

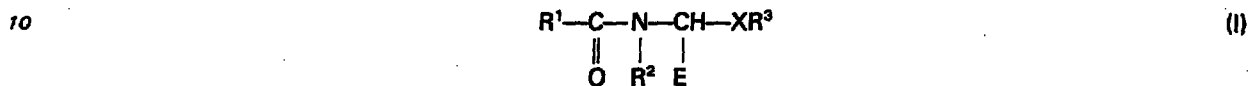
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Description

This invention relates to substituted benzamide derivatives useful as herbicides and fungicides, to processes of combatting weeds and fungal infestations and to herbicidal and fungicidal compositions.

5 Substituted benzamide derivatives have previously been proposed for use as herbicides; by way of example, the compounds disclosed in UK Patent Specifications No. 1209608 and 1395802 may be mentioned.

According to the present invention, there are provided amide derivatives of the formula (I)



wherein R^1 is an optionally substituted alkyl, alkenyl, aryl, heterocyclyl, benzyl, or heterocyclylmethyl radical;

15 R^2 is hydrogen, or an optionally substituted alkyl, alkenyl, benzyl, or heterocyclylmethyl, radical;

X is oxygen, sulphur, or an $-NH-$ group;

R^3 is an optionally substituted alkyl or alkenyl radical when X is oxygen or sulphur, or is COZ where Z is alkyl or alkylene when X is $-NH-$;

20 and E is a $-CN$, $-CONH_2$, $-CSNH_2$, or $-CONR^4R^5$ group wherein each R^4 and R^5 is hydrogen or an optionally substituted alkyl or alkenyl group, provided that X is not sulphur when R^1 is phenyl or phenyl substituted by nitro or methoxy.

When the group R^1 is an optionally substituted alkyl or alkenyl radical, it may be for example C_{1-5} alkyl or C_{2-5} alkenyl radical. Examples of substituents include C_1-C_4 alkoxy, C_1-C_4 alkylthio and halogen (i.e. 25 fluorine, chlorine, bromine or iodine).

When R^1 is a benzyl radical optionally substituted in the phenyl ring, examples of substituents include halogen (fluorine, chlorine, bromine or iodine), C_1-C_4 alkoxy, C_1-C_4 alkylthio, nitro, cyano, C_1-C_4 haloalkyl (e.g. CF_3), and C_1-C_4 alkyl (e.g. CH_3). There may be from one to five substituents, which may be the same or different.

30 When R^1 is an optionally substituted aryl group it may be a phenyl or naphthyl radical. Examples of substituents which may be present include fluorine, chlorine, bromine, iodine, C_1-C_4 alkoxy, methylenedioxy and ethylenedioxy, C_1-C_4 alkyl, C_1-C_4 alkylthio, C_1-C_4 haloalkyl (e.g. CF_3), nitro and cyano. There may be from one to three or more substituents which may be the same or different. When R^1 is a substituted phenyl radical the substituents are preferably in the 3, 4, or 5 positions. When a methylenedioxy or 35 ethylenedioxy substituent is present, it preferably is attached to the 3 and 4 positions of the phenyl ring. A halogen substituent (e.g. Cl or Br) may also be present in the 4- or 5-position, or both, in such compounds.

When R^1 is an optionally substituted heterocyclyl radical, it may for example be a furyl, benzofuryl, thienyl, pyridyl, thiazolyl, or benzthiazolyl radical. Examples of substituents which may be present include those listed above for the case when R^1 is a substituted phenyl radical. There may be from one to three or 40 more substituents which may be the same or different.

When R^1 is an optionally substituted heterocyclylmethyl radical, the heterocyclyl group may be for example a furyl, thienyl, pyridyl, thiazolyl or benzthiazolyl group. Examples of substituents which may be present in the heterocyclyl group include those described above for the case when R^1 is a substituted phenyl radical.

45 R^2 is preferably hydrogen but when it is not, then it may be an optionally substituted alkyl group, for example an C_1-C_4 alkyl group. Examples of substituents which may be present include fluorine, chlorine, bromine, iodine, and C_1-C_4 alkoxy. When R^2 is an optionally substituted alkenyl group it may be for example an alkenyl group of from 3-5 carbon atoms. Examples of substituents which may be present include those listed above for the case when R^2 is an alkyl group.

50 When R^2 is an optionally substituted benzyl group, the substituents may include those described above for the case when R^1 is substituted benzyl.

When R^2 is an optionally substituted heterocyclylmethyl group, the heterocyclyl ring may be for example a furyl, thienyl, pyridyl, thiazolyl, or benzothiazolyl ring. Substituents which may be present include those described above for the case where R^1 is a substituted phenyl radical.

55 When R^3 is an optionally substituted alkyl or alkenyl radical it may have any of the values described above for the group R^2 .

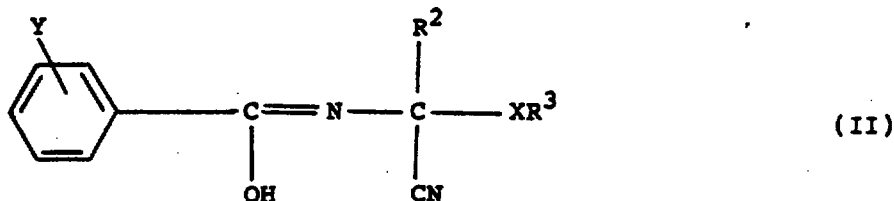
When R^3 is COZ where Z is alkyl or alkylene (i.e. when X is NH) it may for example have from 1 to 4 carbon atoms (e.g. it may be a formyl, acetyl, or propionyl group).

60 R^4 and R^5 are preferably hydrogen, but when they are not, they may be optionally substituted alkyl or alkenyl group it may have any of the values defined above for the group R^2 when it is an optionally substituted alkyl or alkenyl radical.

Within the above definition, one sub-class of compounds according to the invention comprises those compounds wherein R^2 is hydrogen. Within this sub-class, a further sub-class comprises those compounds in which E is a cyano group, X is O or S, and R^3 is C_1-C_4 alkyl. A group within the latter sub-class includes 65 those compounds in which R^1 is phenyl or heterocyclyl. Within the latter group, a sub-group includes

compounds in which the heterocyclyl or phenyl group is substituted, for example by alkyl, alkoxy, methylenedioxy, or halogen, for example fluorine or chlorine. In such compounds the groups or atoms are preferably located in the 3, 4 or 5 positions of the phenyl ring.

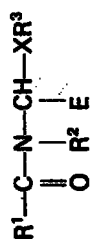
The structural formula (I) given above is believed to be the one which best represents the structure of the compounds. For some compounds within the scope of the formula (I) it may be possible in principle for tautomeric forms of the compound to exist, in which a hydrogen atom is transposed to another part of the molecule and the chemical bonds between the atoms of the molecule are consequently rearranged; thus, where R¹ is hydrogen, it is possible in principle for the molecule to exist in the alternative form (II)



The structural formula (I) is intended to represent and include such tautomeric forms, insofar as they may exist. The structural formula (I) is also intended to include any physically distinguishable modifications of the compounds which may arise, for example, from different ways in which the molecules are arranged in a crystal lattice, or from the inability of parts of the molecules to rotate freely in relation to other parts, or from geometrical and or optical isomerism, or from intra-molecular or inter-molecular bonding, or otherwise.

Particular examples of compounds according to the invention are listed in Table I below:

TABLE 1



Compound No.	R ¹	R ²	XR ³	E	Route	Melting Point °C	Notes (see end of Table)
1	C ₆ H ₅	H	OMe	CONHMe	A	155	
2	C ₆ H ₅	H	OMe	CN	A	83	
3	C ₆ H ₅	H	OEt	CONH ₂	A	148—150	
4	C ₆ H ₅	H	OEt	CN	A	107—110	
5	C ₆ H ₅	H	OPr ⁿ	CONH ₂	A	105—108	
6	C ₆ H ₅	H	OPr ⁱ	CONH ₂	A	119—121	
7	C ₆ H ₅	H	OBu ⁿ	CONH ₂	A	85—88	
8	C ₆ H ₅	H	OPr ⁱ	CN	A	118—119	
9	C ₆ H ₅	H	OBu ⁿ	CN	A	74—77	
10	C ₆ H ₅	H	OBu ^t	CONH ₂	A	150—154	
11	C ₆ H ₅	H	OBu ^s	CONH ₂	A	94—95	
12	C ₆ H ₅	H	OBu ^t	CN	A	117—120	

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TABLE 1 continued

Compound No.	R ¹	R ²	XR ³	E	Route	Melting Point °C	Notes (see end of Table)
13	C ₆ H ₆	H	OBu ^a	CN	A	77-79	
14	4-Cl.C ₆ H ₄ .	H	OMe	CONH ₂	A	164-166	
15	4-Cl.C ₆ H ₄ .	H	OMe	CN	A	123-125	
16	2-Cl.C ₆ H ₄ .	H	OMe	CONH ₂	A	110-112	
17	2-Cl.C ₆ H ₄ .	H	OMe	CN	A	86-89	
18	3,5-Cl ₂ .C ₆ H ₃ .	H	OMe	CN	A	155-158	
19	3-Cl.C ₆ H ₄ .	H	OMe	CONH ₂	A	135-137	
20	3-Cl.C ₆ H ₄ .	H	OMe	CN	A	90-92	
21	3,5(Me) ₂ .C ₆ H ₃ .	H	OMe	CONH ₂	A	171-173	
22	3,5(Me) ₂ .C ₆ H ₃ .	H	OMe	CN	A	107-108	
23	3,5-Cl ₂ .C ₆ H ₃ .	H	OMe	CONH ₂	A	190-192	
24	C ₆ H ₆	H	OPr ^a	CN	A	91-93	
25	3-CF ₃ .C ₆ H ₄ .	H	OEt	CONH ₂	A	151-153	
26	3-CF ₃ .C ₆ H ₄ .	H	OEt	CN	A	54-56	
27	3-NO ₂ .C ₆ H ₄ .	H	OEt	CONH ₂	A	150-152	

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TABLE 1 continued

Compound No.	R ¹	R ²	XR ³	E	Route	Melting Point °C	Notes (see end of Table)
28	3-NO ₂ .C ₆ H ₄ .	H	OEt	CN	A	99—100	
29	3-Me.C ₆ H ₄ .	H	OEt	CONH ₂	A	123—125	
30	3-Me.C ₆ H ₄ .	H	OEt	CN	A	76—77	
31	3,5-Cl ₂ .C ₆ H ₃ .	H	OEt	CONH ₂	A	188—189	
32	3,5-Cl ₂ .C ₆ H ₃ .	H	OPr ⁱ	CONH ₂	A	178—180	
33	3,4-Cl ₂ .C ₆ H ₃ .	H	OEt	CN	A	96—97	
34	3,5-Cl ₂ .C ₆ H ₃ .	H	OEt	CN	A	156	
35	3-Br.C ₆ H ₄ .	H	OEt	CONH ₂	A	152—153	
36	3-Br.C ₆ H ₄ .	H	OEt	CN	A	93—95	
37	3-MeO.C ₆ H ₄ .	H	OEt	CONH ₂	B	143—144	
38	3-MeO.C ₆ H ₄ .	H	OEt	CN	B	72	
39	3,5-Cl ₂ .C ₆ H ₃ .	H	OPr ⁱ	CN	A	128—130	
40	3-Cl.C ₆ H ₄ .	H	Sme	CN	A	115—117	
41	3-Cl.C ₆ H ₄ .	H	OEt	CN	A	90—91	
42	3,5-(CF ₃) ₂ .C ₆ H ₃ .	H	OEt	CN	A	114—116	

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TABLE 1 continued

Compound No.	R ¹	R ²	XR ³	E	Route	Melting Point °C	Notes (see end of Table)
43	3-Cl.C ₆ H ₄ .	H	OP ¹	CN	A	82—84	
44	3-Cl.C ₆ H ₄ .	H	OEt	CSNH ₂	G	136—137	
45	2,5-Cl ₂ .C ₆ H ₄ .	H	OEt	CN	A	123—124	
46	3,5-Cl ₂ .C ₆ H ₃ .	H	OCH ₂ CF ₃	CONH ₂	A	204—205	
47	3,4-Cl ₂ .C ₆ H ₃ .	H	OEt	CSNH ₂	G	140	
48	3-F.C ₆ H ₄ .	H	OEt	CONH ₂	A	112—113	
49	3-F.C ₆ H ₄ .	H	OMe	CONH ₂	A	137—139	
50	2,6-(Me) ₂ .C ₆ H ₃	H	OMe	CN	B	65—67	
51	3-F.C ₆ H ₄ .	H	OEt	CN	A	68—69	
52	3-F.C ₆ H ₄ .	H	OMe	CN	A	86—88	
53	C ₆ H ₅	Me	OMe	CN	F	Oil	a
54	3-Cl.C ₆ H ₄ .	Me	OEt	CN	F	Oil	b
55	3-Cl.C ₆ H ₄ .	Mw	OMe	CN	F	55—56	
56	3-Cl.C ₆ H ₄ .	H	OEt	CONH ₂	A	134—136	

TABLE 1 continued

Compound No.	R ¹	R ²	XR ³	E	Route	Melting Point °C	Notes (see end of Table)
57	3,5-(CF ₃) ₂ .C ₆ H ₃ .	H	OEt	CONH ₂	A	204—206	
58	3-Cl.C ₆ H ₄ .	H	OPr ⁱ	CONH ₂	A	140—143	
59	2,5-Cl ₂ .C ₆ H ₃ .	H	OEt	CONH ₂	A	163—165	
60	3-F.C ₆ H ₄ .	H	OPr ⁱ	CONH ₂	A	140	
61	3-F.C ₆ H ₄ .	H	OPr ⁱ	CN	A	82—83	
62	3-Me.C ₆ H ₄ .	H	OMe	CN	B	68—71	
63	3-Me.C ₆ H ₄ .	H	OPr ⁱ	CN	B	86—87	
64	3,5-Cl ₂ .C ₆ H ₃ .	Me	OMe	CN	F	88—90	
65	3,5-Cl ₂ .C ₆ H ₃ .	Me	OEt	CN	F	46—48	
66	3,5-(Me) ₂ .C ₆ H ₃ .	H	OEt	CN	B	85—87	
67	F ₆ .C ₆ .	H	OEt	CN	A	85—86	
68	3-Me-4-NO ₂ .C ₆ H ₃ .	H	OEt	CONH ₂	A	116—118	
69	4-MeO-3,5-Cl ₂ .C ₆ H ₂ .	H	OEt	CN	B	119—122	
70	3-Me.C ₆ H ₄ .	H	OMe	CSNH ₂	G	130—131	
71	3,5-(Me) ₂ .C ₆ H ₃ .	H	OEt	CSNH ₂	G	170—171	
72	3,5-Cl ₂ .C ₆ H ₃ .	Pr ⁱ	OMe	CN	F	79—81	

TABLE 1 continued

Compound No.	R ¹	R ²	XR ³	E	Route	Melting Point °C	Notes (see end of Table)
73	3,5-Cl ₂ .C ₆ H ₃ .	Et	OMe	CN	F	97—98	c
74	3-Cl.C ₆ H ₄ .	Et	OMe	CN	F	Oil	
75	3-Cl.C ₆ H ₄ .	Pr ¹	OMe	CN	F	Oil	
76	3-Me.C ₆ H ₄ .	Pr ¹	OMe	CN	F	Oil	d
77	3-Me.C ₆ H ₄ .	Et	OMe	CN	F	Oil	e
78	3-Me.C ₆ H ₄ .	Me	OMe	CN	F	Oil	f
79	3,5(Me) ₂ .C ₆ H ₃ .	H	OEt	CONH ₂	B	180—183	g
80	3-CN.C ₆ H ₄ .	H	OEt	CONH ₂	A	157—158	
81	3-CN.C ₆ H ₄ .	H	OEt	CN	A	112—115	
82	3,5-Cl ₂ .C ₆ H ₃ .	H	OPr ⁿ	CN	A	178—180	
83	3,5-Cl ₂ .C ₆ H ₃ .	H	OPr ⁿ	CN	A	137—138	
84	3,5-Cl ₂ .C ₆ H ₃ .	H	OPr ⁿ	CSNH ₂	G	137—138	
85	2-naphthyl	H	OEt	CN	A	117—118	
86	3-Cl-5-NO ₂ .C ₆ H ₃ .	H	OEt	CN	A	133—136	
87	3-chlorobenzyl	H	OEt	CN	B	87—89	
88	2,6-dichloro-4-pyridyl-	H	OMe	CONH ₂	B	190—192	

TABLE 1 continued

Compound No.	R ¹	R ²	XR ³	E	Route	Melting Point °C	Notes (see end of Table)
89	3-Cl. C ₆ H ₄ .	H	OCH ₂ CH=CH ₂	CONH ₂	A	91—92	
90	3,5-Cl ₂ . C ₆ H ₃ .	H	OCH ₂ CH=CH ₂	CONH ₂	A	164—165	
91	3,5-Cl ₂ . C ₆ H ₃ .	H	OCH ₂ CH=CH ₂	CN	A	134—135	
92	3-Cl. C ₆ H ₄ .	H	OCH ₂ CH=CH ₂	CN	A	64—66	
93	3-Cl. C ₆ H ₄ .	H	Sme	CONH ₂	A	154—156	
94	3-Br. C ₆ H ₄ .	H	OMe	CONH ₂	A	141—143	
95	3-Br. C ₆ H ₄ .	H	OMe	CN	A	88—90	
96	3-Et. C ₆ H ₄ .	H	OEt	CN	B	55—56	
97	3-Cl-5-Me. C ₆ H ₃ .	H	OEt	CN	B	114—116	
98	3-Cl-5-Me. C ₆ H ₃ .	H	OMe	CN	B	99—102	
99	2-furyl	H	OMe	CONH ₂	B	113—114	
100	2-furyl	H	OEt	CONH ₂	B	113—114	
101	2-furyl	H	OMe	CN	B	75—77	
102	2-furyl	H	OEt	CN	B	73—74	
103	2,6-dichloro-4-pyridyl	H	OMe	CN	B	134—136	
104	2-benzthiazolyl	H	OMe	CN	B	116—118	

TABLE 1 continued

Compound No.	R ¹	R ²	XR ³	E	Route	Melting Point °C	Notes (see end of Table)
105	<i>iso</i> -pentyl	H	OMe	CONH ₂	B	98—101	
106	<i>iso</i> -pentyl	H	OMe	CN	B	Oil	
107	<i>tert</i> -C ₄ H ₉	H	OMe	CONH ₂	B	86—88	
108	<i>tert</i> -C ₄ H ₉	H	OMe	CN	B	59—60	
109	3,5-Cl ₂ . C ₆ H ₃ .	H	SMe	CN	A	150—152	
110	3-Me. C ₆ H ₄ .	H	SMe	CN	B	119—120	
111	3-Br. C ₆ H ₄ .	H	OEt	CSNH ₂	G	145—146	
112	2-naphthyl	H	OMe	CN	A	117—118	
113	3-MeO. C ₆ H ₄ .	H	OMe	CONH ₂	B	106—108	
114	3-Cl-5-NO ₂ . C ₆ H ₃ .	H	OEt	CONH ₂	A	190—192	
115	5-Cl-2-MeO. C ₆ H ₃ .	H	OEt	CONH ₂	B	177—180	
116	5-Cl-2-MeO. C ₆ H ₃ .	H	OEt	CN	B	109—112	
117	3,5-Cl ₂ . C ₆ H ₃ .	H	OCH ₂ CF ₃	CN	A	148—149	
118	3-MeO. C ₆ H ₄ .	H	OMe	CN	B	80—81	
119	3,5-(MeO) ₂ . C ₆ H ₃ .	H	OMe	CN	B	98—100	
120	3,5-(MeO) ₂ . C ₆ H ₃ .	H	OEt	CN	B	86—88	

TABLE 1 continued

Compound No.	R ¹	R ²	XR ³	E	Route	Melting Point °C	Notes (see end of Table)
121	C ₆ H ₅ CH ₂ .	H	OMe	CN	B	67—68	h
122	3-F.C ₆ H ₄ .	Me	OMe	CN	F	Oil	
123	3-I.C ₆ H ₄ .	H	OEt	CONH ₂	A	174—176	
124	3-I.C ₆ H ₄ .	H	OMe	CONH ₂	A	147—148	
125	3-I.C ₆ H ₄ .	H	OEt	CN	A	123—125	i
126	3-I.C ₆ H ₄ .	H	OMe	CN	A	98—101	
127	3,5-Cl ₂ .C ₆ H ₃ .	CH ₂ Ph	OMe	CN	F	59—61	
128	3-Cl.C ₆ H ₄ .	CH ₂ Ph	OMe	CN	F	Oil	
129	3,5-Cl ₂ .C ₆ H ₃ .	H	OEt	CONHMe	B	184—185	
130	3,5-Cl ₂ .C ₆ H ₃ .	H	OEt	CONMe ₂	B	90—92	
131	3,5-Cl ₂ .C ₆ H ₃ .	H	OEt	CO-N 	B	112—113	
132	3-Cl-5-Me.C ₆ H ₃ .	H	OEt	CONH ₂	B	169—171	
133	3,5-F ₂ .C ₆ H ₃ .	H	OEt	CONH ₂	A	173—175	
134	3,5-F ₂ .C ₆ H ₃ .	H	OEt	CN	A	111—112	
135	3-Cl-4,5-F ₂ .C ₆ H ₂ .	H	OEt	CONH ₂	A	167—168	
136	3-Cl-4,5-F ₂ .C ₆ H ₂ .	H	OEt	CN	A	146—149	

TABLE 1 continued

Compound No.	R ¹	R ²	XR ³	E	Route	Melting Point °C	Notes (see end of Table)
137	C ₆ H ₅ .	H	NHAc	CONH ₂	D	243—245	j
138	C ₆ H ₅ .	H	NHAc	CN	D	193—194	
139	C ₆ H ₅ .	H	NHAc	CONHMe	D	207—209	
140	3,5-Br ₂ .C ₆ H ₃ .	H	OEt	CONH ₂	A	203—205	
141	3,5-Br ₂ .C ₆ H ₃ .	H	OEt	CN	A	165—167	
142	3,5-Cl ₂ .C ₆ H ₃ .	CH ₂ Ph	OEt	CN	F	Oil	
143	3-Eto.C ₆ H ₄ .	H	OEt	CONH ₂	B		
144	3-Eto.C ₆ H ₄ .	H	OEt	CN	B	95—97	
145	3,4,5-Cl ₃ .C ₆ H ₂ .	H	OEt	CONH ₂	A	203—204	
146	3,4,5-Cl ₃ .C ₆ H ₂ .	H	OEt	CN	A	139—141	
147	3,5-Cl ₂ .C ₆ H ₃ .	H	OCH ₂ CH ₂ CH ₂ Cl	CONH ₂	A	169—172	
148	3,5-Cl ₂ .C ₆ H ₃ .	H	OCH ₂ CH ₂ CH ₂ Cl	CN	A	123—124	
149	3-F.C ₆ H ₄ .	H	NHAc	CONH ₂	D	238—240	
150	C ₆ H ₅ .	CH ₂ Ph	OMe	CN	F	Oil	
151	3-F.C ₆ H ₄ .	CH ₂ Ph	OMe	CN	F	Oil	k
152	3,5-Cl ₂ .C ₆ H ₃ .	H	NHAc	CONH ₂	D	267—268	

TABLE 1 continued

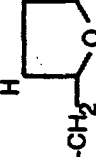
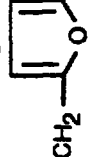
Compound No.	R ¹	R ²	XR ³	E	Route	Melting Point °C	Notes (see end of Table)
153	3,5-Cl ₂ .C ₆ H ₃ .	H	NHAc	CN	D	227—228	k
154	3,5-Me ₂ .C ₆ H ₃ .	H	NHAc	CONH ₂	C	244—245	
155	3-F.C ₆ H ₄ .	H	NHAc	CN	D	175—176	
156	3,5-Me ₂ .C ₆ H ₃ .	CH ₂ Ph	OMe	CN	F	Oil	l
157	3-Me.C ₆ H ₄ .	CH ₂ Ph	OMe	CN	F	Oil	
158	3,5-Me ₂ .C ₆ H ₃ .	H	NHAc	CN	C	195—197	m
159	3,5-Cl ₂ .C ₆ H ₃ .		OMe	CN	E	89—90	
160	3,5-F ₂ .C ₆ H ₃ .	CH ₂ Ph 	OMe	CN	F	Oil	
161	3-Cl.C ₆ H ₄ .		OMe	CN	E	48—49	

TABLE 1 continued

Compound No.	R ¹	R ²	XR ³	E	Route	Melting Point °C	Notes (see end of Table)
162	3,5-Me ₂ .C ₆ H ₃ .	H	NHCOCH=CH ₂	CONH ₂	C	201—203	
163	3,5-Me ₂ .C ₆ H ₃ .	H	NHCOCH=CH ₂	CN	C	191—193	
164	3,5-Cl ₂ .C ₆ H ₃ .	H	NHCOCH=CH ₂	CONH ₂	C	223—225	
165	3,5-Cl ₂ .C ₆ H ₃ .	H	NHCOCH=CH ₂	CN	C	220—222	
166	3,4,5-F ₃ .C ₆ H ₂ .	H	OEt	CONH ₂	A	155—156	
167	3,4,5-F ₃ .C ₆ H ₂ .	H	OEt	CN	A	129—131	
168	3,5-Cl ₂ .C ₆ H ₃ .	Allyl	OMe	CONH ₂	E	176—178	
169	3,5-Cl ₂ .C ₆ H ₃ .	Allyl	OMe	CN	E	Oil	
170	3,5-Cl ₂ .C ₆ H ₃ .	C ₆ H ₅	OMe	CN	E	Oil	
171	3,5-F ₂ .C ₆ H ₃	H	NHAc	CONH ₂	C	197—200	
172	3,4-OCH ₂ O.C ₆ H ₃	H	OEt	CONH ₂	B	159—161	
173	3,4,5-F ₃ .C ₆ H ₂	H	OCH ₂ CH=CH ₂	CONH ₂	A	104—106	
174	3,4,5-F ₃ .C ₆ H ₂	H	OCH ₂ CH=CH ₂	CN	A	109—111	
175	3,4-OCH ₂ OC ₃ H ₆	H	OEt	CN	B	155—156	
176	3-ClC ₆ H ₄	Allyl	OMe	CONH ₂	E	115—116	

TABLE 1 continued

Compound No.	R ¹	R ²	XR ³	E	Route	Melting Point °C	Notes (see end of Table)
177	3-ClC ₆ H ₄	CH ₂ CH=CH ₂	OMe	CN	E	Oil	
178	2-HOC ₆ H ₄	H	OEt	CN	B	Oil	
179	2-AcOC ₆ H ₄	H	OEt	CN	B	83—87	
180	3-FC ₆ H ₄	H	OCH ₂ CF ₃	CONH ₂	A	104—106	
181	3-FC ₆ H ₄	H	OCH ₂ CF ₃	CN	A	106—107	
182	3,4,5-F ₃ C ₆ H ₂	H	NHAc	CONH ₂	C	241—242	
183	3,4,5-F ₃ C ₆ H ₂	H	NHAc	CN	C	210—211	
184	3,5-Cl ₂ C ₆ H ₃	H	OCH ₂ CH ₂ Br	CONH ₂	A	165—166	
185	3,5-F ₂ C ₆ H ₃	H	OCH ₂ CH ₂ Br	CONH ₂	A	160—162	
186	3,5-F ₂ C ₆ H ₃	H	NHAc	CN	C	204—206	
187	3-FC ₆ H ₄	H	NHCOCH ₂ CH CH ₂	CN	C	185—187	
188	3,5-Cl ₂ C ₆ H ₃	H	OCH ₂ CH ₂ Cl	CONH ₂	A	176—178	
189	4-MeOC ₆ H ₄	H	OEt	CONH ₂	B	169—170	

TABLE 1 continued

Compound No.	R ¹	R ²	XR ³	E	Route	Melting Point °C	Notes (see end of Table)
190	4-MeOC ₆ H ₄	H	OEt	CN	B	87—89	
191	3,4-OCH ₂ OC ₆ H ₃	H	SMe	CONH ₂	B	185—187	
192	3,4-OCH ₂ OC ₆ H ₃	H	SMe	CN	B	139—141	
193		H	OMe	CONH ₂	B	214—215	
194		H	OMe	CN	B	110—111	
195	3-ClC ₆ H ₄	Me	SMe	CN	F	Oil	
196	4-MeC ₆ H ₄	H	OEt	CN	B	133—135	
197	4-ClC ₆ H ₄	H	OEt	CN	A	102—103	
198	3,4-Me ₂ C ₆ H ₃	H	OEt	CN	A	94—96	
199	4-BrC ₆ H ₄	H	OEt	CN	A	113—114	
200	4-CNC ₆ H ₄	H	OEt	CN	A	103—104	
201	3,4-(MeO) ₂ C ₆ H ₃	H	OEt	CN	B	121—123	
202	3-Cl-4-HOC ₆ H ₃	H	OEt	CN	B	90—92	
203	3-Cl-4-AcOC ₆ H ₃	H	OEt	CN	B	126—128	
204	3-Cl-4-Me-C ₆ H ₃	H	OEt	CN	A	113—114	

TABLE 1 continued

Compound No.	R ¹	R ²	XR ³	E	Route	Melting Point °C	Notes (see end of Table)
205	3,5-Cl ₂ -4-MeC ₆ H ₂	H	OEt	CN	A		
206	4-CF ₃ C ₆ H ₄	H	OEt	CN	A	114—115	
207	3-Cl-4-OMeC ₆ H ₃	H	OEt	CN	B		
208	3-Br-4-OMeC ₆ H ₃	H	OEt	CN	B		
209	3,4,5-Me ₃ C ₆ H ₂	H	OEt	CN	B		
210	4-EtC ₆ H ₄	H	OEt	CN	A	115—116	

NOTES:

The abbreviations used in Table 1 are standard chemical symbols. Thus the symbols Me, Et, Pr and Ph stand for methyl, ethyl, propyl, and phenyl groups respectively, and the symbols F₆, C₆, and 3-Cl-5-NO₂-C₆H₃, for example, stand for pentafluorophenyl and 3-chloro-5-nitrophenyl respectively.

