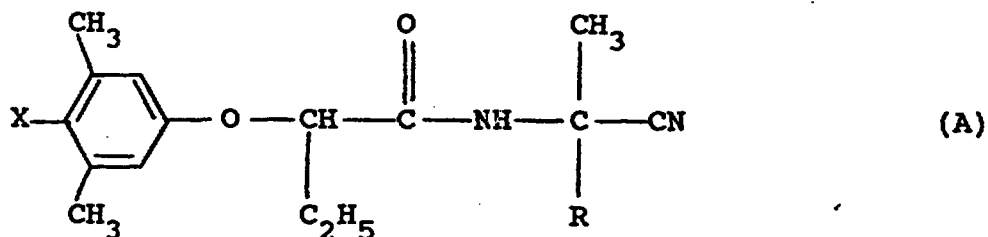


The invention concerns new agents for the control of phytopathogenic fungi, new active substances for these agents and processes for the preparation of these active substances.

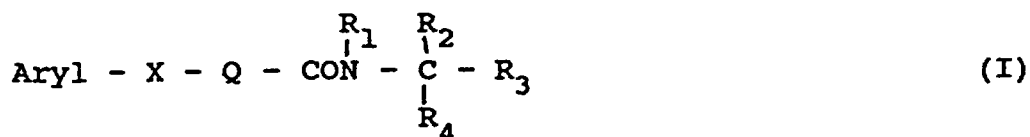
EP-A-1721 discloses certain compounds of the formula:



where X means a chlorine or bromine atom or a methyl group and R means a methyl, ethyl or methoxymethyl group. The use of such compounds in controlling mildew, especially bean mildew (Erysiphe polygoni) is also disclosed.

It has however now been discovered that certain other derivatives of aryloxy- and arylthiocarboxylic acids are useful for controlling phytopathogenic fungi, especially Piricularia on rice plants.

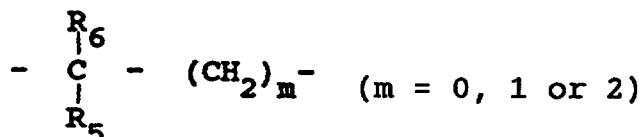
Hence according to the invention the use of compounds is provided, which correspond to the formula I



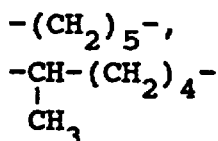
in which

Aryl: means a phenyl residue unsubstituted or one- to three-fold substituted by C₁-C₅-alkyl, C₁-C₅-alkoxy, C₁-C₅-alkyl-SO_n (n = 0, 1 or 2), halogen, NO₂, CF₃, CN, CH₃OCH₂, (CH₃)₂NCH₂, COO-alkyl, CONH₂ or phenyl, a 1- or 2-naphthyl, an

optionally chlorine-substituted 2-, 3- or 4-pyridyl, a pyrimidyl or quinolyl residue,
Q: means



R₁: means H, C₁-C₅-alkyl, Allyl,
R₂ & R₃: mean H, C₁-C₆-alkyl (which can also contain an
O or S atom in the chain),
C₃-C₇-cycloalkyl,
CH₂-COO-(C₁-C₅-alkyl), phenyl,
R₂ and R₃ together also mean -(CH₂)₄-



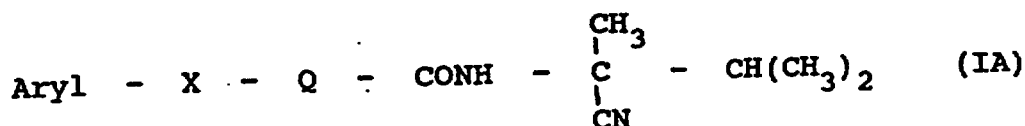
R₄: means CN, CONH₂,
R₅: means H, CH₃, C₂H₅
R₆: means H, CH₃ and
X: means O or S,

optionally in the form of racemates or mixtures of the optical isomers or in the form of the pure enantiomers or diastereomers, for the control of Piricularia on rice.

If the substituents R₁ to R₆ contain hydrocarbon chains, these may be straight or branched and the same or different. Preferred are chains with up to 4, especially up to 3 C-atoms. CH₃ is preferred as alkyl substituent in the aryl residue. Halogen means fluorine, chlorine, bromine, and iodine, preferably chlorine and fluorine. The substituents in the aryl residue may be the same or different. CF₃, CN, NO₂, (CH₃)₂NCH₂, phenyl and C₁-C₅-alkyl-SO_n are in general present only once. If aryl

means a quinolinyl group, this preferably is 8-quinolinyl.

Most of the compounds of the formula I are novel. Consequently compounds of the formula,



Aryl: a phenyl residue unsubstituted or one- to three-fold substituted by C₁-C₅-alkyl, C₁-C₅-alkoxy, C₁-C₅-alkyl-SO_n (n = 0, 1 or 2), halogen, NO₂, CF₃, CN, CH₃OCH₂, (CH₃)₂NCH₂, COO-alkyl, CONH₂ or phenyl, a 1- or 2-naphthyl, an optionally chlorine-substituted 2-, 3- or 4-pyridyl, a pyrimidyl or quinolyl residue,

Q:



R₅: H, CH₃, C₂H₅

R₆: H, CH₃

X: O or S,

optionally in the form of racemates or mixtures of the optical isomers or in the form of the pure enantiomers or diastereomers, are provided in the invention.

Aryl preferably represents 4-chlorophenyl, 4-chloro-2-methylphenyl, 2,4-, 3,4- or 3,5-dichlorophenyl. Moreover it is preferable for X to represent O and Q CH(CH₃).

An especially preferred compound is N-[2-cyano-3-methylbutyl(2)]-2-(4-chloro-2-methylphenoxy)-propionamide. These compounds are prepared in known ways.

1. Reaction of compounds of the formula



where aryl, X and Q have the above meaning and Y is a leaving group, e.g. halogen (preferably chlorine), Oalkyl, OH, acyl, with a compound of the formula



with elimination of HY.

The reaction is preferably performed in an inert solvent, for example methylene chloride, toluene, acetonitrile, an ether, or in a mixture of solvents at temperatures between room temperature and the boiling temperature of the reaction mixture, the reaction being promoted by an HY-binding agent, for example a base, when HY represents an acid such as HCl, or dicyclohexylcarbodiimide or carbonyldiimidazole, when HY means water.

The starting materials are known or else readily preparable by normal procedures. Thus compounds of the formula II with Y = OH can for example be obtained by reaction of appropriate phenols or thiophenols aryl-XH with ethyl 2-bromopropionate ester in the presence of a base and subsequent hydrolysis of the ester. The corresponding carboxylic acid chlorides of the formula II are formed from the carboxylic acids so obtained, e.g. by reaction with thionyl chloride.

The α -aminoacid nitriles (III) can be prepared by the Strecker synthesis from the corresponding ketone or

aldehyde, NaCN and NH_4Cl in water

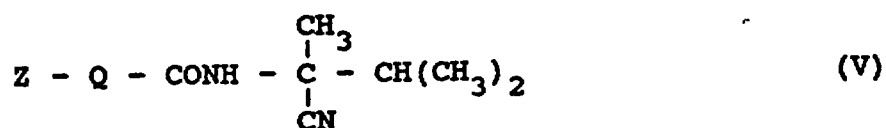
(Houben-Weyl, Vol. VIII, pp 274 ff (1952)).

Compounds of the formula III, in which the cyano group has been replaced by CONH_2 , are formed from the corresponding nitriles by partial hydrolysis.

2. Reaction of a compound of the formula



where aryl and X have the above meaning, and M means hydrogen or an alkali metal cation, with a compound of the formula



