CONVENTION APPLICATION FOR A PATENT

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(c) Insert title of invention.

(d) Insert country in which first basic application was made.

(e) Insert date(s) of basic application(s).

(f) Insert number of basic application(s).

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Dated this (g) 13th day of August, 1981.

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The Commissioner of Patents,
COMMONWEALTH OF AUSTRALIA
ARTHUR S. CAVE & CO.
The compounds of formula I and their acid addition salts have fungicidal properties and are suitable as fungicidal active substances, especially for use in agriculture and in horticulture.

Claim

1. Compounds of the general formula

\[
\begin{align*}
R^1 & \quad \text{-} \\
\text{C} & \quad \text{-} \\
\text{CH} & \quad \text{-} \\
\text{R}^2 & \quad \text{I} \\
\text{N} & \\
\text{OR}^4 &
\end{align*}
\]

wherein \( R^1 \) signifies 2-halo-, 4-halo- or 2,4-di\( \text{halo} \)-phenyl,

\( R^2 \) signifies 3-pyridyl or 2-pyrazinyl,

\( R^3 \) signifies hydrogen or straight-chain \( C_{1-4} \)-alkyl

and \( R^4 \) signifies \( C_{1-6} \)-alkyl, \( C_{3-6} \)-cycloalkyl,

\( C_{3-6} \)-alkenyl or \( C_{3-6} \)-alkynyl,

and acid addition salts of these compounds.
TO BE COMPLETED BY APPLICANT

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Complete Specification for the invention entitled: PYRIDINE AND PYRAZINE DERIVATIVES

The following statement is a full description of this invention, including the best method of performing it known to me:-
The invention is concerned with compounds of the general formula

\[ \begin{align*}
R^3 \\
R^1 - C - CH - R^2 \\
\mid \\
\mid \\
\mid \\
\text{N} \\
\mid \\
\text{OR}^4
\end{align*} \]

wherein \( R^1 \) signifies 2-halo-, 4-halo- or 2,4-dihalo-phenyl,
\( R^2 \) signifies 3-pyridyl or 2-pyrazinyl,
\( R^3 \) signifies hydrogen or straight-chain \( C_{1-4} \)-alkyl and \( R^4 \) signifies straight-chain \( C_{1-6} \)-alkyl, \( C_{3-6} \)-cycloalkyl, \( C_{3-6} \)-alkenyl or \( C_{3-6} \)-alkynyl,

and acid addition salts of these compounds.

The compounds of formula I and their acid addition salts have fungicidal properties and are suitable as fungicidal active substances, especially for use in agriculture and in horticulture.

Pa/5.8.1981
The invention is also concerned with a process for the manufacture of the compounds of formula I and their acid addition salts, compounds of formula I and acid addition salts thereof as fungicidal active substances, fungicidal compositions which contain the compounds of formula I or acid addition salts thereof as the active substances, as well as the use of said compounds, acid addition salts and compositions for the control of fungi in agriculture and in horticulture.

The term "halo" in the definition of formula I embraces fluoro, chloro, bromo and iodo, with chloro being preferred.

The halogen atoms in a 2,4-dihalo-phenyl group denoted by R can be the same or different.

The terms "C_{1-6} -alkyl", "C_{3-6} -alkenyl" and "C_{3-6} -alkynyl" embrace not only straight-chain but also branched-chain hydrocarbon groups. Under alkyl there are to be understood, depending on the number of carbon atoms specified, for example the following groups: methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-butyl, isoamyl and n-hexyl.

If R^4 signifies C_{1-6} -alkyl, C_{3-6} -alkenyl or C_{3-6} -alkynyl, then this is preferably C_{1-4} -alkyl,
C₃ or 4'-alkenyl or C₃ or 4'-alkynyl. The allyl group is an especially preferred alkenyl group and the propargyl group is an especially preferred alkynyl group.

R¹ preferably signifies 4-chlorophenyl or 2,4'-dichlorophenyl, especially the latter group.

R³ preferably signifies hydrogen, methyl or ethyl, especially hydrogen.

