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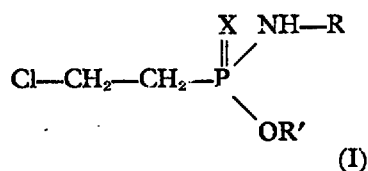
(54) METHODS FOR THE REGULATION OF VASCULAR PLANT GROWTH

- (71) We, FARBENFABRIKEN BAYER AK-
 TIENGESSELLSCHAFT, a body corporate organised
 under the laws of Germany, of Leverkusen,
 Germany, do hereby declare the invention, for
 which we pray that a patent may be granted
 to us, and the method by which it is to be
 performed, to be particularly described in and
 by the following statement:—

- The present invention relates to the use of
 certain 2 - chloroethane - (thiono) - phos-
 phonic acid amido compounds, some of which
 are known, as agents for the regulation of
 vascular plant growth.

- It is known (cf. Dutch Patent Specification
 6,802,633) that 2-chloroethanephosphonic acid
 exhibits plant-growth-regulating properties.

- The present invention provides a method
 for the control of plant growth which comprises
 applying to the vascular plant or seed thereof
 a 2 - chloroethane - (thiono) - phosphonic
 acid amido compound of the general formula



in which

- X stands for an oxygen or sulphur atom,
 R denotes a lower alkyl radical with 1 to 6
 carbon atoms or a phenyl radical, and
 R' denotes a hydrogen atom, an alkali
 metal equivalent, an alkaline earth metal
 equivalent, an ammonium equivalent or a
 phenyl radical which may be substituted by
 nitro, halogen, alkyl or hydroxy,

either alone or in admixture with a solid or
 liquid diluent or carrier.

Some of the above compounds are known
 to have fungicidal effects.

It is, however, very surprising that they
 have plant-growth regulating properties.
 Surprisingly, the 2 - chloroethane - (thiono) -
 phosphonic acid amido compounds according
 to the invention show a considerably higher
 plant-growth-regulating activity than the 2-
 chloroethanephosphonic acid known from the
 prior art which is the chemically closest active
 compound of the same type of activity. The
 substances according to the invention there-
 fore represent a valuable enrichment of the
 art.

The substances to be used according to the
 invention are unambiguously defined by the
 general formula (I).

R stands preferably for lower alkyl radicals
 with 1 to 4 carbon atoms or for a phenyl
 radical, while R' stands preferably for a
 hydrogen atom or a phenyl radical which may
 be substituted by nitro, methyl, hydroxy or
 chlorine.

As examples of the active compounds which
 can be used according to the invention, there
 are mentioned in particular:

- 2 - chloroethane - phosphonic acid mono - N -
 methylamide,
 2 - chloroethane - phosphonic acid mono - N -
 ethylamide,
 2 - chloroethane - phosphonic acid mono - N -
 n-propylamide,
 2 - chloroethane - phosphonic acid mono - N -
 iso-propylamide,
 2 - chloroethane - phosphonic acid mono - N -
 n-butylamide,

- 2 - chloroethane - phosphonic acid mono - N - sec. - butylamide,
 2 - chloroethane - phosphonic acid mono - N - tert. - butylamide,
 5 2 - chloroethane - phosphonic acid mono - N - iso - butylamide,
 2 - chloroethane - phosphonic acid mono - N - phenylamide,
 10 2 - chloroethane - thiono - phosphonic acid mono - N - methylamide,
 2 - chloroethane - thiono - phosphonic acid mono - N - ethylamide,
 2 - chloroethane - thiono - phosphonic acid mono - N - n - propylamide,
 15 2 - chloroethane - thiono - phosphonic acid mono - iso - propylamide,
 2 - chloroethane - thiono - phosphonic acid mono - N - n - butylamide,
 20 2 - chloroethane - thiono - phosphonic acid mono - N - sec. - butylamide,
 2 - chloroethane - thiono - phosphonic acid mono - N - tert. - butylamide,
 2 - chloroethane - thiono - phosphonic acid mono - N - iso - butylamide,
 25 2 - chloroethane - thiono - phosphonic acid mono - N - phenylamide,
 in addition, the sodium, potassium, ammonium, calcium and barium salts of these (thiono)-phosphonic acid amides; further, their:
 30 2'-hydroxyphenyl esters, 3'-hydroxyphenyl esters,
 4'-hydroxyphenyl esters, 2'-nitrophenyl esters, 3'-nitrophenyl esters, 4'-nitrophenyl esters, 2'-cresyl esters, 3'-cresyl esters, 4'-cresyl esters,
 35 2'-chlorophenyl esters, 3'-chlorophenyl esters, 4'-chlorophenyl esters, 2',4'-dichlorophenyl esters and 2',6'-dichlorophenyl esters.
 40 Some of the substances which can be used according to the invention are known, e.g. 2 - chloroethane - thiono - phosphonic acid 2',4'-dichlorophenyl ester mono-N-isopropylamide (cf. Russian Patent Specification
 45 197.359 and Z. Obsc. Chim (Journal of General Chemistry of the U.S.S.R.) 38 (1968), No. 10, pp. 2260-2265).
 Some of the substances used in the invention are new, but they can be prepared in
 50 simple manner according to known processes. They are obtained for example when 2-chloroethane-(thiono)-phosphonic acid amide chlorides are reacted with phenols in the presence of inert solvents, such as benzene,
 55 and acid-binding agents, for example triethylamine, at temperatures of 0° to 70°C. The reaction products may be isolated by filtering off the precipitated solids with suction, washing the organic phase with water, subsequently drying it over sodium sulphate
 60 and, finally, drawing off the solvent in a vacuum.
 As examples of the 2-chloroethane-(thiono)-phosphonic acid amide chlorides which can be
 65 used for preparing compounds to be used in

the invention, there are mentioned in particular:

- 2 - chloroethane - phosphonic acid N - methylamide chloride,
 2 - chloroethane - phosphonic acid N - iso - propylamide chloride,
 2 - chloroethane - phosphonic acid anilide chloride,
 2 - chloroethane - thiono - phosphonic acid N - methylamide chloride,
 2 - chloroethane - thiono - phosphonic acid N - iso - propylamide chloride.

