

The present invention relates to new compounds, containing triazole or imidazole and tetrahydrofuran groups, for use in plant protection. It also relates to
5 the processes for the preparation of the said compounds and products which can be used, if desired, as intermediates in the processes of preparation. It further relates to the use of these compounds as fungicides, to the fungicidal compositions based on these compounds and
10 to the processes, using these compounds, for the control of fungal diseases of crops.

Numerous products, especially fungicides, containing triazole groups are already known, in particular, from European Patent Application No. 151,084. In fact,
15 this patent application describes the compounds the formula of which is given at the end of the description and their use as fungicides.

One object of the present invention is to provide compounds which have improved properties in the treatment
20 of fungal diseases.

Another object of the present invention is to provide compounds which also have an improved spectrum of use in the field of fungal diseases.

It has now been found that these objects could be
25 achieved by means of the products of the invention. The latter are characterised in that they correspond to the formula (I) in which

A is a group $(Y)_n \text{Ph}-(\text{CH}_2)_m$, where Ph is a phenylene ring and $m = 0$ or 1, preferably 0,
30 Y is a halogen atom or a cyano or nitro group, or an optionally halogenated alkyl or alkoxy group,
 n is zero or a positive integer less than 6, it being possible for the groups Y to be identical or different when n is greater than 1,
35 Tr represents a 1,2,4-triazol-1-yl group and Im a 1,3-imidazol-1-yl group,
 R_1 to R_5 , which may be identical or different, represent a hydrogen atom or a (linear or branched) alkyl radical containing at most six carbon atoms,

a cycloalkyl radical containing at most six carbon atoms, a phenyl or benzyl radical or an alkoxy radical containing at most six carbon atoms, it being possible for these various radicals to be optionally substituted (for example with one or more atoms or radicals such as halogen atoms, [lacuna] and alkoxy radicals containing at most six carbon atoms,

5 X_1 and X_2 , which may be identical or different, represent a hydrogen atom, a halogen atom, an alkyl radical containing at most six carbon atoms, a cycloalkyl radical containing at most six carbon atoms or a phenyl or benzyl radical, it being possible for these various radicals to be optionally substituted in a manner similar to the groups R_1 to R_5 ,

10 a group $Q-R_6$, in which Q represents O or S, and R_6 represents a hydrogen atom or an alkyl radical containing at most six carbon atoms, a cycloalkyl radical containing at most six carbon atoms or a phenyl, benzyl, acyl or [sic] benzoyl [sic] radical, it being possible for these radicals to be substituted in a manner similar to the groups R_1 to R_5 and to have identical or different meanings when X_1 and X_2 each correspond to OR_6 or SR_6 ,

15 a group of formula $-Q-R_7-Q-$, where Q has the same meaning as above and in which R_7 is a divalent hydrocarbon radical comprising from 2 to 6 carbon atoms, it being possible for one of these carbon atoms to be replaced by an oxygen or nitrogen atom, the said single divalent radical itself being optionally substituted (for example with one or more halogen atoms [lacuna] or alkyl radicals containing at most six carbon atoms, alkoxy radicals containing at most six carbon atoms, or hydroxyl radicals),

20 a group $-N R_8 R_9$, in which R_8 and R_9 , which may be identical or different, represent a hydrogen atom or an alkyl radical containing at most six carbon

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atoms, a cycloalkyl radical containing at most six carbon atoms or a phenyl radical, it being possible for these various radicals to be optionally substituted in a manner similar to the groups R_1 to R_5 , or alternatively R_8 and R_9 together can form a single divalent hydrocarbon radical comprising from 2 to 6 carbon atoms, it being possible for one of these carbon atoms to be replaced by an oxygen, sulphur or nitrogen atom, the said single divalent radical itself being optionally substituted (for example with one or more halogen atoms, or alkyl radicals containing at most six carbon atoms, optionally halogenated alkoxy radicals containing at most six carbon atoms, or hydroxyl radicals),

5 a group = $N-R_{10}$, in which R_{10} corresponds to an alkyl radical containing at most six carbon atoms, or a cycloalkyl radical containing at most six carbon atoms, or to a group of formula OR_{11} in which R_{11} is an alkyl, it being possible for these radicals to be substituted in a manner similar to the groups R_1 to R_5 , or a hydroxyl group,

10 a group N_3 , on condition that X_2 is other than N_3 , X_1 or X_2 can constitute together =O or =S,

15 on the general conditions that X_1 and X_2 cannot simultaneously correspond to a hydrogen atom or to an alkyl radical containing at most six carbon atoms, a cycloalkyl radical containing at most six carbon atoms, a phenyl radical or a benzyl radical, and if X_1 and X_2 are different and either one of them is OR_6 , then, in this case

20 only, R_6 can be only a benzoyl or acyl [sic] group.

The invention also relates to the salified forms of the compounds according to the invention. The salified forms are the forms which are acceptable in agriculture among which there may be mentioned the hydrochloride, sulphate, oxalate, nitrate or arylsulphonate and the addition complexes of these compounds with metal salts, and especially iron, chromium, copper, manganese, zinc, cobalt, tin, magnesium and aluminium salts.

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By way of example, zinc complexes may be obtained by reacting the compound of formula I with zinc chloride.

It should be noted that the compounds claimed are not described in European Patent Application No. 151,084.

5 Within the meaning of the present text, it is understood that the adjective lower, when it qualifies an organic radical, means that this radical contains at most six carbon atoms. This radical may be linear or branched.

10 The applicant wishes to emphasize that the plates appended should in no way be considered as drawings, but as forming an integral part of the description of the invention.

15 The compounds of formula I and the compounds which may, if appropriate, be used as intermediates in the preparation processes, and which will be defined at the time of describing these processes, may exist in one or more isomeric forms depending on the number of asymmetric centres in the molecule. Therefore, the invention relates to all the optical isomers as well as to their
20 racemic mixtures and to the corresponding diastereoisomers. The separation of the diastereoisomers and/or the optical isomers may be carried out according to methods known per se.

25 For the purpose of fungicidal applications, it has been found that the invention related preferably to the compounds of formula I in which Y is a halogen and $n = 1, 2$ or 3 .

30 It has also been found that it was preferable to use the compounds of formula I in which $n = 1$ or 2 , and Y is a halogen atom placed in the ortho and/or para position.

More preferably, $n = 2$ and Y is a halogen atom, advantageously chlorine, placed in the ortho- and the para-positions.

35 Taking into account the restrictions defined above, considered separately or in combination, it has been found that, by virtue of the fungicidal properties, it was preferable to use the triazole compounds of

formula II in which R_1 to R_5 correspond to a hydrogen atom or to a lower cycloalkyl or alkyl group, Y, n and m have the same meaning as in formula I with the preferred variants listed above, and Hal corresponds to a halogen atom, preferably chlorine or bromine, and X_1 is a halogen atom, preferably chloride or bromine, or a hydrogen atom, and advantageously a hydrogen atom.

Taking into account the restrictions defined above, considered separately or in combination, it has been found that, by virtue of the fungicidal properties, it was preferable to use the triazole compounds of formula III in which R_1 to R_5 correspond to a hydrogen atom or to a lower cycloalkyl or alkyl group, Y, n and m have the same meaning as in formula I, with the preferred variants listed above, X_1 corresponds to a hydrogen atom or to a lower cycloalkyl or alkyl group, Q has the same meaning as in formula I and R^6 corresponds to a hydrogen atom or to a lower cycloalkyl or alkyl group.

The preferred triazole compounds of formula II are those in which the R_1 to R_5 groups correspond to a hydrogen atom.

The preferred triazole compounds of formula III are those of which the R_1 to R_5 groups correspond to a hydrogen atom, where X_1 corresponds to a hydrogen atom or lower cycloalkyl or alkyl, and where R_6 corresponds to a lower cycloalkyl or alkyl group and preferably $Q = 0$.

The present invention also relates to processes for the preparation of the compounds according to the invention.

In the case where the X_2 group corresponds to a halogen atom (compound of formula II), a preparation process consists of the following stages:

Stage a) A halo ketone of formula IIa obtained by a known process, in which Y, n and R_5 have the same meaning as that given for the compounds of formula I and Z corresponds to a halogen atom, is reacted with an organometallic compound of formula IIb, in which R_1 to R_4 and X_1 have the same meaning as above and M

corresponds to an alkali metal or a magnesium-containing group (Mg Hal) or a zinc-containing group (Zn Hal) for example, in a solvent, preferably chosen from ethers such as diethyl ether or tetrahydrofuran, aliphatic, alicyclic or aromatic hydrocarbons such as hexane or toluene at a temperature chosen between -50°C and the reflux temperature of the solvent in question and in a molar ratio of $\text{IIa}:\text{IIb}$ which is preferably of between 1.1 and 0.2. The reaction leads to the compound of formula IIc after neutralisation of the reaction medium.

Stage b) The compound of formula IIc is then reacted with an unsubstituted triazole or imidazole in the presence of an organic or inorganic base, for example pyridine, triethylamine, sodium hydroxide, potassium hydroxide, carbonates and bicarbonates of alkali or alkaline earth metals, and in a suitable solvent such as, for example, alcohols, ketones, amides, nitriles or optionally halogenated aromatic hydrocarbons, at a temperature of between 80° and the reflux temperature of the solvent and in a molar ratio of $\text{IIc}:\text{imidazole}$ or triazole which is preferably of between 1.1 and 0.2, which leads to the compound of formula IId . The reaction generally passes through an epoxide intermediate or formula IIh which may, if appropriate, be isolated or prepared separately by methods known to the man skilled in the art.

Stage c) A molecule of halogen or of mixed halogen is added, preferably mole for mole, to the compound IId in an inert solvent such as saturated or optionally halogenated aromatic hydrocarbons, which leads to the compound IIe .

Stage d) The compound II is preferably obtained at ambient temperature by the cyclisation of the compound IIe in the presence of an organic or inorganic base indicated in b in a molar ratio of compound $\text{II}:\text{base}$ which is preferably of between 1.1

and 0.66. The reaction may be carried out in a protic or aprotic solvent (water, alcohol, ketone, nitrile, ester, saturated or optionally halogenated aromatic hydrocarbon, dimethyl sulphoxide or amide such as dimethylformamide).

A second process for the preparation of the compounds where the X_2 group is a halogen consists in placing stage b) of grafting the imidazole or triazole ring after stage d), using the same procedure for the different stages. Thus, a halogen or halogen halide (mixed halogen) molecule is added to the compound IIc to give the compound II_f, the latter than being cyclised to give the compound II_g, which is then provided with a triazole or imidazole group to give the compound II.

Other preparation processes may, of course, also be suitable.

In the case where the X_2 group corresponds to QR_6 , and X_1 is other than Hal (compounds of formula III), one preparation process consists in reacting a compound of formula II with a heteroatomic nucleophile of formula R_6-Q-E , in which R_6 and Q have the same meaning as in formula I and E is a cation, for example an alkali or alkaline earth metal or a quaternary ammonium. The reaction is carried out in a suitable solvent in the presence of a base and, if appropriate, a phase transfer catalyst and at reaction temperatures which are generally of between -30°C and the reflux temperature of the solvent used and in a molar ration II: R_6Q E which is preferably of between 1.2 and 0.1.

Another process consists in reacting the compound II_g under the same conditions with the same heteroatomic nucleophile to obtain a compound IIIa to which the triazole or imidazole ring is then attached as described previously.