Melting points are given for most compounds in the table. Where the compound is an oil, a refractive index measurement or nuclear magnetic resonance (NMR) data are given in the notes below. In the NMR information, the symbols have the following meanings:—

s singlet
t triplet
q quartet
m multiplet
d doublet

Chemical shifts (δ) are quoted relative to tetramethylsilane. The solvent used was deuteriochloroform.

Notes for individual compounds follow:—

(a) Refractive index $n_D^{25} = 1.5233$

(b) Refractive index $n_D^{25} = 1.5197$

(c) NMR data: δ = 1.3 (3H, t), 3.45 (3H, s), 3.7 (2H, q), 5.95 (1H, s, broad), ca. 7.5 (4H, m)

(d) NMR data: δ = 1.5 (6H, s), 2.35 (3H, s), 3.3 (3H, s), 4.1 (1H, m), 5.5 (1H, s), ca. 7.2 (4H, m)

(e) NMR data: δ = 1.5 (6H, d), 2.35 (3H, s), 3.3 (3H, s), 4.1 (1H, m), 5.5 (1H, s), ca. 7.2 (4H, m)

(f) NMR data: δ = 1.3 (3H, t), 2.4 (3H, s), 3.7 (2H, q), 5.95 (1H, s, broad), ca. 7.3 (4H, m)

(g) NMR data: δ = 2.4 (3H, s), 3.1 (3H, s), 3.4 (3H, s), ca. 6.1 (1H, s, very broad), ca. 7.3 (4H, m)

(h) NMR data: δ = 3.1 (3H, s), 3.4 (3H, s), 6.1 (s, very broad), ca. 7.2 (4H, m)

(i) NMR data: δ = 3.4 (3H, s), 4.75 (2H, q), 4.7 (2H, d), 5.95 (1H, broad), ca. 7.2 (8H, m)

(j) NMR data: δ = 1.2 (3H, t), 3.55 (2H, q), 4.7 (2H, d), 5.95 (1H, broad), ca. 7.2 (9H, m)

(k) NMR data: δ = 3.35 (3H, s), 4.75 (2H, s), 5.9 (1H, s, broad), ca. 7.2 (9H, m)

(l) NMR data: δ = 2.3 (6H, s), 3.3 (3H, s), 4.75 (2H, s), 5.9 (1H, s, broad), 7.0—7.4 (8H, m)

(m) NMR data: δ = 3.4 (3H, s), 4.75 (2H, s), 5.9 (1H, s, broad), ca. 6.8—7.3 (8H, m)

29

In another aspect the invention provides a process of inhibiting the growth of unwanted plants, which comprises applying to the plants, or to the locus thereof, a phytotoxic amount of a compound of the formula (I) as hereinbefore defined. The amount of the compound may vary, depending upon the identity of the particular compound chosen and the plant species whose growth is to be inhibited, but in general amounts of from 0.01 to 5.0 kilograms per hectare will be suitable; usually the amount will be from 0.2 to 1.0 kilograms per hectare. The skilled worker in the herbicide art will readily be able to establish appropriate application rates by standard procedures without undue experimentation.

The compounds of the invention are relatively less toxic towards certain crop plants than they are towards other plant species; accordingly, there is the possibility of using the compounds for selective weed control in these crops. Examples of such crops include cotton, sugar beet, rape, lettuce, peas; the compounds may be useful in a number of crops of the families Compositae and Leguminosae.

The compounds used in the process of the invention are preferably applied in the form of a composition, in which the active ingredient is mixed with a carrier comprising a solid or liquid diluent. In another aspect, therefore, the invention provides a herbicidal composition, comprising as an active ingredient a compound of the formula (I) as hereinbefore defined, in admixture with a solid or liquid diluent. Preferably the composition also comprises a surface-active agent.

The solid compositions of the invention may be for example, in the form of dusting powders, or may take the form of granules. Suitable solid diluents include, for example, kaolin, bentonite, kieselguhr, dolomite, calcium carbonate, talc, powdered magnesia, and Fuller's Earth.

Solid compositions may also be in the form of dispersible powders or grains comprising in addition to the active ingredient, a wetting agent to facilitate the dispersion of the powder or grains in liquids. Such powders or grains may include fillers, suspending agents and the like.

Liquid compositions include aqueous solutions, dispersions and emulsions containing the active ingredient preferably in the presence of one or more surface active agents. Water or organic liquids may be used to prepare solutions, dispersions, or emulsions of the active ingredient. The liquid compositions of the invention may also contain one or more corrosion inhibitors for example lauryl isoquinolinium bromide.

Surface active agents may be of the cationic, anionic or non-ionic type. Suitable agents of the cationic type include for example quaternary ammonium compounds, for example cetyltrimethyl ammonium bromide. Suitable agents of the anionic type include for example soaps, salts of aliphatic mono-esters of sulphuric acid, for example sodium lauryl sulphate; and salts of sulphonated aromatic compounds, for example dodecylbenzenesulphonate, sodium, calcium and ammonium lignosulphonate, butylnaphthalene sulphonate, and a mixture of the sodium salts of diisopropyl- and triisopropyl-naphthalenesulphonic acid. Suitable agents of the non-ionic type include, for example, the condensation products of ethylene oxide with fatty alcohols such as oleyl alcohol and cetyl alcohol, or with alkyl phenols such as octyl-phenol, nonylphenol, and octylcresol. Other non-ionic agents are the partial esters derived from long chain fatty acids and hexitol anhydrides, for example sorbitol monolaurate; the condensation products of the said partial esters with ethylene oxide and the lecithins.

The compositions which are to be used in the form of aqueous solutions, dispersions or emulsions are generally supplied in the form of a concentrate containing a high proportion of the active ingredient, the concentrate being diluted with water before use. These concentrates are usually required to withstand storage for prolonged periods and after such storage to be capable of dilution with water in order to form aqueous preparations which remain homogenous for a sufficient time to enable them to be applied by conventional spray equipment.

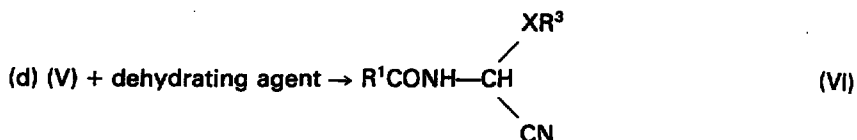
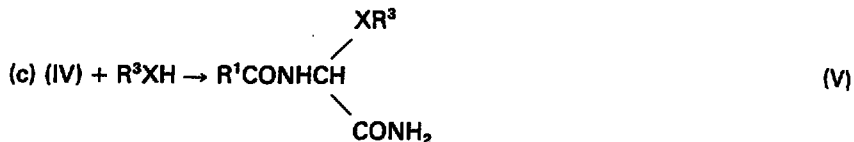
The compositions of the invention may contain, in addition to carriers and surface-active agents, various other constituents to increase their usefulness. They may contain, for example, buffering salts to maintain the pH of the composition within a desired range; antifreeze agents, for example urea or propylene glycol; adjuvants, for example oils and humectants; and sequestrants, for example citric acid and ethylenediaminetetracetic acid, which help to prevent the formation of insoluble precipitates when the compositions are diluted with hard water. Aqueous dispersions may contain anti-settling agents and anti-caking agents. The compositions may in general contain a dye or pigment to impart a characteristic colour. Agents for increasing viscosity may be added to reduce the formation of fine droplets during spraying, and thereby reduce spray drift. Other additives useful for particular purposes will be known to those skilled in the formulation art.

In general concentrates may conveniently contain from 10 to 85% and preferably from 25 to 60% by weight of active ingredient. Dilute preparations ready for use may contain varying amounts of the active ingredient, depending upon the purpose for which they are to be used; however, dilute preparations suitable for many uses contain between 0.01% and 10% and preferably between 0.1% and 1% by weight of the active ingredient.

The invention further provides processes for preparing compounds of formula (I) above. Thus, compounds wherein R^2 is hydrogen may be prepared, for example, by the process of Scheme A below:—

28
(III)

Scheme A



The process outlined in Scheme A begins with step (a), in which an acid chloride R^1COCl is reacted with aminoacetonitrile by a conventional procedure to obtain the acylaminoacetonitrile derivative (III). This is then reacted in step (b) with a brominating agent (for example bromine in glacial acetic acid) to give the brominated derivative (IV). This bromination procedure also simultaneously hydrates the cyano group to a carbamoyl group $-\text{CONH}_2$, and necessitates treatment with a dehydrating agent at a later stage to convert the carbamoyl group back into a cyano group. It may be possible to avoid the undesired conversion of the cyano group to the carbamoyl by use of a different solvent or brominating agent and thereby shorten the process by making step (d) unnecessary.

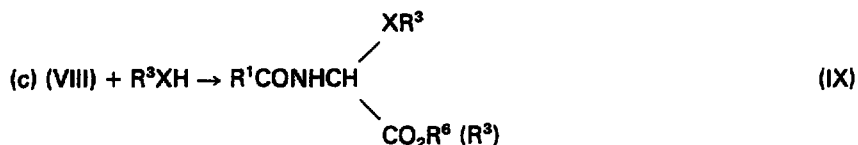
In step (c), the bromo compound (IV) is reacted with an appropriate alcohol, thiol, or amine of formula R^3XH to obtain the carbamoyl compound (V). Preferably the reaction is carried out in a solvent; the solvent should be an aprotic solvent to avoid reaction of the solvent with the bromo-compound (IV). Preferably an acid acceptor is present in at least a stoichiometric proportion. Examples of acid acceptors include tertiary amines, for example triethylamine and pyridine. The reaction takes place readily even at ambient temperatures but may be accelerated if desired by heating for example to 100°C or above.

The intermediate compounds of formula IV and V are novel and constitute a further aspect of the present invention.

The final step (d) of Scheme A is the treatment of the carbamoyl compound (V) with a dehydrating agent to convert it to the corresponding cyano compound. The dehydrating agent may be, for example, a bi-molar amount of *p*-toluene sulphonyl chloride in pyridine as solvent and acid acceptor, or another dehydrating agent, for example phosphorus oxychloride-dimethylformamide. The reaction with *p*-toluene-sulphonyl chloride proceeds readily at ambient temperature. Scheme A has been described in terms of brominated compounds; however, the scheme could equally be carried out using a chlorinating agent (e.g. gaseous chlorine) in place of a brominating agent, to produce the chlorinated compound corresponding to compound (IV); this could then be used in step (c) in place of compound (IV). This route cannot be used where R^1 is readily attacked by elemental bromine or chlorine.

A further process for making compounds of the invention in which R^2 is hydrogen is outlined in Scheme B:—

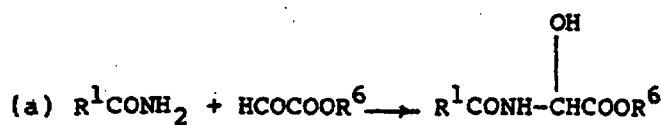
Scheme B



In step (a) of Scheme B, an amide R^1CONH_2 is condensed with a glyoxylic ester $\text{HCO}-\text{CO}_2R^6$ to give the hydroxy intermediate (VII). The group R^6 is an ester radical, for example an alkyl group of 1 to 4 carbon atoms (e.g. a methyl group). In step (b), the hydroxy intermediate (VII) is treated with a chlorinating agent

(e.g. thionyl chloride) to convert it to the chloroderivative (VIII). This is in turn reacted in step (c) with the appropriate alcohol, thiol, or amine R^3XH to give the ester (IX). Treatment of this with ammonia in step (c) gives the carbamoyl derivative (V) which may then be converted to the cyano compound of the invention by the method of step (d) of Scheme A.

An alternative process for preparing the amide derivatives of the invention when $X=O$ in formula I is a variation of the Scheme B process above. This Scheme B variation is outlined below:

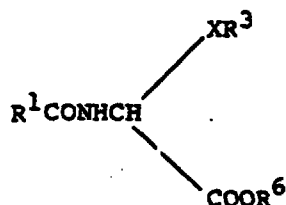


(VII)

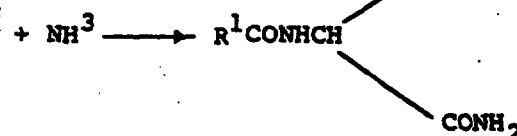
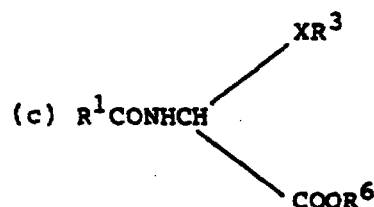


(VII)

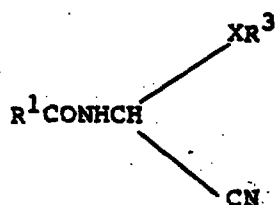
HXR^3
(H_2SO_4 present as catalyst)



(IX)



(V)

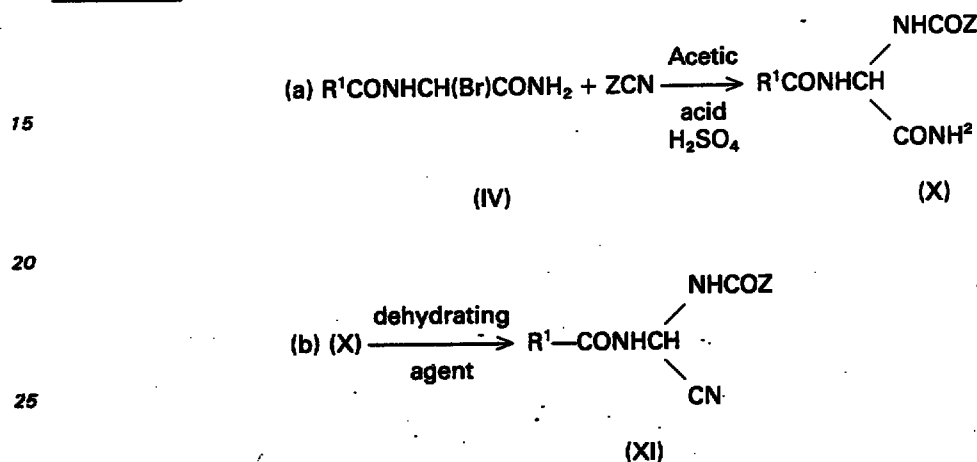


(VI)

In this modified Scheme B procedure it can be seen that one can proceed directly from the hydroxy intermediate (VII) to the ester (IX) in one step. The ester (IX) is then treated with ammonia, as in step d, to produce the carbamoyl derivative (V) which in turn is converted to the cyano compound of the invention (VI) by means of the final step (step d) of the process of Scheme A.

5 A further process for preparing compounds of the invention in which the group XR^3 is an —NHCOZ group where Z is alkyl or alkylene is outlined in Scheme C below.

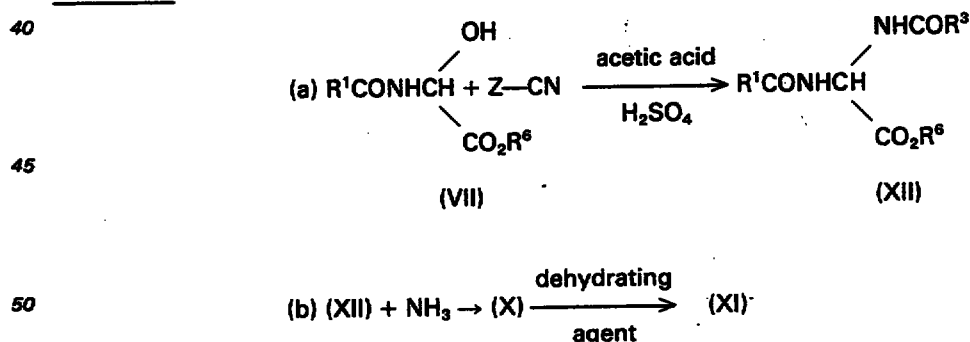
10 Scheme C



30 According to Scheme C the bromo-amide (IV) (prepared as in Scheme A) is reacted with the appropriate nitrile ZCN in acetic acid under the conditions of the Ritter reaction to give the amide (X). This is then treated with a dehydrating agent (e.g. trifluoroacetic anhydride in pyridine) to give the required nitrile (XI).

35 A further method of preparing the nitriles (XI) is shown in Scheme D below.

40 Scheme D

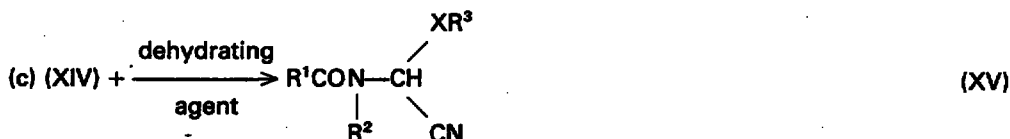
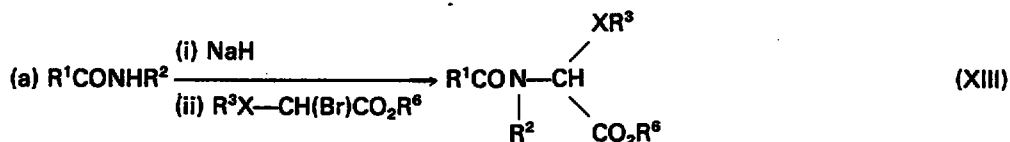


55 In Scheme D, the hydroxy-ester (VII) prepared as in Scheme B is reacted with the appropriate nitrile ZCN, where Z is alkyl or alkylene, in the presence of acetic acid and sulphuric acid (Ritter reaction) to give the amide (XII). This may then be reacted with ammonia to give the amide (X) already prepared in Scheme C. As in Scheme C the amide (X) may then be dehydrated to give the required nitrile (XI). The conversion of (XII) to (X) may be troublesome because the esters (XII) tend to be highly insoluble.

60 A further method of preparing compounds of the invention is outlined in Scheme E.

3

Scheme E

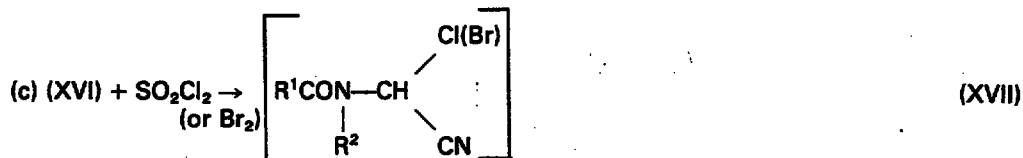
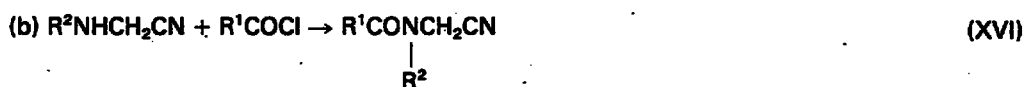
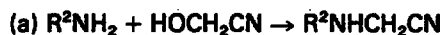


According to Scheme E, an amide R^1CONHR^2 is first treated with sodium hydride and the anion so generated is then reacted with an alpha bromo ester $\text{R}^3\text{X}-\text{CH}(\text{Br})\text{CO}_2\text{R}^6$ to give the ester (XIII). This is then reacted with ammonia to give the amide (XIV), and finally (XIV) is treated with a dehydrating agent to give the nitrile (XV).

This method may conveniently be used to prepare compounds in which R^2 is other than hydrogen, particularly when either R^1 or R^2 is susceptible to reaction with bromine or sulphuryl chloride, which are used as reagents in certain other routes described herein.

A further method for preparing compounds of the invention is outlined in Scheme F.

Scheme F

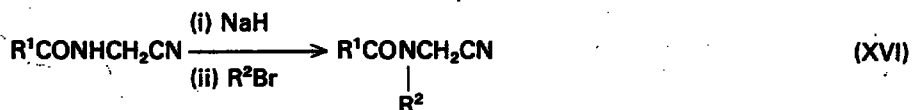


According to Scheme F, an amine R^2NH_2 is condensed with formaldehyde cyanhydrin to give the substituted aminoacetonitrile $\text{R}^2\text{NHCH}_2\text{CN}$. This is then acylated by the appropriate acid chloride R^1COCl to give the amide derivative (XVI).

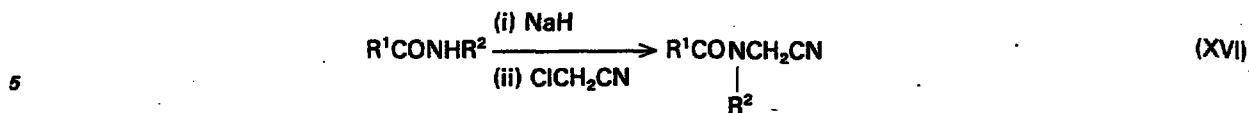
This in turn is chlorinated (e.g. with SO_2Cl_2) or brominated (e.g. with Br_2) to give the highly reactive bromo- or chloro-derivative (XVII). This is treated with the appropriate alcohol, thiol or amine R^3XH in the presence of base to give the required nitrile (XV).

The chloro- or bromo- nitriles (XVII) are too unstable to be isolated and characterised, and are used within a short time after they are prepared. The final stage (d) of the scheme may conveniently be carried out by using an excess of alcohol, thiol, or amine R^3XH as solvent, and anhydrous potassium carbonate as the base. Triethylamine or other tertiary amines may also be used as the base.

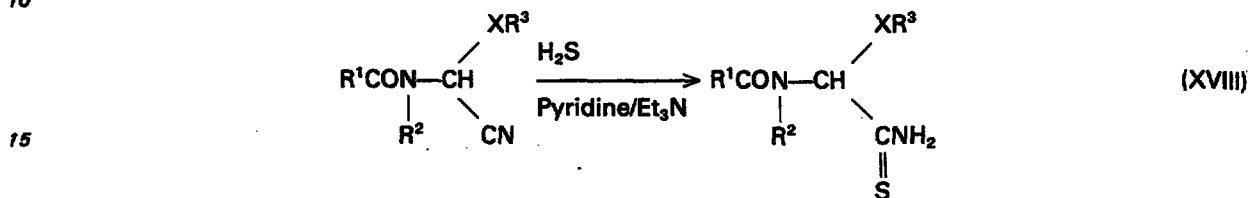
The cyanoamides (XVI) may also be prepared by methods other than that described above. Thus, the R^2 substituent may be introduced by alkylation as shown below:—



Another alternative is shown below:—



Compounds of the invention in which the group E is a thiocarbamoyl radical may be prepared according to Scheme G below:—



The reaction is conveniently carried out by passing gaseous H_2S through a solution of the nitrile in pyridine containing a little triethylamine as catalyst. Usually the solution is externally cooled to $0-10^\circ$. If the product does not separate from the solution, it may be isolated by removal of the solvent.

The amide derivatives of formula I, and compositions containing them, are variously active against a wide range of fungal diseases, particularly, for example, against:

- Plasmopara viticola* (downy mildew) on vines and
- Phytophthora infestans* (late blight) on potatoes and tomatoes and other species of *Phytophthora*
- Phytophthora parasitica*, *Phytophthora cinnamomi*, *Phytophthora palminora* and *Phytophthora capsici* on a range of commercially important crops
- Peronospora tabacina* on tobacco
- Peronospora parasitica* on cabbage
- Peronospora destructor* on onions
- Bremia lactuca* on lettuce
- Pythium* species on a range of commercially important crops
- Other fungal diseases, for example:
- Venturia inaequalis* (scab) on apples
- Cercospora arachidicola* on peanuts and other *Cercospora* species.

A particularly valuable feature of the activity of the amide derivatives is their systemic effect, i.e. their ability to move in a plant to combat an infection or infestation remote from the site of initial application. Thus a derivative, or a composition containing it, may be applied to the soil surrounding the roots of a plant or to the seed or to other plant areas, e.g. leaves, and be taken up by the plant through its roots, or other areas, to combat fungi locally or elsewhere on the plants.

In another aspect, therefore, the invention provides a process for combatting fungi, especially of inhibiting the growth of fungi on plants, which comprises applying to the plants, or the locus thereof, a fungicidally effective amount of a compound of the formula I as hereinbefore defined. The amount of the compound may vary, depending upon the identity of the particular compound chosen, the fungal species whose growth is to be inhibited, and the plant or locus involved.

The skilled worker in the fungicide art will readily be able to establish appropriate application rates by standard procedures without undue experimentation.

Preferred compounds for use in the fungicidal compositions of the invention and the process for combatting fungi are those defined in detail above with reference to formula I wherein R_2 is hydrogen, R^1 is optionally-substituted phenyl, or heterocyclyl, for example 2-furyl, X is O or S (X is preferably O) and R^3 is alkyl, alkenyl, or haloalkyl, and E is CN or CSNH_2 .

Preferred phenyl substitution, when R^1 is phenyl, is at the 3, 4 or 5 positions and is alkyl, alkoxy, methylenedioxy or halogen. Preferred alkyl groups for R^3 are C_{1-4} alkyl. Allyl is also a preferred group for R^3 .

The compounds used in the process and compositions of the invention are preferably applied in the form of a composition, in which the active ingredient is mixed with a carrier comprising a solid or liquid diluent. In another aspect, therefore, the invention provides a fungicidal composition, comprising as an active ingredient a compound of the formula I as hereinbefore defined, in admixture with a solid or liquid diluent. Preferably the composition also comprises a surface-active agent.

The amide derivatives may be used as such for anti-fungal purposes but are more conveniently formulated into compositions for such usage.

The invention also provides fungicidal compositions comprising as active ingredient an amide derivative as defined in any of the paragraphs above.

The amide derivatives and compositions containing them can be used to combat plant fungi and treat plants or seeds in a number of ways, for example they can be applied, formulated or unformulated, directly

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to the foliage of of plant which is infected or likely to become infected, or they can be applied also to bushes and trees, to soil or to other medium in which plants, bushes or trees are growing or to be planted, or they can be sprayed on, dusted on or applied as a cream or paste formulation. Application can be to any part of the plant, bush or tree, for example to the foliage, stems, branches, seeds or roots, or to the soil surrounding the roots.

The terms "combatting" and "treatment" as used herein embrace all the foregoing modes of application and the term "plant" includes seedlings, bushes and trees. Furthermore, the method of the invention includes protectant, prophylactic and eradicant treatment.

The derivatives are preferably used for agricultural and horticultural purposes in the form of compositions. The type of composition used in any instance will depend upon the particular purpose envisaged.