The 2 chloroethane - (thiono) - phosphonic acid amide chlorides used as starting materials are not yet known but can readily be prepared by reacting 2 - chloroethane - (thiono) - phosphonic acid dichloride with primary amines in the presence of an inert solvent, such as e.g. benzene, and an acid-binding agent, for example excess amine, at temperatures from -10° to 50°C. Working up may take place according to customary methods (cf. Examples 1 and 2).

The active compounds which can be used according to the invention interfere with the physiological phenomena of plant growth and can therefore be used as plant growth regulators.

The different effects of the active compounds depend essentially on the point in time of the application, with reference to the development stage of the seed or the plant, as well as on the concentrations applied.

Plant growth regulators are used for various purposes which are connected with the development stage of the plant.

Thus, with plant growth regulators the seed dormancy can be broken in order to cause the seeds to germinate at a certain desired time at which the seed itself shows no readiness to germinate. The seed germination itself can be such active compounds, depending on the concentration applied, either be inhibited or promoted. This inhibition or promotion relates to the seedling development.

The bud dormancy of the plants, that is to say the endogenic annual cycle, can be influenced by the active compounds so that, for example, the plants shoot or blossom at a point in time at which they normally show no readiness to shoot or blossom.

The shoot or root growth can be promoted or inhibited by the active compounds in manner dependent on concentration. Thus, it is possible to inhibit very strongly the growth of the fully formed plant, or to bring the plant as a whole to a more robust habitus or to produce a dwarf growth.

Possible economic applications include the suppression of grass growth at roadsides and waysides, and the inhibition of the growth of lawns so that the frequency of grass-cutting (of lawn-mowing) can be reduced.

During the growth of the plant, the branching to the side can also be multiplied by a

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chemical breaking of the apical dominance. This is particularly useful in the case of propagation of plants by cuttings. In concentration-dependent manner, however, it is also possible to inhibit the growth of side-shoots, for example in order to prevent the formation of side-shoots in tobacco plants after decapitation and thus to promote the leaf growth.

In the case of the influencing of blossom formation, there can be achieved, in manner dependent on concentration and the point in time of the application, either a retarding or an acceleration of blossom formation. In certain circumstances, a multiplication of blossom initiation can also be obtained, these effects occurring when the appropriate treatments are carried out at the time of the normal blossom formation.

The influence of the active compounds on the foliage of the plants can be so regulated that defoliation is achieved, for example in order to facilitate the harvest or to reduce transpiration at a time at which the plants are to be transplanted.

Fruit initiation can be promoted so that more fruits or seedless fruits are formed (parthenocarp). In certain conditions, the premature fall of fruit can also be prevented, or the fruit fall can be promoted up to a certain extent in the sense of a chemical thinning out. The property of promoting the fruit fall can also be exploited by effecting the treatment at the time of the harvest, whereby harvesting may be facilitated.

By spraying the unripe fruits with the compounds according to the invention, the ripening process can also be accelerated and a better colouring of the fruits can be achieved.

The active compounds to be used according to the present invention can be converted into the usual formulations, such as solutions, emulsions, suspensions, powders, pastes and granulates. These may be produced in known manner, for example by mixing the active compounds with extenders, that is, liquid or solid diluents or carriers, optionally with the use of surface-active agents, that is, emulsifying agents and/or dispersing agents. In the case of the use of water as an extender, organic solvents can, for example, also be used as auxiliary solvents.

As liquid diluents or carriers, there are preferably used aromatic hydrocarbons, such as xylenes or benzene, chlorinated aromatic hydrocarbons, such as chlorobenzenes, paraffins, such as mineral oil fractions, alcohols such as methanol or butanol, or strongly polar solvents, such as dimethyl formamide or dimethyl sulfoxide, as well as water.

As solid diluents or carriers, there are preferably used ground natural minerals, such as kaolins, clays, talc or chalk, or ground synthetic minerals, such as highly-dispersed silicic acid or silicates.

Preferred examples of emulsifying agents include non-ionic and anionic emulsifiers, such as polyoxyethylene-fatty acid esters, polyoxyethylene-fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkyl sulphonates and aryl sulphonates; and preferred examples of dispersing agents include lignin, sulphite waste liquors and methyl cellulose.

The formulations contain, in general, from 0.1 to 95, preferably 0.5 to 90, per cent by weight of active compound.

The active compounds may be applied as such or in the form of their formulations or of the application form prepared therefrom, such as ready-to-use solutions, emulsifiable concentrates, emulsions, suspensions, spray powders, pastes, soluble powders, dusting agents and granulates. Application may take place in customary manner, for example by watering, squirting, spraying, scattering, dusting, etc.

The concentrations of active compound can be varied within a fairly wide range for actual application. In general, concentrations of 0.0005 to 2% by weight, preferably 0.01 to 0.5%, are used.

Further, there are applied, in general, 0.1 to 100 kg, preferably 1 to 10 kg, of active compound per hectare.

