

(CONVENTION. By one or more persons and/or a Company.)

Form 4

609579
COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1969

CONVENTION APPLICATION FOR A PATENT

(1) Here
insert (in
full) Name
or Names of
Applicant or
Applicants,
followed by
Address (es).

xx (1) BASF AKTIENGESELLSCHAFT
We
of D-6700 Ludwigshafen, Federal Republic of Germany

(2) Here
insert Title
of Invention.

hereby apply for the grant of a Patent for an invention entitled: (2)
AZOLYLMETHYLCYCLOALKYLOXIRANES, THEIR PREPARATION AND THEIR
USE AS CROP PROTECTION AGENTS

(3) Here insert
number(s)
of basic
application(s)

which is described in the accompanying complete specification. This application is a
Convention application and is based on the application numbered (3)
P38 05 684.4

(4) Here insert
Name of basic
Country or
Countries, and
basic date or
dates

for a patent or similar protection made in (4) Federal Republic of Germany
on 24th February 1988

APPLICATION ACCEPTED AND AMENDMENTS

ALLOWED 29 - 1 - 91

My
xxx address for service is Messrs. Edwd. Waters & Sons, Patent Attorneys,
Our
50 Queen Street, Melbourne, Victoria, Australia.

DATED this 22nd day of February 1989

(5) Signa-
ture (s) of
Applicant (s)
or
Seal of
Company and
Signatures of
its Officers as
per Statute of
Association.

(5)

BASF AKTIENGESELLSCHAFT

by

Louis C. Gebhardt

Registered Patent Attorney

To:

MOOGES

23/02/89

COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1962

DECLARATION IN SUPPORT OF A CONVENTION
APPLICATION FOR A PATENT OR PATENT OF ADDITION(1) Here
insert (in
full) Name of
Company.

In support of the Convention Application made by⁽¹⁾ _____
BASF Aktiengesellschaft, a German Joint Stock Company of
D-6700 Ludwigshafen, Federal Republic of Germany;

(hereinafter referred to as the applicant) for a Patent

(2) Here
insert title
of invention.

for an invention entitled:⁽²⁾ _____
Azolylmethylcycloalkyloxiranes, their preparation and
their use as crop protection agents

(3) Here
insert full Name
and Address
of Company
official
authorized
to make
declaration.

(3) We, Dr. PETER RICHTERS and PETER BARZ, citizens of the
Federal Republic of Germany, residing, respectively, at
40 Kerschensteinerstrasse, D-6700 Ludwigshafen; and
20 Hochfeldstrasse, D-6700 Ludwigshafen; Federal Republic of
Germany;

do solemnly and sincerely declare as follows:

1. We are
~~xxx~~ authorised by the applicant for the patent
 to make this declaration on its behalf.

(4) Here
insert basic
Country or
Countries
followed by
date or dates
and basic
Applicant or
Applicants.

2. The basic application as defined by Section 141 of the Act was
made in⁽⁴⁾ the Federal Republic of Germany under No.
on the 24th day of February 1988, by P 38 05 684.4
BASF Aktiengesellschaft

~~xxx~~ on the ~~xxx~~ day of ~~xxx~~ 19~~xxxxxx~~

RAINER SEELE, STEFAN KARBACH, THOMAS KUEKENHOEHNER,
HUBERT SAUTER, GISELA LORENZ, EBERHARD AMMERMAN,

(5) Here
insert (in
full) Name
and Address
of Actual
Inventor or
Inventors.

3. (5) citizens of the Federal Republic of Germany, residing,
respectively, at 3 Leiblstrasse, 6701 Fussgoenheim; 44 Grund-
wiesenweg, 6730 Neustadt; 2 Seidelstrasse, 6710 Frankenthal;
20 Neckarpromenade, 6800 Mannheim 1; 13 Erlenweg, 6730 Neustadt;
3 Sachsenstrasse, 6700 Ludwigshafen; Federal Republic of Germany;

~~xxx~~/are the actual inventors of the invention and the facts upon which the applicant
 is entitled to make the application are as follow:

The applicant is the assignee of _____
RAINER SEELE, STEFAN KARBACH, THOMAS KUEKENHOEHNER,
HUBERT SAUTER, GISELA LORENZ, EBERHARD AMMERMAN.

4. The basic application referred to in paragraph 2 of this Declaration
 was _____ the first application made in a Convention country in
 respect of the invention the subject of the application.

DECLARED at D-6700 Ludwigshafen, Federal Republic of Germany
 this 2nd day of February 1989

(6) Signature.

(6) BASF Aktiengesellschaft

To: THE COMMISSIONER OF PATENTS

(12) PATENT ABRIDGMENT (11) Document No. AU-B-30245/89
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 609579

(54) Title
AZOLYLMETHYLCYCLOALKYLOXIRANES, THEIR PREPARATION AND THEIR USE AS
CROP PROTECTION AGENTS

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A01N 043/653

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GISELA LORENZ; EBERHARD AMMERMAN

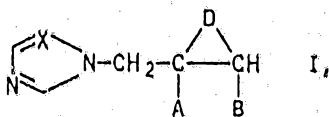
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3122

(56) Prior Art Documents
AU 62275/90 C07D 405/06 405/14
AU 51178/90 C07D 405/06
AU 31133/89 C07D 405/06 405/14

(57) The present invention relates to novel azole com-
pounds, processes for their preparation, fungicides con-
taining these compounds and methods for controlling
fungi.

CLAIM

1. Azolylmethyloxiranes of the general formula I



where A and B are identical or different and each denotes
C₃-C₁₂-cycloalkyl, dioxanyl, tetrahydropyranyl, tetrahydrofuranyl,
norbornyl, C₅-C₈-cycloalkenyl or phenyl, each of these radicals being
unsubstituted or substituted by halogen, nitro, phenoxy, amino, alkyl,
alkoxy or haloalkyl, each of 1 to 4 carbon atoms, with the proviso
that A and B are not simultaneously phenyl, D is O, X is CH or N, and
their pharm-tolerated acid addition salts or metal complexes.

