COMMONWEALTH of AUSTRALIA  
PATENTS ACT 1952
APPLICATION FOR A STANDARD PATENT

We, RHONE-POULENC AGROCHIMIE, of 14-20 Rue Pierre Baizet, Lyon 9e, FRANCE

hereby apply for the grant of a Standard Patent for an invention entitled:

"PROPARGYLOXYBENZENE DERIVATIVES, PREPARATION THEREOF AND FUNGICIDAL COMPOSITIONS CONTAINING THEM"

which is described in the accompanying specification.

Details of basic application(s):

<table>
<thead>
<tr>
<th>Number</th>
<th>Convention Country</th>
<th>Date</th>
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</thead>
<tbody>
<tr>
<td>8606959</td>
<td>FRANCE</td>
<td>12th May 1986</td>
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</tbody>
</table>

The address for service is care of DAVIES & COLLISON, Patent Attorneys, of 1 Little Collins Street, Melbourne, in the State of Victoria, Commonwealth of Australia.

Dated this 11th day of May 1987

To: THE COMMISSIONER OF PATENTS

(a member of the firm of DAVIES & COLLISON for and on behalf of the Applicant).

Davies & Collison, Melbourne and Canberra.
In support of the Application made for a patent for an invention
entitled: "PROPARGYLOXYBENZENE DERIVATIVES, PREPARATION THEREOF AND FUNGICIDAL COMPOSITIONS CONTAINING THEM"

I do solemnly and sincerely declare as follows:-

1. (a) I am the actual inventor of the invention and the facts upon which the applicant is entitled to make the application are as follows:

Employee invention - Contract of employment
- Pierre PLACE : 1.09.1981
- Régis PEPIN : 1.03.1985 whereby the applicant would if a patent were granted on an application made by the said inventors be entitled to have the patent assigned to him.

2. (a) or (b) I am authorized by RHONE-POULENC AGROCHIMIE, a French Body Corporate, of 14-20 Rue Pierre Baizet, Lyon 9e, France

the applicant for the patent to make this declaration on its behalf.

3. Where the basic application referred to in paragraph 3 of this Declaration was made in....FRANCE...on the 12TH MAY 1986

......RHONE-POULENC AGROCHIMIE

4. The basic application referred to in paragraph 3 of this Declaration was the first application...made in a Convention country in respect of the invention the subject of the application.

Declared at LYON this 15 day of April 1987

RHONE-POULENC AGROCHIMIE

BY: François CHRETIEN

DAVIES & COLLISON, MELBOURNE and CANBERRA.
The invention relates to fungicidal compounds which are active especially against strains which are resistant to known fungicides, in particular those of the benzimidazole group.

Claim

1. A propargyloxybenzene derivative of the formula:

\[
\begin{align*}
& X_m \\
& \text{I} \\
& R_1 \\
& \text{I} \\
& (0-C-C \equiv C-Z)_n \\
& \text{I} \\
& R_4 \\
& R_3 \\
& \text{I} \\
& (0-C-C \equiv C-Y) \\
& \text{I} \\
& R_2
\end{align*}
\]
in which

m is zero or an integer from 1 to 5-n;

X, which may be the same or different when m is greater than 1, represents a halogen atom, a cyano or nitro group or an amino group, which may be mono- or dialkylated,

an alkyl, alkoxy or alkylthio radical, the alkyl moiety of which contains 1 to 12 carbon atoms and may be mono- or polyhalogenated, the alkyl moiety, when it contains from 1 to 4 carbon atoms, being optionally substituted with a hydroxy, lower alkoxy or benzyloxy radical or an amino radical, which may be mono- or dialkylated,

an alkenyl or alkenyloxy radical containing 2 to 5 carbon atoms, or

a phenyl, phenoxy, or phenylthio radical, which may be substituted;

Y and Z, which may be identical or different, represent a hydrogen or halogen atom;

n is an integer equal to 1 or 2; and

R₁, R₂, R₃ and R₄, which may be identical or different, each represent a hydrogen atom or a lower alkyl radical, provided that when R₁, R₂, R₃, R₄ each represent hydrogen, m is zero and n is equal to 1, Y and Z do not both represent hydrogen atoms.

10. A fungicidal composition which comprises, as active ingredient, a compound of the formula:
in which

m is zero or an integer from 1 to 5-n;

X, which may be the same or different when m is greater than 1, represents a halogen atom, a cyano or nitro group or an amino group, which may be mono- or dialkylated, an alkyl, alkoxy or alkylthio radical, the alkyl moiety of which contains 1 to 12 carbon atoms and may be mono- or polyhalogenated, the alkyl moiety, when it contains from 1 to 4 carbon atoms, being optionally substituted with a hydroxy, lower alkoxy or benzyloxy radical or an amino radical, which may be mono- or dialkylated, an alkenyl or alkenyloxy radical containing 2 to 5 carbon atoms, or a phenyl, phenoxy, or phenylthio radical, which may be substituted;

Y and Z, which may be identical or different, represent a
hydrogen or halogen atom;
n is an integer equal to 1 or 2; and
R₁, R₂, R₃ and R₄, which may be identical or different,
each represent a hydrogen atom or a lower alkyl radical.

