	65 %	25 %	20 %

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

Example F2: Solutions

	a)	b)	c)	d)
Active ingredient according to Preparation Examples	80 %	10 %	5 %	95 %
Ethylene glycol monomethyl ether	20 %	-	-	-
Polyethylene glycol (MW 400)	-	70 %	-	-
N-Methyl-2-pyrrolidone	-	20 %	-	-
Epoxidised coconut oil	-	-	1 %	5 %
Petroleum spirit (boiling range: 160-190°C)	-	-	94 %	-

The solutions are suitable for use in the form of microdrops.

Example F3: Granules

	a)	b)
Active ingredient according to Preparation Examples	5 %	10 %
Kaolin	94 %	-
Highly disperse silica	1 %	-
Attapulgate	-	90 %

The active ingredient is dissolved in dichloromethane, the solution is sprayed onto the carrier, and the solvent is subsequently removed by evaporation in vacuo.

Example F4: Dusts

	a)	b)
Active ingredient according to Preparation Examples	2 %	5 %
Highly disperse silica	1 %	5 %
Talc	97 %	-
Kaolin	-	90 %

Ready-for-use dusts are obtained by intimately mixing the carriers with the active ingredient.

Example F5: Wetttable powders

	a)	b)	c)
Active ingredient according to Preparation Examples	20 %	50 %	75 %

Sodium ligninsulfonate	5 %	5 %	-
Sodium lauryl sulfate	3 %	-	5 %
Sodium diisobutylnaphthalene-sulfonate	-	6 %	10 %
5 Octylphenol polyethylene glycol ether (7-8 mol EO)	-	2 %	-
Highly disperse silica	5 %	10 %	10 %
Kaolin	67 %	27 %	-

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

Example F6: Emulsion concentrate

	a)	b)
Active ingredient according to Preparation Examples	10 %	10 %
15 Octylphenol polyethylene glycol ether (4-5 mol EO)	3 %	-
Calcium dodecylbenzenesulfonate	3 %	-
Castor oil polyglycol ether (36 mol EO)	4 %	-
20 Castor oil thioxylate	-	25 %
Cyclohexanone	30 %	-
Butanol	-	15 %
Xylene mixture	50 %	-
Ethyl acetate	-	50 %

25 Emulsions of any desired concentration can be prepared from these concentrates by dilution with water.

Example F7: Dusts

	a)	b)
Active ingredient according to Preparation Examples	5 %	8 %
30 Talc	95 %	-
Kaolin	-	92 %

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

Example F8: Extruder granules

Active ingredient according

5	to Preparation Examples	10 %
	Sodium ligninsulfonate	2 %
	Carboxymethylcellulose	1 %
	Kaolin	87 %

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

Example F9: Coated granules

Active ingredient according

	to Preparation Examples	3 %
	Polyethylene glycol (MW 200)	2 %
15	Kaolin	94 %

In a mixer, the finely-ground active ingredient is applied uniformly to the kaolin which has been moistened with polyethylene glycol. Dust-free coated granules are obtained in this manner.

Example F10: Suspension concentrate

20	Active ingredient according	
	to Preparation Examples	40 %
	Ethylene glycol	10 %
	Nonylphenol polyethylene glycol	
	ether (15 mol EO)	6 %
25	Sodium ligninsulfonate	10 %
	Carboxymethylcellulose	1 %
	37% aqueous formaldehyde solution	0.2 %
	Silicone oil in the form of a	
	75% aqueous emulsion	0.8 %
30	Water	32 %

The finely ground active ingredient is mixed intimately with the additives. This gives a suspension concentrate from which suspensions of any desired concentration can be prepared by dilution with water.

Biological Examples

5 Example B1: Activity against Boophilus microplus

Adult ticks (females) which have sucked themselves full are stuck onto a PVC plate and covered with a cottonwool ball. For the treatment, 10 ml of an aqueous test solution comprising 125 ppm of the active ingredient to be tested are poured over the test animals. The cottonwool ball is subsequently removed, and the ticks are incubated for 4 weeks for oviposition. The activity against *Boophilus microplus* becomes apparent either in the female in the form of mortality or sterility, or in the eggs in the form of an ovicidal activity.

In this test, compounds of Tables 2 to 8 have a good activity.

Example B2: Ovicidal activity on Cydia pomonella

15 *Cydia pomonella* eggs which have been deposited on filter paper are briefly immersed into a test solution comprising 400 ppm of the active ingredient to be tested in acetone/water. After the test solution has dried on, the eggs are incubated in Petri dishes. After 6 days, the hatching percentage of the eggs is evaluated by comparison with untreated control batches (% hatching reduction).

