

PATENT SPECIFICATION

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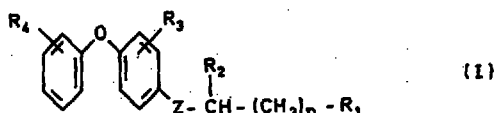


(54) DIPHENYL ETHERS AND THEIR USE IN PEST CONTROL

(71) We, CIBA-GEIGY A.G., a Swiss body Corporate of Basle, Switzerland, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to diphenyl ethers, their preparation, and their use in pest control.

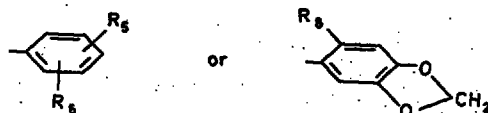
According to the present invention, there are provided compounds of the formula:



wherein n is 0 or 1,

Z represents an oxygen, or sulphur atom or a group of the formula $-N-R_7$ (wherein R_7 represents a hydrogen atom or a C_1 or C_2 alkanoyl group),

R_1 represents a group of the formula



wherein R_3 represents a hydrogen or halogen atom or a C_1-C_4 alkyl, ethynyl, C_1-C_4 alkylthio, C_1-C_4 alkoxy, C_2-C_4 alkenyloxy, C_3-C_4 haloalkenyloxy, C_3-C_4 alkynyloxy, nitro, cyano, C_2-C_4 alkoxycarbonyl, C_3-C_4 alkenyloxycarbonyl, C_3-C_4 alkynyloxycarbonyl, C_1-C_4 alkanoyl, C_1-C_4 alkylcarbonyl or di(C_1-C_4 alkyl) carbamoyl group,

R_5 represents a hydrogen or halogen atom or a methyl, ethyl, isopropyl or methoxy group and

R_6 represents a hydrogen atom or a n -propyl group),

R_2 represents a hydrogen atom or a methyl or ethyl group, and

R_3 and R_4 , which may be the same or different, represents a hydrogen or halogen atom or a methyl, ethyl, methoxy, ethoxy or nitro group.

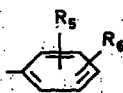
By halogen is meant fluorine, chlorine, bromine or iodine. The alkyl, alkylthio, alkoxy, alkenyloxy, haloalkenyloxy or alkynyloxy, groups given under R_5 , are straight-chain or branched-chain. Examples of such groups are: methyl, ethyl, n-propyl, isopropyl, methylthio, methoxy, ethoxy, allyloxy, β -chloroallyloxy, γ -chloroallyloxy, propargyloxy or 1-butyne-3-yloxy. The alkyl, alkoxy, alkenyloxy or alkynyloxy parts of an alkoxycarbonyl, alkenyloxycarbonyl, alkynyloxycarbonyl or dialkylcarbamoyl group R_6 , can be branched-chain or straight-chain. Examples of alkoxy, alkenyloxy, alkynyloxycarbonyl or dialkylcarbamoyl groups are: carbomethoxy, carbethoxy, allyloxycarbonyl, propargyloxycarbonyl or diethylcarbamoyl. Examples of alkanoyl groups denoted by R_7 and R_8 are as appropriate: formyl, acetyl or propionyl.

Preferred compounds of formula I by virtue of their action are those wherein

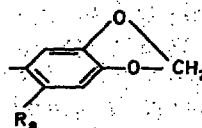
n is 0,

Z represents an oxygen or sulphur atom,

R_1 represents a group of the formula



or



(wherein R_5 represents a hydrogen, fluorine, chlorine, bromine or iodine atom or a methyl, ethyl, propyl, isopropyl, nitro, methoxy, ethoxy, methylmercapto, propargyloxy, allyloxy, C_2 or C_3 alkoxycarbonyl, propargyloxycarbonyl, acetyl or diethylcarbamoyl group,

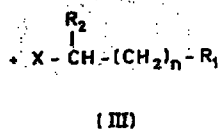
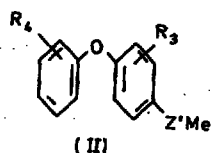
R_6 represents a hydrogen or chlorine atom or a methyl, ethyl or methoxy group and

R_7 represents a hydrogen atom or an n-propyl group)

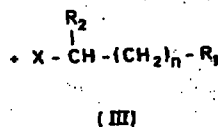
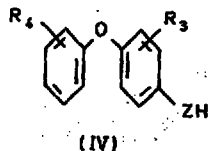
R_8 represents a hydrogen atom or a methyl group, and each of

R_5 and R_6 , which may be the same or different, represents a hydrogen or chlorine atom or a methyl, methoxy or ethoxy group.

The compounds of formula I can be prepared according to the following methods known *per se* by alkylation of a compound of formula II or IV with a halide of formula III, in the presence of a base:

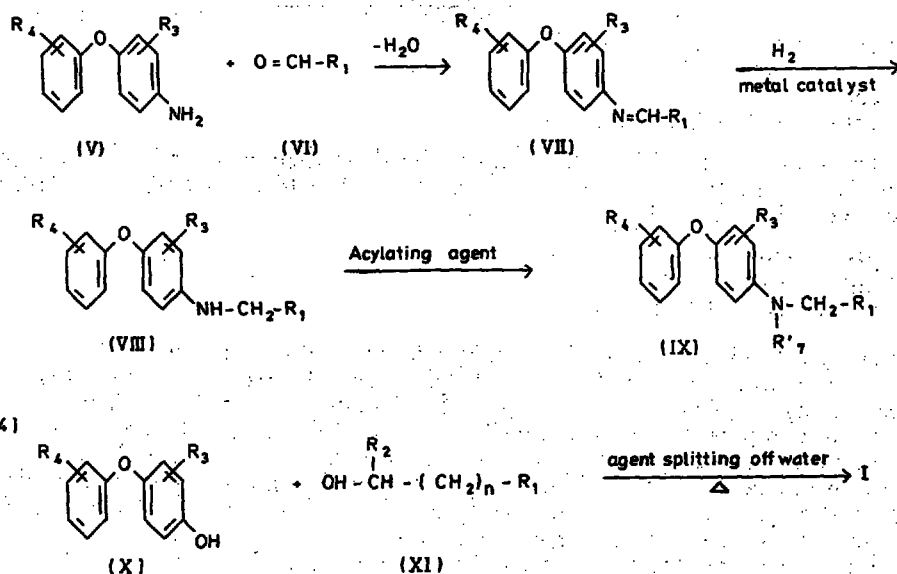


2) If R_7 represents hydrogen:



