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(54) Title: 2-[1-(3-CHLOROALLYLOXYAMINO)ALKYLEDENE]-5-ALKYLTHIOALKYL-CYCLOHEXANE-1,3-DIONE HERBICIDES

(57) Abstract

2-[1-(3-chloroallyloxyamino)propylidene]-5-(2-ethylthiopropyl)-cyclohexane-1,3-dione and salts thereof. The compounds exhibit pre- and post-emergent phytotoxicity and are useful as selective herbicides against grasses.

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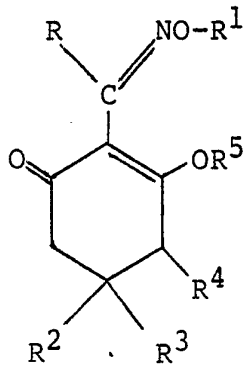
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2-[1-(3-CHLOROALLYLOXYAMINO) ALKYLIDENE]-5-ALKYLTHIOALKYL-CYCLOHEXANE-1,3-DIONE HERBICIDES

BACKGROUND OF THE INVENTION

This invention relates to trans-2-[1-(3-chloroallylamino) propylidene]-5-(2-ethylthiopropyl)cyclohexane-1,3-dione and salts thereof and to the use of such compounds as herbicides.

In my U.S. Patent No. 4,440,566, issued April 3, 1984, I disclosed compounds having the formula:



wherein R is most preferably alkyl or 1 to 3 carbon atoms, most preferably ethyl or propyl;

R^1 is most preferably 3-trans-chloroallyl or 4-chlorobenzyl;

R^2 and R^3 are preferably each alkyl or 1 to 3 carbon atoms or one of R^2 or R^3 is hydrogen and the other is alkylthioalkyl having 2 through 8 carbon atoms, most preferably R^2 and R^3 are each methyl or one of R^2 or R^3 is hydrogen and the other is 2-ethylthiopropyl.

My patent also teaches that these compounds exhibit herbicidal activity against grasses and are safe with respect to broad-leaf crops.

SUMMARY OF THE INVENTION

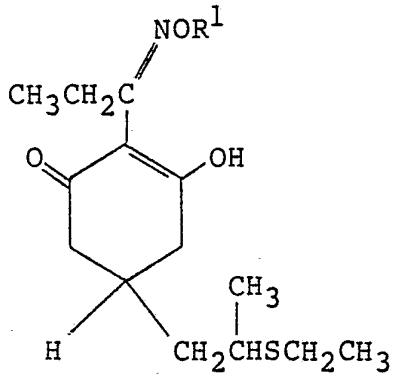
It is has now been discovered that one of the compounds (i.e., see Formula I below R is ethyl) encompassed within U.S. Patent No. 4,440,566, exhibits surprisingly superior herbicidal activity as compared with others, including its homolog where R is propyl. This is

especially surprising because such homolog where R is propyl is a very good herbicide.

As well as exhibiting pre-emergence activity, the present compound exhibits excellent post-emergence herbicidal activity against Bermudagrass, foxtail, crabgrass, volunteer corn, volunteer sorghum, barnyardgrass, broad-leaf signalgrass, goosegrass, red rice, sprangletop, seedling Johnsongrass and Rhizone Johnsongrass.

The compound of Formula I exhibits excellent phytotoxicity against grasses at even very low application rates and may be safely applied with respect to broad-leaf crops at such rates. Thus, the present compound is especially useful for controlling grassy weeds in broad-leaf crops and is especially useful to control grassy weeds in soybean crops.

The compound of the present invention can be represented by the following formula:



(I)

wherein R^1 is 3-transchloroallyl.

The invention also comprises compatible salts of the compound of Formula I.

As is well recognized, compounds of the nature of Formula (I) exist as tautomers. The compounds also have two asymmetric carbon atoms and can also exist as optical isomers. The above formula is intended to encompass the respective tautomeric forms as well as the

individual optical isomers as well as mixtures thereof and the respective tautomers and optical isomers as well as mixtures thereof are encompassed within the invention.

