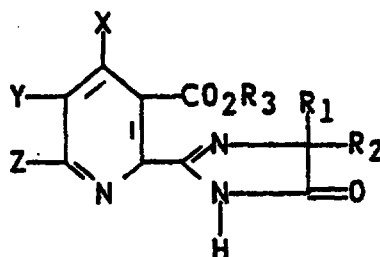


Description

BACKGROUND OF THE DISCLOSURE

Herbicidal imidazolin-2-yl pyridine and quinolinecarboxylic acids, esters and salts of formula I below, methods for their preparation and use are described in European Patent Application EP-A-41623 published December 16, 1981 and, US-A-4647301, filed June 4, 1984



wherein

X is H, halogen, methyl or hydroxyl;

Y and Z are each hydrogen, halogen, C₁-C₆ alkyl, hydroxyloweralkyl, C₁-C₆ alkoxy, C₁-C₄ alkylthio, phenoxy, C₁-C₄ haloalkyl, nitro, cyano, C₁-C₄ alkylamino, diloweralkylamino or C₁-C₄ alkylsulfonyl group, or phenyl optionally substituted with one C₁-C₄ alkyl, C₁-C₄ alkoxy or halogen, difluoromethoxy, trifluoromethoxy, 1,1,2,2-tetrafluoroethoxy, C₃-C₈ straight or branched alkenyloxy optionally substituted with one to three halogens, or C₃-C₈ straight or branched alkynyloxy optionally substituted with one to three halogens;

and when taken together, Y and Z may form a ring which may optionally be substituted, in which YZ are represented by $-(CH_2)_n-$, where n is an integer of 3 or 4, or $(CH)_4$;

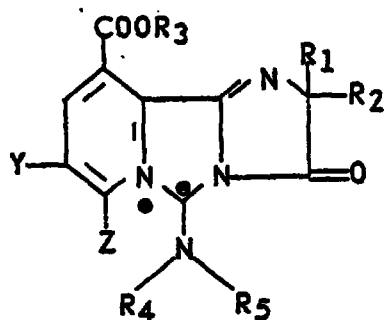
R₁ is C₁-C₄ alkyl;

R₂ is C₁-C₄ alkyl or C₃-C₆ cycloalkyl; and when R₁ and R₂ are taken together with the carbon to which they are attached they may represent C₃-C₆ cycloalkyl optionally substituted with methyl;

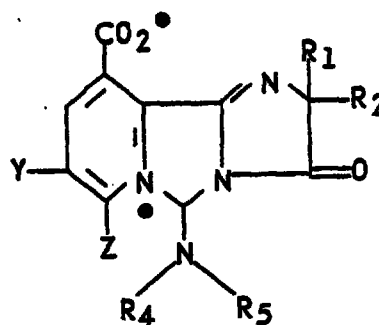
R₃ is hydrogen or COOR₃ represents a salt or ester of the acid.

SUMMARY OF THE INVENTION

The present invention relates to novel herbicidal (2-imidazolin-2-yl)pyridine and quinolinecarboxylic acid and ester inner salts and ylides, represented by formula II and III below



II



III

wherein

Y and Z are each hydrogen, or C₁-C₆ alkyl, and when taken together, Y and Z may form a ring, in which YZ are represented by $-(CH_2)_n-$, where n is an integer of 3 or 4, or $-(CH)_4$;

R₁ is C₁-C₄ alkyl;

R₂ is C₁-C₄ alkyl or C₃-C₆ cycloalkyl; and when R₁ and R₂ are taken together with the carbon to which they are attached they may represent C₃-C₆ cycloalkyl optionally

substituted with methyl;
 R_3 is H or COOR_3 represents an ester of the acid;
 R_4 and R_5 are each $\text{C}_1\text{-C}_4$ alkyl or phenyl or when taken together, may form a C_5 or C_6 cycloalkyl;
 and when R_1 and R_2 are not the same the optical isomers thereof.

5 A preferred group of Formula II and Formula III compounds are those wherein

R_1 is $\text{C}_1\text{-C}_4$ alkyl;
 R_2 is $\text{C}_1\text{-C}_4$ alkyl;
 R_3 is hydrogen, methyl or benzyl;
 R_4 is $\text{C}_1\text{-C}_4$ alkyl;
 10 R_5 is $\text{C}_1\text{-C}_4$ alkyl or phenyl;

and when R_4 and R_5 are taken together, they may represent $\text{C}_5\text{-C}_6$ cycloalkyl;

Y is hydrogen or $\text{C}_1\text{-C}_4$ loweralkyl;
 Z is hydrogen;

and when taken together Y and Z may form a ring represented by $-(\text{CH}_2)_4-$ or $-(\text{CH})_4-$.

15 A most preferred group of Formula II and Formula III compounds are those wherein

R_1 is methyl; and
 R_2 is isopropyl.

The novel compounds of the invention are conveniently prepared by the reaction of a Formula I
 imidazolin-2-yl pyridine or quinolinecarboxylic acid ester or a Formula IV carbamoyl pyridine or
 20 quinolinecarboxylic acid ester from which it may be derived with an approximately equimolar amount of a
 Vilsmeier reagent which is prepared by the reaction of a formamide of Formula V with a chlorinating agent
 such as phosgene, thionylchloride or POCl_3 , treatment of the resulting formula II compound with alcoholic
 base and subsequent acidification yields compounds of formula III as illustrated in Flow Diagram I below.

The reaction is normally conducted in the presence of a chlorinated hydrocarbon solvent such as
 25 methylene chloride, dichloroethane chloroform or the like at ambient temperatures for a period of time
 sufficient to essentially complete the reaction.

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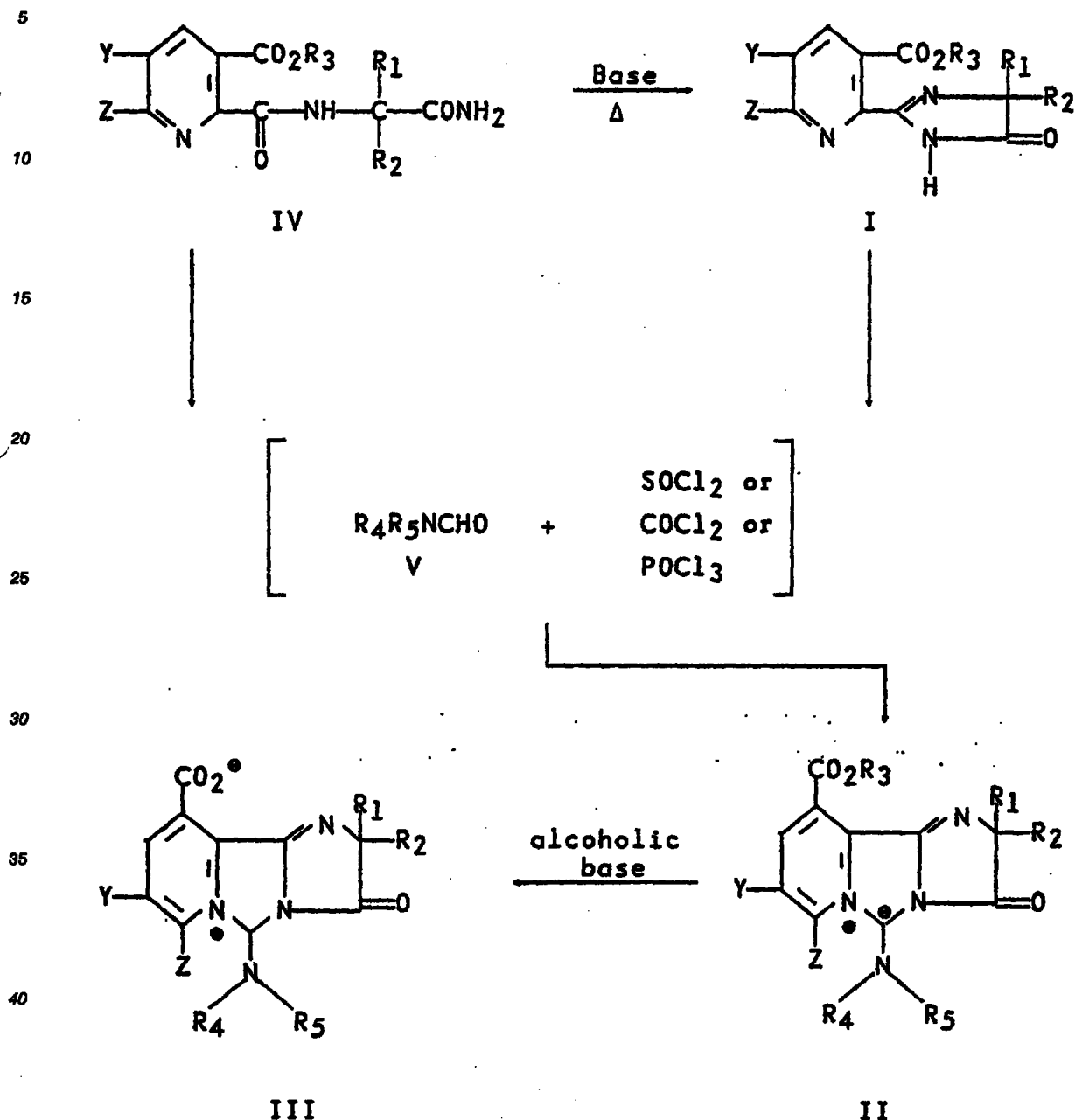
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FLOW DIAGRAM I



wherein X, Y, Z, R₁, R₂, R₃, R₄ and R₅ are as defined for Formula II and Formula III above.

The Formula IV carbamoyl and Formula I (imidazolin-2-yl)pyridine and quinolinecarboxylic acids and esters suitable for use as intermediates for the preparation of the Formula II and Formula III compounds of the present invention may be prepared by a variety of methods which are described in European Patent 0 041,623 issued Aug. 28, 1985 and United States Letters Patent, Numbers 4,467,301 and 4,638,068.

The novel formula II and III (2-imidazolin-2-yl)pyridine and quinolinecarboxylic acid inner salts and ylides of the present invention are exceedingly effective herbicidal agents useful for the control of an exceptionally wide variety of herbaceous and woody annual and perennial monocotyledonous and dicotyledonous plants. Moreover, these compounds are herbicidally effective for controlling weeds indigenous to both dry land and wet land areas. They are also useful as aquatic herbicides and are unique in their effectiveness in controlling the above-said plants when applied to the foliage thereof or to soil or water containing seeds or other propagating organs of said plants such as tubers, rhizomes or stolons, at rates of

from about 0.016 to 4.0 kg/ha, and preferably at rates from about 0.032 to 2.0 kg/ha.