It is also possible to obtain the compounds in the formula of which R_6 is an optionally mono- or polyhalogenated lower alkyl group, by reacting the compounds III or IIIa in the formula of which R_6 cor-

responds to the hydrogen atom with an alkyl halide (mono- or polyhalogenated, is appropriate) in a molar ratio of III or IIa:halide which is preferably of between 1.1 and 0.2, in the presence of an organic or inorganic base. If
5 the starting compound was IIIa, a triazole or imidazole ring is then attached.

In the case where X_2 corresponds to a hydroxyl group (compounds of formula III in which Q corresponds to the oxygen atom and R_6 to the hydrogen atom), compounds
10 of formula IIg or II may also be reacted, if appropriate, in the presence of an inert organic solvent, at a temperature of between -30° and the reflux temperature of the solvent, with a hydroperoxide, hydroxide, oxide or superoxide of an alkali metal, alkaline earth metal or
15 other metal, in a molar ratio which is preferably of between 1.1 and 0.2, and, in the case where compound IIg is the starting compound, an imidazole or triazole ring may then be attached.

In the case where X_2 corresponds to N_3 , the
20 compounds IIg or II are reacted with an alkali metal or ammonium azide in a molar ratio which is preferably of between 1.1 and 0.2, preferably in an aprotic solvent, at a temperature of between -30° and the reflux temperature of the solvent, and, if IIg was the starting compound,
25 the azide compound is then reacted with an imidazole or triazole ring.

In the case where X_2 corresponds to a hydroxyl group, the compounds IIc or IId may also be reacted with a peroxide in order to obtain the epoxide compounds of
30 formula IIIb for IIc, and IIIc for the compound IId. These epoxides may then be hydrated to triols IIId and IIIe respectively in a way which is well known. The cyclisation is carried out in the presence of a dehydrating agent such as hydrochloric, hydrobromic, sulphuric or
35 sulphonic acids, if appropriate in a protic or aprotic solvent. This leads to compound IIIa in which QR_6 corresponds to OH to which a triazole or imidazole ring is then attached, or to compound III in the case of the

compound IIIe. Optionally, if necessary, the alcohol group may be protected in a manner known per se for compounds IIId and IIIe.

5 The compounds of formula II or IIg may also be reacted with an alkali metal or alkaline earth metal carboxylate (acyclic, cyclic, saturated, unsaturated or aromatic) (especially sodium benzoate) in the presence of a phase transfer catalyst and optionally in the presence of an aprotic polar or inert solvent, if required in the
10 presence of water, and at temperatures of between 0° and the reflux temperature of the solvent in question.

In the case where X_1 and X_2 together correspond to an oxygen atom which is doubly bonded to tetrahydrofuran (compounds of formula IV where X_1 corresponds to the
15 oxygen atom), one process of preparation consists in operating from a compound of formula IIIa or III in which QR_6 corresponds to hydroxyl and X_1 to hydrogen, with a well-known oxidising agent in order to obtain a compound IV or IVa onto which an imidazole or triazole ring is
20 grafted.

The gem-halogenated compounds ($X_1 = X_2 = \text{Hal}$) are prepared by reacting phosphorus pentachloride with the ketone (compound of formula IV in which X_1 corresponds to
25 an oxygen atom), if required in the presence of an aprotic inert solvent and if required in the presence of a quaternary ammonium halide, preferably at ambient temperature.

In order to obtain the thioketone group (compound of formula IV or [sic] X_1 corresponds to the sulphur atom)
30 thionation of the ketone group is carried out by reacting the compounds IV or IVa, for example, with H_2S or P_2S_5 in a molar ratio which is preferably of between 1.1 and 0.2, in the presence of an inert organic solvent (pyridine or hydrocarbon, for example) at a temperature of between 20°
35 and the reflux temperature.

In the case where X_1 and X_2 simultaneously correspond to QR_6 (compound of formula V) the compounds of formula (IV) or (IVa) in which X_1 (or X_2) corresponds to

an oxygen or sulphur atom which is doubly bonded to tetrahydrofuran are reacted with a compound of formula HQR_6 , where Q corresponds to O or S in a molar ratio which is preferably of between 1.1 and 0.2, in the presence of
5 an acid catalyst and in a suitable solvent, which may be the alcohol or thiol itself, or an inert solvent such as hydrocarbons or alcohols. If the starting compound was that of formula IVa, the compound of formula Va is obtained and an imidazole or triazole ring is then
10 grafted onto the compound of formula Va.

In the case where X_1 and X_2 correspond to $Q-R_7-Q$ and R_7 constitutes a single divalent radical as defined previously, the compounds of formula (IV) or (IVa) are reacted with a compound $HQ-R_7-QH$ under the same conditions
15 as for the monohydric alcohols or the monothiols. If IVa was the starting compound, the compound Vb is obtained, to which an imidazole or triazole is attached under the same conditions as before.

In the case where X_2 corresponds to $N-R_8R_9$, a preparation process consists in reacting a compound of
20 formula II or of formula IIg with an amine of formula $H-N R_8R_9$ in a molar ratio of between 1.1 and 0.2, if appropriate in the presence of another organic or inorganic base. This leads to the compound of formula VI
25 in the case where the starting compound was that of formula II and to compound VIa to which an imidazole or triazole ring is subsequently attached in the case where the starting compound was that of formula IIg.

In the case where X_1 (or X_2) corresponds to the
30 $= N-R_{10}$ group (compound of formula VII), a compound of formula IV or IVa is reacted with an amine of formula $R_{10}-NH_2$ or with one of its salts in a molar ratio which is preferably of between 1.1 and 0.2, in an inert organic solvent. In the case of the compound IVa, the compound
35 VIIa is obtained, to which an imidazole or triazole ring is then attached.

The compound of formula VII in which R_{10} corresponds to a hydroxyl may also be reacted with an

alkylating agent of formula R_{11} D in which R_{11} is an optionally substituted lower alkyl and in which D corresponds to a sulphonium, ammonium, sulphonate or sulphate group, in the presence of an organic or inorganic base, in order to obtain the oxime substituted on the oxygen.

The subject of the invention is also the compounds which can be used, if appropriate, as intermediates in the preparation processes described above and of formula II, IIc, IID, IIe, IIf, IIg, IIh, III, IIIa, IIIb, IIIc, IIId, IIIe, IV, IVa, V, Va, Vb, VI, VIa, VII and VIIa in which R_1 to R_6 , Y, Tr, Im, m, n, X_1 , X_2 , Q, Hal and Z have any one of the meanings mentioned in the preceding description.

The present invention also relates to the use of the compounds of formula I as fungicides.

The compounds according to the invention may be used for the preventive as well as curative control of fungi, especially of the basidiomycetes, ascomycetes, adelomycetes or fungi imperfecti type, in particular the rusts, mildew, eyespot, fusarium diseases, helminthosporium diseases, septoria diseases and rhizoctonia diseases of crops and of plants in general and, in particular, of cereals such as wheat, barley, rye, oats and their hybrids and also rice and maize. The compounds according to the invention are active, in particular, against fungi, especially of the basidiomycetes, ascomycetes, adelomycetes or fungi imperfecti type such as *Botrytis cinerea*, *Erysiphe graminis*, *Puccinia recondita*, *Piricularia oryzae*, *Cercospora beticola*, *Puccinia striiformis*, *Erysiphe cichoracearum*, *Fusarium oxysporum* (melonis), *Pyrenophora avenae*, *Septoria tritici*, *Venturia inaequalis*, *Whetzelinia sclerotiorum*, *Monilia laxa*, *Mycosphaerella fijiensis*, *Marssonina panettoniana*, *Alternaria solani*, *Aspergillus niger*, *Cercospora arachidicola*, *Cladosporium herbarum*, *Helminthosporium oryzae*, *Penicillium expansum*, *Pestalozzia* sp., *Phialophora cinerescens*, *Phoma betae*, *Phoma foveata*, *Phoma lingam*, *Ustilago maydis*, *Verticillium dahliae*,

Ascochyta pisi, *Guignardia bidwellii*, *Corticium rolfsii*, *Phomopsis viticola*, *Sclerotinia sclerotiorum*, *Sclerotinia minor*, *Coryneum cardinale* and *Rhizoctonia solani*.

They are also and continue to be active against the following fungi: *Acrostalagmus koningi*, the *Alternaria*, the *Colletotrichum*, *Corticium rolfsii*, *Diplodia natalensis*, *Gaeumannomyces graminis*, *Gibberella fujikuroi*, *Hormodendron cladosporioides*, *Lentinus degener* or *tigrinus*, *Lenzites quercina*, *Memnoniella echinata*, *Myrothecium verrucaria*, *Paecilomyces varioti*, *Pellicularia sasakii*, *Phellinus megaloporus*, *Polystictus sanguineus*, *Poria vaporaria*, *Sclerotium rolfsii*, *Stachybotris atra*, the *Stereum*, *Stilbum* sp., *Trametes trabea*, *Trichoderma pseudokoningi* and *Trichothecium roseum*.

The compounds of the invention are of special interest because of their broad spectrum as regards cereal diseases (mildew, rust, eyespot, net blotch, leaf spot and fusarium diseases). They are also of special interest because of their effectiveness against grey mould (*Botrytis*) and cercospora diseases and, because of this, they may be applied on crops as varied as grape vine, market-garden crops and tree crops and tropical crops such as peanut, banana, coffee, pecan nut and others.

In addition to the applications already described above, the products according to the invention additionally have an excellent biocidal activity with respect to many other kinds of microorganisms, among which there may be mentioned in a non-limiting way fungi such as those belonging to the genera:

- *Pullularia* such as the species *P. pullulans*,
- *Chaetomium* such as the species *C. globosum*,
- *Aspergillus* such as the species *Aspergillus niger*,
- *Coniophora* such as the species *C. puteana*.

Owing to their biocidal activity, the products of the invention make it possible to control effectively microorganisms whose proliferation gives rise to numerous problems in the agricultural and industrial fields. To

this end, they are particularly well suited for the protection of plants or of industrial products such as wood, leather, paints, paper, ropes, plastics and industrial water circuits.

5 They are particularly well suited for the protection of lignocellulose products and especially of wood, whether it is timber for furniture or construction, or timber which is exposed to bad weather such as timber for fencing, vine stakes or railway sleepers.

10 The compounds according to the invention, used on their own or in the form of compositions as defined above in the treatments of wood, are generally employed with organic solvents and may, if appropriate, be used in combination with one or more known biocidal products such
15 as pentachlorophenol, metal salts, especially copper, manganese, cobalt, chromium or zinc salts derived from inorganic or carboxylic acids (heptanoic, octanoic or naphthenic acids); organic complexes of tin, mercaptobenzothiazole, insecticides such as pyrethroids or
20 organochlorine compounds.

 Finally, they have an excellent selectivity with respect to crops.

 They are advantageously applied at doses of 0.005 to 5 kg/ha, and more specifically 0.01 to 0.5 kg/ha.

25 In practical use, the compounds according to the invention are rarely used alone. Most often they form part of compositions. These compositions, which can be used for the protection of plants against fungal diseases, or in plant growth regulating compositions,
30 contain as the active substance a compound according to the invention as described previously, in association with solid or liquid carriers which are acceptable in agriculture, and/or surfactants, also acceptable in agriculture. Conventional inert carriers and conventional
35 surfactants can especially be used.