In a further aspect the invention provides a herbicidal composition comprising a compatible carrier and a herbicidally effective amount of the compound(s) of the invention or mixtures thereof.

The present invention also provides a method for preventing or controlling the growth of unwanted grassy vegetation, which comprises treating the growth medium and/or the foliage of such vegetation with a herbicidally effective amount of the compound(s) of the invention or mixtures thereof.

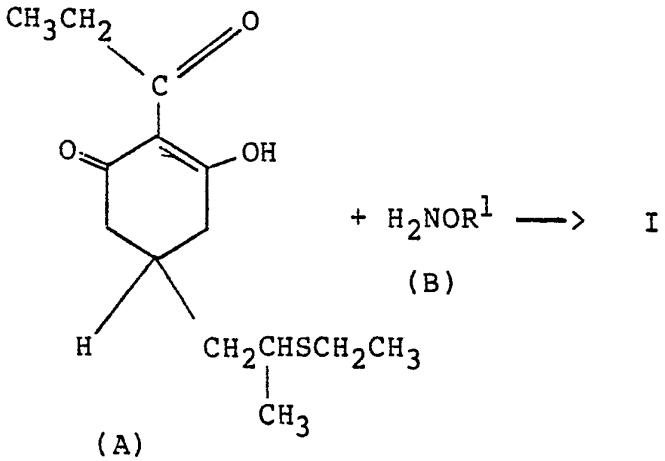
The present invention also provides a method for regulating plant growth which comprises treating the growth medium and/or the foliage of such vegetation with a plant growth regulating effective amount of the compound(s) of the invention or mixtures thereof, effective to alter the normal growth pattern of said plants.

The present invention also provides chemical intermediates and processes for preparing the compounds of the invention.

The invention will be further described hereinbelow.

FURTHER DESCRIPTION OF THE INVENTION AND THE PREFERRED EMBODIMENTS

The compound of Formula (I) can be conveniently prepared by the following schematically represented process:



wherein R^1 is 3-trans-chloroallyl.

This process can be conveniently effected by contacting Compound (A) with 3-trans-chloroallyloxyamine (B), preferably in an inert organic solvent.

Typically, this process is conducted at temperatures in the range of about from 0 to 80°C, preferably about from 20 to 40°C, for about from 1 to 48 hours, preferably about from 4 to 12 hours, using about from 1 to 2, preferably 1.05 to 1.2 moles of 3-trans-chloroallyloxyamine (B) per mole of Compound (A). Suitable inert organic solvents which can be used include, for example, lower alkanols, e.g., methanol, ethanol, ethers, e.g., ethyl ether; methylene chloride. Two-phase water and immiscible organic solvent (e.g., hexane), and the like, and compatible mixtures thereof can also be used.

Trans-chloroallyloxyamine is a known compound and can be prepared via known procedures, such as, for example, described in my U.S. Patent No. 4,440,566. Conveniently, a hydrochloride salt of trans-chloroallyloxyamine can be used by neutralizing the salt with an alkali metal alkoxide, in situ.

The starting materials of Formula (A) can be prepared via the general procedure described in my U.S. Patent No. 4,440,566.

The compatible salts of Formula (I) can be prepared by conventional procedures, for example, via the reaction of the compound of Formula I with a base, such as, for example, sodium hydroxide, potassium hydroxide and the like, having the desired cation. Additional variations in the salt cation can also be effected via ion exchange with an ion exchange resin having the desired cation.

General Process Conditions

The reaction product can be recovered from its reaction product mixture by any suitable separation and purification procedure, such as, for example, chromatography. Suitable separation and purification procedures

are, for example, illustrated in the Examples set forth hereinbelow.

Generally, the reactions described above are conducted as liquid phase reaction and hence pressure is generally not significant except as it affects temperature (boiling point) where reactions are conducted at reflux. Therefore, these reactions are generally conducted at pressures of about from 300 to 3,000 mm of mercury and conveniently are conducted at about atmospheric or ambient pressure.