6. A process for the preparation of a compound
according to claim 1, in the formula of which at least one
of Y or Z represents a halogen atom which comprises the
reaction of a compound of the formula:

\[
\begin{align*}
\text{R}_3 & \\
\mid & \\
(\text{O-C-C} \equiv \text{C-H}) & _n \\
\mid & \\
\text{R}_4 & \\
\mid & \\
\text{R}_1 & \\
\mid & \\
\text{O-C-C} \equiv \text{C-H} & \\
\mid & \\
\text{R}_2 & 
\end{align*}
\]

wherein the various symbols are as defined in claim 1, with
a halogen in the presence of an acid acceptor.
Complete Specification for the invention entitled:

"PROPARGYLOXYBENZENE DERIVATIVES, PREPARATION THEREOF AND FUNGICIDAL COMPOSITIONS CONTAINING THEM"

The following statement is a full description of this invention, including the best method of performing it known to us:-
The present invention relates to new propargyloxybenzene derivatives, to their preparation and to their use in agrochemical compositions, in particular fungicides.

The repeated use for several years of a number of known fungicides has led to the appearance of strains of phytopathogenic fungi which are resistant to these fungicides. This phenomenon is observed with the benzimidazole group, especially carbendazim (methyl benzimidazol-2-ylcarbamate), benomyl (methyl 1-(butylcarbamoyl)benzimidazol-2-ylcarbamate), thiophanate (1,2-di-(3-ethoxycarbonyl-2-thioureido)benzene), thiophanate-methyl (1,2-di-(3-methoxycarbonyl-2-thioureido)benzene) and also with the cyclic imide group, especially iprodione (3-(3,5-dichlorophenyl)-1-isopropylcarbamoylimidazolidine-2,4-dione), procymidone (3-(3,5-dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide) and vinclozolin (3-(3,5-dichlorophenyl)-5-methyl-5-vinlyoxazolidine-2,4-dione). These resistances are observed especially in Botrytis sp, in particular in Botrytis cinerea.

The invention relates to fungicidal compounds which are active especially against strains which are resistant to known fungicides, in particular those of the benzimidazole group.

The present invention accordingly provides propargyloxybenzene derivatives of the formula:
in which

\[ m \text{ is zero or an integer from 1 to } 5-n; \]

\[ X, \text{ which may be the same or different when } m \text{ is} \]
greater than 1, represents a halogen atom, a cyano or nitro group or an amino group, which may be mono- or dialkylated (preferably by lower alkyl), an alkyl, alkoxy or alkylthio radical, the alkyl moiety of which contains 1 to 12 carbon atoms and may be mono- or polyhalogenated, the alkyl moiety, when it contains from 1 to 4 carbon atoms, being optionally substituted with a hydroxy, lower alkoxy or benzyloxy radical or an amino radical which may be mono- or dialkylated (preferably by lower alkyl), an alkenyl or alkenyloxy radical containing 2 to 5 carbon atoms, or

\[ a \text{ phenyl, phenoxy or phenylthio radical, which} \]
may be substituted;
Y and Z, which may be identical or different, represent a hydrogen or halogen atom;
n is an integer equal to 1 or 2; and
R₁, R₂, R₃ and R₄, which may be identical or different, each represent a hydrogen atom or a lower alkyl radical provided that, when R₁, R₂, R₃, R₄ each represent hydrogen, m is zero and n is equal to 1, Y and Z do not both represent hydrogen.

In this specification and the accompanying claims "lower alkyl radical" means an alkyl radical containing from 1 to 4 carbon atoms.

A preferred sub-group comprises derivatives of formula I as defined above, in the formula of which n preferably equals 1 and the group -O-C(R₃R₄)-C=O-C-Z is in the ortho position of the phenyl ring, relative to the group -O-C(R₁R₂)-C=O-C-Y.

Other preferred compounds are such that, in formula I, Y and Z, which may be identical or different, each represent a bromine or iodine atom.

The compounds according to the invention are particularly valuable because of their good fungicidal properties, especially in agriculture.

The compounds of formula I may be prepared by the application or adaptation of methods known per se, ie. methods heretofore used or described in the literature.

Compounds of formula I in which Y and Z both
represent hydrogen atoms, i.e. compounds of formula I', may be prepared by the reaction, known per se (cf. Houben Weil: Methoden der Organischen Chemie [Methods of Organic Chemistry] Vol. VI/3 p. 54 (1965)), of a di- or triphenol with a propargyl halide.

According to a feature of the invention compounds of formula I wherein Y and Z both represent hydrogen atoms are prepared by the process which comprises the reaction of a di- or triphenol of the formula:

\[
\begin{align*}
 X_m & \quad (\text{II}) \\
 \end{align*}
\]
wherein \( R_1 \) and \( R_2 \) are as hereinbefore defined and Hal represents a halogen atom, in the presence of an acid acceptor.