3) Process for the preparation of compounds of formula I wherein $Z = -NR_n-$, $n=0$, $R_2=H$, R_3 =hydrogen, formyl or acetyl, and R_1 , R_5 and R_6 have the meanings given for formula I:

A primary aromatic amine of formula V is condensed, in a known manner, with an aromatic, optionally substituted aldehyde of formula VI, optionally in the presence of an acid catalyst, such as, e.g. *p*-toluenesulphonic acid or sulphuric acid, to an azomethine derivative of formula VII, with the separation of water. The $-N=C$ bond of the azomethine of formula VII is hydrogenated, e.g. catalytically in the presence of a metal catalyst, such as, e.g. finely divided nickel, palladium or platinum. The phenoxy-aniline derivative of formula VIII can, if required, be further treated with an acylating agent, such as, e.g. carboxylic acid anhydrides or carboxylic acid chlorides, whereby compounds of formula IX are obtained.



In the above process, condensation of a compound of formula X with a compound of formula XI with catalytic splitting-off of water is performed preferably at a temperature of 60–110°C. Dicyclohexylcarbodiimide, for example, can be used as the agent splitting off water.

In formula II to XI, the symbols R_1 to R_4 and n have the meanings given for formula I, R'_1 stands for formyl or acetyl Z' for oxygen or sulphur, X for halogen, especially chlorine or bromine, and Me for a metal of the 1st or 2nd main group of the periodic system, particularly sodium, potassium or calcium.

Suitable bases are, e.g. tertiary amines such as trialkylamines, pyridine or dialkylanilines; also inorganic bases such as hydrides or hydroxides; and alkoxides and carbonates of alkali metals and alkaline-earth metals. Processes 1 and 2 are preferably performed at a reaction temperature of between –10 and 130°C, more preferably between 10 and 80°C, under normal pressure and in the presence of solvents or diluents.

Suitable solvents or diluents are, e.g. ethers such as diethyl ether, diisopropyl ether, 1,2-dimethoxyethane, dioxane or tetrahydrofuran; *N,N*-dialkylated carboxylic acid amides such as dimethylformamide; aliphatic and aromatic hydrocarbons, particularly benzene, toluene, xylenes or ethylbenzene; ketones such as acetone, methylethyl ketone or cyclohexanone, as well as hexamethylphosphoric acid triamide or dimethylsulphoxide.

The starting materials of formulae II to VI, X and XI are known compounds, or can be prepared by methods analogous to those described in the literature. The azomethines of formula VII are in some cases new compounds.

The compounds of formula I are suitable for use in the combating pests which are insects or members of the order *Acarina*. Accordingly the invention also provides a method of combating pests which are insects or members of the order *Acarina* at a locus, which method comprises applying to the locus a compound of the formula I. The compounds of formula I are suitable for use in combating insects of the families:

Acrididae, *Blattidae*, *Gryllidae*, *Gryllotalpidae*, *Tettigoniidae*, *Gimicidae*, *Pyrrhocoridae*, *Reduviidae*, *Aphididae*, *Delphacidae*, *Diaspididae*, *Pseudococcidae*, *Chrysomelidae*, *Coccinellidae*, *Bruchidae*, *Scarabaeidae*, *Dermestidae*, *Tenebrionidae*, *Curculionidae*, *Tineidae*, *Noctuidae*, *Lymantriidae*, *Pyrilidae*, *Galleridae*, *Culicidae*, *Tipulidae*, *Stomoxysidae*, *Muscidae*, *Calliphoridae*, *Trypetidae* and *Pulicidae*, as well as acarids of the families: *Ixodidae*, *Argasidae*, *Tetranychidae* and *Dermanyssidae*.

The locus of application of the compounds of formula I suitably comprises corn, maize, rice, vegetables, ornamental plants, fruit trees, grape vines or field fruits.

The insecticidal or acaricidal action of the compounds of formula I can be appreciably widened and adapted to suit given circumstances by the addition of other insecticides and/or acaricides. Suitable additives are, e.g.:

organic phosphorus compounds,

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nitrophenols and derivatives,
formamidines, ureas,
carbamates or
chlorinated hydrocarbons.

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The compounds of formula I can be used on their own or in composition form. The compositions comprise (i) a compound of formula I together with at least one of the following:

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- (ii) a solid extender,
- (iii) a surfactant; or
- (iv) an aerosol propellant.

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The compositions may be solid or liquid, and can contain substances common in formulation practice, such as, e.g. natural or regenerated substances, solvents, dispersing agents, wetting agents, adhesives, thickeners, binders and/or fertilisers.

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Solid compositions may comprise one or both of a solid extender or a surfactant and liquid compositions may comprise one or both of a surfactant and a hydrocarbon which boils at a temperature above 130°C. The aerosol propellant used may be a polyhalogenated hydrocarbon.

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For application, the compounds of formula I can be processed into the form of dusts, emulsion concentrates, granulates, dispersions, sprays or solutions, the formulation of these preparations being effected in a manner commonly known in practice.