20 In this test, compounds of Tables 2 to 8 have a good activity.

Example B3: Ovicidal activity on Adoxophyes reticulana

Adoxophyes reticulana eggs which have been deposited on filter paper are briefly immersed into a test solution comprising 400 ppm of the active ingredient to be tested in acetone/water. After the test solution has dried on, the eggs are incubated in Petri dishes.

25 After 6 days, the hatching percentage of the eggs is evaluated by comparison with untreated control batches (% hatching reduction).

In this test, compounds of Tables 2 to 8 have a good activity.

Example B4: Ovicidal activity on Lobesia botrana

Lobesia botrana eggs which have been deposited on filter paper are briefly immersed into a test solution comprising 400 ppm of the active ingredient to be tested in acetone/water. After the test solution has dried on, the eggs are incubated in Petri dishes. After 6 days, the

hatching percentage of the eggs is evaluated by comparison with untreated control batches (% hatching reduction).

In this test, compounds of Tables 2 to 8 have a good activity.

Example B5: Activity against Aonidiella aurantii

5 Potato tubers are populated with Aonidiella aurantii (orange scale insect) crawlers. After approx. 2 weeks, the potatoes are immersed in an aqueous emulsion, or suspension, spray mixture comprising the active ingredient to be tested at a concentration of 400 ppm. After the treated potato tubers have dried, they are incubated in a plastic container. To evaluate the test, the survival rate of the crawlers of the first subsequent generation of the treated
10 scale insect population is compared after 10-12 weeks with that of the untreated control batches.

In this test, compounds of Tables 2 to 8 have a good activity.

Example B6: Activity against Nilaparvata lugens

15 Rice plants are treated with an aqueous emulsion spray mixture comprising 400 ppm of the active ingredient. After the spray coating has dried on, the rice plants are populated with cicada larvae of the 2nd and 3rd stage. The test is evaluated 21 days later. The percentage reduction in population (% activity) is determined by comparing the number of surviving cicadas on the treated with the number of surviving cicadas on the untreated plants.

20 In this test, compounds of Tables 2 to 8 have a good activity.

Example B7: Activity against Nephotettix cincticeps

25 Rice plants are treated with an aqueous emulsion spray mixture comprising 400 ppm of the active ingredient. After the spray coating has dried on, the rice plants are populated with cicada larvae of the 2nd and 3rd stage. The test is evaluated 21 days later. The percentage reduction in population (% activity) is determined by comparing the number of surviving cicadas on the treated with the number of surviving cicadas on the untreated plants.

In this test, compounds of Tables 2 to 8 have a good activity.

Example B8: Activity against Bemisia tabaci

30 Dwarf bean plants are placed into gauze cages and populated with Bemisia tabaci (whitefly) adults. When oviposition has taken place, all adults are removed, and, 10 days later, the plants together with the nymphs with which they are populated are treated with

an aqueous emulsion spray mixture of the active ingredients to be tested (concentration 400 ppm). The test is evaluated 14 days after the active ingredient has been applied by determining the hatching percentage in comparison with the untreated control batches. In this test, compounds of Tables 2 to 8 have a good activity.

5 Example B9: Activity against *Tetranychus urticae*

Young bean plants are populated with a mixed population of *Tetranychus urticae*, and, 1 day later, sprayed with an aqueous emulsion spray mixture comprising 400 ppm of the active ingredient. The plants are subsequently incubated for 6 days at 25°C and then evaluated. The percentage reduction in population (% activity) is determined by
10 comparing the number of dead eggs, larvae and adults on the treated plants with the number of dead eggs, larvae and adults on the untreated plants.
In this test, compounds of Tables 2 to 8 have a good activity.

Example B10: Ovo/larvicidal activity on *Heliothis virescens*

15 *Heliothis virescens* eggs which have been deposited on cotton are sprayed with an aqueous emulsion spray mixture comprising 400 ppm of the active ingredient. After 8 days, the hatching percentage of the eggs and the survival rate of the caterpillars are evaluated by comparing them with untreated control batches (% reduction in population).
In this test, compounds of Tables 2 to 8 have a good activity.