The reaction proceeds in accordance with the scheme:

\[
\begin{align*}
\text{II} + (n+1) \text{III} & \rightarrow \text{I'} + (n+1)\text{Hal} \\
\end{align*}
\]

wherein B represents an acid acceptor and the formulae and symbols are as hereinbefore defined.

Some starting di- and triphenols of formula II are known, in particular those in the formula of which \( m \) is zero. Others may be prepared by the application or adaptation of known methods.

Suitable acid acceptors include inorganic bases such as alkali metal or alkaline earth metal hydroxides or carbonates, in particular sodium hydroxide, potassium hydroxide and potassium carbonate.
The reaction may advantageously be carried out in a solvent medium, especially an organic solvent, such as a ketone e.g. acetone, a nitrile such as acetonitrile, an amide such as dimethylformamide or dimethyl sulfoxide, a cyclic ether such as tetrahydrofuran, or an aliphatic or aromatic hydrocarbon which is optionally substituted, e.g. toluene, and mixtures of such solvents.

The reaction may advantageously be carried out in the presence of a catalyst, especially a phase transfer catalyst, such as tris(3,6-dioxahexylamine).

Compounds of formula I in which at least one of Y and Z represents a halogen atom (compounds of formula I") may be prepared by methods known per se, especially Houben Weil: Methoden der Organischen Chemie vol. V/3 p. 601, 1977, by reacting a halogen with a di- or tripropargyloxybenzene derivative.

According to a further feature of the invention compounds of formula I wherein at least one of Y and Z represents a halogen atom are prepared by the process which comprises the reaction of a compound of the formula:
wherein the various symbols are as hereinbefore defined with a halogen, preferably chlorine, and more especially bromine or iodine, in the presence of an acid acceptor and optionally in a solvent medium.

The reaction proceeds in accordance with the scheme:

\[ I' + x\text{Hal}_2 \rightarrow I'' + x\text{HalH} \]

wherein the formulae and symbols are as hereinbefore defined.

Certain of the starting compounds of formula I' are known, when m is zero and n is equal to 1. Others may
be prepared by the application or adaptation of known methods as hereinbefore described for compounds of formula \( I' \).

Inorganic bases such as alkali metal or alkaline earth metal hydroxides or carbonates (e.g. sodium hydroxide, potassium hydroxide, sodium carbonate and potassium carbonate), ammonia or organic bases, in particular amines, especially secondary amines such as morpholine, or alkali metal alkoxides, such as e.g. sodium ethoxide or methoxide, may be used as acid acceptors.

Suitable solvents include water, lower alcohols (e.g. methanol, ethanol), ethers [e.g. dimethoxyethane (DME)], and aliphatic or aromatic hydrocarbons, which may be halogenated, and mixtures of such solvents.

The following Examples illustrate the compounds according to the invention, their preparation and their fungicidal properties. The chemical structure of the compounds is confirmed by NMR spectrographic analysis.
Example 1:

Preparation of 1,2,3-tris(propyn-2-yloxy)benzene

(Compound No. 22)

Potassium carbonate (364.3 g; 2.64 moles) and tris(3,6-dioxaheptyl)amine (5.2 g; 0.016 mole) are added to a solution of pyrogallol (i.e. 1,2,3-trihydroxybenzene) (100.8 g; 0.8 mole) in a mixture of acetonitrile (350 cc) and toluene (250 cc). Propargyl bromide (285.6 g; 2.4 moles) is added in the course of 10 min and the mixture is heated for 4 h at 75°C. The reaction mixture is filtered and the filtered materials are washed with acetonitrile. The filtrate is washed several times with dilute sodium hydroxide, and then with water and it is concentrated.

After filtering through silica, an oil (145 g) is obtained, which is crystallized in ether at -20°C.
A white solid, m.p. 54.5°C, is obtained.

The remaining di-(cf. compounds no. 1, 2, 3, 10, 11, 12 and 19) and tri-(cf. compound no. 23) propyn-2-yl-oxybenzene compounds are prepared following the same procedure; their formulae and their physicochemical properties are given in Table I below.

Example 2: Preparation of 1,2-bis(3-bromopropyn-2-yl-oxy)benzene (Compound No. 4)

Bromine (151 g) is added, in the course of approximately 5 min, to a mixture of aqueous 30% sodium hydroxide (288 g) and water (280 cc), at a temperature of between 5 and 15°C. A solution of ortho-di(propyn-2-yl-oxy)benzene (50 g) in dimethoxyethane (675 cc) is then added, at approximately 15°C, in the course of approximately 15 min. The mixture is then stirred for 2 hours at ambient temperature. The reaction mixture is poured into water. The precipitate obtained is filtered and washed thoroughly with water and dried under reduced pressure. After recrystallizing in a mixture of heptane (90 vol) and ethyl acetate (10 vol), a white solid (65 g; i.e. a yield of 70%), m.p. 93-93.5°C, is obtained (percentage composition:
Calculated % C : 41.90; H : 2.34; Br : 46.46
Found % C : 41.95; H : 2.45; Br : 46.30).