For the application time, it is generally true to say that the application of the growth regulators is desirably effected in a preferred space of time, the precise delimitation of which is governed by the climatic and vegetative circumstances.

The substances according to the invention possess also an activity against plant-damaging bacteria.

The activity of the substances to be used according to the invention can be seen from the following experimental results.

EXAMPLE A

Growth inhibition/linseed test

Solvent: 40 parts by weight acetone

Emulsifier: 0.25 part by weight alkylaryl polyglycol ether

To produce a suitable preparation of active compound 1 part by weight of active compound is mixed with the stated amount of solvent which contains the stated amount of emulsifier, and the concentrate is diluted with a disodium hydrogen phosphate-potassium dihydrogen phosphate buffer solution (pH 6) to the desired concentration.

Two batches of 25 linseeds are each laid out on a filter paper in a Petri dish. 10 ml of the preparation of active compound are pipetted into each dish. Germination of the seeds takes place in the dark at 25°C.

After 3 days, the length of the shoot and the roots is determined and the growth inhibition compared with the control plant is expressed as a percentage. 100% denotes the standstill of growth, and 0% denotes a growth

corresponding to that of the untreated plant. The active compounds and results can be seen from Table A.

TABLE A

Growth inhibition/linseed

Active compound	% inhibition with 250 ppm root	shoot
water (control)	0	0
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{O})(\text{OH})_2$	83	36
(known)		
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{O})(\text{NH}-\text{C}_3\text{H}_7-i)(\text{O}-\text{C}_6\text{H}_5)$	82	96
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{O})(\text{NH}-\text{C}_3\text{H}_7-i)(\text{O}-\text{C}_6\text{H}_4-\text{OH})$	90	80
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{O})(\text{NH}-\text{C}_3\text{H}_7-i)(\text{OH})$	42	53

EXAMPLE B

Growth inhibition and defoliation/beans

Solvent: 40 parts by weight acetone

Emulsifier: 0.25 part by weight alkylaryl
polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amount of solvent which contains the stated amount of emulsifier, and the concentrate is diluted with

a disodium hydrogen phosphate-potassium dihydrogen phosphate buffer solution (pH 6) to the desired concentration.

Beans (*Phaseolus vulgaris*) 10 cm high are sprayed with preparations which contain 5000 ppm of active compound. After 6 days, the average length and the number of leaves of 3 beans per experiment are evaluated.

The active compounds and results can be seen from Table B.

TABLE B

Growth inhibition and defoliation/beans

Active compound	Length in cm	Number of leaves
water (control)	17.0	6
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{O})(\text{OH})_2$ (known)	11.0	4
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{O})(\text{NH}-\text{C}_3\text{H}_7-i)(\text{O}-\text{C}_6\text{H}_5)$	11.0	2
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{O})(\text{NH}-\text{C}_3\text{H}_7-i)(\text{OH})$	11.0	3
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{O})(\text{NH}-\text{CH}_3)(\text{O}-\text{C}_6\text{H}_5)$	11.0	4

EXAMPLE C

Growth inhibition/wheat

Solvent: 40 parts by weight acetone

- 5 Emulsifier: 0.25 part by weight alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active com-

pound is mixed with the stated amount of solvent which contains the stated amount of emulsifier, and the concentrate is diluted with a disodium hydrogen phosphate-potassium dihydrogen phosphate buffer solution (pH 6) to the desired concentration.

Wheat plants of a size of 4 cm are sprayed

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(pH 6)

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with a preparation which contains 5000 ppm of active compound. After 10 days, the average length of the wheat is evaluated. The active compounds and results can be seen from Table C.

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TABLE C

Growth inhibition/wheat

Active compound	Length in cm
water (control)	20.0
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{O})(\text{OH})_2$ (known)	6.5
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{S})(\text{NH}-\text{CH}_3)(\text{O}-\text{C}_6\text{H}_5)$	6.0

EXAMPLE D

Growth inhibition/beans (watering test)

Solvent: 40 parts by weight acetone

- 10 Emulsifier: 0.25 part by weight alkylaryl polyglycol ether

- 15 To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amount of solvent which contains the stated amount of emulsifier, and the concentrate is diluted with a disodium hydrogen phosphate-potassium di-

hydrogen phosphate buffer solution (pH 6) to the desired concentration.

Three bean plants (of a height of 10 cm) in a pot (9 cm diameter) are watered once with a preparation of active compound corresponding to an applied amount of 10 kg/hectare. After 8 days, the length of the beans is determined.

The active compounds and results can be seen from Table D.

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TABLE D

Growth inhibition/beans (watering test)

Active compound	Length in cm
water (control)	25.0
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{O})(\text{OH})_2$ (known)	14.0
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{O})(\text{NH}-\text{C}_3\text{H}_7-i)(\text{O}-\text{C}_6\text{H}_5)$	12.0
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{O})(\text{NH}-\text{C}_3\text{H}_7-i)(\text{OH})$	11.5

EXAMPLE E

Growth inhibition/millet

Solvent: 40 parts by weight acetone

5 Emulsifier: 0.25 part by weight alkylaryl polyglycol ether

10 To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amount of solvent which contains the stated amount of emulsifier, and the concentrate is diluted with

a disodium hydrogen phosphate-potassium dihydrogen phosphate buffer solution (pH 6) to the desired concentration.

Millet plants (*Panicum miliaceum*) of a size of 4 cm are sprayed with a preparation which contains 2000 and 1000 ppm of active compound. After 6 days, the growth increase is evaluated.

The active compounds and results can be seen from Table E.