The compositions may be in the form of dusting powders or granules, for example ordinary grains or "slow release" granules wherein the active ingredient is mixed with a solid diluent or carrier, for example, kaolin, bentonite, kieselguhr, dolomite, calcium carbonate, talc, powdered magnesia, Fuller's earth, gypsum, Hewitt's earth, diatomaceous earth and China clay.

Compositions for dressing seed may, for example, comprise an agnet (for example a mineral oil) for assisting the adhesion of the composition to the seed.

The compositions may also be in the form of dispersible powders or grains comprising a wetting agent to facilitate the dispersion in liquids of the powders or grains which may contain also fillers and suspending agents.

The aqueous dispersion of emulsions may be prepared by dissolving the active ingredient(s) in an organic solvent which may contain wetting, dispersing or emulsifying agent(s) and then adding the mixture so obtained to water which may also contain wetting, dispersing or emulsifying agent(s). Suitable organic solvents are ethylene dichloride, isopropyl alcohol, propylene glycol, diacetone alcohol, toluene, kerosene, methylnaphthalene, xylenes and trichloroethylene.

The compositions for spraying may also be in the form of aerosols wherein the formulation is held in a propellant, e.g. fluorotrichloromethane or dichlorodifluoromethane.

By including suitable additives, for example additives for improving the distribution, adhesive power and resistance to rain on treated surfaces, the different compositions can be better adapted for various utilities.

The derivatives can be used in smoke generators and also as mixtures with fertilisers (e.g. nitrogen- or phosphorus- containing fertilisers). Compositions comprising only granules of fertiliser incorporating, for example coated with, the derivative, are preferred.

The invention therefore also provides a fertiliser composition comprising the derivative and a fertiliser.

The compositions may also be in the form of liquid preparations for use as dips or sprays which are generally aqueous dispersions or emulsions containing the active ingredient in the presence of one or more surface active agent(s), dispersing agent(s), emulsifying agent(s) or anionic or non-ionic agents. Suitable cationic agents are quaternary ammonium compounds for example, cetyltrimethylammonium bromide.

Suitable anionic agents are soaps, salts of aliphatic monoesters of sulphuric acid (for example sodium lauryl sulphate), and salts of sulphonated aromatic compounds (for example sodium dodecylbenzenesulphonate, sodium, calcium or ammonium lignosulphonate, butylnaphthalene sulphonate, and a mixture of sodium di-isopropyl- and triisopropyl-naphthalene sulphonates).

Suitable non-ionic agents are the condensation products of ethylene oxide with fatty alcohols such as oleyl alcohol or cetyl alcohol, or with alkyl phenols such as octylphenol, nonylphenol and octylcresol. Other non-ionic agents are the partial esters derived from long chain fatty acids and hexitol anhydrides, the condensation products of the said partial esters with ethylene oxide, and the lecithins. Suitable suspending agents are hydrophilic colloids (for example polyvinylpyrrolidone and sodium carboxymethylcellulose), and the vegetable gums (for example gum acacia and gum tragacanth).

The compositions for use as aqueous dispersions or emulsions are generally supplied in the form of a concentrate containing a high proportion of the active ingredient(s), the concentrate to be diluted with water before use. These concentrates often should be able to withstand storage for prolonged periods and after such form aqueous preparations which remain homogenous for a sufficient time to enable them to be applied by conventional spray equipment. The concentrates may conveniently contain 10—85%, generally 25—60%, by weight of the active ingredient(s).

When diluted to form aqueous preparations, such preparations may contain varying amounts of the active ingredient(s) depending upon the intended purpose, but an aqueous preparation containing 0.0005% or 0.01% to 10% by weight of active ingredient(s) may be used.

The compositions of this invention can comprise also other compound(s) having biological activity, e.g. compounds having similar or complementary fungicidal or plant growth regulating activity or compounds having herbicidal or insecticidal activity.

The other fungicidal compound can be for example one which is capable of combating ear diseases of cereals (e.g. wheat) such as *Septoria*, *Gibberella* and *Helminthosporium* spp., seed and soil borne diseases and downy and powdery mildews on grapes and powdery mildew and scab on apple etc. These mixtures of fungicides can have a broader spectrum of activity than the compound of general formula (I) alone; further

the other fungicide can have a synergistic effect of the fungicidal activity of the compound of general formula (I). Examples of the other fungicidal compound are imazail, benomyl, carbendazim (BCM), thiophanate-methyl, captan, sulphur, dithiocarbamates, carbathiins, copper oxychloride, triforine, dodemorph, tridemorph, dithianon, pyrazophos, binapacryl, quinomethionate, panoctine, furalaxyl, aluminium tris(ethylphosphonate), DPX3217, ethirimol, dimethirimol, bupirimate, chlorothalonil and metazanine.

Suitable insecticides are pirimor, croneton, dimethoate, metasystox and formothion.

The other plant growth regulating compound can be one which controls weeds or seedhead formation, improves the level or longevity of the plant growth regulating activity of the compounds of general formula (I), selectively controls the growth of the less desirable plants (e.g. grasses) or causes the compound of general formula (I) to act faster or slower as a plant growth regulating agent. Some of these other agents will be herbicides. Examples of suitable agents are the gibberellins (e.g. GA₃, GA₄ or GA₇), the auxins (e.g. indoleacetic acid, indolebutyric acid, naphthoxyacetic acid or naphthylacetic acid), the cytokinins (e.g. kinetin, diphenylurea, benzimidazole, benzyladenine or BAP), phenoxyacetic acids (e.g. 2,4-D or MCPA), substituted benzoic acids (e.g. TIBA), morphactins (e.g. chlorfluorecol), maleic hydrazine, glyphosate, glyphosine, long chain fatty alcohols and acids (e.g. Off Shoot O or Off Shoot T), dikegulac, Sustar, Embark, substituted quaternary ammonium and phosphonium compounds (e.g. CCC or Phosfon-D), Ethrel, carbetamide, Racuza, Alar, asulam, abscissic acid, isopyrimol, RH531, hydroxybenzotrioles (e.g. bromoxynil), Avenge, Suffix or Lontrel.

The invention is illustrated by the following Examples, in which unless otherwise stated all parts are by weight and temperatures in degrees Centigrade. The Examples that describe chemical syntheses give details in some cases of the nuclear magnetic resonance (NMR) spectra of the compounds. The information given in the chemical shift (δ) for each peak in the spectrum together with a symbol to indicate the nature of the peak, as follows:—s(singlet); d(doublet); m(multiplet); q(quartet); t(triplet). The solvent used was fully deuterated dimethyl sulphoxide or deuteriochloroform (CDCl₃).

Example 1

This Example illustrates the preparation of compound no. 4 of Table I by the process of Scheme A.

30 (a) Preparation of Benzoylamino(bromo)acetamide

To a suspension of benzoylaminoacetonitrile (5 g) in stirred glacial acetic acid (50 ml) was added all at once bromine (5.0 g). After a brief induction period, the bromine colour was discharged and the product (5.8 g) precipitated from the acetic acid. The product was filtered off, washed with glacial acetic acid, and then with anhydrous ether, and dried. A sample crystallised from glacial acetic acid had m.p. 157° (dec.).

35 Found: C, 42.22; H, 3.7; N, 10.81
C₉H₉BrN₂O₂ requires: C, 42.02; H, 3.5; N, 10.89%.

(b) Preparation of Benzoylamino(ethoxy)acetamide

The foregoing bromoamide (13.4 g) was suspended in anhydrous ethanol (50 ml) and heated on a steam bath just long enough for it to dissolve (ca. 5 min), whereupon the solution was cooled. The ethanol was removed under vacuum and the residual heavy oil was dissolved in water (40 ml) and neutralized by the cautious addition of solid sodium bicarbonate. The solution was then extracted with chloroform (200 ml) and the dried (MgSO₄) extract evaporated to yield a white solid. Crystallisation of this from dichloromethane-hexane gave the product (7.7 g), m.p. 148—150°.

45 Found: C, 59.19; H, 6.27; N, 12.5
C₁₁H₁₄N₂O₃ requires: C, 59.45; H, 6.34; N, 12.6%.
 δ (DMSO-d₆): 1.15 (t, 3H), 3.55 (q, 2H), 5.55 (d, 1H), 7.2—8.0 (m, 7H), 9.0 (d, 1H).

(c) Preparation of Benzoylamino(ethoxy)acetonitrile (Compound No. 4)

50 A solution of the foregoing ethoxyamide (5.55 g) in anhydrous pyridine (40 ml) containing p-toluenesulphonylchloride (4.78 g) was kept at room temperature for 72 hours. The reaction mixture was diluted with water (200 ml) and the precipitated solid filtered off, washed with water and dried. Crystallisation of the solid from carbon tetrachloride gave the product (2.5 g), m.p. 107—110°C.

55 Found: C, 64.31; H, 6.3; N, 13.54
C₁₁H₁₂N₂O₂ requires: C, 64.69; H, 5.92; N, 13.71%.
 δ (CDCl₃): 1.25 (t, 3H), 3.8 (q, 2H), 6.3 (d, 1H), 7.4—8.0 (m, 6H).

Example 2

This Example illustrates the preparation of compound no. 38 of Table I by the process of Scheme B.

60 (a) Preparation of Methyl-[3-Methoxybenzoylamino(hydroxy)]acetate

3-Methoxybenzamide (13.25 g) and methyl glyoxylate (7.72 g) in toluene (150 ml) were heated under reflux in a Dean-Stark apparatus for 6 hours. On cooling the mixture the product separated and was crystallized from toluene. Yield, 12.0 g, m.p. 93—94°C.

65 Found: C, 55.45; H, 5.37; N, 6.3
C₁₁H₁₃NO₅ requires: C, 55.23; H, 5.43; N, 5.85%.

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(b) Preparation of 3-Methoxybenzoylamino(ethoxy)acetamide

The foregoing ester (5.0 g) and thionyl chloride (40 ml) were stirred together for 2 hours, after which the excess of thionyl chloride was removed under vacuum. The residue was dissolved in ethanol (100 ml) and the solution then evaporated under vacuum. The residual oil was treated with aqueous ammonia (d 0.88) and the mixture allowed to stand. The solid so formed was filtered off, dried, and crystallised from chloroform-light petroleum to give the product (1.8 g), m.p. 143—144°.

Found: C, 56.17; H, 6.49; N, 10.73

$C_{12}H_{16}N_2O_4$ requires: C, 57.14; H, 6.35; N, 11.11%.

δ (DMSO- d_6): 1.3 (t, 3H), 3.7 (q, 2H), 4.0 (s, 3H), 5.7 (d, 1H), 7.2—7.8 (m, 6H), 9.15 (d, 1H).

(c) Preparation of 3-Methoxybenzoylamino(ethoxy)acetonitrile

The foregoing ethoxyamide (1.0 g), p-toluenesulphonylchloride (1.28 g) and pyridine (20 ml) were allowed to stand at room temperature for 72 hours. The reaction was then worked up as described in paragraph (c) of Example 1. The product (0.7 g) was crystallised from chloroform-light petroleum and had m.p. 72°.

δ (CDCl₃): 1.2 (t, 3H), 3.7 (q, 2H), 3.8 (s, 3H), 6.2 (d, 1H), 7—7.6 (m, 5H).

Example 3

This Example illustrates the preparation of compound no. 53 of Table 1, using the process of Scheme F.

Preparation of N-Methylbenzoylamino(methoxy)acetonitrile

To a cooled (5—10°) and stirred solution of N-methylbenzoylaminoacetonitrile (5.0 g) in anhydrous carbon tetrachloride (75 ml) was added dropwise bromine (4.6 g). Following the addition the mixture was stirred for a further 5 min. at room temperature, when methanol (25 ml) was added all at once. After stirring the mixture for a further 5 min., triethylamine (5.81 g) was added to the mixture. The solution was then washed with water and the organic phase dried (MgSO₄) and evaporated. The residual oil was chromatographed on a dry silica column using ether-hexane (7:3) as an eluent. Separation of the major band from the column gave the product as a colorless oil (1.0 g) n_D^{25} 1.5233.

δ (CDCl₃): 3.1 (s, 3H), 3.4 (s, 3H), 6.0 (very broad, 1H), 7.4 (s, 5H).

Example 4

This Example illustrates the preparation of compound no. 40 of Table I, using the process of Scheme A.

(a) Preparation of 3-Chlorobenzoylamino(methylthio)acetamide

To a solution of 3-chlorobenzoylamino(bromo)acetamide (5.5 g) in anhydrous tetrahydrofuran (100 ml) containing methyl mercaptan (slight excess) was added 1 equivalent of triethylamine and the mixture kept for 72 hours. The solution was filtered and the filtrate evaporated to give an oil which solidified on treatment with ether. Crystallisation of the solid from ethyl acetate gave the product (0.67 g).

δ (DMSO- d_6): 2.06 (s, 3H), 5.6 (d, 1H), 7.4—7.8 (m, 6H), 8.9 and 9.2 (two doublets, 1H).

(b) Preparation of 3-chlorobenzoylamino(methylthio)acetonitrile (Compound No. 40)

The foregoing amide (0.67 g) and 2 equivalents of p-toluenesulphonyl chloride in pyridine (10 ml) were kept at room temperature for 48 hours. The mixture was then poured into water (100 ml). The solid which separated was dried, and crystallised from chloroform-light petroleum to give the product (0.1 g), m.p. 115—117°.

Found: C, 48.99; H, 3.71; N, 11.01

$C_{10}H_9ClN_2OS$ requires: C, 49.9; H, 3.77; N, 11.64%.

δ (CDCl₃): 2.35 (s, 3H), 6.05 (d, 1H), 7.8—7.2 (m, 5H).

Example 5

This Example illustrates the preparation of compound no 158 of Table 1 by the process of Scheme C.

(a) Preparation of Acetylamino(3,5-dimethylbenzoylamino)acetamide

To a suspension of 3,5-dimethylbenzoylaminoacetonitrile (1 g) in glacial acetic acid (20 ml) was added all at once bromine (0.85 g). After stirring the mixture at room temperature for 15 min. the white solid was separated, washed with anhydrous ether and then re-suspended in glacial acetic acid (10 ml). To this was added concentrated sulphuric acid (1.5 ml) and acetonitrile (8 ml). After 1 hour the mixture was poured into water (30 ml) and extracted with chloroform (2 × 30 ml). The dried (MgSO₄) extract was evaporated and the residue crystallised from aqueous ethanol to give the product (0.38 g) as a white solid (Compound No. 154 of Table I), m.p. 244—5°.

Found: C, 58.49; H, 6.42; N, 15.46

$C_{13}H_{17}N_3O_3$ requires: C, 59.13; H, 6.46; N, 15.97%.

δ (DMSO- d_6): 1.9 (3H, s), 2.3 (6H, s), 5.8 (1H, dd), ca. 7.1—7.5 (5Hm m), 8.3 (1H, d), 8.7 (1H, d).

(b) Preparation of Acetylamino (3,5-dimethylbenzoylamino)acetonitrile

The foregoing acetamide (1.0 g) was dissolved in anhydrous pyridine (25 ml) which was then cooled to

–25°. Trifluoroacetic anhydride (1.5 g) was added dropwise to the cooled and stirred solution, and following the addition the solution was allowed to come to 0° whereupon it was poured into water (70 ml) and extracted with ether (2 × 50 ml). Evaporation of the ethereal extracts and crystallisation of the residue from ethyl acetate-hexane gave the product (0.6 g) as a pale cream solid, m.p. 195–7°.

- 5 Found: C, 62.51; H, 5.98; N, 17.16
 $C_{13}H_{15}N_3O_2$ requires: C, 63.67; H, 6.12; N, 17.14%.
 δ (DMSO- d_6): 1.8 (3H, s), 2.2 (6H, s), 6.2 (1H, dd), 7.1 (1H, s), 7.4 (2H, s), 9.1 (1H, s), 9.5 (1H, s).

EXAMPLE 6

10 This Example illustrates the preparation of compound no. 153 of Table I by the process of Scheme D.

(a) Preparation of Methyl Acetylamino (3,5-dichlorobenzoylamino) acetate

A mixture of 3,5-dichlorobenzamide (19.0 g) and methyl glyoxylate (8.8 g) in ethyl acetate (300 ml) was heated under reflux for 8 hours. The solvent was removed and the residual adduct was crystallised from 15 chloroform-light petroleum. A portion (4.0 g) of the adduct was dissolved in a mixture of glacial acetic acid (30 ml) and acetonitrile (10 ml) with stirring, and then concentrated sulphuric acid (4 ml) was added. The mixture was kept at room temperature overnight when water (100 ml) was added. The precipitated solid was washed with water, dried, and crystallised from ethanol to give the product (2.45 g) as a colourless crystalline solid, m.p. 235–237°.

- 20 Found: C, 45.24; H, 3.88; N, 8.84
 $C_{12}H_{12}Cl_2N_2O_4$ requires: C, 45.14; H, 3.76; N, 8.77%.
 δ (DMSO- d_6): 1.95 (3H, s), 3.7 (3H, s), 5.9 (1H, dd), 7.95 (3H, m), 8.9 (1H, d), 9.75 (1H, d).

(b) Preparation of Acetylamino (3,5-dichlorobenzoylamino)acetamide

25 The foregoing ester (1.46 g) was dissolved in dimethylformamide (70 ml) which was then saturated with ammonia (gas) and the mixture kept for 7 days. The solvent was removed under reduced pressure and the residue crystallised from aqueous dimethylformamide to give the product (0.72 g), m.p. 267–268° (dec).

- 30 Found: C, 43.62; H, 3.72; N, 13.82
 $C_{11}H_{11}Cl_2N_3O_3$ requires: C, 43.42; H, 3.62; N, 13.82%.
 δ (DMSO- d_6): 1.95 (3H, s), 5.9 (1H, dd), 7.3 (2H, d, broad) 7.6 (1H, m), 7.9 (2H, m), 8.35 (1H, d), 9.2 (1H, d).

(c) Preparation of Acetylamino (3,5-dichlorobenzoylamino)acetonitrile

35 The foregoing acetamide (0.5 g) in anhydrous pyridine (10 ml) at –25° was treated with trifluoroacetic anhydride as described above. The product (0.18 g), crystallised from aqueous dimethylformamide, had m.p. 227–228°.

- 40 Found: C, 45.95; H, 3.12; N, 14.43
 $C_{11}H_9Cl_2N_3O_2$ requires: C, 46.15; H, 3.15; N, 14.68%.
 δ (DMSO- d_6): 1.95 (3H, s), 6.4 (1H, dd), 7.9 (3H, m), 9.35 (1H, d), 10.0 (1H, d).

Example 7

This Example illustrates the preparation of compound no. 159 of Table I by the process of Scheme E.

(a) N-Furfuryl-3,5-dichlorobenzamide

45 To a vigorously stirred solution of furfurylamine (2.78 g) in ethyl acetate (40 ml) was added sodium hydroxide (1.15 g) in water (45 ml), followed immediately by the addition of a solution of 3,5-dichlorobenzoyl chloride (6.0 g) in ethyl acetate (20 ml). Following the mild exothermic reaction the ethyl acetate layer was removed, dried (MgSO₄), and evaporated. Crystallisation of the residue from cyclohexane gave the product (6.6 g) as colourless needles.

(b) Preparation of N-Furfuryl-3,5-dichlorobenzoylamino(methoxy) acetonitrile

50 To a stirred suspension of sodium hydride (0.58 g) in anhydrous tetrahydrofuran (40 ml) was added in portions the foregoing amide (3.0 g). Following the addition and cessation of hydrogen evolution was added with stirring methyl 2-bromo-2-methoxy acetate (2.04 g) and the mixture stirred for a further 2 hours 55 at room temperature. Water (100 ml) was then added and the solution extracted with methylene chloride (3 × 50 ml) and the extracts dried and evaporated. The resultant crude oily ester was dissolved in methanol (20 ml) which was then saturated with ammonia gas and kept overnight. The solvent was removed under reduced pressure and the residual oil triturated with ether to give crude amide (1.91 g). The crude amide (1.75 g) was dissolved in anhydrous pyridine (10 ml), cooled to 0° with stirring and phosphorus oxychloride 60 (0.84 g) added dropwise so that the temperature of the mixture did not exceed 0°. After 25 minutes at 0°, water (100 ml) was added and the mixture was extracted with ether (40 ml). The dried (MgSO₄) ether extract was chromatographed on silica using diisopropyl ether as the eluent. Following elution from the column and evaporation of the solvent the product (1.24 g) was obtained as a colourless oil which slowly crystallised, m.p. 89–90°.

- 65 δ (CDCl₃): 3.4 (3H, s), 4.65 (2H, s), 6.1 (1H, s, broad) 6.3 (2H, m), 7.3–7.5 (4H, m).

Example 8

This Example illustrates the preparation of compound no. 142 of Table I by the process of Scheme F.

Preparation of N-Benzyl-3,5-dimethylbenzoylamino(methoxy)acetonitrile

To a stirred solution of glycollonitrile (25 g) in methanol was added dropwise over 45 minutes benzylamine (46.9 g) keeping the temperature of the reaction between 15—20°. Following the addition the reaction mixture was kept overnight at room temperature, and then distilled to give benzylaminoacetonitrile (42.0 g) as a colourless oil, b.p. 120°/15 mm. Reaction of this (3.0 g) with 3,5-dimethylbenzoyl chloride (3.46 g) as described above gave crude N-benzyl-3,5-dimethylbenzoylaminoacetonitrile (5.81 g) as a colourless viscous oil which was used in the next stage without further purification. To this crude amide (2.0 g) in anhydrous methylene chloride (8 ml) was added sulphuryl chloride (0.97 g). Following the cessation of gas evolution (ca. 15 min.), anhydrous methanol (20 ml) and finely powdered anhydrous potassium carbonate (1.95 g) was added to the mixture which was then stirred for 30 minutes. Solids were removed from the solution which was then evaporated and the residual oil chromatographed on a column of silica using methylene chloride as an eluent. Following elution from the column and evaporation of the solvent, the product (1.2 g) was obtained as a very pale-yellow viscous oil.

Found: C, 73.87; H, 6.67; N, 9.22

C₁₉H₂₀N₂O₂ requires: C, 74.02; H, 6.49; N, 9.09%.

(CDCl₃): 2.28 (6H, s), 3.25 (3H, s), 4.75 (2H, s), 5.85 (1H, s, broad), ca. 7.0—7.4 (8H, m).

Example 9

This Example illustrates the preparation of compound no. 84 of Table I by the process of Scheme G.

Preparation of 3-chlorobenzoylamino(ethoxy)thioacetamide

Into a solution of 3-chlorobenzoylamino(ethoxy) acetonitrile (1 g) in toluene (50 ml) containing triethylamine (1 g) was passed hydrogen sulphide gas. The precipitated product (0.72 g) was collected and crystallised from chloroform-light petroleum. m.p. 136—137°.

Found: C, 48.53; H, 4.84; N, 10.19

C₁₁H₁₀ClN₂O₂S requires: C, 48.44; H, 4.80; N, 10.27%.

Example 10

This Example illustrates the herbicidal properties of compounds of Table I. The compounds were submitted to herbicide tests as described below.

Each compound was formulated for tests by mixing an appropriate amount of it with 5 ml of an emulsion prepared by diluting 160 ml of a solution containing 21.8 grams per litre of Span 80 and 78.2 grams per litre of Tween 20 in methylcyclohexanone to 500 ml with water. Span 80 is a Trade Mark for a surface-active agent comprising sorbitan monolaurate. Tween 20 is a Trade Mark for a surface-active agent comprising a condensate of 20 molar proportions of ethylene oxide with sorbitan monolaurate. The mixture of the compound and the emulsion was then shaken with glass beads and diluted to 44 ml with water. The spray composition so prepared was sprayed on to young pot plants (post-emergence test) of the species named in Tables 2 and 3 below, at a rate equivalent to 1000 litres per hectare. Damage to plants was assessed 13 days after spraying by comparison with untreated plants, on a scale of 0 to 5 where 0 is 0 to 20% damage and 5 is complete kill. In the table of results, a dash (—) means no test was made.

A test was also carried out to detect pre-emergence herbicidal activity. Seeds of the test species were placed on the surface of fibre trays of soil and were sprayed with the compositions at the rate of 1000 litres per hectare. The seeds were then covered with further soil. 20 days after spraying, the seedlings in the sprayed fibre trays were compared with the seedlings in unsprayed control trays, the damage being assessed on the same scale of 0 to 5.

The results of the tests are given in Tables 2 and 3 below.