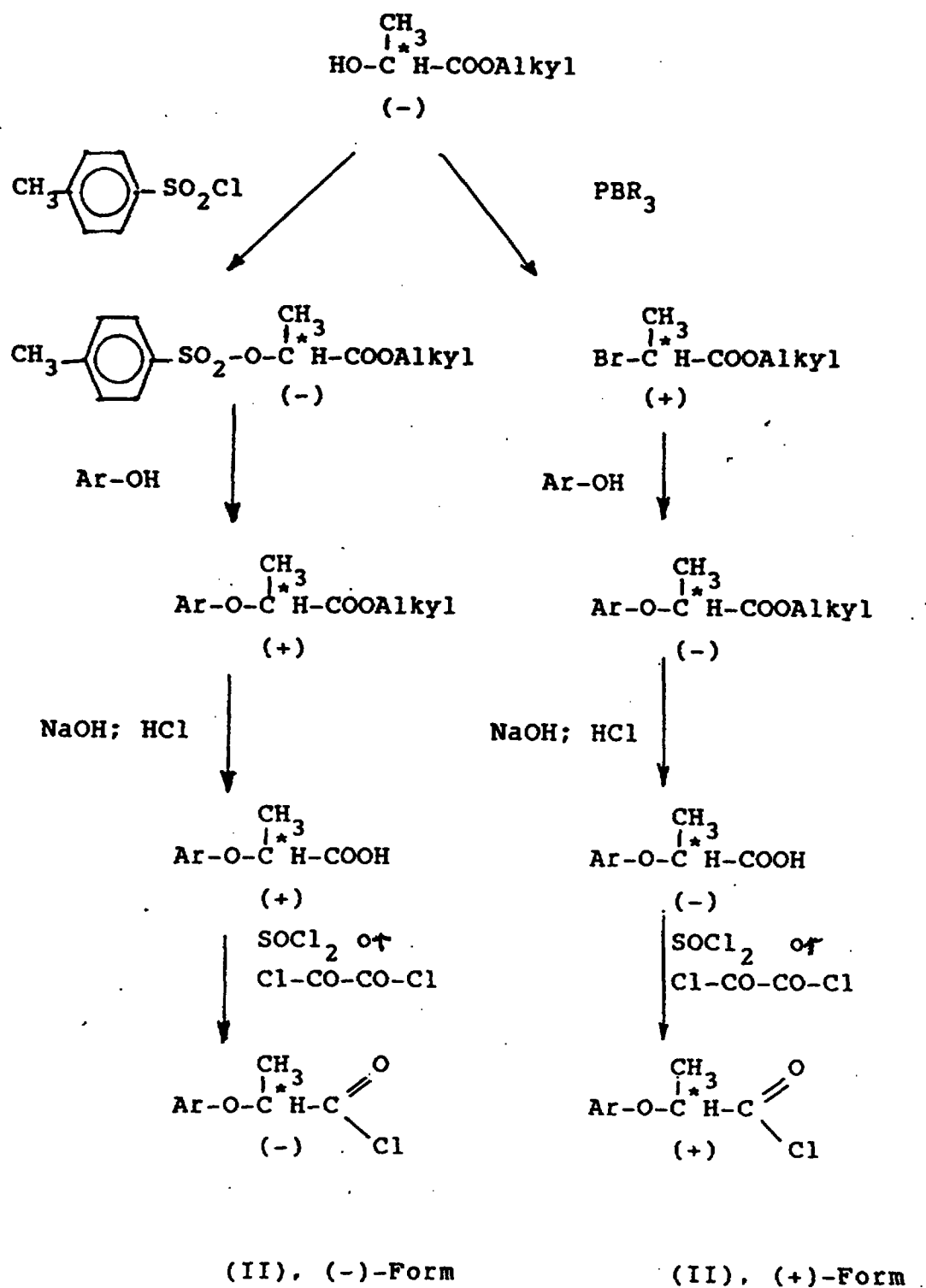
in which Q has the above meaning and Z means halogen or an arylsulphonyloxy group.

The reaction takes place in an inert polar solvent.

When $\text{M} = \text{H}$, a base is added. Conditions under which a compound IV with $\text{M} = \text{K}$ or Na is formed are preferred.

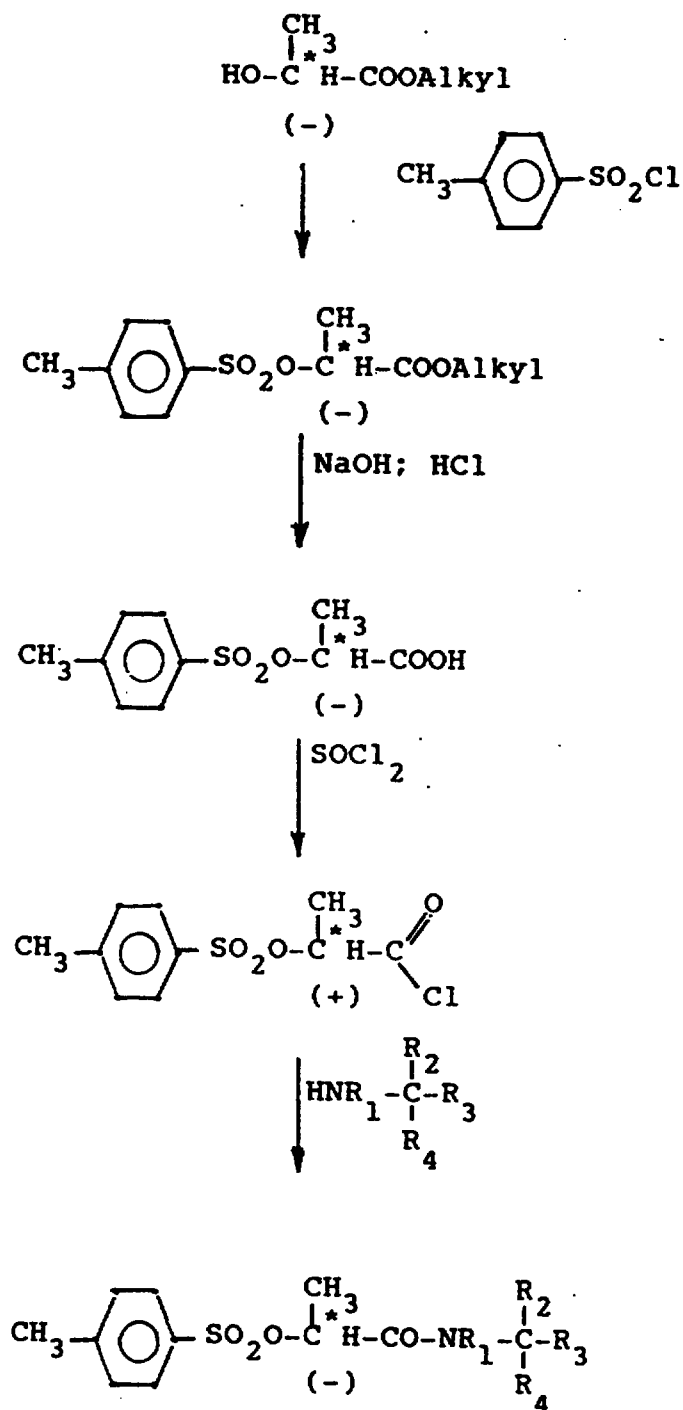
The preferred meaning for Z is bromine and $\text{CH}_3\text{-C}_6\text{H}_4\text{-SO}_3^-$, and the preferred solvent is acetonitrile. The reaction takes place hot, e.g. at reflux temperature. Examples of bases which may be used are alkali metal carbonates, alkali metal hydroxides, and also if necessary adequately basic amines, such as triethylamine.

Depending on the meaning of R_2 to R_6 , compounds of the formula I may occur with one or two asymmetric centres. The isomers may if desired be separated by normal methods or be synthesised directly by the use of optically active starting materials.



"Alkyl" preferably means methyl or ethyl.

Similar steps lead to optically active starting materials of the formula V; in this case also, other optically active compounds of the formula V can be obtained analogously.



(V), (-)-Form.

The compounds of the formula I have a fungitoxic action against phytopathogenic fungi. In particular they can be used against fungal diseases on rice. Although the new compounds are to some extent derived from herbicides (dichlorprop 2,4-DB), they are surprisingly well tolerated by plants.

For use, the compounds of the formula I are processed with normal additives or carriers to produce commonly used preparations, which are diluted with appropriate amounts of water for use in the form of a spray. Examples of such preparations are emulsion and suspension concentrates, suspendable powders, dusting powders and granules, which can contain up to 80 weight percent of active substance.

Examples of the formulation:

1. Emulsion Concentrate

5.0 wt. pts. active substance according to the invention
3.4 wt. pts. epoxidised vegetable oil
13.4 wt. pts. of a combination emulsifier consisting of
fatty alcohol polyglycol ethers and
calcium alkylarylsulphonate
40.0 wt. pts. dimethylformamide
38.2 wt. pts. xylene

The components are mixed and for use are diluted with water to an active substance concentration from 0.01 to 0.1 weight percent.

Suspendable Powder

10 wt. pts. active substance according to the invention
3 wt. pts. sodium fatty alcohol sulphonate
5 wt. pts. salts of naphthalenesulphonic acid
formaldehyde condensate.
82 wt. pts. kaolin

The action of the compounds according to the invention, e.g. against Piricularia was tested under tropical conditions on sown rice. 2 rows of sown rice (I and II) between older rows naturally infected with Piricularia were treated on the 41st, 45th and 49th days after sowing with sprays which contained defined amounts of the active substance. The controls treated only with water were used for comparison. The assessment was made 6, 8, 10 and 13 days after the last spraying (% plants infected).

The compounds according to the invention were found to show effective activity against Piricularia and to be well tolerated by the plants.

Further tests are described below.

Action against Piricularia on Rice

A. Leaf Treatment

Rice plants are raised in transplanting dishes. They are sprayed dripping wet with emulsions or suspensions which contain 1000, 500 or 250 ppm of the particular active substance. Two days after the treatment the transplanting boxes are set out in the open land between infected rice plants for 5-6 days, in order to bring about an infection. Evaluation 5-8 days later.

B. Soil Treatment

Rice plants are raised in flowerpots. Emulsions or suspensions containing 500 ppm of the stated active substance are poured onto the roots. Two days after the treatment the pots are set out for 4-6 days in the open land between rice plants which are infected with Piricularia, in order to bring about an infection. The evaluation is made 5-7 days after the infection.