 The term "carrier", in the present description, denotes a natural or synthetic organic or inorganic material, with which the active substance is combined in

order to facilitate its application on the plant, on seeds or on the soil. Therefore, this carrier is generally inert and it must be acceptable in agriculture, especially on the treated plant. The carrier may be solid
5 (clays, natural or synthetic silicates, silica, resins, waxes, solid fertilizers, etc.) or liquid (water, alcohols, ketones, petroleum fractions, aromatic or paraffinic hydrocarbons, chlorinated hydrocarbons, liquefied gases, etc.).

10 The surfactant may be an emulsifier, dispersant or wetting agent of ionic or non-ionic type. For example, there may be mentioned polyacrylic acid salts, lignosulphonic acid salts, phenolsulphonic or naphthalenesulphonic acid salts, polycondensates of ethylene oxide with
15 fatty alcohols or with fatty acids or with fatty amines, substituted phenols (especially alkylphenols or arylphenols), sulphosuccinic acid ester salts, taurine derivatives (especially alkyltaurates), phosphoric esters of alcohols or of polyoxyethylated phenols. The presence
20 of at least one surfactant is generally indispensable when the active substance and/or the inert carrier are insoluble in water and the vector agent for the application is water.

Therefore, for their application, the compounds
25 of formula (I) are generally in the form of compositions; these compositions according to the invention are themselves in fairly diverse solid or liquid forms.

As solid forms of compositions, there may be mentioned powders for dusting or scattering (with a
30 content of the compound of formula (I) reaching up to 100 %) and granules, especially those obtained by extrusion, by compacting, by impregnation of a granulated carrier, or by granulation starting from a powder (the content of the compound of formula (I) in these granules
35 being between 1 and 80 % in these latter cases).

As liquid forms of compositions, or forms intended to constitute liquid compositions when applied, there may be mentioned solutions, especially water-soluble

concentrates, emulsifiable concentrates, emulsions, flowables, aerosols, wettable powders (or powder for spraying) and pastes.

5 The emulsifiable or soluble concentrates most frequently contain 10 to 80 % of active substance, whereas the emulsions or solutions ready for application contain, for their part, 0.01 to 20 % of active substance.

10 These compositions may also contain any other type of ingredients such as, for example, protective colloids, adhesives, thickeners, thixotropic agents, penetrants, stabilisers, sequestering agents and the like, as well as other known active substances with
15 pesticidal properties (especially insecticidal or fungicidal properties) or properties which promote plant growth (especially fertilizers) or plant growth regulating properties. More generally, the compounds according to the invention may be combined with all those solid or liquid additives which correspond to the usual techniques
20 of formulation.

For example, in addition to the solvent, the emulsifiable concentrates may contain, when necessary, 2 to 20 % of suitable additives such as the stabilisers, surfactants, penetrants, corrosion inhibitors, colouring
25 agents or adhesives mentioned above.

In the case where the compounds according to the invention are used as fungicides, the doses to be used may vary within broad limits according, in particular, to the virulence of the fungi and the climatic conditions.

30 In general, compositions containing 0.5 to 5,000 ppm of active substance are very suitable; these values apply to the compositions ready for application. Ppm denotes "parts per million". The range from 0.5 to 5,000 ppm corresponds to a range from 5×10^{-5} to 0.5 %
35 (percentages by weight).

As regards compositions which are suitable for storage and transportation, they more advantageously contain from 0.5 to 95 % (by weight) of active substance.

Thus, the compositions for agricultural use according to the invention may contain the active substances according to the invention within very broad limits, ranging from $5 \cdot 10^{-5}$ % to 95 % (by weight).

5 By way of example, the compositions of some concentrates are given below:

Example F (formulation) 1

	Active substance	400 g/litre
	Alkali metal dodecyl benzenesulphonate	24 g/litre
10	Oxyethylated nonylphenol containing 10 molecules of ethylene oxide	16 g/litre
	Cyclohexanone	200 g/litre
	Aromatic solvent	q.s. 1 litre

According to another formula for an emulsifiable
15 concentrate, the following are used:

Example F 2:

	Active substance	250 g
	Epoxide-treated vegetable oil	25 g
	Mixture of alkylarylsulphonate, polyglycol ether and fatty alcohols	100 g
20	Dimethylformamide	50 g
	Xylene	575 g

From these concentrates, by dilution with water,
it is possible to obtain emulsions of any desired con-
25 centration, which are especially suitable for application
on leaves.

Flowables, which can also be applied by spraying,
are prepared so as to obtain a stable fluid product which
does not settle; they usually contain from 10 to 75 % of
30 active substance, from 0.5 to 15 % of surfactants, from
0.1 to 10 % of thixotropic agents and from 0 to 10 % of
suitable additives such as antifoams, corrosion inhibi-
tors, stabilisers, penetrants and adhesives, and, as a
carrier, water or an organic liquid in which the active
35 substance is of low solubility or insoluble: some solid
organic substances or inorganic salts may be dissolved in
the carrier to assist in preventing sedimentation, or as
anti-freezes for the water.

The wettable powders (or powder for spraying) are usually prepared so as to contain 20 to 95 % of active substance, and they usually contain, in addition to the solid carrier, from 0 to 5 % of a wetting agent, from 3 to 10 % of a dispersant, and, when necessary, from 0 to 10 % of one or more stabilisers and/or other additives such as penetrants, adhesives, or anti-caking agents, colouring agents etc.

By way of example, various compositions of wettable powders are given below:

Example F 3:

	Active substance	50 %
	Calcium lignosulphonate (deflocculant)	5 %
	Isopropyl naphthalenesulphonate	
15	(anionic wetting agent)	1 %
	Anti-caking silica	5 %
	Kaolin (filler)	39 %

Another composition of powder for spraying, at 70 % strength, uses the following constituents:

Example F 4:

	Active substance	700 g
	Sodium dibutyl naphthalenesulphonate	50 g
	Condensation product of naphthalenesulphonic acid, phenolsulphonic acid and formaldehyde	
25	in proportions 3:2:1	30 g
	Kaolin	100 g
	Whitener	120 g

Another composition of powder for spraying, at 40 % strength, uses the following constituents:

Example F 5:

	Active substance	400 g
	Sodium lignosulphonate	50 g
	Sodium dibutyl naphthalenesulphonate	10 g
	Silica	540 g

Another composition of powder for spraying, at 25 % strength, uses the following constituents:

Example F 6:

	Active substance	250 g
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	Calcium lignosulphonate	45 g
	Mixture of whitener and hydroxyethylcellulose in equal parts by weight	19 g
	Sodium dibutyl-naphthalenesulphonate	15 g
5	Silica	195 g
	Whitener	195 g
	Kaolin	281 g

Another composition of powder for spraying, at 25 % strength, uses the following constituents:

10 Example F 7:

	Active substance	250 g
	Isooctylphenoxy-polyoxyethylene-ethanol	25 g
	Mixture of whitener and hydroxyethylcellulose in equal parts by weight	17 g
15	Sodium aluminosilicate	543 g
	Kieselguhr	165 g

Another composition of powder for spraying, at 10 % strength, uses the following constituents:

Example F 8:

20	Active substance	100 g
	Mixture of sodium salts of sulphates of saturated fatty acids	30 g
	Condensation product of naphthalenesulphonic acid and formaldehyde	50 g
25	Kaolin	820 g

To obtain these powders for spraying or wettable powders, the active substances are intimately mixed in suitable mixers with the additional substances, and the mixtures are ground in mills or other suitable grinders.

30 Powders for spraying are thereby obtained, the wettability and suspendability of which are advantageous; they may be suspended in water at any desired concentration and these suspensions may be very advantageously used, especially for application on plant leaves.

35 Instead of the wettable powders, pastes can be produced. The conditions and means of production and use of these pastes are similar to those for wettable powders or powders for spraying.

As already stated, the dispersions and aqueous emulsions, for example the compositions obtained by diluting with water a wettable powder or an emulsifiable concentrate according to the invention, are included
5 within the general scope of the present invention. The emulsions can be of the water-in-oil or oil-in-water type, and they may have a thick consistency like that of "mayonnaise".

Granules intended for placing on the soil are
10 usually prepared so as to be between 0.1 and 2 mm in size, and they may be manufactured by agglomeration or impregnation. In general, the pellets contain 0.5 to 25 % of active substance and 0 to 10 % of additives such as stabilisers, slow-release modification agents, binders
15 and solvents.

According to an example of granule composition, the following constituents are used:

Example F 9:

	Active substance	50 g
20	Epichlorohydrin	2.5 g
	Cetyl polyglycol ether	2.5 g
	Polyethylene glycol	35 g
	Kaolin (particle size: 0.3 to 0.8 mm)	910 g.

In this particular case, the active substance is
25 mixed with epichlorohydrin and dissolved in 60 g of acetone; polyethylene glycol and cetyl polyglycol ether are then added. The kaolin is wetted with the solution obtained and the acetone is then evaporated under vacuum.

A microgranule of this type is advantageously
30 used to control soil fungi.

The compounds of formula (I) may also be used in the form of powders for dusting; a composition containing 50 g of active substance and 950 g of talc can also be used; a composition containing 20 g of active substance,
35 10 g of finely divided silica and 970 g of talc may also be used; these constituents are mixed and ground, and the mixture is applied by dusting.

Examples I to VII illustrate particular ways of preparing the compounds according to the invention as well as these compounds themselves. The nomenclature of the compounds has been given according to French standards, except that the numbering of the substituents has been placed before the substituents themselves.

Example I: Preparation of 1-[4-bromo-2-(2,4-dichlorophenyl)tetrahydrofuran-2-ylmethyl]-1H-1,2,4-triazole.
Compounds Nos. 1a, 1b and 1a + 1b

10 Stage a) Preparation of 1-chloro-2-(2,4-dichlorophenyl) 4-penten-2-ol:

An organomagnesium derivative is prepared by adding a solution of allyl bromide (110 ml) in ethyl ether (700 ml) and tetrahydrofuran (200 ml) with magnesium (110 g), between 15 and 20°C, over three hours. 15 The mixture is refluxed for 30 min and decanted, and the residue is washed with ether.

A solution of alpha,2,4-trichloroacetophenone (175 g) in tetrahydrofuran (250 g) at -30°C is added to 20 this organic phase and the mixture is neutralised with acetic acid. This is washed with water, dried over sodium sulphate, concentrated and then distilled under vacuum. A colourless oil is obtained (205 g). B.p. (3 10⁻² mm Hg) = 140-142°C.

25 Stage b) Preparation of 1-[2-(2,4-dichlorophenyl)-2-hydroxypenten-4-yl]-1H-1,2,4-triazole

A mixture of the product obtained in stage a) (106 g), triazole (55 g) and potassium carbonate (160 g) is heated in dimethylformamide (600 ml) at 120° for four 30 hours. The insoluble materials are filtered and washed with dimethylformamide, and the reaction mixture is concentrated under vacuum. The residue, dissolved in methylene chloride, is washed with water and then concentrated. The product is obtained by crystallisation in 35 ethyl acetate after dilution with heptane. A pale pink solid, m.p. 101°, is isolated (97 g).