Example 3: Preparation of 1,2-bis(3-iodopropyn-2-yl-oxy)benzene (Compound No. 7)

A solution of sodium hydroxide (35.8 g) in a mixture of methanol (160 cc) and water (40 cc), and iodine
(106.7 g), are added simultaneously and in the course of approximately 15 min to a solution of ortho-di(propyn-2-yloxy)benzene (26 g) in methanol (240 cc), at ambient temperature in small fractions. After allowing the reaction to proceed for approximately 2 hours at ambient temperature, the reaction mixture is poured into 2% sodium thiosulphate solution. The precipitate obtained is filtered, washed thoroughly with water and dried under reduced pressure.

After recrystallizing in cyclohexane, a white solid (51.2 g; i.e. a yield of 83.5%), m.p. 116 - 116.5°C, is obtained (percentage composition:

Calculated % C : 32.91 ; H : 1.84 ; I : 57.94
Found % C : 32.81 ; H : 1.90 ; I : 57.80).

Example 4:
Operating according to the same procedure as in Example 2 (brominated derivatives) and Example 3 (iodinated derivatives), compounds 5 and 6, 13 to 15, 20 and 38 to 53 on the one hand, and 8 and 9, 16 to 18, 21 and 54 to 65 on the other hand respectively, the formulae and the physicochemical properties (melting point) of which are given in Table II below, are obtained. The remaining compounds are prepared as described in Example 1.
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** = C(CH₃)₃
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<td>H</td>
<td></td>
<td>oil</td>
</tr>
<tr>
<td>42</td>
<td>Br</td>
<td>O-CH₂-C≡C-Br</td>
<td>C₂H₅O</td>
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<td>H</td>
<td></td>
<td>105.5</td>
</tr>
<tr>
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<td>Br</td>
<td>O-CH₂-C≡C-Br</td>
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<td></td>
<td></td>
<td></td>
<td>64</td>
</tr>
<tr>
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<td>Br</td>
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<td>H</td>
<td>C(CH₃)₃</td>
<td>H</td>
<td>H</td>
<td>oil</td>
</tr>
<tr>
<td>45</td>
<td>Br</td>
<td>O-CH₂-C≡C-Br</td>
<td>H</td>
<td>NO₂</td>
<td>H</td>
<td>H</td>
<td>145.5</td>
</tr>
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Continuation of Table II

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<tbody>
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<td>H</td>
</tr>
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</tr>
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</tr>
<tr>
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<td>H</td>
</tr>
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</tr>
<tr>
<td>57</td>
<td>I  OCH₂-C≡C-I</td>
<td>H</td>
<td>Br</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>58</td>
<td>I  OCH₂-C≡C-I</td>
<td>H</td>
<td>CN</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>59</td>
<td>I  OCH₂-C≡C-I</td>
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<td>H</td>
</tr>
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<td>60</td>
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<td>H</td>
<td>OC₂H₅</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>61</td>
<td>I  OCH₂-C≡C-I</td>
<td>H</td>
<td>CH₂=CH-CH₂O</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>62</td>
<td>I  OCH₂-C≡C-I</td>
<td>H</td>
<td>C₆H₅-O</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>63</td>
<td>I  OCH₂-C≡C-I</td>
<td>H</td>
<td>CH₃</td>
<td>nC₅H₁₁₀</td>
<td>H</td>
</tr>
<tr>
<td>64</td>
<td>I  OCH₂-C≡C-I</td>
<td>CH₂=C-CH₂</td>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>65</td>
<td>I  OCH₂-C≡C-I</td>
<td>C₂H₅O</td>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
</tbody>
</table>

*** = HOCH₂
Example 5 : In vitro tests on seed fungi and soil fungi

The action of the compounds according to the invention on the following fungi are studied:

Botrytis cinerea: strain resistant to both carbendazim and iprodione

Pseudocercosporella herpotrichoides: strain resistant to carbendazim

Pythium aphanidermatum

Phytophthora cinnamomi

Rhizoctonia solani

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

A solution of the active substance in acetone, prepared so as to obtain the desired final concentration, is injected into the supercooled medium while filling the dishes.

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

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

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

Under these conditions, a good or total (i.e. at least equal to 80%) protection is observed:

- against *Botrytis cinerea*, at a dose of 0.03 g/l for compounds 2 to 9, 11 to 19, 21, 22, 24 to 35, 37, 38, 40, 42, 46, 47, 49 to 51, 57 to 60, 64 and 65,
- against *Pseudocercosporella herpotrichoides*, at a dose of 0.03 g/l for compounds 2, 7 to 11, 16, 17, 19, 21 and 22, 24 to 35, 37 to 40, 42, 46, 47, 49 to 51, 57 to 60 and 65,
- against *Pythium aphanidermatum* and *Phytophthora cinnamomi*, at a dose of 0.1 g/l for compounds 2, 3, 7, 8, 10, 11, 13, 16, 17, 19, 21 and 22, and
- against *Rhizoctonia solani*, at a dose of 0.1 g/l for compounds 2, 5, 7, 8, 10, 11, 16, 17, 19 and 21.