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The compositions according to the invention may be prepared in a manner known *per se* e.g. by the intimate mixing and/or grinding of active substances of formula I with suitable extenders, optionally with the addition of dispersing agents or solvents which are inert to the active substances. The active substances can be obtained and used in the following forms.

solid preparations:—

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dusts, scattering agents, granulates, pellets, coated granulates, coated pellets, impregnated granulates, impregnated pellets, and homogeneous granulates;

liquid preparations:—

- a) water-dispersible active-substance concentrates: wettable powders, pastes or emulsions;
- b) solutions.

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The content of active substance in the compositions is generally between 0.1 and 95% by weight.

The active substances of formula I can be formulated, for example, as follows: [Parts and percentages are by weight]

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Dusts:

The following substances are used in the preparation of a) a 5% dust, and b) a 2% dust:

- a) 5 parts of active substance,
95 parts of talcum;
- b) 2 parts of active substance,
1 part of highly dispersed silicic acid,
97 parts of talcum.

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The active substances are mixed and ground with the extenders.

Granulate:

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The following substances are used to prepare a 5% granulate:

- 5 parts of active substance;
- 0.25 part of epichlorohydrin,
- 0.25 part of cetyl polyglycol ether,
- 3.50 parts of polyethylene glycol,
- 91 parts of kaolin (particle size 0.3—0.8 mm).

The active substance is mixed with epichlorohydrin and dissolved with 6 parts of acetone; the polyethylene glycol and cetyl polyglycol ether are then added. The solution thus obtained is sprayed onto kaolin, and the acetone subsequently evaporated off *in vacuo*.

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Wettable powder:

The following constituents are used for the preparation of a) a 40%, b) and c) a 25%, and d) a 10% wettable powder:

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|----|--|----|
| 10 | a) 40 parts of active substance,
5 parts of sodium lignin sulphonate,
1 part of sodium dibutyl-naphthalene sulphonate,
54 parts of silicic acid; | 10 |
| 15 | b) 25 parts of active substance,
4.5 parts of calcium lignin sulphonate,
1.9 parts of Champagne chalk/hydroxyethyl cellulose mixture (1:1),
1.5 parts of sodium dibutyl naphthalene sulphonate,
19.5 parts of silicic acid,
19.5 parts of Champagne chalk,
28.1 parts of kaolin; | 15 |
| 20 | c) 25 parts of active substance,
2.5 parts of isooctylphenoxy-polyoxyethylene-ethanol,
1.7 parts of Champagne chalk/hydroxyethyl cellulose mixture (1:1),
8.3 parts of sodium aluminium silicate,
16.5 parts of kieselguhr,
46 parts of kaolin; | 20 |
| 25 | d) 10 parts of active substance,
3 parts of a mixture of the sodium salts of saturated fatty alcohol sulphates,
5 parts of naphthalenesulphonic acid/formaldehyde condensate,
82 parts of kaolin. | 25 |

30 The active substances are intimately mixed, in suitable mixers, with the additives, the mixture being then ground in the appropriate mills and rollers. Wettable powders are obtained which can be diluted with water to give suspensions of desired concentration.

Emulsifiable concentrates:

35 The following substances are used to prepare a) a 10% and b) a 25% emulsifiable concentrate:

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| 40 | a) 10 parts of active substance,
3.4 parts of epoxidised vegetable oil,
3.4 parts of a combination emulsifier consisting of fatty alcohol polyglycol ether and alkylarylsulphonate calcium salt,
40 parts of dimethylformamide,
43.2 parts of xylene; | 40 |
| 45 | b) 25 parts of active substance,
2.5 parts of epoxidised vegetable oil,
10 parts of an alkylarylsulphonate/fatty alcohol polyglycol ether mixture,
5 parts of dimethylformamide,
57.5 parts of xylene. | 45 |

From these concentrates it is possible to prepare, by dilution with water, emulsions of desired concentration.

Spray:

50 The following constituents are used to prepare a 5% spray:

- 5 parts of active substance,
1 part of epichlorohydrin,
94 parts of ligroin (boiling limits 160—190°C).
The invention is further illustrated in the following Examples.

Example 1.

(A) Preparation of 1-phenoxy-4-(3',4'-methylenedioxy)-benzyloxybenzene

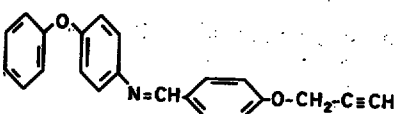
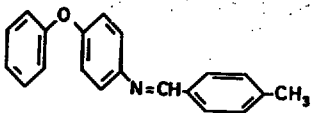
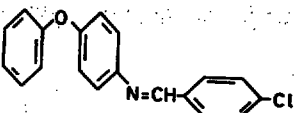
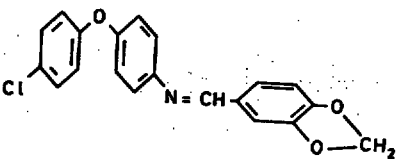
18 g of finely powdered anhydrous potassium carbonate is added to a solution of 18.6 g of 4-hydroxy-diphenyl ether in 100 ml of anhydrous acetone, and the mixture heated to the reflux temperature of the acetone. After half an hour, the solution of 17.1 g of 3,4-methylenedioxychloromethylbenzene in 100 ml of toluene is added dropwise within one hour, and the reaction mixture refluxed for a further 18 hours. The reaction solution is then filtered off from the solid phase, and the solvent completely removed in vacuo from the filtrate. The residue is dissolved in acetic acid ethyl ester/toluene, ca. 1:1; the solution is repeatedly washed with ice-cold 10% by weight potassium hydroxide solution and afterwards with water and saturated sodium chloride solution until neutral. After drying of the organic phase by means of sodium sulphate, the solvent is completely removed in vacuo, and the residue, solidifying in crystalline form, recrystallised twice in acetonitrile to obtain 1-phenoxy-4-(3',4'-methylenedioxy)-benzyloxybenzene, M.P. 90—91°C.