Stage c) Preparation of the compounds No. 1a and No. 1b

The compound obtained in stage b (35 g) in chloroform (200 ml) is treated with bromine at 0°. After decolorising, the solvent is evaporated and the residue redissolved in methanol. An aqueous solution of potassium hydroxide is then added until a basic pH is obtained. After evaporating the medium under vacuum, the residue is extracted with ethyl acetate, washed with water and concentrated. The oil obtained (40 g) consists of a mixture of two diastereoisomers in substantially equal proportions. Using silica column chromatography, the least polar isomer No. 1a: white crystals m.p. 83°, and then the most polar isomer No. 1b: white crystals m.p. 94°, are isolated in sequence. After recrystallisation, 1a, m.p. 96° and 1b, m.p. 104°, are obtained. The 50:50 mixture of 1a and 1b has a melting point of 74°.

The following compounds were prepared in the same way, using the appropriate raw materials: 1-[4-bromo-2-(4-chlorophenyl)tetrahydrofuran-2-ylmethyl)-1H-1,2,4-triazole: 1c: m.p. 74°; 1d: m.p. 78° and 1c+d: m.p. 69°.

Example II - Preparation of 1-(2-(2,4-dichlorophenyl)-4-hydroxytetrahydrofuran-2-ylmethyl)-1H-1,2,4-triazole. Compounds No. 2a and No. 2b.

10 g of the isomer 1a of Example I, which is the least polar isomer, dissolved in 30 ml of chlorobenzene, is refluxed for 48 h, in the presence of 20 g of sodium benzoate in 30 ml of water, and 1 g of the phase transfer catalyst "ADOGEN 464" methyltrialkylammonium chloride. The 4-benzoate compound, that is to say the compound 4a ($X_1 = H$ and $X_2 = OC\phi$) of melting point 98°C, or the

compound 4b ($X_1 = OC\phi$ and $X_2 = H$) of melting point 140°C, is then obtained as an intermediate.

After diluting with ether, the organic phase is washed with water and reduced under vacuum. The residue is then treated with methanol (100 ml) in the presence of

potassium hydroxide (7 g) at reflux temperature for 3 hours. The mixture is cooled, diluted with water and extracted with ethyl acetate, and the product washed to neutrality and purified by chromatography, the crude product being obtained after concentration under vacuum. The alcohol 2a is isolated in the form of a white powder (2.8 g), m.p. 193°.

Operating in the same way, starting from the most polar isomer 1b obtained according to Example I, the optically active alcohol 2b is obtained in the form of a white powder, m.p. 162°C. The 50:50 mixture of 2a and 2b is an oil.

Example III - Preparation of 1-(2-(2,4-dichlorophenyl)-4-ethoxytetrahydrofuran-2-ylmethyl)-1H-1,2,4-triazole.
Compounds No. 3a and No. 3b.

The alcohol 2a (2.2 g) dissolved in dimethylsulphoxide (12 ml) is treated, in sequence, with 80 % strength sodium hydride (0.42 g) and then with ethyl iodide (1.15 ml). After 15 minutes, the medium is diluted with water and extracted with ethyl acetate. After washing with water, the solvent is evaporated and the residue is purified by silica column chromatography to obtain a colourless oil which is the isomer 3a which crystallises on trituration with pentane m.p. 90°; in the same way, starting with 2b, the isomer 3b, which is a white powder, m.p. 63°, is obtained. The 50:50 mixture of 3a + 3b is an oil. The compounds of formula VIII listed in the following table were obtained in the same way, using the appropriate alcohols:

No.	X ₁	X ₂	Melting point
5a	H	O-CH ₃	oil
5b	O-CH ₃	H	oil
6a	H	O-n-Pr	oil
6b	O-n-Pr	H	oil

Example IV - Preparation of 1-[2-(2,4-dichlorophenyl)-
4-ethylthiotetrahydrofuran-2-ylmethyl]-1H-1,2,4-triazole.
Compounds No. 7a and No. 7b

The bromide 1a (3.8 g) dissolved in dimethyl
5 sulphoxide (38 ml) containing water (2 ml) is treated
with sodium hydrogen sulphide (2.8 g) for 2 hours.
Powdered potassium hydroxide (3.3 g) is then added,
followed by ethyl iodide (4 ml). After 10 minutes of
10 stirring, the medium is diluted with water and extracted
with ether. After drying and evaporation, the isomer 7a,
which is a yellow oil (3.9 g), m.p. 88°, is obtained.

Operating in the same way, starting with 1b, 7b
is obtained in the form of a pale yellow powder,
m.p. 64°. The mixture of isomers is an oil. The compounds
15 of formula VIII listed in the following table were
obtained in the same way, using the appropriate thiols:

	No.	X ₁	X ₂	Melting point
20	8a	H	S-CH ₃	96
	8b	S-CH ₃	H	oil
	9a	H	S-n-Pr	110
	9b	S-n-Pr	H	oil
	10a	H	S-2-ClEt	127
25	10b	S-2-ClEt	H	oil
	11a	H	S-i-Bu	68
	11b	S-i-Bu	H	oil
	12a	H	S-i-Pr	75
	12b	S-i-Pr	H	65
30				

Example V - Preparation of 1-[7-(2,4-dichlorophenyl)-1,4,6-trioxospiro[4.4]nonan-7-ylmethyl]-1H-1,2,4-triazole.

Compound No. 13

- 5 Stage a) Preparation of 1-chloro-2-(2,4-dichlorophenyl)-3,4,5-pentanetriol.

 The chlorohydrin obtained in stage a) of Example 1 (91 g) is epoxidised in 1,2-dichloroethane (125 ml) in the presence of vanadyl acetylacetonate (5 g) and 70 % strength tert-butyl peroxide (200 ml) by heating at the reflux temperature for 48 hours. The cooled medium is diluted with water, washed several times with a sodium bisulphite solution and then concentrated. The residue is then converted to triol by heating in water (200 ml) and dioxane (200 ml) in the presence of perchloric acid (5 ml) for 3 hours. After dilution with water, the medium is extracted with toluene (300 ml) and then concentrated.

15 Stage b) Preparation of 2-(2,4-dichlorophenyl)-2-chloromethyltetrahydrofuran-4-one

20 The oily residue obtained in stage a) is then heated in toluene (100 ml) and butanol (200 ml) in the presence of paratoluenesulphonic acid (0.5 g), with the separation of the water formed. After evaporating the reaction medium, the residue is chromatographed on a silica column (40:60 ethyl acetate/heptane eluent) to obtain a colourless oil (14.5 g) corresponding to a mixture of alcohol diastereoisomers, namely 2-(2,4-dichlorophenyl)-4-hydroxy-2-chloromethyltetrahydrofuran. This product is directly oxidised with chromic anhydride in acetic acid to obtain, after purification by silica column chromatography, furanone in the form of white crystals, m.p. 99°C.

25 Stage c) Preparation of 7-chloromethyl-7-(2,4-dichlorophenyl)-1,4,6-trioxaspiro[4.4]nonane.

35 The furanone obtained in stage b) (4.2 g), in toluene (50 ml), is heated at reflux temperature in the presence of ethylene glycol (6.5 ml) and p-toluenesulphonic acid (0.1 g), with the separation of the water

formed, until the disappearance of the starting product.

The medium is washed with sodium hydroxide and then diluted with water, extracted with ether and concentrated. A white solid (5.1 g), m.p. 99°, is obtained.

5 Stage d) Preparation of compound 13

The halide of stage c) (5 g) in dimethyl sulphoxide (20 ml) is heated to 170° in the presence of triazolyl sodium (2.75 g) for 6 hours. The medium is poured into water, extracted with ethyl acetate, concentrated and purified by silica column chromatography. After recrystallisation in an ethyl acetate/heptane mixture, pale yellow crystals (3.6 g), m.p. 123°, are isolated.

15 Example VI - Preparation of 1-[4-chloro-2-(2,4-dichlorophenyl)-tetrahydrofuran-2-ylmethyl]-1H-1,2,4-triazole.
Compounds No. 14a and No. 14b

Stage a) Preparation of 2-(2,4-dichlorophenyl)-1,4,5-trichloro-pentanol.

The chlorohydrin obtained in stage a) of Example I dissolved in dichloromethane (150 ml) is treated with gaseous chlorine (13.4 g) at -15°. The medium is then treated with a 37 % strength sodium bisulphite solution (15 ml), washed with water, dried and then evaporated. A crude product in the form of a colourless oil (49.7 g) containing approximately 70 % of the desired product in the form of a mixture of two diastereoisomers is obtained.

Stage b) Preparation of 1-(2,4-dichlorophenyl)-1-(2,3-dichloro-1-propanyl)oxirane

30 A first method consists in dissolving the crude chlorohydrin (10.3 g) obtained in stage a) above in methanol (30 ml) and treating it with a solution of methanolic potassium hydroxide (12 ml) at a concentration of $2.55 \cdot 10^{-3}$ [sic] moles/litre, at ambient temperature.
35 The precipitate is filtered and the methanolic solution is evaporated under vacuum. The residue is purified by silica column chromatography. A colourless oil is obtained (7.4 g).

A second method consists in dissolving the chlorohydrin (19.9 g) obtained in stage a of Example I in methanol (75 ml), and treating it with a potassium hydroxide (4.9 g) solution in methanol (20 ml) at ambient temperature. After the filtration of the insoluble material and evaporation, epoxide (17.1 g) is obtained in the form of a yellow oil. This epoxide is treated with chlorine until the yellow colour (10.1 g) persists at -15°C. The medium is then washed with a sodium bisulphite solution followed by water, and then evaporated under vacuum. A yellow oil (20.8 g) consisting of a mixture of two diastereoisomers in a ratio of 45:55 is obtained.

Stage c) Preparation of 1-[4-chloro-2-(2,4-dichlorophenyl)tetrahydrofuran-2-ylmethyl]-1H-1,2,4-triazole

The epoxide obtained in stage b) (61.7 g) in 1-butanol (0.5 litre) is heated at 90° for 6 hours in the presence of triazolyl sodium (18.6 g). The inorganic precipitate is filtered and the butanol is evaporated. The residue is purified by silica column chromatography (48 % ethyl acetate:48 % heptane: 4 % methanol eluent) to obtain, in sequence, the first diastereoisomer 14a, m.p. 113°, and then the second diastereoisomer 14b, m.p. 97°. The 50:50 mixture of 14a + 14b has a melting point of 90°.

Example VII

Preparation of 1-[4-oxo-2-(2,4-dichlorophenyl)tetrahydrofuran-2-ylmethyl]-1H-1,2,4-triazole. Compound 15

The alcohol 2a (37.7 g) is added at -60° to a solution of dimethyl sulfoxide (17 ml), in dichloromethane (120 ml), treated at -60° with a solution of trifluoroacetic anhydride (25.4 ml) in dichloromethane (60 ml). After maintaining at -60° for half an hour, the temperature is allowed to rise to ambient temperature and triethylamine (48 ml) is then added. The medium is poured into water, extracted with dichloromethane and evaporated. A white powder (m.p. 91°) is isolated by crystallisation in ether.

Example VIII

Preparation of 1-[4,4-dichloro-2-(2,4-dichlorophenyl)-tetrahydrofuran-2-ylmethyl]-1H-1,2,4-triazole.