**Example 6: Test against Botrytis cinerea on tomato:**

30 to 40 day-old glasshouse-grown tomato plants (variety Marmande) are treated by spraying with aqueous suspensions (called mixtures) of the following composition:

- micronized active substance ................. x mg
- sorbitan monooleate/ethylene oxide (20 moles) condensate ................. x/2 mg
- water qs ........................................ 60 cc

at different concentrations of the compound to be
tested. The trial is repeated twice with each concentration.

After 24 hours, the leaves are cut and placed in 2 Petri dishes (14 cm diameter) whose bases were previously supplied with a moist filter paper disc (5 leaflets per dish).

The inoculum is then introduced with a syringe by depositing drops (3 drops per leaflet) of a spore suspension. This suspension of *Botrytis cinerea* (strain resistant to benzimidazoles) spores was obtained from a 15 day-old culture which was then suspended in a nutrient solution (100,000 spores/cc).

Observations are made 6 days after inoculation by comparing against an untreated control.

Under these conditions, at a dose of 0.1 g/l, a good or total (i.e. at least equal to 80%) protection is observed with compounds no. 4, 7, 13, 16 and 22.

**Example 7 : Glasshouse experiments on grape mildew (Plasmopara viticola)**

Cuttings of vine (*vitis vinifera*), variety Chardonnay, are grown in pots. When these plants are 2 months old (8 to 10 leaf stage, 20 to 30 cm in height), they are treated by spraying with an aqueous solution or suspension of the substance to be tested, as described in Example 6. Each vine plant receives approximately 5 ml of the solution or the dispersion. For each concentration of the active substance to be tested, the treatment is carried out on two plants.
Plants used as controls are treated with a solution which does not contain the active substance, but contains an identical concentration of the same condensate of sorbitan monooleate and ethylene oxide.

After drying for 24 hours, each plant is inoculated by spraying with an aqueous spore suspension of *Plasmopara viticola*, which is responsible for vine mildew, at a rate of approximately 1 cc/plant (i.e. approximately $10^5$ spores per plant).

After this inoculation, the vine plants are incubated for two days at approximately 18°C in a moisture-saturated atmosphere and then for five days at approximately 20-22°C at 90-100% relative humidity.

Seven days after the inoculation, the results obtained in the case of the plants treated with the active substance to be tested are compared with those obtained in the case of the plants used as control.

Under these conditions, it was observed that, at a dose of 1 g/l, compounds no. 7 and 16 bring about 100% inhibition of the development of the fungus.

The doses for use of the compounds according to the invention, when they are used as fungicides, may vary within wide limits, especially according to the virulence of the fungi and the climatic conditions.

The invention provides a fungicidal composition which comprises as active ingredient a compound of general formula I wherein the various symbols are as hereinbefore
defined except that, when $R_1$, $R_2$, $R_3$, $R_4$ each represent hydrogen, $m$ is zero and $n$ is equal to 1, $Y$ and $Z$ may both represent hydrogen, in association with an agriculturally acceptable diluent or carrier and/or an agriculturally acceptable surfactant.

The compositions preferably comprise a compound of formula I wherein, when $R_1$, $R_2$, $R_3$, $R_4$ each represent hydrogen, $m$ is zero and $n$ is equal to 1, $Y$ and $Z$ do not both represent hydrogen.

When the compositions comprise a compound of formula I wherein, when $R_1$, $R_2$, $R_3$, $R_4$ each represent a hydrogen atom, $m$ is zero and $n$ is equal to 1, $Y$ and $Z$ both represent hydrogen, either (a) the carrier or diluent is preferably not water or a common organic solvent or (b) the composition preferably comprises a surfactant.

In general, compositions containing 0.5 to 5,000 ppm of active substance are well suited; these values are given for compositions which are ready for application. Ppm means "parts per million''. The range from 0.5 to 5,000 ppm corresponds to a range from $5 \times 10^{-5}$ to 0.5% (percentages by weight).

As regards compositions suitable for storage and for transport, they more advantageously contain from 0.5 to 95% (by weight) of active substance. Unless otherwise specified percentages referred to hereinafter are by weight.

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

As already stated, the compounds according to the invention are generally combined with carriers and optionally with surfactants.

In the present account, the term "carrier" denotes an organic or inorganic, natural or synthetic material which is in combination with the active substance to facilitate its application to the plant, seeds or soil. This carrier is therefore generally inert, and it must be acceptable in agriculture, especially on the plant treated. The carrier may be solid (e.g. clays, natural or synthetic silicates, silica, resins, waxes and solid fertilizers) or liquid (e.g. water, alcohols, ketones, petroleum fractions, aromatic or paraffinic hydrocarbons, chlorinated hydrocarbons or liquified gases).