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TABLE E
Growth inhibition/millet

Active compound	Concentration in ppm	Growth increase in cm
water (control)	0	9.0
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{O})(\text{OH})_2$	2000	2.0
(known)	1000	5.0
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{O})(\text{OH})(\text{NH}-\text{C}_3\text{H}_7-\text{i})$	2000	3.5
	1000	4.0
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{O})(\text{NH}-\text{C}_3\text{H}_7-\text{i})(\text{O}-\text{C}_6\text{H}_4-\text{OH})$	2000	2.0
	1000	4.0

EXAMPLE F

Acceleration of fruit ripeness/tomato plants
Solvent: 40 parts by weight acetone

5 Emulsifier: 0.25 part by weight alkylaryl
polyglycol ether

To produce a suitable preparation of active
compound, 1 part by weight of active compound
is mixed with the stated amount of
10 solvent which contains the stated amount of
emulsifier, and the concentrate is diluted with

a disodium hydrogen phosphate-potassium
dihydrogen phosphate buffer solution (pH 5)
to be desired concentration.

Green, unripe fruits of tomato plants are
15 sprayed once with a preparation which contains
5000 ppm of active compound. An
accelerated ripening of the fruits is thereby
achieved.

The active compounds and results can be
20 seen from Table F.

TABLE F

Acceleration of fruit ripeness/Tomato plants

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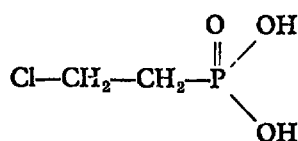
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Active compound

Acceleration of ripeness
in days

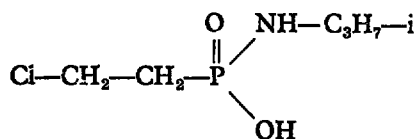
water (control)

0

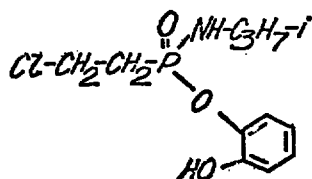


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(known)



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EXAMPLE G

Growth inhibition/linseed

Solvent: 40 parts by weight acetone

5 Emulsifier: 0.25 parts by weight alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amount of solvent which contains the stated amount of emulsifier, and the concentrate is diluted with a disodium hydrogen phosphate/potassium dihydrogen phosphate buffer solution (pH 6) to the desired concentration.

15 Two batches each of 25 linseed are each

laid out on a filter paper in a Petri dish. 10 ml of the preparation of active compound are pipetted into each dish. Germination of the seeds takes place in the dark at 25°C.

After 3 days, the length of the shoot and the roots is determined and the growth inhibition compared with the control plant is expressed as a percentage. 100% denotes the standard of growth, and 0% denotes a growth corresponding to that of the untreated plant.

The active compounds, the concentrations of the active compound in ppm (mg/kg) and results can be seen from the following Table.

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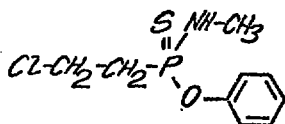
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TABLE G
Growth inhibition/linseed

Active compound	% inhibition of the shoot with	
	50 ppm	250 ppm
water (control)	0	0
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P} \begin{array}{l} \text{O} \text{ OH} \\ \parallel \diagup \\ \text{OH} \end{array}$ (known)	15	36
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P} \begin{array}{l} \text{S} \text{ NH-C}_3\text{H}_7\text{-I} \\ \parallel \diagup \\ \text{O} \text{ } \end{array} \text{O} \text{ } \text{C}_6\text{H}_4 \text{ } \text{Cl}$	33	75
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P} \begin{array}{l} \text{S} \text{ NH-C}_3\text{H}_7\text{-I} \\ \parallel \diagup \\ \text{O} \text{ } \end{array} \text{O} \text{ } \text{C}_6\text{H}_4 \text{ } \text{Cl}$	33	60
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P} \begin{array}{l} \text{S} \text{ NH-C}_4\text{H}_9\text{-n} \\ \parallel \diagup \\ \text{OH} \end{array}$	50	64
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P} \begin{array}{l} \text{O} \text{ NH-C}_4\text{H}_9\text{-n} \\ \parallel \diagup \\ \text{OH} \end{array}$	50	60

The preparation of the compounds to be used according to the invention is illustrated by the following Examples.

EXAMPLE 1



A solution of 19g (0.2 mole) phenol and 20 g (0.2 mole) triethylamine in 100 ml benzene is added dropwise at 50°C, with stirring, to 38.5 g (0.2 mole) 2-chloroethane-

thionophosphonic acid mono-N-methylamide chloride in 200 ml benzene. Stirring is subsequently continued for 2 hours. After suction filtration of the precipitated triethylamine hydrochloride, the benzene solution is washed with 300 ml H₂O, drying is effected over Na₂SO₄, and the solvent is removed in a vacuum. After "slight distillation" at 0.1 mm Hg and 60°C, a pale oil of the refractive index $n_D^{27} = 1.5706$ remains behind. The yield is 35 g (70%) of 2-chloroethanethionophosphonic acid phenyl ether mono-N-methylamide.

Analysis:

Calc. for C₉H₁₁ClNOPS:

Found:

S 12.80 %; N 5.60 %; Cl 14.20 %;
S 12.36 %; N 5.62 %; Cl 14.26 %.