Compound No. 20

5 A mixture of ketone 15 (3.1 g), phosphorus pentachloride (2.3 g) and dichloromethane (30 ml) containing triethylbenzylammonium chloride (0.25 g) is stirred for 2 hours at ambient temperature until the starting material disappears. The medium is evaporated,
10 diluted with water (100 ml), neutralised with sodium bicarbonate and extracted with ether. After drying and evaporation, the oily residue is recrystallised in isopropyl ether (twice). A white powder (0.6 g), m.p. 138°, is obtained.

15 Example IX - Preparation of 1-[4-dimethylamino-2-(2,4-dichlorophenyl)tetrahydrofuran-2-ylmethyl]-1H-1,2,4-triazole. Compound 16

 The ketone of Example III and then sodium cyanoborohydride (0.24 g) are successively added to a solution
20 of potassium hydroxide (0.24 g) and dimethylamine hydrochloride (1.05 g) in methanol. After 15 hours, the medium is diluted with water and extracted with ether. The desired product is then extracted from the organic phase with 6N hydrochloric acid (3 x 20 ml). After neutralisa-
25 tion, extraction and silica column chromatography, compound No. 5 (1.6 g) is isolated in the form of a pale yellow oil (50:50 mixture of 2 isomers).

30 Example X - Preparation of 1-[4-methoxyimino-2-(2,4-dichlorophenyl)tetrahydrofuran-2-ylmethyl]-1H-1,2,4-triazole. Compound 17.

 The ketone of Example III (2 g) in ethanol (30 ml) is heated under reflux in the presence of methoxylamine hydrochloride (5.8 ml of a 25 % solution in water) for 2 hours. The medium is diluted with water,
35 extracted with dichloromethane and evaporated. The product is isolated by crystallisation in a mixture of diisopropyl ether and heptane, in the form of a white powder, m.p. 108° (mixture of the two geometric isomers).

The compounds in which

$R_{11} = \text{H}$ (4-hydroxyimino) [sic] m.p. = 195° 18

$R_{11} = \text{---} \text{<} \text{---}$ (4-isopropoxyimino) oil 19

were prepared in the same manner.

5 Example XI and those which follow illustrate the fungicidal applications of the compounds according to the invention.

10 In these examples, the sprayings of solutions or suspensions of active substances are carried out under conditions such that the spraying of a solution or suspension of concentration equal to 1 g/litre corresponds on average to the application of approximately 2 micrograms of active substance per cm² of leaf area of the plant.

15 Under the conditions of Example XI and those which follow, the compounds illustrated showed no phytotoxicity.

20 In these examples, a product is regarded as providing complete protection against a fungal disease when the protection is at least 95 %; the protection is regarded as good when it is at least 80 % (but less than 95 %), as fairly good when it is at least 70 % (but less than 80 %) and as average when it is at least 50 % (but less than 70 %).

25 In the present account, the percentages are, except where otherwise indicated and except those relating to yields, percentages by weight. In the case where the percentages are expressed relative to the stoichiometry, these are molar percentages. As regards concentrations, some of these are expressed in ppm (part per million) which corresponds to mg/litre.

30 Example XI - In vivo test on Botrytis cinerea on tomato

35 An aqueous emulsion of the active substance to be tested, having the following composition, is prepared by fine grinding:

- active substance under test: 60 mg
- Tween 80 (surfactant) [sic] consisting of an oleate of a polyoxyethylated sorbitan derivative)

diluted to 10 % strength in water: 0.3 ml
the volume is made up to 60 ml with water.

This aqueous emulsion is then diluted with water
to obtain the desired concentration.

5 30- to 40-day-old, greenhouse-cultivated tomatoes
(variety Marmande) are treated by spraying with aqueous
emulsions (called slurries) as defined above and at
various concentrations of the compound to be tested. The
trial is replicated twice with each concentration.

10 After 24 or 48 hours, the leaves are cut and
placed in 2 Petri dishes (diameter 14 cm) the base of
which has previously been provided with a disc of moist
filter paper (5 leaflets per dish).

 The inoculum is then applied by means of a
15 syringe by depositing drops (3 drops per leaflet) of a
spore suspension. This suspension of Botrytis cinerea
spores was obtained from a 15-day-old culture, which was
then suspended in a nutrient solution (100,000 units/cm³).

 Verification is carried out 3 and 6 days after
20 the contamination by comparison with an untreated
control.

 Under these conditions, at a dose of 1 g/litre,
a good or total protection is observed with compounds 1a,
1b, 1a + 1b, 3b, 5b, 6b, 8b, 9b, 12b, 14a, 14b, 14a + 14b
25 and 17.

Example XII - In vivo test on Erysiphe graminis on barley
(barley mildew)

 Barley, in pots, sown in plain soil, is treated
at the 10 cm height stage by spraying with an aqueous
30 emulsion (called slurry) at the concentration indicated
below. The trial is replicated twice. After 24 hours, the
barley plants are dusted with Erysiphe graminis spores,
the dusting being carried out using diseased plants.

 Readings are taken 8 to 14 days after
35 contamination.

 Under these conditions, the following results are
observed: at a dose of 1 g/litre, good or total protec-
tion with compounds 1a, 1b, 1a + 1b, 2a, 2b, 3a, 3b,

3a + 3b, 4a, 4b, 5a, 5b, 6a, 6b, 7a + 7b, 8a, 8b, 13, 14a, 14b, 14a + 14b, 15, 17, 19 and 20.

Example XIII - In vivo test on "Puccinia [sic] recondita" responsible for wheat rust

5 Wheat, in pots, sown in plain soil, is treated at the 10 cm height stage by spraying with aqueous emulsions (called slurries) of the same composition as that described in Example VIII and at various concentrations of the compound to be tested. The trial is replicated twice
10 at each concentration.

 After 24 hours, an aqueous suspension of spores (50,000 sp/cm³) is sprayed onto the wheat; this suspension was obtained from contaminated plants. The wheat is then placed for 48 hours in an incubation cell at approxi-
15 mately 18°C and at 100 % relative humidity.

 After these 2 days, the relative humidity is lowered to 60 %. The condition of the plants is verified between the 11th and the 15th days, after contamination, by comparison with the untreated control.

20 At a dose of 1 g/litre, good or total protection with compounds 1a, 1b, 1a + 1b, 3a, 3b, 3a + 3b, 5b, 6b, 7a, 7a + 7b, 8b, 12b, 13, 14a, 14b, 14a + 14b, 17, 19 and 20.

Example XIV - In vivo test on "Piricularia oryzae" responsible for rice blast

25 Rice, in pots, sown in a 50:50 mixture of enriched peat and pozzolana, is treated at the 10 cm height stage by spraying with an aqueous emulsion (called slurry) defined above at the concentration indicated
30 below. The trial is repeated twice. After 48 hours, treatment is carried out by applying on the leaves a suspension of spores obtained in pure culture.

 The reading is carried out 8 days after contamination. Under these conditions, the following results
35 are observed: at a dose of 1 g/litre, good or total protection with compounds 1a, 1b, 1a + 1b, 3a, 3b, 6a, 8a, 8b, 9a, 9b, 10b, 11a, 11b, 12a, 12b, 14a, 14b, 14a + 14b, 15 and 20.

Example XV - In vitro test on seed fungi and soil fungi

The action of the compounds according to the invention is studied on the following fungi responsible for diseases of cereals and other plants:

- 5 1) *Pyrenophorae avenae*
- 2) *Septoria nodorum*
- 3) *Helminthosporium teres*
- 4) *Fusarium roseum*
- 5) *Fusarium nivale*
- 10 6) *Fusarium culmorum*
- 7) *Rhizoctonia cerealis*
- 8) *Septoria tritici*
- 9) *Botrytis cinerea* sensitive to carbendazime and to cyclic imides
- 15 10) *Botrytis cinerea* resistant to carbendazime and to cyclic imides
- 11) *Pseudocercospora herpotrichoides*
- 12) *Fusarium oxysporum* F. sp. *melonis*
- 13) *Rhizoctonia solani*
- 20 14) *Helminthosporium gramineum*

The numbers which appear before the names will be used to represent these fungi in Table (II).

For each trial, the procedure is as follows: a nutrient medium consisting of potato, glucose and agar
25 (PDA medium) is introduced supercooled into a series of Petri dishes (20 ml per dish) after sterilising in an autoclave at 120°C.

In the course of filling the dishes, an acetone solution of the active substance is injected into the
30 supercooled medium, to obtain the desired final concentration.

Petri dishes similar to the above, into which are poured similar quantities of a nutrient medium which does not contain the active substance, are taken as control.

35 After 24 or 48 h each dish is seeded by depositing a fragment of mycelium originating from a previous culture of the same fungus.

The dishes are stored for 2 to 10 days (depending on the fungus being tested) at 22°C, and the growth of the fungus in the dishes containing the active substance to be tested is compared with that of the same fungus in the dish used as the control.

For each compound tested, the degree of inhibition of the fungus considered, at a dose of 30 ppm, is thus determined. The results are given in the following table.

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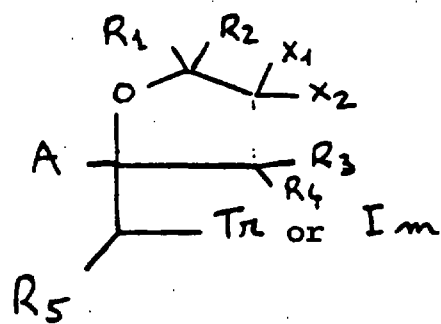
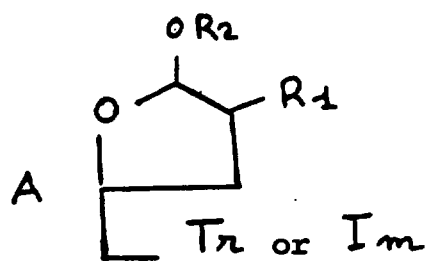
Compound No.	Fungi						
	1	2	3	4	5	6	7
1a	100	100	100	95	100	100	95
1b	100	90	100	100	100	100	90
1a + 1b	100	95	100	95	100	100	90
2a	50	95	80	50	80	100	80
2b	80	110	80	50	90	90	80
3a	95	90	100	50	80	80	90
3b	95	95	100	80	90	100	90
3a + 3b	80	0	80	0	80	80	80
4a	90	0	90	80	80	90	90
4b	95	80	95	80	80	100	90
5a	50	90	50	50	50	50	50
5b	100	100	100	90	95	100	95
6a	50	90	50	50	50	50	50
6b	100	95	95	80	90	90	90
7a	95	95	95	0	0	0	50
7b	95	90	95	0	0	0	50
7a + 7b	50	95	50	0	0	0	50
8a	95	80	95	80	50	100	80
8b	100	90	95	80	80	90	80
9a	95	90	95	80	80	90	80
9b	80	95	95	0	0	80	80
10a	80	0	80	50	90	95	80
10b	90	80	90	0	0	50	80
11a	90	50	95	0	0	0	80
11b	90	80	95	0	0	0	80

	Compound No.	Fungi						
		1	2	3	4	5	6	7
5	12a	90	80	95	0	80	80	80
	12b	95	90	95	80	80	90	80
	13a	--	90	--	--	--	--	--
	14a	95	95	100	95	100	100	90
	14b	95	90	100	90	95	100	90
10	14a + 14b	100	95	100	100	100	100	95
	15	0	95	80	0	0	50	0
	16	80	0	80	0	0	50	0
	17	80	0	80	80	95	80	80
	18							
15	19	90	0	80	80	90	50	80
	20	90	80	95	90	95	90	90