The assessment is made using the scores 1 to 3:

- 1: No attack
- 2: Slight attack
- 3: Attack as in the untreated controls

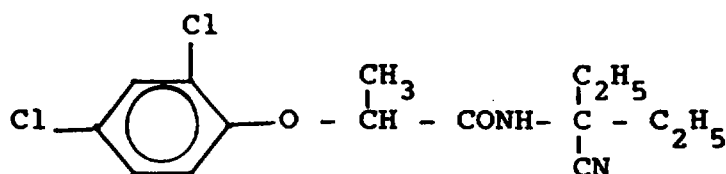
The figures given in the table are mean values from 3 experiments and several assessments made at intervals.

C. Use under Water (Submerged Use)

Rice plants are planted in buckets filled with earth. The earth is covered with a shallow layer of water. A quantity of active ingredient corresponding to an application level of 8 or 4 or 2 kg/ha a.i. is added as suspension or emulsion. 2 days after the treatment the test plants are set out in open land between infected rice plants and remain exposed to the infection during the experiment. The assessment begins one day after an infection occurs in the untreated controls and is performed 4-5 times (3 experiments with each substance). Scoring as in A and B. The figures in the table are mean values from three experiments and several assessments.

Test Results

Act.Subst. from example	Act.Subst. Concn. [ppm]	Infection Count Test A	Test B	Test C kg/ha	Infection Count
Tab. II	1000	1.0			
No. 62	500	1.0	1.8	8	2.0
	250	1.0			
Example	1000	1.0		4	1.8
No. 9	500	1.0	2.0	2	2.2
	250	1.5			
Tab. II	1000	-			
No. 1	500	1.0	2.5	8	1.8
	250	1.0			
Tab. V	1000	1.0			
No. 2	500	1.5	1.0	4	1.5
	250	2.5			
Example	1000	1.0		8	1.8
No. 4	500	1.8	2.1		
	250	2.1			
Tab. II	1000	1.1			
No. 2	500	1.0	-	4	2.0
	250	2.0			
Tab. II	1000	1.0			
No. 33	500	1.0	-		
	250	2.0			
Example	1000	1.5			
No. 6e	500	2.0	2.0		
	250	2.0			
Tab. IV	1000	-			
No. 6	500	1.0	1.9		
	250	1.0			

Example 1N-(1-ethyl-1-cyanopropyl)-2-(2,4-dichlorophenoxy)-propionamide

2.2 g 3-amino-3-cyanopentane and 2.4 g triethylamine are dissolved in 100 ml methylene chloride. To this are added 5.1 g 2-(2,4-dichlorophenoxy)-propionyl chloride and the mixture is stirred overnight at room temperature. The solution is shaken with water and sodium hydrogen carbonate solution, dried and evaporated down. The residue obtained consists of 6.3 g (96 % of theoretical) of a brownish, viscous oil, which crystallises on stirring with diisopropyl ether.

Yield: 4.9 g white solid (74 % of theoretical)

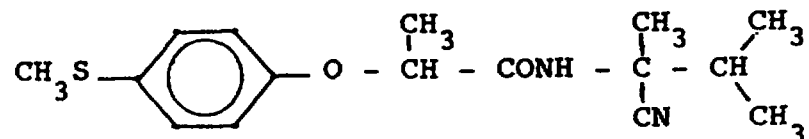
Melting point: 100 - 102°C

The structure is confirmed by spectroscopic examination.

Analysis: $C_{15}H_{18}Cl_2N_2O_2$

M.W. = 329.23

	C %	H %	Cl %	N %
Found:	54.58	5.54	21.06	8.35
Calc:	54.72	5.51	21.54	8.51

Example 2N-(1-cyano-1,2-dimethylpropyl)-2-(4-methylthiophenyl-oxy)-propionamide

2.5 g N-(1-cyano-1,2-dimethyl-propyl)-2-bromopropionamide (made analogously to example 5a) and 1.4 g 4-methylmercaptophenol are dissolved in 50 ml methyl isobutyl ketone. After addition of 1.5 g potash, the mixture is stirred 3 hours at 80°C.

2.8 g of brownish oil (91.5 %) are obtained, which crystallises on stirring with diisopropyl ether.

M.Pt. 83-86°C

Analysis: $C_{16}H_{22}N_2O_2S$ M.W. = 306.43

	C %	H %	N %	S %
Found:	62.48	7.24	9.23	10.34
Calc:	62.71	7.24	9.14	10.46

The structure was confirmed spectroscopically.

Example 3N-[3-cyanopentyl(3)-]-2-(4-chloro-2-methylphenoxy)-propionamide

4.4 g 2-amino-2-ethylbutyronitrile (0.039 moles) and

4.6 g triethylamine (0.046 moles) are dissolved in methylene chloride, and 9.0 g 2-(4-chloro-2-methylphenoxy)-propionyl chloride are added dropwise with stirring. The mixture becomes warm. It is stirred for a further 3 hours without heating, shaken successively with water and bicarbonate solution, dried and evaporated down. The residue obtained consists of a brown oil (10.8 g), which crystallises after stirring with diisopropyl ether. The product is filtered off under suction and dried.

Yield: 10.6 g (88 % of theoretical) white solid
M.Pt.: 125-126°C

Elementary analysis and NMR spectrum confirm the stated formula.

Example 4

N-[2-cyano-3-methylbutyl(2)-]-2-(4-chloro-2-methylphenoxy)-propionamide

Analogously to example 3, the title compound is obtained from equimolar amounts of 2-amino-2,3-dimethylbutyronitrile.

Yield: 76 % of theoretical; M.Pt.: 97-99°C

The product is initially obtained as a brown oil. It consists of 4 isomers. The mixture can be separated into 3 fractions by stepwise precipitation with cold ether.

From 11.1 g oil are obtained:

Fraction I: 1.8 g white solid,
M.Pt.: 117-118°C;
Fraction II: 1.8 g brownish solid,
M.Pt.: 94-96°C;
Fraction III: 5.6 g reddish oil (purified
chromatographically)

The NMR spectrum reveals an enantiomer pair enrichment
in fractions I and II:

Fraction I Enantiomer pair I to enantiomer pair II
89 : 11 (diastereomer ratio)

Fraction II Enantiomer pair I to enantiomer pair II
26 : 74

The enantiomer pairs can be further enriched by
recrystallisation of the fractions.

Analogously to the above examples, the following compounds of the following formula can also be obtained:

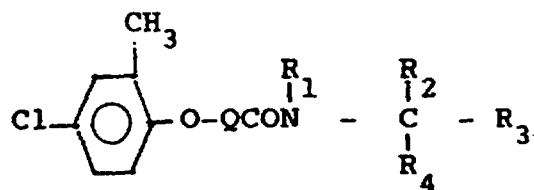
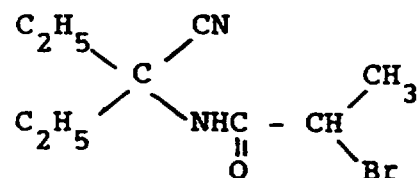


Table I

No.	Q	R ₂	R ₃	R ₁	R ₄	M.Pt. [°C]
1	CH ₂	C ₂ H ₅	C ₂ H ₅	H	CN	86-88
2	CH(CH ₃)	i-C ₃ H ₇	CH ₃	H	CONH ₂	108-111
3	CH ₂	i-C ₃ H ₇	CH ₃	H	CONH ₂	105-107
4	CH ₂	i-C ₃ H ₇	CH ₃	H	CN	102-103
5	CH(CH ₃)	n-C ₃ H ₇	CH ₃	H	CN	71-75
6	CH(CH ₃)	C ₂ H ₅	CH ₃	H	CN	86-87
7	CH(CH ₃)	n-C ₃ H ₇	CH ₃	H	CONH ₂	100-102
8	CH(CH ₃)	n-C ₅ H ₁₁	CH ₃	H	CN	
9	CH(CH ₃)	-(CH ₂) ₅ -		H	CN	134-136
10	CH ₂	-(CH ₂) ₅		H	CN	118-120
11	CH ₂	i-C ₃ H ₇	CH ₃	CH ₃	CN	
12	CH(CH ₃)	i-C ₃ H ₇	CH ₃	CH ₃	CN	Oil
13	CH(CH ₃)	-(CH ₂) ₄ -		H	CN	143-146
14	CH(CH ₃)	-CH-(CH ₂) ₄ CH ₃		H	CN	121-127

Example 5N-(1-ethyl-1-cyanopropyl)-2-(4-chlorophenylthio)-propionamide

a) N-(1-ethyl-1-cyanopropyl)-2-bromopropionamide

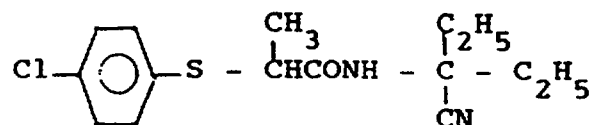


36.5 g 2-amino-2-cyano-n-pentane in 100 ml methylene chloride are added dropwise over 40 minutes with stirring and cooling in the ice-bath to 88.4 g 2-bromopropionic anhydride (0.325 moles) dissolved in 280 ml methylene chloride. After stirring overnight, the solution is shaken with water and sodium bicarbonate solution, dried and evaporated down. The oil which remains is triturated with a little ether, whereupon the product crystallises out.