(B) Preparation of 4-phenoxy-N-(3,4-methylenedioxybenzyl)-aniline

The solution of 47.6 g of 4-phenoxy-(3,4-methylenedioxybenzylidene)-aniline in 500 ml of pure methanol and 450 ml of methyl Cellosolve is, after the addition of 3 g of platinum oxide, catalytically hydrogenated at 20—30°C to effect the absorption of 3.36 l of hydrogen. The catalyst is filtered off, and the solvent removed in vacuo from the filtrate. The residue is chromatographically purified through silica gel (eluant: ether/hexane 1:1), and the resulting pure 4-phenoxy-N-(3,4-methylenedioxybenzyl)-aniline recrystallised in ether/hexane, M.P. 95—96°C. ["Cellosolve" is a registered Trade Mark.]

The starting material used for catalytic hydrogenation, 4-phenoxy-(3,4-methylenedioxy-benzylidene)-aniline, is prepared as follows: the solution of 75 g of 3,4-methylenedioxy-benzaldehyde (piperonal) and 92.5 g of 4-aminodiphenyl ether in 500 ml of benzene is refluxed, with separation of water, for 8 hours. After the water has been completely separated, the reaction mixture is concentrated by evaporation; the crystals precipitated after cooling to about +5°C are filtered off under suction; the crystal mass is recrystallised firstly in anhydrous benzene and subsequently in acetonitrile to thus obtain pure 4-phenoxy-(3,4-methylenedioxy-benzylidene)-aniline, M.P. 89—91°C.

The following azomethine derivatives are prepared in a manner analogous to that described above:

Compounds	Physical data
	M.P.: 76—77°C
	M.P.: 79—80°C
	M.P.: 104—106°C
	M.P.: 120—121°C

C) Preparation of 4-phenoxy-N-acetyl-N-(3,4-methylenedioxybenzyl)-aniline

3.2 ml of acetyl chloride dissolved in 10 ml of anhydrous benzene is added dropwise at 0—5°C in the course of one hour, with stirring, to a solution of 12.7 g of 4-phenoxy-N-(3,4-methylenedioxybenzyl)-aniline and 6 g of N-ethyl-diisopropylamine in 100 ml of anhydrous benzene. The whole is subsequently heated to room temperature and stirred for a further 8 hours. The precipitated N-ethyl-diisopropylamine-hydrochloride is separated by filtration; the filtrate is washed with 10% sodium carbonate solution and then with water. After drying of the organic phase by means of sodium sulphate, the benzene is distilled off *in vacuo*, and the residue recrystallised in hexane to obtain 4-phenoxy-N-acetyl-N-(3,4-methylenedioxybenzyl)-aniline, M.P. 75—76°C.

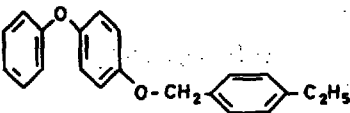
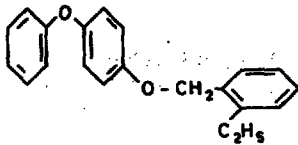
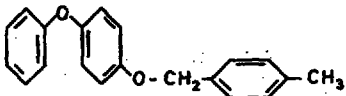
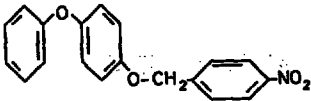
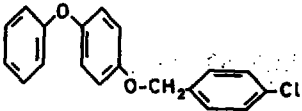
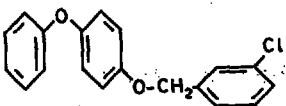
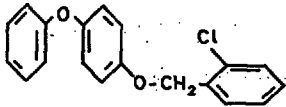
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Table 1.

The following further compounds are prepared in a manner analogous to that previously described:

Compounds	Physical data
	M.P. 55—57°C
	$n_D^{20} = 1.5840$
	M.P.: 69—70°C
	M.P.: 126—128°C
	M.P.: 71—72°C
	M.P.: 60—61°C
	$n_D^{20} = 1.6003$

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Table 1 (Continued).

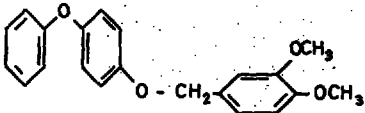
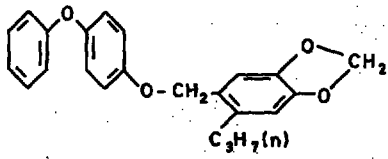
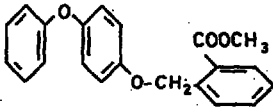
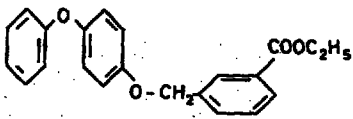
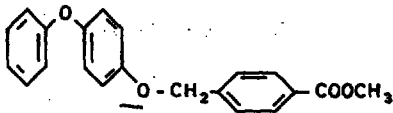
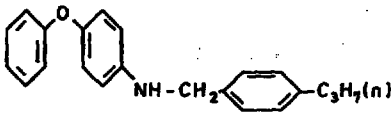
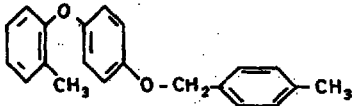
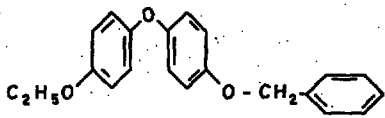
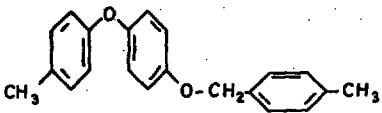
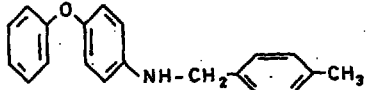
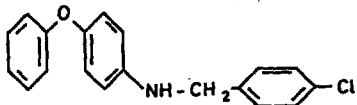
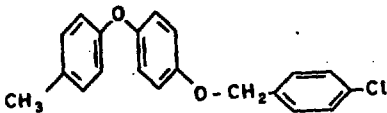
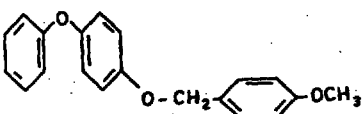
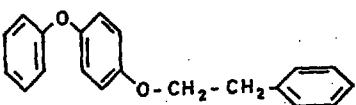
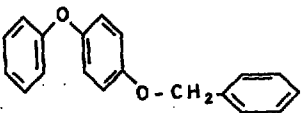
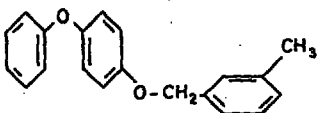
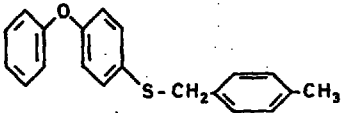
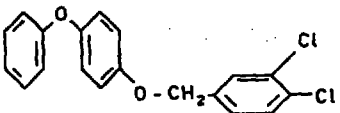
Compounds	Physical data
	M.P.: 107—109°C
	$n_D^{20} = 1.5801$
	M.P.: 60—62°C
	M.P.: 45—47°C
	M.P.: 108—109°C
	M.P.: 65—67°C
	M.P.: 60—61°C
	M.P.: 103—104°C
	M.P.: 97—98°C