TABLE 2

Compound No.	Rate of Application kg/ha	Pre- or Post-emergence Application	TEST PLANTS																								
			Sb	Rp	Ct	Sy	Mz	Ww	Rc	Sn	Ip	Am	Pi	Ca	Po	Xs	Ab	Cv	Ot/Av	Dg	Pu	St	Ec	Sh	Ag	Cn	
2	5.0	Pre	2	3	1	4	2	5	2	2	—	0	4	—	5	1	4	—	5	5	5	5	5	1	5	3	
		Post	2	2	0	2	4	4	2	0	1	4	4	—	4	2	2	1	4	4	2	4	4	0	3	0	
4	1.0	Pre	2	4	3	4	5	5	4	1	4	4	4	—	4	0	5	—	5	5	5	4	5	2	5	2	
		Post	0	0	0	2	3	4	1	—	3	2	3	2	2	0	1	3	4	2	4	3	3	3	3	0	
8	5.0	Pre	1	1	3	3	3	5	0	0	5	2	1	—	4	0	4	—	5	4	4	4	5	1	5	1	
		Post	0	0	0	1	3	4	1	—	0	1	3	3	2	0	1	2	4	3	4	3	3	3	3	2	
15	1.0	Pre	0	0	0	0	0	4	0	0	0	1	0	0	4	0	0	—	4	0	5	1	0	3	5	1	
		Post	0	0	0	0	0	2	0	0	0	0	0	0	3	0	0	1	2	0	4	2	0	0	3	0	
17	1.0	Pre	0	0	0	0	0	0	0	0	0	0	0	—	0	0	0	—	0	1	3	0	0	0	0	0	
		Post	0	0	0	0	0	0	0	1	1	3	—	2	0	0	1	2	0	0	0	1	0	1	0	0	
18	0.2	Pre	4	4	1	4	3	5	4	4	0	4	—	2	5	0	5	—	4	5	5	5	4	4	1	0	
		Post	1	2	0	1	4	3	0	2	3	3	—	—	3	2	2	3	3	4	4	3	1	0	1	0	

TABLE 2 continued

Compound No.	Rate of Application kg/ha	Pre- or Post-emergence Application	TEST PLANTS																								
			Sb	Rp	Ct	Sy	Mz	Ww	Rc	Sn	Ip	Am	Pi	Ca	Po	Xs	Ab	Cv	Or/Av	Dg	Pu	St	Ec	Sh	Ag	Cn	
20	1.0	Pre	4	4	4	4	5	5	5	4	3	5	—	—	5	0	5	—	5	5	5	5	5	5	5	5	3
		Post	1	2	0	2	4	4	2	2	3	3	—	3	3	2	3	3	4	4	4	4	4	4	4	3	3
21	1.0	Pre	0	0	0	0	0	5	0	4	0	0	—	0	—	0	4	—	3	1	—	0	0	0	3	2	2
22	0.2	Pre	1	1	0	4	5	5	4	5	0	5	—	—	5	0	4	—	5	5	5	5	4	3	4	1	1
		Post	0	0	0	1	4	4	1	1	—	3	—	3	3	1	1	3	4	4	4	5	2	1	2	0	0
23	1.0	Pre	0	0	0	1	0	5	0	1	0	0	0	0	0	0	1	—	2	0	3	0	0	0	0	0	0
		Post	0	1	0	0	0	0	0	0	3	—	0	1	1	0	0	0	0	0	0	0	0	0	1	0	0
24	5.0	Pre	0	1	2	0	0	4	0	0	0	—	—	0	3	0	3	—	4	4	5	4	3	—	4	—	—
		Post	1	0	0	0	1	2	0	0	3	3	0	3	3	0	2	3	3	4	0	1	4	2	0	0	0
26	1.0	Pre	4	4	1	4	2	5	4	4	3	4	—	3	5	0	5	—	5	5	5	5	5	4	4	6	6
		Post	2	2	0	2	4	4	2	2	3	3	—	3	1	2	4	—	4	4	4	4	3	3	2	1	1
28	1.0	Pre	3	1	1	0	0	4	0	0	0	4	—	0	4	1	2	—	2	5	5	4	2	0	0	0	0
		Post	0	0	1	0	1	1	0	0	3	1	—	—	1	0	2	3	2	4	2	3	0	1	0	0	0

TABLE 2 continued

Compound No.	Rate of Application kg/ha	Pre- or Post-emergence Application	TEST PLANTS																								
			Sb	Rp	Ct	Sy	Mz	Ww	Rc	Sn	Ip	Am	Pi	Ca	Po	Xs	Ab	Cv	Ol/Av	Dg	Pu	St	Ec	Sh	Ag	Cn	
30	0.2	Pre	3	2	1	2	2	5	2	0	0	4	—	4	5	0	4	—	4	5	5	5	5	2	1	1	
		Post	0	0	0	0	3	3	0	2	1	—	—	2	1	2	3	4	4	4	3	0	0	0	0	—	
31	5.0	Pre	1	0	0	0	0	4	3	0	0	5	5	—	5	0	3	—	4	2	5	4	2	3	0	0	
		Post	0	0	0	1	0	2	1	0	4	0	0	2	2	0	0	3	3	2	0	2	0	0	0	0	
32	3.0	Pre	0	0	1	0	0	4	0	0	0	1	1	—	3	2	3	—	3	0	4	0	0	0	0	0	
		Post	0	0	0	1	0	1	1	0	0	1	0	1	0	0	0	0	3	3	0	1	0	1	0	0	
33	5.0	Pre	3	4	2	4	4	4	4	4	0	5	5	—	5	0	4	—	4	5	5	5	5	4	1	0	
		Post	0	1	1	4	2	3	0	0	3	4	3	4	2	0	2	2	3	4	1	3	3	2	1	0	
34	0.2	Pre	4	4	0	4	3	4	4	4	1	5	—	3	5	0	4	—	4	5	5	5	4	4	1	2	
		Post	1	1	1	0	3	3	0	2	3	3	—	—	3	1	2	3	3	4	4	3	0	1	2	0	
36	1.0	Pre	4	4	3	5	4	5	5	4	4	5	5	5	5	0	5	—	5	5	5	5	5	5	4	—	
		Post	3	1	0	2	4	4	2	0	3	3	3	3	3	1	2	1	4	4	4	4	3	4	2	1	

TABLE 2 continued

Compound No.	Rate of Application kg/ha	Pre- or Post-emergence Application	TEST PLANTS																								
			Sb	Rp	Ct	Sy	Mz	Ww	Rc	Sn	Ip	Am	Pi	Ca	Po	Xs	Ab	Cv	Ol/Av	Dg	Pu	St	Ec	Sh	Ag	Cn	
38	1.0	Pre	4	4	3	3	3	5	4	4	3	5	4	5	5	0	4	—	5	5	5	5	5	5	5	5	—
		Post	0	0	0	2	4	4	2	0	3	2	2	0	2	0	2	2	4	4	4	4	4	3	2	0	
39	1.0	Pre	5	2	0	3	1	4	3	3	1	5	5	4	5	0	4	—	4	5	5	5	5	5	2	—	
		Post	3	0	1	3	3	3	0	1	4	2	2	2	2	1	2	2	3	4	4	4	4	1	2	0	
40	1.0	Pre	4	4	1	4	5	5	4	5	2	5	5	—	5	0	5	—	4	5	5	5	5	4	4	0	
		Post	0	1	1	3	3	3	2	1	3	1	3	1	2	1	2	2	3	4	4	3	4	3	3	0	
41	0.2	Pre	4	4	0	2	3	5	4	4	1	5	5	—	5	0	5	—	4	5	5	5	5	4	4	0	
		Post	0	0	0	2	2	3	0	0	2	0	2	0	1	0	0	1	4	4	2	3	3	2	2	0	
42	1.0	Pre	4	4	1	4	3	5	5	4	0	5	5	—	5	2	5	—	4	5	5	5	4	4	2	1	
		Post	0	2	0	3	3	4	1	2	3	2	2	1	1	2	2	2	3	4	2	2	4	2	2	0	
43	1.0	Pre	4	2	1	2	3	4	4	4	4	—	5	5	5	0	5	—	4	5	5	5	5	4	5	2	
		Post	1	0	1	2	2	3	0	0	3	1	2	2	1	1	2	3	4	4	3	2	2	1	0	0	

TABLE 2 continued

Compound No.	Rate of Application kg/ha	Pre- or Post-emergence Application	TEST PLANTS																								
			Sb	Rp	Ct	Sy	Mz	Ww	Rc	Sn	Ip	Am	Pl	Ca	Po	Xs	Ab	Cv	Ol/Av	Dg	Pu	St	Ec	Sh	Ag	Cn	
44	0.2	Pre	4	3	1	3	2	4	3	4	2	—	5	4	5	0	4	—	4	5	5	5	4	4	4	4	0
		Post	0	0	0	3	1	2	1	1	3	1	1	2	1	0	2	2	3	4	3	2	0	0	0	0	0
45	1.0	Pre	3	0	0	0	0	2	0	0	0	—	0	0	5	0	0	—	3	3	5	1	0	0	4	0	0
		Post	1	1	0	1	1	0	0	0	0	1	0	1	0	0	1	1	0	2	0	0	0	0	0	0	0
46	5.0	Pre	0	0	0	0	0	4	0	3	1	4	0	2	2	0	0	—	4	1	3	2	0	1	1	—	
47	1.0	Pre	0	0	0	0	1	4	1	1	0	—	5	—	5	1	0	—	3	4	5	2	2	3	0	0	0
		Post	0	0	0	0	0	0	0	0	1	3	0	2	0	1	2	1	0	3	0	2	0	1	0	0	0
48	5.0	Pre	4	0	1	2	1	5	1	0	0	5	1	4	5	0	4	—	3	5	5	3	5	1	0	0	0
		Post	0	0	0	2	0	2	0	0	0	1	1	1	2	1	1	—	3	2	1	5	0	0	0	0	0
51	0.05	Pre	0	0	0	1	1	3	0	0	0	—	1	0	5	0	4	—	2	4	5	1	1	2	5	0	0
51	0.2	Pre	3	3	1	3	5	5	3	3	5	—	5	4	5	0	5	—	5	5	5	5	5	5	5	5	5
		Post	1	0	0	3	2	3	0	2	3	4	2	1	2	1	2	2	4	4	4	4	1	1	1	0	0

TABLE 2 continued

Compound No.	Rate of Application kg/ha	Pre- or Post-emergence Application	TEST PLANTS																								
			Sb	Rp	Ct	Sy	Mz	Ww	Rc	Sn	Ip	Am	Pi	Ca	Po	Xs	Ab	Cv	Ot/Av	Dg	Pu	St	Ec	Sh	Ag	Cn	
52	0.2	Pre	2	1	0	0	1	5	2	0	5	—	5	3	5	0	4	—	5	4	5	4	4	4	4	5	1
		Post	1	0	1	1	3	3	1	0	3	4	2	2	2	1	1	3	4	4	4	3	1	0	3	1	
53	5.0	Pre	0	0	0	0	0	4	0	2	0	—	0	0	0	1	0	—	5	0	0	0	0	0	0	0	
		Post	1	0	0	2	0	0	0	1	2	—	0	4	1	0	0	0	0	1	0	1	0	0	0	0	
54	5.0	Pre	0	0	—	1	2	5	3	5	4	5	0	1	5	0	3	—	4	4	5	4	4	3	0	5	
		Post	0	0	0	0	2	0	0	1	3	—	1	1	2	0	1	2	0	1	0	0	1	0	0	0	
55	5.0	Pre	0	0	0	4	4	5	0	1	4	5	5	4	4	0	3	—	5	5	5	5	5	2	5	0	
		Post	0	1	3	1	1	1	0	0	3	—	2	2	2	0	1	1	4	2	2	1	0	0	1	0	
56	5.0	Pre	0	0	0	0	1	0	0	3	1	0	—	2	—	0	0	—	1	1	—	0	0	0	2	1	
		Post	0	0	0	0	0	0	0	0	0	—	0	0	—	0	0	—	0	0	—	3	0	0	0	0	
59	4.0	Pre	2	3	0	2	0	0	0	3	1	—	—	3	—	0	2	—	0	0	—	—	1	2	0	3	0
		Post	0	1	0	0	0	0	0	0	0	—	0	0	—	0	0	—	0	0	—	—	0	0	0	0	

TABLE 2 continued

Compound No.	Rate of Application kg/ha	Pre- or Post-emergence Application	TEST PLANTS																							
			Sb	Rp	Ct	Sy	Mz	Ww	Rc	Sn	Ip	Am	Pi	Ca	Po	Xs	Ab	Cv	Ot/Av	Dg	Pu	St	Ec	Sh	Ag	Cn
61	1.0	Pre	5	3	3	4	3	4	4	2	3	5	5	2	5	0	5	—	4	5	5	5	3	4	1	
		Post	0	0	0	2	2	3	0	1	3	3	0	3	3	1	2	3	2	4	2	3	3	1	0	
62	0.05	Pre	0	0	0	0	0	5	0	1	0	—	0	0	—	0	0	—	3	4	5	4	2	0	3	0
62	0.2	Pre	4	2	1	1	3	5	3	1	3	—	5	5	5	0	4	—	5	5	5	5	1	5	0	
		Post	2	0	0	0	3	4	0	0	2	2	2	1	3	1	2	2	3	4	4	3	1	0	3	1
63	1.0	Pre	3	0	2	1	2	4	2	0	1	—	2	4	5	0	5	—	4	4	5	5	3	2	0	
		Post	1	0	0	0	2	2	1	1	1	0	0	1	1	0	2	2	1	4	3	4	0	2	0	
64	1.0	Pre	0	0	0	1	2	2	0	0	0	—	0	0	2	0	2	—	3	4	4	3	0	1	0	0
65	1.0	Pre	1	0	0	0	0	0	0	0	0	—	0	0	3	0	1	—	0	0	0	1	0	0	0	
66	0.05	Pre	2	0	0	1	2	3	2	4	0	3	2	2	3	0	3	—	3	5	5	4	3	4	1	—
66	0.2	Pre	4	2	2	3	5	5	4	4	2	5	5	5	5	0	5	—	5	5	5	5	4	4	3	1
		Post	2	1	1	3	3	3	0	2	3	1	1	—	2	1	2	—	4	4	4	3	2	2	2	0

TABLE 2 continued

Compound No.	Rate of Application, kg/ha	Pre- or Post-emergence Application	TEST PLANTS																								
			Sb	Rp	Ct	Sy	Mz	Ww	Rc	Sn	Ip	Am	Pi	Ca	Po	Xs	Ab	Cv	Ot/Av	Dg	Pu	St	Ec	Sh	Ag	Cn	
69	1.0	Pre	0	0	0	0	1	2	0	0	0	—	0	4	—	0	0	—	3	4	—	2	0	0	0	0	0
		Post	1	0	0	2	0	1	0	0	0	1	0	1	—	0	1	—	0	2	—	4	0	0	0	0	0
70	1.0	Pre	3	2	2	2	2	5	3	4	3	5	5	5	—	0	4	—	5	5	—	5	5	2	5	2	2
		Post	0	0	0	1	3	4	1	1	2	2	1	2	—	0	2	—	4	4	—	3	4	1	3	0	0
71	1.0	Pre	5	4	1	4	4	5	5	4	3	5	5	5	—	0	4	—	5	5	—	5	5	4	3	1	1
		Post	2	2	0	3	4	3	0	1	2	2	1	2	—	0	1	—	4	4	—	4	4	2	2	1	1
72	5.0	Pre	1	0	0	0	1	4	1	0	0	—	—	2	—	0	0	—	4	3	—	2	2	2	1	0	0
		Post	0	1	2	0	1	0	0	0	0	—	1	—	—	0	1	—	0	0	—	5	3	3	2	0	0
73	5.0	Pre	0	—	0	0	0	4	2	0	1	5	4	5	—	0	4	—	4	4	—	4	0	1	1	—	—
		Post	0	0	0	2	2	1	0	0	3	3	2	1	—	0	2	—	4	2	—	1	1	0	0	0	0
74	1.0	Pre	0	0	0	0	3	5	0	0	0	—	—	0	—	0	0	—	3	3	—	5	3	0	2	0	0
		Post	0	0	0	0	3	0	0	0	1	—	0	0	—	0	0	—	0	0	—	0	0	0	0	0	0

TABLE 2 continued

Compound No.	Rate of Application kg/ha	Pre- or Post-emergence Application	TEST PLANTS																								
			Sb	Rp	Ct	Sy	Mz	Ww	Rc	Sn	Ip	Am	Pi	Ca	Po	Xs	Ab	Cv	Ot/Av	Dg	Pu	St	Ec	Sh	Ag	Cn	
75	5.0	Pre	0	—	0	0	2	5	0	0	0	1	2	0	—	1	1	—	1	0	—	0	0	2	4	0	
		Post	0	0	0	1	1	0	0	0	0	0	0	0	—	0	0	—	0	0	—	1	1	0	0	0	
78	5.0	Pre	0	—	0	1	0	4	0	2	0	5	—	4	—	0	0	—	4	0	—	3	0	0	4	—	
		Post	0	0	0	0	0	1	0	0	0	0	0	0	—	0	0	—	1	0	—	0	0	0	0	0	
81	1.0	Pre	4	3	2	4	3	4	3	4	3	—	—	4	—	0	4	—	5	4	—	5	5	3	1	0	
		Post	2	1	0	2	3	4	1	1	3	1	1	2	—	0	1	—	3	4	—	3	3	3	2	0	
82	5.0	Pre	0	—	0	0	0	5	0	1	0	0	1	0	—	0	0	—	3	1	—	0	0	0	0	—	
		Post	0	0	0	0	2	3	0	0	0	0	0	0	—	0	0	—	1	0	—	1	0	0	1	0	

TABLE 2 continued

Compound No.	Rate of Application kg/ha	Pre- or Post-emergence Application	TEST PLANTS																								
			Sb	Rp	Ct	Sy	Mz	Ww	Rc	Sn	Ip	Am	Pi	Ca	Po	Xs	Ab	Cv	Ot/Av	Dg	Pu	St	Ec	Sh	Ag	Cn	
83	1.0	Pre	3	0	1	2	2	3	3	1	0	—	—	4	—	0	2	—	4	4	—	3	2	0	1	0	
		Post	0	0	0	2	2	0	0	0	3	1	0	2	—	0	1	—	1	2	—	1	1	1	0	0	
84	1.0	Pre	0	0	0	2	1	2	2	0	0	—	—	0	—	0	0	—	3	4	—	3	1	0	0	0	
		Post	0	0	0	1	2	1	0	0	2	0	1	2	—	0	2	—	1	0	—	2	0	1	0	0	
85	4.0	Pre	2	—	2	1	2	4	3	1	—	2	4	0	—	0	—	—	3	5	—	4	3	2	0	—	
		Post	0	1	1	2	1	2	0	1	0	1	0	1	—	0	1	—	2	3	—	2	2	0	0	0	
91	1.0	Pre	5	4	1	3	1	4	2	3	0	5	—	5	—	0	5	—	5	5	—	5	5	4	0	—	
		Post	—	2	1	1	3	2	0	2	3	2	1	0	—	2	2	—	2	3	—	1	1	2	0	—	
92	1.0	Pre	3	3	1	3	5	4	4	5	0	5	—	5	—	0	5	—	4	5	—	5	5	1	5	—	
		Post	—	1	1	1	3	1	0	0	1	3	0	0	—	0	2	—	3	4	—	3	0	3	1	—	
95	0.2	Pre	5	2	0	2	1	5	3	3	0	5	—	5	—	0	4	—	4	5	—	5	4	0	0	—	
		Post	—	0	0	1	2	3	0	1	1	3	0	0	—	1	1	—	3	1	—	1	0	1	2	—	

TABLE 2 continued

Compound No.	Rate of Application kg/ha	Pre- or Post-emergence Application	TEST PLANTS																							
			Sb	Rp	Ct	Sy	Mz	Ww	Rc	Sn	Ip	Am	Pi	Ca	Po	Xs	Ab	Cv	Ot/Av	Dg	Pu	St	Ec	Sh	Ag	Cn
96	1.0	Pre	4	4	1	3	4	5	3	3	0	5	1	5	—	0	4	—	5	5	—	5	4	0	—	—
		Post	—	1	1	2	3	4	1	0	1	3	0	1	—	1	2	—	4	3	—	3	3	2	—	—
97	1.0	Pre	4	4	4	4	5	5	5	5	4	5	5	5	—	4	5	—	5	5	—	5	4	4	—	—
		Post	2	3	0	3	4	4	3	4	3	—	3	2	—	3	3	—	4	4	—	4	4	4	—	—
98	1.0	Pre	4	4	3	4	5	5	5	4	3	5	5	5	—	2	4	—	5	5	—	5	4	4	—	—
		Post	2	2	0	2	4	4	2	3	3	—	2	1	—	2	3	—	4	4	—	3	3	2	—	—
103	5.0	Pre	4	3	3	3	2	5	2	3	5	—	1	3	—	2	4	—	5	5	—	5	4	4	—	—
		Post	1	4	2	3	3	4	1	3	3	—	3	3	—	2	2	—	4	3	—	3	2	0	2	—
104	1.0	Pre	0	0	0	0	0	0	0	0	0	0	0	3	—	0	0	—	0	0	—	0	1	0	3	—
		Post	0	0	0	2	0	0	0	0	0	0	0	0	—	0	0	—	0	0	—	1	0	0	0	—

TABLE 2 continued

Compound No.	Rate of Application kg/ha	Pre- or Post-emergence Application	TEST PLANTS																									
			Sb	Rp	Ct	Sy	Mz	Ww	Rc	Sn	Ip	Am	Pi	Ca	Po	Xs	Ab	Cv	Ot/Av	Dg	Pu	St	Ec	Sh	Ag	Cn		
106	5.0	Pre	0	0	1	0	0	3	0	0	0	3	0	1	—	0	1	—	—	2	0	—	0	0	1	5	—	
		Post	0	0	0	0	2	0	0	0	1	0	0	0	—	0	1	—	—	1	1	—	1	0	0	0	—	
109	1.0	Pre	5	5	2	5	3	5	4	4	5	5	—	5	—	4	5	—	—	4	5	—	5	5	4	4	—	
		Post	2	3	1	3	3	3	1	3	3	2	2	3	—	3	3	—	—	4	4	—	2	2	0	2	—	

TABLE 3

Compound No.	Rate of Application kg/ha	Pre- or Post-emergence Application	TEST PLANTS																							
			Sb	Rp	Ct	Sy	Mz	Ww	Rc	Sn	Ip	Am	Pi	Ca	Ga	Xa	Ab	Co	Av	Dg	Al	St	Ec	Sh	Ag	Cn
110	1.0	Pre	4	4	2	4	3	5	2	—	1	5	—	5	—	0	4	3	4	5	5	5	5	3	5	—
		Post	1	1	1	2	1	4	0	1	3	2	—	1	2	1	2	0	4	3	3	1	2	1	3	—
111	1.0	Pre	5	4	2	4	3	4	4	3	2	5	—	5	—	0	4	1	3	5	5	5	5	4	5	—
		Post	1	1	1	0	2	4	0	2	3	4	—	2	3	1	2	0	4	3	4	3	2	1	2	—
112	5.0	Pre	3	2	0	0	0	3	0	2	0	0	—	1	—	0	0	0	0	1	3	3	2	0	—	—
		Post	0	0	0	2	1	0	0	0	0	1	—	0	1	1	1	0	1	0	0	2	0	0	0	—
117	1.0	Pre	2	1	0	2	0	2	2	2	0	3	—	5	—	0	3	0	0	4	1	1	3	3	2	—
		Post	0	0	0	2	0	1	0	1	2	2	—	2	1	0	1	1	0	0	0	1	0	0	1	—
119	1.0	Pre	2	0	0	0	0	4	2	1	3	3	—	4	—	0	2	0	3	4	5	3	2	2	5	—
		Post	0	0	0	1	1	3	0	0	2	1	—	0	1	0	1	0	3	0	0	0	0	2	3	—

TABLE 3 continued

Compound No.	Rate of Application kg/ha	Pre- or Post-emergence Application	TEST PLANTS																							
			Sb	Rp	Ct	Sy	Mz	Ww	Rc	Sn	Ip	Am	Pi	Ca	Ga	Xa	Ab	Co	Av	Dg	Al	St	Ec	Sh	Ag	Cn
120	1.0	Pre	4	3	3	3	3	4	4	4	3	4	—	4	—	0	4	2	2	5	5	5	5	4	5	—
		Post	0	1	0	2	2	3	0	1	3	3	—	2	2	0	2	1	3	2	0	2	0	1	2	—
122	5.0	Pre	1	0	1	3	0	4	0	0	3	0	—	—	—	0	2	0	5	0	5	0	1	1	0	2
		Post	0	0	0	0	0	0	0	1	3	0	—	0	—	1	0	0	2	0	0	0	0	0	3	0
125	0.2	Pre	4	1	0	2	2	3	2	1	—	3	—	3	0	5	—	1	5	4	5	4	5	5	1	
125	1.0	Pre	5	4	3	3	4	4	5	5	—	5	—	5	5	4	—	5	5	5	5	5	5	5	5	4
		Post	2	2	1	2	4	4	2	2	2	—	—	3	1	2	2	1	3	3	2	2	3	1	3	0
126	1.0	Pre	4	4	3	4	3	5	5	5	—	5	—	5	5	4	—	5	5	5	5	5	5	5	5	4
		Post	1	2	0	1	3	4	0	2	2	—	—	3	2	2	2	0	4	2	2	3	1	0	2	0

TABLE 3 continued

Compound No.	Rate of Application kg/ha	Pre- or Post-emergence Application	TEST PLANTS																								
			Sb	Rp	Ct	Sy	Mz	Ww	Rc	Sn	Ip	Am	Pi	Ca	Ga	Xa	Ab	Co	Av	Dg	Al	St	Ec	Sh	Ag	Cn	
127	5.0	Pre	0	0	0	0	0	0	0	0	0	—	0	—	0	2	0	3	0	3	0	1	0	0	0	2	0
		Post	1	3	0	0	2	0	0	2	—	—	—	2	0	3	1	2	0	—	—	—	—	0	0	0	0
134	.025	Pre	1	0	0	2	0	0	0	0	0	1	—	—	—	1	0	1	0	3	0	0	0	0	2	0	
134	1.0	Pre	5	5	4	5	4	5	4	4	4	—	4	—	3	5	4	5	5	5	5	5	5	5	5	5	5
		Post	3	3	1	3	3	4	4	2	2	3	—	3	3	2	3	2	4	4	4	4	4	4	3	3	2
136	1.0	Pre	3	3	2	1	2	4	5	4	4	3	3	3	1	4	4	5	4	5	5	5	5	5	4	4	
138	5.0	Pre	—	—	—	—	—	4	—	—	—	—	—	—	—	—	—	5	—	—	—	—	—	—	—	—	—
		Post	—	—	—	—	—	2	—	—	—	—	—	—	—	—	—	1	—	—	—	—	—	—	—	—	—

TABLE 3 continued

Compound No.	Rate of Application kg/ha	Pre- or Post-emergence Application	TEST PLANTS																								
			Sb	Rp	Ct	Sy	Mz	Ww	Rc	Sn	Ip	Am	Pi	Ca	Ga	Xa	Ab	Co	Av	Dg	Al	St	Ec	Sh	Ag	Cn	
141	1.0	Pre	4	4	0	4	2	4	3	3	4	3	3	4	—	0	5	3	5	5	5	3	5	5	4	5	2
		Post	2	2	0	2	2	2	0	2	2	3	—	3	3	0	2	2	3	3	3	1	2	1	0	1	1
144	1.0	Pre	1	2	0	0	1	2	2	0	3	1	0	1	0	0	3	1	4	5	5	5	5	5	5	5	3
		Post	1	1	1	1	2	3	0	0	2	—	0	0	0	0	1	1	2	1	0	1	0	0	0	2	1
146	1.0	Pre	3	2	0	1	1	2	2	0	3	2	3	3	0	0	0	2	3	4	5	2	2	3	4	2	
		Post	0	0	1	0	0	2	0	0	1	—	0	0	0	0	0	0	1	0	0	0	0	0	0	—	0
148	1.0	Pre	0	0	0	0	0	0	1	—	0	0	0	0	0	0	—	0	0	1	0	0	0	0	0	0	
		Post	0	0	0	1	1	2	0	0	1	—	1	—	2	1	2	1	0	5	1	3	1	0	0	0	
153	1.0	Pre	2	0	0	1	1	3	1	0	2	3	2	2	0	0	—	0	3	3	1	2	0	0	3	0	
		Post	0	0	1	0	2	2	0	1	2	—	0	2	0	0	1	0	2	2	0	3	0	0	2	0	

Names of test plants in Tables 2 and 3

	Sb	Sugar beet
	Rp	Rape
5	Ct	Cotton
	Sy	Soya Bean
	Mz	Maize
	Ww	Winter wheat
	Rc	Rice
10	Sn	<i>Senecio vulgaris</i>
	Ip	<i>Ipomoea purpurea</i>
	Sm	<i>Amaranthus retroflexus</i>
	Pi	<i>Polygonum aviculare</i>
	Ca	<i>Chenopodium album</i>
15	Po	<i>Portulaca oleracea</i>
	Xs and Xa	<i>Xanthium spinosum</i>
	Ab	<i>Abutilon theophrastii</i>
	Cv	<i>Convolvulus arvensis</i>
	Ot/Av	Oats (cultivated in pre-emergence test and <i>Avena fatua</i> (wild oats) in post-emergence test (Applies to Table 2; in Table 3 only <i>Avena fatua</i> is used)
20	Dg	<i>Digitaria sanguinalis</i>
	Pu	<i>Poa annua</i>
	St	<i>Setaria viridis</i>
	Ec	<i>Echinochloa crus-galli</i>
25	Sh	<i>Sorghum halepense</i>
	Ag	<i>Agropyron repens</i>
	Cn	<i>Cyperus rotundus</i>
	Ga	<i>Galium aparine</i>
	Co	<i>Cassia obtusifolia</i>
30	Al	<i>Alopecurus myosuroides</i>

Example 11

35 This Example further illustrates the herbicidal properties of compounds according to the invention. Tests were carried out as described in Example 10, but using different ranges of test plants. The post-emergence test was slightly different from the one described in Example 10 in that the seeds were sown in trays of soil and covered with a few millimetres of soil before spraying the test compound, whereas in the previous test the seeds were sprayed directly.

40 The compounds were formulated in a similar way to that described in Example 10, but using cyclohexanone solution containing Synperonic NPE 1800 (a nonyl-phenolpropylene oxide — ethylene oxide condensate) and Tween 85 (a condensate of sorbitan tri-oleate with 20 molar proportions of ethylene oxide) instead of the methylcyclohexanone solution of surfactants described in that Example. The damage to the test plants was assessed on a scale of 0 to 9 wherein 0 represents 0 to 10% damage to the plant and 9 is 90 to 100% damage. Assessments were made 26 days after spraying the compounds. The results are given in Tables 4 and 5 below.