It is of course, obvious that the rates of application above the 4.0 kg/ha level can also be used to effectively kill undesirable plant species; however, rates of application of toxicant above the level necessary to kill the undesirable plants should be avoided since application of excessive amounts of toxicant is costly and serves no useful function in the environment.

Among the plants which may be controlled with the compounds of this invention are: Elatine triandra, Sagittaria pygmaea, Scirpus hotarui, Cyperus serotinus, Eclipta alba, Cyperus difformis, Rotala indica, Lindernia pyridonoria, Echinochloa crus-galli, Digitaria sanguinalis, Setaria viridis, Cyperus rotundus, Convolvulus arvensis, Agropyron repens, Datura stramonium, Alopecurus myosuroides, Ipomoea spp., Sida spinosa, Ambrosia artemisiifolia, Eichornia crassipes, Xanthium pensylvanicum, Sesbania exaltata, Avena fatua, Abutilon theophrasti, Bromus tectorum, Sorghum halepense, Lolium spp., Panicum dichotomiflorum, Matricaria spp., Amaranthus retroflexus, Cirsium arvense and Rumex japonicus.

It has been found that the Formula II and III (2-imidazolin-2-yl)pyridine and quinoline compounds are generally selective herbicides, particularly effective for controlling undesirable weeds in the presence of leguminous crops such as soybeans, and cereal crops such as wheat, barley, oats and rye. However, certain compounds are less selective than others in this series.

It has also been found that several of the Formula II and Formula III compounds are effective as antilodging agents in cereal crops when applied at rates of application between about 0.016 to 4.0 kg hectare. At rates of application not exceeding about 0.010 kg per hectare, it has also been found that certain of these compounds are effective for increasing branching of leguminous crops and tillering of cereal crops.

Those Formula II and III compounds which are water soluble, can simply be dispersed in water and applied as a dilute aqueous spray to the foliage of plants or to soil containing propagating organs thereof. These salts also lend themselves to formulation as flowable concentrates.

The compounds also lend themselves to formulation as emulsifiable concentrates, flow concentrates, wettable powders, granular formulation and the like, thus providing a wide range of formulation options for specific purposes.

The formula II and III (2-imidazolin-2-yl)pyridine and quinoline compounds can also be formulated as wettable powders, flow concentrates, granular formulations and the like.

Wettable powders can be prepared by grinding together about 20% to 45% by weight of a finely divided carrier such as kaolin, bentonite, diatomaceous earth, attapulgite, or the like, 45% to 80% by weight of the active compound, 2% to 5% by weight of a dispersing agent such as sodium lignosulfonate, and 2% to 5% by weight of a nonionic surfactant, such as octylphenoxy polyethoxy ethanol, nonylphenoxy polyethoxy ethanol or the like.

A typical flowable liquid can be prepared by admixing about 40% by weight of the active ingredient with about 2% by weight of a gelling agent such as bentonite, 3% by weight of a dispersing agent such as sodium lignosulfonate, 1% by weight of polyethylene glycol and 54% by weight of water.

A typical emulsifiable concentrate can be prepared by dissolving about 5% to 25% by weight of the active ingredient in about 65% to 90% by weight of N-methylpyrrolidone, isophorone, butyl cellosolve, methylacetate or the like and dispersing therein about 5% to 10% by weight of a nonionic surfactant such as an alkylphenoxy polyethoxy alcohol. This concentrate is dispersed in water for application as a liquid spray.

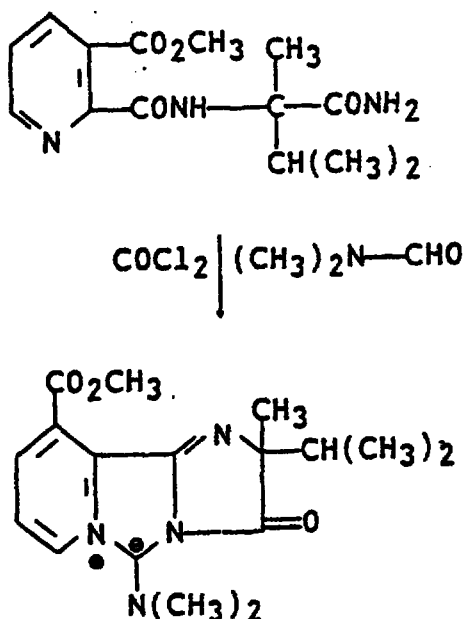
When the compounds of the invention are to be used as herbicides where soil treatments are involved, the compounds may be prepared and applied as granular products. Preparation of the granular product can be achieved by dissolving the active compound in a solvent such as methylene chloride, N-methylpyrrolidone or the like and spraying the thus prepared solution on a granular carrier such as corncob grits, sand, attapulgite, kaolin or the like.

The granular product thus prepared generally comprises about 3% to 20% by weight of the active ingredient and about 97% to 80% by weight of the granular carrier.

In order to facilitate a further understanding of the invention, the following examples are presented primarily for the purpose of illustrating certain more specific details thereof. Unless otherwise noted, all parts are by weight.

EXAMPLE 1

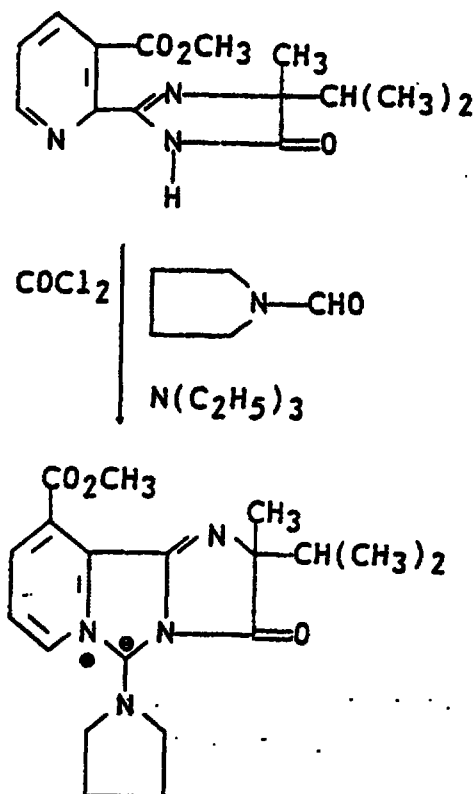
Preparation of methyl 10-carboxy-5-(dimethylamino)-2,3-
dihydro-2-isopropyl-2-methyl-3-oxo-5H-imidazo[2',1':4,3]-
imidazo[1,5-a]pyridin-6-ium-5-ylide



A 12.5% solution of phosgene in benzene (16.5 mL) is added dropwise to a stirred methylene chloride solution (125 mL) of N,N-dimethylformamide (1.18 g). After stirring the resulting precipitate for 45 minutes, solid methyl 2-[(1-carbamoyl-1,2-dimethylpropyl)carbamoyl]nicotinate (5.0 g) is added in portions over a ten minute period and the resulting solution is stirred at ambient temperature overnight. The reaction mixture is washed with a saturated aqueous sodium bicarbonate solution and the aqueous layer separated and extracted with methylene chloride. The organic phases are combined, dried and the solvent removed under reduced pressure. The resulting residue is triturated with diethyl ether to give 2.38 g of the crude title product, which on recrystallization from a methylene chloride-hexane mixture has mp 193-195°C (dec).

EXAMPLE 2

Preparation of methyl 10-carboxy-2,3-dihydro-2-isopropyl-2-methyl-3-oxo-5-(1-pyrrolidinyl)-5H-imidazo[2',1':4,3]-imidazo[1,5-a]pyridin-6-ium-5-ylide

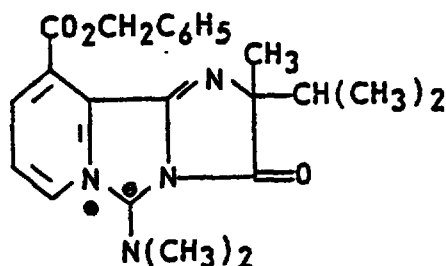
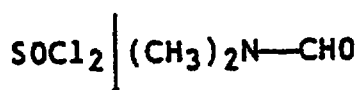
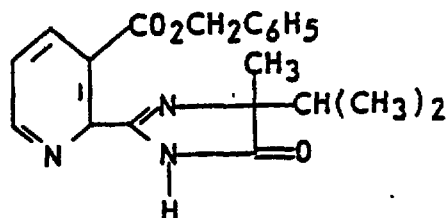


A solution of phosgene in toluene (5.7 mL, 12.5% phosgene, 0.0073 mol) is added dropwise to a stirred solution of pyrrolidine-1-carboxaldehyde (0.76 mL, 0.008 mol) in dry methylene chloride (20 mL) and the resulting mixture allowed to stir for one hour. A methylene chloride (20 mL) solution containing methyl 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinate (2.0 g) and triethylamine (1.0 mL) is added over a two minute period and the reaction mixture is then allowed to stand at ambient temperature overnight. Water (50 mL) is added and the mixture allowed to stir for ten minutes. The aqueous phase is separated and the pH adjusted to 5 to 6 with a saturated sodium bicarbonate solution before extracting with methylene chloride. The pH of the separated aqueous phase is adjusted to 8 with saturated sodium bicarbonate before extracting with additional methylene chloride. The organic extracts are combined, dried and concentrated under reduced pressure to give 1.92 g of the title product which after recrystallization from a methylene chloride-hexane mixture has mp 184-185°C(dec).

Elemental analysis indicates the product is obtained containing 0.2 H₂O.

EXAMPLE 3-10

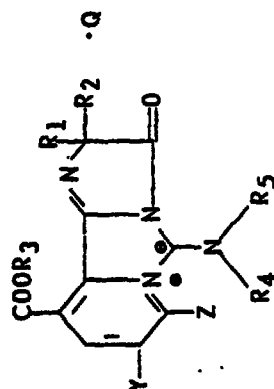
Preparation of benzyl 10-carboxy-5-(dimethylamino)-2,3-
dihydro-2-isopropyl-2-methyl-3-oxo-5H-imidazo[2',1':4,3]-
imidazo[1,5-a]pyridin-6-ium-5-ylide



Thionyl chloride (7 mL, 0.096 mol) is added to a stirred suspension of benzyl 2-(4-isopropyl-4-methyl-5-oxo-2-yl)nicotinate (2.5 g, 0.0071 mol) in chloroform (4 mL). After stirring the mixture for five minutes, N,N-dimethylformamide (1.51 g, 0.021 mol) is added and stirring is continued for three hours. The reaction mixture is concentrated under reduced pressure and the residue is treated with ice. The pH of the aqueous mixture is adjusted to 8 with dilute ammonium hydroxide and the basic solution extracted with several portions of diethyl ether. The combined organic extracts are washed with water and the aqueous washes are extracted with methylene chloride. The organic extracts are combined, dried and concentrated in vacuo to afford 2.91 g of the title product, which upon recrystallization from an acetone-ether mixture has mp 166°C.