Table 1 (Continued).

Compounds	Physical data
	M.P.: 50—51°C
	$n_D^{20} = 1.6313$
	M.P.: 112—113°C
	M.P.: 94—95°C
	M.P.: 43—45°C
	M.P.: 68—69°C
	M.P.: 55—56°C
	M.P.: 61—62°C
	M.P.: 89—90°C

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Table 1 (Continued).

Compounds	Physical data
	M.P.: 74—75°C
	M.P.: 81—83°C
	M.P.: 90—91°C
	M.P.: 44—45°C
	M.P.: 90—91°C
	M.P.: 66—67°C
	M.P.: 103—105°C
	M.P.: 45—46°C
	n_D^{20} : 1.5858
	n_D^{20} : 1.5988

Table 1 (Continued).

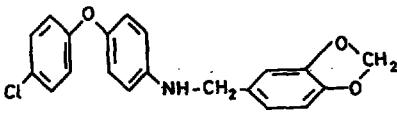
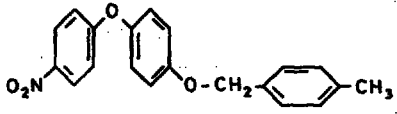
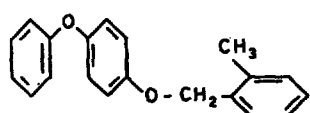
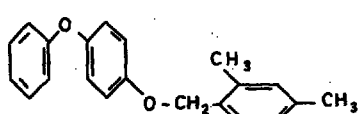
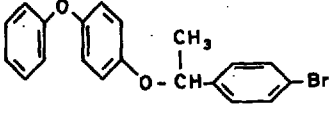
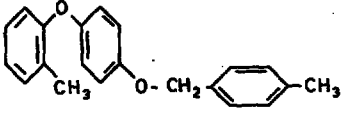
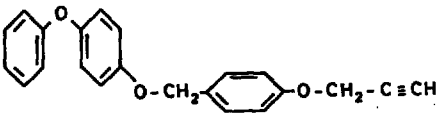
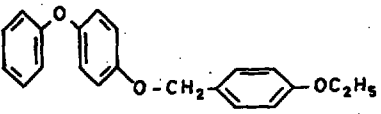
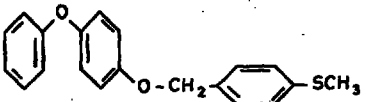
Compounds	Physical data
	M.P.: 112—113°C
	M.P.: 133—134°C
	M.P.: 41—43°C
	M.P.: 59—60°C
	$n_D^{20} = 1.6064$
	M.P.: 60—61°C
	M.P.: 92—93°C
	M.P.: 79—80°C
	M.P.: 90—91°C

Table 1 (Continued).

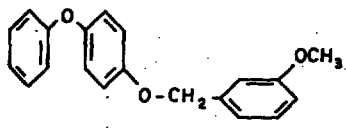
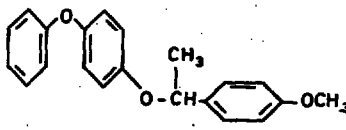
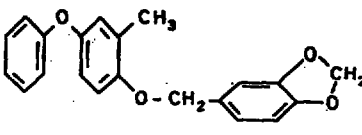
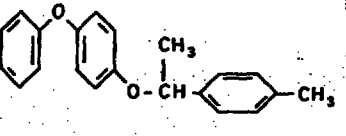
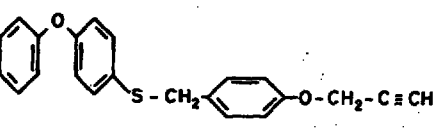
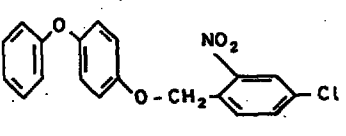
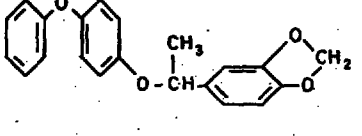
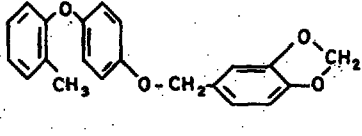
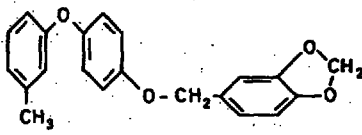
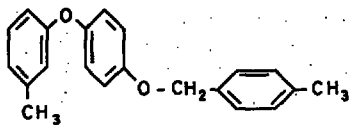
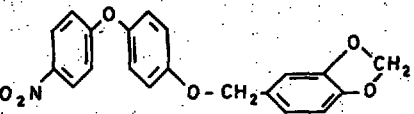
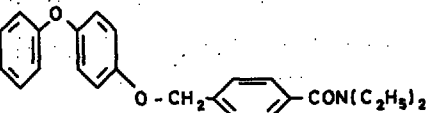
Compounds	Physical data
	$n_D^{20} = 1.5972$
	$n_D^{20} = 1.5778$
	
	
	M.P.: 76—77°C
	
	
	
	

Table 1 (Continued).

