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(54) Title: FUNGICIDE MIXTURES BASED ON TRIPLE OXIME ETHER DERIVATIVES AND ADDITIONAL FUNGICIDES

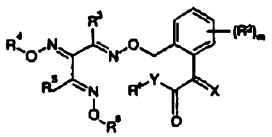
(54) Bezeichnung: FUNGIZIDE MISCHUNGEN AUF DER BASIS VON TRIPELOXIMETHERDERIVATEN UND WEITEREN FUNGIZIDEN

(57) Abstract

The invention relates to fungicide mixtures comprised as active components a) phenylacetic acid derivatives of formula (I) in which the substituents and the index have the meanings cited in the description, and the salts thereof, and b) at least one compound of formulas (II) to (V), whereby the substituents which have the meanings cited in the description are provided in a synergistically effective quantity.

(57) Zusammenfassung

Fungizide Mischungen, enthaltend als aktive Komponenten a) Phenylessigsäurederivate der Formel (I), in der die Substituenten und der Index die in der Beschreibung genannte Bedeutung haben, sowie deren Salze, und b) mindestens eine Verbindung der Formeln (II) bis (V), wobei die Substituenten die in der Beschreibung angegebene Bedeutung haben, in einer synergistisch wirksamen Menge.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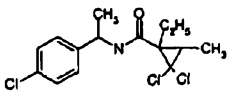
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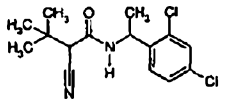
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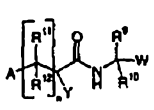
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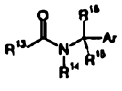
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LEDIGLICH ZUR INFORMATION

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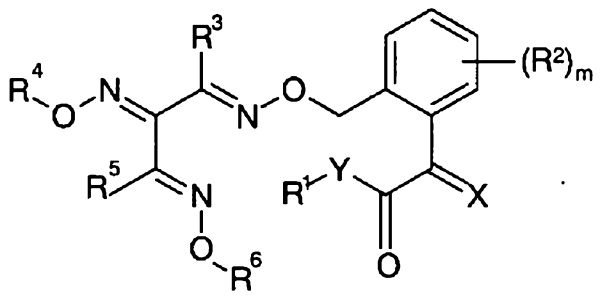
Fungicidal mixtures based on tris(oxime ether) derivatives and further fungicides

The present invention relates to fungicidal mixtures for controlling harmful fungi [lacuna]

a) phenylacetic acid derivatives of the formula I



(I)

in which the substituents and the index have the following meaning:

X is $NOCH_3$, $CHOCH_3$, $CHCH_3$;

Y is O, NR

R^1, R independently of one another are each hydrogen and C_1-C_4-alkyl;

R^2 is cyano, nitro, trifluoromethyl, halogen, C_1-C_4-alkyl and C_1-C_4-alkoxy;

m is 0, 1 or 2, where the radicals R^2 may be different if m is 2;

R^3 is hydrogen, cyano, C_1-C_4-alkyl, C_1-C_4-haloalkyl, C_3-C_6-cycloalkyl;

R^4, R^6 independently of one another are each hydrogen,

are C_1-C_{10}-alkyl, C_3-C_6-cycloalkyl, C_2-C_{10}-alkenyl, C_2-C_{10}-alkynyl, C_1-C_{10}-alkylcarbonyl, C_2-C_{10}-alkenylcarbonyl, C_3-C_{10}-alkynylcarbonyl or C_1-C_{10}-alkylsulfonyl, where these radicals may be partially or fully halogenated or may carry one to

three of the following groups: cyano, nitro, hydroxyl, mercapto, amino, carboxyl, aminocarbonyl, aminothiocarbonyl, halogen, C_1-C_6-alkyl, C_1-C_6-haloalkyl, C_1-C_6-alkylsulfonyl, C_1-C_6-alkylsulfoxyl, C_1-C_6-alkoxy, C_1-C_6-haloalkoxy, C_1-C_6-alkoxycarbonyl, C_1-C_6-alkylthio, C_1-C_6-alkylamino, di-C_1-C_6-alkylamino, C_1-C_6-alkylaminocarbonyl, di-C_1-C_6-alkylaminocarbonyl, C_1-C_6-alkylaminothiocarbonyl, di-C_1-C_6-alkylaminothiocarbonyl, C_2-C_6-alkenyl, C_2-C_6-alkenyloxy, C_3-C_6-cycloalkyl, C_3-C_6-cycloalkyloxy, heterocyclyl, heterocyclyloxy, benzyl, benzyloxy, aryl, aryloxy, arylthio, hetaryl, hetaryloxy and hetarylthio, where the cyclic groups for their part may be partially or fully halogenated or may carry one to three of the following groups: cyano, nitro, hydroxyl, mercapto, amino, carboxyl, aminocarbonyl, aminothiocarbonyl, halogen, C_1-C_6-alkyl, C_1-C_6-haloalkyl, C_1-C_6-alkylsulfonyl, C_1-C_6-alkylsulfoxyl, C_3-C_6-cycloalkyl, C_1-C_6-alkoxy, C_1-C_6-haloalkoxy, C_1-C_6-alkyloxycarbonyl, C_1-C_6-alkylthio, C_1-C_6-alkylamino, di-C_1-C_6-alkylamino, C_1-C_6-alkylaminocarbonyl, di-C_1-C_6-alkylaminocarbonyl, C_1-C_6-alkylaminothiocarbonyl, di-C_1-C_6-alkylaminothiocarbonyl, C_2-C_6-alkenyl, C_2-C_6-alkenyloxy, benzyl, benzyloxy, aryl, aryloxy, arylthio, hetaryl, hetaryloxy, hetarylthio or $C(=NOR^7)$-A_n-R^8;

are aryl, arylcarbonyl, arylsulfonyl, hetaryl, het-arylcarbonyl or hetarylsulfonyl, where these radicals may be partially or fully halogenated or may carry one to three of the following groups: cyano, nitro, hydroxyl, mercapto, amino, carboxyl, aminocarbonyl, aminothiocarbonyl, halogen, C_1-C_6-alkyl, C_1-C_6-haloalkyl, C_1-C_6-alkylcarbonyl, C_1-C_6-alkylsulfonyl, C_1-C_6-alkylsulfoxyl, C_3-C_6-cycloalkyl, C_1-C_6-alkoxy, C_1-C_6-haloalkoxy, C_1-C_6-alkyloxycarbonyl, C_1-C_6-alkylthio, C_1-C_6-alkylamino, di-C_1-C_6-alkylamino, C_1-C_6-alkylaminocarbonyl, di-C_1-C_6-alkylaminocarbonyl, C_1-C_6-alkylaminothiocarbonyl, di-C_1-C_6-alkylaminothiocarbonyl, C_2-C_6-alkenyl, C_2-C_6-alkenyloxy, benzyl, benzyloxy, aryl, aryloxy, hetaryl, hetaryloxy or $C(=NOR^7)$-A_n-R^8;

R^5 is hydrogen,

is C_1-C_6-alkyl, C_2-C_6-alkenyl, C_2-C_6-alkynyl, where the hydrocarbon radicals of these groups may be partially or fully halogenated or may carry one to three of the following radicals: cyano, nitro, hydroxyl, mercapto, amino, carboxyl, aminocarbonyl, aminothiocarbonyl, halogen, C_1-C_6-alkylaminocarbonyl, di-C_1-C_6-alkylaminocarbonyl, C_1-C_6-alkylaminothiocarbonyl, di-C_1-C_6-alkylaminothiocarbonyl, C_1-C_6-alkylsulfonyl, C_1-C_6-alkylsulfoxyl, C_1-C_6-alkoxy, C_1-C_6-haloalkoxy, C_1-C_6-alkoxycarbonyl, C_1-C_6-alkylthio, C_1-C_6-alkylamino, di-C_1-C_6-alkylamino, C_2-C_6-alkenyloxy, C_3-C_6-cycloalkyl, C_3-C_6-cycloalkyloxy, heterocyclyl, heterocyclyloxy, aryl, aryloxy, aryl-C_1-C_4-alkoxy, arylthio, aryl-C_1-C_4-alkylthio, hetaryl, hetaryloxy, hetaryl-C_1-C_4-alkoxy, hetarylthio, hetaryl-C_1-C_4-alkylthio, where the cyclic radicals for their part may be partially or fully halogenated and/or may carry one to three of the following groups: cyano, nitro, hydroxyl, mercapto, amino, carboxyl, aminocarbonyl, aminothiocarbonyl, C_1-C_6-alkyl, C_1-C_6-haloalkyl, C_1-C_6-alkylsulfonyl, C_1-C_6-alkylsulfoxyl, C_3C_6-cycloalkyl [sic], C_1-C_6-alkoxy, C_1-C_6-haloalkoxy, C_1-C_6-alkoxycarbonyl, C_1-C_6-alkylthio, C_1-C_6-alkylamino, di-C_1-C_6-alkylamino, C_1-C_6-alkylaminocarbonyl, di-C_1-C_6-alkylaminocarbonyl, C_1-C_6-alkylaminothiocarbonyl, di-C_1-C_6-alkylaminothiocarbonyl, C_2-C_6-alkenyl, C_2-C_6-alkenyloxy, benzyl, benzyloxy, aryl, aryloxy, arylthio, hetaryl, hetaryloxy, hetarylthio and $C(=NOR^7)$-A_n-R^8;

is C_3-C_6-cycloalkyl, C_3-C_6-cycloalkenyl, heterocyclyl, aryl, hetaryl, where the cyclic radicals may be partially or fully halogenated or may carry one to three of the following groups: cyano, nitro, hydroxyl, mercapto, amino, carboxyl, aminocarbonyl, aminothiocarbonyl, halogen, C_1-C_6-alkyl, C_1-C_6-haloalkyl, C_1-C_6-alkylsulfonyl, C_1-C_6-alkylsulfoxyl, C_3-C_6-cycloalkyl, C_1-C_6-alkoxy, C_1-C_6-haloalkoxy, C_1-C_6-alkoxycarbonyl, C_1-C_6-alkylthio, C_1-C_6-alkylamino, di-C_1-C_6-alkylamino, C_1-C_6-alkylaminocarbonyl, di-C_1-C_6-alkylaminocarbonyl, C_1-C_6-alkylaminothiocarbonyl, di-C_1-C_6-alkylaminothiocarbonyl, C_2-C_6-alkenyl, C_2-C_6-alkenyloxy, benzyl, benzyloxy, aryl, aryloxy, hetaryl and hetaryloxy;

where

A is oxygen, sulfur or nitrogen and where the nitrogen carries hydrogen or C_1-C_6-alkyl;

n is 0 or 1;

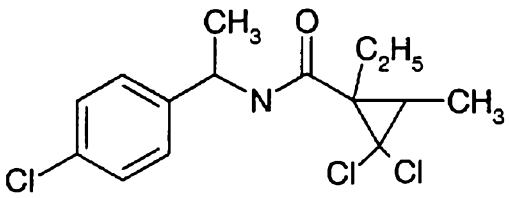
R^7 is hydrogen or C_1-C_6-alkyl and

R^8 is hydrogen or C_1-C_6-alkyl,

and their salts,

and

b) at least one fungicide selected from the fungicides of the formulae II to V



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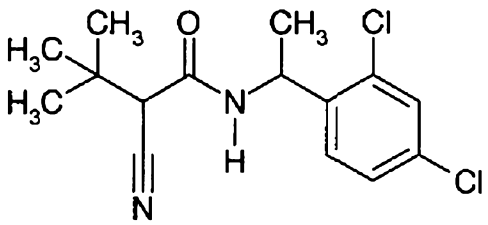

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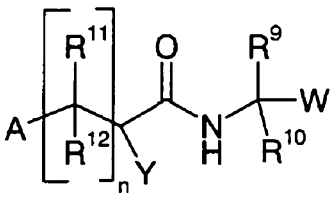

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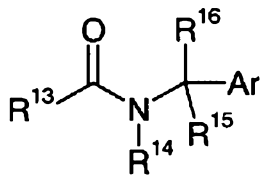


(V)

where the substituents have the following meaning:

A is C_3-C_6-cycloalkyl which may carry one to three substituents selected from the group consisting of halogen and C_1-C_3-alkyl;

R^9 is C_1-C_6-alkyl or C_2-C_6-alkenyl, where these radicals may be partially or fully halogenated and/or may carry one or two of the following groups: C_1-C_4-alkoxy, C_1-C_4-haloalkoxy, C_1-C_4-alkylthio, C_1-C_4-alkoxycarbonyl, C_3-C_6-cycloalkyl and phenyl, where the phenyl may be partially or fully halogenated and/or may carry one to three of the following radicals: nitro, cyano, C_1-C_4-alkyl, C_1-C_4-haloalkyl, C_1-C_4-alkoxy, C_1-C_4-haloalkoxy, C_1-C_4-alkylthio, C_3-C_6-cycloalkyl or heterocyclyl;

R^{10}, R^{11}, R^{12} are each hydrogen or have one of the meanings of the radical R^9 independently of this meaning;

n is 0 or 1;

Y is cyano or halogen;

W is phenyl, naphthyl or heteroaryl, where these radicals may carry one to three of the following groups: nitro, halogen, cyano, C_1-C_4-alkyl, C_1-C_4-haloalkyl, C_1-C_4-alkoxy, C_1-C_4-haloalkoxy, C_1-C_4-alkylthio, C_3-C_6-cycloalkyl and C_1-C_4-alkoxycarbonyl,