Utilizing the above procedure and substituting the appropriate formamide and (imidazolin-2-yl)pyridine or quinolinecarboxylic acid ester yields the formula II products listed in Table I below.

TABLE I



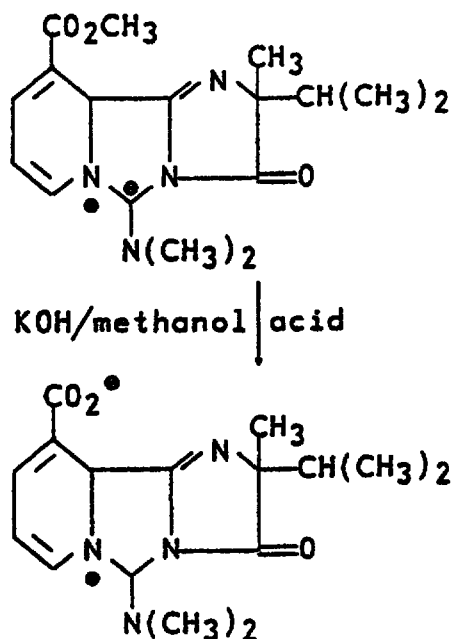
II

Example	R ₁	R ₂	R ₃	R ₄	R ₅	Y	Z	Q	mp°C
4	CH ₃	iPr	CH ₃	C ₂ H ₅	C ₂ H ₅	H	H	-	208 - 210
5	CH ₃	iPr	CH ₃	-(CH ₂) ₅ -	-	H	H	3/4 H ₂ O	220 - 226 (dec)
6	CH ₃	iPr	CH ₃	CH ₃	CH ₃	-CH=CH-CH=CH-	H	-	204 - 206
7	CH ₃	iPr	CH ₃	CH ₃	CH ₃	CH ₃	H	-	222 - 224
8	CH ₃	iPr	CH ₃	CH ₃	C ₆ H ₅	H	H	H ₂ O	120 - 161 (dec)
9	CH ₃	iPr	CH ₃	CH ₃	CH ₃	C ₂ H ₅	H	.07CH ₂ Cl	195 - 200 (dec)
10	CH ₃	iPr	CH ₃	CH ₃	CH ₃	H	H	-	120 - 132 (dec)

(R-isomer)

EXAMPLE 11

Preparation of 10-carboxy-5-(dimethylamino)-2-dihydro-2-
isopropyl-2-methyl-3-oxo-5H-imidazo[2'1':4,3]imidazo-
[1,5-a]pyridin-6-ium hydroxide inner salt



A stirred mixture of the methyl carboxylate ylide (3.5 g, 0.016 mol) and potassium hydroxide (0.84 g, 0.0127 mol) in methanol (50 mL) is heated at 40°C for two hours. After cooling to ambient temperature the mixture is acidified to pH 4 with dilute methanolic sulfuric acid and then filtered. The filtrate is concentrated in vacuo and the residue is dissolved in methylene chloride. The organic solution is filtered through diatomaceous earth and partially concentrated in vacuo to give a small amount of solid having mp 220°C, which is collected by filtration. Further concentration of the solution yields the title product as the monohydrate (1.58 g, 44%) which after recrystallization from acetone/methylene chloride/hexanes mixture has mp 178-183°C. Elemental analysis indicates the product is obtained containing 1.0 H₂O.

Utilizing the above procedure and substituting the appropriate carboxylate ylide yields the formula I compounds listed in Table II below.

EXAMPLE 19**Postemergence herbicidal evaluation of test compounds**

The postemergence herbicidal activity of the compounds of the present invention is demonstrated by the following tests, wherein a variety of monocotyledonous and dicotyledonous plants are treated with test compounds dispersed in aqueous acetone mixtures. In the tests, seedling plants are grown in jiffy flats for about two weeks. The test compounds are dispersed in 50/50 acetone/water mixtures containing 0.5% TWEEN® 20, a polyoxyethylene sorbitan monolaurate surfactant of Atlas Chemical Industries, in sufficient quantity to provide the equivalent of about .016 kg to 10 kg per hectare of active compound when applied to the plants through a spray nozzle operating at 40 psig for a pre-determined time. After spraying, the plants are placed on greenhouse benches and are cared for in the usual manner, commensurate with conventional greenhouse practices. From four to five weeks after treatment, the seedling plants are examined and rated according to the rating system provided below. The data obtained are recorded in Table III below.

Rating System	% Difference in Growth from the Check
0 - No effect	0
1 - Possible effect	1 - 10
2 - Slight effect	11 - 25
3 - Moderate effect	26 - 40
5 - Definite injury	41 - 60
6 - Herbicidal effect	61 - 75
7 - Good herbicidal effect	76 - 90
8 - Approaching complete kill	91 - 99
9 - Complete kill	100
4 - Abnormal growth, that is, a definite physiological malformation but with an over-all effect less than a 5 on the rating scale.	

In most cases the data are for a single test, but in several instances, they are average values obtained from more than one test.

Plant Species Used	
Barnyardgrass	(<u>Echinochloa crusgalli</u>)
Green foxtail	(<u>Setaria viridis</u>)
Purple Nutsedge	(<u>Cyperus rotundus L.</u>)
Wild Oats	(<u>Avena fatua</u>)
Quackgrass	(<u>Agropyron repens</u>)
Field Bindweed	(<u>Convolvulus arvensis L.</u>)
Cocklebur	(<u>Xanthium pensylvanicum</u>)
Morningglory	(<u>Ipomoea purpurea</u>)
Ragweed	(<u>Ambrosia artemisiifolia</u>)
Velvetleaf	(<u>Abutilon theophrasti</u>)

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TABLE III

POST-EMERGENCE TESTS -- RATES IN KG/HA

Example Number

	RATE	BARNY ARDGR	LARGE CRAB	GREEN FOX	P NUT SEGE	MILD OATS	QUACK GRASS	FLD B INDAO	COCKL EDUR	MRHSL RY SP	NILD MUSTO	RAGNE ED	PHIKY SIDA	VELVE TLEAF
1	8.000	9.0	9.0	9.0	9.0	9.0	9.0	1.0	9.0	9.0	9.0	9.0	9.0	9.0
	1.000							7.0	9.0	8.0	9.0	3.0	9.0	9.0
	.500							7.0	7.0	8.0		3.0		9.0
	.250							7.0	6.0	7.0		2.0		9.0
	.125							6.0		7.0		0.0		9.0
2	.063							1.0	8.0	6.0		0.0		6.0
												0.0		2.0
3	5.000	9.0	9.0	9.0	9.0	9.0	9.0	9.0		8.0	9.0	9.0	9.0	8.0
	1.000							6.0		7.0		8.0		8.0
	.500							5.0		7.0		6.0		8.0
	.250							5.0		7.0		4.0		7.0
	.125							5.0		3.0		1.0		3.0
11	1.000	9.0			8.0	9.0	9.0	9.0		9.0		9.0		9.0
	.500				9.0	9.0	9.0	9.0		9.0		7.0		9.0
	.250				2.0	9.0	9.0	9.0		9.0		2.0		9.0
	.125				1.0	8.0	6.0	8.0		9.0		2.0		9.0
	.063				0.0	8.0	4.0	6.0		8.0		0.0		6.0
11	1.000	9.0			8.0	9.0	9.0	9.0		9.0		9.0		9.0
	.500				8.0	9.0	9.0	9.0		9.0		9.0		9.0
	.250				4.0	9.0	9.0	9.0		8.0		7.0		9.0
	.125				2.0	9.0	6.0	9.0		8.0		1.0		9.0
	.063				0.0	6.0	6.0	7.0		8.0		0.0		7.0
11	.032				0.0	6.0	6.0	7.0		6.0		0.0		4.0

TABLE III (Continued)

Example Number	POST-EMERGENCE TESTS -- RATES IN KG/HA															
	RATE	BARNY ANDGR	LARGE CRAB	GREEN FOX	P NJT SEDE	WILD OATS	QUACK GRASS	FLO B INDND	COCKL EBUR	FRNGL RY SP	MILD MUSTD	RAGNE ED	PRIKY SIDA	VELVE TLEAF		
4	1.000	8.5	9.0	9.0	6.0	8.0	6.5	7.5		9.0	9.0	5.5		8.0		
	.500	7.0	8.0	9.0	6.0	7.0	7.0	7.5		9.0	7.0	2.5		6.5		
	.250	6.0*	4.0	5.0	0.0	6.5	3.5*	6.0		7.0	7.0	0.0		5.0*		
	.125	3.0	4.0	5.0	0.0	3.0*	3.5*	2.0		7.0	5.0	0.0		3.5*		
5	1.000	9.0			6.0	9.0	7.0	9.0		9.0		9.0		9.0		
	.500	9.0			2.0	9.0	8.0	9.0		7.0		6.0		9.0		
	.250	7.0			0.0	9.0	8.0	4.0		9.0		2.0		9.0		
	.125	7.0			0.0	6.0	7.0	4.0		7.0		0.0		7.0		
12	.063	2.0			0.0	2.0	4.0	4.0		7.0		0.0		6.0		
	1.000	9.0			9.0	9.0	9.0	8.0		8.0		8.0		8.0		
	.500	9.0			8.0	9.0	7.0	7.0		8.0		4.0		8.0		
	.250	9.0			7.0	9.0		7.0		8.0		0.0		6.0		
6	.125	8.0			5.0	9.0	7.0	5.0		6.0		0.0		2.0		
	.063	8.0			2.0	9.0	7.0	4.0		7.0		0.0		2.0		
	1.000	7.0			8.0	8.0	2.0	0.0		8.0		0.0		0.0		
	.500	6.0			8.0	4.0	8.0	0.0		8.0		0.0		0.0		
	.250	2.0			8.0	2.0	8.0	0.0		8.0		0.0		0.0		

TABLE III (Continued)