609579

Form 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952-69

COMPLETE SPECIFICATION

(ORIGINAL)

Class

Int. Class

Application Number:
Lodged:

Complete Specification Lodged:
Accepted:
Published:

Priority:

Related Art:

Name of Applicant: BASF AKTIENGESELLSCHAFT

Address of Applicant: D-6700 Ludwigshafen, Federal Republic of Germany

Actual Inventor: RAINER SEELE, STEFAN KARBACH, THOMAS KUEKENHOEHNER, HUBERT SAUTER, GISELA LORENZ and EBERHARD AMMERMAN

Address for Service: EDWD. WATERS & SONS,
50 QUEEN STREET, MELBOURNE, AUSTRALIA, 3000.

Complete Specification for the invention entitled:

AZOLYLMETHYLCYCLOALKYLOXIRANES, THEIR PREPARATION AND THEIR
USE AS CROP PROTECTION AGENTS

The following statement is a full description of this invention, including the best method of performing it known to the inventor

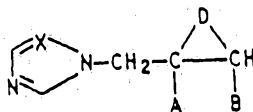
O.Z. 0050/39759

Azolylmethylcycloalkyloxiranes, their preparation and
their use as crop protection agents

5 The present invention relates to novel azole compounds, processes for their preparation, fungicides containing these compounds and methods for controlling fungi.

10 It is known that cis-2-(1,2,4-triazol-1-ylmethyl)-2-(tert-butyl)-3-(4-chlorophenyl)-oxirane can be used as a fungicide (DE-32 18 130.2). However, its action is unsatisfactory.

We have found that azolylmethyloxiranes of the formula I



15 where A and B are identical or different and are each C₃-C₁₂-cycloalkyl, dioxanyl, tetrahydropyranyl, tetrahydrofuranyl, norbornyl, C₅-C₈-cycloalkenyl or phenyl, and these radicals may be monosubstituted to trisubstituted by halogen, nitro, phenoxy, amino, alkyl, alkoxy or haloalkyl, each of 1 to 4 carbon atoms, with the proviso that
20 A and B are not simultaneously phenyl, D is O and X is CH or N, and their plant-tolerated addition salts with acids or metal complexes have a better fungicidal action than the known azole compound.

25 The compounds of the formula I contain chiral centers and are generally obtained in the form of racemates or as diastereomer mixtures of erythro or threo forms. The erythro or threo diastereomers can be separated in a conventional manner, for example on the basis of their different solubilities or by column chromatography, and can be isolated in pure form. Pure enantiomers can be obtained from such an isolated diastereomer by a conventional method. The present invention embraces both the pure diastereomers or enantiomers
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and their mixtures obtained in the synthesis.

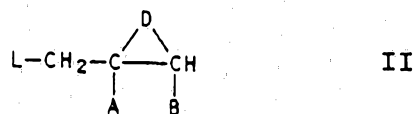
A and B are each, for example, phenyl, halo-phenyl, such as 2-chlorophenyl, 2-fluorophenyl, 2-bromophenyl, 3-chlorophenyl, 3-bromophenyl, 3-fluorophenyl, 4-fluorophenyl, 4-chlorophenyl, 4-bromophenyl, 2,4-dichlorophenyl, 2,3-dichlorophenyl, 2,5-dichlorophenyl, 2,6-dichlorophenyl or 2-chloro-6-fluorophenyl, alkoxyphenyl, such as 2-methoxyphenyl, 3-methoxyphenyl, 4-methoxyphenyl or 2,4-dimethoxyphenyl, alkylphenyl, such as 4-ethylphenyl, 4-isopropylphenyl or 4-tert-butylphenyl, 4-tert-butoxyphenyl, 2-chloro-4-fluorophenyl, 2-chloro-6-methylphenyl, 3,4-dimethoxyphenyl, 3-phenoxyphenyl, 4-phenoxyphenyl, 3-nitrophenyl, 4-nitrophenyl, 3-aminophenyl, 4-aminophenyl, 2-trifluoromethylphenyl, 3-trifluoromethylphenyl, 4-trifluoromethylphenyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclooctyl, cyclododecyl, tetrahydropyranyl, tetrahydrofuranyl, 2-cyclohexenyl, 3-cyclohexenyl, norbornyl, 1,3-dioxan-2-yl or 1,4-dioxan-2-yl.

Addition salts with acids are, for example, the hydrochlorides, bromides, sulfates, nitrates, phosphates, oxalates or dodecylbenzenesulfonates. The activity of the salts is due to the cation, so that in general any anion may be used. The novel active ingredient salts are prepared by reacting the azolymethyloxiranes with the acids.

The metal complexes of the active ingredients or their salts can be formed, for example, with copper, zinc, tin, manganese, iron, cobalt or nickel, by reacting the azolymethyloxiranes with corresponding metal salts, for example with copper sulfate, zinc chloride, tin chloride, manganese sulfate, iron chloride, cobalt sulfate or nickel sulfate.

The compounds of the formula I can be prepared, for example, by

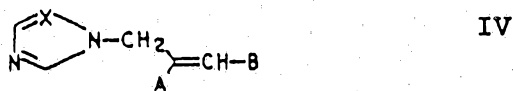
a) reacting a compound of the formula II



where A, B and D have the abovementioned meanings and L is a leaving group which can be nucleophilically substituted (eg. halogen or OH), with a compound of the formula III



where Me is hydrogen or a metal atom (eg. Na or K) and X has the abovementioned meanings, or
b) converting a compound of the formula IV



where A, B and X have the abovementioned meanings, into the epoxide.

If Me is hydrogen, reaction a) is carried out in the presence or absence of a solvent or diluent and with or without the addition of an inorganic or organic base and of a reaction accelerator, at from 10 to 120°C. The preferred solvents and diluents include ketones, such as acetone, methyl ethyl ketone or cyclohexanone, nitriles, such as acetonitrile or propionitrile, alcohols, such as methanol, ethanol, isopropanol, n-butanol or glycol, esters, such as ethyl acetate, methyl acetate or butyl acetate, ethers, such as tetrahydrofuran, diethyl ether, dimethoxyethane, dioxane or diisopropyl ether, amides, such as dimethylformamide, dimethylacetamide or N-methylpyrrolidone, and dimethyl sulfoxide, sulfolane or mixtures of these.