It should also be appreciated that where typical or preferred process conditions (e.g., reaction temperatures, times, mole ratios of reactants, solvents, etc.) have been given, that other process conditions could also be used. Optimum reaction conditions (e.g., temperature, reaction time, mol ratios, solvents, etc.) may vary with the particular reagents or organic solvents used but can be determined by routine optimization procedures.

Where optical isomer mixtures are obtained, the respective optical isomers can be obtained by conventional resolution procedures. Geometric isomers can be separated by conventional separation procedures which depend upon differences in physical properties between the geometric isomers. However, it is generally preferable to use the desired isomeric starting material in the reaction.

Definitions

As used herein the following terms have the following meanings unless expressly stated to the contrary:

The term "compatible salts" refers to salts which do not significantly adversely alter the herbicidal properties of the parent compound. Suitable salts include cation salts such as, for example, the cation salts of lithium, sodium, potassium, alkali earth metals, copper, zinc, ammonia, quaternary ammonium salts, and the like.

The term "room temperature" or "ambient temperature" refers to about 20-25°C.

Utility

The compound of Formula (I) and its salts exhibit both pre- and post-emergent herbicidal activity and exhibit especially good herbicidal activity against grasses. The compounds exhibit especially good phytotoxicity against foxtail, Bermudagrass, crabgrass, rhizone Johnsongrass and volunteer corn which are weed species which are generally very difficult to control.

Generally, for post-emergent applications, the herbicidal compounds are applied directly to the foliage or other plant parts. For pre-emergence applications, the herbicidal compounds are applied to the growth medium, or prospective growth medium, for the plant. The optimum amount of the herbicidal compound or composition will vary with the particular plant species, and the extent of plant growth, if any, and the particular part of the plant which is contacted and the extent of contact. The optimum dosage can also vary with the general location, or environment (e.g., sheltered areas such as greenhouses compared to exposed areas such as fields), and type and degree of control desired. Generally, for both pre- and post-emergent control, the present compounds are applied at rates of about from 0.02 to 60 kg/ha, preferably about from 0.02 to 10 kg/ha.

Also, although in theory the compounds can be applied undiluted, in actual practice they are generally applied as a composition or formulation comprising an effective amount of the compound(s) and an acceptable carrier. An acceptable or compatible carrier (agriculturally acceptable carrier) is one which does not significantly adversely affect the desired biological effect achieved by the active compounds, save to dilute it. Typically, the composition contains about from 0.05 to 95% by weight of the compound of Formula (I) or mixtures thereof. Concentrates can also be made having high concentrations designed for dilution prior to application. The carrier can be a solid, liquid, or aerosol. The actual compositions can take the form of granules, powders,

dusts, solutions, emulsions, slurries, aerosols, and the like.

Suitable solid carriers which can be used include, for example, natural clays (such as kaolin, attapulgite, montmorillonite, etc.), talcs, pyrophyllite, diatomaceous silica, synthetic fine silica, calcium aluminosilicate, tricalcium phosphate, and the like. Also, organic materials, such as, for example, walnut shell flour, cotton-seed hulls, wheat flour, wood flour, wood bark flour, and the like can also be used as carriers. Suitable liquid diluents which can be used include, for example, water, organic solvents (e.g., hydrocarbons such as benzene, toluene, dimethylsulfoxide, kerosene, diesel fuel, fuel oil, petroleum naphtha, etc.), and the like. Suitable aerosol carriers which can be used include conventional aerosol carriers such as halogenated alkanes, etc.

The composition can also contain various promoters and surface-active agents which enhance the rate of transport of the active compound into the plant tissue such as, for example, organic solvents, wetting agents and oils, and in the case of compositions designed for pre-emergence application agents which reduce the leachability of the compound or otherwise enhance soil stability. Crop oils, such as, for example, soybean oils, paraffin oils and olefinic oils, are especially advantageous as carriers or additives in that they enhance phytotoxicity.