R^{13} is C_6-C_{15}-bicycloalkyl or C_7-C_{15}-bicycloalkenyl, where these radicals may be completely halogenated and, if they are not completely halogenated, two carbon atoms of these radicals together with a C_3-C_5-alkylidene group may form a five- to seven-membered saturated carbocyclic ring and/or may carry one or independently of one another two,

three, four or five of the following groups: cyano, C_1-C_4-alkyl, C_1-C_4-haloalkyl, C_1-C_4-alkoxy, C_1-C_4-haloalkoxy and aryl, where the aryl may be partially or fully halogenated and/or may carry one or independently of one another two or three of the following substituents: nitro, cyano, C_1-C_4-alkyl, C_1-C_4-haloalkyl, C_1-C_4-alkoxy, C_1-C_4-haloalkoxy and C_1-C_4-alkylthio;

R^{14}, R^{15}, R^{16} independently of one another are hydrogen,

are C_1-C_8-alkyl which may be partially or fully halogenated and/or may carry one or two of the following groups: C_1-C_4-alkoxy, C_1-C_4-haloalkoxy, C_1-C_4-alkylthio, C_3-C_7-cycloalkyl, C_5-C_7-cycloalkenyl, where the cyclic groups for their part may carry one or independently of one another two or three halogen atoms, C_1-C_3-alkyl groups and/or C_1-C_3-alkoxy groups and aryl, where the aryl may be partially or fully halogenated and/or may carry one or independently of one another two or three of the following substituents: nitro, cyano, C_1-C_4-alkyl, C_1-C_4-haloalkyl, C_1-C_4-alkoxy, C_1-C_4-haloalkoxy ad C_1-C_4-alkylthio or

are C_3-C_6-cycloalkyl, C_3-C_6-cycloalkenyl or heterocyclyl, where these radicals may be partially or fully halogenated and/or may carry one or independently of one another two or three of the following groups: cyano, C_1-C_6-alkyl, C_1-C_6-haloalkyl, C_2-C_6-alkenyl, C_1-C_6-alkoxy and C_1-C_6-alkylthio;

Ar is aryl or heteroaryl, where these radicals may carry one or independently of one another two or three of the following groups: halogen, cyano, C_1-C_4-alkyl, C_1-C_4-alkoxyalkyl, C_1-C_4-haloalkyl, C_1-C_4-alkoxy, C_1-C_4-haloalkoxy, C_1-C_4-alkylthio, C_1-C_4-alkoxycarbonyl, aryl, aryloxy and heteroaryl, where the rings in these groups for their part may carry one or independently of one another two or three of the following substituents: halogen, cyano, C_1-C_4-alkyl, C_1-C_4-alkoxyalkyl, C_1-C_4-haloalkyl, C_1-C_4-alkoxy, C_1-C_4-haloalkoxy, C_1-C_4-alkylthio and C_1-C_4-alkoxycarbonyl,

[lacuna]

It is an object of the present invention to provide fungicidal mixtures having good fungicidal activity, in particular against fungal diseases in rice, exceeding the activity of the mixture components on their own.

We have found that this object is achieved by the mixtures according to claim 1.

The compounds of the formula I are known per se and are described in the literature (WO 97/15552).

The fungicides of the formulae II and III are also known and described in the literature. Moreover, they are commercially available under the trade names given hereinbelow in brackets:

II: EP 341,475, common name: carpropamide (trade name:WIN®, from Bayer)

III: CAS RN 139 920-32-4, proposed common name: dichlocymet (development product of Sumitomo)

The compounds V, and also processes for their preparation, are described in WO 97/35838.

The compounds IV and processes for their preparation are explained in a more detailed manner below; the corresponding compounds are described in the older patent application PCT/EP 98/01031 or DE 19710618.8.

Owing to their C=C and C=N double bonds, the preparation of the compounds I may yield E/Z isomer mixtures which can be separated into the individual compounds in a customary manner, for example by crystallization or chromatography.

However, if the synthesis yields isomer mixtures, a separation is generally not necessarily required since in some cases the individual isomers can be converted into one another during the preparation for use or upon use (for example under the action of light, acids or bases). Similar conversions may also occur after the use, for example in the treatment of plants in the treated plant or in the harmful fungus or animal pest to be controlled.

With regard to the C=X double bond, preference is given to the cis isomers of the compounds I (configuration based on the $-OCH_3$ or the $-CH_3$ group in relation to the $-CO_2R^1$ group) with respect to their activity.

With regard to the $-C(R^3)=NOCH_2-$ double bond, preference is given to the cis isomers of the compounds I (configuration based on the radical R^3 in relation to the $-OCH_2-$ group) with respect to their activity.

With respect to their biological activity, preference is given to compounds of the formula I in which m is 0.

Likewise, preference is given to compounds of formula I in which R^1 is methyl.

Besides, preference is given to compounds I in which R^3 is hydrogen, cyano, cyclopropyl, methyl, ethyl, 1-methylethyl or CF_3.

Moreover, preference is given to compounds I in which R^3 is methyl.

Besides, preference is given to compounds I in which R^3 is cyano.

Furthermore, preference if given to compounds I in which R^3 is cyclopropyl.

Additionally, preference is given to compounds I in which R^3 is CF_3.

Additionally, preference is given to compounds I in which R^5 is hydrogen, cyclopropyl, methyl, ethyl, isopropyl, unsubstituted or substituted aryl or hetaryl.

Moreover, preference is given to compounds I in which R^5 is methyl.

Additionally, preference is given to compounds I in which R^5 is ethyl.

Moreover, preference is given to compounds I in which R^5 is isopropyl.

Moreover, preference is given to compounds I in which R^5 is cyclopropyl.

Moreover, preference is given to compounds I in which R^5 is CF_3.

Additionally, preference is given to compounds I in which R^5 is unsubstituted or substituted aryl or hetaryl.

Additionally, preference is given to compounds I in which R^5 is unsubstituted or substituted pyridyl, pyrimidyl, pyrazinyl, pyridazinyl or triazinyl.

Additionally, preference is given to compounds I in which R^5 is unsubstituted or substituted furyl, thienyl or pyrrolyl.

Additionally, preference is given to compounds I in which R^5 is unsubstituted or substituted oxazolyl, thiazolyl, isoxazolyl, isothiazolyl, pyrazolyl or imidazolyl.

Additionally, preference is given to compounds I in which R^5 is unsubstituted or substituted oxdiazolyl [sic], thiadiazolyl or tri-azolyl.

Moreover, preference is given to compounds I in which R^5 is phenyl which is unsubstituted or carries one or two of the following groups: nitro, cyano, hydroxyl, amino, aminocarbonyl, aminothiocarbonyl, halogen, C_1-C_4-alkyl, C_1-C_4-haloalkyl, C_1-C_4-alkoxy, C_1-C_4-haloalkoxy, C_1-C_4-alkylamino, di-C_1-C_4-alkylamino, C_1-C_4-alkylsulfonyl, C_1-C_4-alkoxycarbonyl, C_1-C_4-alkylaminocarbonyl or di-C_1-C_4-alkylaminocarbonyl.

Moreover, preference is given to compounds I in which R^4 is hydrogen, C_1-C_6-alkyl, C_2-C_6-alkenyl, C_2-C_6-alkynyl, allyl, arylalkyl, hetarylalkyl, aryloxyalkyl, hetaryloxyalkyl, aryl or hetaryl.

Additionally, preference is given to compounds I in which R^4 is C_1-C_6-alkyl.

Further preferred compounds I are disclosed in WO 97/15,552.

With respect to the fungicidal activity against harmful fungi, such as, for example, *Pyricularia oryzae*, preference is given to the cycloalkylalkanecarboxamides IV which have the substituents

below, where the preference in each case can be seen on its own or in combination:

The carbon atom carrying the groups R^9 and R^{10} preferably has the R configuration.

Preference is given to cycloalkylalkanecarboxamides IV in which R^9 is methyl and R^{10} is either methyl or hydrogen; particular preference is given to compounds IV in which R^9 is methyl and R^{10} is hydrogen.

Furthermore, preference is given to cycloalkylalkanecarboxamides of the formula IV in which W is unsubstituted or substituted phenyl which is in particular substituted in the 2-position or in positions 2 and 4. Very particular preference is given to substitution in the 4-position of the phenyl ring and here preferably to substitution by cyano or methoxy, preferably by methyl and in particular by halogen, where in this case preference is in turn given to chlorine.

Additionally, preference is given to cycloalkylalkanecarboxamides IV where n = 1. The substituents R^3 and R^4 are preferably C_1-C_4-alkyl and in particular methyl. Preference is also given to the combination in which one of the two substituents is hydrogen and the other is C_1-C_4-alkyl and in particular methyl.

Furthermore, preference is given to α-chloro or α-bromocycloalkylalkanecarboxamides IV (Y = bromine or chlorine). Particular preference is given to α-cyanocycloalkylalkanecarboxamides IV (Y = cyano).

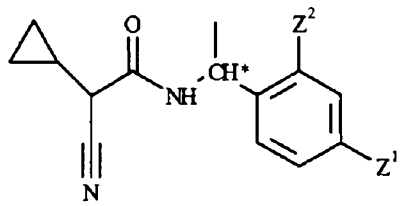
Finally, preference is given to cycloalkylalkanecarboxamides of the formula IV in which A is unsubstituted or substituted cyclopropyl. Particular preference is given to cyclopropyl carrying one to three substituents selected from the group consisting of chlorine and C_1-C_3-alkyl, in particular methyl. Chlorinated cyclopropyl preferably carries two chlorine atoms, these being in a *geminal* position at the cyclopropane ring. Alkylated or preferably methylated cyclopropyl preferably carries one of the alkyl(methyl) substituents at the carbon atom of the site where the cyclopropane ring is linked to the remainder of the molecule.

With respect to their use, particular preference is given to the compounds I which are compiled in the Tables 1 to 13 below.

Table 1

Carboxamides IVa.001 to IVa.108 of the formula IVa

(* = Configuration of the atom labeled "*"; R = R configuration; S = S configuration; rac. = racemic)



IVa

No.	Z^1	Z^2	*
IVa.001	H	H	R
IVa.002	H	H	S
IVa.003	H	H	rac.
IVa.004	H	Cl	R
IVa.005	H	Cl	S
IVa.006	H	Cl	rac.
IVa.007	H	CH_3	R
IVa.008	H	CH_3	S
IVa.009	H	CH_3	rac.
IVa.010	H	OCH_3	R
IVa.011	H	OCH_3	S
IVa.012	H	OCH_3	rac.
IVa.013	H	F	R
IVa.014	H	F	S
IVa.015	H	F	rac.
IVa.016	H	CN	R
IVa.017	H	CN	S
IVa.018	H	CN	rac.
IVa.019	Cl	H	R
IVa.020	Cl	H	S
IVa.021	Cl	H	rac.
IVa.022	Cl	Cl	R
IVa.023	Cl	Cl	S

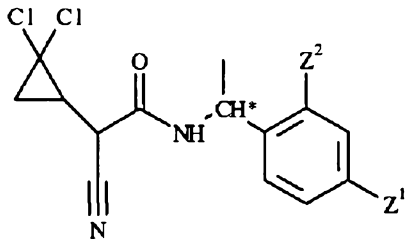
No.	Z^1	Z^2	*
IVa.024	Cl	Cl	rac.
IVa.025	Cl	CH_3	R
IVa.026	Cl	CH_3	S
IVa.027	Cl	CH_3	rac.
IVa.028	Cl	OCH_3	R
IVa.029	Cl	OCH_3	S
IVa.030	Cl	OCH_3	rac.
IVa.031	Cl	F	R
IVa.032	Cl	F	S
IVa.033	Cl	F	rac.
IVa.034	Cl	CN	R
IVa.035	Cl	CN	S
IVa.036	Cl	CN	rac.
IVa.037	CH_3	H	R
IVa.038	CH_3	H	S
IVa.039	CH_3	H	rac.
IVa.040	CH_3	Cl	R
IVa.041	CH_3	Cl	S
IVa.042	CH_3	Cl	rac.
IVa.043	CH_3	CH_3	R
IVa.044	CH_3	CH_3	S
IVa.045	CH_3	CH_3	rac.
IVa.046	CH_3	OCH_3	R
IVa.047	CH_3	OCH_3	S
IVa.048	CH_3	OCH_3	rac.
IVa.049	CH_3	F	R
IVa.050	CH_3	F	S
IVa.051	CH_3	F	rac.
IVa.052	CH_3	CN	R
IVa.053	CH_3	CN	S
IVa.054	CH_3	CN	rac.
IVa.055	OCH_3	H	R
IVa.056	OCH_3	H	S
IVa.057	OCH_3	H	rac.
IVa.058	OCH_3	Cl	R
IVa.059	OCH_3	Cl	S
IVa.060	OCH_3	Cl	rac.
IVa.061	OCH_3	CH_3	R
IVa.062	OCH_3	CH_3	S

No.	Z^1	Z^2	*
IVa.063	OCH_3	CH_3	rac.
IVa.064	OCH_3	OCH_3	R
IVa.065	OCH_3	OCH_3	S
IVa.066	OCH_3	OCH_3	rac.
IVa.067	OCH_3	F	R
IVa.068	OCH_3	F	S
IVa.069	OCH_3	F	rac.
IVa.070	OCH_3	CN	R
IVa.071	OCH_3	CN	S
IVa.072	OCH_3	CN	rac.
IVa.073	F	H	R
IVa.074	F	H	S
IVa.075	F	H	rac.
IVa.076	F	Cl	R
IVa.077	F	Cl	S
IVa.078	F	Cl	rac.
IVa.079	F	CH_3	R
IVa.080	F	CH_3	S
IVa.081	F	CH_3	rac.
IVa.082	F	OCH_3	R
IVa.083	F	OCH_3	S
IVa.084	F	OCH_3	rac.
IVa.085	F	F	R
IVa.086	F	F	S
IVa.087	F	F	rac.
IVa.088	F	CN	R
IVa.089	F	CN	S
IVa.090	F	CN	rac.
IVa.091	CN	H	R
IVa.092	CN	H	S
IVa.093	CN	H	rac.
IVa.094	CN	Cl	R
IVa.095	CN	Cl	S
IVa.096	CN	Cl	rac.
IVa.097	CN	CH_3	R
IVa.098	CN	CH_3	S
IVa.099	CN	CH_3	rac.
IVa.100	CN	OCH_3	R
IVa.101	CN	OCH_3	S

No.	Z^1	Z^2	*
IVa.102	CN	OCH_3	rac.
IVa.103	CN	F	R
IVa.104	CN	F	S
IVa.105	CN	F	rac.
IVa.106	CN	CN	R
IVa.107	CN	CN	S
IVa.108	CN	CN	rac.