An especially preferred compound of formula I is 2',4'-dichloro-2-(3-pyridyl)-acetophenone O-methyl oxime.

Representative compounds of formula I are:

4'-chloro-2-(3-pyridyl)-acetophenone O-allyl oxime and

2',4'-dichloro-2-(2-pyrazinyl)-acetophenone O-isopropyl oxime.

As a consequence of the presence of the C=N double bond in the compounds of formula I geometric isomerism occurs. In addition, asymmetric carbon atoms can be present and, therefore, the compounds can exist as optical antipodes. Formula I is accordingly intended to embrace all of these possible isomeric forms.

As acid addition salts of the compounds of formula I
there come into consideration physiologically compatible salts. These salts are preferably salts of the compounds of formula I with inorganic or organic acids such as hydrochloric acid, nitric acid, phosphoric acid, mono- and bifunctional carboxylic acids and hydroxy carboxylic acids (e.g. acetic acid, maleic acid, succinic acid, fumaric acid, tartaric acid, citric acid, salicylic acid, sorbic acid and lactic acid) and sulphonic acids (e.g. 1,5-naphthalene-disulphonic acid).

The process in accordance with the invention for the manufacture of the compounds of formula I and of their salts comprises

(a) reacting an oxime of the formula

\[
\begin{align*}
R^1 \quad C \quad CH \quad R^2.
\end{align*}
\]

wherein \(R^1, R^2\) and \(R^3\) have the significances given above,

with a compound of the formula

\[
\begin{align*}
R^4U
\end{align*}
\]
wherein $R_4^4$ has the significance given above and $U$ signifies a leaving group (e.g. chlorine, bromine, iodine, mesyloxy, tosyloxy or an alkysulphate group),

or

(b) reacting a ketone of the formula

$$\begin{align*}
R^3
R^1 - \text{CH} - R^2
\end{align*}$$

wherein $R^1$, $R^2$ and $R^3$ have the significances given above,

with a $O$-substituted hydroxylamine of the formula

$$R^{41} \text{ONH}_2$$

wherein $R^{41}$ signifies $C_{1-6}$-alkyl, $C_{3-6}$-cycloalkyl or $C_{3-6}$-alkenyl,

and, if desired, converting a compound of formula I obtained into an acid addition salt.

Process variant (a) can be carried out by treating the starting material of formula II with the compound of
formula III, conveniently in the presence of a base, in an organic solvent and in a temperature range between 0°C and the reflux temperature of the reaction mixture.

The solvent can be protic or non-protic. When protic solvents such as, for example, alcohols, especially methanol or ethanol, are used, an alkali metal hydroxide (e.g. sodium or potassium hydroxide) or an alkali metal alcoholate is preferably used as the base. When non-protic solvents such as, for example, ethers or ether-like compounds, especially tetrahydrofuran or dimethoxyethane, and dialkylamides, especially dimethylformamide, are used, an alkali metal hydride (e.g. sodium hydride) is preferably used as the base.

In a preferred embodiment of variant (a), sodium hydride is used as the base and an ether or an ether-like compound, especially tetrahydrofuran or dimethoxyethane, or a dialkylamide, especially dimethylformamide, is used as the solvent.

In accordance with process variant (b), which leads to compounds of formula I in which R signifies C\textsubscript{1-6}-alkyl, C\textsubscript{3-6}-cycloalkyl or C\textsubscript{3-6}-alkenyl, the reaction is conveniently carried out in an organic solvent, for example an alcohol such as methanol or ethanol, a dialkylamide such as dimethylformamide or a tertiary amine such as pyridine. The reaction is preferably carried out in a temperature range between room temperature and the...
reflux temperature of the reaction mixture. Since the starting material of formula V is preferably used in the form of an acid addition salt (e.g. the hydrochloride or hydrosulphate), a base such as sodium or potassium carbonate, triethylamine or pyridine is conveniently added to the reaction mixture.