The surfactant may be an emulsifier, dispersant or wetting agent of ionic or nonionic type. There may be mentioned e.g. salts of polyacrylic acids, salts of
lignosulphonic acids, salts of phenolsulphonic or naphthalenesulphonic acids, polycondensates of ethylene oxide with fatty alcohols or fatty acids or fatty amines, substituted phenols (especially alkylphenols or arylphenols), salts of sulphisuccinic acid esters, taurine derivatives (especially alkyltaurates), and phosphoric acid esters of polycondensates of ethylene oxide with alcohols or phenols. The presence of at least one surfactant is generally essential when the active substance and/or the inert carrier are not water-soluble and the vector agent for application is water.

These compositions may also contain other types of ingredient, e.g. protective colloids, adhesives, thickeners, thixotropic agents, penetrants, stabilizers and sequestering agents, as well as other known active substances having pesticidal properties (especially insecticidal or fungicidal properties) or plant growth promoting properties (especially fertilizers) or plant growth regulating properties. More generally, the compounds according to the invention may be combined with all the solid or liquid additives which correspond to the customary techniques of formulation.

The compositions used in the invention may be in fairly diverse, solid or liquid forms.

As solid forms of compositions, there may be mentioned powders for dusting (with a content of active substances which may range up to 100%).
As liquid forms of compositions or forms designed 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), granules and pastes.

The emulsifiable or soluble concentrates most frequently contain 10 to 80% of active substance, whereas the emulsions or solutions ready for application generally contain 0.001 to 20% of active substance. In addition to the active substance and the solvent, the emulsifiable concentrates may contain, when required, a suitable co-solvent and from 2 to 20% of suitable additives such as stabilizers, surfactants, especially emulsifiers, penetrants, corrosion inhibitors, colourants and adhesives.

From these concentrates, by dilution with water, it is possible to obtain emulsions of any desired concentration which are particularly suitable for application to crops.

Flowables, which may also be applied by spraying, are prepared so as to obtain a stable fluid product which does not settle, and they usually contain from 10 to 75% of active substance, from 0.5 to 15% of surfactants, from 0.1 to 10% of thixotropic agents, from 0 to 10% of suitable additives such as antifoams, corrosion inhibitors, stabilizers, penetrants and adhesives and, as a carrier, water or an organic liquid in which the active 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 antifreezes for the water.

By way of example, the composition of several aqueous suspensions according to the invention is as follows:

**Example A:**

An aqueous suspension containing the following is prepared:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active substance (compound no. 4)</td>
<td>500</td>
</tr>
<tr>
<td>Wetting agent (C₁₃ synthetic alcohol/ethylene oxide polycondensate)</td>
<td>10</td>
</tr>
<tr>
<td>Dispersant (salified phosphate of polyaryl-phenol/ethylene oxide condensate)</td>
<td>50</td>
</tr>
<tr>
<td>Antifreeze (propylene glycol)</td>
<td>100</td>
</tr>
<tr>
<td>Thickener (polysaccharide)</td>
<td>1.6</td>
</tr>
<tr>
<td>Biocide (sodium 4-hydroxymethylbenzoate)</td>
<td>3.3</td>
</tr>
<tr>
<td>Water</td>
<td>qs 1 litre</td>
</tr>
</tbody>
</table>

A fluid flowable is thereby obtained.

**Example B - Aqueous suspension:**

An aqueous suspension containing the following is prepared:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active substance (compound no. 7)</td>
<td>100</td>
</tr>
<tr>
<td>Wetting agent (alkylphenol/ethylene oxide polycondensate)</td>
<td>5</td>
</tr>
<tr>
<td>Dispersant (Na naphthalenesulphonate)</td>
<td>10</td>
</tr>
</tbody>
</table>
antifreeze (propylene glycol) ............... 100 g/l
thickener (polysaccharide) .................. 3 g/l
biocide (formaldehyde) ....................... 1 g/l
water ........................................... qs 1 litre

5 Example C - Aqueous suspension:

An aqueous suspension containing the following is prepared:

active substance (compound no. 22) ........ 250 g/l
wetting agent (C_{13} synthetic alcohol/ethylene oxide polycondensate) .............. 10 g/l
dispersant (sodium lignosulphonate) ...... 15 g/l
antifreeze (urea) .............................. 50 g/l
thickener (polysaccharide) ................. 2.5 g/l
biocide (formaldehyde) ...................... 1 g/l
water ........................................... qs 1 litre.

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 20% of a dispersant and, when required, from 0 to 10% of one or more stabilizers and/or other additives such as penetrants, adhesives, or anticaking agents and colourants.