Example B11: Activity against *Panonychus ulmi* (OP- and Carb.-resistant)



20 Apple seedlings are populated with adult *Panonychus ulmi* females. After seven days, the infected plants are sprayed to drip point with an aqueous emulsion spray mixture comprising 400 ppm of the compound to be tested and grown in the greenhouse. The test is evaluated after 14 days. The percentage population reduction (% activity) is determined by comparing the number of dead spider mites on the treated plants with the number of
25 dead spider mites on the untreated plants.
In this test, compounds of Tables 2 to 8 have a good activity.

Example B12: Activity against *Ctenocephalides felis*

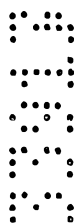
20 to 25 flea eggs are placed into a horizontally positioned 50 ml cell culture flask into which 15 g of flea larvae medium comprising 100 ppm of the active ingredient to be tested
30 had been introduced. The test flasks are incubated in an incubator at 26 to 27°C and 60-70% atmospheric humidity. The presence of adult fleas, unhatched pupae and larvae is

checked after 21 days.

In this test, compounds of Tables 2 to 8 have a good activity.

Example B13: Activity against Bemisia tabaci eggs

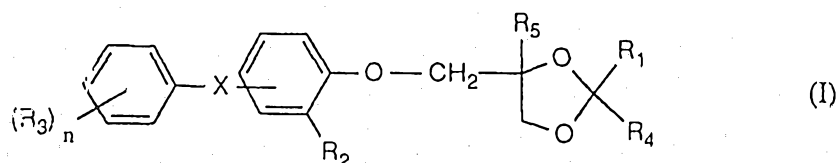
Dwarf bean plants are placed into gauze cages and populated with Bemisia tabaci
5 (whitefly) adults. When oviposition has taken place, all adults are removed, and, 2 days
later, the plants together with the nymphs with which they are populated are treated with
an aqueous emulsion spray mixture of the active ingredients to be tested (concentration
400 ppm). The test is evaluated 10 days after the active ingredient has been applied by
determining the hatching percentage in comparison with the untreated control batches.
10 In this test, compounds of Tables 2 to 8 have a good activity.



~~WHAT IS CLAIMED IS:~~

The claims defining the invention are as follows:

1. A compound of the formula



in which:

n is 0, 1 or 2, and, if n is 2, the two radicals R_3 are identical or different;

either R_1 is C_1 - C_6 alkyl, halo- C_1 - C_3 alkyl, C_2 - C_4 alkenyl, C_2 - C_4 alkynyl, C_1 - C_3 alkoxy or C_3 - C_6 cycloalkyl and R_4 is hydrogen or C_1 - C_3 alkyl, or R_1 and R_4 together with the carbon atom to which R_1 and R_4 are bonded are a ring having 4, 5 or 6 ring members, and the ring skeleton, which may contain a carbon-carbon double bond, is composed either only of carbon atoms or of 1 oxygen atom and 3, 4 or 5 carbon atoms, and the ring is unsubstituted or mono- or disubstituted by identical or different C_1 - C_3 alkyl radicals;

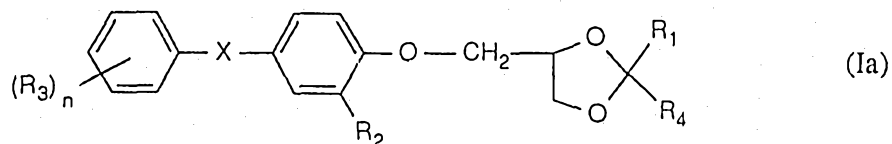
R_2 is C_1 - C_3 alkyl, halo- C_1 - C_3 alkyl, C_1 - C_3 alkoxy, halo- C_1 - C_3 alkoxy, fluorine, chlorine or bromine;

R_3 is C_1 - C_3 alkyl, halo- C_1 - C_3 alkyl, C_1 - C_3 alkoxy, halo- C_1 - C_3 alkoxy, fluorine, chlorine or bromine;

R_5 is hydrogen or C_1 - C_3 alkyl and

X is methylene, O, S or $C(=O)$.

2. A compound according to claim 1 of the formula



in which:

n is 0, 1 or 2, and, if n is 2, the two radicals R_3 are identical or different;

R_1 is C_1 - C_4 alkyl, vinyl or cyclopropyl;

R_2 is methyl or chlorine;

R_3 is methyl, fluorine or chlorine;

R_4 is hydrogen or methyl and

X is oxygen or methylene.