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60

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TABLE 4

Compound No.	Rate of Application kg/ha	Pre- or Post-emergence Application	TEST PLANTS															
			Ww	Br	Pe	Rp	Sb	Lt	Av	Al	Bt	Ag	Ga	Sm	Ca	Pi	Ma	Sp
18	0.2	Pre	6	7	2	8	9	7	9	9	9	6	7	9	9	9	9	6
		Post	8	7	1	0	1	0	8	3	0	5	7	7	4	7	0	—
20	0.1	Pre	8	9	0	0	9	0	9	9	9	9	5	9	9	9	8	3
		Pre	9	9	2	7	6	5	9	9	9	9	9	9	9	9	8	4
	0.1	Post	8	6	0	0	1	0	3	1	0	1	5	3	3	4	1	4
		Post	9	8	0	0	1	0	5	5	2	5	7	5	2	9	2	6
	0.4	Post	9	9	3	0	3	0	9	6	7	9	7	7	6	9	3	6
		Post	7	8	0	0	5	1	9	9	9	8	8	8	9	9	7	1
22	0.1	Pre	9	9	0	3	8	2	9	9	9	9	9	9	9	9	6	3
		Post	7	7	0	0	0	0	4	2	2	3	3	1	2	6	0	3
	0.2	Post	9	6	1	0	1	0	5	4	2	5	6	5	4	7	1	3
		Post	9	7	1	1	1	0	8	8	6	8	7	6	6	7	1	3
	0.4	Post	9	7	1	1	1	0	8	8	6	8	7	6	6	7	1	3
		Post	9	7	1	1	1	0	8	8	6	8	7	6	6	7	1	3

The names of the test plants in Table 4

Ww	Winter wheat	Bt	<i>Bromus tectorum</i>
Br	Barley	Ag	<i>Agropyron repens</i>
Pe	Peas	Ga	<i>Galium aparine</i>
Rp	Rape	Sm	<i>Stellaria media</i>
Sb	Sugar beet	Ca	<i>Chenopodium album</i>
Lt	Lettuce	Pi	<i>Polygonum aviculare</i>
Av	<i>Avena fatua</i>	Ma	<i>Matricaria inodora</i>
Al	<i>Alopecurus myosuroides</i>	Sp	<i>Sinapis alba</i>

TABLE 5

Compound No.	Rate of Application kg/ha	TEST PLANTS																			
		Mz	Rc	Sy	Ct	To	Sg	Eh	Ip	Ab	Se	Si	Ds	Xa	Ec	Dg	St	Sh	Pm	Cd	Cn
2	1.1	9	7	2	2	5	5	4	1	2	1	2	4	0	1	8	6	2	—	0	0
4	1.1	7	8	3	2	5	8	4	6	6	7	7	6	2	3	9	9	4	—	4	0
18	0.4	0	1	2	1	1	3	2	3	1	2	2	3	0	0	1	5	1	7	1	0
20	0.2	7	4	2	1	1	4	4	5	2	2	1	5	1	0	8	6	0	5	0	0
22	0.4	7	7	2	2	1	3	5	6	1	4	4	4	0	3	7	7	4	7	0	0

The names of test plants in Table 5

Mz	Maize
Rc	Rice
Sy	Soya bean
Ct	Cotton
To	Tomato
Sg	Sorghum
Eh	<i>Euphorbia heterophylla</i>
Ip	<i>Ipomoea purpurea</i>
Ab	<i>Abutilon theophrasti</i>
Se	<i>Sesbania exaltata</i>
Si	<i>Sida spinosa</i>
Ds	<i>Datura stramonium</i>
Xa	<i>Xanthium pensylvanicum</i>
Ec	<i>Echinochloa crus-galli</i>
Dg	<i>Digitaria sanguinalis</i>
St	<i>Setaria viridis</i>
Sh	<i>Sorghum halepense</i>
Pm	<i>Panicum maximum</i>
Cd	<i>Cyperus difformis</i>
Cn	<i>Cyperus rotundus</i>

56

Example 12

This Example illustrates a composition according to the invention which comprises an emulsifiable concentrate. The following ingredients were thoroughly mixed to give a solution.

5	Compound No. 2 of Table I	10%
	Ethylene dichloride	40%
	Calcium dodecylbenzenesulphate	5%
10	"Lubrol" L	10%
	"Aromasol" H	35%

15

Example 13

A composition in the form of grains readily dispersible in a liquid, e.g. water, was prepared by grinding together the first three ingredients in the presence of added water and then mixing in the sodium acetate. The resultant mixture was dried and passed through a British Standard mesh sieve, size 44—100, to obtain the desired size of grains.

	Compound No. 4 of Table I	50%
	"Dispersol" T	25%
25	"Lubrol" APN 5	1.5%
	Sodium acetate	23.5%

30

Example 14

The following ingredients were ground together to produce a powder formulation readily dispersible in liquids.

35	Compound No. 8 of Table I	45%
	"Dispersol" T	5%
	"Lissapol" NX	0.5%
40	"Cellofas" B600	2%
	Sodium acetate	47.5%

45

Example 15

The active ingredient was dissolved in acetone and the resultant liquid was sprayed on to the granules of china clay. The solvent was then allowed to evaporate to produce a granular composition.

50	Compound No. 18 of Table I	5%
	China clay granules	95%

55

Example 16

A composition suitable for use as a seed dressing was prepared by mixing the following three ingredients.

60	Compound No. 2 of Table I	50%
	Mineral oil	2%
	China clay	48%

65

Example 17

A dusting powder was prepared by mixing the active ingredient with talc.

5	Compound No. 4 of Table I	5%
	Talc	95%

Example 18

10 A Col formulation was prepared by ball-milling the constituents set out below and then forming an aqueous suspension of the ground mixture with water.

	Compound No. 8 of Table I	40%
15	"Dispersol" T	10%
	"Lubrol" APN5	1%
20	Water	49%

Example 19

25 A dispersible powder formulation was made by mixing together the ingredients set out below and then grinding the mixture until all were thoroughly mixed.

	Compound No. 18 of Table I	25%
	"Aerosol" OT/B	2%
30	"Dispersol" A.C.	5%
	China clay	28%
35	Silica	40%

Example 20

40 This Example illustrates the preparation of a dispersible powder formulation. The ingredients were mixed and the mixture then ground in a comminution mill.

	Compound No. 20 of Table I	25%
	"PERMINAL" BX	1%
45	"Dispersol" T	5%
	Polyvinylpyrrolidone	10%
50	Silica	25%
	China clay	34%

Example 21

55 The ingredients set out below were formulated into a dispersible powder by mixing then grinding the ingredients.

	Compound No. 2 of Table I	25%
60	"Aerosol" OT/B	2%
	"Dispersol" A	5%
65	China clay	68%

In Examples 1 to 10 the proportions of the ingredients given are by weight and the Examples were all repeated using, as active ingredients, the other compounds of Table I.

There now follows an explanation of the compositions or substances represented by the various Trade Marks and Trade Names mentioned above.

5	LUBROL L:	a condensate of nonyl phenol (1 mole) with ethylene oxide (13 moles).
10	AROMASOL H:	a solvent mixture of alkyl- benzenes
15	DISPERSOL T AND AC:	a mixture of sodium sulphate and a condensate of formalde- hyde with sodium naphthalene sulphonate
20	LUBROL APN 5:	a condensate of nonyl phenol (1 mole) with ethylene oxide (5.5 moles).
25	CELLOFAS B600:	a sodium carboxymethyl cellulose thickener.

Example 22

The compounds were tested against a variety of foliar fungal diseases of plants. The techniques employed were as follows:

The plants were grown in John Innes Potting Compost (No. 1 or 2) in 4 cm diameter mini-pots. A layer of fine sand was placed at the bottom to facilitate uptake of test compound by the roots. The test compounds were formulated either by bead milling with aqueous Dispersol T or as a solution in acetone or acetone/ethanol which was diluted to the required concentration immediately before use. For the foliage diseases suspensions (100 ppm active ingredient) were sprayed on to the foliage and applied to the roots of the same plant via the soil. Exceptions were the tests on *Plasmopara viticola* and *Venturia inaequalis* in which the compound was sprayed on to the foliage only. Sprays were applied to maximum retention, and root drenches were applied to a final concentration equivalent to approximately 40 ppm a.i./dry soil. Tween 20, to give a final concentration of 0.05% was added when the sprays were applied to cereals.

For most of the tests the compound was applied to the soil (roots) and to the foliage (by spraying) one or two days before the plant was inoculated with the diseases. An exception was the test on *Erysiphe graminis* in which the plants were inoculated 24 hours before treatment. After inoculation, the plants were put into an appropriate environment to allow infection to take place and then incubated until the disease was ready for assessment.

The period between inoculation and assessment varied from four to fourteen days according to the disease and environment.

The disease control was recorded by the following grading:

- 4 = no disease
- 3 = trace—5% of disease on untreated plants
- 2 = 6—25% of disease on untreated plants
- 1 = 26—59% of disease on untreated plants
- 0 = 60—100% of disease on untreated plants

The results are shown in Table 6 below.

In the table below the following compounds have been omitted for the reasons stated.

Compounds Nos. 5, 6, 7, 14, 16, 21, 23, 25, 27, 29, 32, 40, 58, 88, 115, 123, 140 were not tested at the standard primary screen rate.

Compounds Nos. 135, 136, 138, 142—145, 147, 148 and 160 were not tested.

A dash, thus "—", in the table in any column indicates that the particular compound was not tested against that particular disease.

An asterisk, thus "*", against the disease grading in the column headed "*BOTRYTIS CINEREA* (TOMATO)" signifies that the test plant material used in this instance were grape berries.

TABLE 6

Compound Number	Puccinia recondita (Wheat)	Erysiphe graminis (Barley)	Plasmopara viticola (Vine)	Phytophthora infestans (Tomato)	Botrytis cinerea (Tomato)	Cercospora arachidicola (Peanut)	Venturia inequalis (Apple)
1	0	0	0	2	0	0	2
2	0	4	3	3	0	3	3
3	0	0	0	0	0	0	1
4	0	0	4	4	0	3	0
8	0	1	4	4	0	3	—
9	0	0	0	0	0	1	0
10	0	0	0	0	0	1	0
11	0	1	0	0	2	0	1
12	0	0	0	0	0	0	0
13	0	0	0	0	0	3	0
15	0	0	0	1	0	2	0
17	0	0	0	2	0	2	0

TABLE 6 continued

Compound Number	Puccinia recondita (Wheat)	Erysiphe graminis (Barley)	Plasmopara viticola (Vine)	Phytophthora infestans (Tomato)	Botrytis cinerea (Tomato)	Cercospora arachidicola (Peanut)	Venturia inequalis (Apple)
18	0	0	4	4	0	4	0
19	0	0	2	1	0	0	0
20	—	4	4	3	1	3	0
22	0	4	4	4	0	4	4
24	0	0	4	3	0	0	—
26	—	—	—	—	—	—	—
28	0	0	4	3	0	1	0
30	0	1	4	3	0	3	0
31	0	3	4	3	0	3	0
33	0	3	4	4	0	3	0
34	0	2	4	4	0	2	2
35	0	4	4	0	1	—	—

TABLE 6 continued

Compound Number	Puccinia recondita (Wheat)	Erysiphe graminis (Barley)	Plasmopara viticola (Vine)	Phytophthora infestans (Tomato)	Botrytis cinerea (Tomato)	Cercospora arachidicola (Peanut)	Venturia inequalis (Apple)
36	0	4	4	4	1	—	—
37	0	1	2	0	0	0	0
38	0	3	4	4	1	—	—
39	0	0	4	3	—	1	0
41	0	3	2	4	0	—	—
42	0	2	4	4	0	—	—
43	0	3	4	1	1	—	—
44	0	3	4	4	0	—	—
45	0	2	4	2	1	—	—
46	—	0	0	2	0	0	0
47	—	0	2	3	0	0	1
48	—	0	0	0	1	2	0

TABLE 6 continued

Compound Number	Puccinia recondita (Wheat)	Erysiphe graminis (Barley)	Plasmopara viticola (Vine)	Phytophthora infestans (Tomato)	Botrytis cinerea (Tomato)	Cercospora arachidicola (Peanut)	Venturia inequalis (Apple)
49	—	0	0	2	0	0	0
50	0	3	0	0	0	—	—
51	0	0	4	4	1	—	—
52	0	0	4	3	1	—	—
53	—	0	0	0	0	2	0
54	—	4	0	0	0	0	2
55	—	4	1	0	0	2	4
56	0	1	0	0	—	0	0
57	0	0	0	0	0	0	0
59	—	—	—	—	—	—	—
60	0	1	—	2	0	3	0
61	0	1	—	4	1	4	1

TABLE 6 continued

Compound Number	Puccinia recondita (Wheat)	Erysiphe graminis (Barley)	Plasmopara viticola (Vine)	Phytophthora infestans (Tomato)	Botrytis cinerea (Tomato)	Cercospora arachidicola (Peanut)	Venturia inequalis (Apple)
62	0	1	—	4	2	4	0
63	0	4	—	4	2	1	0
64	0	2	—	0	1	1	0
65	0	2	—	4	1	1	1
66	0	2	—	4	0	2	1
67	0	1	0	0	2	0	0
68	0	—	0	0	0	1	0
69	0	0	—	3	0	2	0
70	0	2	0	3	0	4	—
71	0	3	—	3	0	3	3
72	0	4	0	0	0	0	1
73	0	0	0	0	0	1	0

TABLE 6 continued

Compound Number	Puccinia recondita (Wheat)	Erysiphe graminis (Barley)	Plasmopara viticola (Vine)	Phytophthora infestans (Tomato)	Botrytis cinerea (Tomato)	Cercospora arachidicola (Peanut)	Venturia inequalis (Apple)
74	0	1	0	0	0	0	0
75	0	0	0	0	0	0	0
76	0	0	0	0	0	0	0
77	0	0	0	0	0	0	0
78	0	0	1	0	0	0	0
79	0	0	0	0	0	0	3
80	0	0	0	0	0	0	0
81	0	0	4	3	0	2	0
82	0	0	1	0	0	0	0
83	0	0	3	2	0	1	0
84	0	0	4	1	0	0	0
85	0	0	4	4	0	0	2

TABLE 6 continued

Compound Number	Puccinia recondita (Wheat)	Erysiphe graminis (Barley)	Plasmopara viticola (Vine)	Phytophthora infestans (Tomato)	Botrytis cinerea (Tomato)	Cercospora arachidicola (Peanut)	Venturia inequalis (Apple)
86	0	0	3	0	0	2	2
87	—	—	—	—	—	—	—
89	0	2	0	0	1	0	0
90	0	0	0	0	0	1	0
91	0	0	4	4	1	0	0
92	0	1	4	3	0	0	0
93	1	3	0	0	3	2	0
94	—	—	—	—	—	—	—
95	0	0	4	4	2	0	—
95	0	0	3	4	0	0	0

TABLE 6 continued

Compound Number	Puccinia recondita (Wheat)	Erysiphe graminis (Barley)	Plasmopara viticola (Vine)	Phytophthora infestans (Tomato)	Botrytis cinerea (Tomato)	Cercospora arachidicola (Peanut)	Venturia inequalis (Apple)
97	0	0	4	4	0	0	0
98	0	0	4	4	0	0	2
99	0	0	0	3	0	0	0
100	0	0	1	0	0	0	0
101	0	1	0	0	0	0	0
102	0	0	4	4	0	2	0
103	0	0	0	0	0	0	2
104	—	—	—	—	—	—	—
105	0	0	0	0	0	0	0
106	0	0	0	0	0	0	0
107	0	0	0	0	0	0	0
108	1	0	4	0	0	0	0

TABLE 6 continued

Compound Number	Puccinia recondita (Wheat)	Erysiphe graminis (Barley)	Plasmopara viticola (Vine)	Phytophthora infestans (Tomato)	Botrytis cinerea (Tomato)	Cercospora arachidicola (Peanut)	Venturia inequalis (Apple)
109	0	0	4	4	0	3	0
110	0	0	4	4	0	0	0
111	0	0	4	4	0	2	0
112	0	0	1	0	0	0	0
113	0	0	0	1	0	0	0
114	0	0	0	0	—	0	0
115	0	0	0	1	0	0	0
117	0	0	4	4	0	2	0

TABLE 6 continued

Compound Number	Puccinia recondita (Wheat)	Erysiphe graminis (Barley)	Plasmopara viticola (Vine)	Phytophthora infestans (Tomato)	Botrytis cinerea (Tomato)	Cercospora arachidicola (Peanut)	Venturia inequalis (Apple)
118	0	0	4	3	0	3	—
119	0	0	4	3	0	0	0
120	0	0	4	4	0	2	0
121	0	0	0	0	0	0	0
122	0	0	0	0	0	0	0
124	0	0	2	0	2	0	0
125	0	0	4	4	0	0	0
126	0	0	4	3	0	2	0
127	0	0	0	0	2	0	0
128	0	0	0	0	1	0	0
129	1	0	0	0	2	1	0

TABLE 6 continued

Compound Number	Puccinia recondita (Wheat)	Erysiphe graminis (Barley)	Plasmopara viticola (Vine)	Phytophthora infestans (Tomato)	Botrytis cinerea (Tomato)	Cercospora arachidicola (Peanut)	Venturia inequalis (Apple)
130	4	2	3	0	2	2	0
131	3	0	2	0	1	0	0
132	—	—	—	—	—	—	—
133	0	0	0	0	0	2	0
134	0	1	4	4	0	3	2
137	0	0	0	—	0*	0	0
139	0	0	0	—	0*	0	0
141	0	0	4	—	0*	—	0
146	0	1	3	2	0*	0	0
149	0	3	0	0	0*	1	0
150	0	2	0	0	0*	0	2
151	0	0	2	1	0*	3	0

TABLE 6 continued

Compound Number	Puccinia recondita (Wheat)	Erysiphe graminis (Barley)	Plasmopara viticola (Vine)	Phytophthora infestans (Tomato)	Botrytis cinerea (Tomato)	Cercospora arachidicola (Peanut)	Venturia inequalis (Apple)
152	0	0	0	0	0*	3	0
153	0	0	1	3	0*	4	0
154	0	0	1	0	0*	3	1
155	0	0	4	2	0*	4	0
156	0	0	0	0	0*	3	0
157	0	0	0	0	0*	2	0
158	0	0	4	4	0*	4	0
159	0	0	0	0	0*	3	0

TABLE 6 continued

Compound Number	Puccinia recondita (Wheat)	Erysiphe graminis (Barley)	Plasmopara viticola (Vine)	Phytophthora infestans (Tomato)	Botrytis cinerea (Grape)	Cercospora arachidicola (Peanut)	Venturia inequalis (Apple)
161	0	2	0	0	0	0	0
162	0	2	0	0	0	0	0
163	0	1	0	0	0	0	0
164	0	3	0	0	0	0	0
165	0	4	0	0	0	0	0
166	0	0	0	0	0	0	0
167	0	3	3	3	0	2	0
169	0	0	1	0	0	0	0
171	0	2	0	0	0	0	0
172	0	0	2	0	0	0	0
173	0	0	0	0	0	0	0
174	0	0	4	3	0	0	2

TABLE 6 continued

Compound Number	Puccinia recondita (Wheat)	Erysiphe graminis (Barley)	Plasmopara viticola (Vine)	Phytophthora infestans (Tomato)	Botrytis cinerea (Grape)	Cercospora arachidicola (Peanut)	Venturia inequalis (Apple)
175	0	0	4	4	0	0	0
176	0	0	1		0	2	0
177	0	0	0		0	0	0
178	0	1	0		0	0	0
179	0	1	0		0	0	0
180	0	3	0		0	0	0
181	0	4	4		0	0	0
182	0	0	0		0	0	0
183	0	0	0		0	0	0
184	0	0	0		0	0	0
185	0	0	0		0	0	0
186	0	1	4		0	0	0

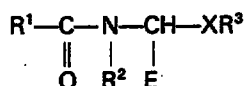
TABLE 6 continued

Compound Number	Puccinia recondita (Wheat)	Erysiphe graminis (Barley)	Plasmopara viticola (Vine)	Phytophthora infestans (Tomato)	Botrytis cinerea (Grape)	Cercospora arachidicola (Peanut)	Venturia inequalis (Apple)
187	0	0	0		0	0	0
188	0	0	0		0	0	0
189	0	0	0		0	0	0
190	0	0	4		0	0	0
191	0	0	0		0	0	0
192	0	2	3		0	0	0
193	0	0	0		0	0	0
194	0	1	0		0	0	2
195	0	1	0		0	0	3

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Claims for the Contracting States: BE CH DE FR GB IT LI NL SE

1. Amide derivatives of the formula (I):



wherein

- 10 R¹ is an optionally substituted alkyl, alkenyl, aryl, heterocyclyl, benzyl, or heterocyclylmethyl radical;
 R² is hydrogen, or an optionally substituted alkyl, alkenyl, benzyl or heterocyclylmethyl radical;
 X is oxygen, sulphur, or an —NH— group;
 R³ is an optionally substituted alkyl or alkenyl radical when X is oxygen or sulphur, or is COZ where Z is
 alkyl or alkylene when X is —NH—; and

- 15 E is a —CN, —CONH₂, —CSNH₂, or —CONR⁴R⁵ group wherein each R⁴ and R⁵ is hydrogen or an
 optionally substituted alkyl or alkenyl group, provided that X is not sulphur when R¹ is phenyl or phenyl
 substituted by nitro or methoxy.

2. Amide derivatives according to claim 1 wherein R¹ is an optionally substituted C₁₋₅ alkyl or C₃₋₅
 alkenyl radical; a phenyl, naphthyl or benzyl radical each optionally substituted in the ring with fluorine,
 20 chlorine, bromine or iodine, C₁₋₄ alkyl, C₁₋₄ alkoxy, methylenedioxy, ethylenedioxy, C₁₋₄ alkylthio, nitro,
 cyano or C₁₋₄ haloalkyl; an optionally substituted furyl, thienyl, pyridyl, thiazolyl, or benzthiazolyl radical;
 or an optionally substituted heterocyclylmethyl radical wherein the heterocyclyl group is furyl, thienyl,
 pyridyl, thiazolyl or benzthiazolyl; R² is hydrogen, C₁₋₄ alkyl, allyl, phenyl, benzyl or a furylmethyl group; R³
 is C₁₋₄ alkyl, C₁₋₄ haloalkyl or C₃₋₄ alkenyl radical, or is a C₁₋₄ alkanoyl group when X is NH; and each R⁴
 25 and R⁵ is hydrogen or methyl.

3. Amide derivatives according to claim 1 or 2 wherein R¹ is an optionally substituted aryl or
 heterocyclic group.

4. Amide derivatives according to any of the preceding claims wherein R¹ is phenyl optionally
 substituted at any of the 3-, 4- or 5- position with an alkyl, alkoxy or methylenedioxy group or with halogen.

- 30 5. Amide derivatives according to any of the preceding claims wherein R¹ is furyl, benzfuryl, thienyl,
 pyridyl, thiazolyl or benzthiazolyl.

6. Amide derivatives according to claim 1, 2 or 3 wherein R² is hydrogen.

7. Amide derivatives according to any of the preceding claims wherein R³ is allyl or a C₁₋₄ alkyl group.

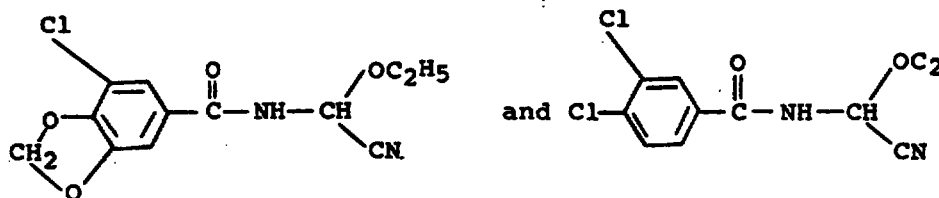
8. Amide derivatives according to any of the preceding claims wherein X is oxygen or sulphur.

- 35 9. Amide derivatives according to any of the preceding claims where X is oxygen.

10. Amide derivatives according to any of the preceding claims wherein E is CN or CSNH₂.

11. Amide derivatives according to formula I wherein R¹ is as defined in claim 4 and wherein R² is
 hydrogen, X is oxygen, R³ is C₁₋₄ alkyl and E is a cyano group.

12. The amide derivatives of formula:



- 50 13. A process for preparing amide derivatives as defined in any of claims 1 to 12 and wherein R² in
 formula I is hydrogen which comprises bringing into reaction an acid chloride:—



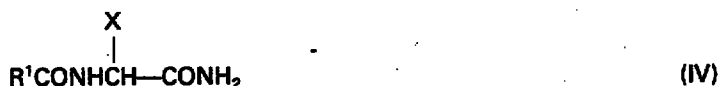
with aminoacetonitrile:—



to obtain the acylaminoacetonitrile of formula



and reacting this with a brominating agent or a chlorinating agent to give the halogenated derivative



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wherein X is a bromine or chlorine, which in turn is brought into reaction with the appropriate alcohol, thiol or amine of formula



to obtain the carbamoyl compound



thereafter treating the latter with a dehydrating agent to convert it to the corresponding cyano compound:—



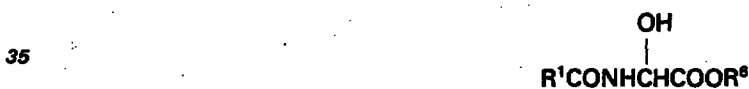
14. A process for preparing amide derivatives as defined in any of claims 1 to 12 which comprise condensing an amide:



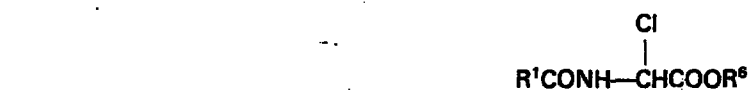
with a glyoxylic ester:



to give the hydroxy intermediate:



which is treated with a chlorinating agent (e.g. thionyl chloride) to convert it to the corresponding chloro derivative:



which is then reacted with the appropriate alcohol, thiol or amine R^3XH to give the ester derivative:



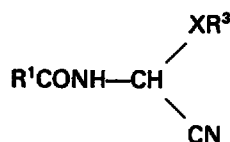
which itself is treated with ammonia to give the carbamoyl derivative:



which is then dehydrated to produce the desired cyano amide derivative of the invention:



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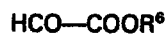


(VI)

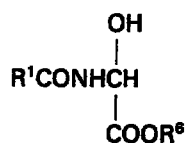
15. A process for preparing amide derivatives as defined in any of claims 1 to 12, and wherein X in formula I is oxygen, which comprises condensing an amide



with a glyoxylic ester



to give the hydroxy intermediate

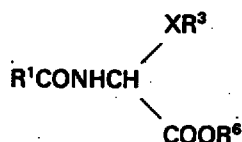


(VII)

which is then reacted with a compound

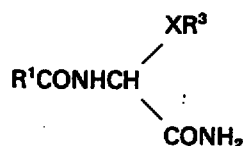


in the presence of H_2SO_4 as a catalyst to give the ester



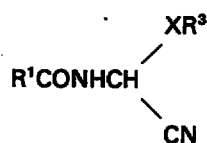
(IX)

which is treated with ammonia to produce the carbamoyl derivative



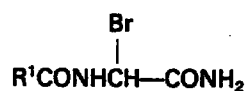
(V)

which is then dehydrated to produce the cyanoamide derivative of the invention



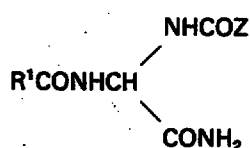
(VI)

16. A process for preparing amide derivatives as defined in any of claims 1 to 12 which comprises bringing into reaction a bromoamide:



(XII)

with the appropriate nitrile ZCN, where Z is alkyl or alkylene, in acetic acid under the conditions of the Ritter reaction to give the amide:

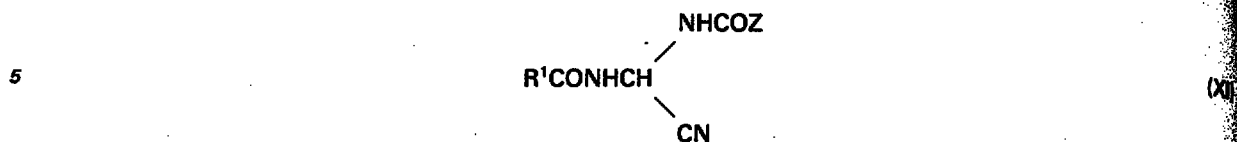


(X)

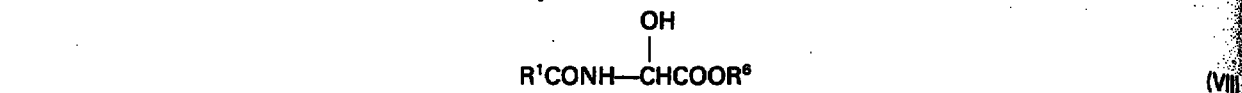


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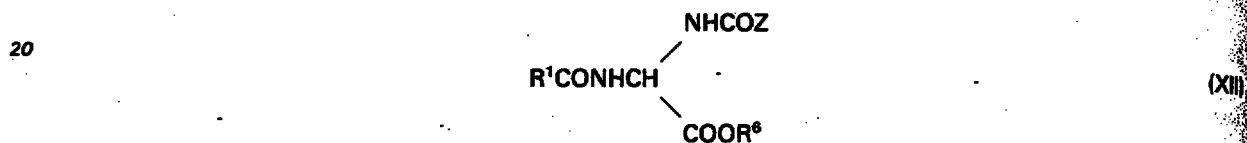
which is treated with a dehydrating agent (e.g. trifluoroacetic anhydride in pyridine) to give the nitrile:



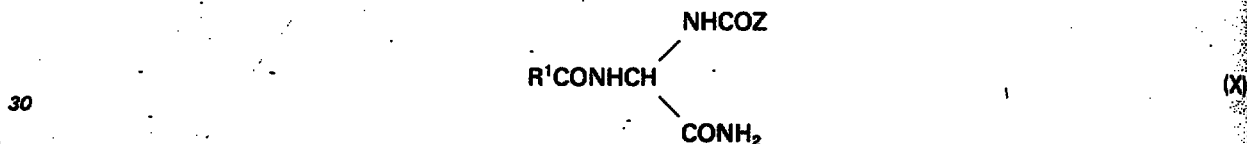
17. A process for preparing amide derivatives as defined in any of claims 1 to 12 which comprises bringing a hydroxy ester:



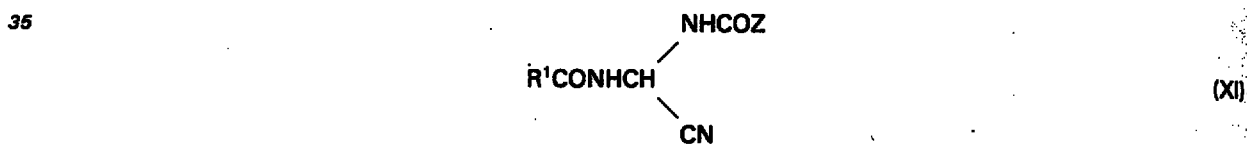
into reaction with the appropriate nitrile ZCN, where Z is alkyl or alkylene, in the presence of acetic acid and sulphuric acid (Ritter reaction) to give the amide:



25 which is then reacted with ammonia to give the amide:



which is then dehydrated to the nitrile:



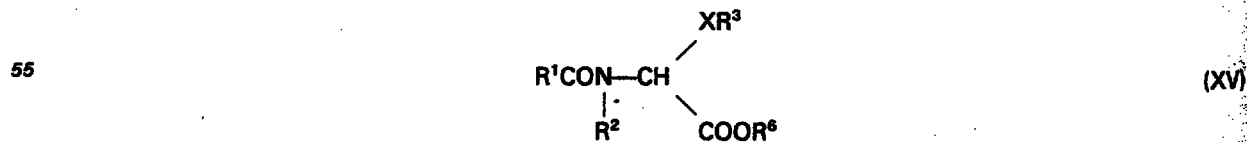
18. A process for preparing amide derivatives as defined in any of claims 1 to 12 which comprises treating an amide:



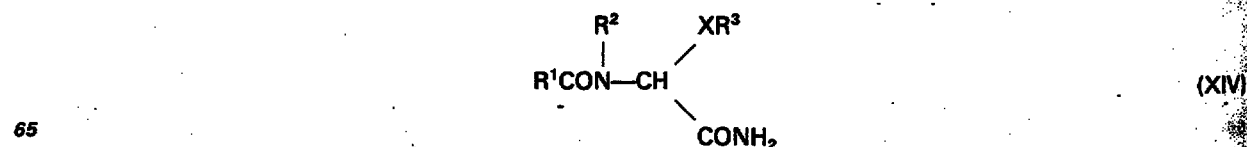
with sodium hydride and reacting the ion so generated with an alpha bromo ester:



to give the ester:



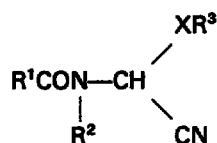
60 which is then reacted with ammonia to give the amide:



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which is then dehydrated to produce the desired nitrile:

(XI)

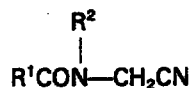


(XV)

19. A process for preparing amide derivatives as defined in any of claims 1 to 12 which comprises condensing an amine R^2NH_2 with formaldehyde cyanhydrin to give a substituted aminoacetonitrile:

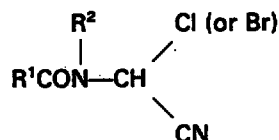


which is then acylated by the appropriate acid chloride R^1COCl to give the amide derivative:



(XVI)

which is chlorinated (e.g. with SO_2Cl_2) or brominated (e.g. with Br_2) to give the chloro; or bromo-derivative:



(XVII)

which is treated with the appropriate alcohol, thiol or amine HXR^3 in the presence of a base to give the required nitrile (XV).