By way of example, the composition of several wettable powders is as follows:

active substance (compound no. 1 according to the invention) ....................... 50 %
fatty alcohol/ethylene oxide condensate
(wetting agent) .......................... 2.5 %

styrylphenol/ethylene oxide condensate
(dispersant) .............................. 5 %

chalk (inert carrier) ...................... 42.5 %

Example E: 10% wettable powder

active substance (compound no. 4) ............. 10 %

condensate of branched type C_{13} oxo

synthetic alcohol and ethylene oxide,
containing 8 to 10 units of ethylene oxide
(wetting agent) ............................. 0.75 %

neutral calcium lignosulphonate
(dispersant) .................................. 12 %

calcium carbonate (inert filler) .............. qs 100 %

Example F: 75% wettable powder containing the same ingredients as in the previous example, in the following proportions:

active substance (compound no. 7) ........... 75 %

wetting agent ................................ 1.50 %

dispersant .................................. 8 %

calcium carbonate (inert filler) ............... qs 100 %

Example G: 90% wettable powder

active substance (compound no. 22) ........... 90 %

fatty alcohol/ethylene oxide condensate ...
(wetting agent) ............................. 4 %

styrylphenol/ethylene oxide condensate
(dispersant) ................................. 6 %
Example H: 50% wettable powder

active substance (compound no. 4 according to the invention) .................. 50 %

mixture of anionic and nonionic surfactants (wetting agent) ............... 2.5 %
neutral sodium lignosulphonate (dispersant) ................................. 5 %
kaolin clay (inert carrier) ........................................... 42.5 %

In order to obtain these powders for spraying or wettable powders, the active substance is intimately mixed in suitable mixers with the additional substances, and the mixtures are ground in mills or other suitable grinders. 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 this suspension may be very advantageously used, especially for application on plant leaves.

The compounds according to the invention may advantageously be formulated in the form of water dispersible granules which are also included within the scope of the invention.

These dispersible granules, of apparent specific gravity generally between approximately 0.3 and 0.6, have a particle size generally between approximately 150 and 2000 and preferably between 300 and 1500 microns.

The active substance (compound no. 4) content of these granules is generally between approximately 1% and
90% and preferably between 25% and 90%.

The rest of the granule generally comprises a solid filler and, where appropriate, of surfactant adjuvants which give water dispersibility properties to the granule. These granules may be essentially of two distinct types depending on whether the filler used is soluble or insoluble in water. When the filler is water-soluble, it may be inorganic but is preferably organic.

Excellent results were obtained with urea. In the case of an insoluble filler, the latter is preferably inorganic, such as e.g. kaolin or bentonite. It is then accompanied by surfactants (at a rate of 2 to 20% by weight of the granule), surfactant adjuvants, more than half of which consist of at least one essentially anionic dispersant, such as poly(alkali metal or alkaline earth metal naphthalenesulphonate) or an alkali metal or alkaline earth metal lignosulphonate, the remaining part consisting of nonionic or anionic wetting agents such as an alkali metal or alkaline earth metal alkyl naphthalenesulphonate.

Furthermore, other adjuvants such as antifoams may be added, although they are not indispensable.

The granule according to the invention may be prepared by mixing the necessary ingredients and then granulating according to several techniques known per se (using, for example a pelletizer, fluidized bed, atomizer or extrusion). This is generally completed by a crushing followed by a sieving to the chosen particle size within the limits.
mentioned above.

It is preferably obtained by extrusion, operating as mentioned in the examples below.

Example I: Dispersible granules containing 90% of active substance

90% by weight of active substance (compound no. 7) and 10% of urea pellets are mixed in a mixer. The mixture is then ground in a toothed roll crushe. A powder is obtained, which is moistened with approximately 8% by weight of water. The moist powder is extruded in a perforated roller extruder. Granules are obtained, which are dried and then crushed and sieved, so as to retain only the granules with a size between 150 and 2000 microns respectively.

Example J: Dispersible granules containing 75% of active substance

The following constituents are mixed in a mixer:

active substance (compound no. 22) .......... 75 %

wetting agent (sodium alkyl naphthalene-sulphonate) ........................................ 2 %

dispersant (sodium naphthalenepoly-sulphonate) ............................................. 8 %

water-insoluble inert filler (kaolin) ....... 15 %

This mixture is granulated in a fluidized bed, in the presence of water, and then dried, crushed and sieved so as to obtain granules of size between 0.16 and 0.40 mm.

These granules may be used alone, in solution or
dispersion in water so as to obtain the dose sought. They may also be used to prepare combinations with other active substances, especially fungicides, the latter being in the form of wettable powders, or granules or aqueous suspensions.

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

The invention further relates to a method for the treatment of crops against diseases caused by phytopathogenic fungi belonging to very different families and especially against Botrytis sp strains which are sensitive or resistant to benzimidazoles, eyespot (strains sensitive or resistant to benzimidazoles), seed-borne fungi such as Pythium sp, Fusarium sp, Septoria sp, Rhizoctonia sp, and also against fungi responsible for rots such as Monilia sp, Penicillium sp, Rhizopus sp, or Venturia sp and Phytophthora sp.

The invention provides a method for the control of fungal disease of plants at a locus which comprises applying thereto an effective amount of a compound of formula (I) wherein the various symbols are as hereinbefore defined except that when R1, R2, R3, R4 each represent hydrogen, m is zero and n is equal to 1, Y and Z may both represent hydrogen. The term "effective amount" refers to an amount which is sufficient to achieve the control or destruction of fungi.
present on these crops. However, the doses for use may vary within wide limits according to the fungus to be controlled, the type of crop, the climatic conditions and the compound used.