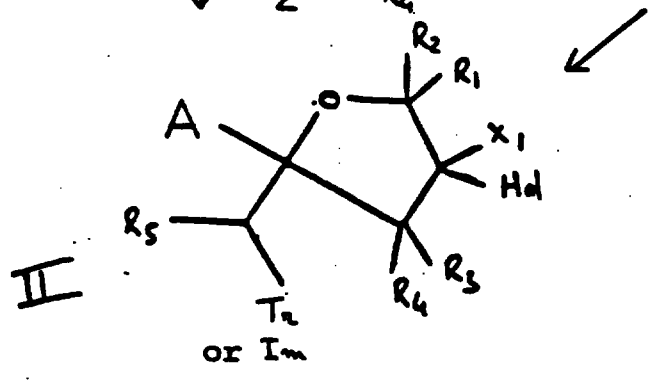
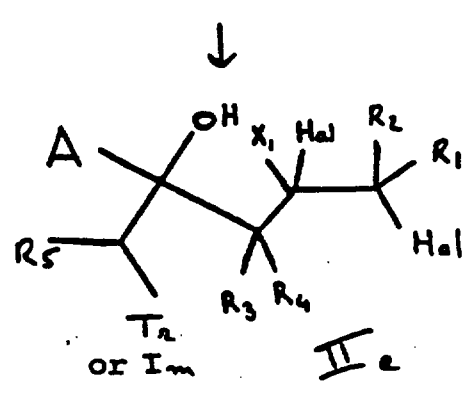
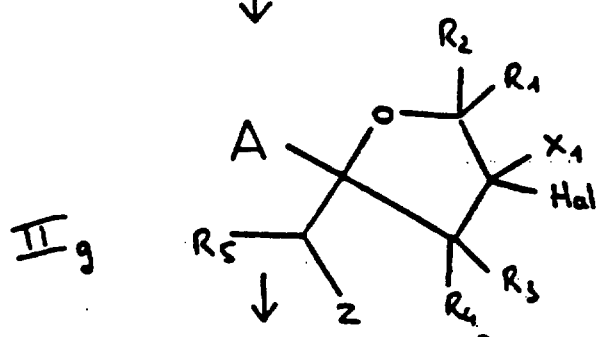
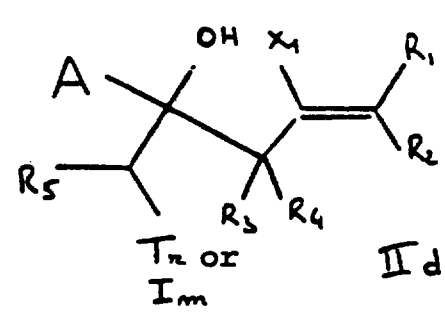
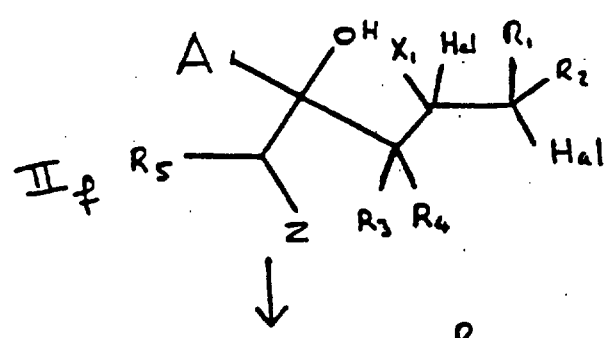
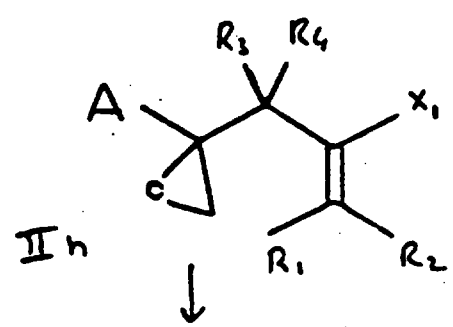
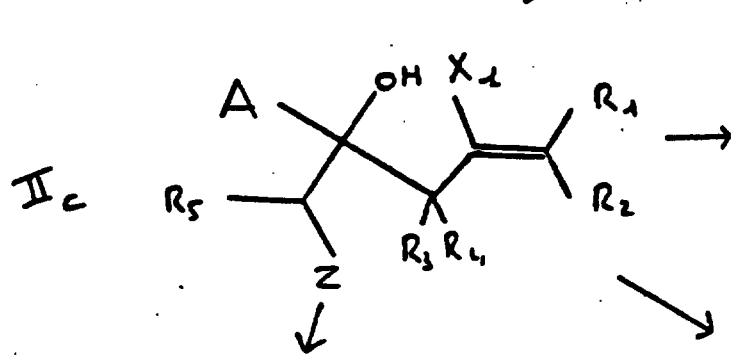
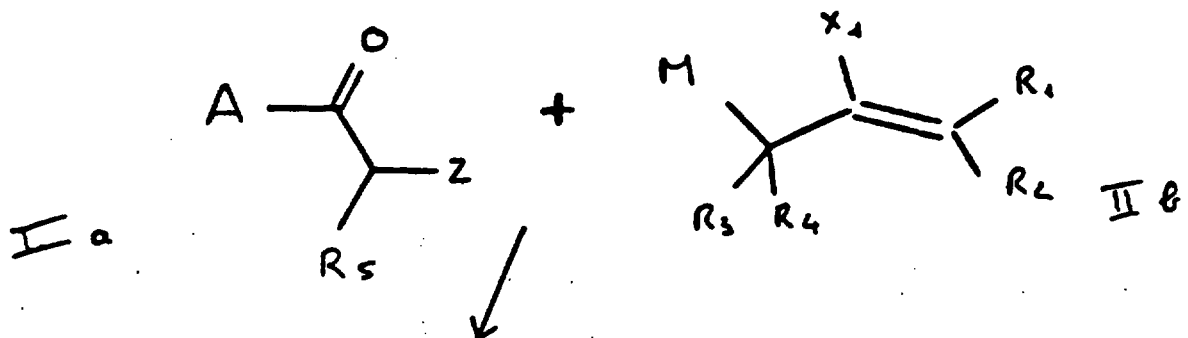
	Compound No.	Fungi						
		8	9	10	11	12	13	14
20	1a	100	100	100	100	100	80	100
	1b	-	95	95	100	100	80	100
	1a + 1b	100	95	95	100	100	90	95
25	2a	0	95	95	100	0	0	80
	2b	0	80	50	100	80	0	80
	3a	95	90	90	95	0	0	90
	3b	100	95	100	95	80	80	95
	3a + 3b	0	80	95	0	0	0	80
30	4a	0	95	95	0	0	0	90
	4b	0	95	95	90	95	0	95
	5a	0	0	0	100	0	0	50
	5b	0	95	90	100	95	90	90
	6a	0	50	50	100	0	0	50
35	6b	50	95	95	100	80	80	95
	7a	0	95	95	95	0	80	80
	7b	0	90	95	90	0	50	50

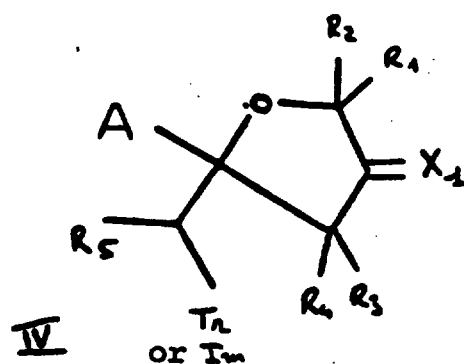
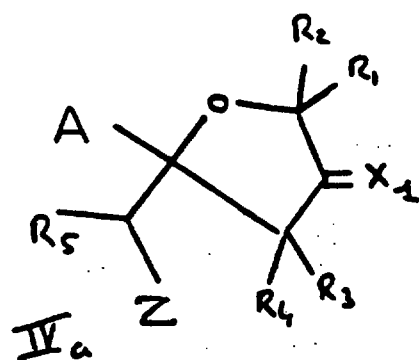
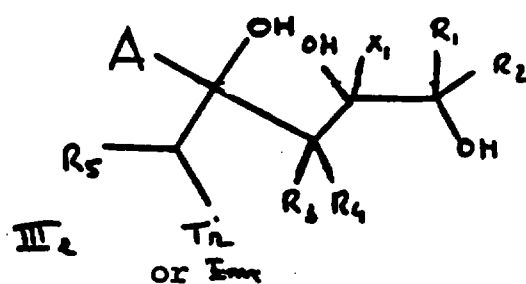
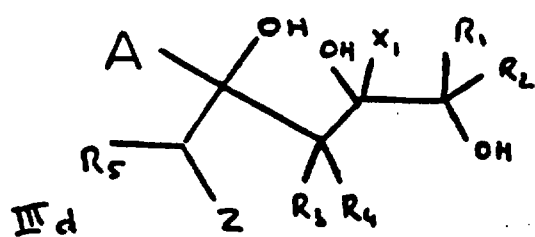
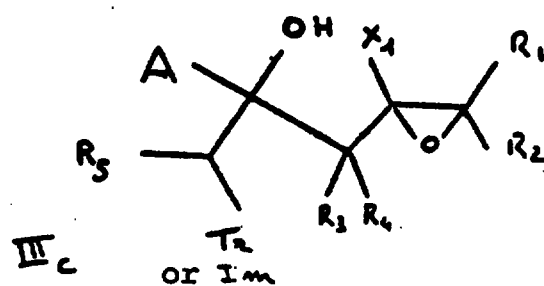
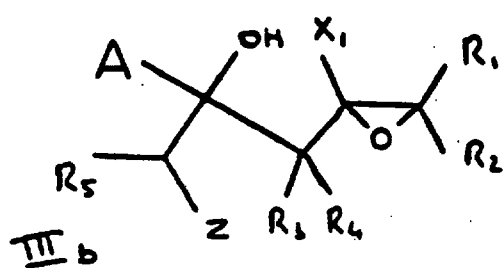
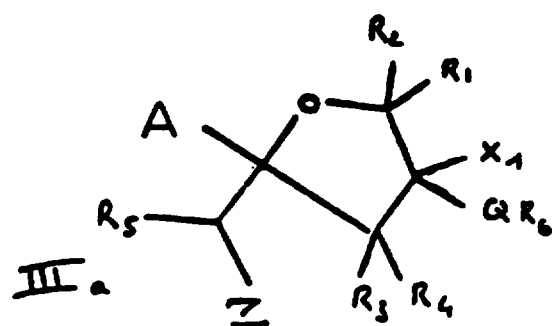
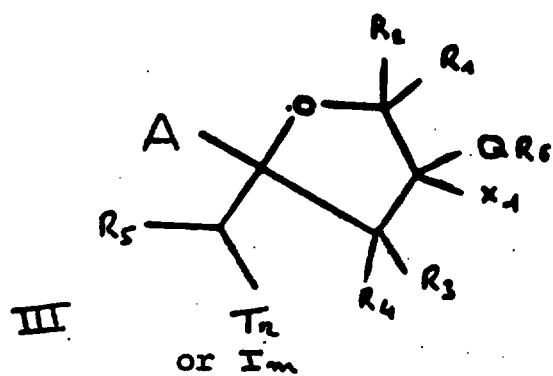
	Compound No.	Fungi						
		8	9	10	11	12	13	14
5	7a + 7b	-	95	95	100	50	80	50
	8a	0	80	80	80	80	80	95
	8b	0	95	95	90	80	80	95
	9a	0	90	90	90	80	80	95
	9b	0	95	90	100	80	80	50
10	10a	50	80	0	0	0	0	0
	10b	0	90	95	80	50	50	90
	11a	0	0	80	50	50	50	95
	11b	0	80	80	80	80	80	95
	12a	0	50	80	80	0	80	90
15	12b	0	95	95	90	80	80	100
	13a	-	0	0	100	50	0	-
	14a	-	100	100	100	100	80	100
	14b	0	95	95	100	80	80	100
	14a+14b	50	95	95	100	100	80	95
20	15	-	0	0	95	0	0	0
	16	0	0	0	0	0	0	80
	17	0	80	80	0	0	0	80
	18							
	19	0	0	0	0	0	0	90
25	20	0	80	90	100	50	80	90