M.Pt. 85-87°C

Yield: 61.2 g (76.5 % of theoretical)

b)



5.8 g 4-chlorothiophenol (0.04 moles) are stirred in 150 ml methyl isobutyl ketone for 10 minutes at 90°C with 12.2 g potassium carbonate. 9.9 g N-(1-ethyl-1-cyanopropyl)-2-bromopropionamide are added to the resulting suspension with stirring, and the mixture is stirred for ca. 5 hours at ca. 90°C. The solution is filtered, shaken successively with water, 2N sodium hydroxide and

water, dried over magnesium sulphate and evaporated down. A brown oil is obtained, which solidifies to a brownish crystalline mass on stirring with a little ether.

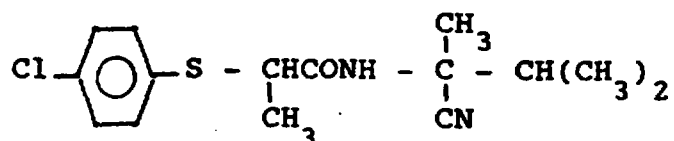
M.Pt. 108-110°C

Yield: 7.2 g (58.1 % of theoretical)

Elementary analysis:

	C	H	Br	Cl	S
Found:	57.96 %	6.16 %	9.01 %	11.4 %	10.32 %
Calc:	57.77 %	6.35 %	8.86 %	11.32 %	10.28 %

Analogously to the above example, the following compound is also obtained



M.Pt. 106-109°C

Example 6

(+)-N-(1-ethyl-1-cyanopropyl)-2-(4-chloro-2-methylphenoxy)-propionamide

a) (-) Methyl O-(4-methylphenylsulphonyl)-lactate

26.9 g triethylamine are added dropwise to a solution of 25.2 g S-(-) methyl lactate and 46.1 g p-toluenesulphonyl chloride in 160 ml toluene. The mixture is stirred overnight and the precipitate is removed by suction filtration. The toluene solution is shaken with dilute hydrochloric acid and water, dried with sodium sulphate and evaporated down. 55.9 g of a colourless oil are obtained, which is purified by vacuum distillation.

B.Pt._{0.2}: 148-152°C [α]_D²⁴: -50.1° (ethanol)

Yield: 43.5 g (70 % of theoretical)

b) (+) Methyl (4-chloro-2-methylphenoxy)-propionate

41.9 g S-(-) methyl O-(4-methylsulphonyl)-lactate and 23.1 g 4-chloro-2-methylphenol are dissolved in 100 ml acetonitrile, treated with 50 g potash and stirred for 10 hours under reflux. The solution is suction filtered and evaporated down. The residue is taken up in toluene, shaken with 1 N sodium hydroxide solution, dried and evaporated down. 32.2 g of reddish liquid are obtained (87 % of theoretical).

c) (+)-4-chloro-2-methylphenoxypropionic acid

The crude product (32.2 g) prepared according to b) is dissolved in 100 ml acetone. A solution of 6.8 g NaOH in 30 ml water is added dropwise with stirring and ice-cooling. After stirring overnight, the mixture is diluted with water and shaken with methylene chloride. The aqueous solution is acidified with conc. hydrochloric acid and the product that separates is extracted with methylene chloride. The methylene chloride solution is separated, dried and evaporated down. An oily residue is obtained, which immediately solidifies. M.Pt. 62-72°C (pressed dry on clay)
[α]_D²⁴: + 14.1° (ethanol)
Yield: 27.7 g (91 % of theoretical)

d) (+)-4-Chloro-2-methylphenoxypropionyl chloride

27.2 g (+)-4-Chloro-2-methylphenoxypropionic acid and 30.2 g thionyl chloride are stirred with 100 ml toluene for 3 hours at 100°C. The solution is evaporated down in vacuo. 29.6 g of brown oil is obtained, which is reacted without purification.

e) (+)-N-(1-ethyl-1-cyanopropyl)-2-(4-chloro-2-methylphenoxy)-propionamide

8.4 g of the crude product from d) are added dropwise with stirring at -20° to -30°C to 4 g 3-amino-3-cyanopentane and 4.4 g triethylamine, dissolved in 100 ml toluene. Next the mixture is stirred 3 hours at RT, shaken with water and the solution evaporated down. The oily residue (8.8 g) is stirred with diisopropyl ether, whereupon a crystalline product comes out, which is separated.

Yield 2.8 g (25 % of theoretical)

M.Pt. $98 - 100^{\circ}\text{C}$

$[\alpha]_D^{22}$: $+ 9.1^{\circ}$ (ethanol)

Example 7

(-)-N-(1-ethyl-1-cyanopropyl)-2-(4-chloro-2-methylphenoxy)-propionamide

a) (+) Methyl 2-bromopropionate

47.2 g S(-) ethyl lactate are dissolved in 300 ml methylene chloride. 108 g phosphorus tribromide are added dropwise. The reaction is exothermic. After stirring overnight at RT the mixture is poured onto ice and stirred with water. The methylene chloride solution is shaken with bicarbonate solution, dried and evaporated down. The residue is distilled.

Yield: 33.8 g; colourless oil (47 % of theoretical)

B.Pt._{25 mbar} $55-56^{\circ}\text{C}$

b) (-) Ethyl (4-chloro-2-methylphenoxy)-propionate

The product described in a) (33.8 g) is dissolved in 300 ml toluene together with 26.7 g 4-chloro-2-methylphenol

and stirred for 10 hours under reflux after addition of 52 g K_2CO_3 . The solution is suction filtered, shaken twice with 1 N sodium hydroxide solution, dried and evaporated down. 34.3 g clear liquid are obtained. (76 % of theoretical).

$[\alpha]_D^{22}$: - 14.46° (ethanol)

c) (-)-(4-chloro-2-methylphenoxy)-propionic acid
(-)-CMPP

The hydrolysis of the ester obtained according to b) is effected analogously to example 6c).

From 24.2 g (-) ethyl (4-chloro-2-methylphenoxy)-propionate, 19.7 g (-)-(4-chloro-2-methylphenoxy)-propionic acid are obtained (92 % of theoretical).

M.Pt.: 69-75°C

$[\alpha]_D^{22}$: - 9.679° (ethanol)

d) (+)-(4-chloro-2-methylphenoxy)-propionyl chloride
(+)-CMPP-chloride

The acid described in 7c) is converted to the acid chloride analogously to example 6d), and this is further processed without purification.

From 8.6 g (-)-CMPP, 8.4 g (+)-CMPP-chloride are obtained as a brownish oil (90 % of theoretical).

$[\alpha]_D^{22}$: + 4.486° (CCl_4)

e) (-)-N-(1-ethyl-1-cyanopropyl)-2-(4-chloro-2-methylphenoxy)-propionamide

The (+)-CMPP-chloride is reacted with 3-amino-3-cyano-n-pentane as described in example 6e). From 8 g (+)-CMPP-chloride, 3 g (-)-N-(1-ethyl-1-cyanopropyl)-2-(4-chloro-2-methylphenoxy)-propionamide (28 % of theoretical) are obtained.

M.Pt. 98-100°C

$[\alpha]_D^{22}$: - 8.584° (ethanol)

An alternative for the preparation of the dextrorotatory phenoxypropionamides is presented below taking (+)-N-(1-ethyl-1-cyanopropyl)-2-(4-chloro-2-methylphenoxy)-propionamide as the example:

Example 8

(+)-N-(1-ethyl-1-cyanopropyl)-2-(4-chloro-2-methylphenoxy)-propionamide

a) (+)-O-(4-methylphenylsulphonyl)-lactyl chloride

17.9 g (-)-O-(4-methylphenylsulphonyl)-lactic acid (Helv. Chim. Acta 65/1240 (1982)) and 13 g thionyl chloride are stirred for 3 hours at 95-100°C.

The product is evaporated down and degassed in vacuo.

19.2 g of brown oil (100 % of theoretical) are obtained.

b) (-)-N-(1-ethyl-1-cyanopropyl)-O-(4-methylsulphonyl)-lactamide

18.8 g of the crude product from 8a) are added dropwise at -20 to -30°C to a solution of 8 g 3-amino-3-cyano-n-pentane and 8.8 g triethylamine in 200 ml toluene. The mixture is stirred 3 hours at -20°C and then overnight at RT. The solution is shaken with water and evaporated down. 23.4 g (96 % of theoretical) of brown, clear oil are obtained, which are crystallised by stirring with diisopropyl ether.

M.Pt. 57-60°C $[\alpha]_D^{22}$: - 40.4° (ethanol)

Yield: 8.4 g (34 % of theoretical)

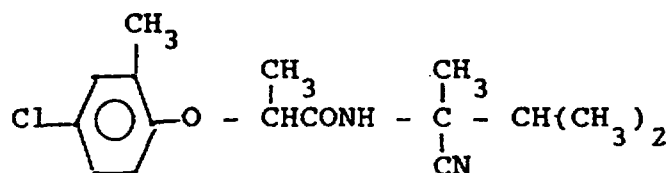
c) (+)-N-(1-ethyl-1-cyanopropyl)-2-(4-chloro-2-methylphenoxy)-propionamide

4.7 g (-)-N-(1-ethyl-1-cyanopropyl)-O-(4-methylsulph-

onyl)-lactamide and 2 g 4-chloro-2-methylphenol are dissolved in 100 ml toluene. 4.5 g powdered potassium carbonate are added, and the mixture is heated 12 hours under reflux with stirring. The solution is suction filtered, shaken with 1 N sodium hydroxide solution and evaporated down. 3.1 g of yellow oil are obtained (72 % of theoretical), which crystallises on stirring with diisopropyl ether. 2.2 g of white crystalline solid are obtained (51 % of theoretical).