In practice, doses ranging from 1 g/hl to 500 g/hl, which correspond substantially to active substance doses per hectare of approximately 10 g/ha to 5000 g/ha, generally give good results.
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A propargyloxybenzene derivative of the formula:

\[
\begin{align*}
R_3 & \\
| & \\
(\text{O-C-C} \equiv \text{C-Z})_n & \\
| & \\
R_4 & \\
| & \\
\text{X}_m & \\
| & \\
\text{O-C-C} \equiv \text{C-Y} & \\
| & \\
R_1 & \\
| & \\
R_2 & 
\end{align*}
\]

in which

m is zero or an integer from 1 to 5-n;

X, which may be the same or different when m is greater than 1, represents a halogen atom, a cyano or nitro group or an amino group, which may be mono- or dialkylated,

an alkyl, alkoxy or alkylthio radical, the alkyl moiety of which contains 1 to 12 carbon atoms and may be mono- or polyhalogenated, the alkyl moiety, when it contains from 1 to 4 carbon atoms, being optionally substituted with a hydroxy, lower alkoxy or benzyloxy radical or an amino radical, which may be mono- or dialkylated,

an alkenyl or alkenyloxy radical containing 2 to 5 carbon atoms, or
a phenyl, phenoxy, or phenylthio radical, which may be substituted;

Y and Z, which may be identical or different, represent a hydrogen or halogen atom;

n is an integer equal to 1 or 2; and

R₁, R₂, R₃ and R₄, which may be identical or different, each represent a hydrogen atom or a lower alkyl radical, provided that when R₁, R₂, R₃, R₄ each represent hydrogen, m is zero and n is equal to 1, Y and Z do not both represent hydrogen atoms.

2. A compound according to claim 1, wherein n equals 1 and the group \(-O-C(R₃R₄)-C=O\) is in the ortho-position of the phenyl ring relative to the group \(-O-C(R₁R₂)-C=O\).

3. A compound according to claim 1, wherein Y and Z, which may be identical or different, each represent a bromine or iodine atom.

4. A compound according to claim 1, hereinbefore identified as any one of compounds 1 to 65.

5. A process for the preparation of a compound according to claim 1, in the formula of which Y and Z both represent hydrogen atoms, which comprises the reaction of a di- or tri-phenol of the formula:
wherein X, m and n are as defined in claim 1, with a propargyl halide of the formula:

\[
\begin{align*}
X_m & - (\text{OH})_{n+1} \\
\end{align*}
\]

wherein \( R_1 \) and \( R_2 \) are as defined in claim 1, in the presence of an acid acceptor.

6. A process for the preparation of a compound according to claim 1, in the formula of which at least one of \( Y \) or \( Z \) represents a halogen atom which comprises the reaction of a compound of the formula:
wherein the various symbols are as defined in claim 1, with a halogen in the presence of an acid acceptor.

7. A process according to claim 6, wherein the halogen is iodine or bromine.

8. A process according to claim 6 or 7 substantially as hereinbefore described in any one of Examples 1 to 4.

9. A compound according to claim 1 when prepared by a process according to claim 6, 7 or 8.

10. A fungicidal composition which comprises, as active ingredient, a compound of the formula:
in which

m is zero or an integer from 1 to 5-n;

X, which may be the same or different when m is greater than 1, represents a halogen atom, a cyano or nitro group or an amino group, which may be mono- or dialkylated, an alkyl, alkoxy or alkylthio radical, the alkyl moiety of which contains 1 to 12 carbon atoms and may be mono- or polyhalogenated, the alkyl moiety, when it contains from 1 to 4 carbon atoms, being optionally substituted with a hydroxy, lower alkoxy or benzyloxy radical or an amino radical, which may be mono- or dialkylated, an alkenyl or alkenyloxy radical containing 2 to 5 carbon atoms, or a phenyl, phenoxy, or phenylthio radical, which may be substituted;

Y and Z, which may be identical or different, represent a
hydrogen or halogen atom;
n is an integer equal to 1 or 2; and
R₁, R₂, R₃ and R₄, which may be identical or different,
each represent a hydrogen atom or a lower alkyl radical.

11. A composition according to claim 10 wherein when
R₁, R₂, R₃, R₄ each represent hydrogen, m is zero and n is equal
to 1, Y and Z do not both represent hydrogen.

12. A composition according to claim 10 substantially
as hereinbefore described in any one of Examples A to J.

13. A method for the control of fungal diseases of
plants at a locus which comprises applying thereto an
effective amount of a compound of formula I as defined in
claim 10 or 11.

14. A method according to claim 13 substantially as
hereinbefore described.

15. The steps, features, compositions and compounds
referred to or indicated in the specification and/or
claims of this application, individually or collectively
and any and all combinations of any two or more of said
steps or features.

Dated this 11th day of May 1987
RHONE-POULENC AGROCHIMIE
By its Patent Attorneys
DAVIES & COLLISON