Table 2

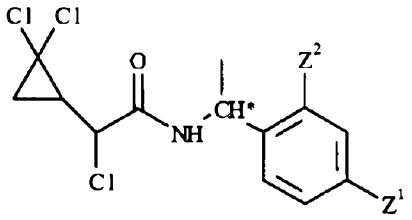
Carboxamides IVb.001 to IVb.108 of the formula IVb in which the meanings of the combinations of Z^1, Z^2 and "*" are given by the rows of Table 1.



IVb

Table 3

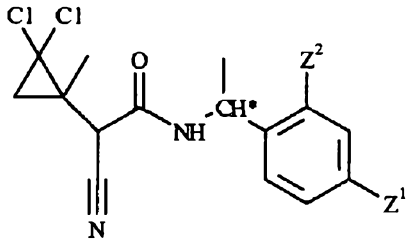
Carboxamides IVc.001 to IVc.108 of the formula IVc in which the meanings of the combinations of Z^1, Z^2 and "*" are given by the rows of Table 1.



IVc

Table 4

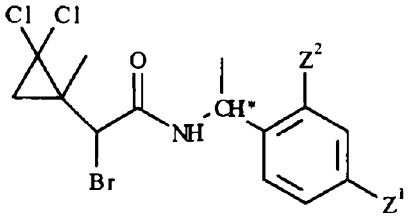
Carboxamides IVd.001 to IVd.108 of the formula IVd in which the meanings of the combinations of Z^1, Z^2 and "*" are given by the rows of Table 1.



IVd

Table 5

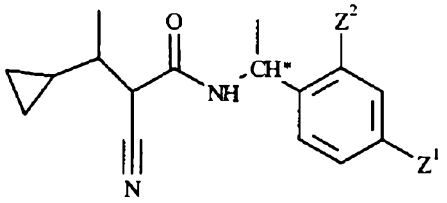
Carboxamides IVe.001 to IVe.108 of the formula IVe in which the meanings of the combinations of Z^1, Z^2 and "*" are given by the rows of Table 1.



Ie

Table 6

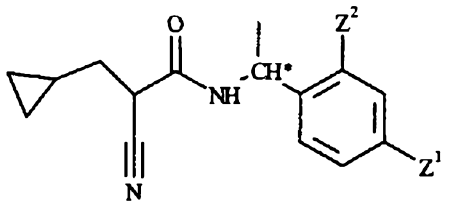
Carboxamides IVf.001 to IVf.108 of the formula IVf in which the meanings of the combinations of Z^1, Z^2 and "*" are given by the rows of Table 1.



IVf

Table 7

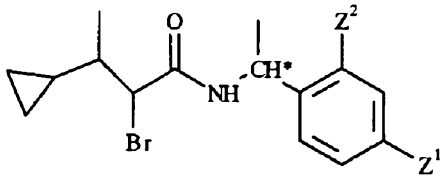
Carboxamides IVg.001 to IVg.108 of the formula IVg in which the meanings of the combinations of Z^1, Z^2 and "*" are given by the rows of Table 1.



IVg

Table 8

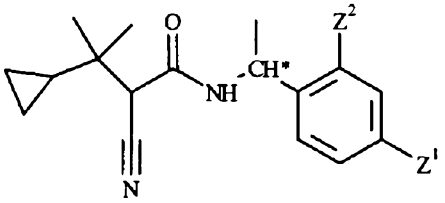
Carboxamides IVh.001 to IVh.108 of the formula IVh in which the meanings of the combinations of Z^1, Z^2 and "*" are given by the rows of Table 1.



IVh

Table 9

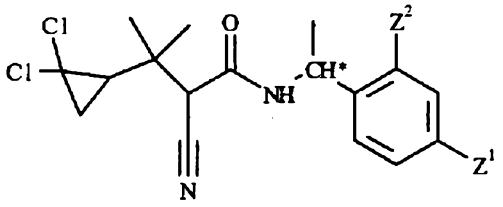
Carboxamides IVi.001 to IVi.108 of the formula IVi in which the meanings of the combinations of Z^1, Z^2 and "*" are given by the rows of Table 1.



IVi

Table 10

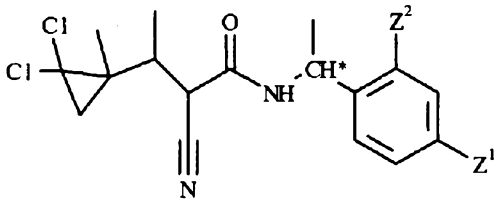
Carboxamides IVk.001 to IVk.108 of the formula IVk in which the meanings of the combinations of Z^1, Z^2 and "*" are given by the rows of Table 1.



IVk

Table 11

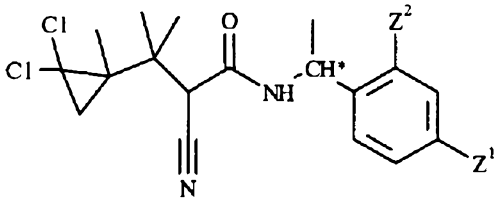
Carboxamides IVm.001 to IVm.108 of the formula IVm in which the meanings of the combinations of Z^1, Z^2 and "*" are given by the rows of Table 1.



IVm

Table 12

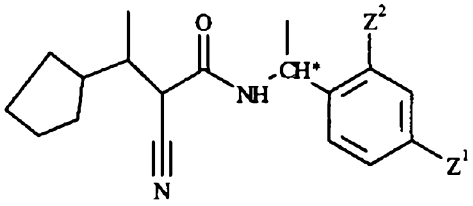
Carboxamides IVn.001 to IVn.108 of the formula IVn in which the meanings of the combinations of Z^1, Z^2 and "*" are given by the rows of Table 1.



IVn

Table 13

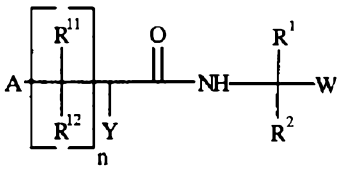
Carboxamides IVo.001 to IVo.108 of the formula IVo in which the meanings of the combinations of Z^1, Z^2 and "*" are given by the rows of Table 1.



IVo

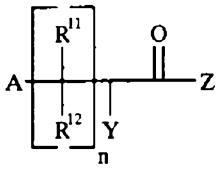
Furthermore, we have found processes by which the carboxamides IV can be prepared in good yields.

In a preferred process, the carboxamides IV



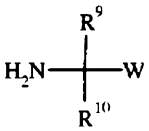
IV

are obtained by reacting the carboxylic acid derivatives VI,



VI

with amines of the formula VII



VII

The amide formation is carried out according to the processes known from the literature. The free carboxylic acids of the formula VI' where Z is hydroxyl are generally first converted into an activated carboxylic acid derivative VI where Z is, for example, chlorine.

The activation of the carboxylic acids VI' can preferably also be carried out in situ by using the carboxylic acids VI' directly with addition of, for example, dicyclohexylcarbodiimide, ethyl chloroformate, diethyl cyanophosphonate, triphenylphosphine/azodicarboxylic ester, 2-pyridine disulfide/triphenylphosphine,

carbonyldiimidazole, thionyl chloride, phosphorus trichloride, phosphorus pentachloride, etc. In general, for example the carbodiimides are added in equimolar amounts, based on the carboxylic acids VI'.

Activation of the carboxylic acids via acyl cyanides is carried out, for example, by reacting the carboxylic acids VI' with diethyl cyanophosphonate, preferably in an inert solvent such as tetrahydrofuran, toluene or dichloromethane (cf. Tetrahedron Lett. 18 (1973), 1595-8).

Activation via anhydrides is carried out, for example, by reacting the carboxylic acids VI' with chloroformates such as ethyl chloroformate, generally in the presence of bases and, if appropriate, in an inert solvent, such as toluene or tetrahydrofuran (cf. "Houben-Weyl", 4th Ed. (1974), 15/1, pages 28-32).

The amide formation is preferably carried out in the presence of bases, such as tertiary amines, for example triethylamine or dimethylcyclohexylamine, alkali metal carbonates, alkali metal hydroxides, pyridine, etc. The starting materials and the auxiliary base are advantageously employed in equimolar amounts. In certain cases, a slight excess of auxiliary base of from 0.1 - 0.5 equivalents may be advantageous.

Suitable solvents are aliphatic hydrocarbons such as hexane and ligroin, aromatic hydrocarbons such as toluene and xylene, chlorinated hydrocarbons such as methylene chloride and 1,2-dichloroethane, ethers such as methyl tert-butyl ether and tetrahydrofuran, polar aprotic solvents, such as acetonitrile and dimethylformamide or esters such as ethyl acetate, or mixtures of these.

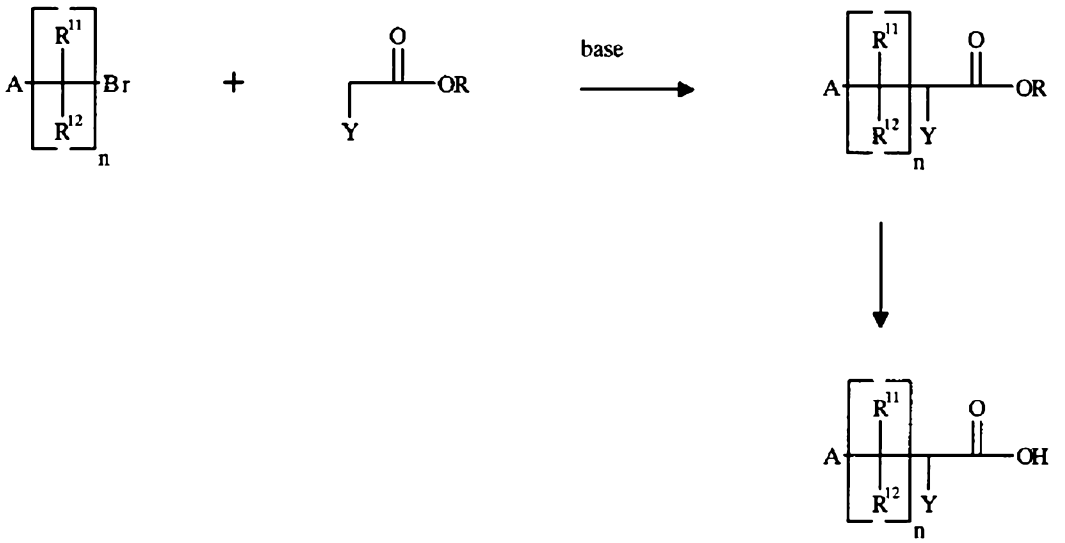
The molar ratio of carboxylic acid derivative VI to amine VII is generally from 0.8 to 1.5 and preferably from 0.9 to 1.1.

After the reaction has gone to completion, work-up is carried out as usual, for example by introducing the reaction mixture into water, followed by extraction of the amide.

The amines of the formula VII are known or can be easily obtained (cf. Organikum (1993) Barth Verlagsgesellschaft mbH Leipzig, p. 509 ff.; Indian J. Chem. 10 (1972), 366).

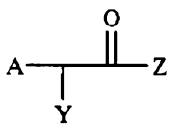
The preparation of α-cyanocyclopropane acetic acid is described in Org. Prep. Proced. Int. 5 (1973), 25-29. Scheme 1 shows a general route for constructing carboxylic acids of the formula VI' (cf. Collect. Czech. Chem. Commun. 48 (1983), 1597-1601 and J. Polym. Sci., Polym. Chem. Ed. 14 (1976), 2357-9).

Scheme 1

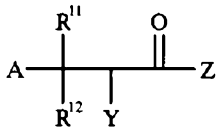


VI'

Carboxylic acid derivatives of the formula VIA can furthermore be prepared in accordance with Scheme 2.