Example Number	POST-EMERGENCE TESTS -- RATES IN KG/HA													
	RATE	BARNY ARGR	LARGE CRAB	GREEN FOX	P NUT SEDGE	WILD OATS	GRASS	QUACK	FLO B INDI	COCKL EBUR	HRSL RY SP	WILD MUSTO	MAGHE ED	PRIKY SIDA
7	1.000	9.0			8.0	9.0	0.0	0.0	8.0		8.0		4.0	
	.500	8.0			8.0	9.0	0.0	0.0	7.0		7.0		4.0	
	.250	8.0			8.0	9.0	0.0	0.0	6.0		6.0		0.0	
	.125	3.0			2.0	6.0	8.0	8.0	4.0		3.0		0.0	
	.063	1.0			1.0	3.0	0.0	0.0	2.0		1.0		0.0	
13	1.000	9.0			9.0	9.0	4.0	4.0	9.0		8.0		9.0	
	.500	9.0			9.0	9.0	1.0	1.0	9.0		9.0		6.0	
	.250	9.0			9.0	9.0	0.0	0.0	6.0		7.0		6.0	
	.125	7.0			6.0	9.0	0.0	0.0	7.0		7.0		2.0	
	.063	5.0			7.0	4.0	0.0	0.0	4.0		3.0		1.0	
14	1.000	8.0			9.0	9.0	9.0	9.0	7.0		9.0		8.0	
	.500	8.0			8.0	9.0	9.0	9.0	7.0		9.0		3.0	
	.250	9.0			7.0	9.0	2.0	2.0	7.0		6.0		1.0	
	.125	8.0			4.0	9.0	1.0	1.0	4.0		4.0		0.0	
8	1.000	6.0			4.0	9.0	6.0	6.0	7.0		4.0		0.0	
	.500	2.0			2.0	9.0	6.0	6.0	6.0		2.0		0.0	
	.250	1.0			1.0	6.0	2.0	2.0	2.0		2.0		0.0	

TABLE III (Continued)

Example Number	RATE	POST-EMERGENCE TESTS -- RATES IN KG/HA													
		BARNY ARDGR	LARGE CRAB	GREEN FOX	P NUT SEGE	WILD OATS	QUACK GRASS	FLD B INDIO	COCKL EBUR	WRNGL RY SP	WILD HJSTO	MAGNE ED	PRIKY SIDA	VELVE TLEAF	
15	1.000	8.0			4.0	9.0	8.0	4.0		0.0		7.0		4.0	
	.500	8.0			1.0	9.0	8.0	2.0		0.0		7.0		2.0	
	.250	3.0			0.0	9.0	2.0	1.0		0.0		3.0		1.0	
	.125	1.0			0.0	6.0	1.0	0.0		0.0		1.0		0.0	
9	1.000	8.0			6.0	8.0	2.0	7.0		0.0		8.0		7.0	
	.500	6.0			4.0	2.0	1.0	7.0		0.0		4.0		6.0	
	.250	2.0			1.0	2.0	0.0	2.0		4.0		0.0		2.0	
16	1.000	9.0			8.0	9.0	8.0	9.0		9.0		9.0		8.0	
	.500	9.0			8.0	9.0	7.0	8.0		9.0		8.0		8.0	
	.250	8.0			7.0	4.0	4.0	9.0		9.0		3.0		8.0	
	.125	8.0			2.0	2.0	2.0	5.0		8.0		2.0		2.0	
10	1.000	9.0			8.0	9.0	9.0	9.0		9.0		4.0		9.0	
	.500	9.0			9.0	9.0	9.0	7.0		9.0		2.0		9.0	
	.250	8.0			6.0	8.0	9.0	7.0		9.0		8.0		9.0	
	.125	6.0			5.0	6.0	7.0	6.0		8.0		0.0		8.0	
	.063	3.0			0.0	4.0	7.0	5.0		6.0		0.0		6.0	

TABLE III (Continued)

Example Number	RATE	POST-EMERGENCE TESTS -- RATES IN KG/HA												
		BARNY ARDGR	LARGE CRAB	GREEN FOX	P NUT SEDE	WILD OATS	QUACK GRASS	FLD B INDID	COCKL EBUR	FRINGL RY SP	WILD HUSTO	RAGME ED	PRIKY SIDA	VELVE TLEAF
17	1.000	9.0			9.0	9.0	9.0	8.0		9.0		6.0		9.0
	.500	9.0			7.0	9.0	9.0	7.0		9.0		2.0		8.0
	.250	8.0			7.0	9.0	9.0	7.0		7.0		0.0		7.0
	.125	8.0			2.0	8.0	9.0	4.0		7.0		0.0		3.0
	.063	4.0			2.0	6.0	6.0	0.0		4.0		0.0		1.0
18	1.000	9.0			9.0	9.0	9.0	9.0		9.0		8.0		9.0
	.500	9.0			9.0	9.0	9.0	9.0		9.0		6.0		9.0
	.250	9.0			8.0	9.0	9.0	8.0		9.0		2.0		9.0
	.125	6.0			7.0	9.0	9.0	8.0		9.0		2.0		9.0
	.063	5.0			7.0	7.0	9.0	7.0		8.0		0.0		7.0
	.032	2.0			2.0	5.0	2.0	7.0		7.0		0.0		6.0

EXAMPLE 20**Preemergence herbicidal evaluation of test compounds**

- 5 The preemergence herbicidal activity of the compounds of the present invention is exemplified by the following tests in which the seeds of a variety of monocotyledonous and dicotyledonous plants are separately mixed with potting soil and planted on top of approximately one inch of soil in separate pint cups. After planting, the cups are sprayed with the selected aqueous acetone solution containing test compound in sufficient quantity to provide the equivalent of about 0.016 to 10 kg per hectare of test
10 compound per cup. The treated cups are then placed on greenhouse benches, watered and cared for in accordance with conventional greenhouse procedures. From four to five weeks after treatment, the tests are terminated and each cup is examined and rated according to the rating system set forth above. The herbicidal proficiency of the active ingredients of the present invention is evident from the test results which are recorded in Table IV below. Where more than one test is involved for a given compound, the data are
15 averaged.

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TABLE IV

PRE-EMERGENCE TESTS --- RATES IN KG/Ha

Example Number

RATE	BARNY ARGR	LARGE CRAB	GREEN FOX	P NUT SEGE	WILD OATS	QUACK GRASS	FLO S INDIO	COCKL EBUR	WINGL RY SP	HILD RUSTD	RAGHE ED	PRIKY SIDA	VELVE TLEAF
6.000	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0
.500	6.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0
.250	7.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0
.125	3.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0
.063	1.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0
.032	0.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0
.016	0.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0
5.000	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0
.500	6.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0
.250	6.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0
.125	0.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0
.063	0.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0
.032	0.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0
.016	0.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0
.500	6.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0
.250	0.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0
.125	0.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0

TABLE IV (Continued)

PRE-EMERGENCE TESTS -- RATES IN KG/HA

Example Number	RATE	BARNY ARDCR	LARGE CRAB	GREEN FOX	P SEGE	NUT OATS	WILD OATS	QUACK GRASS	FLO & TIN:ED	COCKL EBUR	HINGL RY SP	WILD MUSTO	RAGHE ED	PRIKY SIDA	VELVE TLEAF
13	.500	0.0			9.0	9.0	9.0	9.0	9.0		0.0		4.0		9.0
	.250	4.0			7.0	5.0	9.0	9.0	9.0		7.0		2.0		0.0
	.125	3.0			7.0	1.0	9.0	2.0	2.0		6.0		1.0		0.0
	.063	0.0			0.0	0.0	0.0	4.0	0.0		2.0		0.0		2.0
	.032	0.0			0.0	0.0	0.0	2.0	0.0		0.0		0.0		0.0
14	.016	0.0			0.0	0.0	0.0	0.0	0.0		0.0		0.0		0.0
	.500	0.0			4.0	0.0	9.0	9.0	9.0		7.0		0.0		9.0
	.250	6.0			2.0	7.0	9.0	3.0	3.0		4.0		4.0		3.0
8	.125	2.0			2.0	3.0	9.0	9.0	0.0		1.0		2.0		3.0
	.500	2.0			6.0	6.0	8.0	8.0	6.0		2.0		0.0		4.0
	.250	2.0			3.0	0.0	4.0	4.0	2.0		1.0		0.0		2.0
15	.125	1.0			1.0	0.0	2.0	2.0	0.0		0.0		0.0		1.0
	.500	4.0			9.0	4.0	9.0	9.0	5.0		5.0		7.0		6.0
	.250	2.0			7.0	2.0	2.0	2.0	1.0				2.0		3.0

TABLE IV (Continued)

Example Number	PRE-EMERGENCE TESTS -- RATES IN KG/HA														
	RATE	BARNY AROGR	LARGE CRAB	GREEN FOX	P SEGE	NUT	WILD OATS	QUACK GRASS	FLO B INDND	COCKL EDUR	HRNGL RY SP	WILD RUSTD	RAGHE ED	PRIKY SIDA	VELVE TLEAF
9	.500	8.0			6.0	8.0	8.0	4.0	8.0		0.0	0.0	0.0		7.0
	.250	2.0			4.0	8.0	8.0	0.0	8.0		0.0	0.0	0.0		3.0
16	.500	7.0			4.0	2.0	7.0	7.0	9.0		0.0	0.0	0.0		8.0
	.250	4.0			4.0	1.0	7.0	7.0	9.0		0.0	0.0	0.0		7.0
	.125	8.0			4.0	0.0	2.0	2.0	9.0		0.0	0.0	0.0		3.0
10	.500	8.0			9.0	9.0	9.0	9.0	9.0		8.0	8.0	2.0		8.0
	.250	5.0			9.0	7.0	9.0	9.0	9.0		8.0	8.0	1.0		8.0
	.125	2.0			8.0	5.0	9.0	9.0	9.0		4.0	4.0	0.0		7.0
	.063	1.0			2.0	3.0	2.0	2.0	2.0		1.0	1.0	0.0		5.0
17	.500	2.0			7.0	2.0	9.0	9.0	9.0		4.0	4.0	0.0		6.0
	.250	0.0			2.0	8.0	9.0	9.0	2.0		1.0	1.0	0.0		2.0
	.125	0.0			1.0	8.0	2.0	2.0	8.0		0.0	0.0	0.0		1.0

TABLE IV (Continued)

Example Number	PRE-EMERGENCE TESTS -- RATES IN KG/HA													
	RATE	DARNY ARDGR	LARGE CRAB	GREEN FOX	P HUT SEDE	WILD OATS	QUACK GRASS	FLO B INDKO	COCKL EBUR	WYNGL RY SP	HILD HJSTO	RAGIE ED	PRIKY SIDA	VELVE TLEAF
18	.500	7.0			9.0	8.0	9.0	9.0		8.0		2.0		8.0
	.250	3.0			6.0	7.0	9.0	9.0		4.0		1.0		8.0
	.125	1.0			2.0	5.0	9.0	9.0		4.0		0.0		7.0
	.063	0.0			2.0	3.0	5.0	9.0		2.0		0.0		4.0