The composition can also contain various compatible adjuvants, stabilizers, conditioners, insecticides, fungicides, and if desired, other herbicidally active compounds.

One convenient concentrate formulation which can be used comprises 23-27% by weight of the active herbicide of the invention, 2 to 4% by weight of an emulsifier, for example, calcium alkylbenzene sulfonates, octylphenol-ethoxylate, etc., or mixtures thereof, and about 70-75% organic solvent, for example, xylene, etc. The concentrate is mixed with water and preferably a crop oil prior

to application and applied as a water emulsion containing about 0.5 to 2% of a crop oil, for example, soybean oils, and paraffinic oils and olefinic oils. Conveniently, the herbicide is applied as water emulsion containing about 0.02-0.6 wt. %, preferably 0.07-0.15 wt. % of the herbicide, of the invention; about 0.001-0.01 wt. % of an emulsifier; about 0.08-2.5 wt. % of an organic solvent and about 95 to 99 wt. % water. Preferably, the composition also contains about 0.25 to 2 wt. % of a crop oil. The application composition can be conveniently prepared by mixing the concentrate formulation with about 1/4 to 1/2 the desired amount of water. Then admixing the crop oil and then adding the remaining amount of water. If no crop oil is used, then the water and concentrate formulation are simply admixed together.

A further understanding of the invention can be had in the following non-limiting Preparation(s) and Example(s). Wherein, unless expressly stated to the contrary, all temperatures and temperature ranges refer to the Centigrade system and the term "ambient" or "room temperature" refers to about 20-25°C. The term "percent" or "%" refers to weight percent and the term "mole" or "moles" refers to gram moles. The term "equivalent" refers to a quantity of reagent equal in moles, to the moles of the preceding or succeeding reactant recited in that example in terms of finite moles or finite weight or volume. Where given, proton-magnetic resonance spectrum (p.m.r. or NMR) were determined at 60 mHz, signals are assigned as singlets (s), broad singlets (bs), doublets (d), double doublets (dd), triplets (t), double triplets (dt), quartets (q), and multiplets (m); and cps refers to cycles per second. Also where necessary examples are repeated to provide additional starting material for subsequent examples.

EXAMPLES

Example 1

Trans-2-[1-(3-chloroallyloxyamino) propylidene]-5-(2-ethylthiopropyl)-cyclohexane-1,3-dione

In this example, 17.2 g (0.0636 mol) of 2-propionyl-5-(2-ethylthiopropyl)cyclohexane-1,3-dione; 0.9 g (0.0153 mol) of acetic acid, and 10.9 g (0.0757 mol) of 3-trans-chloroallyloxyamine in 35 ml of water were added to 20 ml of hexane and stirred. Aqueous 5 wt. % sodium hydroxide was slowly added over about 15 minutes until 3.0 g (0.0757 m + small excess) of sodium hydroxide had been added - pH of reaction mixture about 6. The mixture was heated to and maintained at 40°C for 2-1/2 hours and then cooled to room temperature. The organic (i.e., hexane) phase was separated and washed with 10 ml of aqueous 5 wt. % hydrochloric acid and then aqueous 6.25 wt. % sodium hydroxide added until pH12. The aqueous phase was separated and admixed with 25 ml of hexane and the pH adjusted to 5.4 by the dropwise addition of aqueous 36 wt. % hydrochloric acid over an ice bath. The organic phase was separated, dried over magnesium sulfate and then concentrated by evaporation affording 18.0 g of a crude product. The crude product was purified by column chromatography over silica gel eluting with hexane:methylene chloride affording the purified title compound as an oil. Elemental analysis carbon calculated 56.73%, found 56.63%; Hydrogen calculated 7.28%, found 7.55%; Nitrogen 3.89%, found 3.55%.

Example 2

Sodium 2-[1-(3-trans-chloroallyloxyamino) propylidene-3-oxo-5-(2-ethylthiopropyl)-cyclohex-1-en-1-olate

This example illustrates a procedure which can be used to prepare the title compound.