Compounds	Physical data
	M.P.: 142—144°C n_D^{20} : 1.5893
	
	
	
	

Example 2.

A) Contact action on *Dysdercus-fasciatus* larvae

A specific amount of a 0.1% acetonic active-substance solution (corresponding to 10 mg of active substance per square metre) was transferred by pipette to an aluminium dish and uniformly distributed. After evaporation of the acetone, 10 larvae in the 5th stage of *Dysdercus fasciatus* were placed into the treated dish containing feed and moist cotton wool. The dish was then covered with a perforated lid. After about 10 days, i.e. as soon as the control insects had moulted into adults, the test insects were examined to determine the number of normal adults.

Compounds according to Example 1 and Table 1 exhibited a good action in the above test.

B) Contact action on *Aedes-aegypti* larvae

About 20 two-day-old larvae of the yellow-fever mosquito (*Aedes aegypti*) were placed in position in a beaker containing a solution of the active substance (concentration 5 ppm). The beaker was then covered with a perforated lid. After the control insects had moulted into adults, the test insects were examined and the percentage of normal adults in comparison with the control adults determined.

Compounds according to Example 1 and Table 1 exhibited a good action in the above test.

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C) *Contact action on Tenebrio-mollitor pupae*

A specific amount of a 0.1% acetic active-substance solution corresponding to 10 mg of active substance per square metre was transferred by pipet into an aluminium dish and uniformly distributed. After evaporation of the acetone, 10 freshly formed pupae were placed on the treated surface, and the dish covered with a perforated lid. After the control insects had left the cocoon as imagines, the test insects were examined to determine the number of normal adults.

Compounds according to Example 1 and Table 1 exhibited a good action in the above test.

Example 3.

A) *Action against Musca domestica*

An amount in each case of 50 g of CSMA maggot substrate was weighed off in beakers. For each active substance, 2.5 ml of a 1% by weight of acetic solution of the respective substance was transferred twice to 50 g of maggot substrate each time. After a thorough mixing of the treated substrate, the solvent was allowed to evaporate off. There were then deposited per active substance in each 25 one-, two- and three-day-old maggots and about 50 fly eggs. After completion of pupation, the pupae were flushed out and counted. After a period of ten days, the number of emerged flies was determined and hence any effect on metamorphosis established.

Compounds according to Example 1 and Table 1 exhibited in this test a good action against *Musca domestica*.

B) *Action against Ephestia kühniella*

50 g of wheat flour was made up in two beakers with a specific amount of active substance to give a 5% by weight dust, the concentration thus being 0.05%. Into each beaker (25 g of flour) were placed 10 larvae of *Ephestia kühniella*. The course of population was ascertained over a period of 8 weeks and the number of moths determined.

Compounds according to Example 1 and Table 1 exhibited a good action in the test against *Ephestia kühniella*.

Example 4.

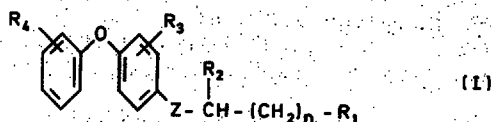
Action against red spider mites

Phaseolus vulgaris (bush beans) were infested, 12 hours before the test for acaricidal action, with an infested piece of leaf from a mass culture of *Tetranychus urticae*. The transferred mobile stages were sprayed with the emulsified test preparations, at a concentration of 0.04% by weight, by means of a chromatography-sprayer in a manner ensuring no running off of the spray liquor. An assessment was made after 2 to 7 days, by examination under a microscope, of the living and of the dead larvae, adults and eggs. The treated plants were kept during the holding time in greenhouse compartments at 25°C.

The compounds according to Example 1 and Table 1 exhibited in the above test a good action against eggs, larvae and adults of *Tetranychus urticae*.

WHAT WE CLAIM IS:—

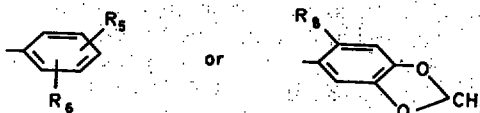
1. Compounds of the formula



wherein n is 0 or 1,

Z represents an oxygen, or sulphur atom or a group of the formula —N—R₇, (wherein R₇ represents a hydrogen atom or a C₁ or C₂ alkanoyl group),

R₁ represents a group of the formula



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C) *Contact action on Tenebrio-molitor pupae*

A specific amount of a 0.1% acetic active-substance solution corresponding to 10 mg of active substance per square metre was transferred by pipet into an aluminium dish and uniformly distributed. After evaporation of the acetone, 10 freshly formed pupae were placed on the treated surface, and the dish covered with a perforated lid. After the control insects had left the cocoon as imagines, the test insects were examined to determine the number of normal adults.

Compounds according to Example 1 and Table 1 exhibited a good action in the above test.

Example 3.

A) *Action against Musca domestica*

An amount in each case of 50 g of CSMA maggot substrate was weighed off in beakers. For each active substance, 2.5 ml of a 1% by weight of acetic solution of the respective substance was transferred twice to 50 g of maggot substrate each time. After a thorough mixing of the treated substrate, the solvent was allowed to evaporate off. There were then deposited per active substance in each 25 one-, two- and three-day-old maggots and about 50 fly eggs. After completion of pupation, the pupae were flushed out and counted. After a period of ten days, the number of emerged flies was determined and hence any effect on metamorphosis established.

Compounds according to Example 1 and Table 1 exhibited in this test a good action against *Musca domestica*.