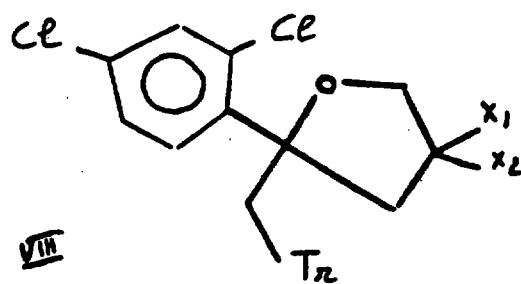
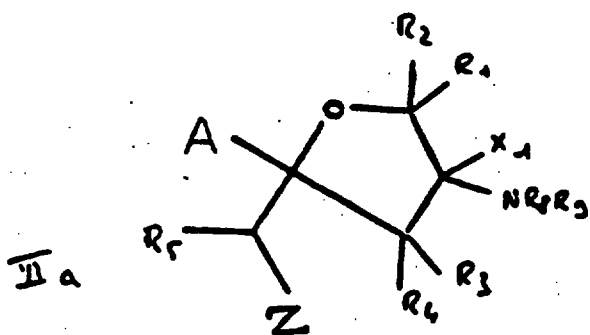
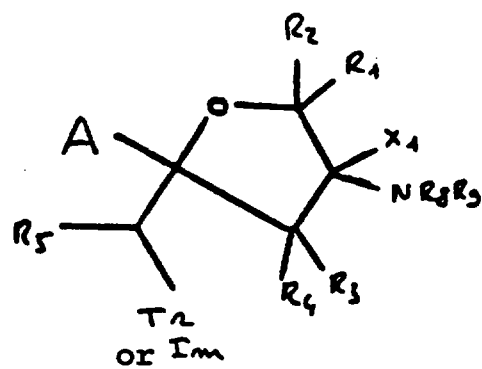
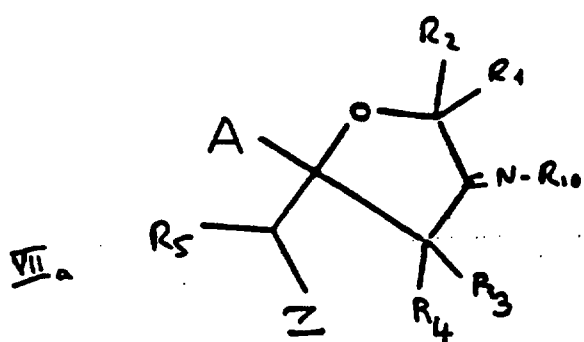
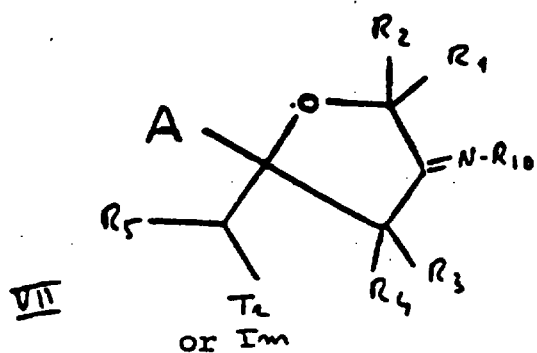
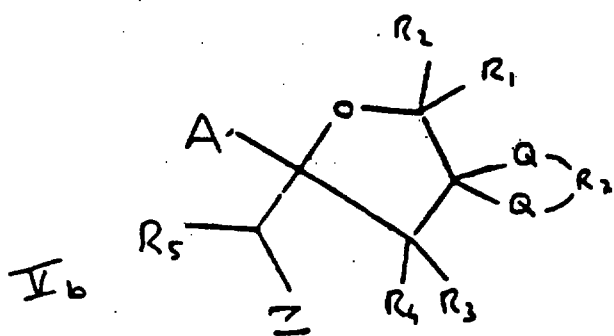
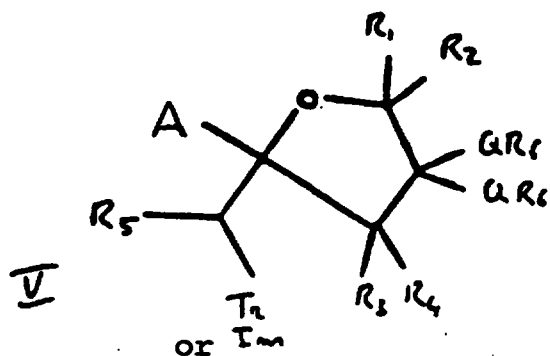
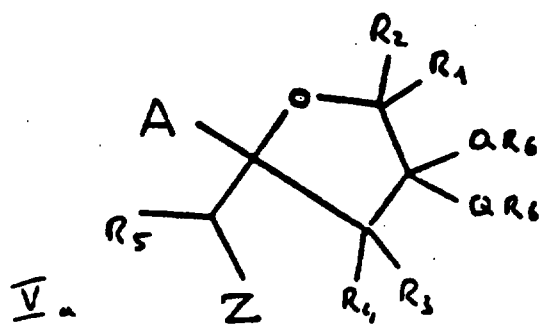
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(I)



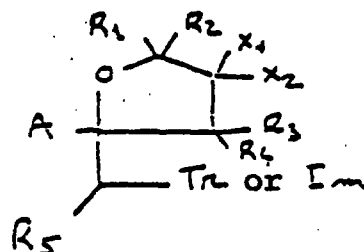






CLAIMS

1. Compounds containing triazole or imidazole, tetrahydrofuran and phenyl groups, characterised in that they correspond to the general formula (I)



5 in which

A is a group $(Y)_n\text{-Ph-(CH}_2)_m\text{-}$, where Ph is a phenylene ring and $m = 0$ or 1 ,

Y is a halogen atom or a cyano or nitro group, or an optionally halogenated alkyl or alkoxy group,

10 n is zero or a positive integer less than 6, it being possible for the groups Y to be identical or different when n is greater than 1,

Tr represents a 1,2,4-triazol-1-yl group and Im a 1,3-imidazol-1-yl [sic] group,

15 R_1 to R_5 , which may be identical or different, represent a hydrogen atom or a linear or branched alkyl radical containing at most six carbon atoms, a cycloalkyl radical containing at most six carbon atoms, a phenyl or benzyl radical or an alkoxy radical containing at most
20 six carbon atoms, it being possible for these various radicals to be optionally substituted with one or more halogen atoms or alkoxy radicals containing at most six carbon atoms;

25 X_1 and X_2 , which may be identical or different, represent a hydrogen atom, a halogen atom, an alkyl radical containing at most six carbon atoms, a cycloalkyl radical containing at most six carbon atoms or a phenyl or benzyl radical, it being possible for these various radicals to be optionally substituted in a manner similar
30 to the groups R_1 to R_5 ,



a group $Q-R_6$, in which Q represents O or S , and R_6 represents a hydrogen atom or an alkyl radical containing at most six carbon atoms, a cycloalkyl radical containing at most six carbon atoms or a phenyl, benzyl, benzoyl or acyl [sic] radical, it being possible for these radicals to be substituted in a manner similar to the groups R_1 to R_5 and to have identical or different meanings when X_1 and X_2 each correspond to OR_6 or SR_6 ,

a group of formula $-Q-R_7-Q-$, where Q has the same meaning as above and in which R_7 is a divalent hydrocarbon radical comprising from 2 to 6 carbon atoms, it being possible for one of these carbon atoms to be replaced by an oxygen or nitrogen atom, the said single divalent radical itself being optionally substituted with one or more halogen atoms or hydroxyl [lacuna], alkyl radicals containing at most six carbon atoms or alkoxy radicals containing at most six carbon atoms,

a group $-N-R_8R_9$, in which R_8 and R_9 , which may be identical or different, represent a hydrogen atom or an alkyl radical containing at most six carbon atoms, a cycloalkyl radical containing at most six carbon atoms or a phenyl radical, it being possible for these various radicals to be optionally substituted in a manner similar to the groups R_1 to R_5 , or alternatively R_8 and R_9 together can form a single divalent hydrocarbon radical comprising from 2 to 6 carbon atoms, it being possible for one of these carbon atoms to be replaced by an oxygen, sulphur or nitrogen atom, the said single divalent radical itself being optionally substituted with one or more halogen atoms, hydroxyl groups, alkyl radicals containing at most six carbon atoms or optionally halogenated alkoxy radicals containing at most six carbon atoms,

a group $=N-R_{10}$, in which R_{10} corresponds to an alkyl radical containing at most six carbon atoms, or a cycloalkyl radical containing at most six carbon atoms, or to a group of formula OR_{11} in which R_{11} is an alkyl, it being possible for these radicals to be substituted in a manner similar to the groups R_1 to R_5 , or a hydroxyl

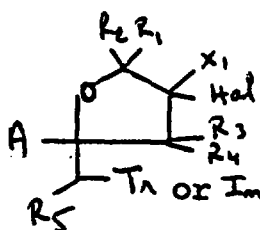
group,

a group N_3 , on condition that X_2 is other than N_3 , X_1 or X_2 can correspond to $=O$ or $=S$, the other group being eliminated,

- 5 on the general conditions that X_1 and X_2 cannot simultaneously correspond to a hydrogen atom or to an alkyl radical containing at most six carbon atoms, a cycloalkyl radical containing at most six carbon atoms, a phenyl radical or a benzyl radical, and if X_1 and X_2 are different and either one of them is OR_6 , then, in this case only, R_6 can be only a benzoyl or acyl [sic] group;
- 10

and their salified forms.