A solution containing 0.01 mole of sodium hydroxide dissolved in 2 ml of water is added to a solution containing 0.01 mole of 2-[1-(3-trans-chloroallyloxyamino) propylidene-5-(2-ethylthiopropyl)-cyclohexane 1,3-dione at room temperature. After the reaction is

completed, the solvents are evaporated off under vacuum affording the 1-hydroxy sodium salt of 2-[1-(3-trans-chloroallyloxyamino) propylidene-3-oxo-5-(2-ethylthiopropyl)-cyclohex-1-en-1-ol.

Example 3

In this example, the title compound of Example 1, i.e., 2-[1-(3-trans-chloroallyloxyamino) propylidene]-5-(2-ethylthiopropyl)-cyclohexane-1,3-dione was tested, using the procedures described hereinbelow, for pre-emergent and post-emergent phytotoxic activity against a variety of grasses and broad-leaf plants including one grain crop and one broad-leaf crop.

Pre-Emergent Herbicide Test

Pre-emergence herbicidal activity was determined in the following manner.

Test solutions of the respective compounds were prepared as follows:

355.5 mg of test compound was dissolved in 15 ml of acetone. 2 ml of acetone containing 110 mg of a nonionic surfactant was added to the solution. 12 ml of this stock solution was then added to 47.7 ml of water which contained the same nonionic surfactant at a concentration of 625 mg/l.

Seeds of the test vegetation were planted in a pot of soil and the test solution was sprayed uniformly onto the soil surface at a test compound dose of 27.5 micrograms/cm^2 unless otherwise specified in the following Tables. The pot was watered and placed in a greenhouse. The pot was watered intermittently and observed for seedling emergence, health of emerging seedlings, etc., for a 3-week period. At the end of this period, the herbicidal effectiveness of the compound was rated based on the physiological observations. A 0-to-100 scale was used, 0 representing no phytotoxicity, 100 representing complete kill. The results of these tests are summarized in Table 1.

Post-Emergent Herbicidal Test

The test compound was formulated in the same manner as described above for the pre-emergent test. This formulation was uniformly sprayed on 2 similar pots containing plants 2 to 3 inches tall (except wild oats, soybean and watergrass which were 3 to 4 inches tall) (approximately 15 to 25 plants per pot) at a test compound dose of 27.5 microgram/cm^2 unless otherwise specified in the following Tables. After the plants had dried, they were placed in a greenhouse and then watered intermittently at their bases as needed. The plants were observed periodically for phytotoxic effects and physiological and morphological responses to the treatment. After 3 weeks, the herbicidal effectiveness of the compound was rated based on these observations. A 0-to-100 scale was used, 0 representing no phytotoxicity, 100 representing complete kill. The results of these tests are summarized in Table 2.

TABLE 1

Pre-Emergence Herbicidal Activity

Application Rate: 27.5 micrograms/cm^2, unless otherwise noted

Compound No.	Broad-leaf Plants % Phytotoxicity				Grasses % Phytotoxicity			
	Lambsquarter	Mustard	Pigweed	Soybean	Barnyard Grass	Crabgrass	Wild Oats	Rice
1	25	30	25	30	100	100	100	100

TABLE 2

Post-Emergence Herbicidal Activity

Application Rate: 27.5 micrograms/cm^2, unless otherwise noted

Compound No.	Broadleaf Plants % Phytotoxicity				Grasses % Phytotoxicity				
	Lambsquarter	Mustard	Pigweed	Soybean	Barnyard Grass	Crabgrass	Wild Oats		Rice
1	30	45	40	40	100	100	100		100

Example 3

In this example, the title compound of Example 1, of the present invention, ("1") was tested for post-emergence herbicidal activity at moderately low dosage rates side-by-side with its butylidene homolog, i.e., trans-2-[1-(3-chloroallyloxyamino)butylidene]-5-(2-ethylthiopropyl)-cyclohexane-1,3-dione.