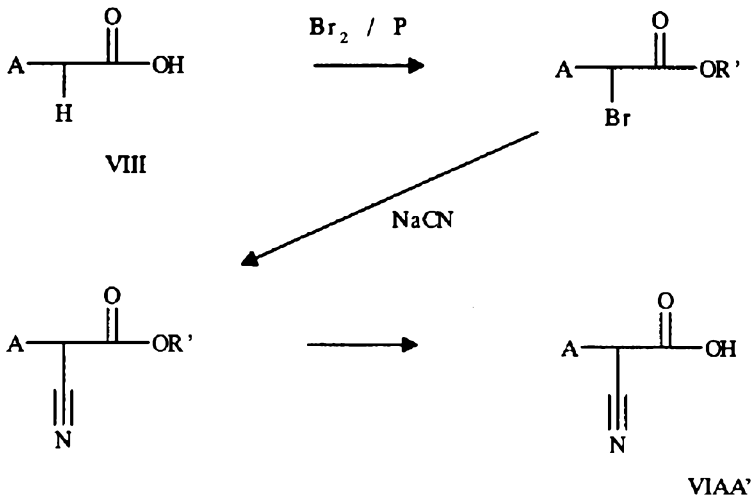


VIA



VIB

Scheme 2

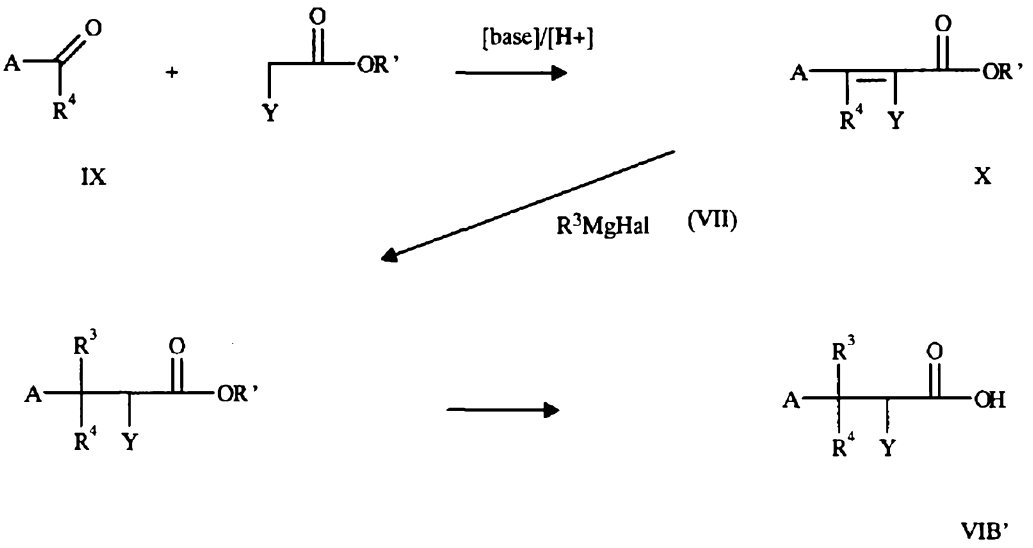


The cycloalkylacetic acids of the formula VIII where A is as defined in claim 1 are known (J. Chem. Technol. Biotechnol., Chem. Technol., 33A (1983), 109-15; NL 65 06 881; Chem. Ber. 41 (1908), 2627; Chem. Ber. 35 (1902), 2688).

The cycloalkylacetic acids VIII can be brominated in the α position in accordance with the protocol in J. Am. Chem. Soc 70 (1948), 3626. Work-up in the presence of a C_1-C_6-alcohol leads directly to the corresponding ester. The subsequent bromine/cyano exchange is carried out as described in Synth. Commun. 23 (1993), 2323-9. The hydrolysis of the esters to give the carboxylic acids VIAA' is carried out by standard procedures (Organikum 1993 Barth Verlagsgesellschaft mbH, Leipzig, p. 431ff.).

The carboxylic acid derivatives of the formula VIB can be obtained, for example, by the route shown in Scheme 3.

Scheme 3



The starting materials, acyl- or formylcycloalkanes of the formula IX, are generally accessible (cf. inter alia J. Chem. Soc., Perkin Trans. I, 6 (1994), 739 -52). These are reacted in a Knoevenagel reaction with C_1-C_6-alkyl α-halo- or α-cyanoacetates to give the Michael systems X (cf. Chem. Heterocycl. Compd. 24 (1988), 860-4).

The condensation is generally carried out in a solvent that is immiscible with water, such as hexane, toluene or xylene, with removal of the water that is formed during the reaction. To this end, the reaction mixture is heated at the boil and under reflux for several hours.

Bases, such as, for example, piperidine, pyridine, ammonia or β-alanine, in the presence of an acid, such as, for example, glacial acetic acid, serve as catalysts.

An alkyl Grignard reagent of the formula XI where R^3 is as defined in claim 1 and Hal is chlorine, bromine or iodine is subsequently added to a Michael system of the formula X to give saturated systems of the type VIB.

The reaction is carried out in solvents which are inert under the reaction conditions. Particular preference is given to ethers such as tetrahydrofuran, diethyl ether, dimethoxyethane or methyl tert-butyl ether. The reaction temperature is generally set to from -10 to 80°C and preferably to from 10 to 60°C.

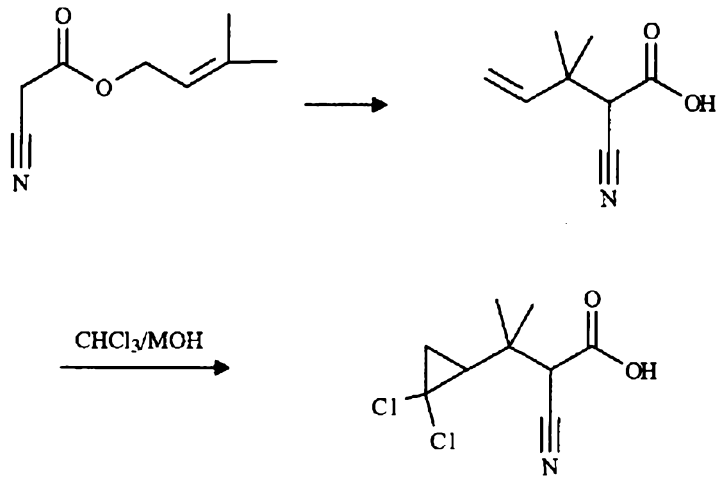
The Grignard reagent XI is generally employed in equimolar amounts, based on the Michael system X. In some cases, it proves advantageous to employ an excess of from 0.2 to 0.5 molar equivalents of the Grignard reagent.

In general, the addition is carried out, catalyzed by copper, by addition of 1 - 10 mol% of, for example, copper(I) iodide. This results in a higher selectivity for 1,2-addition versus 1,4-addition.

The free carboxylic acids VIB' are finally prepared by alkaline hydrolysis of the corresponding esters (Organikum 1993 Barth Verlagsgesellschaft mbH, Leipzig, p. 431ff.).

An elegant route to 2-cyano-3-(2,2-dichlorocyclopropyl)-3-methylbutanoic acid is shown in Scheme 4.

Scheme 4



The preparation of 2-cyano-3,3-dimethylpent-4-enoic acid from the 3-methylbut-2-enyl ester of cyanoacetic acid is described in DE 26 49 711 and Res. Discl. 249 (1985), 55. By addition of dichlorocarbene, which is obtainable from chloroform and alkali metal hydroxides by standard methods, 2-cyano-3-(2,2-dichloro-cyclopropyl)-3-methylbutanoic acid can be obtained directly. To increase the yield it is advantageous to protect the carboxylic acid function prior to the cyclopropanation step (for example by conversion into the tert-butyl ester).

By the abovementioned processes, carboxylic acid derivatives VI are obtainable which are suitable, for example, for preparing the carboxamides IV according to the invention.

The particularly preferred embodiments of the carboxylic acid derivatives VI with respect to the substituents R^{11}, R^{12}, A and Y correspond to those of the carboxamides IV.

Z is a nucleophilically replaceable radical, such as hydroxyl, C_1-C_4-alkoxy, halogen, for example bromine or chlorine, hetaryl, for example imidazolyl or pyridyl, carboxylate, for example acetate or trifluoroacetate, etc.

Particular preference is given to carboxylic acid derivatives of the formula VI in which n is 1 and/or A is unsubstituted or substituted cyclopropyl. In the case that n is 0, preference is given to carboxylic acid derivatives of the formula VIA in which A is cyclopropyl which may carry one to three substituents, such as, for example, chlorine and/or C_1-C_3-alkyl. Chlorinated cyclopropyl preferably carries two chlorine atoms in a *geminal* position at the cyclopropane ring.

The compounds V can be prepared starting from the corresponding carboxylic acids XIIa

$$R^{13}\text{-COOH} \quad \text{(XIIa)}$$

by reaction with amines XIII (the literature references "Houben-Weyl" are based on : Houben-Weyl, Methoden der Organischen Chemie, 4th Edition, Thieme Verlag, Stuttgart).

The carboxylic acids XIIa are known from EP-A 653 418.

The amines XIII are also generally known or obtainable by known methods (cf. WO-A 95/23 784).

The reaction is preferably carried out by initially converting the carboxylic acids XIIa into carboxyl-activated derivatives XII, especially into acyl halides - for example the chlorides -, acyl cyanides or anhydrides (cf. Tetrahedron Letters, Volume 18, page 1595 to page 1598 (1973) or "Houben-Weyl", Volume 15/1, page

28 to page 32). These derivatives XII are then reacted with the amines XIII in the presence of bases.

Suitable for preparing the acyl cyanides is, for example, the reaction of the carboxylic acids XIIa with diethyl cyanophosphonate, especially in an inert solvent such as tetrahydrofuran, toluene or dichloromethane.

To prepare the carboxyl-activated anhydrides, preference is given to reacting the carboxylic acids XIIa with chloroformates such as isobutyl chloroformate in the presence of bases and, if appropriate, in an inert solvent such as toluene or tetrahydrofuran.

The reaction of the amines XIII with the carboxyl-activated carboxylic acids III [sic] is preferably carried out in a solvent such as dichloromethane, tetrahydrofuran or toluene.

The amines XIII themselves may also act as the bases, and they are usually recovered from the crude product.

In a preferred embodiment of this process step, the carboxylic acid XII [sic], the amine XIII, the reagent suitable for preparing the carboxyl-activated derivative of the carbamoylcarboxylic acid XII and the base are reacted in a one-pot process, if appropriate in an inert solvent.

The reaction mixture obtained in this manner is worked-up in a customary manner to give the compounds V, for example by mixing with water, separation of the phases and, if appropriate, chromatographic purification of the crude products. Some of the end products are obtained in the form of colorless or slightly brownish, viscous oils, which can be freed of volatile components under reduced pressure and at moderately elevated temperature. If the end products are obtained as solids, purification can also be carried out, for example, by recrystallization or digestion.

Depending on the nature of the substituents, the compounds of the formula V may be present as geometrical and/or optical isomers or isomer mixtures. In particular, the carbon atom in the compounds V which carries the groups R^3 and R^4 may have R or S configuration according to IUPAC nomenclature. Both the pure isomers described here and the mixtures of the isomers have fungicidal activity.

In the compounds V, with respect to the radical R^{13}, the remaining part of the molecule may be arranged exo or endo. Both isomers and their mixtures are in each case fungicidally active.

With respect to their biological action against harmful fungi, preference is given to compounds V in which the carbon atom carrying groups R^{15} and R^{16} has R configuration.

Moreover, preference is given to compounds V in which R^{15} is hydrogen and R^{16} is C_1-C_4-alkyl, especially methyl.

Furthermore, preference is given to compounds V in which Ar is optionally substituted phenyl which is substituted in particular in the 2-position or in the 2- and 4-position and especially in the 4-position. Preferred sole substituents in the 4-position are cyano, preferably methyl and in particular halogen, especially chlorine.

Additionally, preference is given to compounds V in which R^{13} is unsubstituted or substituted bicycloalkyl having 6 to 10 carbon atoms.

Moreover, preference is given to compounds V in which R^{13} is unsubstituted or substituted bicycloalkenyl having 7 to 10 carbon atoms.

Particular preference with respect to their use is given to the compounds compiled in Tables 1 to 29 of WO-A 97/35838.

In the definition of the compounds I, IV and V given at the outset, collective terms were used which generally represent the following groups:

Halogen: fluorine, chlorine, bromine and iodine;

Alkyl: straight-chain or branched alkyl groups having 1 to 4, 6 or 10 carbon atoms, for example C_1-C_6-alkyl such as methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, 1,1-dimethylethyl, pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl, hexyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,1-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,2-dimethylbutyl, 2,3-dimethylbutyl, 3,3-dimethylbutyl, 1-ethylbutyl, 2-ethylbutyl,

1,1,2-trimethylpropyl, 1,2,2-trimethylpropyl, 1-ethyl-1-methylpropyl and 1-ethyl-2-methylpropyl;

Haloalkyl: straight-chain or branched alkyl groups having 1 to 6 carbon atoms, it being possible for some or all of the hydrogen atoms in these groups to be replaced by halogen atoms as mentioned above, for example C_1-C_2-haloalkyl, such as chloromethyl, dichloromethyl, trichloromethyl, fluoromethyl, difluoromethyl, trifluoromethyl, chlorofluoromethyl, dichlorofluoromethyl, chlorodifluoromethyl, 1-fluoroethyl, 2-fluoroethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, 2-chloro-2-fluoroethyl, 2-chloro-2,2-difluoroethyl, 2,2-dichloro-2-fluoroethyl, 2,2,2-trichloroethyl and pentafluoroethyl;

C_1-C_4-Alkoxy and the alkoxy moieties of C_1-C_4-alkoxycarbonyl: methoxy, ethoxy, propoxy, 1-methylethoxy, butoxy, 1-methylpropoxy, 2-methylpropoxy and 1,1-dimethylethoxy;