M.Pt. 97-99°C $[\alpha]_D^{22}$: + 11.94° (ethanol)

Analogously to the examples 6 to 8, dextro- and laevo-rotatory enantiomers of the following compound are also obtained:



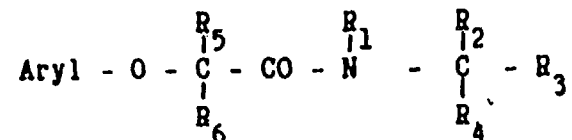
Example 9: $[\alpha]_D^{22}$: + 9.1°
(ethanol)

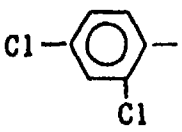
Oils, diastereomer
mixtures

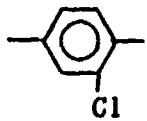
Example 10: $[\alpha]_D^{22}$: - 7.65°
(ethanol)

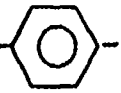
TABLE II

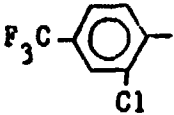
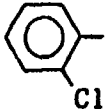
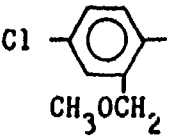
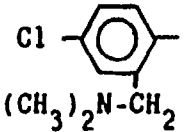
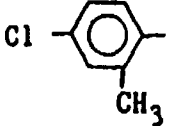
Compounds of the formula

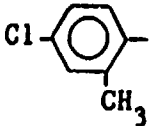
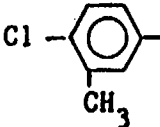
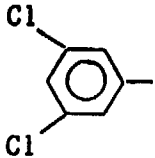


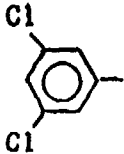
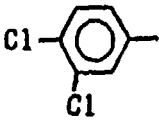
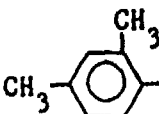
No.	Aryl	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	M.Pt. (°C)
1		H	CH ₃	CH(CH ₃) ₂	CN	H	CH ₃	79-80
2	"	H	CH ₃	C ₂ H ₅	CN	H	CH ₃	105-107
3	"	CH ₃	CH ₃	CH(CH ₃) ₂	CN	H	CH ₃	Oil
4	"	H		-(CH ₂) ₅ -	CN	H	CH ₃	142-144
5	"	H	CH ₃	n-C ₅ H ₁₁	CN	H	CH ₃	65-67
6	"	H	CH ₃	CH ₂ CH ₂ CH(CH ₃) ₂	CN	H	CH ₃	74-76

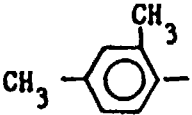
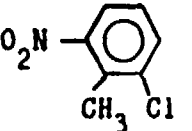
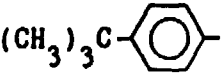
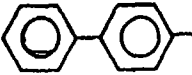
No.	Aryl	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	M.Pt. (°C)
7	Cl 	H	C ₂ H ₅ -	CH ₂ CH(CH ₃) ₂	CN	H	CH ₃	70-75
8	"	H	CH ₃	CH ₂ CH(CH ₃) ₂	CN	H	CH ₃	74-75
9	"	H	-(CH ₂) ₄		CN	H	CH ₃	117-119
10	"	H	H	CH(CH ₃) ₂	CN	H	CH ₃	Oil
11	"	H	CH ₃	-CH ₂ OCH ₃	CN	H	CH ₃	Oil
12	"	H	-CH(CH ₃)-(CH ₂) ₄		CN	H	CH ₃	129-134
13	"	H	CH ₃	-CH ₂ COOC ₂ H ₅	CN	H	CH ₃	

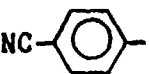
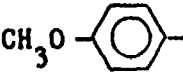
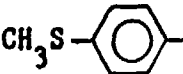
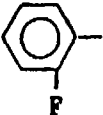
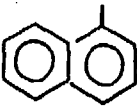
No.	Aryl	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	M.Pt. (°C)
14	Cl- 	H	CH ₃	CH(CH ₃) ₂	CN	H	H	85-87
15		H	-(CH ₂) ₅ -		CN	H	H	94-96
16	"	H	C ₂ H ₅	C ₂ H ₅	CN	H	H	50-52
17	"	H	CH ₃	CH(CH ₃) ₂	CN	H	CH ₃	80-81
18	"	CH ₃	CH ₃	CH(CH ₃) ₂	CN	H	CH ₃	0-11
19	"	H	C ₂ H ₅	C ₂ H ₅	CN	H	CH ₃	83-84
20	"	H	CH ₃	n-C ₅ H ₁₁	CN	H	CH ₃	75-77
21	"	H	CH ₃	CH ₂ CH(CH ₃) ₂	CN	H	CH ₃	58-62

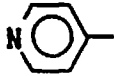
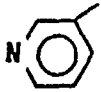
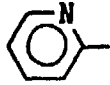
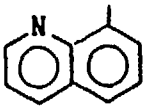
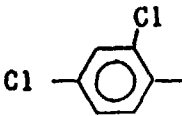
No.	Aryl	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	M.Pt. (°C)
22	C ₆ H ₅	H	CH ₃	CH(CH ₃) ₂	CN	H	CH ₃	81-83
23		H	CH ₃	CH(CH ₃) ₂	CN	H	CH ₃	120-124
24		H	CH ₃	CH(CH ₃) ₂	CN	H	CH ₃	60-62
25	"	H	CH ₃	n-C ₅ H ₁₁	CN	H	CH ₃	97-100
26		H	CH ₃	CH(CH ₃) ₂	CN	H	CH ₃	011
27		H	CH ₃	CH(CH ₃) ₂	CN	H	CH ₃	011
28		H	CH ₃	CH(CH ₃) ₂	CN	H	C ₂ H ₅	98-100

No.	Aryl	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	M.Pt. (°C)
29		H	CH ₃	CH(CH ₃) ₂	CN	CH ₃	CH ₃	94-97
30		H	CH ₃	CH(CH ₃) ₂	CN	H	CH ₃	110
31	"	H	CH ₃	n-C ₅ H ₁₁	CN	H	CH ₃	011 30
32	"	H	CH ₃	CH(CH ₃) ₃	CONH ₂	H	CH ₃	155
33		H	CH ₃	CH(CH ₃) ₃	CN	H	CH ₃	105
34	"	H	CH ₃	CH(CH ₃) ₃	CONH ₂	H	CH ₃	140

No.	Aryl	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	M.Pt. (°C)
35		H	CH ₃	n-C ₅ H ₁₁	CN	H	CH ₃	81
36		H	CH ₃	CH(CH ₃) ₂	CN	H	CH ₃	103
37	"	H	CH ₃	CH(CH ₃) ₂	CONH ₂	H	CH ₃	150
38	"	H	CH ₃	n-C ₅ H ₁₁	CN	H	CH ₃	111
39		H	CH ₃	CH(CH ₃) ₂	CN	H	CH ₃	106
40	"	H	CH ₃	n-C ₅ H ₁₁	CN	H	CH ₃	142

No.	Aryl	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	M.Pt. (°C)
41		H	C ₂ H ₅	C ₂ H ₅	CN	H	CH ₃	114
42	"	H	-(CH ₂) ₅		CN	H	CH ₃	121
43	"	CH ₃	CH ₃	CH(CH ₃) ₂	CONH ₂	H	CH ₃	85-90
44		H	CH ₃	CH(CH ₃) ₂	CN	H	CH ₃	160
45	"	H	C ₂ H ₅	C ₂ H ₅	CN	H	CH ₃	152-154
46		H	CH ₃	CH(CH ₃) ₂	CN	H	CH ₃	88-90
47		H	CH ₃	CH(CH ₃) ₂	CN	H	CH ₃	106-108

No.	Aryl	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	M.Pt. (°C)
48		H	CH ₃	CH(CH ₃) ₂	CN	H	CH ₃	98-100
49		H	CH ₃	CH(CH ₃) ₂	CN	H	CH ₃	57-63
50		H	C ₂ H ₅	C ₂ H ₅	CN	H	CH ₃	
51		H	CH ₃	CH(CH ₃) ₂	CN	H	CH ₃	78-81
52		H	CH ₃	CH(CH ₃) ₂	CN	H	CH ₃	72-75
53		H	CH ₃	CH(CH ₃) ₂	CN	H	CH ₃	98-102
54		H	CH ₃	CH(CH ₃) ₂	CN	H	CH ₃	152-157

No.	Aryl	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	M.Pt. (°C)
55		H	CH ₃	CH(CH ₃) ₂	CN	H	CH ₃	90-95
56		H	CH ₃	CH(CH ₃) ₂	CN	H	CH ₃	
57		H	CH ₃	CH(CH ₃) ₂	CN	H	CH ₃	80
58		H	CH ₃	CH(CH ₃) ₂	CN	H	CH ₃	125-128
59		H	CH ₃	CH(CH ₃) ₂	CN	H	CH ₃	105-107
60	"	H	CH ₃	CH ₂ CH(CH ₃) ₂	CN	H	CH ₃	
61		H	CH(CH ₃) ₂	CH(CH ₃) ₂	CN	H	CH ₃	82-84