The tests were conducted in the same manner as described in Example 2, hereinabove, with the exception that the application rates specified in Table 3 were used and 4 replicate pots were used per test instead of 2. The average result of the four replicates are reported in Table 3 herein below, wherein 0 indicates no phytotoxicity and 100 indicates complete kill. Generally, phytotoxicities below about 20-30% are not considered significant because the plant can typically grow out of this amount of injury.

TABLE 3

Post-Emergence Herbicidal Activity

Moderate Low Dosage Tests

		Broadleaf Plants % Phytotoxicity					Grasses % Phytotoxicity			
Compound No.*	Dosage γ/cm²**	Lambs-quarter	Mustard	Pig-weed	Soybean	Crab-grass	Barn-yard grass	Wild Oats	Rice
1	1.8	0	3	0	7	100	100	98	98
1	0.7	0	0	0	2	100	100	80	85
C-1	1.8	0	0	0	N.T.	87	100	95	97
C-1	0.7	0	0	0	N.T.	60	98	80	87

N.T. = Not tested, but based on other tests the comparison compound is also safe with respect to soybeans at this dosage rate.

1 = trans-2-[1-(3-chloroallyloxyamino)propylidene]-5-(2-ethylthiopropyl)-cyclohexane-1,3-dione

C-1 = trans-2-[1-(3-chloroallyloxyamino)butylidene]-5-(2-ethylthiopropyl)-cyclohexane-1,3-dione

**γ/cm² = micrograms per square centimeter.

As can be seen from Table 3, Compound 1 was substantially superior to comparison Compound C-1 against crabgrass, even at moderately low dosages. The superiority of Compound 1 will become more apparent at the low dosages used in Example 4 hereinbelow.

Example 4

In this example, the title compound ("1") was tested for post-emergence herbicidal activity at very low dosage rate side by side with trans-2-[1-(3-chloroallyloxyamino)butylidene]-5-(2-ethylthiopropyl)-cyclohexane-1,3-dione ("C-1") and the commercial herbicide Sethoxdm ("C-2") (i.e., 2-[1-(ethoxyamino)butylidene]-5-(2-ethylthiopropyl)-cyclohexane-1,3-dione against an expanded list of weed grasses.

The tests were conducted in the same manner as described in Example 3, hereinabove, with the exception that the dosages indicated in Table 4 were used. The results of this testing are summarized in Table 4 wherein 0 indicates no phytotoxicity and 100 indicates complete kill. Generally, phytotoxicities below about 20-30% are not considered meaningful because the plant can typically grow out of this amount of injury.

TABLE 4

Post-Emergence Herbicidal Activity

Low Dosage Tests

Compound No.*	Dosage γ/cm²*	Broadleaf Plants % Phytotoxicity				Grasses % Phytotoxicity			
		Crabgrass	Barnyard grass	Wild Oats	Rhizone Johnsongrass	Yellow Foxtail	Yellow Nutsedge	Soybean	Rice
1	0.28	71	99	66	99	99	0	0	93
1	0.11	63	90	46	92	92	0	0	83
1	0.05	40	60	6	63	63	0	0	71
1	0.02	5	8	0	21	21	0	0	1
C-1	0.28	55	96	60	68	80	0	0	78
C-1	0.11	25	70	43	43	53	0	0	70
C-1	0.05	15	40	26	21	40	0	0	40
C-1	0.02	0	8	0	0	0	0	0	10
C-2	0.28	53	80	36	73	68	0	0	63
C-2	0.11	16	68	16	31	48	0	0	41
C-2	0.05	10	20	0	0	10	0	0	10
C-2	0.02	0	0	0	0	0	0	0	0