20. A process for preparing amide derivatives according to claim 19 characterised in that the cyanoamides (XVI) are produced by either (a) subjecting a nitrile of formula:

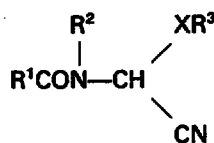


to alkylation with a bromide R^2Br in the presence of sodium hydride to give the cyanoamide; or (b) an amide of formula:



is reacted with ClCH_2CN in the presence of sodium hydride to give the desired cyanoamide.

21. A process for preparing amide derivatives as defined in any of claims 1 to 12 wherein E is a thiocarbamoyl radical which comprises passing gaseous H_2S through a solution of a nitrile:



in pyridine containing a small amount of a catalyst such as triethylamine.

22. A pesticidal composition, and especially fungicidal and herbicidal compositions, comprising as an active ingredient an amide derivative as defined in any of claims 1 to 12 together with a carrier or diluent.

23. A process of inhibiting the growth of unwanted plants, which comprises applying to the plants, or to the locus thereof, a phytotoxic amount of a compound as defined in any of the claims 1 to 12 or a composition as claimed in claim 22.

24. A process for combating fungi which comprises applying to the fungi, or the locus thereof, a fungicidally effective amount of a compound as defined in any of claims 1 to 12 or a composition as defined in claim 22.

25. A method of combating fungal disease in a plant which comprises applying to the plant, to the seed of the plant, or to the locus of the plant, or seed, a compound as defined in any of claims 1 to 12 or a fungicidal composition as defined in claim 22.

26. As novel chemical compounds the novel intermediates of formulae IV and V as defined in claim 13; of formula IX as defined in claim 14; and of formulae XIV and XV as defined in claim 18.

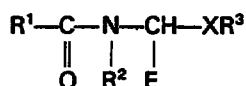


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Claims for the Contracting State: AT

1. A process for preparing amide derivatives of the formula (I):

5



wherein

- 10 R^1 is an optionally substituted alkyl, alkenyl, aryl, heterocyclyl, benzyl, or heterocyclylmethyl radical;
 R^2 is hydrogen;
 X is oxygen sulphur, or an $-\text{NH}-$ group;
 R^3 is an optionally substituted alkyl or alkenyl radical when X is oxygen or sulphur, or is COZ where Z is alkyl or alkylene when X is $-\text{NH}-$; and
 15 E is a $-\text{CN}-$, $-\text{CONH}_2$, or $-\text{CONR}^4\text{R}^5$ group wherein each R^4 and R^5 is hydrogen or an optionally substituted alkyl or alkenyl group, provided that X is not sulphur when R^1 is phenyl or phenyl substituted by nitro or methoxy which comprises bringing into reaction an acid chloride:



20

with aminoacetonitrile:



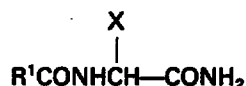
25 to obtain the acylaminoacetonitrile of formula



(III)

and reacting this with a brominating agent or a chlorinating agent to give the halogenated derivative

30

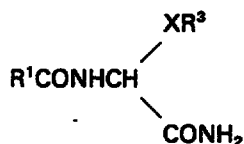


(IV)

35 where X is a bromine or chlorine, which in turn is brought into reaction with the appropriate alcohol, thiol or amine of formula



40 to obtain the carbamoyl compound

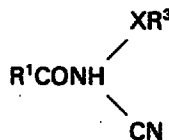


45

(V)

thereafter treating the latter with a dehydrating agent to convert it to the corresponding cyano compound:

50

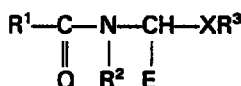


(VI)

55

2. A process for preparing amide derivatives of the formula (I):

60



wherein

- R^1 is an optionally substituted alkyl, alkenyl, aryl, heterocyclyl, benzyl, or heterocyclylmethyl radical;
 R^2 is hydrogen, or an optionally substituted alkyl, alkenyl, benzyl or heterocyclylmethyl radical;
 65 X is oxygen, sulphur, or an $-\text{NH}-$ group;



R^3 is an optionally substituted alkyl or alkenyl radical when X is oxygen or sulphur, or is COZ where Z is alkyl or alkylene when X is —NH—; and

E is a —CN, —CONH₂, or —CONR⁴R⁵ group wherein each R⁴ and R⁵ is hydrogen or an optionally substituted alkyl or alkenyl group, provided that X is not sulphur when R¹ is phenyl or phenyl substituted by nitro or methoxy, which comprises condensing an amide



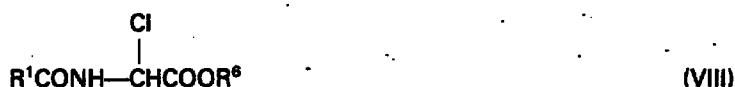
with a glyoxylic ester:



to give the hydroxy intermediate:



which is treated with a chlorinating agent (e.g. thionyl chloride) to convert it to the corresponding chloro derivative:



which is then reacted with the appropriate alcohol, thiol or amine R³XH to give the ester derivative:



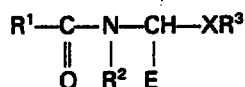
which itself is treated with ammonia to give the carbamoyl derivative:



which is then dehydrated to produce the desired cyano amide derivative of the invention:



3. A process for preparing amide derivatives of the formula (I):



wherein

R¹ is an optionally substituted alkyl, alkenyl, aryl, heterocyclyl, benzyl, or heterocyclylmethyl radical;

R² is hydrogen, or an optionally substituted alkyl, alkenyl, benzyl or heterocyclylmethyl radical;

X is oxygen;

R³ is optionally substituted alkyl or alkenyl radical when X is oxygen or sulphur, or is COZ where Z is alkyl or alkylene when X is —NH—; and

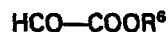
E is a —CN, —CONH₂, —CSNH₂, or —CONR⁴R⁵ group wherein each R⁴ and R⁵ is hydrogen or an optionally substituted alkyl or alkenyl group, provided that X is not sulphur when R¹ is phenyl or phenyl substituted by nitro or methoxy.



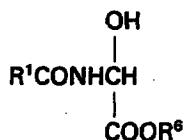
Which comprises condensing an amide



5 with a glyoxylic ester



to give the hydroxy intermediate

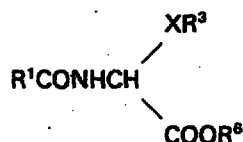


(VII)

which is then reacted with a compound

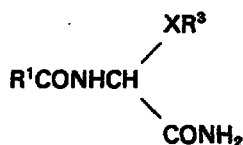


in the presence of H_2SO_4 as a catalyst to give the ester



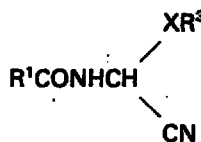
(IX)

which is treated with ammonia to produce the carbamoyl derivative



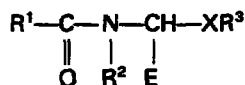
(V)

which is then dehydrated to produce the cyanoamide derivative of the invention



(VI)

4. A process for preparing amide derivatives of the formula (I):



wherein

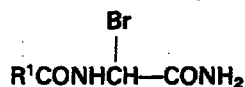
R^1 is an optionally substituted alkyl, alkenyl, aryl, heterocyclyl, benzyl, or heterocyclylmethyl radical;

R^2 is hydrogen, or an optionally substituted alkyl, alkenyl, benzyl or heterocyclylmethyl radical;

X is an $-NH-$ group;

R^3 is COZ where Z is alkyl or alkylene; and

E is a $-CN$, $-CONH_2$, $-CSNH_2$, or $-CONR^4R^5$ group wherein each R^4 and R^5 is hydrogen or an optionally substituted alkyl or alkenyl group, provided that X is not sulphur when R^1 is phenyl or phenyl substituted by nitro or methoxy, which comprises bringing into reaction a bromoamide:

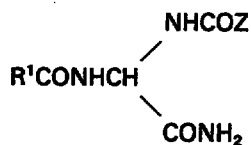


(XIII)

with the appropriate nitrile ZCN , where Z is alkyl or alkylene, in acetic acid under the conditions of the Ritter reaction to give the amide:

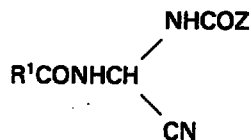


82



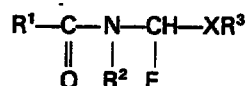
(X)

which is treated with a dehydrating agent (e.g. trifluoroacetic anhydride in pyridine) to give the nitrile:



(XI)

5. A process for preparing amide derivatives of the formula (I):



wherein

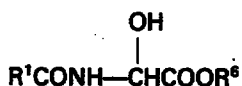
R¹ is an optionally substituted alkyl, alkenyl, aryl, heterocyclyl, benzyl, or heterocyclmethyl radical;

R² is hydrogen, or an optionally substituted alkyl, alkenyl, benzyl, or heterocyclmethyl radical;

X is an —NH— group;

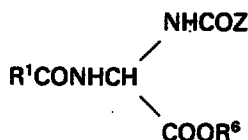
R³ is COZ where Z is alkyl or alkylene; and

E is a —CN, —CONH₂, or —CONR⁴R⁵ group wherein each R⁴ and R⁵ is hydrogen or an optionally substituted alkyl or alkenyl group, provided that X is not sulphur when R¹ is phenyl or phenyl substituted by nitro or methoxy, which comprises bringing a hydroxy ester:



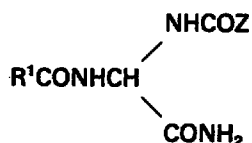
(VII)

into reaction with the appropriate nitrile ZCN, where Z is alkyl or alkylene, in the presence of acetic acid and sulphuric acid (Ritter reaction) to give the amide:



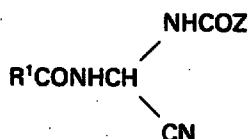
(XII)

which is then reacted with ammonia to give the amide:



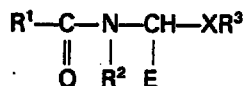
(X)

which is then dehydrated to the nitrile:



(XI)

6. A process for preparing amide derivatives of the formula (I):



wherein

R¹ is an optionally substituted alkyl, alkenyl, aryl, heterocyclyl, benzyl, or heterocyclylmethyl radical;

R² is hydrogen;

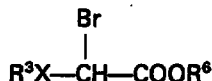
X is oxygen, sulphur, or an —NH— group;

R³ is an optionally substituted alkyl or alkenyl radical when X is oxygen or sulphur, or is COZ where Z is alkyl or alkylene when X is —NH; and

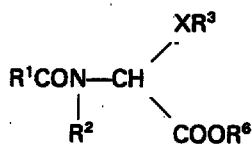
E is a —CN—, —CONH₂, —CSNH₂, or —CONR⁴R⁵ group wherein each R⁴ and R⁵ is hydrogen or an optionally substituted alkyl or alkenyl group, provided that X is not sulphur when R¹ is phenyl or phenyl substituted by nitro or methoxy which comprises treating an amide:



with sodium hydride and reacting the ion so generated with an alpha bromo ester:

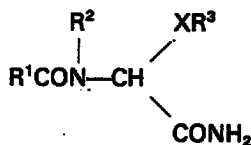


to give the ester:



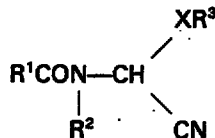
(XIII)

which is then reacted with ammonia to give the amide:



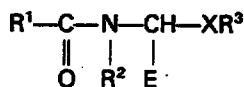
(XIV)

which is then dehydrated to produce the desired nitrile:



(XV)

7. A process for preparing amide derivatives of the formula (I):



wherein

R¹ is an optionally substituted alkyl, alkenyl, aryl, heterocyclyl, benzyl, or heterocyclylmethyl radical;

R² is hydrogen;

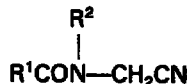
X is oxygen, sulphur, or an —NH— group;

R³ is an optionally substituted alkyl or alkenyl radical when X is oxygen or sulphur, or is COZ where Z is alkyl or alkylene when X is —NH; and

E is a —CN—, —CONH₂, —CSNH₂, or —CONR⁴R⁵ group wherein each R⁴ and R⁵ is hydrogen or an optionally substituted alkyl or alkenyl group, provided that X is not sulphur when R¹ is phenyl or phenyl substituted by nitro or methoxy which comprises condensing an amine R²NH₂ with formaldehyde cyanhydrin to give a substituted aminoacetonitrile:



which is then acylated by the appropriate acid chloride R¹COCl to give the amide derivative:



(XVI)



which is chlorinated (e.g. with SO_2Cl_2) or brominated (e.g. with Br_2) to give the chloro- or bromo-derivative:



which is treated with the appropriate alcohol, thiol or amine HXR^3 in the presence of a base to give the required nitrile (XV).

8. A process for preparing amide derivatives according to claim 7 characterised in that the cyanoamides (XVI) are produced by either (a) subjecting a nitrile of formula:

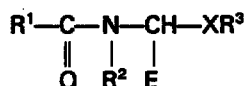


to alkylation with a bromide R^2Br in the presence of sodium hydride to give the cyanoamide, or (b) an amide of formula:



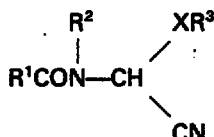
is reacted with ClCH_2CN in the presence of sodium hydride to give the desired cyanoamide.

9. A process for preparing amide derivatives of the formula (I):



wherein

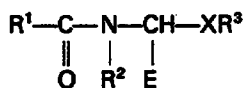
- R^1 is an optionally substituted alkyl, alkenyl, aryl, heterocyclyl, benzyl, or heterocyclylmethyl radical;
- R^2 is hydrogen;
- X is oxygen, sulphur, or an $-\text{NH}-$ group;
- R^3 is an optionally substituted alkyl or alkenyl radical when X is oxygen or sulphur, or is COZ where Z is alkyl or alkylene when X is $-\text{NH}-$; and
- E is a $-\text{CSNH}_2$ group wherein each R^4 and R^5 is hydrogen or an optionally substituted alkyl or alkenyl group, provided that X is not sulphur when R^1 is phenyl or phenyl substituted by nitro or methoxy, which comprises passing gaseous H_2S through a solution of a nitrile



in pyridine containing a small amount of a catalyst such as triethylamine.

Patentansprüche für die Vertragsstaaten: BE CH DE FR GB IT LI NL SE

1. Amid-Derivate der Formel (I):



worin

- R^1 für einen gegebenenfalls substituierten Alkyl-, Alkenyl-, Aryl-, Heterocyclyl-, Benzyl- oder Heterocyclylmethyl-Rest steht;
- R^2 für Wasserstoff oder einen gegebenenfalls substituierten Alkyl-, Alkenyl-, Benzyl- oder Heterocyclylmethyl-Rest steht;
- X für Sauerstoff, Schwefel oder eine $-\text{NH}-$ Gruppe steht;
- R^3 für einen gegebenenfalls substituierten Alkyl- oder Alkenyl-Rest steht, wenn X Sauerstoff oder Schwefel bedeutet, oder für COZ steht, worin Z Alkyl oder Alkylen ist, wenn X die $-\text{NH}-$ Gruppe bedeutet; und
- E für eine $-\text{CN}-$, CONH_2- , $-\text{CSNH}_2-$ oder CONR^4R^5 -Gruppe steht, worin jeder Rest R^4 und R^5 Wasserstoff oder eine gegebenenfalls substituierte Alkyl- oder Alkenylgruppe bedeutet,



wobei gilt, daß X nicht für Schwefel steht, wenn R¹ Phenyl oder durch Nitro oder Methoxy substituiertes Phenyl bedeutet.

2. Amid-Derivate nach Anspruch 1, worin R¹ für einen gegebenenfalls substituierten C₁₋₅-Alkyl- oder C₃₋₅-Alkenyl-Rest; einen Phenyl-, Naphthyl- oder Benzyl-Rest, von denen jeder gegebenenfalls im Ring mit Fluor, Chlor, Brom oder Jod, C₁₋₄-Alkyl, C₁₋₄-Alkoxy, Methylendioxy, Ethylendioxy, C₁₋₄-Alkylthio, Nitro, Cyano oder C₁₋₄-Halogenalkyl substituiert ist; einen gegebenenfalls substituierten Furyl-, Thienyl-, Pyridyl-, Thiazolyl- oder Benzthiazolyl-Rest; oder einen gegebenenfalls substituierten Heterocyclymethyl-Rest, worin die Heterocyclylgruppe Furyl, Thienyl, Pyridyl, Thiazolyl oder Benzthiazolyl bedeutet, steht; R² für Wasserstoff, C₁₋₄-Alkyl-, Allyl-, Phenyl-, Benzyl- oder eine Furylmethylgruppe steht; R³ für einen C₁₋₄-Alkyl-, C₁₋₄-Halogenalkyl- oder C₃₋₄-Alkenyl-Rest steht oder eine C₁₋₄-Alkanoylgruppe bedeutet, wenn X für NH steht; und jeder der Reste R⁴ und R⁵ für Wasserstoff oder Methyl steht.

3. Amid-Derivate nach Anspruch 1 oder 2, worin R¹ für eine gegebenenfalls substituierte Aryl- oder Heterocyclylgruppe steht.

4. Amid-Derivate nach einem der vorhergehenden Ansprüche, worin R¹ für Phenyl steht, das gegebenenfalls in einer der 3-, 4- oder 5-Stellungen mit einer Alkyl-, Alkoxy- oder Methylendioxygruppe oder mit Halogen substituiert ist.

5. Amid-Derivate nach einem der vorhergehenden Ansprüche, worin R¹ für Furyl, Benzfuryl, Thienyl, Pyridyl, Thiazolyl oder Benzthiazolyl steht.

6. Amid-Derivate nach Anspruch 1, 2 oder 3 worin R² für Wasserstoff steht.

7. Amid-Derivate nach einem der vorhergehenden Ansprüche, worin R³ für Allyl- oder eine C₁₋₄-Alkylgruppe steht.

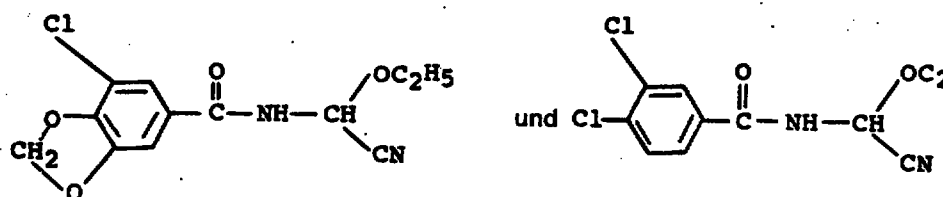
8. Amid-Derivate nach einem der vorhergehenden Ansprüche, worin X für Sauerstoff oder Schwefel steht.

9. Amid-Derivate nach einem der vorhergehenden Ansprüche, worin X für Sauerstoff steht.

10. Amid-Derivate nach einem der vorhergehenden Ansprüche, worin E für .CN oder CSNH₂ steht.

11. Amid-Derivate gemäß Formel I, worin R¹ die in Anspruch 4 angegebene Bedeutung hat und worin R² für Wasserstoff, X für Sauerstoff, R³ für C₁₋₄-Alkyl und E für eine Cyanogruppe steht.

12. Amid-Derivate der Formel:



13. Verfahren zur Herstellung von Amid-Derivaten nach einem der Ansprüche 1 bis 12, wobei R² in Formel I für Wasserstoff steht, bei welchem ein Säurechlorid:



mit Aminoacetonitril:

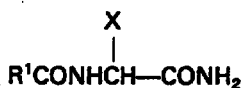


zur Reaktion gebracht wird unter Bildung des Acylaminoacetonitrils der Formel:



(III)

und dieses mit einem Bromierungsmittel oder einem Chlorierungsmittel umgesetzt wird unter Bildung des halogenierten Derivats



(IV)

worin X für Brom oder Chlor steht, welches seinerseits mit dem entsprechenden Alkohol, Thiol oder Amin der Formel:



zur Reaktion gebracht wird unter Bildung der Carbamoylverbindung:



worauf letztere mit einem Dehydrationsmittel umgesetzt wird, um sie in die entsprechende Cyanoverbindung:



zu überführen.

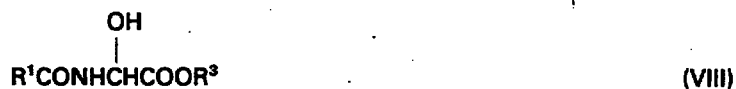
14. Verfahren zur Herstellung von Amid-Derivaten nach einem der Ansprüche 1 bis 12, bei welchem ein Amid:



mit einem Glyoxylester:



kondensiert wird unter Bildung des Hydroxy-Zwischen-produktes:



welches mit einem Chlorierungsmittel (z.B. Thionylchlorid) umgesetzt wird, um es in das entsprechende Chlor-Derivat:



zu überführen, das sodann mit dem entsprechenden Alkohol, Thiol oder Amin R^3XH umgesetzt wird, um das Ester-Derivat:



zu erzielen, das seinerseits mit Ammoniak umgesetzt wird unter Bildung des Carbamoyl-Derivats:



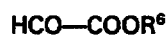
welches sodann dehydratisiert wird zu Bildung des gewünschten erfindungsgemäßen Cyanoamid-Derivats:



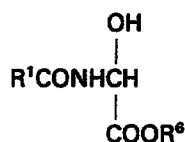
15. Verfahren zur Herstellung von Amid-Derivaten nach einem der Ansprüche 1 bis 12, worin X in Formel I für Sauerstoff steht, bei welchem ein Amid



mit einem Glyoxylester:



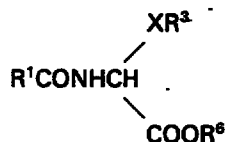
10 kondensiert wird unter Bildung des Hydroxy-Zwischenprodukts:



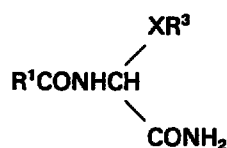
welche sodann mit einer Verbindung



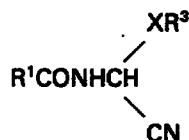
in Gegenwart von H_2SO_4 als Katalysator umgesetzt wird unter Bildung des Esters:



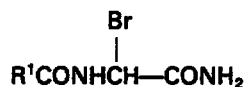
30 der mit Ammoniak behandelt wird zur Bildung des Carbamoyl-Derivats:



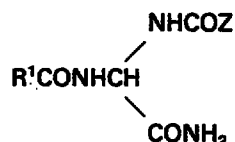
das sodann dehydratisiert wird zur Bildung des erfindungsgemäßen Cyanoamid-Derivats:



16. Verfahren zur Herstellung von Amid-Derivaten nach einem der Ansprüche 1 bis 12, bei welchem ein Bromamid:

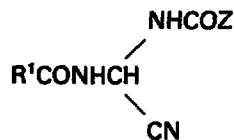


55 mit dem geeigneten Nitril ZCN, worin Z für Alkyl oder Alkylen steht, in Essigsäure unter den Bedingungen der Ritter-Reaktion zur Reaktion gebracht wird unter Bildung des Amids:



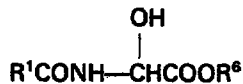
65 das mit einem Dehydratisierungsmittel (z.B. Trifluoroessigsäureanhydrid in Pyridin) behandelt wird unter Bildung des Nitrils:





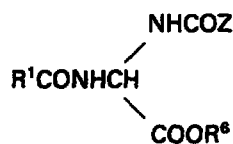
(XI)

17. Verfahren zur Herstellung von Amid-Derivaten nach einem der Ansprüche 1 bis 12, bei welchem ein Hydroxyester:



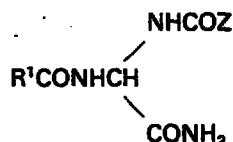
(VII)

mit dem geeigneten Nitril ZCN, worin Z für Alkyl oder Alkylen steht, in Gegenwart von Essigsäure und Schwefelsäure (Ritter-Reaktion) zur Reaktion gebracht wird unter Bildung des Amids:



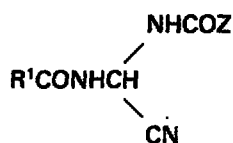
(XII)

das sodann mit Ammoniak umgesetzt wird unter Bildung des Amids:



(X)

welches anschließend dehydratisiert wird zu dem Nitril:

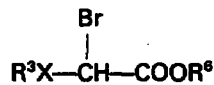


(XI)

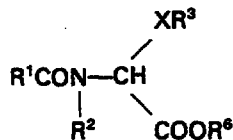
18. Verfahren zur Herstellung von Amid-Derivaten nach einem der Ansprüche 1 bis 12, bei welchem ein Amid:



mit Natriumhydrid behandelt und das auf diese Weise erzeugte Ion mit einem α -Bromoester:

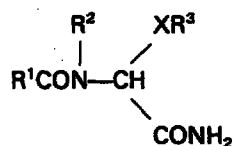


umgesetzt wird unter Bildung des Esters:



(XIII)

der sodann mit Ammoniak umgesetzt wird unter Bildung des Amids:

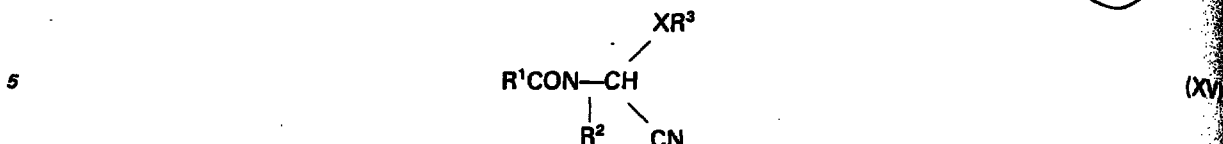


(XIV)



89

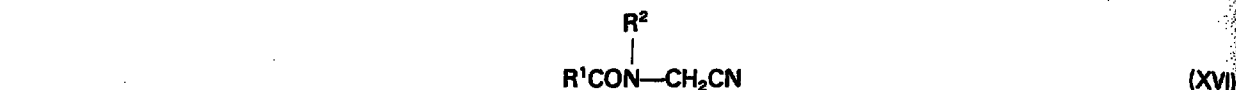
welches sodann dehydratisiert wird zur Bildung des gewünschten Nitrils:



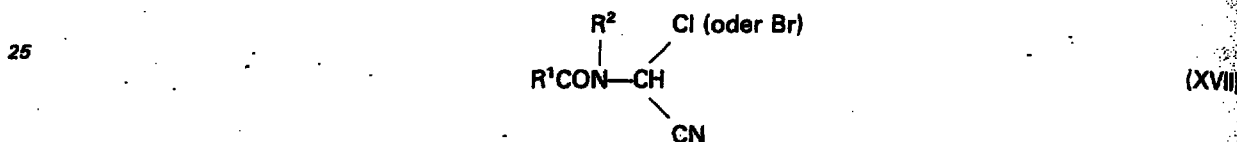
19. Verfahren zur Herstellung von Amid-Derivaten nach einem der Ansprüche 1 bis 12, bei welchem ein Amin R^2NH_2 mit Formaldehydcyanhydrin kondensiert wird unter Bildung eines substituierten Aminoacetonitrils:



15 das sodann durch das geeignete Säurechlorid R^1COCl acyliert wird unter Bildung des Amid-Derivats:



das chloriert (z.B. mit SO_2Cl_2) oder bromiert (z.B. mit Br_2) wird unter Bildung des Chloro- oder Bromo-Derivats:



30 das mit dem geeigneten Alkohol, Thiol oder Amin HXR^3 in Gegenwart einer Base behandelt wird unter Bildung des gewünschten Nitrils (XV).