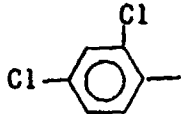
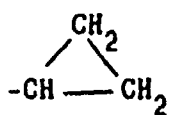
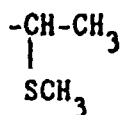
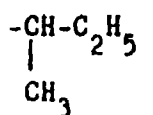
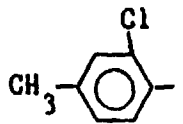
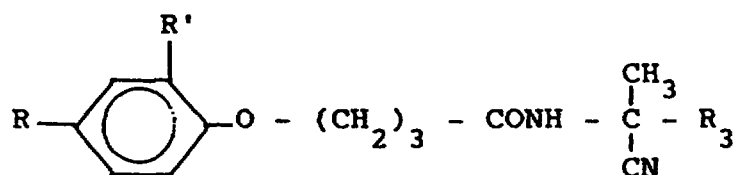
No.	Aryl	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	M.Pt. (°C)
62		H	CH ₃		CN	H	CH ₃	89-94
63	"	H	CH ₃		CN	H	CH ₃	124-128
64	"	H	CH ₃	CH ₂ -COOC ₂ H ₅	CN	H	CH ₃	
65	"	H	CH ₃		CN	H	CH ₃	107-110
66		H	CH ₃	CH(CH ₃) ₂	CN	H	CH ₃	

TABLE III

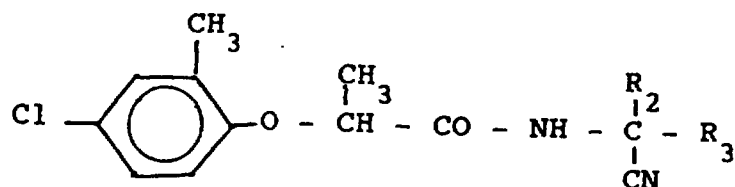
Compounds of the formula



No.	R ₃	R	R'	M.Pt. (°C)
1	CH(CH ₃) ₂	Cl	CH ₃	Oil
2	n-C ₅ H ₁₁	Cl	CH ₃	Oil
3	CH(CH ₃) ₂	CH ₃	Cl	
4	n-C ₅ H ₁₁	CH ₃	Cl	

Table IV

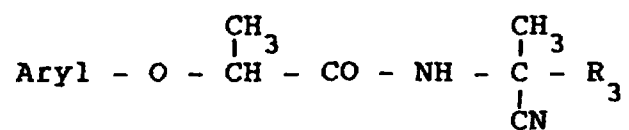
Compounds of the formula

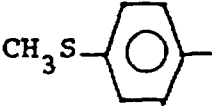
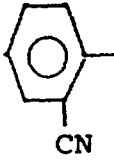
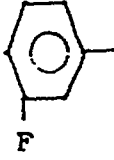
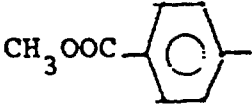
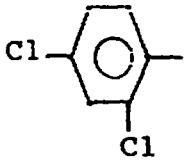


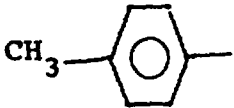
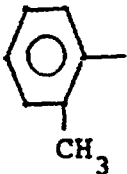
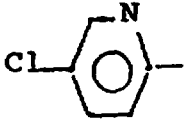
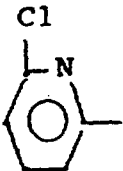
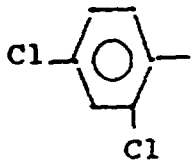
No.	R ₂	R ₃	M.Pt. [°C]
1	CH ₃	n-C ₃ H ₇	71-75
2	CH ₃	C ₂ H ₅	86-87
3	C ₂ H ₅	C ₂ H ₅	125-126
4	CH ₃	CH ₂ CH(CH ₃) ₂	101-102
5	CH ₃	CH ₂ OCH ₃	Öl
6	H	CH(CH ₃) ₂	86-88
7	CH ₃	CH ₂ CH ₂ CH(CH ₃) ₂	92-94
8	C ₂ H ₅	CH ₂ CH(CH ₃) ₂	68-70
9	CH ₃	CH(CH ₃)C ₂ H ₅	103-109
10	CH(CH ₃) ₂	CH(CH ₃) ₂	106-109
11	CH ₃		87-88
12	CH ₃	-CH-CH ₃ SCH ₃	127-129
13	CH ₃	CH ₃	128-130
14	CH ₃	C(CH ₃) ₃	110-115
15	H	C ₂ H ₅	64-66
16	H	CH ₃ CH ₂ CH ₃	66-70
17	CH ₃	C ₆ H ₅	148-152
18	CH ₃	CH ₂ SC ₂ H ₅	78-82

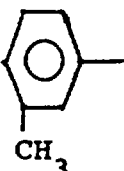
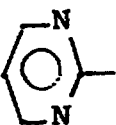
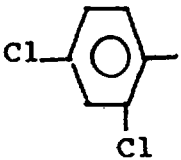
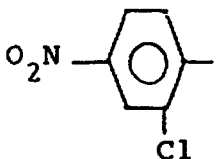
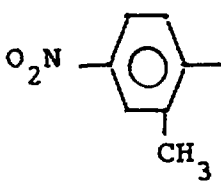
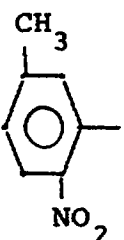
Table V

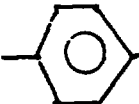
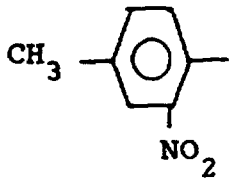
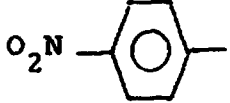
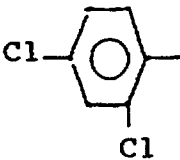
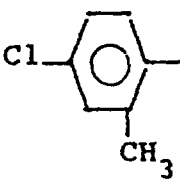
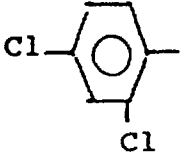
Compounds of the formula



No.	Aryl	R ₃	M.Pt. [°C]
1		CH(CH ₃) ₂	83-86
2		CH(CH ₃) ₂	74-76
3		CH(CH ₃) ₂	71-75
4		CH(CH ₃) ₂	110-115
5		CH ₃	134-137

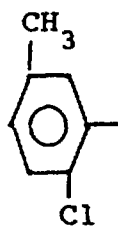
No.	Aryl	R ₃	M.Pt. [°C]
6		CH(CH ₃) ₂	80-82
7		CH(CH ₃) ₂	74-76
8		CH(CH ₃) ₂	134-136
9		CH(CH ₃) ₂	101-105
10		CH(CH ₃) ₂	94-99
11		C(CH ₃) ₃	126-130

No.	Aryl	R ₃	M.Pt. [°C]
12		CH(CH ₃) ₂	85-88
13		CH(CH ₃) ₂	170-174
14		C ₆ H ₅	129-145
15		CH(CH ₃) ₂	139-142
16		CH(CH ₃) ₂	124-126
17		CH(CH ₃) ₂	102-104

No.	Aryl	R ₃	MPt. [°C]
18		CH(CH ₃) ₂	78-80
19		CH(CH ₃) ₂	87-92
20		CH(CH ₃) ₂	110-112
21		CH ₂ SC ₂ H ₅	oil
22			from 112
23			from 112

No.	Aryl	R ₃	M.Pt. [°C]
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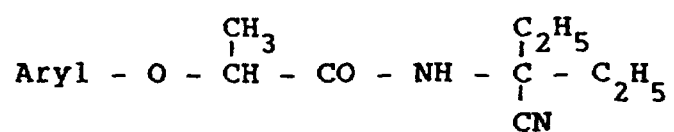
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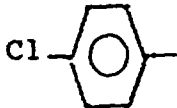
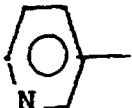
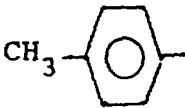
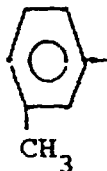
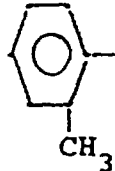
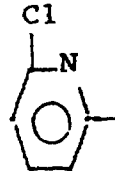
CH(CH₃)₂