Examples of suitable bases, which may also be used as acid acceptors in the reaction, are alkali metal

hydroxides, such as lithium hydroxide, sodium hydroxide or potassium hydroxide, alkali metal carbonates, such as sodium carbonate, potassium carbonate or cesium carbonate, or sodium bicarbonate, potassium bicarbonate or cesium bicarbonate, pyridine or 4-dimethylaminopyridine. However, it is also possible to use other conventional bases.

Preferred reaction accelerators are metal halides, such as sodium iodide or potassium iodide, quaternary ammonium salts, such as tetrabutylammonium chloride, bromide, iodide or bisulfate or benzyltriethylammonium chloride or bromide, and crown ethers, such as 12-crown-4, 15-crown-6, dibenzo-18-crown-6 or dicyclohexano-18-crown-6.

The reaction is generally carried out at from 20 to 150°C, under atmospheric or superatmospheric pressure, continuously or batchwise.

If Me is a metal atom, reaction a) is carried out in the presence or absence of a solvent or diluent and with or without the addition of a strong inorganic or organic base, at from -10 to 120°C. The preferred solvents and diluents include amides, such as dimethylformamide, diethylformamide, dimethylacetamide, diethylacetamide, N-methylpyrrolidone or hexamethylphosphorotriamide, sulfoxides, such as dimethyl sulfoxide and finally sulfolane.

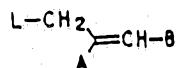
Examples of suitable bases, which may also be used as acid acceptors in the reaction, are alkali metal hydrides, such as lithium hydride, sodium hydride and potassium hydride, alkali metal amides, such as sodium amide and potassium amide, and sodium tert-butoxide, potassium tert-butoxide, triphenylmethyllithium, triphenylmethylsodium, triphenylmethylpotassium, naphthalenelithium, naphthalenesodium and naphthalenepotassium.

Suitable diluents for reaction b) are polar organic solvents, such as nitriles, eg. acetonitrile, sulfoxides, eg. dimethyl sulfoxide, formamides,

eg. dimethylformamide, ketones, eg. acetone, ethers, eg. diethyl ether or tetrahydrofuran, and in particular chlorohydrocarbons, eg. methylene chloride or chloroform.

5 The reaction is carried out in general at from 0 to 100°C, preferably from 20 to 80°C. If a solvent is present, the reaction is advantageously carried out at the boiling point of the particular solvent.

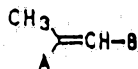
The novel starting compounds II are obtained by epoxidation of the corresponding olefins V



V

(cf. G. Dittus in Houben-Weyl-Müller, Methoden der Organischen Chemie, Georg Thieme Verlag, Stuttgart, 1965, Vol. VI, 3, page 385 et seq.).

15 The compound V is prepared by halogenating or oxidizing an olefin of the formula VI



VI

by a known method in the allyl position.

20 Suitable halogenation reagents are N-chloro- and N-bromosuccinimide in halohydrocarbons, such as carbon tetrachloride, trichloroethane or methylene chloride, at from 20 to 100°C. Allyl oxidation is carried out using peresters, such as tert-butyl perbenzoate or tert-butyl peracetate, in the presence of a heavy metal salt, eg. copper(I) chloride, or copper(I) bromide. The reaction is carried out in an inert solvent at from 10 to 100°C.

25 The allyl halides or alcohols V thus obtained are then converted into the corresponding epoxides II (L = halogen or OH). For this purpose, the olefins V are oxidized with peroxy-carboxylic acids, such as perbenzoic acid, 3-chloroperbenzoic acid, 4-nitroperbenzoic acid, monoperphthalic acid, peracetic acid, perpropionic acid,

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monoperphthalic acid, peracetic acid, perpropionic acid, permaleic acid, monopersuccinic acid, perpelargonic acid or trifluoroperacetic acid, in an inert solvent, preferably a chlorohydrocarbon, eg. methylene chloride, chloroform, carbon tetrachloride or dichloroethane, or, if required, in acetic acid, ethyl acetate, acetone or dimethylformamide, in the presence or absence of a buffer, such as sodium acetate, sodium carbonate or disodium hydrogen phosphate. The reaction is carried out at from 10 to 100°C and may be catalyzed, for example, with iodine, sodium tungstate or light. Alkaline solutions of hydrogen peroxide (about 30% strength) in methanol, ethanol, acetone or acetonitrile at from 25 to 30°C and alkyl hydroperoxides, eg. tert-butyl hydroperoxide, with the addition of a catalyst, eg. sodium tungstate, per-tungstic acid, molybdenum hexacarbonyl or vanadyl acetylacetonate are also suitable for the oxidation. Some of the stated oxidizing agents can be prepared in situ.

While the resulting epoxyhalides II (L = halogen) can be reacted directly in process a), the corresponding epoxyalcohols II (L = OH) are converted into reactive esters, which are then reacted with the compounds III in process a).

The reactive esters which are reacted with III are prepared by generally known methods (Houben-Weyl-Müller, Methoden der organischen Chemie, Georg Thieme Verlag, Stuttgart, 1955, Volume 9, pages 388, 663 and 671). Examples of esters of this type are methanesulfonates, trifluoromethanesulfonates, 2,2,2-trifluoroethanesulfonates, nonafluorobutanesulfonates, 4-methylbenzenesulfonates, 4-bromobenzenesulfonates, 4-nitrobenzenesulfonates and benzenesulfonates.

The compounds V can be prepared by generally known processes for olefin synthesis (Houben-Weyl-Müller, Methoden der organischen Chemie, Georg Thieme Verlag, Stuttgart, 1972, Vol. V, 1b).

The compounds of the formula IV are obtained, for

example, by reacting a compound of the formula V with a compound of the formula III, for example in a solvent.

The Examples which follow illustrate the preparation of the active ingredients.

5 I. Preparation of the starting materials

Method A

3.9 g of sodium hydroxide in 30 ml of water are added to a solution of 42 g of 2,4-dichlorobenzaldehyde in 200 ml of methanol. The reaction mixture is cooled to 10°C and 30.7 g of tetrahydropyranylacetaldehyde are rapidly added dropwise, the temperature of the solution increasing to 30°C. Stirring is carried out for 2 hours at room temperature, after which 200 ml of water are added to the colorless reaction solution, and the resulting emulsion is extracted by shaking with methyl tert-butyl ether. The organic phase is separated off, dried over sodium sulfate and evaporated down under reduced pressure. 43 g (63%) of E/Z-2-(tetrahydropyran-4-yl)-3-(2,4-dichlorophenyl)-propenal of melting point 82-85°C are obtained from methyl tert-butyl ether/n-hexane.