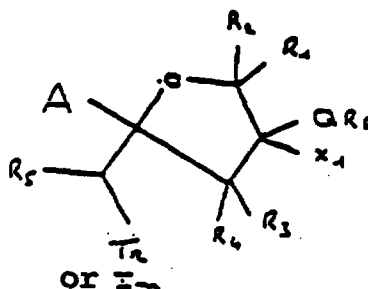
2. Compounds according to Claim 1, characterised in that $m = 0$, $n = 1, 2$ or 3 and Y is a halogen atom.
- 15 3. Compounds according to Claims 1 and 2, characterised in that $n = 1$ or 2 and Y is a halogen atom in the ortho and/or para position.
4. Compounds according to Claim 3, characterised in that Y is a chlorine or bromine atom.
- 20 5. Triazole compounds according to one of Claims 1 to 4, characterised in that they correspond to the formula II



- in which Y , m and n have one of the meanings indicated in the compound of formula I, R_1 to R_5 correspond to a hydrogen atom or to an alkyl or cycloalkyl group containing at most six carbon atoms, Hal corresponds to a halogen atom and X_1 is a halogen or hydrogen atom.
- 25
6. Compounds according to Claim 5, characterised in that Hal is chlorine or bromine and X_1 is chlorine or bromine.
- 30



7. Triazole compounds according to one of Claims 1 to 4, characterised in that they correspond to the formula III

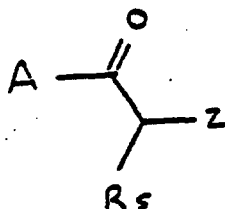


in which Y, n and m have one of the meanings indicated in the compound of the formula I, R₁ to R₅ correspond to a hydrogen atom or to an alkyl or cycloalkyl group containing at most six carbon atoms, X₁ corresponds to a hydrogen atom or to an alkyl or cycloalkyl group containing at most six carbon atoms, Q has the same meaning as in the formula I and R₆ corresponds to a hydrogen atom or to an alkyl or cycloalkyl group containing at most six carbon atoms.

8. Compounds according to Claim 7, characterised in that the groups R₁ to R₅ correspond to a hydrogen atom or to an alkyl or cycloalkyl group containing at most six carbon atoms, and R₆ corresponds to an alkyl or cycloalkyl group containing at most six carbon atoms and optionally substituted in a manner similar to the groups R₁ to R₅ [sic].

9. Process for the preparation of the compounds of formula II, in which R₁ to R₅, A, Y, n and X₁ have the same meaning as in Claim 1 and Hal corresponds to a halogen atom, characterised in that it consists of the following steps:

Step a) A halo ketone of formula IIa,

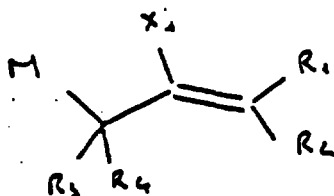


IIa



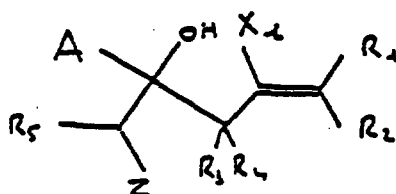
in which Y, n and R₃ have the same meaning as that given for the compounds of formula I and Z corresponds to a halogen atom, is reacted with an organometallic compound of formula IIb,

5



IIb

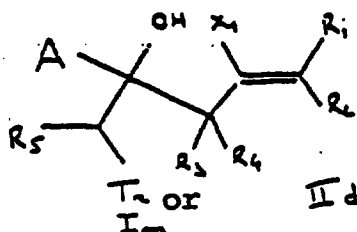
to obtain the compound of formula IIc,



IIc

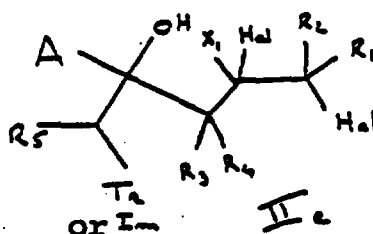
10 Step b) The compound of formula IIc is then reacted with an unsubstituted imidazole or triazole in the presence of an organic or inorganic base and in a suitable solvent,

Step c) A halogen molecule or mixed halogen molecule is added to the compound IIc



IIc

in an inert solvent, leading to the compound IIe,

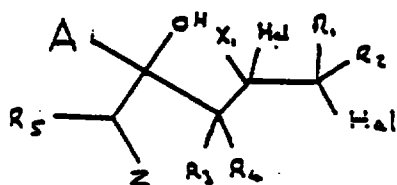


15

IIe

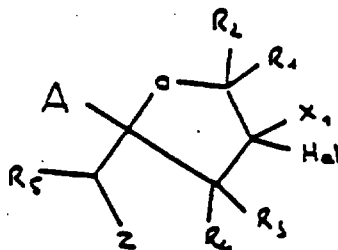
Step d) The compound II is obtained by cyclisation of the compound IIe in the presence of an organic or inorganic base.

10. Process for the preparation of the compounds of formula II, in which R_1 to R_5 , Y, n, A and X_1 have the same meaning as in Claim 1 and Hal corresponds to a halogen atom, characterised in that a halogen molecule or mixed halogen molecule is added in an inert solvent to the compound IIc according to Claim 9, to obtain the compound IIf,



II f

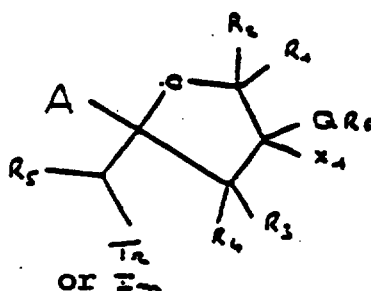
the latter being cyclised in the presence of an organic or inorganic base to lead to the compound IIg,



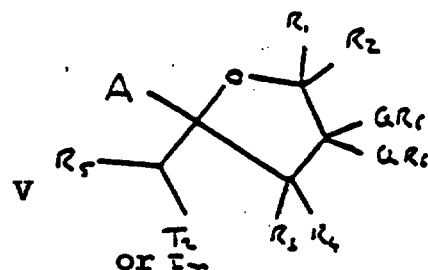
II g

- 15 to which an unsubstituted triazole or imidazole group is attached in the presence of an organic or inorganic base and in a suitable solvent.

11. Process for the preparation of the compounds of formula III or V,



III

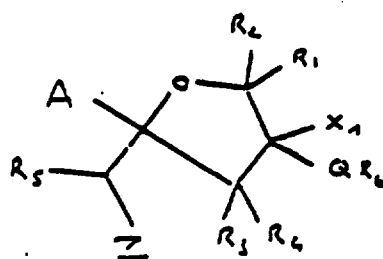


V



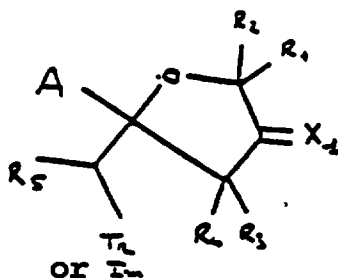
in which R_1 to R_6 , Y , n , A and X_1 have the same meaning as in Claim 1 and Q corresponds to an oxygen or sulphur atom, characterised in that a compound of formula II or IIg is reacted with a nucleophile containing a hetero atom, of formula R_6-Q-E in which R_6 and Q have the same meaning as in the compound of formula I and E is a cation, in the presence of a base and optionally of a phase transfer catalyst, and in the case where the starting material is the compound IIg, an unsubstituted imidazole or triazole is attached.

12. Process for the preparation of the compounds of formula III in which R_6 is an optionally mono- or poly-halogenated alkyl group containing at most six carbon atoms, characterised in that a compound of formula III or IIIa in which R_6 corresponds to a hydrogen atom is reacted with an alkyl halide (where appropriate mono- or poly-halogenated) in the presence of an organic or inorganic base, and in that an imidazole or triazole ring is then attached if the starting material is the compound IIIa



IIIa

13. Process for the preparation of the compounds of formula IV



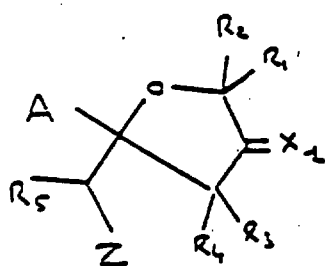
IV

in which R_1 to R_5 , n , Y and A have the same meaning as in Claim 1 or [sic] X_1 and X_2 together correspond to an oxygen atom, characterised in that a compound of formula III or IIIa in which Y , n and R_1 to R_5 have the same meaning as in Claim 1 and Z is a halogen atom, and in

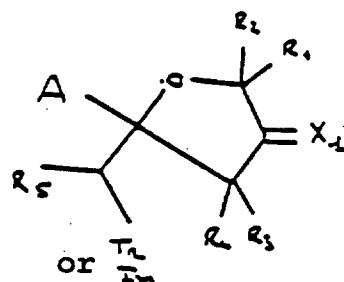
which QR_6 corresponds to a hydroxyl group and X_1 to a hydrogen atom, is oxidised, and in that, when the starting material is the compound IIIa, an unsubstituted imidazole or triazole ring is then attached.

- 5 14. Process for the preparation of compounds of formula IV in which X_1 and X_2 together correspond to a sulphur atom and Y, n and R_1 to R_5 have the same meaning as in Claim 1, characterised in that the compound of the formula IV in which X_1 and X_2 together correspond to an oxygen atom is subjected to a thionation.

15. Process for the preparation of the compounds of formula V, characterised in that the compounds of formula IV or IVa



15 IVa



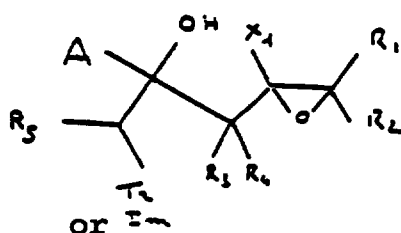
IV

- in which X_1 and X_2 together correspond to an oxygen or sulphur atom doubly bonded to the tetrahydrofuran are reacted with a compound of formula HQR_6 , or [sic] Q corresponds to O or S, in the presence of an acid catalyst and in a suitable solvent, which can be the alcohol or thiol itself or an inert solvent; if the starting material is the compound of formula IVa, the compound of formula Va is obtained, and an imidazole or triazole ring is then grafted onto the compound of formula Va.

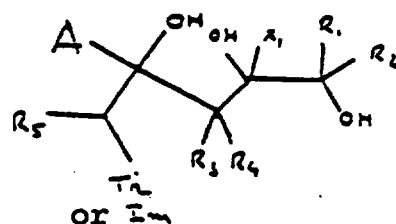
- 25 16. Process for the preparation of the compounds of formula II in which R_1 to R_5 , n, Y and A have the same meaning as in Claim 1 or [sic] X_1 and X_2 correspond to a halogen atom, preferably chlorine or bromine, characterised in that a compound of formula III or IIIa in which Y, n, R_1 to R_5 and A have the same meaning as in Claim 1 and Z is a halogen atom, and in which QR_6 corresponds to a hydroxyl group and X_1 to a hydrogen atom, is

oxidised and in that phosphorous pentachloride is then added to the ketone (compound of formula IV in which X_1 corresponds to an oxygen atom), optionally in the presence of an aprotic polar solvent and optionally of a quaternary ammonium halide, preferably at room temperature.

17. Compounds which can be used, where appropriate, as intermediates in the preparation processes of Claims 9 to 16, characterised in that they correspond to the formulae IIIc and IIIe



IIIc



IIIe

in which R_1 to R_5 , Y , A , m , n , X_1 and X_2 have any one of the meanings stated in Claim 1 or 8.

18. Use of the compounds according to one of Claims 1 to 8 as a fungicide, in particular in the form of fungicidal compositions containing as active substance a compound according to one of Claims 1 to 8, preferably 0.5 to 95 % by weight, this active substance being in combination with at least one agriculturally acceptable inert carrier.

19. Process for the control of fungal diseases of crops, characterised in that an effective dose of an active substance according to one or Claims 1 to 8 is applied, preferably at a rate of 0.005 to 5 kg/ha, and advantageously 0.01 to 0.5 kg/ha.