The 2-chloroethanethionophosphonic acid mono-N-methylamide chloride required as starting product is prepared as follows:

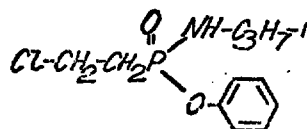
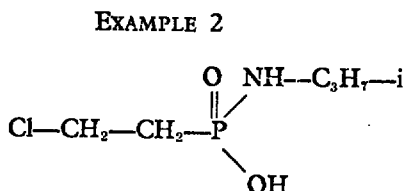
15.5 g (0.5 mole) methylamine in 200 ml toluene are added to 49.5 g (0.25 mole) 2-chloroethanethionophosphonic acid dichloride in 500 ml toluene. Stirring is effected for one hour, the salts are then filtered off with suction; washing with water is effected, followed by drying over sodium sulphate, and the solvent is drawn off. After "slight distillation" at 0.1 mm Hg/80°C a yellow oil remains behind.

Yield: 41 g (85% of the theory); $n_D^{25} = 1.5613$

59 g (1 mole) i-propylamine are added at 0°C to 91 g (0.5 mole) 2-chloroethanephosphonic acid dichloride in 1.5 l of toluene. Stirring is then effected for one hour at room temperature. The salts are filtered off with suction, then washed with a little water, and the solvent is drawn off. After "slight distillation" at 0.01 mmHg/80°C, a yellowish oil remains behind.

Yield: 93 g (91%) $n_D^{25} = 1.4854$

EXAMPLE 3



12 g (0.3 mole) NaOH in 20 ml water are added dropwise at 40°C, with stirring, to 61 g (0.3 mole) 2-chloroethanephosphonic acid mono-N-isopropylamide chloride in 500 ml acetone. Stirring is continued for a further 2 hours at room temperature, suction filtration from precipitated salt is effected and the solvent is subsequently drawn off. There remain behind 53 g (69%) of 2-chloroethanephosphonic acid mono-N-isopropylamide, hygroscopic crystals of m.p. 102—108°C.

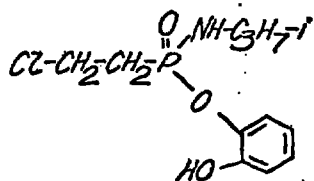
The 2-chloroethanephosphonic acid mono-N-isopropylamide chloride required as starting product is prepared as follows:

61 g (0.3 mole) 2-chloroethanephosphonic acid mono-N-isopropylamide chloride (cf Example 2) are added at 40°C to 28 g (0.3 mole) phenol, 46 g (0.33 mole) potassium carbonate and 500 ml acetonitrile. Stirring is then effected for 2 hours at 60°C, suction filtration from the solid is effected, the solvent is drawn off in a vacuum and the residue is taken up in methylene chloride. The organic phase is washed with water dried over sodium sulphate, and the solvent is drawn off. "Slight distillation" is effected at 0.1 mmHg and 80°C. 31 g (40%) of 2-chloroethanephosphonic acid phenyl ester mono-N-isopropylamide remain behind as pale oil, $n_D^{27} = 1.5144$.

Analysis:

calc. for C₁₁H₁₇ClNO₂P: P 11.9 %, Cl 13.60 %;
found. P 12.5 %, Cl 12.03%.

EXAMPLE 4



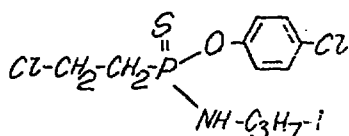
30 g (0.3 mole) triethylamine are added at room temperature to 500 ml benzene, 61 g (0.3 mole) 2-chloroethanephosphonic acid

mono-N-isopropylamide chloride (cf. Example 2) and 33 g (0.3 mole) catechol. Stirring is then effected for 2 hours at room temperature; suction filtration from precipitated salts is effected, followed by washing with a little water (about 100 ml) and drying over sodium sulphate. The solvent is subsequently drawn off and, finally, "slight distillation" is effected at 0.01 mmHg and 60°C. A pale oil remains behind. Yield: 48 g (58%) of 2-chloroethanephosphonic acid 2'-hydroxyphenyl ester mono-N-isopropylamide; $n_D^{27} = 1.5344$.

Analysis:

20 calcd: for $C_{11}H_{17}ClNO_3P$: N 5.03 %, Cl 12.8%;
found: N 5.22 %, Cl 11.0%.

EXAMPLE 5



24 g (0.4 mole) isopropylamine are added to 58 g (0.2 mole) 2-chloroethanethionophos-

phonic acid 4'-chlorophenyl ester chloride in 300 ml benzene. Stirring is then effected for two hours at room temperature; the salts are subsequently filtered off with suction, followed by washing with water, and, after drying with sodium sulphate, the solvent is drawn off. The residue is "slightly distilled". There remains behind a pale oil, $n_D^{24} = 1.5705$, yield: 54 g (86% of the theory) 2-chloroethanethionophosphonic acid 4'-chlorophenyl ester N-monoisopropylamide.

Analysis:

Calculated for $C_{11}H_{16}Cl_2NOPS$:
Found:

22.70 % Cl 4.50 % N 10.25 % S
23.15 % Cl 4.02 % N 10.27 % S

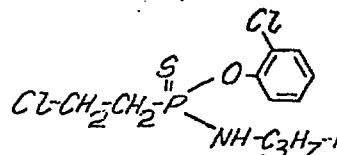
40 The starting product used is prepared as follows:

A solution of 65 g (0.5 mole) 4-chlorophenol and 20 g (0.5 mole) sodium hydroxide in 200 ml water is added to 99 g (0.5 mole) 2-chloroethanethionophosphonic acid dichloride. 45 Stirring is then effected for one hour at room temperature, followed by taking up in methylene chloride and separation of the aqueous phase. After washing with water and 50 drying with sodium sulphate, the solvent is drawn off and slight distillation is effected. Yield: 86 g (59% of the theory) 2-chloroethanethionophosphonic acid 4'-chlorophenyl ester chloride, $n_D^{23} = 1.5856$.