Method B

21.3 g of E/Z-2-(tetrahydropyran-4-yl)-3-(2,4-dichlorophenyl)-propenal are dissolved in 200 ml of methanol, and 0.85 ml of concentrated sodium hydroxide solution is added. The reaction solution is stirred at 0°C while 5.5 g of hydrogen peroxide (about 50% strength by weight) are slowly added dropwise, the internal temperature not exceeding 30°C. After the addition has ended, stirring is continued for 6 hours at room temperature, after which 0.91 g of sodium borohydride, dissolved in a little 10% strength sodium hydroxide solution, is added. After the reaction mixture has been stirred for 18 hours at room temperature, 100 ml of water are added to the solution and the resulting emulsion is extracted by shaking with methylene chloride. The organic phase is dried over sodium sulfate and evaporated down, and the residue is recrystallized from isopropanol. 19.5 g (86%)

of cis-2-hydroxymethyl-2-(tetrahydropyran-4-yl)-3-(2,4-dichloro-phenyl)-oxirane of melting point 89°C are obtained.

Method C

5 14.1 g of 4-methylbenzenesulfonyl chloride are added, at room temperature, to a solution of 19.5 g of cis-2-hydroxymethyl-2-(tetrahydropyran-4-yl)-3-(2,4-dichlorophenyl)-oxirane in 100 ml of methylene chloride and 20 g of triethylamine. After 24 hours, the reaction mixture is washed with aqueous sodium bicarbonate solution and water, dried over sodium sulfate and evaporated down under reduced pressure. Crystallization of the remaining residue from methyl tert-butyl ether/n-hexane gives 26 g (89%) of cis-2-(4-methylphenylsulfonyloxymethyl)-2-(tetrahydropyran-4-yl)-3-(2,4-dichlorophenyl)-oxirane of melting point 102-104°C.

Method D

20 5.5 g of sodium hydroxide in 30 ml of water are added to a solution of 40 g of 3-cyclohexenecarbaldehyde in 300 ml of methanol. The reaction mixture is cooled to 10°C, and 49.7 g of 4-fluorophenylacetaldehyde are rapidly added dropwise, the temperature of the solution not exceeding 30°C. After the mixture has been stirred for 2 hours at room temperature, 200 ml of water are added to the colorless reaction solution and the resulting emulsion is extracted by shaking with methyl tert-butyl ether. The organic phase is separated off, and 34 g (41%) of Z-2-(4-fluorophenyl)-3-(3-cyclohexenyl)-propenal are obtained under 0.5 mbar and at 136-142°C by distillation of the remaining residue.

Method E

35 2 g of sodium borohydride dissolved in a little 10% strength sodium hydroxide solution are added to a solution of 34 g of Z-2-(4-fluorophenyl)-3-(3-cyclohexenyl)-propenal in 200 ml of methanol. After the reaction mixture has been stirred for 18 hours at room temperature, 100 ml of water are added to the solution and the

chloride. The organic phase isolated is then dried over sodium sulfate and evaporated down. 34 g (99%) of Z-1-hydroxymethyl-1-(4-fluorophenyl)-2-(3-cyclohexenyl)-ethene are obtained.

5 Method F

32.5 g of 4-methylbenzenesulfonyl chloride are added, at room temperature, to a solution of 34 g of Z-1-hydroxymethyl-1-(4-fluorophenyl)-2-(3-cyclohexenyl)-ethene in 200 ml of methylene chloride and 29 g of triethylamine. After 24 hours, the reaction mixture is washed with aqueous sodium bicarbonate solution and water, dried over sodium sulfate and evaporated down under reduced pressure. 49.7 g (95%) of Z-1-(4-methylphenylsulfonyloxymethyl)-1-(4-fluorophenyl)-2-(3-cyclohexenyl)-ethene are obtained from the residue.

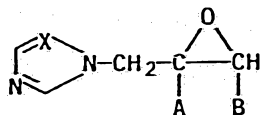
II. Preparation of the end products

EXAMPLE 1

2.7 g of sodium hydroxide are added to a solution of 4.9 g of 1,2,4-triazole in 100 ml of N-methylpyrrolidone and the mixture is heated at 50°C for 30 minutes. After the reaction mixture has been cooled to room temperature, 26 g of cis-2-(4-methylphenylsulfonyloxymethyl)-2-(tetrahydropyran-4-yl)-3-(2,4-dichlorophenyl)-oxirane, dissolved in 100 ml of N-methylpyrrolidone, are slowly added dropwise to the solution, and the mixture is stirred for 12 hours at room temperature. Thereafter, 200 ml of water are added and the mixture is extracted several times with methyl tert-butyl ether; the organic phase is washed with water, dried over sodium sulfate and evaporated down under reduced pressure. 14 g of cis-2-(1,2,4-triazol-1-ylmethyl)-2-(tetrahydropyran-4-yl)-3-(2,4-dichlorophenyl)-oxirane of melting point 155-158°C (compound No. 1) are obtained from methyl tert-butyl ether/n-hexane.

35 The compounds listed in Table 1 can be prepared similarly to Example 1.

Table 1



No.	A	B	X	M.p./IR	Isomer
1	4-tetrahydropyranyl	2,4-Cl ₂ -C ₆ H ₃	N	155-158 °C	cis
2	4-tetrahydropyranyl	2-Cl-C ₆ H ₄	N	101-103 °C	cis
3	4-tetrahydropyranyl	4-Cl-C ₆ H ₄	N	157-163 °C	cis
4	4-tetrahydropyranyl	2-F-C ₆ H ₄	N	131-134 °C	cis
5	4-F-C ₆ H ₄	cyclopropyl	N	105-108 °C	cis/trans 35:65
6	4-F-C ₆ H ₄	cyclopentyl	N	50- 56 °C	cis/trans 60:40
7	4-F-C ₆ H ₄	cyclohexyl	N	resin	cis
8	4-F-C ₆ H ₄	cyclooctyl	N	-	-
9	4-F-C ₆ H ₄	cyclododecyl	N	-	-
10	2-Cl-C ₆ H ₄	cyclopropyl	N	-	-
11	2-Cl-C ₆ H ₄	cyclopentyl	N	-	-
12	2-Cl-C ₆ H ₄	cyclohexyl	N	-	-
13	4-Cl-C ₆ H ₄	cyclopropyl	N	-	-
14	4-Cl-C ₆ H ₄	cyclopentyl	N	-	-
15	4-Cl-C ₆ H ₄	cyclohexyl	N	-	-
16	2,4-Cl ₂ -C ₆ H ₃	cyclopropyl	N	-	-
17	2,4-Cl ₂ -C ₆ H ₃	cyclopentyl	N	-	-
18	2,4-Cl ₂ -C ₆ H ₃	cyclohexyl	N	-	-
19	4-F-C ₆ H ₄	norbornyl	N	212-215 °C	cis/trans 50:50
20	2-F-C ₆ H ₄	norbornyl	N	-	-
21	2-Cl-C ₆ H ₄	norbornyl	N	-	-