20. Verfahren zur Herstellung von Amid-Derivaten nach Anspruch 19, dadurch gekennzeichnet, daß die Cyanoamide (XVI) entweder dadurch gebildet werden, daß

(a) ein Nitril der Formel:



der Alkylierung mit einem Bromid R^2Br in Gegenwart von Natriumhydrid unterworfen wird unter Bildung des Cyanoamids, oder

40 (b) ein Amid der Formel:



mit ClCH_2CN in Gegenwart von Natriumhydrid umgesetzt wird unter Bildung des gewünschten Cyanoamids.

21. Verfahren zur Herstellung von Amid-Derivaten nach einem der Ansprüche 1 bis 12, wobei E für einen Thiocarbamoyl-Rest steht, bei welchem gasförmiges H_2S durch eine Lösung eines Nitrils:



55 in Pyridin, die eine geringe Menge eines Katalysators wie Triethylamin enthält, geleitet wird.

22. Pesticide Zusammensetzung und insbesondere fungicide und herbicide Zusammensetzung die als eine aktive Komponente ein Amid-Derivat gemäß einem der Ansprüche 1 bis 12 zusammen mit einem Träger- oder Verdünnungsmittel aufweist.

60 23. Verfahren zur Hemmung des Wachstums von unerwünschten Pflanzen, bei welchem auf die Pflanzen oder die Wachstumsstelle derselben eine phytotoxische Menge einer Verbindung gemäß einem der Ansprüche 1 bis 12 oder eine Zusammensetzung gemäß Anspruch 22 aufgebracht wird.

24. Verfahren zur Bekämpfung von Fungi, bei welchem auf die Fungi oder die Wachstumsstelle derselben eine fungicidische wirksame Menge einer Verbindung gemäß einem der Ansprüche 1 bis 12 oder 65 eine Zusammensetzung gemäß Anspruch 22 aufgebracht wird.



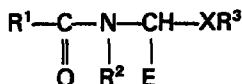
90

25. Verfahren zur Bekämpfung von Pilzkrankheiten in einer Pflanze, bei welchem auf die Pflanze, auf den Samen der Pflanze oder auf die Wachstumsstelle der Pflanze oder des Samens eine Verbindung gemäß einem der Ansprüche 1 bis 12 oder eine fungicide Zusammensetzung gemäß Anspruch 22 aufgebracht wird.

26. Neue chemische Verbindungen in Form der neuen Zwischenprodukte der Formel IV und V gemäß Anspruch 13; der Formel IX gemäß Anspruch 14 und der Formeln XIV und XV gemäß Anspruch 18.

Patentansprüche für den Vertragsstaat: AT

1. Verfahren zur Herstellung von Amid-Derivaten der Formel (I):



15 worin

R¹ für einen gegebenenfalls substituierten Alkyl-, Alkenyl-, Aryl-, Heterocyclyl-, Benzyl- oder Heterocyclymethyl-Rest steht;

R² für Wasserstoff steht;

X für Sauerstoff, Schwefel oder eine —NH-Gruppe steht;

20 R³ für einen gegebenenfalls substituierten Alkyl- oder Alkenyl-Rest steht, wenn X Sauerstoff oder Schwefel bedeutet, oder für COZ, worin Z Alkyl oder Alkylen ist, steht, wenn X eine —NH-Gruppe bedeutet; und

E für eine —CN—, —CONH₂— oder —CONR⁴R⁵-Gruppe steht, worin jeder der Reste R⁴ und R⁵ Wasserstoff oder eine gegebenenfalls substituierte Alkyl- oder Alkenylgruppe bedeutet,

25 wobei gilt, daß X nicht für Schwefel steht, wenn R¹ Phenyl oder durch Nitro oder Methoxy substituiertes Phenyl bedeutet, bei welchem ein Säurechlorid:



mit Aminoacetonitril:



zur Reaktion gebracht wird unter Erzielung des Acylaminoacetonitrils der Formel:



und dieses mit einem Bromierungsmittel oder einem Chlorierungsmittel umgesetzt unter Bildung des halogenierten Derivats



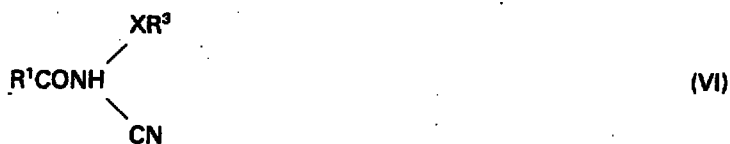
45 worin X für Brom oder Chlor steht, welches seinerseits mit dem geeigneten Alkohol, Thiol oder Amin der Formel:



zur Reaktion gebracht wird zur Gewinnung der Carbamoylverbindung:



worauf letztere mit einem Dehydratisierungsmittel behandelt wird, um sie in die entsprechende Cyanoverbindung:



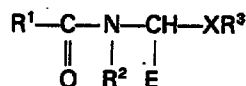
65 zu überführen.



91

2. Verfahren zur Herstellung von Amid-Derivaten der Formel (I):

5



worin

- R¹ für einen gegebenenfalls substituierten Alkyl-, Alkenyl-, Aryl-, Heterocyclyl-, Benzyl- oder
 10 Heterocyclymethyl-Rest steht;
 R² für Wasserstoff oder einen gegebenenfalls substituierten Alkyl-, Alkenyl-, Benzyl- oder
 Heterocyclymethyl-Rest steht;
 X für Sauerstoff, Schwefel oder eine —NH-Gruppe steht;
 R³ für einen gegebenenfalls substituierten Alkyl- oder Alkenylrest steht, wenn X Sauerstoff oder
 15 Schwefel bedeutet, oder für COZ, worin Z Alkyl oder Alkylen ist, steht, wenn X —NH— bedeutet; und
 E für eine —CN—, —CONH₂— oder —CONR⁴R⁵-Gruppe steht, worin jeder Rest R⁴ und R⁵ Wasserstoff
 oder eine gegebenenfalls substituierte Alkyl- oder Alkenylgruppe bedeutet,
 wobei gilt, daß X nicht für Schwefel steht, wenn R¹ Phenyl oder durch Nitro oder Methoxy substituiertes
 Phenyl bedeutet, bei welchem ein Amid:

20



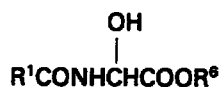
mit einem Glyoxylester:

25



kondensiert wird unter Bildung des Hydroxy-Zwischenproduktes:

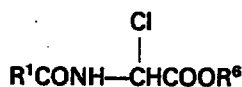
30



(VII)

das mit einem Chlorierungsmittel (z.B. Thionylchlorid) behandelt wird, um es in das entsprechende Chlor-Derivat:

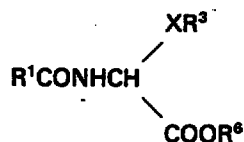
35



(VIII)

40 zu überführen, das sodann mit dem geeigneten Alkohol, Thiol oder Amin R³XH umgesetzt wird unter Bildung des Ester-Derivats:

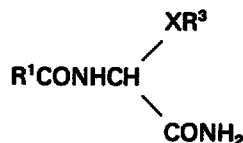
45



(IX)

das mit Ammoniak behandelt wird unter Bildung des Carbamoyl-Derivats:

50

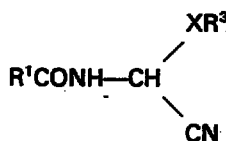


(V)

55

das sodann dehydratisiert wird zur Bildung des gewünschten erfindungsgemäßen Cyanoamid-Derivats:

60



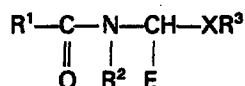
(VI)

65

3. Verfahren zur Herstellung von Amid-Derivaten der Formel (I):



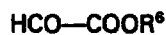
92



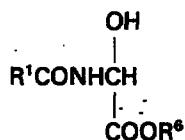
- 5 worin
 R¹ für einen gegebenenfalls substituierten Alkyl-, Alkenyl-, Aryl-, Heterocyclyl-, Benzyl- oder Heterocyclylmethyl-Rest steht;
 R² für Wasserstoff oder einen gegebenenfalls substituierten Alkyl-, Alkenyl-, Benzyl- oder Heterocyclylmethyl-Rest steht,
 X für Sauerstoff steht;
 10 R³ für einen gegebenenfalls substituierten Alkyl- oder Alkenyl-Rest steht, wenn X Sauerstoff oder Schwefel bedeutet, oder für COZ, worin Z Alkyl oder Alkylen ist, steht, wenn X —NH— bedeutet; und
 E für eine —CN—, —CONH₂—, —CSNH₂— oder —CONR⁴R⁵-Gruppe steht, worin jeder der Reste R⁴ und R⁵ Wasserstoff oder eine gegebenenfalls substituierte Alkyl- oder Alkenylgruppe bedeutet,
 15 wobei gilt, daß X nicht für Schwefel steht, wenn R¹ Phenyl oder durch Nitro oder Methoxy substituiertes Phenyl bedeutet, bei welchem ein Amid:



- 20 mit einem Glyoxylester:



- 25 kondensiert wird unter Bildung des Hydroxy-Zwischenprodukts

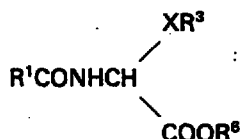


(VII)

- das sodann mit einer Verbindung

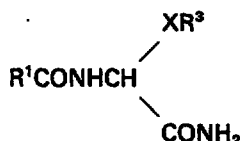


- 35 in Gegenwart von H₂SO₄ als Katalysator umgesetzt wird unter Bildung des Esters:



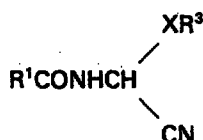
(IX)

- 45 der mit Ammoniak behandelt wird zur Bildung des Carbamoyl-Derivats:



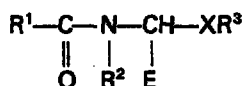
(V)

- das sodann dehydratisiert wird zur Bildung des erfindungsgemäßen Cyanoamid-Derivats:



(VI)

- 60 4. Verfahren zur Herstellung von Amid-Derivaten der Formel (I):



93

worin

R^1 für einen gegebenenfalls substituierten Alkyl-, Alkenyl-, Aryl-, Heterocyclyl-, Benzyl- oder Heterocyclymethyl-Rest steht;

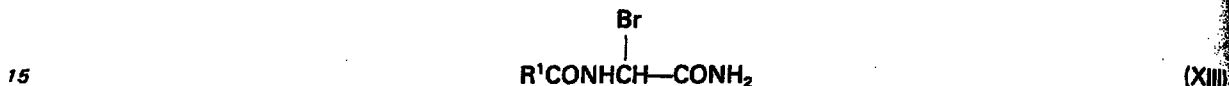
R^2 für Wasserstoff oder einen gegebenenfalls substituierten Alkyl-, Alkenyl-, Benzyl- oder Heterocyclymethyl-Rest steht;

X für eine —NH-Gruppe steht;

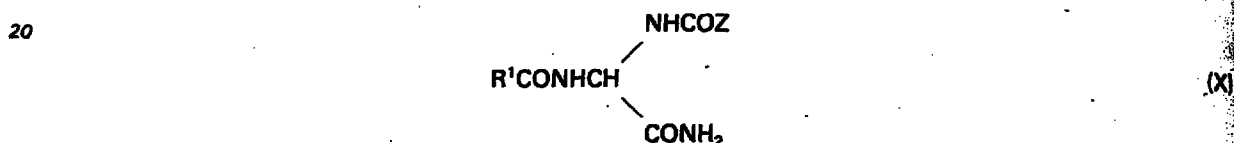
R^3 für COZ, worin Z Alkyl oder Alkylen ist, steht; und

E für eine —CN—, —CONH₂—, —CSNH₂— oder —CONR⁴R⁵-Gruppe steht, worin jeder der Rest R^4 und R^5 Wasserstoff oder eine gegebenenfalls substituierte Alkyl- oder Alkenylgruppe bedeutet,

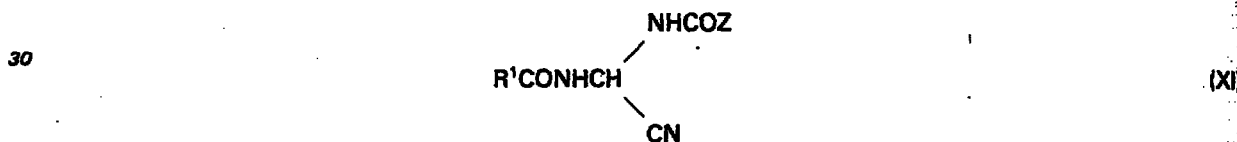
wobei gilt, daß X nicht für Schwefel steht, wenn R^1 Phenyl oder durch Nitro oder Methoxy substituiertes Phenyl bedeutet, bei welchem ein Bromoamid:



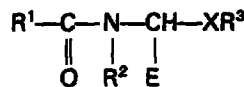
mit dem geeigneten Nitril ZCN, worin Z für Alkyl oder Alkylen steht, in Essigsäure unter den Bedingungen der Ritter-Reaktion zur Umsetzung gebracht wird unter Bildung des Amids:



das mit einem Dehydratisierungsmittel (z.B. Trifluoroessigsäureanhydrid in Pyridin) behandelt wird unter Bildung des Nitrils:



5. Verfahren zur Herstellung von Amid-Derivaten der Formel (I):



worin

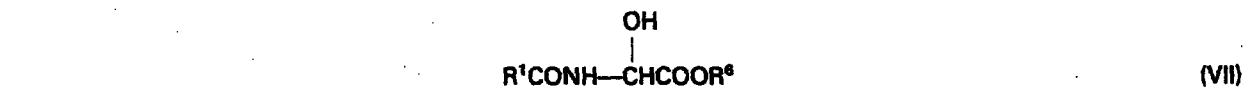
R^1 für einen gegebenenfalls substituierten Alkyl-, Alkenyl-, Aryl-, Heterocyclyl-, Benzyl- oder Heterocyclymethyl-Rest steht;

R^2 für Wasserstoff oder einen gegebenenfalls substituierten Alkyl-, Alkenyl-, Benzyl- oder Heterocyclymethyl-Rest steht;

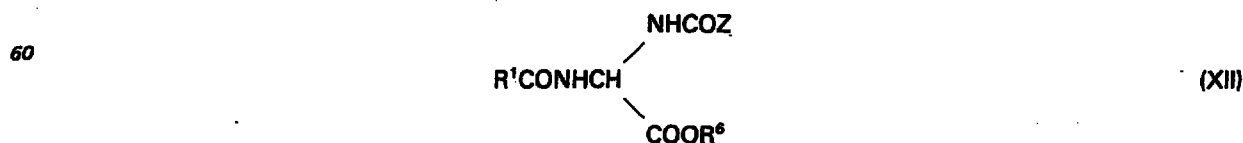
X für eine —NH-Gruppe steht;

R^3 für COZ, worin Z Alkyl oder Alkylen bedeutet, steht und E für eine —CN—, —CONH₂— oder —CONR⁴R⁵-Gruppe steht, worin jeder Rest R^4 und R^5 Wasserstoff oder eine gegebenenfalls substituierte Alkyl- oder Alkenylgruppe bedeutet,

wobei gilt, daß X nicht für Schwefel steht, wenn R^1 Phenyl oder durch Nitro oder Methoxy substituiertes Phenyl bedeutet, bei welchem ein Hydroxyester:

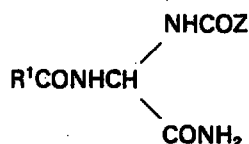


mit dem geeigneten Nitril ZCN, worin Z für Alkyl oder Alkylen steht, in Gegenwart von Essigsäure und Schwefelsäure (Ritter-Reaktion) zur Reaktion gebracht wird unter Bildung des Amids:

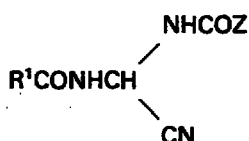


das sodann mit Ammoniak umgesetzt wird unter Bildung des Amids:



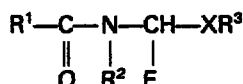


welches sodann zu dem Nitril:



dehydratisiert wird.

6. Verfahren zur Herstellung von Amid-Derivaten der Formel (I):



worin

R^1 für einen gegebenenfalls substituierten Alkyl-, Alkenyl-, Aryl-, Heterocyclyl-, Benzyl- oder Heterocyclylmethyl-Rest steht;

R^2 für Wasserstoff steht;

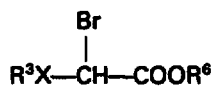
X für Sauerstoff, Schwefel oder eine $-\text{NH}$ -Gruppe steht;

R^3 für einen gegebenenfalls substituierten Alkyl- oder Alkenyl-Rest steht, wenn X Sauerstoff oder Schwefel bedeutet, oder für COZ , worin Z Alkyl oder Alkylen ist, steht, wenn $\text{X} -\text{NH}$ bedeutet; und

E für eine $-\text{CN}-$, $-\text{CONH}_2-$, $-\text{CSNH}_2-$ oder CONR^4R^5 -Gruppe steht, worin beide Reste R^4 und R^5 Wasserstoff oder eine gegebenenfalls substituierte Alkyl- oder Alkenylgruppe bedeuten, wobei gilt, daß X nicht für Schwefel steht, wenn R^1 Phenyl oder durch Nitro oder Methoxy substituiertes Phenyl bedeutet, bei welchem ein Amid:



mit Natriumhydrid behandelt wird und das auf diese Weise erzeugte Ion mit einem α -Bromoester:



umgesetzt wird unter Bildung des Esters:



der sodann mit Ammoniak umgesetzt wird unter Bildung des Amids:



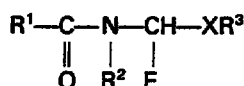
das sodann dehydratisiert wird zur Bildung des gewünschten Nitrils:



7. Verfahren zur Herstellung von Amid-Derivaten der Formel (I):



98



5 worin

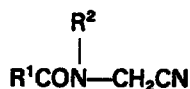
R¹ für einen gegebenenfalls substituierten Alkyl-, Alkenyl-, Aryl-, Heterocyclyl-, Benzyl- oder Heterocyclylmethyl-Rest steht; R² für Wasserstoff steht; X für Sauerstoff, Schwefel oder eine —NH-Gruppe steht; R³ für einen gegebenenfalls substituierten Alkyl- oder Alkenyl-Rest steht, wenn X Sauerstoff oder Schwefel bedeutet, oder für COZ, worin Z Alkyl oder Alkylen ist, steht, wenn X —NH bedeutet; und E für eine —CN-, —CONH₂-, —CSNH₂- oder —CONR⁴R⁵-Gruppe steht, worin jeder Rest R⁴ und R⁵ Wasserstoff oder eine gegebenenfalls substituierte Alkyl- oder Alkenylgruppe bedeutet, wobei gilt, daß X nicht für Schwefel steht, wenn R¹ Phenyl oder durch Nitro oder Methoxy substituiertes Phenyl bedeutet, bei welchem ein Amin R²NH₂ mit Formaldehydcyanhydrin kondensiert wird unter Bildung eines substituierten Aminoacetonitrils:

15



das sodann durch das geeignete Säurechlorid R¹COCl acyliert wird unter Bildung des Amid-Derivats:

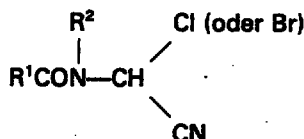
20



(XVI)

welches chloriert (z.B. mit SO₂Cl₂) oder bromiert (z.B. mit Br₂) wird unter Bildung des Chloro- oder Bromo-Derivats:

25



(XVII)

30

das mit dem geeigneten Alkohol, Thiol oder Amin HXR³ in Gegenwart einer Base behandelt wird unter Bildung des gewünschten Nitrils (XV).

35 8. Verfahren zur Herstellung von Amid-Derivaten nach Anspruch 7, dadurch gekennzeichnet, daß die Cyanoamide (XVI) dadurch erzeugt werden, daß entweder
(a) ein Nitril der Formel:



40

einer Alkylierung mit einem Bromid R²Br in Gegenwart von Natriumhydrid unterworfen wird unter Bildung des Cyanoamids, oder

(b) ein Amid der Formel:

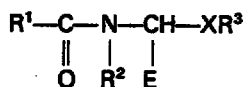
45



mit ClCH₂CN in Gegenwart von Natriumhydrid umgesetzt wird unter Bildung des gewünschten Cyanoamids.

9. Verfahren zur Herstellung von Amid-Derivaten der Formel (I):

50



55 worin

R¹ für einen gegebenenfalls substituierten Alkyl-, Alkenyl-, Aryl-, Heterocyclyl-, Benzyl- oder Heterocyclylmethyl-Rest steht;

R² für Wasserstoff steht;

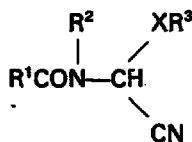
X für Sauerstoff, Schwefel oder eine —NH-Gruppe steht;

60 R³ für einen gegebenenfalls substituierten Alkyl- oder Alkenyl-Rest steht, wenn X Sauerstoff oder Schwefel bedeutet, oder für COZ, worin Z Alkyl oder Alkylen ist, steht, wenn X —NH bedeutet; und

E für eine —CSNH₂-Gruppe steht, wobei jeder der Reste R⁴ und R⁵ Wasserstoff oder eine gegebenenfalls substituierte Alkyl- oder Alkenylgruppe bedeutet, wobei gilt, daß X nicht für Schwefel steht, wenn R¹ Phenyl oder durch Nitro oder Methoxy substituiertes Phenyl bedeutet, bei welchem gasförmiges

65 H₂S durch eine Lösung eines Nitrils:

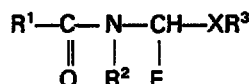




in Pyridin, die eine geringe Menge eines Katalysators wie Triethylamin enthält, geleitet wird.

Revendications pour les Etats Contractants: BE CH DE FR GB IT LI NL SE

1. Dérivés amidiques de formule (I):



dans laquelle

R¹ est un radical alkyle, alcényle, aryle, hétérocyclyle, benzyle ou hétérocyclylméthyle éventuellement substitué;

R² est l'hydrogène ou un radical alkyle, alcényle, benzyle ou hétérocyclylméthyle éventuellement substitué;

X est l'oxygène, le soufre ou un groupe —NH—;

R³ est un radical alkyle ou alcényle facultativement substitué lorsque X est l'oxygène ou le soufre ou est un radical COZ dans lequel Z est un radical alkyle ou alkylène lorsque X est un groupe —NH—; et

E est un groupe —CN, —CONH₂, —CSNH₂, ou —CONR⁴R⁵ dans lequel chacun de R⁴ et R⁵ représente l'hydrogène ou un radical alkyle ou alcényle facultativement substitué, sous réserve que X ne soit pas du soufre, lorsque R¹ est un groupe phényle ou phényle substitué par un radical nitro ou méthoxy.

2. Dérivés amidiques suivant la revendication 1, dans lesquels R¹ est un radical alkyle en C₁ à C₅ ou alcényle en C₃ à C₅ facultativement substitué; un radical phényle, naphtyle ou benzyle, chacun facultativement substitué dans le noyau avec du fluor, du chlore, du brome ou de l'iode, un radical alkyle en C₁ à C₄, alkoxy en C₁ à C₄, méthylènedioxy, éthylènedioxy, alkylthio en C₁ à C₄, nitro, cyano ou halogénalkyle en C₁ à C₄; un radical furyle, thiényle, pyridyle, thiazolyle ou benzothiazolyle facultativement substitué; ou un radical hétérocyclylméthyle facultativement substitué dont le groupe hétérocyclyle est un groupe furyle, thiényle, pyridyle, thiazolyle ou benzothiazolyle; R² est l'hydrogène ou un groupe alkyle en C₁ à C₄, allyle, phényle, benzyle ou furylméthyle; R³ est un radical alkyle en C₁ à C₄, halogénalkyle en C₁ à C₄ ou alcényle en C₃ à C₄, ou est un groupe alcanoyle en C₁ à C₄ lorsque X est un groupe NH; et chacun de R⁴ et R⁵ représente l'hydrogène ou un groupe méthyle.

3. Dérivés amidiques suivant la revendication 1 ou 2, dans lesquels R¹ est un groupe aryle ou hétérocyclique facultativement substitué.

4. Dérivés amidiques selon l'une quelconque des revendications précédentes, dans lesquels R¹ est un radical phényle facultativement substitué au niveau de l'une quelconque des positions 3, 4 et 5 avec un groupe alkyle, alkoxy ou méthylènedioxy ou avec un halogène.

5. Dérivés amidiques suivant l'une quelconque des revendications précédentes, dans lesquels R¹ est un groupe furyle, benzofuryle, thiényle, pyridyle, thiazolyle ou benzothiazolyle.

6. Dérivés amidiques suivant la revendication 1, 2 ou 3 dans lesquels R² est l'hydrogène.

7. Dérivés amidiques selon l'une quelconque des revendications précédentes, dans lesquels R³ est un groupe allyle ou un groupe alkyle en C₁ à C₄.