55 Analogously with Example 5, the following compounds are prepared:

thiono-phosphonic acid 4'-methyl-phenyl ester N-mono-isopropylamide, $n_D^{24} = 1.5542$. The starting product 2-chloroethane-thiono-phosphonic acid 4'-methyl-phenyl ester chloride is obtained analogously with Example 5 in a yield of 64%, $n_D^{24} = 1.5686$.

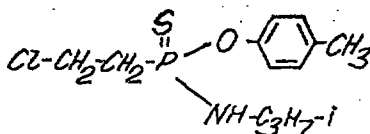
EXAMPLE 7



Yield: 66% 2-chloroethane-thiono-phosphonic acid 2'-chlorophenyl ester N-mono-isopropylamide, $n_D^{24} = 1.5687$

Starting product: 2-chloroethane-thiono-phosphonic acid 2'-chlorophenyl ester chloride, Yield: 66%, $n_D^{24} = 1.5862$.

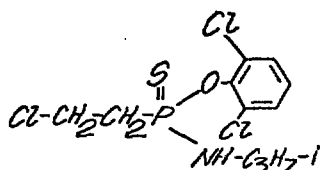
EXAMPLE 6



Yield: 76% of the theory 2-chloroethane-

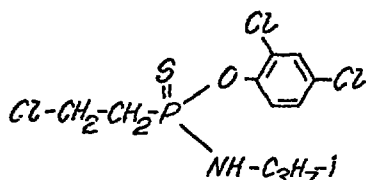
Example
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EXAMPLE 8



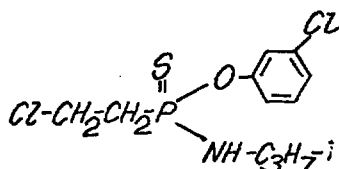
Yield: 53% 2-chloroethane-thiono-phosphonic acid 2', 6'-dichlorophenyl ester -N-mono-isopropylamide, melting point 101°C. Starting product: 2 - chloroethane - thionophosphonic acid 2',6'-dichloro-phenyl ester chloride, yield: 53%, n_D^{24} : 1.5944.

EXAMPLE 9



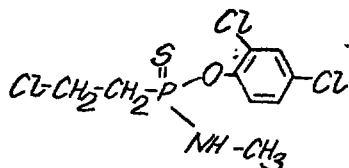
Yield: 73% 2-chloroethane-thiono-phosphonic acid 2',4'-dichloro-phenyl ester N-mono-isopropylamide, n_D^{24} : 1.5790. Starting product: 2-chloroethane-thiono-phosphonic acid 2', 4'-dichloro-phenyl ester chloride, yield: 60%, n_D^{20} : 1.5962.

EXAMPLE 10



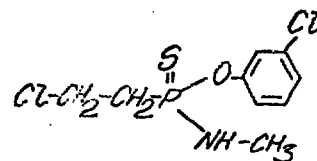
Yield: 84% 2-chloroethane-thiono-phosphonic acid 3'-chlorophenyl ester N-mono-isopropylamide, n_D^{24} : 1.5668. Starting product: 2-chloroethane-thiono-phosphonic acid 3'-chlorophenyl ester chloride, yield: 73%, n_D^{24} : 1.5851.

EXAMPLE 11



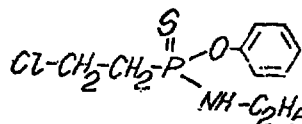
Yield: 66% 2-chloroethane-thiono-phosphonic acid 2',4'-dichloro-phenyl ester N-mono-methylamide, n_D^{24} : 1.5900. Starting product compare Example 9.

EXAMPLE 12



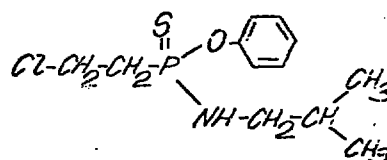
Yield: 79% 2-chloroethane-thiono-phosphonic acid 3'-chlorophenyl ester N-mono-methylamide, n_D^{24} : 1.5840. Starting product: compare Example 10.

EXAMPLE 13



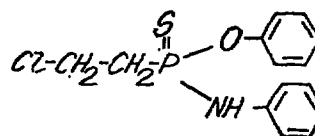
Yield: 81% 2-chloroethane-thiono-phosphonic acid phenyl ester N-mono-ethylamide, n_D^{24} : 1.5626. Starting product: 2-chloroethane-thiono-phosphonic acid phenyl ester chloride, yield: 77%, n_D^{28} : 1.5688.

EXAMPLE 14



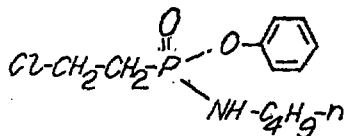
Yield: 87% 2-chloroethane-thiono-phosphonic acid phenyl ester N-mono-isobutylamide, n_D^{24} : 1.5511. Starting product: compare Example 13.

EXAMPLE 15



Yield: 55% 2-chloroethane-thiono-phosphonic acid phenyl ester N-mono-phenylamide, melting point: 60-62°C. Starting product: compare Example 13.