No.	A	B	X	M.p./IR	Isomer
22	4-Cl-C ₆ H ₄	norbornyl	N	-	-
23	2,4-Cl ₂ -C ₆ H ₃	norbornyl	N	-	-
24	2-Cl-C ₆ H ₄	3-cyclohexenyl	N	-	-
25	4-Cl-C ₆ H ₄	3-cyclohexenyl	N	-	-
26	2,4-Cl ₂ -C ₆ H ₃	3-cyclohexenyl	N	-	-
27	2-F-C ₆ H ₄	3-cyclohexenyl	N	-	-
28	4-F-C ₆ H ₄	3-cyclohexenyl	N	1510, 1273, 1139 840 cm ⁻¹	cis/trans 60:40
29	4-F-C ₆ H ₄	2-cyclohexenyl	N	-	-
30	2-F-C ₆ H ₄	2-cyclohexenyl	N	-	-
31	2-Cl-C ₆ H ₄	2-cyclohexenyl	N	-	-
32	4-Cl-C ₆ H ₄	2-cyclohexenyl	N	-	-
33	2,4-Cl ₂ -C ₆ H ₃	2-cyclohexenyl	N	-	-
34	2,4-Cl ₂ -C ₆ H ₃	3-cyclopentenyl	N	-	-
35	2-Cl-C ₆ H ₄	3-cyclopentenyl	N	-	-
36	cyclohexyl	2-Cl-C ₆ H ₄	N	106-108°C	cis
37	cyclohexyl	4-Cl-C ₆ H ₄	N	resin	cis/trans 50:50
38	cyclohexyl	2,4-Cl ₂ -C ₆ H ₃	N	109-111°C	cis
39	cyclohexyl	2-F-C ₆ H ₄	N	90-92°C	cis
40	cyclohexyl	4-F-C ₆ H ₄	N	2928, 2854, 1511 1225, 1020 cm ⁻¹	cis
41	cyclopentyl	2-Cl-C ₆ H ₄	N	-	-
42	cyclopentyl	4-Cl-C ₆ H ₄	N	-	-
43	cyclopentyl	2-OCH ₃ -C ₆ H ₄	N	-	-
44	cyclohexyl	Cyclohexyl	N	-	-
45	cyclohexyl	Cyclopentyl	N	-	-
46	cyclopropyl	2,4-Cl ₂ -C ₆ H ₃	N	-	-
47	cyclopropyl	2-Cl-C ₆ H ₄	N	-	-
48	cyclopropyl	4-Cl-C ₆ H ₄	N	-	-

No.	A	B	X	M.p./IR	Isomer
49	cyclopropyl	4-F-C ₆ H ₄	N	-	-
50	cyclopropyl	2-F-C ₆ H ₄	N	-	-
51	3-cyclohexenyl	2-Cl-C ₆ H ₄	N	-	-
52	3-cyclohexenyl	4-Cl-C ₆ H ₄	N	-	-
53	3-cyclohexenyl	2,4-Cl ₂ -C ₆ H ₃	N	-	-
54	3-cyclohexenyl	2-F-C ₆ H ₄	N	-	-
55	3-cyclohexenyl	4-F-C ₆ H ₄	N	-	-
56	2-cyclohexenyl	2-Cl-C ₆ H ₄	N	-	-
57	2-cyclohexenyl	4-Cl-C ₆ H ₄	N	-	-
58	2-cyclohexenyl	2-F-C ₆ H ₄	N	-	-
59	2-cyclohexenyl	4-F-C ₆ H ₄	N	-	-
60	2-tetrahydrofuranyl	2-Cl-C ₆ H ₄	N	-	-
61	2-tetrahydrofuranyl	4-Cl-C ₆ H ₄	N	-	-
62	2-tetrahydrofuranyl	2,4-Cl ₂ -C ₆ H ₃	N	-	-
63	2-tetrahydrofuranyl	2-F-C ₆ H ₄	N	-	-
64	2-tetrahydrofuranyl	4-F-C ₆ H ₄	N	-	-
65	4-F-C ₆ H ₄	2-tetrahydrofuranyl	N	-	-
66	2-Cl-C ₆ H ₄	2-tetrahydrofuranyl	N	-	-
67	4-Cl-C ₆ H ₄	2-tetrahydrofuranyl	N	-	-
68	2,4-Cl ₂ -C ₆ H ₃	2-tetrahydrofuranyl	N	-	-
69	2-F-C ₆ H ₄	2-tetrahydrofuranyl	N	-	-
70	cyclohexyl	2,4-Cl ₂ -C ₆ H ₃	CH	72 - 74°C	cis
71	cyclohexyl	4-F-C ₆ H ₄	CH	resin	cis/trans 50:50

In general terms, the novel compounds are extremely effective on a broad spectrum of phytopathogenic fungi, in particular those from the class consisting of the Ascomycetes and Basidiomycetes. Some of them have a systemic action and can be used as foliar and soil fungicides.

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The fungicidal compounds are of particular interest for controlling a large number of fungi in various crops or their seeds, especially wheat, rye, barley, oats, rice, Indian corn, lawns, cotton, soybeans, coffee, sugar cane, fruit and ornamentals in horticulture and viticulture, and in
10 vegetables such as cucumbers, beans and cucurbits.