69-71

Table VI

Compounds of the formula



No.	Aryl	M.Pt. [°C]
	Cl	
1		100-102
2		Oil
3		93-94
4		64-66
5		92-93
6		88-90

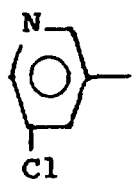
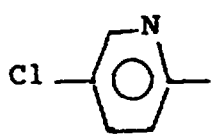
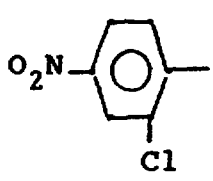
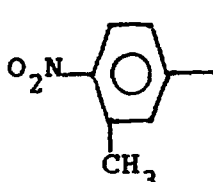
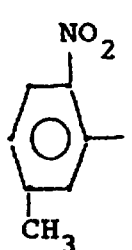
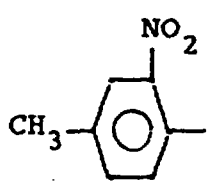
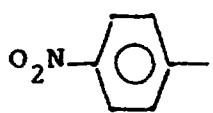
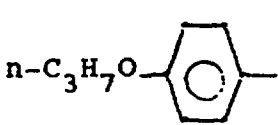
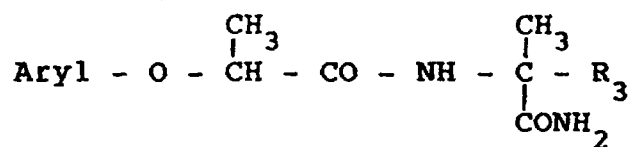
No.	Aryl	M.Pt. (°C)
7		84-87
8		129-131
9		117-120
10		117-118
11		132-133
12		120-122
13		108-110
14		71-75

Table VII

Compounds of the formula



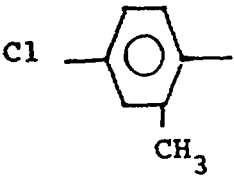
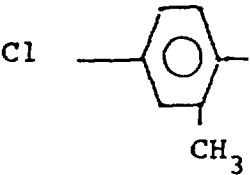
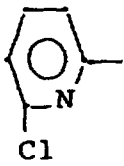
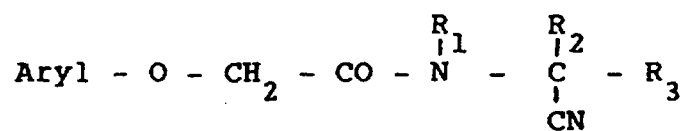
No.	Aryl	R ₃	M.Pt. [°C]
1		n-C ₃ H ₇	100-102
2		n-C ₃ H ₇	108-111
3		n-C ₃ H ₇	111-113
4		n-C ₃ H ₇	115-117

Table VIII

Compounds of the formula



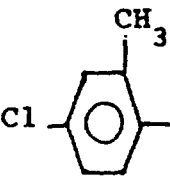
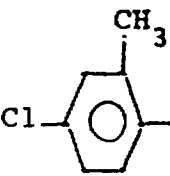
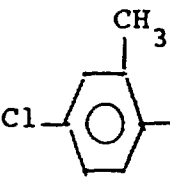
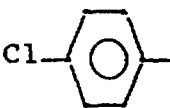
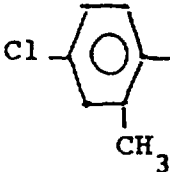
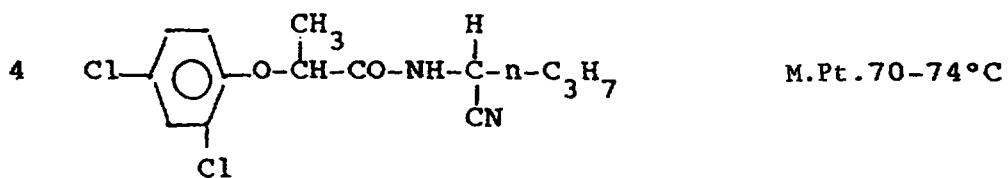
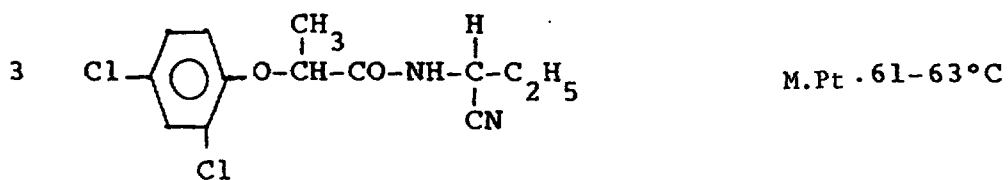
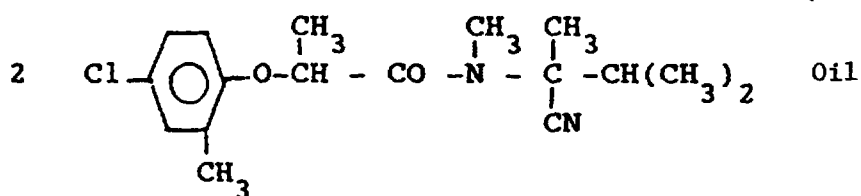
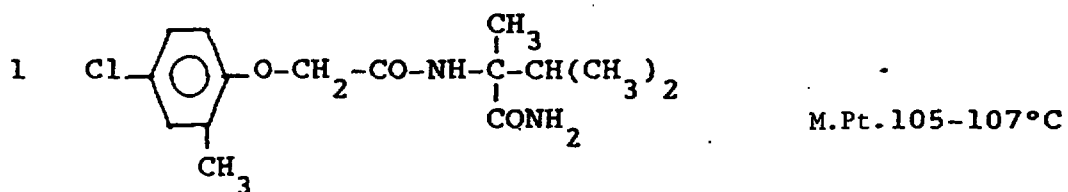
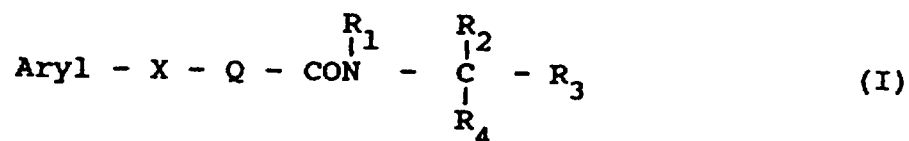
No.	Aryl	R ₁	R ₂	R ₃	M.Pt. - [°C]
1		H	CH ₃	CH(CH ₃) ₂	100-103
2		H	C ₂ H ₅	C ₂ H ₅	86-88
3		CH ₃	C ₂ H ₅	CH(CH ₃) ₂	Oil
4		H	C ₂ H ₅	C ₂ H ₅	50-52
5		H	CH ₃	n-C ₅ H ₁₁	Oil

Table IXOther Compounds According to the Invention

Patent Claims

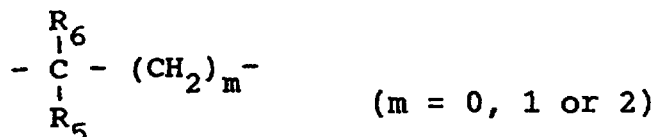
1. Use of compounds of the formula



in which

Aryl: a phenyl residue unsubstituted or one- to three-fold substituted by C₁-C₅-alkyl, C₁-C₅-alkoxy, C₁-C₅-alkyl-SO_n (n = 0, 1 or 2), halogen, NO₂, CF₃, CN, CH₃OCH₂, (CH₃)₂NCH₂, COO-alkyl, CONH₂ or phenyl, a 1- or 2-naphthyl, an optionally chlorine-substituted 2-, 3- or 4-pyridyl, a pyrimidyl or quinolyl residue,

Q:



R₁: H, C₁-C₅-alkyl, allyl,

R₂ and

R₃: H, C₁-C₆-alkyl (which can also contain an O or S atom in the chain), C₃-C₇-cycloalkyl, CH₂-COO-(C₁-C₅-alkyl), phenyl, R₂ and R₃ together also mean -(CH₂)₄-, -(CH₂)₅-, -CH-(CH₂)₄-
 $\begin{array}{c} | \\ \text{CH}_3 \end{array}$

R₄: CN, CONH₂,

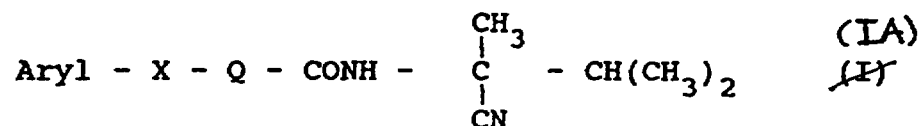
R₅: H, CH₃, C₂H₅

R₆: H, CH₃

X: O or S,

optionally in the form of racemates or mixtures of the optical isomers or in the form of the pure enantiomers or diastereomers, for the control of Piricularia on rice.

2. Compounds of the formula,



in which

Aryl: a phenyl residue unsubstituted or one- to three-fold substituted by C₁-C₅-alkyl, C₁-C₅-alkoxy, C₁-C₅-alkyl-SO_n (n = 0, 1 or 2), halogen, NO₂, CF₃, CN, CH₃OCH₂, (CH₃)₂NCH₂, COO-alkyl, CONH₂ or phenyl, a 1- or 2-naphthyl, an optionally chlorine-substituted 2-, 3- or 4-pyridyl, a pyrimidyl or quinolyl residue,

Q:

R₅: H, CH₃, C₂H₅R₆: H, CH₃

X: O or S,

optionally in the form of racemates or mixtures of the optical isomers or in the form of the pure enantiomers or diastereomers.