C_1-C_4-Haloalkoxy: a C_1-C_4-alkoxy radical as mentioned above which is partially or fully substituted by fluorine, chlorine, bromine and/or iodine, i.e., for example, fluoromethoxy, difluoromethoxy, trifluoromethoxy, chlorodifluoromethoxy, bromodifluoromethoxy, 2-fluoroethoxy, 2-chloroethoxy, 2-bromomethoxy, 2-iodoethoxy, 2,2-difluoroethoxy, 2,2,2-trifluoroethoxy, 2-chloro-2-fluoroethoxy, 2-chloro-2,2-difluoroethoxy, 2,2-dichloro-2-fluoroethoxy, 2,2,2-trichloroethoxy, pentafluoroethoxy, 2-fluoropropoxy, 3-fluoropropoxy, 2-chloropropoxy, 3-chloropropoxy, 2-bromopropoxy, 3-bromopropoxy, 2,2-difluoropropoxy, 2,3-difluoropropoxy, 2,3-dichloropropoxy, 3,3,3-trifluoropropoxy, 3,3,3-trichloropropoxy, 2,2,3,3,3-pentafluoropropoxy, heptafluoropropoxy, 1-(fluoromethyl)-2-fluoroethoxy, 1-(chloromethyl)-2-chloroethoxy, 1-(bromomethyl)-2-bromoethoxy, 4-fluorobutoxy, 4-chlorobutoxy, 4-bromobutoxy and nonafluorobutoxy;

Cycloalkyl: monocyclic alkyl groups having 3 to 6 carbon ring members, for example cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl;

Alkenyl: straight-chain or branched alkenyl groups having 2 to 6 or 10 carbon atoms and a double bond in any position, for example C_2-C_6-alkenyl, such as ethenyl, 1-propenyl, 2-propenyl, 1-methylethenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1-methyl-1-propenyl, 2-methyl-1-propenyl, 1-methyl-2-propenyl, 2-methyl-2-propenyl, 1-pentenyl, 2-pentenyl, 3-pentenyl,

4-pentenyl, 1-methyl-1-butenyl, 2-methyl-1-butenyl, 3-methyl-1-butenyl, 1-methyl-2-butenyl, 2-methyl-2-butenyl, 3-methyl-2-butenyl, 1-methyl-3-butenyl, 2-methyl-3-butenyl, 3-methyl-3-butenyl, 1,1-dimethyl-2-propenyl, 1,2-dimethyl-1-propenyl, 1,2-dimethyl-2-propenyl, 1-ethyl-1-propenyl, 1-ethyl-2-propenyl, 1-hexenyl, 2-hexenyl, 3-hexenyl, 4-hexenyl, 5-hexenyl, 1-methyl-1-pentenyl, 2-methyl-1-pentenyl, 3-methyl-1-pentenyl, 4-methyl-1-pentenyl, 1-methyl-2-pentenyl, 2-methyl-2-pentenyl, 3-methyl-2-pentenyl, 4-methyl-2-pentenyl, 1-methyl-3-pentenyl, 2-methyl-3-pentenyl, 3-methyl-3-pentenyl, 4-methyl-3-pentenyl, 1-methyl-4-pentenyl, 2-methyl-4-pentenyl, 3-methyl-4-pentenyl, 4-methyl-4-pentenyl, 1,1-dimethyl-2-butenyl, 1,1-di-methyl-3-butenyl, 1,2-dimethyl-1-butenyl, 1,2-dimethyl-2-butenyl, 1,2-dimethyl-3-butenyl, 1,3-dimethyl-1-butenyl, 1,3-dimethyl-2-butenyl, 1,3-dimethyl-3-butenyl, 2,2-dimethyl-3-butenyl, 2,3-dimethyl-1-butenyl, 2,3-dimethyl-2-butenyl, 2,3-dimethyl-3-butenyl, 3,3-dimethyl-1-butenyl, 3,3-dimethyl-2-butenyl, 1-ethyl-1-butenyl, 1-ethyl-2-butenyl, 1-ethyl-3-butenyl, 2-ethyl-1-butenyl, 2-ethyl-2-butenyl, 2-ethyl-3-butenyl, 1,1,2-trimethyl-2-propenyl, 1-ethyl-1-methyl-2-propenyl, 1-ethyl-2-methyl-1-propenyl and 1-ethyl-2-methyl-2-propenyl;

Alkynyl: straight-chain or branched alkynyl groups having 2 to 10 carbon atoms and a triple bond in any position, for example C_2-C_6-alkynyl, such as ethynyl, 2-propynyl, 2-butynyl, 3-butynyl, 1-methyl-2-propynyl, 2-pentynyl, 3-pentynyl, 4-pentynyl, 1-methyl-2-butynyl, 1-methyl-3-butynyl, 2-methyl-3-butynyl, 1,1-dimethyl-2-propynyl, 1-ethyl-2-propynyl, 2-hexynyl, 3-hexynyl, 4-hexynyl, 5-hexynyl, 1-methyl-2-pentynyl, 1-methyl-3-pentynyl, 1-methyl-4-pentynyl, 2-methyl-3-pentynyl, 2-methyl-4-pentynyl, 3-methyl-4-pentynyl, 4-methyl-2-pentynyl, 1,1-dimethyl-2-butynyl, 1,1-dimethyl-3-butynyl, 1,2-dimethyl-3-butynyl, 2,2-dimethyl-3-butynyl, 1-ethyl-2-butynyl, 1-ethyl-3-butynyl, 2-ethyl-3-butynyl and 1-ethyl-1-methyl-2-propynyl;

Heterocyclyl or heterocyclyloxy, heterocyclylthio and heterocyclylamino: three- to six-membered saturated or partially unsaturated mono- or polycyclic heterocycles which contain one to three hereroatoms [sic] selected from a group consisting of oxygen, nitrogen and sulfur and which are attached to the skeleton directly or (heterocyclyloxy) via an oxygen atom or (heterocyclylthio) via a sulfur atom or (heterocyclylamino) via a nitrogen atom, such as, for example, 2-tetrahydrofuranyl, oxiranyl, 3-tetrahydrofuranyl, 2-tetrahydrothienyl,

3-tetrahydrothienyl, 2-pyrrolidinyl, 3-pyrrolidinyl, 3-isoxazoldinyl, 4-isoxazolidinyl, 5-isoxazolidinyl, 3-isothiazolidinyl, 4-isothiazolidinyl, 5-isothiazolidinyl, 3-pyrazolidinyl, 4-pyrazolidinyl, 5-pyrazolidinyl, 2-oxazolidinyl, 4-oxazolidinyl, 5-oxazolidinyl, 2-thiazolidinyl, 4-thiazolidinyl, 5-thiazolidinyl, 2-imidazolidinyl, 4-imidazolidinyl, 1,2,4-oxadiazolidin-3-yl, 1,2,4-oxadiazolidin-5-yl, 1,2,4-thiadiazolidin-3-yl, 1,2,4-thiadiazolidin-5-yl, 1,2,4-triazol-idin-3-yl, 1,3,4-oxadiazolidin-2-yl, 1,3,4-thiadiazolidin-2-yl, 1,3,4-triazolidin-2-yl, 2,3-dihydrofur-2-yl, 2,3-dihydrofur-3-yl, 2,3-dihydrofur-4-yl, 2,3-dihydrofur-5-yl, 2,5-dihydrofur-2-yl, 2,5-dihydrofur-3-yl, 2,3-dihydrothien-2-yl, 2,3-dihydrothien-3-yl, 2,3-dihydrothien-4-yl, 2,3-dihydrothien-5-yl, 2,5-dihydrothien-2-yl, 2,5-dihydrothien-3-yl, 2,3-dihydropyrrol-2-yl, 2,3-dihydropyrrol-3-yl, 2,3-dihydropyrrol-4-yl, 2,3-dihydropyrrol-5-yl, 2,5-dihydropyrrol-2-yl, 2,5-dihydropyrrol-3-yl, 2,3-dihydroisoxazol-3-yl, 2,3-dihydroisoxazol-4-yl, 2,3-dihydroisoxazol-5-yl, 4,5-dihydroisoxazol-3-yl, 4,5-dihydroisoxazol-4-yl, 4,5-dihydroisoxazol-5-yl, 2,5-dihydroisothiazol-3-yl, 2,5-dihydroisothiazol-4-yl, 2,5-dihydroisothiazol-5-yl, 2,3-dihydroisopyrazol-3-yl, 2,3-dihydroisopyrazol-4-yl, 2,3-dihydroisopyrazol-5-yl, 4,5-dihydroisopyrazol-3-yl, 4,5-dihydroisopyrazol-4-yl, 4,5-dihydroisopyrazol-5-yl, 2,5-dihydroisopyrazol-3-yl, 2,5-dihydroisopyrazol-4-yl, 2,5-dihydroisopyrazol-5-yl, 2,3-dihydrooxazol-3-yl, 2,3-dihydrooxazol-4-yl, 2,3-dihydrooxazol-5-yl, 4,5-dihydrooxazol-3-yl, 4,5-dihydrooxazol-4-yl, 4,5-dihydrooxazol-5-yl, 2,5-dihydrooxazol-3-yl, 2,5-dihydrooxazol-4-yl, 2,5-dihydrooxazol-5-yl, 2,3-dihydrothiazol-2-yl, 2,3-dihydrothiazol-4-yl, 2,3-dihydrothiazol-5-yl, 4,5-dihydrothiazol-2-yl, 4,5-dihydrothiazol-4-yl, 4,5-dihydrothiazol-5-yl, 2,5-dihydrothiazol-2-yl, 2,5-dihydrothiazol-4-yl, 2,5-dihydrothiazol-5-yl, 2,3-dihydroimidazol-2-yl, 2,3-dihydroimidazol-4-yl, 2,3-dihydroimidazol-5-yl, 4,5-dihydroimidazol-2-yl, 4,5-dihydroimidazol-4-yl, 4,5-dihydro-imidazol-5-yl, 2,5-dihydroimidazol-2-yl, 2,5-dihydroimidazol-4-yl, 2,5-dihydroimidazol-5-yl, 2-morpholinyl, 3-morpholinyl, 2-piperidinyl, 3-piperidinyl, 4-piperidinyl, 3-tetrahydropyridazinyl, 4-tetrahydropyridazinyl, 2-tetrahydropyrimidinyl, 4-tetrahydropyrimidinyl, 5-tetrahydropyrimidinyl, 2-tetrahydropyrazinyl, 1,3,5-tetrahydrotriazin-2-yl, 1,2,4-tetrahydrotriazin-3-yl, 1,3-dihydrooxazin-2-yl, 1,3-dithian-2-yl, 2-tetrahydropyranyl,

1,3-dioxolan-2-yl, 3,4,5,6-tetrahydropyridin-2-yl, 4H-1,3-thiazin-2-yl, 4H-3,1-benzothiazin-2-yl, 1,1-dioxo-2,3,4,5-tetrahydrothien-2-yl, 2H-1,4-benzothiazin-3-yl, 2H-1,4-benzoxazin-3-yl, 1,3-dihydrooxazin-2-yl, 1,3-dithian-2-yl;

Aryl or aryloxy, arylthio, arylcarbonyl and arylsulfonyl: aromatic mono- or polycyclic hydrogen radicals which are attached to the skeleton directly or (aryloxy) via an oxygen atom (-O-) or (arylthio) a sulfur atom (-S-), (arylcarbonyl) via a carbonyl group (-CO-) or (arylsulfonyl) via a sulfonyl group ($-SO_2-$), for example phenyl, naphthyl and phenanthrenyl or phenyloxy, naphthyloxy and phenanthrenyloxy and the corresponding carbonyl and sulfonyl radicals;

Hetaryl or hetaryloxy, hetarylthio, hetarylcarbonyl and hetarylsulfonyl: aromatic mono- or polycyclic radicals which, beside carbon ring members, can additionally contain one to four nitrogen atoms or one to three nitrogen atoms and one oxygen or one sulfur atom or one oxygen or one sulfur atom and which are attached to the skeleton directly or (hetaryloxy) via an oxygen atom (-O-) or (hetarylthio) a sulfur atom (-S-), (hetarylcarbonyl) via a carbonyl group (-CO-) or (hetarylsulfonyl) via a sulfonyl group ($-SO_2-$), for example

- 5-membered heteroaryl, containing one to three nitrogen atoms: 5-membered heteroaryl groups which, beside carbon atoms, can contain one to three nitrogen atoms as ring members, for example 2-pyrrolyl, 3-pyrrolyl, 3-pyrazolyl, 4-pyrazolyl, 5-pyrazolyl, 2-imidazolyl, 4-imidazolyl, 1,2,4-triazol-3-yl and 1,3,4-triazol-2-yl;

- 5-membered heteroaryl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom or one oxygen or one sulfur atom: 5-membered heteroaryl groups which, beside carbon atoms, can contain one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom or one oxygen or sulfur atom as ring members, for example 2-furyl, 3-furyl, 2-thienyl, 3-thienyl, 2-pyrrolyl, 3-pyrrolyl, 3-isoxazolyl, 4-isoxazolyl, 5-isoxazolyl, 3-isothiazolyl, 4-isothiazolyl, 5-isothiazolyl, 3-pyrazolyl, 4-pyrazolyl, 5-pyrazolyl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl, 2-thiazolyl, 4-thiazolyl, 5-thiazolyl, 2-imidazolyl, 4-imidazolyl, 1,2,4-oxadiazol-3-yl, 1,2,4-oxadiazol-5-yl, 1,2,4-thiadiazol-3-yl, 1,2,4-thiadiazol-5-yl,

1,2,4-triazol-3-yl, 1,3,4-oxadiazol-2-yl, 1,3,4-thiadiazol-2-yl, 1,3,4-triazol-2-yl;

- benzo-fused 5-membered heteroaryl, containing one to three nitrogen atoms or one nitrogen atom and/or one oxygen or sulfur atom: 5-membered heteroaryl groups which, beside carbon atoms, can contain one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom or one oxygen or one sulfur atom as ring members, and in which two adjacent carbon ring members or one nitrogen and one adjacent carbon ring member may be bridged by a buta-1,3-dien-1,4-diyl group;

- 5-membered heteroaryl bonded via nitrogen and containing one to four nitrogen atoms, or benzo-fused 5-membered heteroaryl, bonded via nitrogen and containing one to three nitrogen atoms: 5-membered heteroaryl groups which, beside carbon atoms, can contain one to four nitrogen atoms and one to three nitrogen atoms, respectively, as ring members, and in which two adjacent carbon ring members or one nitrogen and one adjacent carbon ring member can be bridged by a buta-1,3-dien-1,4-diyl group, these rings being attached to the skeleton via one of the nitrogen ring members;

- 6-membered heteroaryl containing one to three and one to four nitrogen atoms, respectively: 6-membered heteroaryl groups which, beside carbon atoms, can contain one to four nitrogen atoms as ring members, for example 2-pyridinyl, 3-pyridinyl, 4-pyridinyl, 3-pyridazinyl, 4-pyridazinyl, 2-pyrimidinyl, 4-pyrimidinyl, 5-pyrimidinyl, 2-pyrazinyl, 1,3,5-triazin-2-yl, 1,2,4-triazin-3-yl and 1,2,4,5-tetrazin-3-yl;

- benzo-fused 6-membered heteroaryl containing one to four nitrogen atoms: 6-membered heteroaryl groups in which two adjacent carbon ring members can be bridged by a buta-1,3-dien-1,4-diyl group, for example quinoline, isoquinoline, quinazoline and quinoxaline,

and the corresponding oxy, thio, carbonyl or sulfonyl groups.