Claims

55 Claims for the contracting States : BE, CH, DE, FR, GB, IT, LI, LU, NL, SE

1. (2-imidazolin-2-yl)pyridine and quinolinecarboxylic acid and ester inner salts and ylides, having the structure

TABLE IV (Continued)

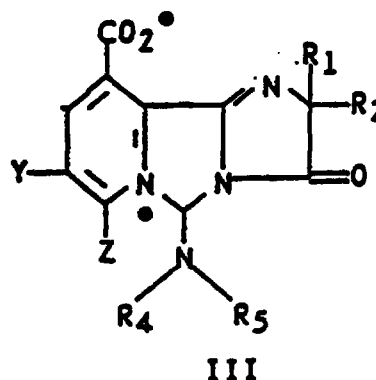
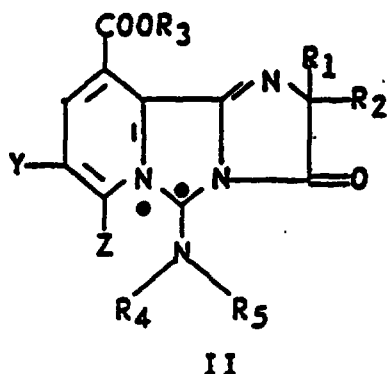
Example Number	PRE-EMERGENCE TESTS --- RATES IN KG/HA													
	RATE	BARNY AROG	LARGE CRAB	GREEN FOX	P NUT SEGE	WILD OATS	QUACK GRASS	FLD B INDO	COCKL EBUR	WINGL RY SP	WILD HJSTO	RAGUE ED	PRIKY SIDA	VELVE TLEAF
18	.500	7.0			9.0	8.0	9.0	9.0		8.0		2.0		8.0
	.250	3.0			8.0	7.0	9.0	9.0		4.0		1.0		8.0
	.125	1.0			2.0	5.0	9.0	9.0		4.0		0.0		7.0
	.063	0.0			2.0	3.0	5.0	9.0		2.0		0.0		4.0

Claims

55 **Claims for the contracting States : BE, CH, DE, FR, GB, IT, LI, LU, NL, SE**

1. (2-imidazolin-2-yl)pyridine and quinolinecarboxylic acid and ester inner salts and ylides, having the structure





wherein

Y and Z are each hydrogen or alkyl C₁-C₆, and when taken together, Y and Z may form a ring, in which YZ are represented by -(CH₂)_n- where n is an integer of 3 or 4, or -(CH)₄-;

R₁ and R₂ are each alkyl C₁-C₄;

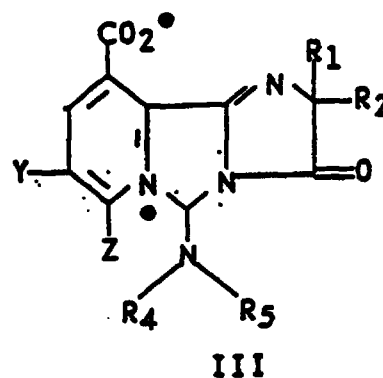
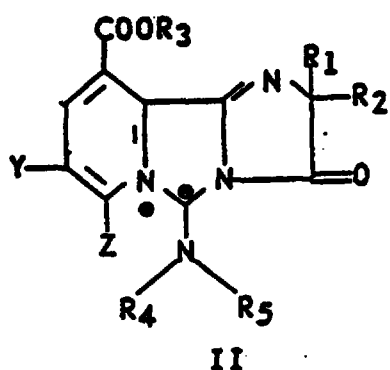
R₃ is H or COOR₃ represents an ester of the acid;

R₄ and R₅ are each C₁-C₄ alkyl or phenyl, or, when taken together, may form a C₅ or C₆ cycloalkyl;

and when R₁ and R₂ are not the same, the optical isomers thereof.

2. A compound according to Claim 1 methyl 10-carboxy-5-(dimethylamino)-2,3-dihydro-2-isopropyl-2-methyl-3-oxo-5H-imidazo[2',1':4,3]-imidazo[1,5-a]pyridin-6-ium-5-ylide and the R isomer thereof.
3. A compound according to Claim 1 methyl 10-carboxy-2,3-dihydro-2-isopropyl-2-methyl-3-oxo-5-(1-pyrrolidinyl)-5H-imidazo[2',1':4,3]-imidazo[1,5-a]pyridin-6-ium-5-ylide and the R isomer thereof.
4. A compound according to Claim 1 benzyl 10-carboxy-5-(dimethylamino)-2,3-dihydro-2-isopropyl-2-methyl-3-oxo-5H-imidazo[2',1':4,3]-imidazo[1,5-a]pyridin-6-ium-5-ylide and the R isomer thereof.
5. A compound according to Claim 1, 10-carboxy-5-(dimethylamino)-2-dihydro-2-isopropyl-2-methyl-3-oxo-5H-imidazo[2',1':4,3]imidazo[1,5-a]pyridin-6-ium hydroxide inner salt and the R isomer thereof.
6. A compound according to Claim 1, 10-carboxy-5-(diethylamino)-2-dihydro-2-isopropyl-2-methyl-3-oxo-5H-imidazo[2',1':4,3]imidazo[1,5-a]pyridin-6-ium hydroxide inner salt and the R isomer thereof.
7. A compound according to Claim 1, 10-carboxy-5-(dimethylamino)-2-dihydro-2-isopropyl-(2,8-dimethyl)-3-oxo-5H-imidazo[2',1':4,3]imidazo[1,5-a]pyridin-6-ium hydroxide inner salt and the R isomer thereof.
8. A method for control of monocotyledonous and dicotyledonous annual, perennial and aquatic plant species comprising: applying to the foliage of said plants or to soil or water containing seeds or other propagating organs thereof, a herbicidally effective amount of a compound having a structure:





wherein Y, Z, R₁, R₂, R₃, R₄ and R₅ are as defined in claim 1.

9. A method according to Claim 8 wherein

- R₁ is C₁-C₄ alkyl;
- R₂ is C₁-C₄ alkyl;
- R₃ is hydrogen, methyl or benzyl;
- R₄ is C₁-C₄ alkyl;
- R₅ is C₁-C₄ alkyl or phenyl;

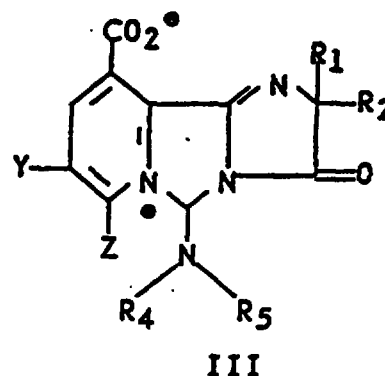
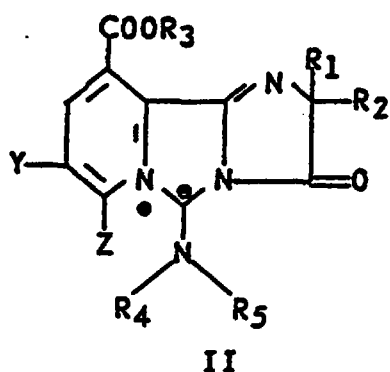
and when R₄ and R₅ are taken together, they may be represented C₅-C₆ cycloalkyl;

Y is hydrogen or C₁-C₄ loweralkyl;

Z is hydrogen;

and when taken together Y and Z may form a ring represented by -(CH₂)₄- or -(CH)₄-.

10. A method for the preparation of (2-imidazolin-2-yl)pyridine and quinolinecarboxylic acid and ester inner salts and ylides, having the structure:

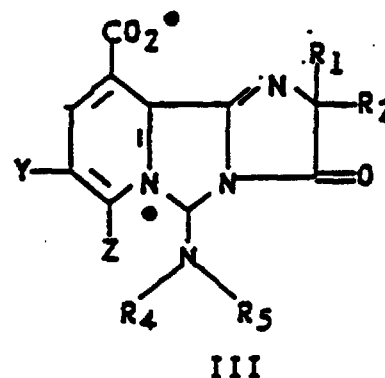
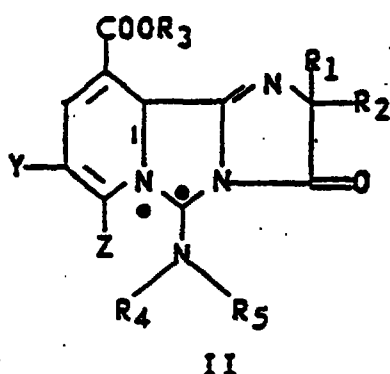


wherein Y, Z, R₁, R₂, R₃, R₄ and R₅ are as defined in claim 1; Comprising reacting an imidazolin-2-yl pyridine or quinolinecarboxylic acid ester or a carbamoylpyridine or quinolinecarboxylic acid ester with an approximately equimolar amount of a Vilsmeier reagent and optionally treating the resulting product with alcoholic base, followed by acidification and isolation of the product.

Claims for the following Contracting States : AT, ES, GR

1. A method for the preparation of (2-imidazolin-2-yl)pyridine and quinolinecarboxylic acid and ester inner salts and ylides, having the structure





wherein

Y and Z are each hydrogen or alkyl C₁-C₆, and when taken together, Y and Z may form a ring, in which YZ are represented by -(CH₂)_n- where n is an integer of 3 or 4, or -(CH)₄-;

R₁ and R₂ are each alkyl C₁-C₄;

R₃ is H or COOR₃ represents an ester of the acid;

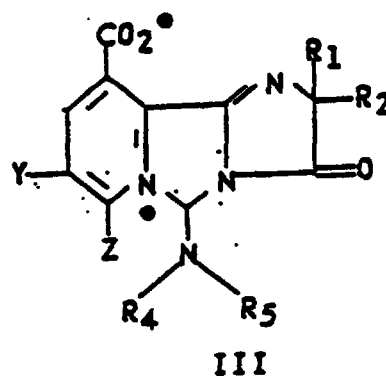
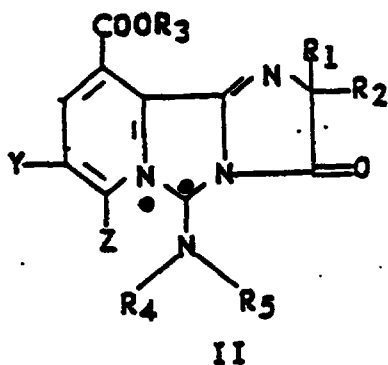
R₄ and R₅ are each C₁-C₄ alkyl or phenyl, or, when taken together, may form a C₅ or C₆ cycloalkyl;

and when R₁ and R₂ are not the same, the optical isomers thereof;

Comprising reacting an imidazolin-2-yl pyridine or quinolinecarboxylic acid ester or a carbamoyl-pyridine or quinolinecarboxylic acid ester with an approximately equimolar amount of a Vilsmeier reagent and optionally treating the resulting product with alcoholic base, followed by acidification and isolation of the product.