The novel compounds are particularly useful for controlling the following plant diseases:

- 15 Erysiphe graminis in cereals,
Erysiphe cichoracearum and Sphaerotheca fuliginea in cucurbits,
Diosphaera leucotricha in apples,
Uncinula necator in vines,
Puccinia species in cereals,
- 20 Rhizoctonia solani in cotton,
Ustilago species in cereals and sugar cane,
Venturia inaequalis (scab) in apples,
Helminthosporium species in cereals,
Septoria nodorum in wheat,
- 25 Botrytis cinerea (gray mold) in strawberries and grapes,
Cercospora arachidicola in groundnuts,
Pseudocercospora herpotrichoides in wheat and barley,
Pyricularia oryzae in rice,
Phytophthora infestans in potatoes and tomatoes,
- 30 Fusarium and Verticillium species in various plants,
Plasmopara viticola in grapes,
Alternaria species in fruit and vegetables.

The compounds are applied by spraying or dusting the plants with the
35 active ingredients, or treating the seeds of the plants with the active ingredients. They may be applied before or after infection of the plants or seeds by the fungi.

The novel substances can be converted into conventional formulations such
0 as solutions, emulsions, suspensions, dusts, powders, pastes and granules. The application forms depend entirely on the purposes for which they are intended; they should at all events ensure a fine and uniform distribution of the active ingredient. The formulations are produced in known manner, for example by extending the active ingredient with solvents and/or carriers, with or without the use of emulsifiers and dispersants; if water

is used as solvent, it is also possible to employ other organic solvents as auxiliary solvents. Suitable auxiliaries for this purpose are solvents such as aromatics (e.g., xylene), chlorinated aromatics (e.g., chlorobenzenes), paraffins (e.g., crude oil fractions), alcohols (e.g., 5 methanol, butanol), ketones (e.g., cyclohexanone), amines (e.g., ethanolamine, dimethylformamide), and water; carriers such as ground natural minerals (e.g., kaolins, aluminas, talc and chalk) and ground synthetic minerals (e.g., highly disperse silica and silicates); emulsifiers such as nonionic and anionic emulsifiers (e.g., polyoxyethyl- 10 ene fatty alcohol ethers, alkyl sulfonates and aryl sulfonates); and dispersants such as lignin, sulfite waste liquors and methylcellulose.

The fungicides generally contain from 0.1 to 95, and preferably from 0.5 to 90, wt% of active ingredient. The application rates are from 0.02 to 3 15 kg or more of active ingredient per hectare, depending on the type of effect desired. The novel compounds may also be used for protecting materials, e.g., on *Paecilomyces variotii*.

The agents and the ready-to-use formulations prepared from them, such as 20 solutions, emulsions, suspensions, powders, dusts, pastes and granules, are applied in conventional manner, for example by spraying, atomizing, dusting, scattering, dressing or watering.

Examples of formulations are given below.

25 I. 90 parts by weight of compound no. 2 is mixed with 10 parts by weight of N-methyl- α -pyrrolidone. A mixture is obtained which is suitable for application in the form of very fine drops.

30 II. 20 parts by weight of compound no. 6 is dissolved in a mixture consisting of 80 parts by weight of xylene, 10 parts by weight of the adduct of 8 to 10 moles of ethylene oxide and 1 mole of oleic acid-N-monoethanolamide, 5 parts by weight of the calcium salt of dodecylbenzene-sulfonic acid, and 5 parts by weight of the adduct of 40 moles of ethylene 35 oxide and 1 mole of castor oil. By pouring the solution into water and uniformly distributing it therein, an aqueous dispersion is obtained.

III. 20 parts by weight of compound no. 7 is dissolved in a mixture consisting of 40 parts by weight of cyclohexanone, 30 parts by weight of iso- 40 butanol, 20 parts by weight of the adduct of 40 moles of ethylene oxide and 1 mole of castor oil. By pouring the solution into water and finely distributing it therein, an aqueous dispersion is obtained.

IV. 20 parts by weight of compound no. 19 is dissolved in a mixture consisting of 25 parts by weight of cyclohexanol, 65 parts by weight of a mineral oil fraction having a boiling point between 210 and 280°C, and 10 parts by weight of the adduct of 40 moles of ethylene oxide and 1 mole of castor oil. By pouring the solution into water and uniformly distributing it therein, an aqueous dispersion is obtained.

V. 80 parts by weight of compound no. 28 is well mixed with 3 parts by weight of the sodium salt of diisobutyl naphthalene- α -sulfonic acid, 10 10 parts by weight of the sodium salt of a lignin-sulfonic acid obtained from a sulfite waste liquor, and 7 parts by weight of powdered silica gel, and triturated in a hammer mill. By uniformly distributing the mixture in water, a spray liquor is obtained.

VI. 3 parts by weight of compound no. 36 is intimately mixed with 97 parts by weight of particulate kaolin. A dust is obtained containing 3% by weight of the active ingredient.

VII. 30 parts by weight of compound no. 2 is intimately mixed with a 20 mixture consisting of 92 parts by weight of powdered silica gel and 8 parts by weight of paraffin oil which has been sprayed onto the surface of this silica gel. A formulation of the active ingredient is obtained having good adherence.

VIII. 40 parts by weight of compound no. 6 is intimately mixed with 10 parts of the sodium salt of a phenolsulfonic acid-urea-formaldehyde condensate, 2 parts of silica gel and 48 parts of water to give a stable aqueous dispersion. Dilution in water gives an aqueous dispersion.

IX. 20 parts by weight of compound no. 7 is intimately mixed with 2 parts by weight of the calcium salt of dodecylbenzenesulfonic acid, 8 parts by weight of a fatty alcohol polyglycol ether, 2 parts by weight of the sodium salt of a phenolsulfonic acid-urea-formaldehyde condensate and 68 parts by weight of a paraffinic mineral oil. A stable oily dispersion is 35 obtained.

In these application forms, the agents according to the invention may also be present together with other active ingredients, for example herbicides, insecticides, growth regulators, and fungicides, and may furthermore be 40 mixed and applied together with fertilizers. Admixture with other fungicides frequently results in a greater fungicidal action spectrum.

The following list of fungicides with which the novel compounds may be combined is intended to illustrate possible combinations but not to impose any restrictions.