Hetarylamino: aromatic mono- or polycyclic radicals which, beside carbon ring members, can additionally contain one to four nitrogen atoms or one to three nitrogen atoms and one oxygen or

one sulfur atom and which are attached to the skeleton via a nitrogen atom.

Bicycloalkyl: bicyclic alkyl groups having 6 to 15 carbon ring members, for example bicyclo[2.1.1]hex-5-yl, bicyclo[2.2.1]-hept-2-yl, bicyclo[2.2.2]oct-2-yl, bicyclo[3.2.1]oct-6-yl, bicyclo[3.2.2]non-6-yl, bicyclo[4.2.2]dec-7-yl, bicyclo[3.1.0]-hex-1-yl, bicyclo[4.1.0]hept-1-yl, bicyclo[4.3.0]non-1-yl, bicyclo[4.4.0]dec-1-yl, particularly preferably 5-methylbicyclo-[2.1.1]hex-5-yl, 2-methylbicyclo[2.2.1]hept-2-yl, 2-methyl-bicyclo[2.2.2]oct-2-yl, 6-methylbicyclo[3.2.1]oct-6-yl, 6-methylbicyclo[3.2.2]non-6-yl, 7-methylbicyclo[4.2.2]dec-7-yl, 1-methylbicyclo[3.1.0]hex-1-yl, 1-methylbicyclo[4.1.0]hept-1-yl, 1-methylbicyclo[4.3.0]non-1-yl, 1-methylbicyclo[4.4.0]dec-1-yl, 2-methylbicyclo[3.1.0]hex-1-yl, 2-methylbicyclo[4.1.0]hept-1-yl, 2-methylbicyclo[4.3.0]non-1-yl, 2-methylbicyclo[4.4.0]dec-1-yl, adamantyl;

Bicycloalkenyl: bicyclic alkenyl groups having 7 to 15 carbon ring members, for example bicyclo[2.2.1]hept-2-en-5-yl, bicyclo[2.2.2]oct-2-en-5-yl, bicyclo[4.2.2]dec-7-en-2-yl, bicyclo-[4.3.0]non-7-en-1-yl, bicyclo[4.4.0]dec-3-en-1-yl, bicyclo-[4.1.0]hept-3-en-1-yl, 5-methylbicyclo[2.2.1]hept-2-en-5-yl, 5-methylbicyclo[2.2.2]oct-2-en-5-yl, 2-methylbicyclo-[4.2.2]dec-7-en-2-yl, 2-methylbicyclo[4.3.0]non-7-en-1-yl, 2-methyl-bicyclo[4.4.0]dec-3-en-1-yl, 2-methylbicyclo[4.1.0]hept-3-en-1-yl;

Alkylidene: straight-chained or branched alkylidene groups having 3 to 5 carbon atoms, for example 1,3-propylidene, 1,4-butylidene, 1-methyl-1,3-propylidene, 2-methyl-1,3-propylidene, 2,2-dimethyl-1,3-propylidene, 1,5-pentylidene, 1-methyl-1,4-butylidene;

Cycloalkenyl: monocyclic alkyl groups having 5 to 7 carbon ring members and containing one or more double bonds, for example C_5-C_7-cycloalkenyl, such as cyclopentenyl, cyclohexenyl and cycloheptenyl;

Heterocyclyl: three to six-membered saturated or partially unsaturated mono- or polycyclic heterocycles which contain one to three hereroatoms [sic] selected from a group consisting of oxygen, nitrogen and sulfur and which are attached to the skeleton, for example 2-tetrahydrofuranyl, oxiranyl, 3-tetrahydrofuranyl, 2-tetrahydrothienyl, 3-tetrahydrothienyl, 2-pyrrolidinyl,

3-pyrrolidinyl, 3-isoxazolidinyl, 4-isoxazolidinyl, 5-isoxazolidinyl, 3-isothiazolidinyl, 4-isothiazolidinyl, 5-isothiazolidinyl, 3-pyrazolidinyl, 4-pyrazolidinyl, 5-pyrazolidinyl, 2-oxazolidinyl, 4-oxazolidinyl, 5-oxazolidinyl, 2-thiazolidinyl, 4-thiazolidinyl, 5-thiazolidinyl, 2-imidazolidinyl, 4-imidazolidinyl, 1,2,4-oxadiazolidin-3-yl, 1,2,4-oxadiazolidin-5-yl, 1,2,4-thiadiazolidin-3-yl, 1,2,4-thiadiazolidin-5-yl, 1,2,4-triazolidin-3-yl, 1,3,4-oxadiazolidin-2-yl, 1,3,4-thiadiazolidin-2-yl, 1,3,4-triazolidin-2-yl, 2,3-dihydrofur-2-yl, 2,3-dihydrofur-3-yl, 2,3-dihydro-fur-4-yl, 2,3-dihydro-fur-5-yl, 2,5-dihydro-fur-2-yl, 2,5-dihydro-fur-3-yl, 2,3-dihydrothien-2-yl, 2,3-dihydrothien-3-yl, 2,3-dihydrothien-4-yl, 2,3-dihydrothien-5-yl, 2,5-dihydrothien-2-yl, 2,5-dihydrothien-3-yl, 2,3-dihydropyrrol-2-yl, 2,3-dihydropyrrol-3-yl, 2,3-dihydropyrrol-4-yl, 2,3-dihydropyrrol-5-yl, 2,5-dihydropyrrol-2-yl, 2,5-dihydro-pyrrol-3-yl, 2,3-dihydroisoxazol-3-yl, 2,3-dihydroisoxazol-4-yl, 2,3-dihydroisoxazol-5-yl, 4,5-dihydroisoxazol-3-yl, 4,5-dihydro-isoxazol-4-yl, 4,5-dihydroisoxazol-5-yl, 2,5-dihydroisothiazol-3-yl, 2,5-dihydroisothiazol-4-yl, 2,5-dihydroisothiazol-5-yl, 2,3-dihydroisopyrazol-3-yl, 2,3-dihydroisopyrazol-4-yl, 2,3-dihydroisopyrazol-5-yl, 4,5-dihydroisopyrazol-3-yl, 4,5-dihydroisopyrazol-4-yl, 4,5-dihydroisopyrazol-5-yl, 2,5-dihydroisopyrazol-3-yl, 2,5-dihydroisopyrazol-4-yl, 2,5-dihydroisopyrazol-5-yl, 2,3-dihydrooxazol-3-yl, 2,3-dihydrooxazol-4-yl, 2,3-dihydrooxazol-5-yl, 4,5-dihydrooxazol-3-yl, 4,5-dihydrooxazol-4-yl, 4,5-dihydrooxazol-5-yl, 2,5-dihydrooxazol-3-yl, 2,5-dihydrooxazol-4-yl, 2,5-dihydrooxazol-5-yl, 2,3-dihydrothiazol-2-yl, 2,3-dihydrothiazol-4-yl, 2,3-dihydrothiazol-5-yl, 4,5-dihydrothiazol-2-yl, 4,5-dihydrothiazol-4-yl, 4,5-dihydrothiazol-5-yl, 2,5-dihydrothiazol-2-yl, 2,5-dihydrothiazol-4-yl, 2,5-dihydrothiazol-5-yl, 2,3-dihydroimidazol-2-yl, 2,3-dihydroimidazol-4-yl, 2,3-dihydroimidazol-5-yl, 4,5-dihydroimidazol-2-yl, 4,5-dihydroimidazol-4-yl, 4,5-dihydro-imidazol-5-yl, 2,5-dihydroimidazol-2-yl, 2,5-dihydroimidazol-4-yl, 2,5-dihydroimidazol-5-yl, 2-morpholinyl, 3-morpholinyl, 2-piperidinyl, 3-piperidinyl, 4-piperidinyl, 3-tetrahydropyridazinyl, 4-tetrahydropyridazinyl, 2-tetrahydropyrimidinyl, 4-tetrahydropyrimidinyl, 5-tetrahydropyrimidinyl, 2-tetrahydropyrazinyl, 1,3,5-tetrahydrotriazin-2-yl, 1,2,4-tetrahydrotriazin-3-yl, 1,3-dihydrooxazin-2-yl, 1,3-dithian-2-yl, 2-tetrahydropyranyl, 1,3-dioxolan-2-yl, 3,4,5,6-tetrahydropyridin-2-yl,

4H-1,3-thiazin-2-yl, 4H-3,1-benzothiazin-2-yl, 1,1-dioxo-2,3,4,5-tetrahydrothien-2-yl, 2H-1,4-benzothiazin-3-yl, 2H-1,4-benzoxazin-3-yl, 1,3-dihydrooxazin-2-yl, 1,3-dithian-2-yl.

The specification "partially or fully halogenated" is meant to express that some or all of the hydrogen atoms in the groups thus characterized may be replaced by identical or different halogen atoms as mentioned above.

When preparing the mixtures, it is preferred to employ the pure active ingredients I and II to V, with which further active ingredients against harmful fungi or other pests, such as insects, arachnids or nematodes, or else herbicidal or growth-regulating active ingredients or fertilizers can be admixed.

The mixtures of the compounds I and at least one compound II to V can be applied simultaneously, that is joined or separately, and have outstanding action against a wide range of phytopathogenic fungi, in particular from the classes of the Ascomycetes, Basidiomycetes, Phycomycetes and Deuteromycetes. Some of them act systematically and are therefore also suitable for use as folio and soil-acting fungicides.

They are especially important for controlling a large number of fungi in a variety of crop plants, such as cotton, vegetable species (for example cucumbers, beans, tomatoes, potatoes and cucurbits), barley, grass, oats, bananas, coffee, maize, fruit species, rice, rye, soya, grapevine, wheat, ornamentals, sugar cane, and a variety of seeds.

They are particularly suitable for controlling the following phytopathogenic fungi: Erysiphe graminis (powdery mildew) in cereals, Erysiphe cichoracearum and Sphaerotheca fuliginea in cucurbits, Podosphaera leucotricha in apples, Uncinula necator in grapevines, Puccinia species in cereals, Rhizoctonia species in cotton, rice and lawns, Ustilago species in cereals and sugar cane, Venturia inaequalis (scab) in apples, Helminthosporium species in cereals and rice, Septoria nodorum in wheat, Botrytis cinera [sic] (gray mold) in strawberries, vegetables, ornamentals and grapevines, Cercospora arachidicola in groundnuts, Pseudocercosporella herpotrichoides in wheat and barley, Pyricularia oryzae in rice and lawns, Phytophthora infestans in potatoes and tomatoes, Plasmopara viticola in grapevines, Pseudoperonospora species in hops and cucumbers, Alternaria

species in vegetables and fruit, Mycosphaerella species in bananas and Fusarium and Verticillium species.

The mixtures according to the invention are particularly preferably utilizable for controlling Pyricularia oryzae.

The compounds I and at least one of the compounds II to V can be applied simultaneously, either together or separately, or in succession, the sequence, in the case of separate application, generally not having any effect on the control results.

Depending on the nature of the desired effect, the application rates of the mixtures according to the invention are, in particular in agricultural crops, from 0.01 to 8 kg/ha, preferably from 0.1 to 5 g/ha [sic], in particular from 0.5 to 3.0 kg/ha.

In the case of the compounds I, the application rates are from 0.01 to 2.5 kg/ha, preferably from 0.05 to 2.5 kg/ha, in particular from 0.1 to 1.0 kg/ha.

Correspondingly, in the case of the compounds II to V, the application rates are from 0.001 to 5 kg/ha, preferably from 0.005 to 2 kg/ha, in particular from 0.01 to 1.0 kg/ha.

For seed treatment, the application rates of the mixture are generally from 0.001 to 250 g/kg of seed, preferably 0.01 to 100 g/kg, in particular 0.01 to 50 g/kg.

If phytopathogenic harmful fungi are to be controlled, the separate or joint application of the compounds I and at least one of the compounds II to V is effected by spraying or dusting the seeds, the plants or the soils before or after sowing the plants, or before or after plant emergence.