For the manufacture of acid addition salts, the compounds of formula I can, if desired, be reacted with inorganic or organic acids such as, for example, hydrochloric acid, nitric acid, phosphoric acid, monofunctional carboxylic acids and hydroxycarboxylic acids or sulphonic acids.

The isolation and purification of the thus-manufactured compounds of formula I and their acid addition salts is carried out according to methods known per se.

The compounds of formulae II, III, IV and V used as the starting materials are either known or can be prepared according to methods known per se. For example, the oximes of formula II can be prepared from the corresponding ketones of formula IV by reaction with hydroxylamine, and the ketones themselves can be prepared in accordance with the processes described in DOS 2 221 546, DOS 2 800 010 and British Patent Specification No. 2 015 524.
The compounds in accordance with the invention (i.e. the compounds of formula I and their acid addition salts) have fungicidal activity and can accordingly be used for the control of fungi in agriculture and in horticulture. They are especially suitable for eradicating or checking phytopathogenic fungi on parts of plants (e.g. leaves, stems, roots, tubers, fruits or flowers) and on seeds as well as in the soil and are especially effective in the control of powdery mildew fungi such as, for example, Erysiphe graminis (powdery mildew of cereals), Erysiphe cichoracearum (powdery mildew of cucumbers), Podosphaera leucotricha (powdery mildew of apples) and Sphaerotheca pannosa (powdery mildew of roses); of Venturia inaequalis (apple scab); and of rust fungi such as, for example, those of the genera Puccinia, Uromyces and Hemileia, especially Puccinia coronata (crown rust of oats), Puccinia recondita (leaf rust of cereals), Uromyces appendiculatus (bean rust) and Hemileia vastatrix (coffee rust).

Further, various compounds in accordance with the invention are also active against phytopathogenic fungi of the following genera:

Helminthosporium, Rhizoctonia, Septoria, Cercospora, Corticium, Tilletia and Ustilago.

Moreover, individual compounds in accordance with
the invention have a pronounced activity against wood-
destroying fungi such as, for example, Coniophora puteana
and Lenzites trabea. Moreover, individual compounds are
also active against phytopathogenic bacteria such as,
for example, Xanthomonas oryzae.

The compounds in accordance with the invention are
distinguished by systemic activity as well as by a good
plant tolerance.

The compounds in accordance with the invention are
active under greenhouse conditions even at a concentration
of 5 mg to 500 mg of active substance per litre of spray
liquor. In the open, concentrations of 50 g to 1000 g
of active substance of formula I per hectare and treatment
are advantageously used. For example, for the effective
control of apple mildew and apple scab a concentration of
50 g to 400 g of active substance of formula I is used
per hectare and treatment. For the control of seed-
borne fungi in a disinfecting process there are advantage-
ously used 0.1 g to 2.5 g of active substance of formula I
per kg of seeds.

The compounds in accordance with the invention can
be formulated to give various compositions (e.g. spray
liquors, aqueous suspensions, emulsions, emulsifiable
concentrates and pulverous preparations). The fungicidal
compositions in accordance with the invention contain an
effective amount of at least one compound of general formula
I, as defined above, or an acid addition salt of such a
compound as well as inert carrier material.

A composition generally contains, depending on its
type, between 0.0001 and 95 weight percent of compound in
accordance with the invention or compounds in accordance
with the invention as the active substance(s).

Various inert pulverous carrier substances such as,
for example, kaolin, bentonite, talc, whiting, magnesium
carbonate and siliceous earth can be used for the prepara-
tion of pulverous fungicidal compositions. The active
components are mixed with such carrier substances (e.g.
by grinding together) or the inert carrier substance is
impregnated with a solution of the active components and
then the solvent is removed by evaporation, heating or by
sucking-off under reduced pressure. Such pulverous
compositions can be applied to the plants to be protected
as dusting compositions using the usual dusting apparatuses.