2. A method according to Claim 1 for preparing methyl 10-carboxy-5-(dimethylamino)-2,3-dihydro-2-isopropyl-2-methyl-3-oxo-5H-imidazo[2',1':4,3]-imidazo[1,5-a]pyridin-6-ium-5-ylide and the R isomer thereof.
3. A method according to Claim 1 for preparing methyl-10-carboxy-2,3-dihydro-2-isopropyl-2-methyl-3-oxo-5-(1-pyrrolidinyl)-5H-imidazo[2',1':4,3]-imidazo[1,5-a]pyridin-6-ium-5-ylide and the R isomer thereof.
4. A method according to Claim 1 for preparing benzyl 10-carboxy-5-(dimethylamino)-2,3-dihydro-2-isopropyl-2-methyl-3-oxo-5H-imidazo[2',1':4,3]-imidazo[1,5-a]pyridin-6-ium-5-ylide and the R isomer thereof.
5. A method according to Claim 1 for preparing 10-carboxy-5-(dimethylamino)-2-dihydro-2-isopropyl-2-methyl-3-oxo-5H-imidazo[2',1':4,3]-imidazo[1,5-a]pyridin-6-ium hydroxide inner salt and the R isomer thereof.
6. A method according to Claim 1 for preparing 10-carboxy-5-(diethylamino)-2-dihydro-2-isopropyl-2-methyl-3-oxo-5H-imidazo[2',1':4,3]-imidazo[1,5-a]pyridin-6-ium hydroxide inner salt and the R isomer thereof.
7. A method according to Claim 1 for preparing 10-carboxy-5-(dimethylamino)-2-dihydro-2-isopropyl-(2,8-dimethyl)-3-oxo-5H-imidazo[2',1':4,3]-imidazo[1,5-a]pyridin-6-ium hydroxide inner salt and the R isomer thereof.
8. A method for control of monocotyledonous and dicotyledonous annual, perennial and aquatic plant species comprising: applying to the foliage of said plants or to soil or water containing seeds or other propagating organs thereof, a herbicidally effective amount of a compound having a structure:





wherein Y, Z, R₁, R₂, R₃, R₄ and R₅ are as defined in claim 1.

9. A method according to Claim 8 wherein

R₁ is C₁-C₄ alkyl;

R₂ is C₁-C₄ alkyl;

R₃ is hydrogen, methyl or benzyl;

R₄ is C₁-C₄ alkyl;

R₅ is C₁-C₄ alkyl or phenyl;

and when R₄ and R₅ are taken together, they may represent C₅-C₆ cycloalkyl;

Y is hydrogen or C₁-C₄ loweralkyl;

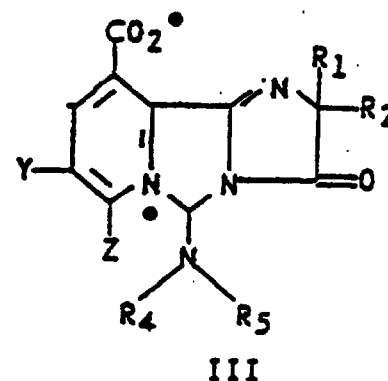
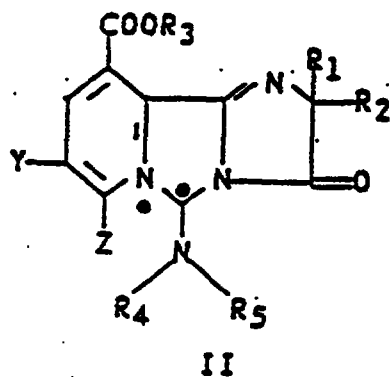
Z is hydrogen;

and when taken together Y and Z may form a ring represented by -(CH₂)₄- or -(CH)₄-.

Patentansprüche

Patentansprüche für folgende Vertragsstaaten : BE, CH, DE, FR, GB, IT, LI, LU, NL, SE

1. Innere (2-Imidazolin-2-yl)pyridin- und Chinolincarbonsäure- und Ester-Salze und -Ylide der Struktur



worin Y und Z jeweils Wasserstoff oder C₁-C₆-Alkyl sind und Y und Z zusammengekommen einen Ring bilden können, in dem YZ durch -(CH₂)_n-, worin n eine ganze Zahl von 3 oder 4 ist, oder durch -(CH)₄- repräsentiert ist;

R₁ und R₂ sind jeweils C₁-C₄-Alkyl;

R₃ ist H oder COOR₃ repräsentiert einen Ester der Säure;

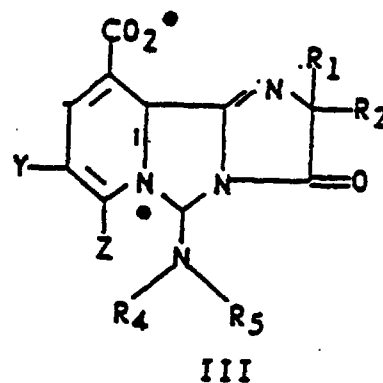
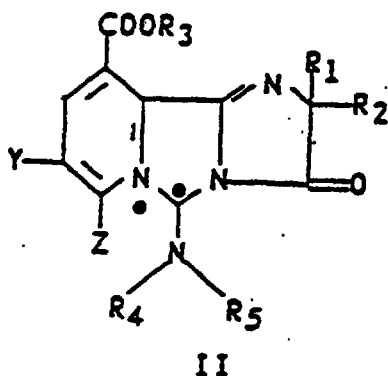
R₄ und R₅ sind jeweils C₁-C₄-Alkyl oder Phenyl oder, zusammengekommen, können sie ein C₅- oder C₆-Cycloalkyl bilden;

und, wenn R₁ und R₂ nicht gleich sind, die optischen Isomere davon.

2. Eine Verbindung nach Anspruch 1, Methyl-10-carboxy-5-(dimethylamino)-2,3-dihydro-2-isopropyl-2-methyl-3-oxo-5H-imidazo[2',1':4,3]-imidazo[1,5-a]pyridin-6-ium-5-ylid und das R-Isomere davon.



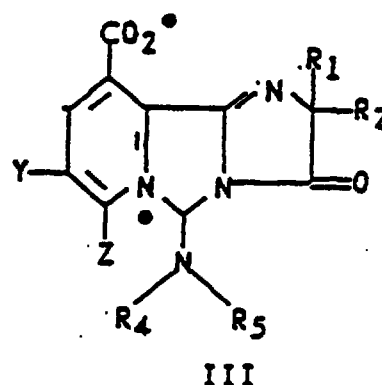
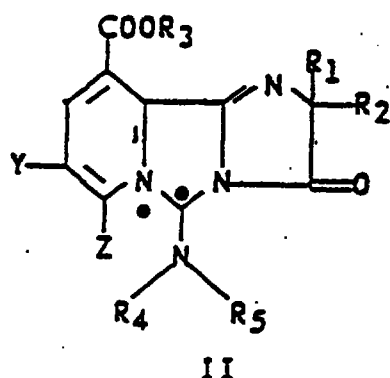
3. Eine Verbindung nach Anspruch 1, Methyl-10-carboxy-2,3-dihydro-2-isopropyl-2-methyl-3-oxo-5-(1-pyrrolidiny)-5H-imidazo[2',1':4,3]-imidazo[1,5-a]pyridin-6-ium-5-ylid und das R-Isomere davon.
4. Eine Verbindung nach Anspruch 1, Benzyl-10-carboxy-5-(dimethylamino)-2,3-dihydro-2-isopropyl-2-methyl-3-oxo-5H-imidazo[2',1':4,3]-imidazo[1,5-a]pyridin-6-ium-5-ylid und das R-Isomere davon.
5. Eine Verbindung nach Anspruch 1, inneres 10-Carboxy-5-(dimethylamino)-2-dihydro-2-isopropyl-2-methyl-3-oxo-5H-imidazo[2',1':4,3]-imidazo[1,5-a]pyridin-6-ium-Hydroxidsalz und das R-Isomere davon.
6. Eine Verbindung nach Anspruch 1, inneres 10-Carboxy-5-(diethylamino)-2-dihydro-2-isopropyl-2-methyl-3-oxo-5H-imidazo[2',1':4,3]-imidazo[1,5-a]pyridin-6-ium-Hydroxidsalz und das R-Isomere davon.
7. Eine Verbindung nach Anspruch 1, inneres 10-Carboxy-5-(dimethylamino)-2-dihydro-2-isopropyl-(2,8-dimethyl)-3-oxo-5H-imidazo[2',1':4,3]-imidazo[1,5-a]pyridin-6-ium-Hydroxidsalz und das R-Isomere davon.
8. Ein Verfahren zur Kontrolle einkeimblättriger und zweikeimblättriger, jährlicher, mehrjähriger bzw. winterharter und Wasserpflanzen-Arten umfassend: das Aufbringen auf das Blattwerk der genannten Pflanzen oder den Boden oder Wasser, der oder das Samen enthält oder auf andere Fortpflanzungsorgane einer herbizid wirksamen Menge einer Verbindung mit einer Struktur



worin Y, Z, R₁, R₂, R₃, R₄ und R₅ die gleiche Bedeutung haben wie in Anspruch 1.