The fungicidal synergistic mixtures according to the invention can be formulated for example in the form of ready-to-spray solutions, powders and suspensions or in the form of highly concentrated aqueous, oily or other suspensions, dispersions, emulsions, oil dispersions, pastes, dusts, materials for broadcasting or granules, and applied by spraying, atomizing, dusting, broadcasting or watering. The use form depends on the intended purpose; in any case, it should ensure as fine and

uniform as possible a distribution of the mixture according to the invention.

The formulations are prepared in a known manner, for example by expanding the active ingredient with solvents and/or carriers, if desired by use of emulsifiers and dispersants. If the diluent used is water, it is also possible to use other organic solvents as auxiliary solvents. Suitable auxiliaries are essentially: solvents, such as aromatics (for example xylene), chlorinated aromatics (for example chlorobenzenes), paraffins (for example mineral oil fractions), alcohols (for example methanol, butanol), ketones (for example cyclohexanone), amines (for example ethanolamine, dimethylformamide) and water; carriers, such as natural ground minerals (for example kaolins, clays, talc, chalk) and ground synthetic minerals (for example finely divided silica gel, silicates); emulsifiers, such as nonionic and anionic emulsifiers (for example polyoxyethylene fatty alcohol ethers, alkylsulfonates and arylsulfonates), and dispersants, such as ligninsulfite waste liquors and methylcellulose.

Suitable surfactants are the alkali metal salts, alkaline earth metal salts and ammonium salts of aromatic sulfonic acids, e.g. ligno-, phenol-, naphthalene- and dibutylnaphthalenesulfonic acid, and of fatty acids, alkyl- and alkylarylsulfonates, alkyl, lauryl ethers and fatty alcohol sulfates, and salts of sulfated hexa-, hepta- and octadecanols, or of fatty alcohol glycol ethers, condensates of sulfonated naphthalene and its derivatives with formaldehyde, condensates of naphthalene or of the naphthalenesulfonic acids with phenol and formaldehyde, polyoxyethylene octylphenol ether, ethoxylated isooctyl-, octyl- or nonylphenol, alkylphenol polyglycol ethers, tributylphenyl polyglycol ethers, alkylaryl polyether alcohols, isotridecyl alcohol, fatty alcohol ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers or polyoxypropylene [sic], lauryl alcohol polyglycol ether acetate, sorbitol esters, lignosulfite waste liquors or methylcellulose.

Powders, materials for broadcasting and dusts can be prepared by mixing or jointly grinding the compounds I and at least one of the compounds II to V or the mixture of the compounds I and at least one of the compounds II to V with a solid carrier.

Granules (eg. coated granules, impregnated granules or homogeneous granules) are usually prepared by binding the active ingredient, or active ingredients, to a solid carrier.

Fillers or solid carriers are, for example, mineral earths, such as silica gel, silicic acids, silica gels [sic], silicates, talc, kaolin, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic materials, and fertilizers, such as ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas, and products of vegetable origin, such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders or other solid carriers.

The formulations generally comprise 0.1 to 95% by weight, preferably 0.5 to 90% by weight, of one of the compounds I and at least one of the compounds II to V or of the mixture of the compounds I and at least one of the compounds II to V. The active ingredients are employed in a purity of from 90% to 100%, preferably 95% to 100% (according to NMR or HPLC spectrum [sic].

The corresponding formulations are applied by treating the harmful fungi, their habitat or the plants, seeds, soils, areas, materials or spaces to be kept free from them with a fungicidally effective amount of the mixture, or of the compounds I and at least one of the compounds II to V in the case of separate application.

Application can be effected before or after infection by the harmful fungi.

Examples of such preparations comprising the active ingredients are:

I. A solution of 90 parts by weight of the active ingredients and 10 parts by weight of N-methylpyrrolidone; this solution is suitable for use in the form of microdrops;

II. A mixture of 20 parts by weight of the active ingredients, 80 parts by weight of xylene, 10 parts by weight of the adduct of 8 to 10 mol of ethylene oxide and 1 mol of oleic acid N-monoethanolamide, 5 parts by weight of the calcium salt of dodecylbenzenesulfonate, 5 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil; a dispersion is obtained by finely distributing the solution in water;

III. An aqueous dispersion of 20 parts by weight of the active ingredients, 40 parts by weight of cyclohexanone, 30 parts by weight of isobutanol, 20 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil;

IV. An aqueous dispersion of 20 parts by weight of the active ingredients, 25 parts by weight of cyclohexanol, 65 parts by weight of a mineral oil fraction of boiling point 210 to 280°C, and 10 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil;

V. A mixture, ground in a hammer mill, of 80 parts by weight of the active ingredients, 3 parts by weight of the sodium salt of diisobutylnaphthalene-1-sulfonic acid, 10 parts by weight of the sodium salt of a lignosulfonic acid from a sulfite waste liquor and 7 parts by weight of pulverulent silica gel; a spray mixture is obtained by finely distributing the mixture in water;

VI. An intimate mixture of 3 parts by weight of the active ingredients and 97 parts by weight of finely divided kaolin; this dust comprises 3% by weight of active ingredient;

VII. An intimate mixture of 30 parts by weight of the active ingredients, 92 parts by weight of pulverulent silica gel and 8 parts by weight of paraffin oil which had been sprayed onto the surface of this silica gel; this formulation imparts good adhesion to the active ingredient;

VIII. A stable aqueous dispersion of 40 parts by weight of the active ingredients, 10 parts by weight of the sodium salt of a phenolsulfonic acid/urea/formaldehyde condensate, 2 parts by weight of silica gel and 48 parts by weight of water; this dispersion may be diluted further;

IX. A stable oily dispersion of 20 parts by weight of the active ingredients, 2 parts by weight of the calcium salt of dodecylbenzenesulfonic acid, 8 parts by weight of fatty alcohol polyglycol ether, 20 parts by weight of the sodium salt of a phenolsulfonic acid/urea/formaldehyde condensate and 88 parts by weight of a paraffinic mineral oil.

The synergistic activity of the mixtures according to the invention can be demonstrated by the following experiments:

The active ingredients, separately or together, are formulated as a 10% emulsion in a mixture of 63% by weight of cyclohexanone and 27% by weight of emulsifier, and correspondingly diluted with water to the desired concentration.

Evaluation is carried out by determining the infected leaf areas in percent. These percentages are converted into efficacies. The efficacy (W) is calculated as follows using Abbot's formula:

$$W = (1 - \alpha) \cdot 100/\beta$$

α corresponds to the fungal infection of the treated plants in % and

β corresponds to the fungal infection of the untreated (control) plants in %

An efficacy of 0 means that the infection level of the treated plants corresponds to that of the untreated control plants; an efficacy of 100 means that the treated plants were not infected.

The expected efficacies of the mixtures of the active ingredients were determined using Colby's formula [R.S. Colby, Weeds 15, 20-22 (1967)] and compared with the observed efficacies.

Colby's formula: $E = x + y - x \cdot y/100$

E expected efficacy, expressed in % of the untreated control, when using the mixture of the active ingredients A and B at the concentrations a and b

x efficacy, expressed in % of the untreated control, when using active ingredient A at the concentration a

y efficacy, expressed in % of the untreated control, when using active ingredient B at the concentration b

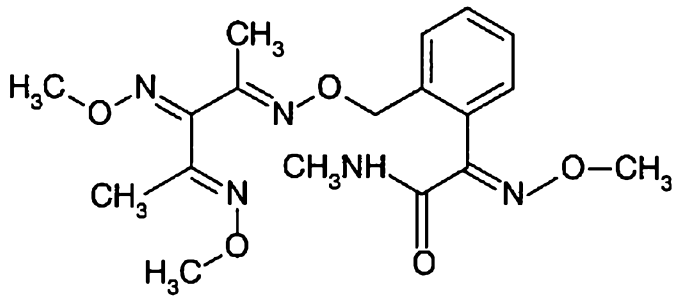
Use Example 1 - Activity against Pyricularia oryzae (protective)

Leaves of potted rice seedlings c.v. "Tai-Nong 67" were sprayed to runoff point with an aqueous preparation of active ingredient prepared using a stock solution comprising 10% of active ingredient, 63% of cyclohexanone and 27% of emulsifier. The following day, the plants were inoculated with an aqueous spore suspension of Pyricularia oryzae. The test plants were subsequently placed in climatized chambers at 22-24°C and 95-99% relative atmospheric humidity for 6 days. The extent of the development of the disease on the leaves was then determined visually.

The visually determined values for the percentage of diseased leaf areas were converted into efficacies as percent of the untreated control. An efficacy of 0 is the same disease level as in the untreated control, an efficacy of 100 is 0% disease. The expected efficacies for the active ingredient combinations were determined using Colby's formula (Colby, S. R. (Calculating

synergistic and antagonistic responses of herbicide combinations", Weeds, 15, pp. 20-22, 1967) and compared with the observed efficacies.

The compound I' below was employed as component a):



The test results are shown in Tables 1 and 2 below:

Table 1:

Ex.	Active ingredient	conc. in ppm	Efficacy in % of the untreated control
1C	without	(100% disease)	0
2C	Compound I'	2.0 0.5	20 0
3C	Compound II	2.0 0.5	20 0

Table 2:

Ex.	Mixture according to the invention (conc. in ppm)	Observed efficacy	Calculated efficacy*
4	2 ppm I' + 2 ppm II	99	36
5	0.5 ppm I' + 0.5 ppm II	25	0

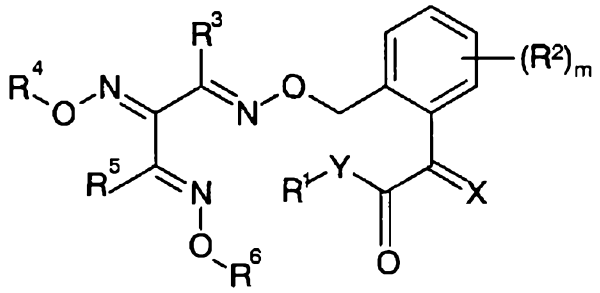
* Calculated using Colby's formula

The test results show that for all mixing ratios the observed efficacy is higher than the efficacy which had been calculated beforehand using Colby's formula.

We claim:

1. A mixture for crop protection, comprising as active components

a) phenylacetic acid derivatives of the formula I



(I)

in which the substituents and the index have the following meaning:

X is $NOCH_3$, $CHOCH_3$, $CHCH_3$;

Y is O, NR;

R^1, R independently of one another are each hydrogen and C_1-C_4-alkyl;

R^2 is cyano, nitro, trifluoromethyl, halogen, C_1-C_4-alkyl and C_1-C_4-alkoxy;

m is 0, 1 or 2, where the radicals R^2 may be different if m is 2;

R^3 is hydrogen, cyano, C_1-C_4-alkyl, C_1-C_4-haloalkyl, C_3-C_6-cycloalkyl;

R^4, R^6 independently of one another are each hydrogen,

are C_1-C_{10}-alkyl, C_3-C_6-cycloalkyl, C_2-C_{10}-alkenyl, C_2-C_{10}-alkynyl, C_1-C_{10}-alkylcarbonyl, C_2-C_{10}-alkenylcarbonyl, C_3-C_{10}-alkynylcarbonyl or C_1-C_{10}-alkylsulfonyl, where these radicals may be partially or fully halogenated or may carry one to

three of the following groups: cyano, nitro, hydroxyl, mercapto, amino, carboxyl, aminocarbonyl, aminothiocarbonyl, halogen, C_1-C_6-alkyl, C_1-C_6-haloalkyl, C_1-C_6-alkylsulfonyl, C_1-C_6-alkylsulfoxyl, C_1-C_6-alkoxy, C_1-C_6-haloalkoxy, C_1-C_6-alkoxycarbonyl, C_1-C_6-alkylthio, C_1-C_6-alkylamino, di-C_1-C_6-alkylamino,

are C_1-C_6-alkylaminocarbonyl, di-C_1-C_6-alkylamino-carbonyl, C_1-C_6-alkylaminothiocarbonyl, di-C_1-C_6-alkylaminothiocarbonyl, C_2-C_6-alkenyl, C_2-C_6-alkenyloxy, C_3-C_6-cycloalkyl, C_3-C_6-cycloalkyloxy, heterocyclyl, heterocyclyloxy, benzyl, benzyloxy, aryl, aryloxy, arylthio, hetaryl, hetaryloxy and hetarylthio, where the cyclic groups for their part may be partially or fully halogenated or may carry one to three of the following groups: cyano, nitro, hydroxyl, mercapto, amino, carboxyl, aminocarbonyl, aminothiocarbonyl, halogen, C_1-C_6-alkyl, C_1-C_6-haloalkyl, C_1-C_6-alkylsulfonyl, C_1-C_6-alkylsulfoxyl, C_3-C_6-cycloalkyl, C_1-C_6-alkoxy, C_1-C_6-haloalkoxy, C_1-C_6-alkyloxycarbonyl, C_1-C_6-alkylthio, C_1-C_6-alkylamino, di-C_1-C_6-alkylamino, C_1-C_6-alkylaminocarbonyl, di-C_1-C_6-alkylaminocarbonyl, C_1-C_6-alkylaminothiocarbonyl, di-C_1-C_6-alkylaminothiocarbonyl, C_2-C_6-alkenyl, C_2-C_6-alkenyloxy, benzyl, benzyloxy, aryl, aryloxy, arylthio, het-aryl, hetaryloxy, hetarylthio or $C(=NOR^7)$-A_n-R^8;

are aryl, arylcarbonyl, arylsulfonyl, hetaryl, hetarylcarbonyl or hetarylsulfonyl, where these radicals may be partially or fully halogenated or may carry one to three of the following groups: cyano, nitro, hydroxyl, mercapto, amino, carboxyl, aminocarbonyl, aminothiocarbonyl, halogen, C_1-C_6-alkyl, C_1-C_6-haloalkyl, C_1-C_6-alkylcarbonyl, C_1-C_6-alkylsulfonyl, C_1-C_6-alkylsulfoxyl, C_3-C_6-cycloalkyl, C_1-C_6-alkoxy, C_1-C_6-haloalkoxy, C_1-C_6-alkyloxycarbonyl, C_1-C_6-alkylthio, C_1-C_6-alkylamino, di-C_1-C_6-alkylamino, C_1-C_6-alkylaminocarbonyl, di-C_1-C_6-alkylamino-carbonyl, C_1-C_6-alkylaminothiocarbonyl, di-C_1-C_6-alkylaminothiocarbonyl, C_2-C_6-alkenyl,