By adding wetting and/or dispersing agents such pulverous
compositions can be made readily wettable with water, so
that they can be used as spray compositions in the form
of aqueous suspensions.
In order to produce emulsifiable concentrates, the active substances can, for example, be mixed with an emulsifying agent or dissolved in an inert solvent and mixed with an emulsifier. By diluting such concentrates with water there are obtained ready-for-use emulsions. Such concentrates can contain 5 to 95 weight percent, especially 25 to 75 weight percent, of active substance.

The fungicidal compositions in accordance with the invention can contain, in addition to the active substances of formula I, other active substances (e.g. other fungicidal agents, insecticidal and acaridical agents, other bactericides, plant growth regulators and fertilizers). Such combination compositions are suitable for broadening the spectrum of activity or for specifically influencing the plant growth.

The compositions in accordance with the invention can be used according to application methods which are usual in plant protection or in agriculture. The method in accordance with the invention for the control of fungi is characterized by treating the goods to be protected (e.g. plants, parts of plants or seeds) with an effective amount of a compound in accordance with the invention or of a composition in accordance with the invention.
The following Examples illustrate the invention.

All temperatures are given in °C.

I. Manufacture of the active substances

Example 1

A solution of 13.3 g of 2',4'-dichloro-2-(3-pyridyl)-acetophenone in 40 ml of ethanol is treated with 10 g of sodium carbonate and 8.3 g of O-methylhydroxylamine hydrochloride and the mixture is subsequently heated at reflux temperature while stirring. After 4 hours, the mixture is poured onto ice and extracted with ethyl acetate. The organic phase is washed, dried over sodium sulphate and concentrated under reduced pressure. There is obtained 2',-dichloro-2-(3-pyridyl)-acetophenone O-methyl oxime as the E,Z-isomer mixture in the form of a yellowish oil. By chromatographic separation on silica gel with n-hexane/ethyl acetate (4:1) there is eluted firstly the E-isomer (nD20 = 1.5845) and then the Z-isomer (nD20 = 1.5745).

In an analogous manner,

from 4'-chloro-2-(3-pyridyl)-acetophenone and O-methylhydroxylamine hydrochloride there is obtained 4'-chloro-2-(3-pyridyl)-acetophenone O-methyl oxime, m.p. 55-58°;

from 4'-chloro-2-(2-pyrazinyl)-acetophenone and O-methylhydroxylamine hydrochloride there is obtained
and acid addition salts of these compounds.

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4'-chloro-2-(2-pyrazinyl)-acetophenone O-methyl oxime,
m.p. 53-58°;

from 4'-chloro-2-(2-pyrazinyl)-acetophenone and
O-ethylhydroxylamine hydrochloride there is obtained.

54'-chloro-2-(2-pyrazinyl)-acetophenone O-ethyl oxime,
m.p. 44-46°;

from 4'-chloro-2-(2-pyrazinyl)-acetophenone and
O-allylhydroxylamine hydrochloride there is obtained
4'-chloro-2-(2-pyrazinyl)-acetophenone O-allyl oxime as
a yellowish oil,

from 2',4'-dichloro-2-(3-pyridyl)-acetophenone and
O-allylhydroxylamine hydrochloride there is obtained
2',4'-dichloro-2-(3-pyridyl)-acetophenone O-allyl oxime
as a colourless oil.

Example 2

3 g of 2'-chloro-2-(2-pyrazinyl)-acetophenone and
0.8 g of O-methylhydroxylamine hydrochloride are dissolved
in 10 ml of pyridine and the mixture is heated at 80° for
30 minutes. The pyridine is then removed under reduced
pressure and water is added to the crude product. There-
upon, the mixture is extracted with ethyl acetate and the
organic phase is dried over sodium sulphate and concentrated. There is obtained 2'-chloro-2-(2-pyrazinyl)-acetophenone O-methyl oxime as an oil.