EXAMPLE 16



19 g (0.2 mole) phenol are added to 44 g (0.2 mole) 2-chloroethanephosphonic acid N-

Analysis:

Calculated for $\text{C}_{12}\text{H}_{19}\text{ClNO}_2\text{P}$:

Found:

12.90 % Cl 5.10 % N

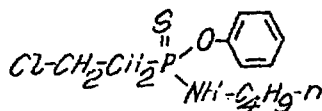
12.16 % Cl 5.35 % N

The 2-chloroethanephosphonic acid N-mono-n-butylamide chloride used as starting product is prepared as follows:

73 g (1 mole) n-butylamine are added to 91 g (0.5 mole) 2-chloroethanephosphonic acid dichloride in 1500 ml toluene. Stirring is then effected for two hours at room temperature, the salts are filtered off with suction, and, after washing with water and drying with sodium sulphate, the solvent is drawn off. After "slight distillation", a colourless oil remains behind, yield: 75 g (69% of the theory) 2-chloroethanephosphonic acid N-mono-n-butylamide chloride, n_D^{25} : 1.4962.

The following compounds are prepared in a manner analogous to that of Example 16.

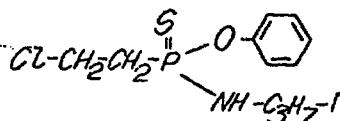
EXAMPLE 17



Yield: 70% 2-chloroethane-thiono-phosphonic acid phenyl ester N-mono-n-butylamide, n_D^{25} : 1.5479.

Starting product: 2-chloroethane-thiono-phosphonic acid N-mono-n-butylamide chloride from 2-chloroethane-thiono-phosphonic acid dichloride and n-butylamine, yield: 90%, n_D^{25} : 1.5363.

EXAMPLE 18

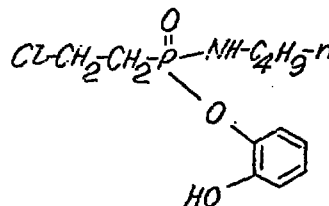


Yield: 43% 2-chloroethane-thiono-phosphonic phenyl ester N-mono-isopropylamide, n_D^{24} : 1.5611.

mono-n-butylamide chloride in 400 ml benzene. 21 g (0.2 mole) triethylamine are subsequently added dropwise at room temperature and stirring is effected for one hour. The salts are filtered off with suction; washing with water is effected, followed by drying with sodium sulphate, and the solvent is drawn off. After "slight distillation", a pale oil remains behind, yield: 24 g (44% of the theory) 2-chloroethanephosphonic acid phenyl ester N-mono-n-butylamide, n_D^{25} : 1.5160.

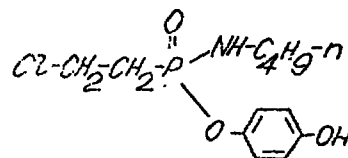
Starting product: 2-chloroethane-thiono-phosphonic acid N-mono-isopropylamide chloride, yield: 87%, n_D^{26} : 1.5476.

EXAMPLE 19



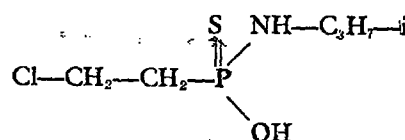
Yield: 35% 2-chloroethane-phosphonic acid 2'-hydroxy-phenyl ester N-mono-n-butylamide, n_D^{24} : 1.5273. Starting product: compare Example 16.

EXAMPLE 20



Yield: 32% 2-chloroethane-phosphonic acid 4'-hydroxy-phenyl ester N-mono-n-butylamide, n_D^{24} : 1.5241. Starting product: compare Example 16.

EXAMPLE 21



A solution of 5.5 g (0.3 mole) of water and 30 g (0.3 mole) triethylamine in 20 ml acetone

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is added at room temperature to 66 g (0.3 mole) 2-chloroethanethionophosphonic acid N-monoisopropylamide chloride in 100 ml benzene. Stirring is then effected for one hour, the precipitated salt is removed and the sol-

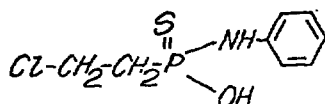
vent is drawn off. After "slight distillation", a pale oil remains behind. Yield: 54 g (89% of the theory) 2-chloroethanethiophosphonic acid N-monoisopropylamide, n_D^{25} : 1.5419.

Analysis:

Calculated for $C_5H_9ClNOPS$: 17.65 % Cl 6.95 % N
Found: 17.43 % Cl 6.49 % N

Starting product: compare Example 18.
Analogously with Example 21, the following compounds are prepared:

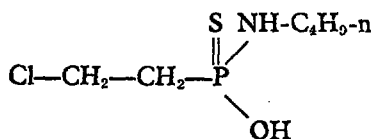
EXAMPLE 22



Yield: 92% 2-chloroethane-thiono-phosphonic acid-N-mono-phenylamide, n_D^{24} : 1.5662.

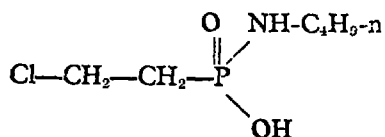
Starting product: 2-chloroethane-thiono-phosphonic acid N-mono-phenylamide chloride from 2-chloroethane-thiono-phosphonic acid dichloride and aniline, yield: 79%, n_D^{23} : 1.6145.

EXAMPLE 23



Yield: 93% 2-chloroethane-thiono-phosphonic acid N-mono-n-butylamide, n_D^{24} : 1.5402.
Starting product: cf. Example 17.

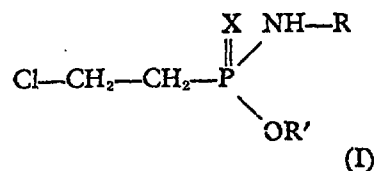
EXAMPLE 24



Yield: 61% 2-chloroethane-phosphonic acid N-mono-n-butylamide, n_D^{24} : 1.4884. Starting product: compare Example 16.