C_2-C_6-alkenyloxy, benzyl, benzyloxy, aryl, aryloxy, hetaryl, hetaryloxy or C(=NOR^7)-A_n-R^8;

R^5 is hydrogen,

is C_1-C_6-alkyl, C_2-C_6-alkenyl, C_2-C_6-alkynyl, where the hydrocarbon radicals of these groups may be partially or fully halogenated or may carry one to three of the following radicals: cyano, nitro, hydroxyl, mercapto, amino, carboxyl, aminocarbonyl, aminothiocarbonyl, halogen, C_1-C_6-alkylaminocarbonyl, di-C_1-C_6-alkylaminocarbonyl, C_1-C_6-alkylaminothiocarbonyl, di-C_1-C_6-alkylaminothiocarbonyl, C_1-C_6-alkylsulfonyl, C_1-C_6-alkylsulfoxyl, C_1-C_6-alkoxy, C_1-C_6-haloalkoxy, C_1-C_6-alkoxycarbonyl, C_1-C_6-alkylthio, C_1-C_6-alkylamino, di-C_1-C_6-alkylamino, C_2-C_6-alkenyloxy, C_3-C_6-cycloalkyl, C_3-C_6-cycloalkyloxy, heterocyclyl, heterocyclyloxy, aryl, aryloxy, aryl-C_1-C_4-alkoxy, arylthio, aryl-C_1-C_4-alkylthio, hetaryl, hetaryloxy, hetaryl-C_1-C_4-alkoxy, hetarylthio, hetaryl-C_1-C_4-alkylthio, where the cyclic radicals for their part may be partially or fully halogenated and/or may carry one to three of the following groups: cyano, nitro, hydroxyl, mercapto, amino, carboxyl, aminocarbonyl, aminothiocarbonyl, C_1-C_6-alkyl, C_1-C_6-haloalkyl, C_1-C_6-alkylsulfonyl, C_1-C_6-alkylsulfoxyl, C_3C_6-cycloalkyl [sic], C_1-C_6-alkoxy, C_1-C_6-haloalkoxy, C_1-C_6-alkoxycarbonyl, C_1-C_6-alkylthio, C_1-C_6-alkylamino, di-C_1-C_6-alkylamino, C_1-C_6-alkylaminocarbonyl, di-C_1-C_6-alkylaminocarbonyl, C_1-C_6-alkylaminothiocarbonyl, di-C_1-C_6-alkylaminothiocarbonyl, C_2-C_6-alkenyl, C_2-C_6-alkenyloxy, benzyl, benzyloxy, aryl, aryloxy, arylthio, hetaryl, hetaryloxy, hetarylthio and C(=NOR^7)-A_n-R^8;

is C_3-C_6-cycloalkyl, C_3-C_6-cycloalkenyl, heterocyclyl, aryl, hetaryl, where the cyclic radicals may be partially or fully halogenated or may carry one to three of the following groups:

cyano, nitro, hydroxyl, mercapto, amino, carboxyl, aminocarbonyl, aminothiocarbonyl, halogen, C_1-C_6-alkyl, C_1-C_6-haloalkyl, C_1-C_6-alkylsulfonyl, C_1-C_6-alkylsulfoxyl, C_3-C_6-cycloalkyl, C_1-C_6-alkoxy, C_1-C_6-haloalkoxy, C_1-C_6-alkoxycarbonyl, C_1-C_6-alkylthio, C_1-C_6-alkylamino, di-C_1-C_6-alkylamino, C_1-C_6-alkylaminocarbonyl, di-C_1-C_6-alkylaminocarbonyl, C_1-C_6-alkylaminothiocarbonyl, di-C_1-C_6-alkylaminothiocarbonyl, C_2-C_6-alkenyl, C_2-C_6-alkenyloxy, benzyl, benzyloxy, aryl, aryloxy, hetaryl and hetaryloxy;

where

A is oxygen, sulfur or nitrogen and where the nitrogen carries hydrogen or C_1-C_6-alkyl;

n is 0 or 1;

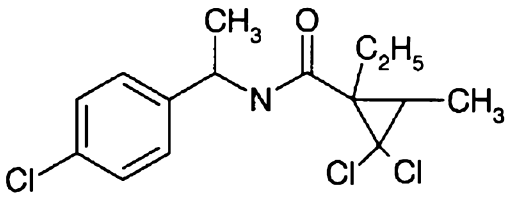
R^7 is hydrogen or C_1-C_6-alkyl and

R^8 is hydrogen or C_1-C_6-alkyl,

and their salts,

and

b) at least one compound of the formulae II to V



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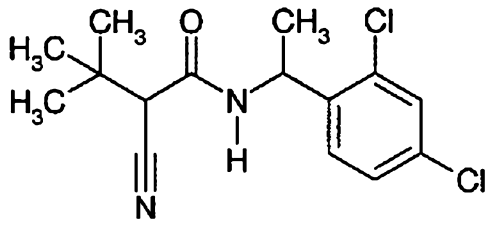

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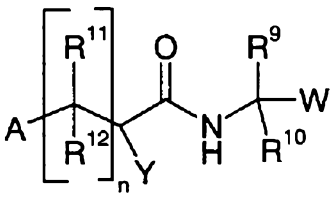

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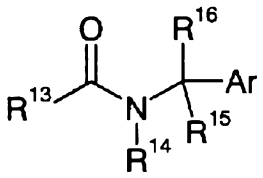


(V)

where the substituents have the following meaning:

A is C_3-C_6-cycloalkyl which may carry one to three substituents selected from the group consisting of halogen and C_1-C_3-alkyl;

R^9 is C_1-C_6-alkyl or C_2-C_6-alkenyl, where these radicals may be partially or fully halogenated and/or may carry one or two of the following groups: C_1-C_4-alkoxy, C_1-C_4-haloalkoxy, C_1-C_4-alkylthio, C_1-C_4-alkoxycarbonyl, C_3-C_6-cycloalkyl and phenyl, where the phenyl may be partially or fully halo-genated and/or may carry one to three of the following radicals: nitro, cyano, C_1-C_4-alkyl, C_1-C_4-haloalkyl, C_1-C_4-alkoxy, C_1-C_4-haloalkoxy, C_1-C_4-alkylthio, C_3-C_6-cycloalkyl or heterocyclyl;

R^{10}, R^{11}, R^{12} are each hydrogen or have one of the meanings of the radical R^9 independently of this meaning;

n is 0 or 1;

Y is cyano or halogen;

W is phenyl, naphthyl or heteroaryl, where these radicals may carry one to three of the following groups: nitro, halogen, cyano, C_1-C_4-alkyl, C_1-C_4-haloalkyl, C_1-C_4-alkoxy, C_1-C_4-haloalkoxy, C_1-C_4-alkylthio, C_3-C_6-cycloalkyl and C_1-C_4-alkoxycarbonyl,

R^{13} is C_6-C_{15}-bicycloalkyl or C_7-C_{15}-bicycloalkenyl, where these radicals may be completely halogenated and, if they are not completely halogenated, two carbon atoms of these radicals together with a C_3-C_5-alkylidene group may form a five- to seven-membered saturated carbocyclic ring and/or may carry one or independently of one another two, three, four or five of the following groups: cyano, C_1-C_4-alkyl, C_1-C_4-haloalkyl, C_1-C_4-alkoxy, C_1-C_4-haloalkoxy and aryl, where the aryl may be partially or fully halogenated and/or may carry one or independently of one another two or three of the following substituents: nitro, cyano, C_1-C_4-alkyl, C_1-C_4-haloalkyl, C_1-C_4-alkoxy, C_1-C_4-haloalkoxy and C_1-C_4-alkylthio;

R^{14}, R^{15}, R^{16} independently of one another are hydrogen,

are C_1-C_8-alkyl which may be partially or fully halogenated and/or may carry one or two of the following groups: C_1-C_4-alkoxy, C_1-C_4-haloalkoxy, C_1-C_4-alkylthio, C_3-C_7-cycloalkyl, C_5-C_7-cycloalkenyl, where the cyclic groups for their part may carry one or independently of one another two or three halogen atoms, C_1-C_3-alkyl groups and/or C_1-C_3-alkoxy groups and aryl, where the aryl may be partially or fully halogenated and/or may carry one or independently of one another two or three of the following substituents: nitro, cyano, C_1-C_4-alkyl,

C_1-C_4-haloalkyl, C_1-C_4-alkoxy, C_1-C_4-haloalkoxy ad C_1-C_4-alkylthio or

are C_3-C_6-cycloalkyl, C_3-C_6-cycloalkenyl or heterocyclyl, where these radicals may be partially or fully halogenated and/or may carry one or independently of one another two or three of the following groups: cyano, C_1-C_6-alkyl, C_1-C_6-haloalkyl, C_2-C_6-alkenyl, C_1-C_6-alkoxy and C_1-C_6-alkylthio;

Ar is aryl or heteroaryl, where these radicals may carry one or independently of one another two or three of the following groups: halogen, cyano, C_1-C_4-alkyl, C_1-C_4-alkoxyalkyl, C_1-C_4-haloalkyl, C_1-C_4-alkoxy, C_1-C_4-haloalkoxy, C_1-C_4-alkylthio, C_1-C_4-alkoxycarbonyl, aryl, aryloxy and heteroaryl, where the rings in these groups for their part may carry one or independently of one another two or three of the following substituents: halogen, cyano, C_1-C_4-alkyl, C_1-C_4-alkoxyalkyl, C_1-C_4-haloalkyl, C_1-C_4-alkoxy, C_1-C_4-haloalkoxy, C_1-C_4-alkylthio and C_1-C_4-alkoxycarbonyl,

in a synergistically effective amount.

2. A fungicidal mixture as claimed in claim 1, which is conditioned in two parts, one part comprising the compound I in a solid or liquid carrier and the other part comprising at least one of the compounds II to V in a solid or liquid carrier.

3. A method for controlling harmful fungi, which comprises treating the fungi, their habitat, or the materials, plants, seeds, soils, areas or spaces to be protected against fungal attack with a fungicidal mixture as claimed in any of claims 1 to 2, where the application of the compound I and at least one of the compounds II to V may be carried out simultaneously, either together or separately, or in succession.

4. A method as claimed in claim 3, wherein the harmful fungi, their habitat or the plants, seeds, soils, areas, materials or spaces to be kept free from them are treated with from 0.005 to 1 kg/ha of a compound I as set forth in claim 1.

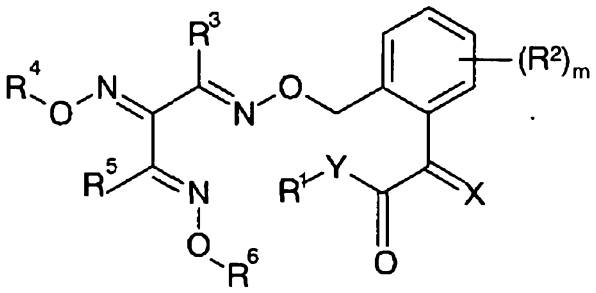
5. A method as claimed in claim 3, wherein the harmful fungi, their habitat or the plants, seeds, soils, areas, materials or spaces to be kept free from them are treated with from 0.01 to 1 kg/ha of at least one of the compounds II to V as set forth in claim 1.

Fungicidal mixtures based on tris(oxime ether) derivatives and further fungicides

Abstract

Fungicidal mixtures, comprising as active components

a) Phenylacetic acid derivatives of the formula I

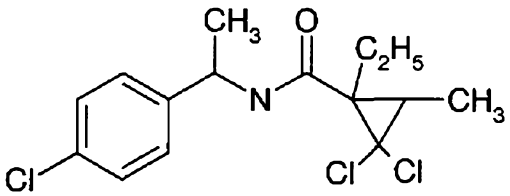


(I)

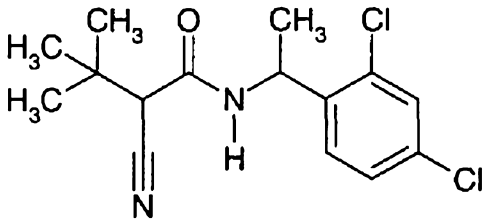
in which the substituents and the index are each as defined in the description, and salts thereof,

and

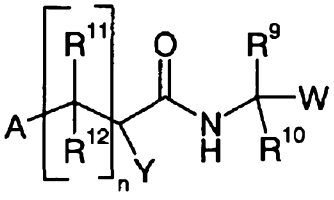
b) at least one compound of the formulae II to V



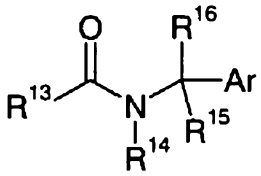
(II)



(III)



(IV)



(V)

where the substituents are each as defined in the description, in a synergistically effective amount.