In an analogous manner,

from 4'-fluoro-2-(2-pyrazinyl)-acetophenone and O-methylhydroxylamine hydrochloride there is obtained 4'-fluoro-2-(2-pyrazinyl)-acetophenone O-methyl oxime, m.p. 52-54°;

from 4'-bromo-2-(2-pyrazinyl)-acetophenone and O-methylhydroxylamine hydrochloride there is obtained 4'-bromo-2-(2-pyrazinyl)-acetophenone O-methyl oxime, m.p. 81-84°;

from 4'-chloro-2-(2-pyrazinyl)-propiophenone and O-methylhydroxylamine hydrochloride there is obtained 4'-chloro-2-(2-pyrazinyl)-propiophenone O-methyl oxime as an oil;

from 2',4'-dichloro-2-(2-pyrazinyl)-acetophenone and O-methylhydroxylamine hydrochloride there is obtained 2',4'-dichloro-2-(2-pyrazinyl)-acetophenone O-methyl oxime as an oil;
from 2',4'-dichloro-2-(2-pyrazinyl)-acetophenone and O-ethyl hydroxylamine hydrochloride there is obtained 2',4'-dichloro-2-(2-pyrazinyl)-acetophenone O-ethyl oxime as an oil;

from 2',4'-dichloro-2-(2-pyrazinyl)-acetophenone and O-allyl hydroxylamine hydrochloride there is obtained 2',4'-dichloro-2-(2-pyrazinyl)-acetophenone O-allyl oxime as an oil;

from 2',4'-dichloro-2-(2-pyrazinyl)-propiophenone and O-methyl hydroxylamine hydrochloride there is obtained 2',4'-dichloro-2-(2-pyrazinyl)-propiophenone O-methyl oxime as an oil.

Example 3

A solution of 3 g of 2',4'-dichloro-2-(3-pyridyl)-acetophenone oxime in 25 ml of dimethoxyethane is treated portionwise with 0.51 g of sodium hydride dispersion (55% in oil) and the mixture is stirred for 30 minutes at room temperature. Thereupon, 2.0 g of ethyl iodide are added and the mixture is heated at reflux temperature. After 4 hours, the mixture is poured onto ice and extracted with ethyl acetate, and the organic phase is dried over sodium sulphate and concentrated under reduced pressure. The
If $R^4$ signifies $C_{1-6}$-alkyl, $C_{3-6}$-alkenyl or $C_{3-6}$-alkynyl, then this is preferably $C_{1-4}$-alkyl,

crude product is purified by chromatography on silica gel. There is obtained 2',4'-dichloro-2-(3-pyridyl)-acetophenone O-ethyl oxime as a yellowish oil.

In an analogous manner,

from 2',4'-dichloro-2-(3-pyridyl)-acetophenone oxime and isopropyl bromide there is obtained 2',4'-dichloro-2-(3-pyridyl)-acetophenone O-isopropyl oxime as a yellowish oil;

from 2',4'-dichloro-2-(3-pyridyl)-acetophenone oxime and propargyl bromide there is obtained 2',4'-dichloro-2-(3-pyridyl)-acetophenone O-propargyl oxime, m.p. 60-62º;

from 4'-chloro-2-(2-pyrazinyl)-acetophenone oxime and propargyl bromide there is obtained 4'-chloro-2-(2-pyrazinyl)-acetophenone O-propargyl oxime, m.p. 76-77º;

from 2',4'-dichloro-2-(2-pyrazinyl)-acetophenone oxime and propargyl bromide there is obtained 2',4'-dichloro-2-(2-pyrazinyl)-acetophenone O-propargyl oxime as an oil.
possible isomeric forms.

As acid addition salts of the compounds of formula I

**II Preparation of the starting materials**

**Example 4**

The 2',4'-dichloro-2-(3-pyridyl)-acetophenone required as the starting material in Example 1 can be prepared as follows:

A mixture of 27.6 g of ethyl 2,4-dichlorobenzoate and 20.81 g of ethyl 3-pyridylacetate at 20-25° is treated portionwise with 10.59 g of sodium methoxide. The mixture is subsequently heated at 65-70° and resulting readily volatile products are blown off with dry nitrogen. After 20 hours, the mixture is treated with 40 ml of concentrated hydrochloric acid and heated at reflux temperature for 18 hours. The mixture is washed with diethyl ether and the aqueous phase is made basic by adding concentrated ammonia and extracted with methylene chloride. The organic phase is concentrated and the crude product is chromatographed on silica gel with methylene chloride/methanol (98:2). The product, 2',4'-dichloro-2-(3-pyridyl)-acetophenone, can be crystallized from diethyl ether/n-pentane and melts at 55-56°.
The 2',4'-dichloro-2-(2-pyrazinyl)-acetophenone required as the starting material in Example 2 can be prepared as follows:

20 g of 2-methylpyrazine are added dropwise to a suspension of sodium amide in liquid ammonia (from 200 ml of ammonia and 4.83 g of sodium) at -30° and the mixture is left to stir for 30 minutes. 20.5 g of methyl 2,4-dichlorobenzoate are then slowly added dropwise and the mixture is left to react at -30° for 1 hour. Then the mixture is treated with ammonium chloride, ammonia is driven off and diethyl ether is added. The organic phase is washed with water, dried over sodium sulphate and concentrated. After treatment with a small amount of ethanol, 2',4'-dichloro-2-(2-pyrazinyl)-acetophenone crystallises out from the crude reaction product. The product melts at 96-98°.

In an analogous manner,

from 2-methylpyrazine and methyl 2-chlorobenzoate there is obtained 2'-chloro-2-(2-pyrazinyl)-acetophenone as an oil;
Process variant (a) can be carried out by treating the starting material of formula II with the compound of

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from 2-methylpyrazine and methyl 4-fluorobenzoate there is obtained 4'-fluoro-2-(2-pyrazinyl)-acetophenone, m.p. 100-103°;

from 2-methylpyrazine and methyl 4-bromobenzoate there is obtained 4'-bromo-2-(2-pyrazinyl)-acetophenone, m.p. 121-122°;

from 2-ethylpyrazine and methyl 4-chlorobenzoate there is obtained 4'-chloro-2-(2-pyrazinyl)-propiophenone, m.p. 85°;

from 2-ethylpyrazine and methyl 2,4-dichlorobenzoate there is obtained 2',4'-dichloro-2-(2-pyrazinyl)-propiophenone as an oil.

Example 6

The 4'-chloro-2-(2-pyrazinyl)-acetophenone oxime required as the starting material in Example 3 can be prepared as follows:

10 g of 4'-chloro-2-(2-pyrazinyl)-acetophenone, 10 g of hydroxylamine hydrochloride and 12 g of anhydrous sodium carbonate are stirred at 60° in 100 ml of ethanol for 2 hours. The mixture is then treated with water and
alcohol such as methanol or ethanol, a dialkylamide such as dimethylformamide or a tertiary amine such as pyridine. The reaction is preferably carried out in a temperature range between room temperature and the

extracted with ethyl acetate, and the organic phase is dried over sodium sulphate and subsequently concentrated. The residue is crystallized from acetone/n-hexane. There is obtained 4'-chloro-2-(2-pyrazinyl)-acetophenone oxime, m.p. 134°.

In an analogous manner,

from 2',4'-dichloro-2-(2-pyrazinyl)-acetophenone and hydroxylamine hydrochloride there is obtained 2',4'-dichloro-2-(2-pyrazinyl)-acetophenone oxime as a viscous oil;

from 2',4'-dichloro-2-(3-pyridyl)-acetophenone and hydroxylamine hydrochloride there is obtained 2',4'-dichloro-2-(3-pyridyl)-acetophenone oxime, m.p. 134-136°.

III. **Formulation Examples**

15 **Example 7**

1. Spray powder (for active substances which are liquid or which melt below 75°)
Active substance of formula I  50
Hydrated silicic acid  37
Kaolin  5
Alkylphenol ethoxylate  4
Sodium polynaphthalenesulphonate  4

100

The liquid or molten active substance is absorbed onto the silicic acid, the remaining components are admixed and the mixture is finely ground in a suitable mill.