3. A compound according to claim 2 of the formula Ia in which X is oxygen.
4. A compound according to claim 2 or 3 of the formula Ia in which R₂ is chlorine.
5. A compound according to any one of claims 2 to 4 of the formula Ia in which R₄ is hydrogen.
6. A compound according to any one of claims 2 to 5 of the formula Ia in which R₁ is C₁-C₄alkyl.
7. A compound according to claim 6 of the formula Ia in which n is 1 or 2 and R₃ is fluorine or chlorine.
8. A compound according to claim 7 of the formula Ia in which the radical R₃ or one of the radicals R₃ is bonded in the 3-position.
9. A compound according to claim 2 of the formula Ia in which X is methylene, R₂ is chlorine and R₄ is hydrogen.
10. A compound according to claim 9 of the formula Ia in which R₁ is C₁-C₄alkyl.
11. A compound according to claim 10 of the formula Ia in which n is 1 or 2 and R₃ is fluorine or chlorine and the radical R₃ or one of the radicals R₃ is bonded in the 3-position.
12. A compound according to claim 2 of the formula Ia, selected from the group of compounds ~~comprising~~ ^{consisting of}
 - 4-(2-chloro-4-phenoxyphenoxyethyl)-2-ethyl-1,3-dioxolane;
 - 4-(2-chloro-4-phenoxyphenoxyethyl)-2-propyl-1,3-dioxolane;
 - 4-(2-chloro-4-phenoxyphenoxyethyl)-2-isopropyl-1,3-dioxolane;
 - 4-(2-chloro-4-phenoxyphenoxyethyl)-2-cyclopropyl-1,3-dioxolane;
 - 4-[2-chloro-4-(3-fluorophenoxy)phenoxyethyl]-2-ethyl-1,3-dioxolane;
 - 4-[2-chloro-4-(3-fluorophenoxy)phenoxyethyl]-2-propyl-1,3-dioxolane;
 - 4-[2-chloro-4-(3-fluorophenoxy)phenoxyethyl]-2-isopropyl-1,3-dioxolane;
 - 4-[2-chloro-4-(3-fluorophenoxy)phenoxyethyl]-2-cyclopropyl-1,3-dioxolane;



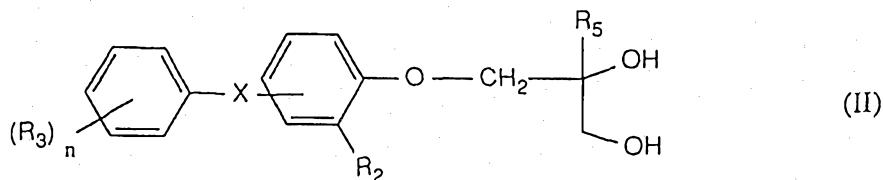
4-[2-chloro-4-(3-chlorophenoxy)phenoxy)methyl]-2-ethyl-1,3-dioxolane;
 4-[2-chloro-4-(3-chlorophenoxy)phenoxy)methyl]-2-propyl-1,3-dioxolane;
 4-[2-chloro-4-(3-chlorophenoxy)phenoxy)methyl]-2-isopropyl-1,3-dioxolane;
 4-[2-chloro-4-(3,5-difluorophenoxy)phenoxy)methyl]-2-ethyl-1,3-dioxolane;
 4-[2-chloro-4-(3,5-difluorophenoxy)phenoxy)methyl]-2-propyl-1,3-dioxolane;
 4-[2-chloro-4-(3,5-difluorophenoxy)phenoxy)methyl]-2-isopropyl-1,3-dioxolane;
 4-[2-chloro-4-(3,4-dichlorophenoxy)phenoxy)methyl]-2-ethyl-1,3-dioxolane and
 4-[2-chloro-4-(3-chloro-4-fluorophenoxy)phenoxy)methyl]-2-ethyl-1,3-dioxolane.

13. A compound according to claim 2 of the formula Ia, selected from the group of compounds ~~comprising~~ ^{consisting of}

4-(2-chloro-4-benzylphenoxy)methyl)-2-ethyl-1,3-dioxolane;
 4-(2-chloro-4-benzylphenoxy)methyl)-2-propyl-1,3-dioxolane;
 4-(2-chloro-4-benzylphenoxy)methyl)-2-isopropyl-1,3-dioxolane;
 4-(2-chloro-4-benzylphenoxy)methyl)-2-cyclopropyl-1,3-dioxolane;
 4-[2-chloro-4-(3-fluorobenzyl)phenoxy)methyl]-2-ethyl-1,3-dioxolane;
 4-[2-chloro-4-(3-fluorobenzyl)phenoxy)methyl]-2-propyl-1,3-dioxolane;
 4-[2-chloro-4-(3,5-difluorobenzyl)phenoxy)methyl]-2-ethyl-1,3-dioxolane and
 4-[2-chloro-4-(3,4-dichlorobenzyl)phenoxy)methyl]-2-ethyl-1,3-dioxolane.