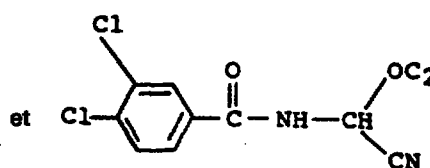
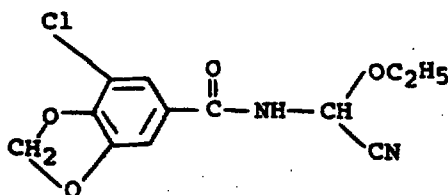
8. Dérivés amidiques selon l'une quelconque des revendications précédentes, dans lesquels X est l'oxygène ou le soufre.

9. Dérivés amidiques selon l'une quelconque des revendications précédentes, dans lesquels X est l'oxygène.

10. Dérivés amidiques selon l'une quelconque des revendications précédentes, dans lesquels E est un groupe CN ou CSNH₂.

11. Dérivés amidiques de formule I dans laquelle R¹ est tel que défini dans la revendication 4 et R² est l'hydrogène, X est l'oxygène, R³ est un groupe alkyle en C₁ à C₄ et E est un groupe cyano.

12. Dérivés amidiques de formule:



13. Procédé de préparation de dérivés amidiques tels que définis dans l'une quelconque des revendications 1 à 12 et dans lesquels R^2 , dans la formule I, est l'hydrogène, qui consiste à mettre en réaction un chlorure d'acide:



avec l'aminooacétonitrile:



10 pour obtenir l'acylaminoacétonitrile de formule



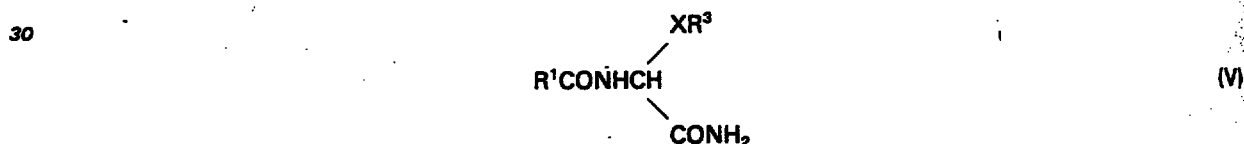
15 et à faire réagir ce composé avec un agent de bromation ou un agent de chloration pour obtenir le dérivé halogéné



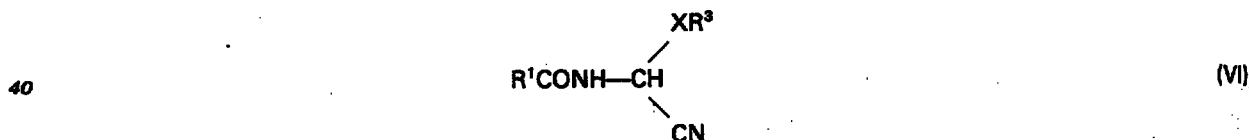
dans lequel X est un atome de brome ou de chlore, que l'on met à son tour en réaction avec l'alcool, le thiol ou l'amine approprié de formule



pour obtenir le composé carbamoylique



35 puis à traiter ce dernier avec un agent déshydratant pour le convertir en le composé cyano correspondant



14. Procédé de préparation de dérivés amidiques tels que définis dans l'une quelconque des revendications 1 à 12, qui consiste à condenser un amide:



avec un ester glyoxylique:



pour obtenir le composé intermédiaire hydroxylé:



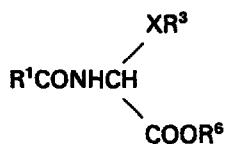
60 qu'on traite avec un agent de chloration (par exemple le chlorure de thionyle) pour le convertir en le dérivé chloro correspondant:



65 que l'on fait ensuite réagir avec l'alcool, le thiol ou l'amine approprié R^3XH pour obtenir l'ester:

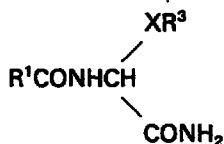


(IX)



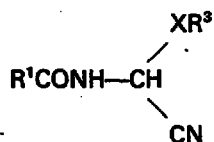
qu'on traite lui-même avec l'ammoniac pour obtenir le dérivé carbamoylique:

(V)



qui est ensuite déshydraté en donnant le dérivé cyanamidé désiré de l'invention:

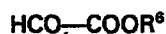
(VI)



15. Procédé de préparation de dérivés amidiques tels que définis dans l'une quelconque des revendications 1 à 12, et dans lesquels X, dans la formule I, est l'oxygène, qui consiste à condenser un amide

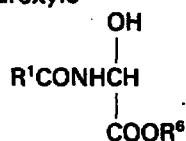


avec un ester glyoxylique:



pour obtenir le composé intermédiaire hydroxylé

(VII)

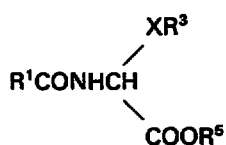


qu'on fait ensuite réagir avec un composé



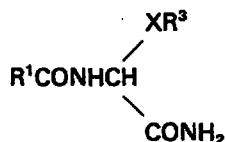
en présence de H_2SO_4 comme catalyseur pour obtenir l'ester

(IX)



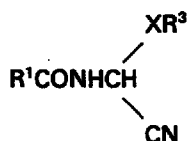
qu'on traite avec de l'ammoniac pour produire le dérivé carbamoylique

(V)

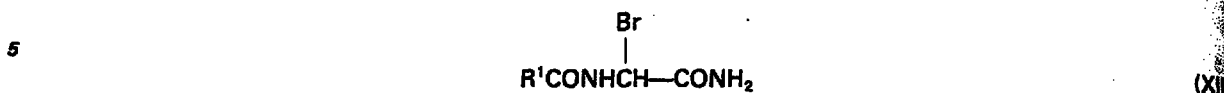


qui est ensuite déshydraté pour produire le dérivé cyanamidique de l'invention

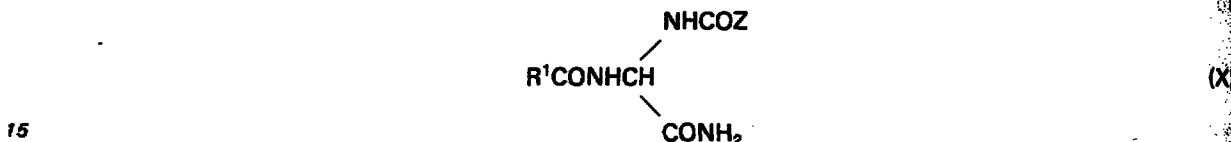
(VI)



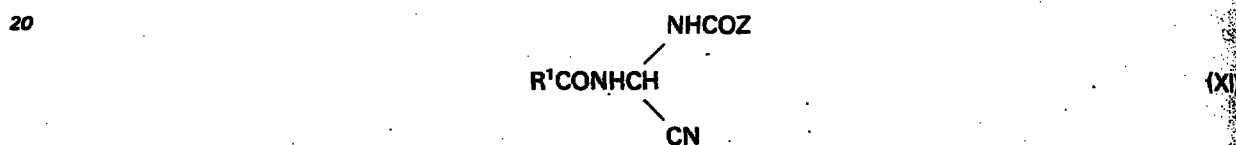
16. Procédé de préparation de dérivés amidiques tels que définis dans l'une quelconque des revendications 1 à 12, qui consiste à mettre en réaction un bromamide:



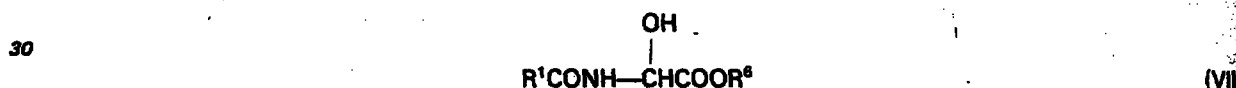
avec le nitrile ZCN approprié dans lequel Z est un radical alkyle ou alkylène, dans l'acide acétique dans les conditions de la réaction de Ritter pour obtenir l'amide



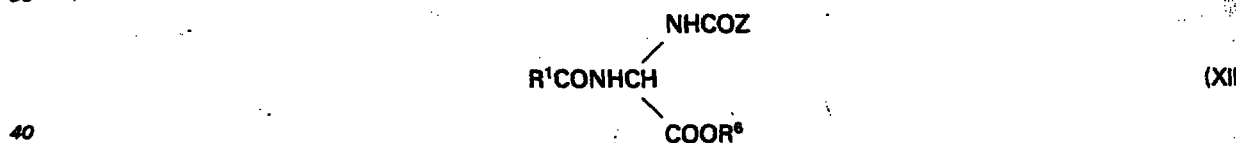
qu'on traite avec un agent déshydratant (par exemple l'anhydride trifluoroacétique dans la pyridine) pour obtenir le nitrile:



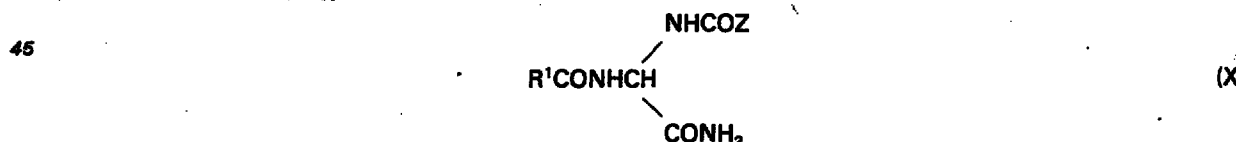
17. Procédé de préparation de dérivés amidiques tels que définis dans l'une quelconque des revendications 1 à 12, qui consiste à mettre en réaction un hydroxyester:



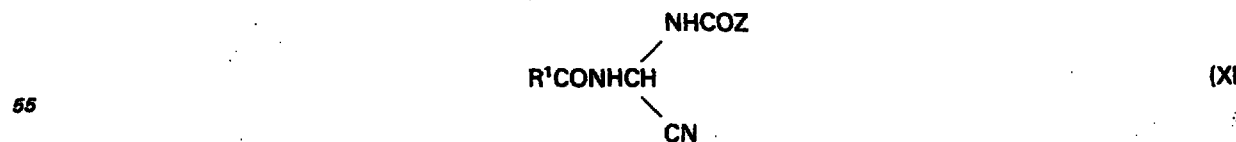
avec le nitrile ZCN approprié dans lequel Z est un radical alkyle ou alkylène, en présence d'acide acétique et d'acide sulfurique (réaction de Ritter) pour obtenir l'amide:



qu'on fait ensuite réagir avec l'ammoniac pour obtenir l'amide:



qui est ensuite déshydraté en le nitrile:



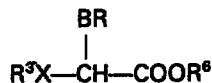
18. Procédé de préparation de dérivés amidiques tels que définis dans l'une quelconque des revendications 1 à 12, qui consiste à traiter un amide:



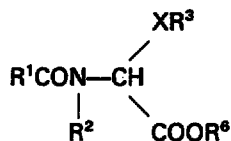
avec l'hydruire de sodium et à faire réagir l'ion ainsi engendré avec l'alpha-bromester:



100

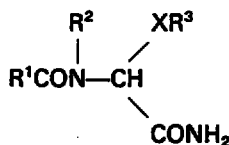


pour obtenir l'ester:



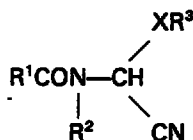
(XIII)

qu'on fait ensuite réagir avec l'ammoniac pour obtenir l'amide:



(XIV)

qui est ensuite déshydraté pour produire le nitrile désiré:

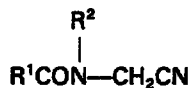


(XV)

19. Procédé de préparation de dérivés amidiques tels que définis dans l'une quelconque des revendications 1 à 12, qui consiste à condenser une amine R^2NH_2 avec la cyanhydrine du formaldéhyde pour obtenir un aminoacétonitrile substitué:

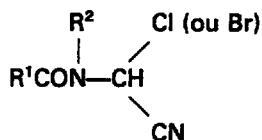


qui est ensuite acylé par le chlorure d'acide R^1COCl approprié pour former le dérivé amidique:



(XVI)

qui est chloré (par exemple avec SO_2Cl_2) ou bromé (par exemple avec Br_2) pour obtenir le dérivé chloré ou bromé



(XVII)

qu'on traite avec l'alcool, le thiol ou une amine HXR^3 approprié en présence d'une base pour obtenir le nitrile (XV) désiré.

20. Procédé de préparation de dérivés amidiques suivant la revendication 19, caractérisé en ce que les cyanamides (XVI) sont produits (a) en soumettant un nitrile de formule:



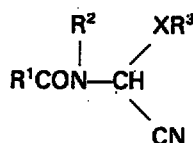
à une alkylation avec un bromure R^2Br en présence d'hydrure de sodium pour obtenir le cyanamide ou (b) en faisant réagir un amide de formule:



avec ClCH_2CN en présence d'hydrure de sodium pour obtenir le cyanamide désiré.

21. Procédé de préparation de dérivés amidiques tels que définis dans l'une quelconque des revendications 1 à 12, dans lesquels E est un radical thiocarbamoyl, qui consiste à faire passer du H_2S gazeux dans une solution d'un nitrile:





dans la pyridine contenant une petite quantité d'un catalyseur tel que la triéthylamine.

22. Composition pesticide, et notamment compositions fongicide et herbicide, comprenant comme ingrédient actif un dérivé amidique tel que défini dans l'une quelconque des revendications 1 à 12 en association avec un support ou diluant.

23. Procédé pour inhiber la croissance de plantes non désirées, qui consiste à appliquer aux plantes ou au site des plantes une quantité phytotoxique d'un composé tel que défini dans l'une quelconque des revendications 1 à 12 ou d'une composition telle que définie dans la revendication 22.

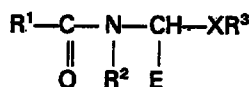
24. Procédé pour combattre des champignons, qui consiste à appliquer aux champignons ou à leur site une quantité efficace du point de vue fongicide d'un composé tel que défini dans l'une quelconque des revendications 1 à 12 ou d'une composition telle que définie dans la revendication 22.

25. Procédé pour combattre une maladie fongique chez une plante, qui consiste à appliquer à la plante, à la graine de la plante ou au site de la plante ou de la graine un composé tel que défini dans l'une quelconque des revendications 1 à 12 ou une composition fongicide telle que définie dans la revendication 22.

26. A titre de composés chimiques nouveaux, les composés intermédiaires nouveaux de formules IV et V telles que définies dans la revendication 13; de formule V telle que définie dans la revendication 14; et de formules XIV et XV telles que définies dans la revendication 18.

25 Revendications pour l'Etat contractant: AT

1. Procédé de préparation de dérivés amidiques de formule (I):



dans laquelle

R¹ est un radical alkyle, alcényle, aryle, hétérocyclyle, benzyle ou hétérocyclyméthyle éventuellement substitué;

R² est l'hydrogène, X est l'oxygène, le soufre ou un groupe —NH—;

R³ est un radical alkyle ou alcényle facultativement substitué lorsque X est l'oxygène ou le soufre, ou est un groupe COZ dans lequel Z est un radical alkyle ou alkylène lorsque X représente —NH—; et

E est un groupe —CH, —CONH₂ ou —CONR⁴R⁵ dans lequel chacun de R⁴ et R⁵ est l'hydrogène ou un groupe alkyle ou alcényle facultativement substitué, sous réserve que X ne soit pas le soufre lorsque R¹ est un groupe phényle ou phényle substitué par un radical nitro ou méthoxy, qui consiste à mettre en réaction un chlorure d'acide:



avec l'aminooacétonitrile:



pour obtenir l'acylaminoacétonitrile de formule



et à faire réagir ce composé avec un agent de bromation ou un agent de chloration pour obtenir le dérivé halogéné



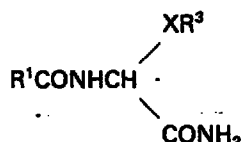
dans lequel X est le brome ou de chlore, qu'on met à son tour en réaction avec l'alcool, le thiol ou l'amine approprié de formule



pour obtenir le composé carbamoylique

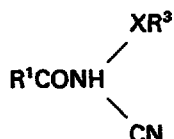


(102)



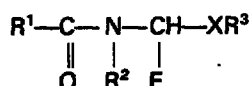
(V)

puis à traiter ce dernier avec un agent déshydratant pour le convertir en le composé cyano correspondant



(VI)

2. Procédé de préparation de dérivés amidiques de formule (I):



dans laquelle

R¹ est un radical alkyle, alcényle, aryle, hétérocyclyle, benzyle ou hétérocyclylméthyle facultativement substitué;

R² est l'hydrogène ou un radical alkyle; alcényle, benzyle ou hétérocyclylméthyle facultativement substitué;

X est l'oxygène, le soufre ou un groupe —NH—;

R³ est un radical alkyle ou alcényle facultativement substitué lorsque X est l'oxygène ou le soufre ou est un groupe COZ dans lequel Z est un radical alkyle ou alkylène lorsque X est un groupe —NH—; et

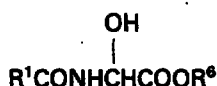
E est un groupe —CN, —CONH₂ ou —CONR⁴R⁵ dans lequel chacun de R⁴ et R⁵ est l'hydrogène ou un groupe alkyle ou alcényle facultativement substitué, sous réserve que X ne soit pas le soufre lorsque R¹ est un groupe phényle ou phényle substitué par un radical nitro ou méthoxy, qui consiste à condenser un amide



avec un ester glyoxylique:

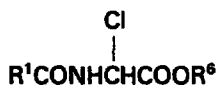


pour obtenir le composé intermédiaire hydroxylé:



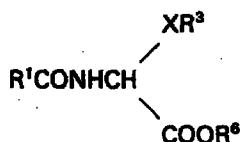
(VII)

qui est traité avec un agent de chloration (par exemple le chlorure de thionyle) pour le convertir en le dérivé chloré correspondant:



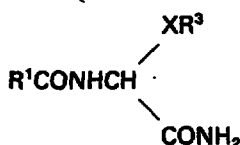
(VIII)

qu'on fait ensuite réagir avec l'alcool, le thiol ou l'amine R³XH approprié pour obtenir l'ester:



(IX)

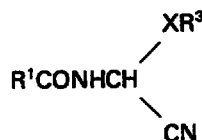
qu'on traite lui-même avec l'ammoniac pour obtenir le dérivé carbamoylique:



(V)

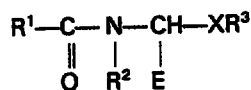


qu'on déshydrate ensuite pour produire le dérivé cyanamidé désiré de l'invention:



(VI)

3. Procédé de préparation de dérivés amidiques de formule (I):



dans laquelle

R¹ est un radical alkyle, alcényle, aryle, hétérocyclyle, benzyle ou hétérocyclylméthyle facultativement substitué;

R² est l'hydrogène ou un radical alkyle, alcényle, benzyle ou hétérocyclylméthyle facultativement substitué;

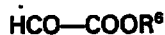
X est un l'oxygène;

R³ est un radical alkyle ou alkylène facultativement substitué lorsque X est l'oxygène ou le soufre, ou représente un group COZ dans lequel Z est un radical alkyle ou alkylène lorsque X est un groupe —NH—; et

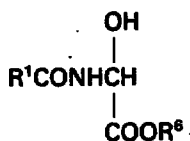
E est un groupe —CN, —CONH₂, —CSNH₂ ou —CONR⁴R⁵ dans lequel chacun de R⁴ et R⁵ est l'hydrogène ou un groupe alkyle ou alcényle facultativement substitué, sous réserve que X ne soit pas le soufre lorsque R¹ est un groupe phényle ou phényle substitué par un radical nitro ou méthoxy, qui consiste à condenser un amide



avec un ester glyoxylique



pour obtenir le composé intermédiaire hydroxylé

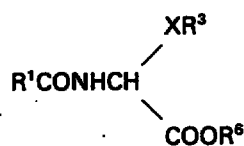


(VII)

qu'on fait ensuite réagir avec un composé

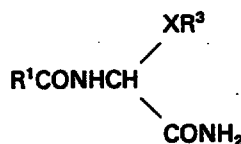


en présence de H₂Si₄ comme catalyseur pour obtenir l'ester:



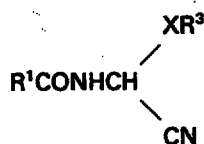
(IX)

qu'on traite avec l'ammoniac pour produire le dérivé carbamoylique



(V)

qu'on déshydrate ensuite pour produire le dérivé cyanamidé dique de l'invention:

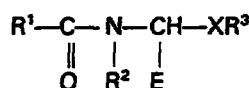


(VI)



16H

4. Procédé de préparation de dérivés amidiques de formule (I):



5

dans laquelle

R¹ est un radical alkyle, alcényle, aryle, hétérocyclyle, benzyle ou hétérocyclylméthyle facultativement substitué;10 R² est l'hydrogène ou un radical alkyle, alcényle, benzyle ou hétérocyclylméthyle facultativement substitué;

X est un group —NH—;

R³ est un group COZ dans lequel Z est un radical alkyle ou alkylène; et15 E est un groupe —CN, —CONH₂, —CSNH₂ ou —CONR⁴R⁵ dans lequel chacun de R⁴ et R⁵ est l'hydrogène ou un groupe alkyle ou alcényle facultativement substitué, sous réserve que X ne soit pas le soufre lorsque R¹ est un groupe phényle ou phényle substitué par un radical nitro ou méthoxy, qui consiste à mettre en réaction un bromamide:

20



avec le nitrile ZCN approprié dans lequel Z est un radical alkyle ou alkylène, dans l'acide acétique dans les conditions de la réaction de Ritter pour obtenir l'amide:

25



30

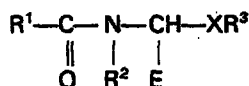
qu'on traite avec un agent déshydratant (par exemple l'anhydrite trifluoroacétique dans la pyridine) pour obtenir le nitrile:

35



40

5. Procédé de préparation de dérivés amidiques de formule (I):



45

dans laquelle

R¹ est un radical alkyle, alcényle, aryle, hétérocyclyle, benzyle ou hétérocyclylméthyle facultativement substitué;50 R² est l'hydrogène ou un radical alkyle, alcényle, benzyle ou hétérocyclylméthyle facultativement substitué;

X est un groupe —NH—;

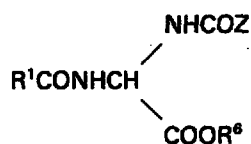
R³ est un groupe COZ dans lequel Z est un radical alkyle ou alkylène; et55 E est un groupe —CN, —CONH₂, ou —CONR⁴R⁵ dans lequel chacun de R⁴ et R⁵ est l'hydrogène ou un groupe alkyle ou alcényle facultativement substitué, sous réserve que X ne soit pas le soufre, lorsque R¹ est un groupe phényle ou phényle substitué par un radical nitro ou méthoxy, qui consiste à mettre en réaction un hydroxyester:

60

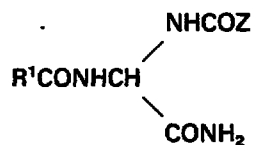


65 avec le nitrile ZCN approprié dans lequel Z est un radical alkyl ou alkylène, en présence d'acide acétique et d'acide sulfurique (réaction de Ritter) pour obtenir l'amide de formule:

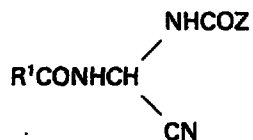




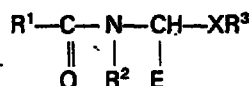
qu'on fait ensuite réagir avec l'ammoniac pour obtenir l'amide:



qu'on déshydrate ensuite en le nitrile:



6. Procédé de préparation de dérivés amidiques de formule (I):



dans laquelle

R^1 est un radical alkyle, alcényle, aryle, hétérocyclyle, benzyle ou hétérocyclylméthyle facultativement substitué;

R^2 est l'hydrogène;

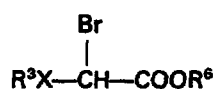
X est l'oxygène, le soufre ou un groupe $-\text{NH}-$;

R^3 est un radical alkyle ou alcényle facultativement substitué lorsque X est l'oxygène ou le soufre, ou un groupe COZ dans lequel Z est un radical alkyle ou alkylène lorsque X est un groupe $-\text{NH}-$; et

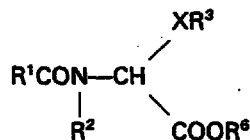
E est un groupe $-\text{CN}$, $-\text{CONH}_2$, $-\text{CSNH}_2$ ou $-\text{CONR}^4\text{R}^5$ dans lequel chacun de R^4 et R^5 est l'hydrogène ou un groupe alkyle ou alcényle facultativement substitué, sous réserve que X ne soit pas le soufre lorsque R^1 est un groupe phényle ou phényle substitué par un radical nitro ou méthoxy, qui consiste à traiter un amide:



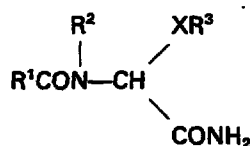
avec l'hydrure de sodium et à faire réagir l'ion ainsi engendré avec un alpha-bromester:



pour obtenir l'ester:



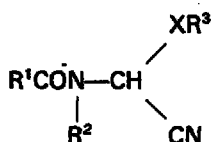
qu'on fait ensuite réagir avec l'ammoniac pour obtenir l'amide:



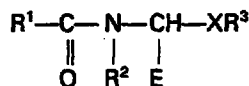
qu'on déshydrate ensuite pour produire le nitrile désiré



(XV)



7. Procédé de préparation de dérivés amidiques de formule (I):



dans laquelle

R¹ est un radical alkyle, alcényle, aryle, hétérocyclyle, benzyle ou hétérocyclylméthyle facultativement substitué;

R² est l'hydrogène;

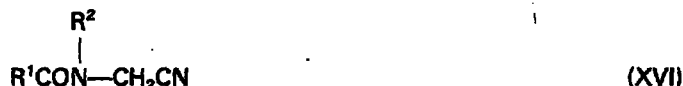
X est un l'oxygène, le soufre ou un groupe —NH—;

R³ est un radical alkyle ou alcényle facultativement substitué lorsque X est l'oxygène ou le soufre, ou représente un groupe COZ dans lequel Z est un radical alkyle ou alkylène lorsque X est un group —NH; et

E est un groupe —CN, —CONH₂, —CSNH₂ ou —CONR⁴R⁵ dans lequel chacun de R⁴ et R⁵ est l'hydrogène ou un groupe alkyle ou alcényle facultativement substitué, sous réserve que X ne soit pas le soufre, lorsque R¹ est un groupe phényle ou phényle substitué par un radical nitro ou méthoxy, qui consiste à condenser une amine R²NH₂ avec la cyanhydrine du formaldéhyde pour obtenir un aminoacétonitrile substitué:



qui est ensuite acylé par le chlorure d'acide R¹COCl approprié pour former le dérivé amidique:



qui est chloré (par exemple avec SO₂Cl₂) ou bromé (par exemple avec Br₂) pour former le dérivé chloré ou bromé:



qu'on traite avec l'alcool, le thiol ou une amine HXR³ approprié en présence d'une base pour obtenir le nitrile (XV) désiré.

8. Procédé de préparation de dérivés amidiques suivant la revendiction 7, caractérisé en ce que les cyanamides (XVI) sont produits (a) en soumettant un nitrile de formule:

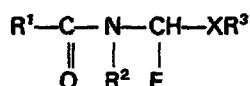


à une alkylation avec un bromure R²Br en présence d'hydrure de sodium pour obtenir le cyanamide ou (b) en faisant réagir un amide de formule:



avec ClCH₂CN en présence d'hydrure de sodium pour obtenir le cyanamide désiré.

9. Procédé de préparation de dérivés amidiques de formule (I):



dans laquelle

R¹ est un radical alkyle, alcényle, aryle, hétérocyclyle, benzyle ou hétérocyclylméthyle facultativement substitué;

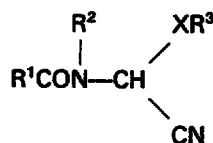
R² est l'hydrogène;



X est un l'oxygène, le soufre ou un groupe —NH—;

R³ est un radical alkyle ou alcényle facultativement substitué lorsque X est l'oxygène ou le soufre ou représente un groupe COZ dans lequel Z est un radical alkyle ou alkylène lorsque X est un group —NH—;

E est un groupe —CSNH₂, sous réserve que X ne soit pas le soufre lorsque R¹ est un groupe phényle ou phényle substitué par un radical nitro ou méthoxy, qui consiste à faire passer du H₂S gazeux dans une solution d'un nitrile



dans la pyridine contenant une petite quantité d'un catalyseur tel que la triéthylamine.