2. Spray powder (for solid active substances which melt above 75°C)

Active substance of formula I  50
Hydrated silicic acid  5
Kaolin  42
Sodium lauryl sulphate  1
Sodium lignosulphonate  2

100

The components are mixed with one another and the mixture is finely ground in a suitable mill.
Moreover, individual compounds in accordance with Exampel 8

**Example 8**

Emulsifiable concentrate (for active substances which are liquid at 20-25°C)

<table>
<thead>
<tr>
<th>Parts by weight</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>5 Active substance of formula I</td>
<td>500</td>
</tr>
<tr>
<td>100 Castor oil ethoxylate</td>
<td></td>
</tr>
<tr>
<td>25 Calcium dodecylbenzene sulphonate</td>
<td></td>
</tr>
<tr>
<td>100 Mixture of C10-alkylbenzenes ad 1000 parts by volume.</td>
<td></td>
</tr>
</tbody>
</table>

The components are mixed with one another until a clear solution results.
be formulated to give various compositions (e.g. spray liquors, aqueous suspensions, emulsions, emulsifiable concentrates and pulverous preparations). The fungicidal
The claims defining the invention are as follows:

1. Compounds of the general formula

   \[
   R^3 \quad \begin{array}{c} R^1 \quad - \quad C \quad - \quad CH \quad - \quad R^2 \\ \| \quad \| \quad \| \\ N \quad \| \\ OR^4 \end{array} 
   \]

   wherein \( R^1 \) signifies 2-halo-, 4-halo- or 2,4-dihalo-phenyl,
   \( R^2 \) signifies 3-pyridyl or 2-pyrazinyl,
   \( R^3 \) signifies hydrogen or straight-chain \( C_{1-4} \)-alkyl and
   \( R^4 \) signifies \( C_{1-6} \)-alkyl, \( C_{3-6} \)-cycloalkyl, \( C_{3-6} \)-alkenyl or \( C_{3-6} \)-alkynyl,

   and acid addition salts of these compounds.

2. Compounds according to claim 1, wherein \( R^1 \) signifies 4-chlorophenyl or 2,4-dichlorophenyl.

3. Compounds according to claim 1 or claim 2, wherein \( R^3 \) signifies hydrogen.

4. 2',4'-Dichloro-2-(3-pyridyl)-acetophenone O-methyl oxime.

5. A compound according to claim 1, selected from:
of a composition in accordance with the invention.

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4'-Chloro-2-(3-pyridyl)-acetophenone O-methyl oxime,
4'-chloro-2-(2-pyrazinyl)-acetophenone O-methyl oxime,
4'-chloro-2-(2-pyrazinyl)-acetophenone O-ethyl oxime,
4'-chloro-2-(2-pyrazinyl)-acetophenone O-allyl oxime,
2',4'-dichloro-2-(3-pyridyl)-acetophenone O-ethyl oxime,
2',4'-dichloro-2-(3-pyridyl)-acetophenone O-isopropyl oxime and
2',4'-dichloro-2-(3-pyridyl)-acetophenone O-propargyl oxime.

6. A compound according to claim 1, selected from:

2',4'-Dichloro-2-(3-pyridyl)-acetophenone O-allyl oxime,
2'-chloro-2-(2-pyrazinyl)-acetophenone O-methyl oxime,
4'-fluoro-2-(2-pyrazinyl)-acetophenone O-methyl oxime,
4'-bromo-2-(2-pyrazinyl)-acetophenone O-methyl oxime,
4'-chloro-2-(2-pyrazinyl)-propiophenone O-methyl oxime,
2',4'-dichloro-2-(2-pyrazinyl)-acetophenone O-methyl oxime,
2',4'-dichloro-2-(2-pyrazinyl)-acetophenone O-ethyl oxime,
2',4'-dichloro-2-(2-pyrazinyl)-acetophenone O-allyl oxime,
from 4'-chloro-2-(2-pyrazinyl)-acetophenone and
O-methylhydroxylamine hydrochloride there is obtained

2',4'-dichloro-2-(2-pyrazinyl)-propiophenone O-methyl oxime,
4'-chloro-2-(2-pyrazinyl)-acetophenone O-propargyl oxime and
2',4'-dichloro-2-(2-pyrazinyl)-acetophenone O-propargyl oxime.