9. Verfahren nach Anspruch 8, worin R₁ ein C₁-C₄-Alkyl ist, R₂ ein C₁-C₄-Alkyl ist, R₃ Wasserstoff, Methyl oder Benzyl ist, R₄ ein C₁-C₄-Alkyl ist, R₅ ein C₁-C₄-Alkyl oder Phenyl ist und, wenn R₄ und R₅ zusammengekommen werden, sie C₅-C₆-Cycloalkyl repräsentieren können, Y Wasserstoff oder C₁-C₄-Niederalkyl ist, Z Wasserstoff ist und, wenn Y und Z zusammengekommen werden, sie einen Ring bilden können, der durch -(CH₂)₄- oder -(CH)₄- repräsentiert ist.
10. Verfahren zum Herstellen von inneren (2-Imidazolin-2-yl)pyridin- und Chinolincarbonsäure- und Ester-Salzen und -Yliden der Struktur

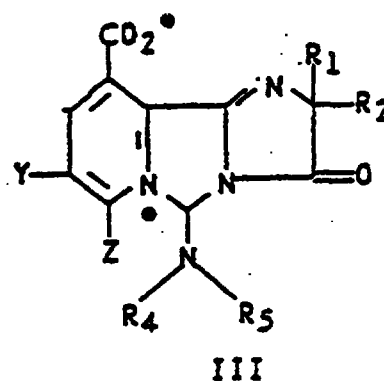
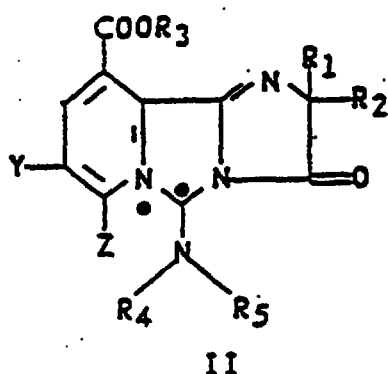




worin Y, Z, R₁, R₂, R₃, R₄ und R₅ die gleiche Bedeutung haben wie sie in Anspruch 1 angegeben ist, umfassend die Umsetzung eines Imidazolin-2-yl-pyridins oder Chinolincarbonsäureesters oder eines Carbamoylpyridins oder Chinolincarbonsäureesters mit einer etwa äquimolaren Menge eines Vilsmeier-Reagenz und wahlweises Behandeln des erhaltenen Produktes mit alkoholischer Base, gefolgt mit einem Ansäuern und Isolieren des Produktes.

Patentansprüche für folgende Vertragsstaaten : AT, ES, GR

- Verfahren zum Herstellen von inneren (2-Imidazolin-2-yl)pyridin- und Chinolincarbonsäure- und Ester-Salzen und -Yliden der Struktur



worin Y und Z jeweils Wasserstoff oder C₁-C₆-Alkyl sind und Y und Z zusammengekommen einen Ring bilden können, in dem YZ durch -(CH₂)_n, worin n eine ganze Zahl von 3 oder 4 ist, oder durch -(CH)₄-repräsentiert ist;

R₁ und R₂ sind jeweils C₁-C₄-Alkyl;

R₃ ist H oder COOR₃ repräsentiert einen Ester der Säure;

R₄ und R₅ sind jeweils C₁-C₄-Alkyl oder Phenyl oder, zusammengekommen, können sie ein C₅- oder C₆-Cycloalkyl bilden;

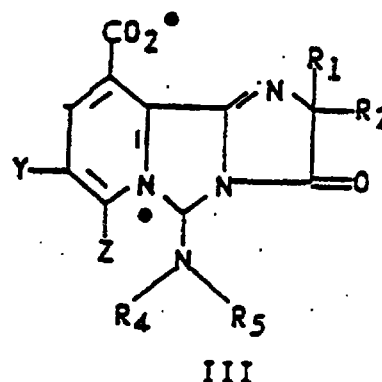
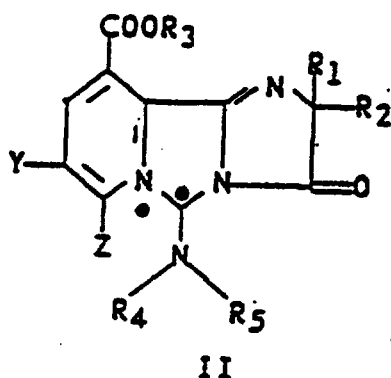
und, wenn R₁ und R₂ nicht gleich sind, die optischen Isomeren davon,

umfassend die Umsetzung eines Imidazolin-2-yl-pyridins oder Chinolincarbonsäureesters oder eines Carbamoylpyridins oder Chinolincarbonsäureesters mit einer etwa äquimolaren Menge eines Vilsmeier-Reagenz und wahlweises Behandeln des erhaltenen Produktes mit alkoholischer Base, gefolgt mit einem Ansäuern und Isolieren des Produktes.

- Ein Verfahren nach Anspruch 1, zum Herstellen von Methyl-10-carboxy-5-(dimethylamino)-2,3-dihydro-2-isopropyl-2-methyl-3-oxo-5H-imidazo[2',1':4,3]imidazo[1,5-a]pyridin-6-ium-5-ylid und dem R-Isomeren davon.



3. Ein Verfahren nach Anspruch 1, zum Herstellen von Methyl-10-carboxy-2,3-dihydro-2-isopropyl-2-methyl-3-oxo-5-(1-pyrrolidinyl)-5H-imidazo[2',1':4,3]imidazo[1,5-a]pyridin-6-ium-5-ylid und dem R-Isomeren davon.
4. Ein Verfahren nach Anspruch 1, zum Herstellen von Benzyl-10-carboxy-5-(dimethylamino)-2,3-dihydro-2-isopropyl-2-methyl-3-oxo-5H-imidazo[2',1':4,3]imidazo[1,5-a]pyridin-6-ium-5-ylid und dem R-Isomeren davon.
5. Ein Verfahren nach Anspruch 1, zum Herstellen von innerem 10-Carboxy-5-(dimethylamino)-2-dihydro-2-isopropyl-2-methyl-3-oxo-5H-imidazo[2',1':4,3]imidazo[1,5-a]pyridin-6-ium-Hydroxidsalz und dem R-Isomeren davon.
6. Ein Verfahren nach Anspruch 1, zum Herstellen von innerem 10-Carboxy-5-(diethylamino)-2-dihydro-2-isopropyl-2-methyl-3-oxo-5H-imidazo[2',1':4,3]imidazo[1,5-a]pyridin-6-ium-Hydroxidsalz und dem R-Isomeren davon.
7. Ein Verfahren nach Anspruch 1, zum Herstellen von innerem 10-Carboxy-5-(dimethylamino)-2-dihydro-2-isopropyl-(2,8-dimethyl)-3-oxo-5H-imidazo[2',1':4,3]imidazo[1,5-a]pyridin-6-ium-Hydroxidsalz und dem R-Isomeren davon.
8. Ein Verfahren zur Kontrolle einkeimblättriger und zweikeimblättriger, jährlicher, mehrjähriger bzw. winterharter und Wasserpflanzen-Arten umfassend: das Aufbringen auf das Blattwerk der genannten Pflanzen oder den Boden oder Wasser, der oder das Samen enthält oder auf andere Fortpflanzungsorgane einer herbizid wirksamen Menge einer Verbindung mit einer Struktur



worin Y, Z, R₁, R₂, R₃, R₄ und R₅ die gleiche Bedeutung haben wie in Anspruch 1.

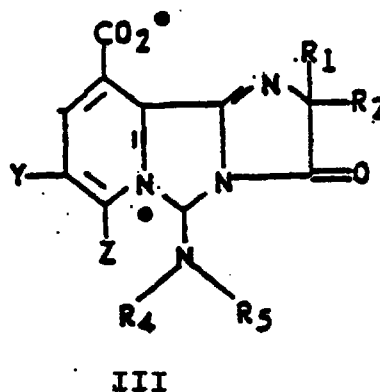
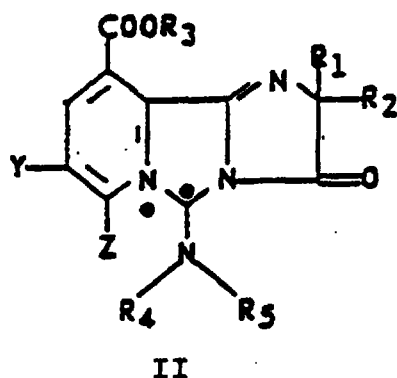
9. Verfahren nach Anspruch 8, worin R₁ ein C₁-C₄-Alkyl ist, R₂ ein C₁-C₄-Alkyl ist, R₃ Wasserstoff, Methyl oder Benzyl ist, R₄ ein C₁-C₄-Alkyl ist, R₅ ein C₁-C₄-Alkyl oder Phenyl ist und, wenn R₄ und R₅ zusammengekommen werden, sie C₅-C₆-Cycloalkyl repräsentieren können, Y Wasserstoff oder C₁-C₄-Niederalkyl ist, Z Wasserstoff ist und, wenn Y und Z zusammengekommen werden, sie einen Ring bilden können, der durch -(CH₂)₄- oder -(CH)₄- repräsentiert ist.

Revendications

Revendications pour les Etats contractants suivants : BE, CH, DE, FR, GB, IT, LI, LU, NL, SE

1. Sels internes et ylures d'acides (2-imidazolin-2-yl)pyridine et quinoléinecarboxyliques et d'esters de ceux-ci, de formule :





dans lesquelles

Y et Z représentent chacun un atome d'hydrogène ou un groupe alkyle en C₁-C₆, et Y et Z peuvent former ensemble un cycle, auquel cas YZ représente un groupe -(CH₂)_n, n étant un entier égal à 3 ou 4, ou un groupe -(CH)₄-;

R₁ et R₂ représentent chacun un groupe alkyle en C₁-C₄;

R₃ représente un atome d'hydrogène, ou COOR₃ représente un ester de l'acide;

R₄ et R₅ représentent chacun un groupe alkyle en C₁-C₄ ou phényle, ou ils peuvent former ensemble un groupe cycloalkyle en C₅ ou C₆;

et lorsque R₁ et R₂ ne sont pas identiques, leurs isomères optiques.

2. Composé selon la revendication 1, qui est le méthyl 10-carboxy-5-(diméthylamino)-2,3-dihydro-2-isopropyl-2-méthyl-3-oxo-5H-imidazo[2',1':4,3]imidazo[1,5-a]pyridin-6-ium-5-ylure et son isomère R.

3. Composé selon la revendication 1, qui est le méthyl 10-carboxy-2,3-dihydro-2-isopropyl-2-méthyl-3-oxo-5-(1-pyrrolidinyl)-5H-imidazo[2',1':4,3]imidazo[1,5-a]pyridin-6-ium-5-ylure et son isomère R.

4. Composé selon la revendication 1, qui est le benzyl 10-carboxy-5-(diméthylamino)-2,3-dihydro-2-isopropyl-2-méthyl-3-oxo-5H-imidazo[2',1':4,3]imidazo[1,5-a]pyridin-6-ium-5-ylure et son isomère R.