WHAT WE CLAIM IS:—

1. A method for the control of vascular plant growth which comprises applying to the plant or seed thereof a 2-chloroethane-(thiono)-phosphonic acid amido compound of the general formula



in which

X stands for an oxygen or sulphur atom, R denotes a lower alkyl radical with 1 to 6 carbon atoms or a phenyl radical, and R' denotes a hydrogen atom, an alkali metal equivalent, an alkaline earth metal equivalent, an ammonium equivalent or a phenyl radical which may be substituted by nitro, halogen, alkyl or hydroxy, either alone or in admixture with a solid or liquid diluent or carrier.

2. A method for the control of vascular plant growth which comprises applying to the plant or seed thereof a compound as defined in claim 1 in which R is an alkyl radical with 1 to 4 carbon atoms or a phenyl radical and R' is a hydrogen atom or a phenyl radical which may be substituted by nitro, methyl, hydroxy or chlorine, alone or in admixture with a solid or liquid diluent or carrier.

3. A method for the control of vascular plant growth which comprises applying to the plant or seed thereof a 2-chloro-ethane-(thiono)-phosphonic acid amido compound which is hereinbefore specifically identified, alone or in admixture with a solid or liquid diluent or carrier.

4. A method according to any of claims 1—3 in which a composition is used containing from 0.0005 to 2% by weight of the stated compound.

5. A method according to claim 4 in which a composition is used containing from 0.01 to 0.5% by weight of the stated compound.

6. A method according to any of claims 1—5 in which from 0.1 to 100 kg of the stated compound are applied per hectare.

7. A method according to claim 6 in which from 1 to 10 kg of the stated compound is used per hectare.

8. A method according to claim 1 substantially as hereinbefore described.

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is added at room temperature to 66 g (0.3 mole) 2-chloroethanethionophosphonic acid N-monoisopropylamide chloride in 100 ml benzene. Stirring is then effected for one hour, the precipitated salt is removed and the sol-

vent is drawn off. After "slight distillation", a pale oil remains behind. Yield: 54 g (89% of the theory) 2-chloroethanethiophosphonic acid N-monoisopropylamide, n_D^{25} : 1.5419.

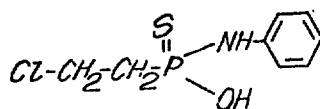
10 Analysis:

Calculated for $C_5H_{11}ClNOPS$:
Found:

17.65 % Cl 6.95 % N
17.43 % Cl 6.49 % N

Starting product: compare Example 18.
Analogously with Example 21, the following compounds are prepared:

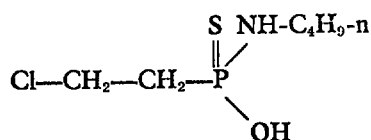
EXAMPLE 22



Yield: 92% 2-chloroethane-thiono-phosphonic acid-N-mono-phenylamide, n_D^{24} : 1.5662.

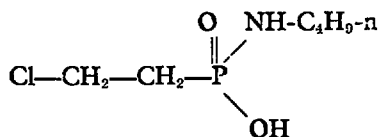
20 Starting product: 2-chloroethane-thiono-phosphonic acid N-mono-phenylamide chloride from 2-chloroethane-thiono-phosphonic acid dichloride and aniline, yield: 79%, n_D^{25} : 1.6145.

EXAMPLE 23



Yield: 93% 2-chloroethane-thiono-phosphonic acid N-mono-n-butylamide, n_D^{24} : 1.5402.
Starting product: cf. Example 17.

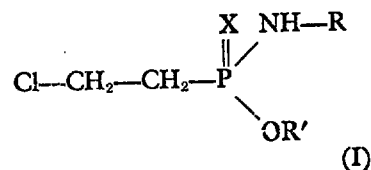
EXAMPLE 24



Yield: 61% 2-chloroethane-phosphonic acid N-mono-n-butylamide, n_D^{24} : 1.4884. Starting product: compare Example 16.

WHAT WE CLAIM IS:—

1. A method for the control of vascular plant growth which comprises applying to the plant or seed thereof a 2-chloroethane-(thiono)-phosphonic acid amido compound of the general formula



in which

X stands for an oxygen or sulphur atom, R denotes a lower alkyl radical with 1 to 6 carbon atoms or a phenyl radical, and R' denotes a hydrogen atom, an alkali metal equivalent, an alkaline earth metal equivalent, an ammonium equivalent or a phenyl radical which may be substituted by nitro, halogen, alkyl or hydroxy, either alone or in admixture with a solid or liquid diluent or carrier.

2. A method for the control of vascular plant growth which comprises applying to the plant or seed thereof a compound as defined in claim 1 in which R is an alkyl radical with 1 to 4 carbon atoms or a phenyl radical and R' is a hydrogen atom or a phenyl radical which may be substituted by nitro, methyl, hydroxy or chlorine, alone or in admixture with a solid or liquid diluent or carrier.

3. A method for the control of vascular plant growth which comprises applying to the plant or seed thereof a 2-chloro-ethane-(thiono)-phosphonic acid amido compound which is hereinbefore specifically identified, alone or in admixture with a solid or liquid diluent or carrier.

4. A method according to any of claims 1—3 in which a composition is used containing from 0.0005 to 2% by weight of the stated compound.

5. A method according to claim 4 in which a composition is used containing from 0.01 to 0.5% by weight of the stated compound.

6. A method according to any of claims 1—5 in which from 0.1 to 100 kg of the stated compound are applied per hectare.

7. A method according to claim 6 in which from 1 to 10 kg of the stated compound is used per hectare.

8. A method according to claim 1 substantially as hereinbefore described.



* C L M S *

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