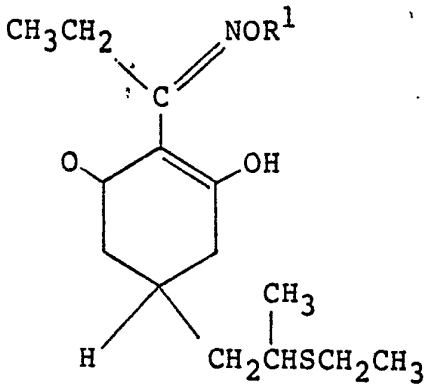
As can be seen from Table 4, with the exception of wild oats and yellow nutsedge, Compound 1 was superior to Comparison Compound C-1 with respect to teach of the other weed species tested. Compounds 1 and C-1 were about equivalent with respect to wild oats and both compounds were inactive at these dosage rates against yellow nutsedge. Compounds 1 and C-1 were both superior to Compound C-2.

In terms of dosages required to evoke equivalent responses, an application rate of Compound 1 of 0.11 q/cm^2 was about equivalent to an application rate of Compound C-1 of 0.28 q/cm^2 to control crabgrass and barnyardgrass. An application rate of Compound 1 of 0.05 q/cm^2 was about equivalent to an application rate of Compound C-1 of 0.28 q/cm^2 to control yellow foxtail and an application rate of Compound 1 of 0.11 q/cm^2 was superior to an application rate of Compound C-1 of 0.28 q/cm^2 to control Johnsongrass.

Obviously, many modifications and variations of the invention described hereinabove and below can be made without departing from the essence and scope thereof.

WHAT IS CLAIMED IS:

1. A compound having the formula:



wherein R^1 is 3-trans-chloroallyl;
and compatible salts thereof.

2. The compound of Claim 1 wherein said compound is 2-[1-(3-trans-chloroallylamino) propylidene]-5-(2-ethylthiopropyl)-cyclohexane-1,3-dione.

3. A herbicidal composition comprising a herbicidally effective amount of a compound according to Claim 1, and a compatible carrier.

4. A herbicidal composition comprising a herbicidally effective amount of the compound of Claim 2, and a compatible carrier.

5. A herbicidal composition comprising a herbicidally effective amount of the compound according to Claim 1 and a crop oil.

6. A method for controlling grassy plants which comprises applying a herbicidally effective amount of a compound according to Claim 1, to the foliage or habitat of said plants.

7. A method for controlling grassy plants which comprises applying a herbicidally effective amount of the compound of Claim 2, or mixtures thereof, to the foliage or habitat of said plants.

8. A method for controlling the grass species of foxtail, Bermudagrass, volunteer sorghum, broad-leaf signalgrass, goosegrass, red rice, sprangletop, Johnsongrass or volunteer corn which comprises applying a herbicidally effective amount of the compound of Claim 1 to said grass species or their habitat.

9. A method for preparing the compound of Claim 1 which comprises the step of contacting 2-propionyl-5-(2-methylthiopropyl)-cyclohexane-1,3-dione with 3-trans-chloroallyloxyamine under reactive conditions thereby producing the corresponding compound of Formula I.

10. The method of Claim 9 wherein said method is conducted in an inert organic solvent at temperatures in the range of about from 0 to 80°C.

11. A process for preparing the compounds of Claim 1, substantially as described herein.

12. A herbicidal composition comprising 0.02-0.6 wt. % of a compound according to Claim 1; 0.001-0.15 wt. % of an emulsifier; 0.08-2.5 wt. % of an organic solvent and about 95 to 99 wt. % water.

13. The composition of Claim 12 wherein said composition comprises about 0.25-2 wt. % of a crop oil.

14. A herbicidal concentrate composition comprising 23-27 wt. % of a compound according to Claim 1; 2 to 4 wt. % of an emulsifier and about 70-75 wt. % of an organic solvent.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 85/01786

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[4]: C 07 C 149/00; A 01 N 35/10

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC[4]	C 07 C 149/00

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	US, A, 4440566 (T. LUO) 3 April 1984, see claims; example 54 (cited in the application)	1-14

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* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
24th April 1986	22 MAI 1986
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	M. VAN MOL

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/US 85/01786 (SA 10802)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 06/05/86

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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