14. A process for the preparation of a compound according to claim 1 of the formula I, which comprises

a) reacting a compound of the formula

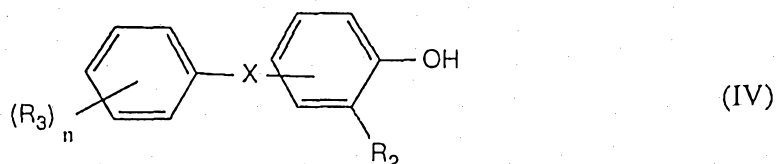


with a compound of the formula



preferably in the presence of an acidic catalyst, or

b) reacting a compound of the formula



with a compound of the formula



preferably in the presence of a base, or

c) reacting a compound of the formula II with a compound of the formula



preferably in the presence of an acidic catalyst, where n, R₁, R₂, R₃, R₄, R₅ and X are in each case as defined for formula I, R₆ and R₇ either independently of one another are C₁-C₈alkyl or together are -(CH₂)₂- or -(CH₂)₃- and Z is chlorine, bromine, iodine, methanesulfonyloxy or p-toluenesulfonyloxy and, if desired, in each case a mixture of isomers which can be obtained according to the process is separated and the desired isomer is isolated.

15. A pesticide, which comprises at least one compound according to claim 1 as active ingredient and at least one adjuvant.

16. A composition according to claim 15 for protecting plants or animals against infestation with insects and/or pests from the order of the Acarina.

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17. A process for the preparation of a composition according to claim 15, which comprises intimately mixing the active ingredient with the adjuvant(s).

18. A 4-(4-phenoxyphenoxyethyl)-1,3 dioxolane derivative substantially as hereinbefore described with reference to any one of the Preparation Examples.

5 19. A process for the preparation of a 4-(4-phenoxyphenoxyethyl)-1,3 dioxolane derivative substantially as hereinbefore described with reference to any one of the Preparation Examples.

20. A pesticidal composition substantially as hereinbefore described with reference to any one of the Formulation Examples.

10 21. A method of controlling pests, which comprises treating the pests or the various development stages of the pests or their locus with a pesticidally effective amount of a compound according to any one of claims 1 to 13 or 18 or a composition according to any one of claims 15, 16 or 20.

22. A method according to claim 21 for protecting plants or animals against 15 infestation with insects and/or pests from the order of the Acarina.

23. A method according to claim 21 for protecting seed, which comprises treating the seed or the seed furrow.

24. Seed treated according to the method described in claim 23.

Dated 24 May, 1996

Ciba-Geigy AG

Patent Attorneys for the Applicant/Nominated Person

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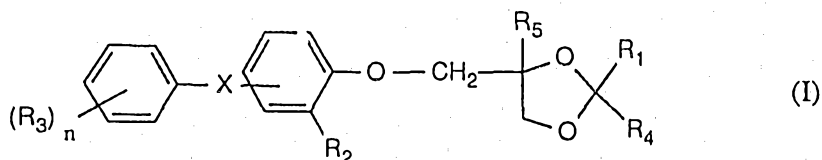


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Dioxolane derivatives

Abstract

Compounds of the formula



5 in which:

n is 0, 1 or 2, and, if n is 2, the two radicals R₃ are identical or different;

either R₁ is C₁-C₆alkyl, halo-C₁-C₃alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₃alkoxy or C₃-C₆cycloalkyl and R₄ is hydrogen or C₁-C₃alkyl, or R₁ and R₄ together with the carbon

10 skeleton, which may contain a carbon-carbon double bond, is composed either only of carbon atoms or of 1 oxygen atom and 3, 4 or 5 carbon atoms, and the ring is unsubstituted or mono- or disubstituted by identical or different C₁-C₃alkyl radicals; R₂ is C₁-C₃alkyl, halo-C₁-C₃alkyl, C₁-C₃alkoxy, halo-C₁-C₃alkoxy, fluorine, chlorine or bromine; R₃ is

15 C₁-C₃alkyl, halo-C₁-C₃alkyl, C₁-C₃alkoxy, halo-C₁-C₃alkoxy, fluorine, chlorine or bromine;

R₅ is hydrogen or C₁-C₃alkyl and X is methylene, O, S or C(=O), can be used as agrochemical active ingredients and can be prepared in a manner known per se.