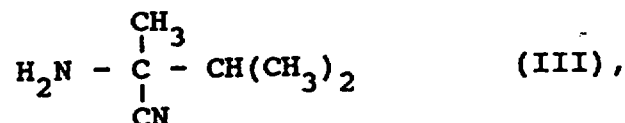
3. Compounds according to Claim 2, wherein aryl is 4-chlorophenyl, 4-chloro-2-methylphenyl, 2,4-, 3,4- or 3,5-dichlorophenyl.
4. Compounds according to Claim 2 or 3, wherein X means O.
5. Compounds according to Claim 2, 3 or 4, wherein Q means CH(CH₃).
6. N-[2-cyano-3-methylbutyl(2)]-2-(4-chloro-2-methylphenoxy)-propionamide.
7. Fungicidal agents, characterised by a content of a compound of the formula IA according to Claim 2 to 6, optionally in the form of racemates or mixtures of the optical isomers or in the form of the pure enantiomers or diastereomers, with normal additives and/or carrier substances.

8. Process for the preparation of compounds according to Claims 2 to 6 by known methods, characterised in that

- a) a compound of the formula



where aryl, X and Q have the above meaning and Y is a leaving group, is reacted with a compound of the formula

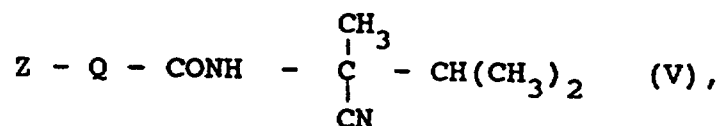


or that

- b) a compound of the formula



where aryl and X have the above meaning, and M means hydrogen or an alkali metal cation, is reacted with a compound of the formula

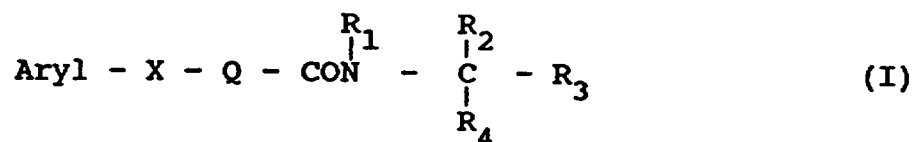


in which Q has the above meaning and Z means halogen or an arylsulphonyloxy group

and that if desired mixtures of enantiomers present are separated by normal methods into the individual enantiomers or into diastereomer pairs.

Patent Claims for Following Convention States: AT, ES

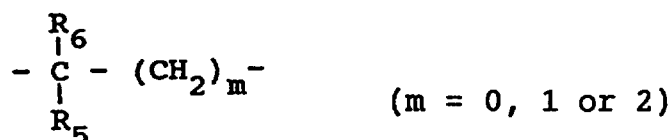
1. Use of compounds of the formula I



in which

Aryl: a phenyl residue unsubstituted or one- to three-fold substituted by C₁-C₅-alkyl, C₁-C₅-alkoxy, C₁-C₅-alkyl-SO_n (n = 0, 1 or 2), halogen, NO₂, CF₃, CN, CH₃OCH₂, (CH₃)₂NCH₂, COO-alkyl, CONH₂ or phenyl, a 1- or 2-naphthyl, an optionally chlorine-substituted 2-, 3- or 4-pyridyl, a pyrimidyl or quinolyl residue,

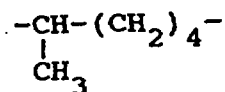
Q:



R₁: H, C₁-C₅-alkyl, allyl,

R₂ and

R₃: H, C₁-C₆-alkyl (which can also contain an O or S atom in the chain), C₃-C₇-cycloalkyl, CH₂-COO-(C₁-C₅-alkyl), phenyl, R₂ and R₃ together also mean -(CH₂)₄-, -(CH₂)₅-



R₄: CN, CONH₂,

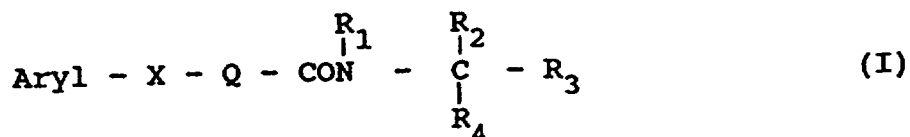
R₅: H, CH₃, C₂H₅

R₆: H, CH₃,

X: O or S,

optionally in the form of racemates or mixtures of the optical isomers or in the form of the pure enantiomers or diastereomers, for the control of Piricularia on rice.

2. Process for the control of Piricularia on rice, which involves the treatment of the rice plants with a compound of the formula



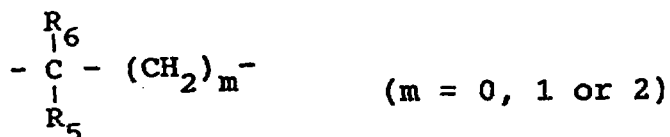
in which

Aryl: a phenyl residue unsubstituted or one- to three-fold substituted by C₁-C₅-alkyl, C₁-C₅-alkoxy, C₁-C₅-alkyl-SO_n (n = 0, 1 or 2), halogen, NO₂, CF₃, CN, CH₃OCH₂, (CH₃)₂NCH₂, COO-alkyl, CONH₂ or phenyl, a 1- or 2-naphthyl, an optionally chlorine-



substituted 2-, 3- or 4-pyridyl, a pyrimidyl or quinolyl residue,

Q:



R₁: H, C₁-C₅-alkyl, allyl,

R₂ and

R₃: H, C₁-C₆-alkyl (which can also contain an O or S atom in the chain),
C₃-C₇-cycloalkyl,
CH₂-COO-(C₁-C₅-alkyl), phenyl,
R₂ and R₃ together also mean -(CH₂)₄-,
-(CH₂)₅-,
-CH-(CH₂)₄-
|
CH₃

R₄: CN, CONH₂,

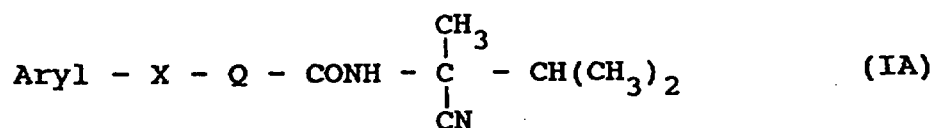
R₅: H, CH₃, C₂H₅

R₆: H, CH₃,

X: O or S,

optionally in the form of racemates or mixtures of the optical isomers or in the form of the pure enantiomers or diastereomers.

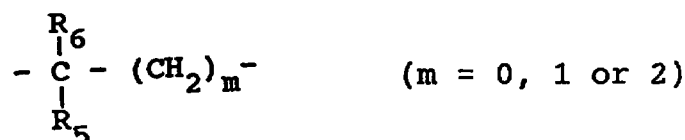
3. Process for the preparation of compounds of the formula



in which

Aryl: a phenyl residue unsubstituted or one- to three-fold substituted by C₁-C₅-alkyl, C₁-C₅-alkoxy, C₁-C₅-alkyl-SO_n (n = 0, 1 or 2), halogen, NO₂, CF₃, CN, CH₃OCH₂, (CH₃)₂NCH₂, COO-alkyl, CONH₂ or phenyl, a 1- or 2-naphthyl, an optionally chlorine-substituted 2-, 3- or 4-pyridyl, a pyrimidyl or quinolyl residue,

Q:



R₅: H, CH₃, C₂H₅

R₆: H, CH₃

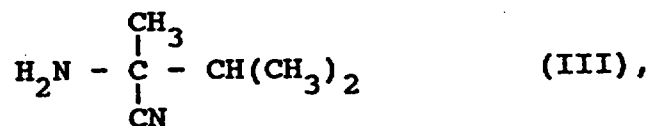
X: O or S,

optionally in the form of racemates or mixtures of the optical isomers or in the form of the pure enantiomers or diastereomers by known methods, characterised in that

a) a compound of the formula



where aryl, X and Q have the above meaning and Y is a leaving group, is reacted with a compound of the formula

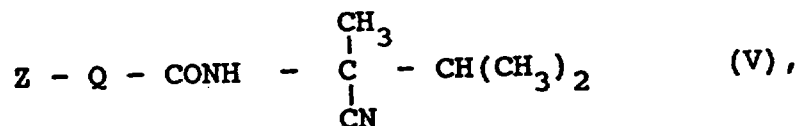


or that

b) a compound of the formula



where aryl and X have the above meaning, and M means hydrogen or an alkali metal cation, is reacted with a compound of the formula



in which Q has the above meaning and Z means halogen or an arylsulphonyloxy group

and that if desired mixtures of enantiomers present are separated by normal methods into the individual enantiomers or into diastereomer pairs.

4. Process according to Claim 3, wherein aryl is



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4-chlorophenyl, 4-chloro-2-methylphenyl, 2,4-, 3,4-
or 3,5-dichlorophenyl.

5. Process according to Claim 3 or 4, wherein X means O.
6. Process according to Claim 3, 4 or 5, wherein Q means $\text{CH}(\text{CH}_3)$.
7. Process according to Claim 3, 4, 5 or 6, wherein the compound of the formula IA is N-[2-cyano-3-methylbutyl(2)]-2-(4-chloro-2-methylphenoxy)-propionamide.
8. Process for the preparation of fungicidal agents, characterised by a compound of the formula IA, as defined in one of the Claims 3 to 7, optionally in the form of racemates or mixtures of the optical isomers or in the form of the pure enantiomers or diastereomers, combined with the normal additives and/or carrier substances.