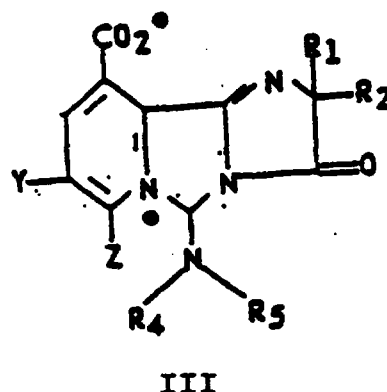
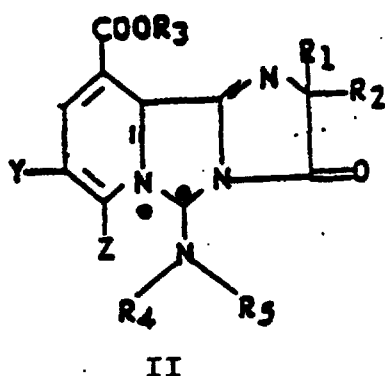
5. Composé selon la revendication 1, qui est le sel interne 10-carboxy-5-(diméthylamino)-2-dihydro-2-isopropyl-2-méthyl-3-oxo-5H-imidazo[2',1':4,3]imidazo[1,5-a]pyridin-6-ium-hydroxyde et son isomère R.

6. Composé selon la revendication 1, qui est le sel interne 10-carboxy-5-(diéthylamino)-2-dihydro-2-isopropyl-2-méthyl-3-oxo-5H-imidazo[2',1':4,3]imidazo[1,5-a]pyridin-6-ium-hydroxyde et son isomère R.

7. Composé selon la revendication 1, qui est le sel interne 10-carboxy-5-(diméthylamino)-2-dihydro-2-isopropyl-(2,8-diméthyl)-3-oxo-5H-imidazo[2',1':4,3]imidazo[1,5-a]pyridin-6-ium-hydroxyde et son isomère R.

8. Procédé de lutte contre des espèces végétales monocotylédones et dicotylédones, annuelles, pérennes et aquatiques, selon lequel on applique sur le feuillage des plantes ou sur le sol ou dans l'eau contenant des graines ou d'autres organes de propagation de celles-ci, une quantité à effet herbicide d'un composé de formule :





dans lesquelles Y, Z, R₁, R₂, R₃, R₄ et R₅ sont tels que définis dans la revendication 1.

9. Procédé selon la revendication 8, dans lequel :

R₁ représente un groupe alkyle en C₁-C₄ ;

R₂ représente un groupe alkyle en C₁-C₄ ;

R₃ représente un atome d'hydrogène, un groupe méthyle ou benzyle ;

R₄ représente un groupe alkyle en C₁-C₄ ;

R₅ représente un groupe alkyle en C₁-C₄ ou phényle ;

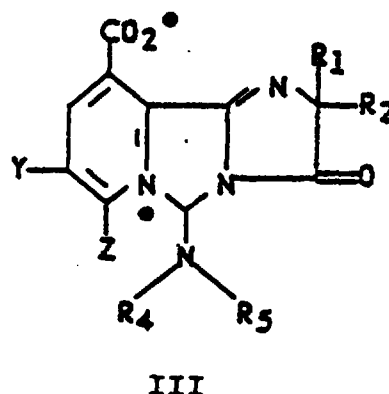
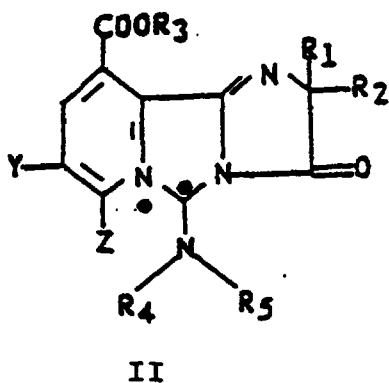
et R₄ et R₅ peuvent former ensemble un groupe cycloalkyle en C₅-C₆ ;

Y représente un atome d'hydrogène ou un groupe alkyle inférieur en C₁-C₄ ;

Z représente un atome d'hydrogène ;

et Y et Z peuvent former ensemble un cycle représenté par un groupe -(CH₂)₄- ou -(CH)₄-.

10. Procédé de préparation de sels internes et d'ylures dérivés d'acides (2-imidazolin-2-yl)pyridine et quinoléinecarboxyliques et d'esters de ceux-ci, de formule :

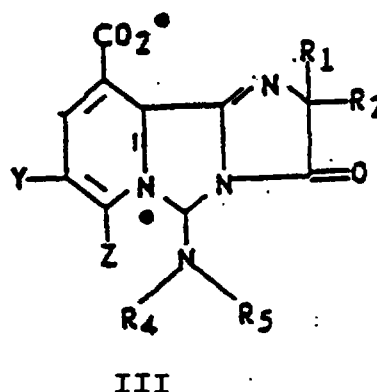
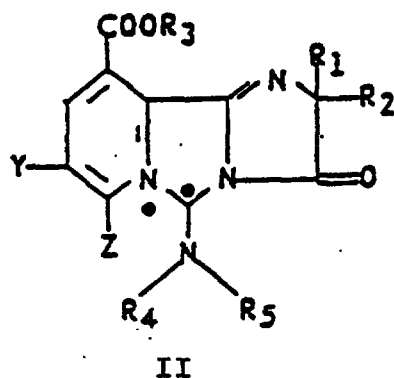


dans lesquelles Y, Z, R₁, R₂, R₃, R₄ et R₅ sont tels que définis dans la revendication 1 ; selon lequel on fait réagir un ester d'acide imidazolin-2-yl pyridine ou quinoléinecarboxylique, ou un ester d'acide carbamoylpyridine ou quinoléinecarboxylique, avec une quantité à peu près équimolaire d'un réactif de Vilsmeier, et on traite éventuellement le produit résultant avec une base alcoolique, puis on acidifie et on isole le produit.

Revendications pour les Etats contractants suivants : AT, ES, GR

1. Procédé de préparation de sels internes et d'ylures dérivés d'acides (2-imidazolin-2-yl)pyridine et quinoléinecarboxyliques et d'esters de ceux-ci, de formule :





dans lesquelles

Y et Z représentent chacun un atome d'hydrogène ou un groupe alkyle en C₁-C₆, et Y et Z peuvent former ensemble un cycle, auquel cas YZ représente un groupe -(CH₂)_n, n étant un entier égal à 3 ou 4, ou un groupe -(CH)₄- ;

R₁ et R₂ représentent chacun un groupe alkyle en C₁-C₄ ;

R₃ représente un atome d'hydrogène, ou COOR₃ représente un ester de l'acide ;

R₄ et R₅ représentent chacun un groupe alkyle en C₁-C₄ ou phényle, ou ils peuvent former ensemble un groupe cycloalkyle en C₅ ou C₆ ;

et lorsque R₁ et R₂ ne sont pas identiques, leurs isomères optiques, procédé selon lequel on fait réagir un ester d'acide imidazolin-2-yl pyridine ou quinoléinecarboxylique, ou un ester d'acide carbamoylpyridine ou quinoléinecarboxylique, avec une quantité à peu près équimolaire d'un réactif de Vilsmeier, et on traite éventuellement le produit résultant avec une base alcoolique, puis on acidifie et on isole le produit.

2. Procédé selon la revendication 1, pour préparer le méthyl 10-carboxy-5-(diméthylamino)-2,3-dihydro-2-isopropyl-2-méthyl-3-oxo-5H-imidazo[2',1':4,3]imidazo[1,5-a]pyridin-6-ium-5-ylure et son isomère R.

3. Procédé selon la revendication 1, pour préparer le méthyl 10-carboxy-2,3-dihydro-2-isopropyl-2-méthyl-3-oxo-5-(1-pyrrolidinyl)-5H-imidazo[2',1':4,3]imidazo[1,5-a]pyridin-6-ium-5-ylure et son isomère R.

4. Procédé selon la revendication 1, pour préparer le benzyl 10-carboxy-5-(diméthylamino)-2,3-dihydro-2-isopropyl-2-méthyl-3-oxo-5H-imidazo[2',1':4,3]imidazo[1,5-a]pyridin-6-ium-5-ylure et son isomère R.

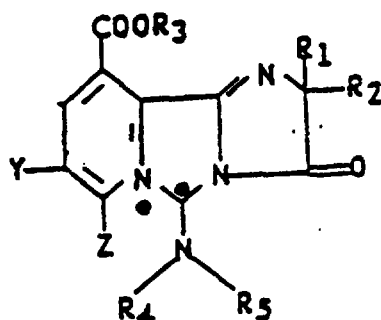
5. Procédé selon la revendication 1, pour préparer le sel interne 10-carboxy-5-(diméthylamino)-2-dihydro-2-isopropyl-2-méthyl-3-oxo-5H-imidazo[2',1':4,3]imidazo[1,5-a]pyridin-6-ium-hydroxyde et son isomère R.

6. Procédé selon la revendication 1, pour préparer le sel interne 10-carboxy-5-(diéthylamino)-2-dihydro-2-isopropyl-2-méthyl-3-oxo-5H-imidazo[2',1':4,3]imidazo[1,5-a]pyridin-6-ium-hydroxyde et son isomère R.

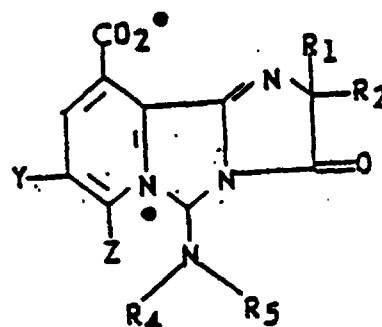
7. Procédé selon la revendication 1, pour préparer le sel interne 10-carboxy-5-(diméthylamino)-2-dihydro-2-isopropyl-(2,8-diméthyl)-3-oxo-5H-imidazo[2',1':4,3]imidazo[1,5-a]pyridin-6-ium-hydroxyde et son isomère R.

8. Procédé de lutte contre des espèces végétales monocotylédones et dicotylédones, annuelles, pérennes et aquatiques, selon lequel on applique sur le feuillage des plantes ou sur le sol ou dans l'eau contenant des graines ou d'autres organes de propagation de celles-ci, une quantité à effet herbicide d'un composé de formule :





II



III

dans lesquelles Y, Z, R₁, R₂, R₃, R₄ et R₅ sont tels que définis dans la revendication 1.

9. Procédé selon la revendication 8, dans lequel :

R₁ représente un groupe alkyle en C₁-C₄ ;

R₂ représente un groupe alkyle en C₁-C₄ ;

R₃ représente un atome d'hydrogène, un groupe méthyle ou benzyle ;

R₄ représente un groupe alkyle en C₁-C₄ ;

R₅ représente un groupe alkyle en C₁-C₄ ou phényle ;

et R₄ et R₅ peuvent former ensemble un groupe cycloalkyle en C₅-C₆ ;

Y représente un atome d'hydrogène ou un groupe alkyle inférieur en C₁-C₄ ;

Z représente un atome d'hydrogène ;

et Y et Z peuvent former ensemble un cycle représenté par un groupe -(CH₂)₄- ou -(CH)₄-.