7. Compounds according to one of claims 1 to 6 as fungicidal active substances.

8. A fungicidal composition, which contains an effective amount of at least one compound of the general formula

\[
\begin{align*}
R^1 &\quad \text{C} - \text{CH} - R^2 \\
\text{N} &\quad \text{OR}^4
\end{align*}
\]

wherein \(R^1\) signifies 2-halo-, 4-halo- or 2,4-dihalo-phenyl,
\(R^2\) signifies 3-pyridyl or 2-pyrazinyl,
\(R^3\) signifies hydrogen or straight-chain \(\text{C}_{1-4}\)-alkyl
and \(R^4\) signifies \(\text{C}_{1-6}\)-alkyl, \(\text{C}_{3-6}\)-cycloalkyl, \(\text{C}_{3-6}\)-alkenyl or \(\text{C}_{3-6}\)-alkynyl,
or an acid addition salt of such a compound as well as inert carrier material.
9. A fungicidal composition according to claim 8, which contains an effective amount of 2',4'-dichloro-2-(3-pyridyl)-acetophenone O-methyl oxime as well as inert carrier material.

10. A process for the manufacture of compounds of the general formula

\[
R^3
\]

\[
R^1 - C - CH - R^2
\]

\[
\begin{array}{c}
\parallel \\
N \\
\mid \\
OR^4
\end{array}
\]

wherein \( R^1 \) signifies 2-halo-, 4-halo- or 2,4-dihalo-phenyl, \( R^2 \) signifies 3-pyridyl or 2-pyrazinyl, \( R^3 \) signifies hydrogen or straight-chain \( C_{1-4} \)-alkyl and \( R^4 \) signifies \( C_{1-6} \)-alkyl, \( C_{3-6} \)-cycloalkyl, \( C_{3-6} \)-alkenyl or \( C_{3-6} \)-alkynyl, and of their acid addition salts, which process comprises

(a) reacting an oxime of the formula

\[
R^3
\]

\[
R^1 - C - CH - R^2
\]

\[
\begin{array}{c}
\parallel \\
N \\
\mid \\
OH
\end{array}
\]
wherein \( R_1, R_2 \) and \( R_3 \) have the significances given earlier in this claim,

with a compound of the formula

\[
R^4U
\]

wherein \( R^4 \) has the significance given earlier in this claim

and \( U \) signifies a leaving group,

or

(b) reacting a ketone of the formula

\[
R_1 - C - CH - R_2
\]

wherein \( R_1, R_2 \) and \( R_3 \) have the significances given earlier in this claim,

with a 0-substituted hydroxylamine of the formula

\[
R^4\text{ONH}_2
\]

wherein \( R^4 \) signifies \( C_{1-6}\)-alkyl, \( C_{3-6}\)-cycloalkyl

or \( C_{3-6}\)-alkenyl,
sulphate and concentrated under reduced pressure. The

and, if desired, converting a compound of formula I

obtained into an acid addition salt.

11. A method for the control of fungi in agriculture

and in horticulture, which method comprises treating the
goods to be protected with an effective amount of at
least one of the compounds set forth in claims 1 to 6 or
one of the compositions set forth in claims 8 and 9.

12. The use of one of the compounds set forth in claims

1 to 6 or of one of the compositions set forth in claims
8 and 9 for the control of fungi in agriculture and in
horticulture.

13. A compound of the general formula I, as defined in

claim 1, or an acid addition salt thereof, whenever pro-
duced by a process according to claim 10 or by an obvious
chemical equivalent thereof.

14. A fungicidal composition according to claim 8,

substantially as described herein with reference to
Example 7 or Example 8.

15. A process according to claim 10, substantially as
described herein with reference to any one of Examples 1 to 3.

16. A compound as herein defined.

Dated this 24th day of August 1981

F. HOFFMAN - LA ROCHE & CO.
By its Patent Attorneys
ARTHUR S. CAVE & CO.
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