B) *Action against Ephestia kühniella*

50 g of wheat flour was made up in two beakers with a specific amount of active substance to give a 5% by weight dust, the concentration thus being 0.05%. Into each beaker (25 g of flour) were placed 10 larvae of *Ephestia kühniella*. The course of population was ascertained over a period of 8 weeks and the number of moths determined.

Compounds according to Example 1 and Table 1 exhibited a good action in the test against *Ephestia kühniella*.

Example 4.

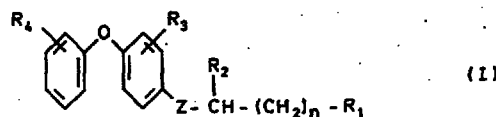
Action against red spider mites

Phaseolus vulgaris (bush beans) were infested, 12 hours before the test for acaricidal action, with an infested piece of leaf from a mass culture of *Tetranychus urticae*. The transferred mobile stages were sprayed with the emulsified test preparations, at a concentration of 0.04% by weight, by means of a chromatography-sprayer in a manner ensuring no running off of the spray liquor. An assessment was made after 2 to 7 days, by examination under a microscope, of the living and of the dead larvae, adults and eggs. The treated plants were kept during the holding time in greenhouse compartments at 25°C.

The compounds according to Example 1 and Table 1 exhibited in the above test a good action against eggs, larvae and adults of *Tetranychus urticae*.

WHAT WE CLAIM IS:—

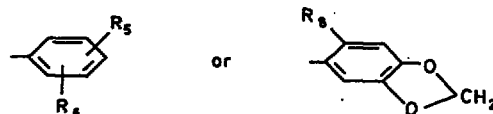
1. Compounds of the formula



wherein n is 0 or 1,

Z represents an oxygen, or sulphur atom or a group of the formula —N—R₇ (wherein R₇ represents a hydrogen atom or a C₁ or C₂ alkanoyl group),

R₁ represents a group of the formula



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(wherein R_1 represents a hydrogen or halogen atom or a C_1-C_4 alkyl, ethynyl, C_1-C_4 alkylthio, C_1-C_4 alkoxy, C_2-C_3 alkenyloxy, C_2-C_3 haloalkenyloxy, C_2-C_3 alkynyloxy, nitro, cyano, C_2-C_3 alkoxy-carbonyl, C_2-C_3 alkenyloxycarbonyl, C_2-C_3 alkynyloxycarbonyl, C_1-C_3 alkanoyl, C_1-C_4 alkylcarbamoyl or di(C_1-C_4 alkyl) carbamoyl group,

R_6 represents a hydrogen or halogen atom or a methyl, ethyl, isopropyl or methoxy group and

R_3 represents a hydrogen atom or a n-propyl group),

R_2 represents a hydrogen atom or a methyl or ethyl group, and

each of

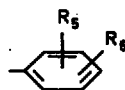
R_3 and R_4 , which may be the same or different, represents a hydrogen or halogen atom or a methyl, ethyl, methoxy, ethoxy or nitro group.

2. Compounds according to Claim 1 wherein

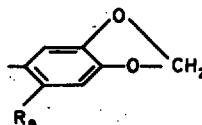
n is 0,

Z represents an oxygen or sulphur atom,

R_1 represents a group of the formula



or



(wherein R_5 represents a hydrogen, fluorine, chlorine, bromine or iodine atom or a methyl, ethyl, propyl, isopropyl, nitro, methoxy, ethoxy, methylmercapto, propargyloxy, allyloxy, C_2 or C_3 alkoxycarbonyl, propargyloxycarbonyl, acetyl or diethyl-carbamoyl group,

R_6 represents a hydrogen or chlorine atom or a methyl, ethyl or methoxy group and

R_7 represents a hydrogen atom or an n-propyl group)

R_2 represents a hydrogen atom or a methyl group, and each of

R_3 and R_4 , which may be the same or different, represents a hydrogen or chlorine atom or a methyl, methoxy or ethoxy group.

3. 1-Phenoxy-4-[(4'-ethyl)-benzyloxy]benzene.

4. 1-Phenoxy-4-[(2'-ethyl)-benzyloxy]benzene.

5. 1-Phenoxy-4-[(4'-methyl)-benzyloxy]benzene.

6. 1-Phenoxy-4-[(4'-chloro)-benzyloxy]benzene.

7. 1-Phenoxy-4-[(2'-chloro)-benzyloxy]benzene.

8. 1-Phenoxy-4-[(3',4'-methylenedioxy)-benzyloxy]benzene.

9. 1-Phenoxy-4-[(2'-n-propyl-3',4'-methylenedioxy)-benzyloxy]benzene.

10. 1-Phenoxy-4-[(3'-carbethoxy)-benzyloxy]benzene.

11. 4-Phenoxy-1-[(3',4'-methylenedioxy)-benzyl]aniline.

12. 1-(2'-Toluyloxy)-1-[(4'-methyl)-benzyloxy]benzene.

13. 1-(4'-Toluyloxy)-1-[(4'-methyl)-benzyloxy]benzene.

14. 1-Phenoxy-4-[(4'-methoxy)-benzyloxy]benzene.

15. 1-Phenoxy-4-(2'-phenethyloxy)-benzene.

16. 1-Phenoxy-4-benzyloxybenzene.

17. 1-Phenoxy-4-[(4'-methyl)-benzylthio]benzene.

18. 1-Phenoxy-4-[(3',4'-dichloro)-benzyloxy]benzene.

19. 1-Phenoxy-4-[(4'-fluoro)-benzyloxy]benzene.

20. 1-Phenoxy-4-[(4'-bromo)-benzyloxy]benzene.

21. 1-Phenoxy-4-[(4'-acetyl)-benzyloxy]benzene.

22. 1-Phenoxy-4-[(3',4'-methylenedioxy)-benzylthio]benzene.

23. 1-Phenoxy-4-[(4'-iodo)-benzyloxy]benzene.