5 Examples of fungicides which may be combined with the novel compounds are:

sulfur,
dithiocarbamates and their derivatives, such as
ferric dimethyldithiocarbamate,

10 zinc dimethyldithiocarbamate,
zinc ethylenebisdithiocarbamate,
manganese ethylenebisdithiocarbamate,
manganese zinc ethylenediaminebisdithiocarbamate,
tetramethylthiuram disulfides,

15 ammonia complex of zinc N,N'-ethylenebisdithiocarbamate,
ammonia complex of zinc N,N'-propylenebisdithiocarbamate,
zinc N,N'-propylenebisdithiocarbamate and
N,N'-polypropylenebis(thiocarbamyl) disulfide;

20 nitro derivatives, such as
dinitro(1-methylheptyl)-phenyl crotonate,
2-sec-butyl-4,6-dinitrophenyl 3,3-dimethylacrylate,
2-sec-butyl-4,6-dinitrophenyl isopropylcarbonate and
diisopropyl 5-nitroisophthalate;

25 heterocyclic substances, such as
2-heptadecylimidazol-2-yl acetate,
2,4-dichloro-6-(o-chloroanilino)-s-triazine,
O,O-diethyl phthalimidophosphonothioate,
30 5-amino-1-[-bis-(dimethylamino)-phosphinyl]-3-phenyl-1,2,4-triazole,
2,3-dicyano-1,4-dithioanthraquinone,
2-thio-1,3-dithio[4,5-b]quinoxaline,
methyl 1-(butylcarbamyl)-2-benzimidazolecarbamate,
2-methoxycarbonylaminobenzimidazole,

35 2-(fur-2-yl)-benzimidazole,
2-(thiazol-4-yl)benzimidazole,
N-(1,1,2,2-tetrachloroethylthio)-tetrahydrophthalimide,
N-trichloromethylthiotetrahydrophthalimide,
N-trichloromethylthiophthalimide,

40 N-dichlorofluoromethylthio-N',N'-dimethyl-N-phenylsulfuric acid diamide,
5-ethoxy-3-trichloromethyl-1,2,3-thiadiazole,
2-thiocyanatomethylthiobenzothiazole,
1,4-dichloro-2,5-dimethoxybenzene,

- 4-(2-chlorophenylhydrazono)-3-methyl-5-isoxazolone,
 2-thiopyridine 1-oxide,
 8-hydroxyquinoline and its copper salt,
 2,3-dihydro-5-carboxanilido-6-methyl-1,4-oxathiine,
 5 2,3-dihydro-5-carboxanilido-6-methyl-1,4-oxathiine 4,4-dioxide,
 2-methyl-5,6-dihydro-4H-pyran-3-carboxanilide,
 2-methylfuran-3-carboxanilide,
 2,5-dimethylfuran-3-carboxanilide,
 2,4,5-trimethylfuran-3-carboxanilide,
 10 2,5-dimethyl-N-cyclohexylfuran-3-carboxamide,
 N-cyclohexyl-N-methoxy-2,5-diethylfuran-3-carboxamide,
 2-methylbenzanilide,
 2-iodobenzanilide,
 N-formyl-N-morpholine-2,2,2-trichloroethylacetal,
 15 piperazine-1,4-diylbis-(1-(2,2,2-trichloroethyl)-formamide),
 1-(3,4-dichloroanilino)-1-formylamino-2,2,2-trichloroethane,
 2,6-dimethyl-N-tridecylmorpholine and its salts,
 2,6-dimethyl-N-cyclododecylmorpholine and its salts,
 N-[3-(p-tert.-butylphenyl)-2-methylpropyl]-cis-2,6-dimethylmorpholine,
 20 N-[3-(p-tert.-butylphenyl)-2-methylpropyl]-piperidine,
 1-[2-(2,4-dichlorophenyl)-4-ethyl-1,3-dioxolan-2-ylethyl]-1H-1,2,4-
 -triazole,
 1-[2-(2,4-dichlorophenyl)-4-n-propyl-1,3-dioxolan-2-ylethyl]-1H-1,2,4-
 -triazole,
 25 N-(n-propyl)-N-(2,4,6-trichlorophenoxyethyl)-N'-imidazolyl-urea,
 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-butan-2-one,
 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-butan-2-ol,
 1-(4-phenylphenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-2-butanol,
 α-(2-chlorophenyl)-α-(4-chlorophenyl)-5-pyrimidinemethanol,
 30 5-butyl-(2-dimethylamino-4-hydroxy-6-methylpyrimidine,
 bis-(p-chlorophenyl)-3-pyridinemethanol,
 1,2-bis-(3-ethoxycarbonyl-2-thioureido)-benzene,
 1,2-bis-(3-methoxycarbonyl-2-thioureido)-benzene,
 and various fungicides, such as
 35 dodecylguanidine acetate,
 3-[3-(3,5-dimethyl-2-oxycyclohexyl)-2-hydroxyethyl]-glutaramide,
 hexachlorobenzene,
 DL-methyl-N-(2,6-dimethylphenyl)-N-fur-2-yl alanate,
 methyl DL-N-(2,6-dimethylphenyl)-N-(2'-methoxyacetyl)-alanate,
 40 N-(2,6-dimethylphenyl)-N-chloroacetyl-DL-2-aminobutyrolactone,
 methyl DL-N-(2,6-dimethylphenyl)-N-(phenylacetyl)-alanate,
 5-methyl-5-vinyl-3-(3,5-dichlorophenyl)-2,4-dioxo-1,3-oxazolidine,
 3-[3,5-dichlorophenyl]-5-methyl-5-methoxymethyl-1,3-oxazolidine-2,4-dione,
 3-(3,5-dichlorophenyl)-1-isopropylcarbamyldantoin,

- N-(3,5-dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide,
 2-cyano-[N-(ethylaminocarbonyl)-2-methoximino]-acetamide,
 1-[2-(2,4-dichlorophenyl)-pentyl]-1H-1,2,4-triazole,
 2,4-difluoro- α -(1H-1,2,4-triazol-1-ylmethyl)-benzhydryl alcohol,
 5 N-(3-chloro-2,6-dinitro-4-trifluoromethylphenyl)-5-trifluoromethyl-3-chloro-2-aminopyridine, and
 1-((bis-(4-fluorophenyl)-methylsilyl)-methyl)-1H-1,2,4-triazole.