24. 1-Phenoxy-4-[(4'-isopropyl)-benzyloxy]benzene.

25. 5-Phenoxy-2-[(4'-chloro)-benzyloxy]toluene.

26. 1-Phenoxy-4-[(2'-methyl)-benzyloxy]benzene.

27. 1-Phenoxy-4-[(2',4'-dimethyl)-benzyloxy]benzene.

28. 1-(2'-Toluyloxy)-4-[(4'-methyl)-benzyloxy]benzene.

29. 1-Phenoxy-4-[(4'-propargyloxy)-benzyloxy]benzene.

30. 1-Phenoxy-4-[(4'-ethoxy)-benzyloxy]benzene.

31. 1-Phenoxy-4-[(4'-methylthio)-benzyloxy]benzene.





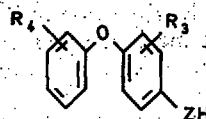
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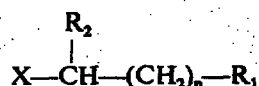
32. 5-Phenoxy-2-[(3',4'-methylenedioxy)-benzyloxy]toluene.
33. 1-Phenoxy-4-[(4'-propargyloxy)-benzylthio]benzene.
34. 1-Phenoxy-4-[(α-methyl-3',4'-methylenedioxy)-benzyloxy]benzene.
35. 1-(2'-Toluyloxy)-4-[(3',4'-methylenedioxy)-benzyloxy]benzene.
36. 1-(3'-Toluyloxy)-4-[(3',4'-methylenedioxy)-benzyloxy]benzene.
37. 1-(3'-Toluyloxy)-4-[(4'-methyl)-benzyloxy]benzene.

38. A process for preparing a compound of formula I as defined in Claim 1 wherein Z represents an oxygen or sulphur atom or a group of the formula

—N—R₇ (wherein R₇ represents a hydrogen atom) of the formula:

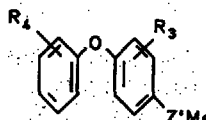


(wherein R₃ and R₄ are as defined in Claim 1 and Z is as defined above) in the presence of a base, with a compound of the formula:

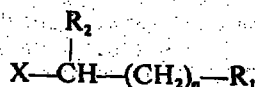


(wherein R₁, R₂ and n are as defined in Claim 1, and X represents a halogen atom).

39. A process for preparing a compound of formula I as defined in Claim 1 wherein Z represents an oxygen or sulphur atom which process comprises reacting a compound of the formula

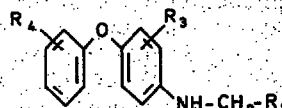


(wherein R₃ and R₄ are as defined in Claim 1, Z' represents an oxygen or sulphur atom and Me represents a metal atom) in the presence of a base, with a compound of the formula

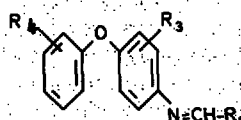


(wherein R₁, R₂ and n are as defined in Claim 1, and X represents a halogen atom).

40. A process for preparing a compound of formula



(wherein R₁, R₃ and R₄ are as defined in Claim 1) which process comprises hydrogenating a compound of the formula

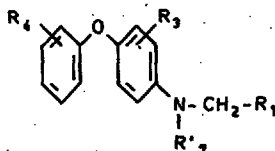


(wherein R₁, R₂ and R₄ are as defined in Claim 1) in the presence of a metal catalyst.

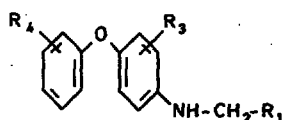


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41. A process for preparing a compound of the formula



(wherein R_1 , R_3 and R_4 are as defined in Claim 1 and R' , represents a formyl or acetyl group) which process comprises reacting an aniline derivative of the formula



with an acylating agent.

42. A process for preparing a compound as claimed in Claim 1 substantially as hereinbefore described with reference to Example 1.

43. A compound according to Claim 1 when prepared by the process claimed in any one of claims 38 to 42.

44. A pesticidal composition which comprises (i) a compound according to any one of Claims 1 to 37 together with at least one of the following:

(ii) a solid extender;

(iii) a surfactant; or

(iv) an aerosol propellant.

45. A solid composition according to claim 44 which comprises one or both of (ii) and (iii).

46. A composition according to claim 45 in the form of a granulate or pellets.

47. A composition according to claim 46 wherein the granules or pellets are coated or impregnated with (i).

48. A liquid composition according to claim 44 which comprises one or both of (iii) or (iv).

49. A composition according to claim 48 comprising (iii) and a hydrocarbon which boils at a temperature above 130°C .

50. A composition according to claim 48 comprising, as (iv), a polyhalogenated hydrocarbon.

51. A composition containing a compound of formula I as defined in claim 1 in the form of a dust, granulate, wettable powder, emulsifiable concentrate or spray specifically described herein.

52. A pesticidal composition which comprises (i) a compound according to any one of claims 3 to 9, 11 to 14, 16 to 24, 27, 29 and 31 together with at least one of (ii) a solid extender or (iii) a surfactant.

53. A pesticidal composition which comprises (i) a compound according to any one of claims 10, 15, 25, 26, 28, 30 and 32 to 36 together with at least one of (ii) a solid extender or (iii) a surfactant.

54. A method of combating pests which are insects or members of the order *Acarina* at a locus, which method comprises applying to the locus a compound according to claim 1 or 2.

55. A method according to claim 54 wherein the compound applied is as claimed in any one of claims 3 to 9, 11 to 14, 16 to 24, 27, 29 and 31.

56. A method according to claim 54 wherein the compound applied is as claimed in any one of claims 10, 15, 25, 26, 28, 30 and 32 to 36.

57. A method according to any one of claims 54 to 56 wherein the locus comprises corn, maize, rice, vegetables, ornamental plants, fruit trees, grape vines or field fruits.

58. A method according to claim 54 substantially as hereinbefore described with reference to any one of Examples 2 to 4.

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