Use examples

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For comparison purposes, cis-2-(1,2,4-triazolylmethyl)-2-(tert-butyl)-3-(4-chlorophenyl)-oxirane (A) disclosed in DE 3 218 130.2 was employed.

Use Example 1

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Action on wheat brown rust

Leaves of pot-grown wheat seedlings of the "Frühgold" variety were dusted with spores of brown rust (*Puccinia recondita*). The pots were then placed for 24 hours at 20 to 22°C in a high-humidity (90 - 95%) chamber. During this period the spores germinated and the germ tubes penetrated the leaf tissue. The infected plants were then sprayed to runoff with aqueous liquors containing (dry basis) 80% of active ingredient and 20% of emulsifier. After the sprayed-on layer had dried, the plants were set up in the greenhouse at 20 to 22°C and a relative humidity of 65 to 70%. The extent of rust fungus spread on the leaves was assessed after 8 days.

The results show that active ingredients 2, 6, 7 and 19 have, when applied as 0.025wt% spray liquors, a better fungicidal action (97%) than prior art comparative agent A (60%).

Use Example 2

Action on Botrytis cinerea in paprika

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Paprika seedlings of the "Neusiedler Ideal Elite" variety were sprayed, after 4 to 5 leaves were well developed, to runoff with aqueous suspensions containing (dry basis) 80% of active ingredient and 20% of emulsifier. After the sprayed-on layer had dried, the plants were sprinkled with a conidial suspension of the fungus *Botrytis cinerea*, and placed at 22 to 24°C in a chamber of high humidity. After 5 days, the disease had spread to such a great extent on the untreated plants that the necroses covered the major portion of the leaves.

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The results show that active ingredients 28 and 36, when applied as 0.05% spray liquors, have a better fungicidal action (90%) than prior art comparative agent A (60%).

5 Use Example 3

Action on *Pyrenophora teres*

Leaves of pot-grown barley seedlings of the "Igri" variety were sprayed to runoff at the 2-leaf stage with aqueous suspensions containing (dry basis) 80% of active ingredient and 20% of emulsifier. After 24 hours the plants were inoculated with a spore suspension of *Pyrenophora teres* and set up for 48 hours in a high-humidity climatic cabinet at 18°C. The plants were then cultivated for a further 5 days in the greenhouse at 20 to 22°C and a relative humidity of 70%. The extent of the spread of the symptoms was then assessed.

The results show that active ingredients 6, 7, 28 and 36 have a good fungicidal action (97%) when applied as 0.05% spray liquors.

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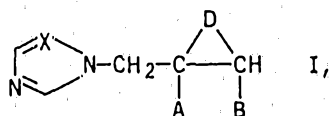
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~~Maximum:~~

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Azolymethyloxiranes of the general formula I

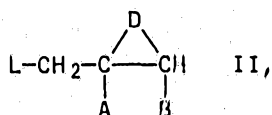


where A and B are identical or different and each denotes C₃-C₁₂-cycloalkyl, dioxanyl, tetrahydropyranyl, tetrahydrofuranyl, norbornyl, C₅-C₈-cycloalkenyl or phenyl, each of these radicals being unsubstituted or substituted by halogen, nitro, phenoxy, amino, alkyl, alkoxy or haloalkyl, each of 1 to 4 carbon atoms, with the proviso that A and B are not simultaneously phenyl, D is O, X is CH or N, and their plant-tolerated acid addition salts or metal complexes.

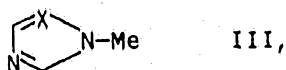
2. Azolymethyloxiranes of the general formula I, where A is unsubstituted or fluoro- or chloro-substituted phenyl, D is O, and B and X have the meanings given in claim 1.

3. A process for the manufacture of the azolymethyloxiranes of the formula I as set forth in claim 1, D denoting O, wherein

- a) a compound of the formula II

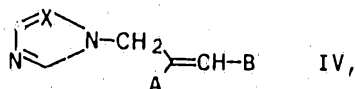


where A, B and D have the above meanings and L is a nucleophilically substitutable leaving group, is reacted with a compound of the formula III



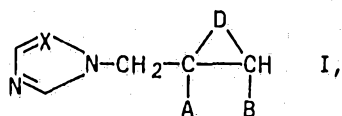
where Me is a hydrogen atom or a metal atom and X has the above meanings, or

- b) a compound of the formula IV



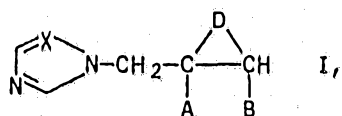
where A, B and X have the above meanings, is converted into the corresponding oxirane and the compounds thus obtained are, if desired, converted into their salts with plant-tolerated acids.

4. A fungicidal agent containing a carrier and an azolymethyloxirane of the formula I



where A and B are identical or different and each denotes C₃-C₁₂-cycloalkyl, dioxanyl, tetrahydropyranyl, tetrahydrofuranyl, norbornyl, C₅-C₈-cycloalkenyl or phenyl, each of these radicals being unsubstituted or substituted by halogen, nitro, phenoxy, amino, alkyl, alkoxy or haloalkyl, each of 1 to 4 carbon atoms, with the proviso that A and B are not simultaneously phenyl, D is O, X is CH or N, or a plant-tolerated acid addition salt or metal complex thereof.

5. A process for combating fungi, wherein a fungicidally effective amount of an azolymethyloxirane of the formula I



where A and B are identical or different and each denotes C₃-C₁₂-cycloalkyl, dioxanyl, tetrahydropyranyl, tetrahydrofuranyl, norbornyl, C₅-C₈-cycloalkenyl or phenyl, each of these radicals being unsubstituted or substituted by halogen, nitro, phenoxy, amino, alkyl, alkoxy or haloalkyl, each of 1 to 4 carbon atoms, with the proviso that A and B are not simultaneously phenyl, D is O, X is CH or N, or a plant-tolerated acid addition salt or metal complex thereof, is allowed to act on the fungi, or the materials, areas, plants or seed threatened by fungus attack.

6. A compound as set forth in claim 1, where A is 4-fluorophenyl, B is cyclopentyl, D is O, and X is N.

7. A compound as set forth in claim 1, where A is 4-fluorophenyl, B is cyclohexyl, D is O, and X is M.

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DATED this 22nd day of February 1989.

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