

PATENT SPECIFICATION

(11) 1 274 350

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NO DRAWINGS

- (21) Application No. 47009/70 (22) Filed 2 Oct. 1970
 (31) Convention Application No. P 19 50 099.3
 (32) Filed 4 Oct. 1969
 (31) Convention Application No. P 19 50 099.3
 (32) Filed 28 Jan. 1970 in
 (33) Germany (DT)
 (45) Complete Specification published 17 May 1972
 (51) International Classification C07F 9/28; A01N 5/00
 (52) Index at acceptance
 C2P 1L1 2E11A 2E12B 2E18A 2E18B 2E26D 2J 2L12B
 2L18A 2L18B 2L26D 3B12B 3B18A 3B18B 3B18C
 3B19D 3B21 3C12B 3C18A 3C18B 3C18C 3C19F
 3C21
 C1B 3F1 3FX
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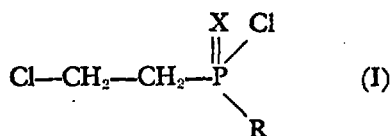
(54) 2-CHLOROETHANE-(THIONO)-PHOSPHONIC ACID DERIVATIVES, PROCESS FOR THEIR PREPARATION, AND THEIR USE FOR THE REGULATION OF PLANT GROWTH

(71) We, FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT, 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:—

10 The present invention relates to certain new 2 - chloroethane - (thiono) - phosphonic acid derivatives, to a process for their preparation and to their use as agents for regulating plant growth.

15 It is known (cf. Dutch Patent Specification 6802633) that 2-chloroethanephosphonic acid exhibits plant-growth-regulating properties.

20 The present invention provides 2 - chloroethane - (thiono) - phosphonic acid derivatives of the general formula



in which

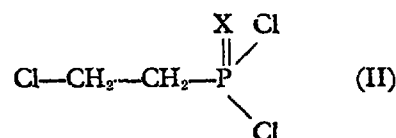
X stands for an oxygen or sulphur atom, and

25 R stands for an aryloxy radical which may be substituted by hydroxy, alkyl, halogen or nitro groups or for a monoaryl-amino radical or a mono-alkylamino radical with 1 to 6 carbon atoms.

30 Such compounds exhibit strong plant-growth-regulating properties.

[Price 25p]

The invention also provides a process for the production of a 2 - chloroethane - (thiono)-phosphonic acid derivative of the formula (I) in which a 2 - chloroethane - (thiono)-phosphonic acid dichloride of the general formula



in which

X has the meaning stated above, is reacted with a phenol or primary amine of the general formula



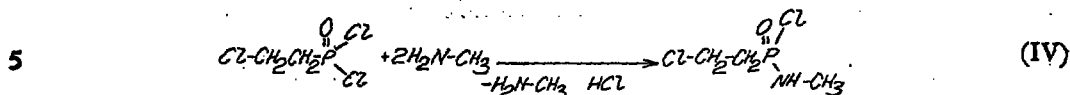
in which

R has the meaning stated above (in the case of a phenol, this may be used in the form of its alkali metal, alkaline earth metal or ammonium salt), optionally (when the amine or free phenol is used) in the presence of an acid-binding agent and optionally in the presence of a solvent.

Surprisingly, the 2-chloroethane-(thiono)-phosphonic acid derivatives according to the invention show a noteworthy greater plant-growth-regulating activity than the 2-chloroethane-phosphonic 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 therefore represent a valuable enrichment of the art.

If 2-chloroethanephosphonic acid dichloride and methylamine are used as starting mater-

ials, the reaction course can be represented by the following formula scheme:



The starting materials are defined generally by the formulae (II) and (III).

R stands preferably for a phenyloxy radical which is unsubstituted or substituted by nitro, methyl, hydroxyl and/or chlorine, for a monophenylamino radical, or for a mono-alkylamino radical with 1 to 4 carbon atoms.

As examples of the amines or phenols which can be used according to the invention, there may be mentioned in particular: phenylamine, methylamine, ethylamine, n-propylamine, iso-propylamine, and n-, sec-, tert- and iso-butylamine; 2-, 3- and 4-chlorophenol, 2-, 3- and 4-nitrophenol, 2-, 3- and 4-methylphenol and resorcinol, catechol and hydroquinone.

The 2-chloroethane-(thiono)-phosphonic acid dichlorides, the primary amines and the phenols which may be used as starting materials are generally known and can be prepared according to known methods.

The solvent (this term includes a mere diluent) which may be used in the process according to the invention may for example be water or an inert organic solvent. Preferred examples include aliphatic and aromatic hydrocarbons (which may be chlorinated), such as benzene, toluene, xylene, benzine, methylene chloride, chloroform, carbon tetrachloride and chlorobenzene; ethers, such as diethyl ether, dibutyl ether and dioxan; ketones, such as acetone, methylethyl ketone, methylisopropyl ketone and methylisobutyl ketone; and nitriles, such as acetonitrile.

As acid acceptors, all customary acid-binding agents are suitable. Particularly suitable have proved to be the alkali metal carbonates and alcoholates, such as sodium or potassium carbonate, or sodium or potassium methylate or ethylate; and aliphatic, aromatic or heterocyclic amines, for example triethylamine, dimethylamine, dimethylaniline, dimethylbenzylamine and pyridine. Preferably an excess (for example of about one mole equivalent) of the amine of the general formula (III) to be used is employed as acid-binder.

The reaction temperature can be varied within a fairly wide range. In general, the reaction is carried out at -10° to 50° , preferably at 0° to 20°C .

The reactions are, in general, carried out at normal pressure.

When carrying out the process according to the invention, 2 moles of primary amine or 1 mole of phenol and about 1 mole of acid-binder or 1 mole of alkali metal phenol-

ate, alkaline earth metal phenolate or ammonium phenolate may generally be used per mole of 2-chloroethane-(thiono)-phosphonic acid dichloride. As indicated above, the reaction may be carried out in water or another suitable solvent, in most cases at room temperature.

Working up may take place according to customary methods. The substances according to the invention are obtained in most cases in the form of colourless to slightly yellow-coloured, viscous, water-insoluble oils, which cannot be distilled without decomposition but can, by so-called "slight distillation" (that is, longer heating to moderately elevated temperatures under reduced pressure), be freed from the last volatile components and in this way be purified. They may be characterised especially by their refractive index as well as their elementary analysis.

The chloroethane-(thiono)-phosphonic acid derivatives interfere with the physiological phenomena of plant growth and can therefore be used as plant growth regulators.

The different effects of these active compounds depends 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 plants. Thus, with plant growth regulators, the seed germination can, 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 the plants for example 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 branch-

- ing to the side can be multiplied by a 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 attained, these effects occurring when the appropriate treatments are carried out at the time of the normal blossom formation.
- The influence of the active compound on the foliage of the plants can be so regulated that a 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 (parthenocarpy). 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 promotion of 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 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 sulphoxide, 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 nonionic 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 forms 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 the usual manner, for example by watering, squirting, spraying, scattering or dusting.
- 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 effected in a preferred space of time, the precise delimitation of which is governed by the climatic and vegetative circumstances.
- The compounds according to the invention also have an activity against plant-damaging bacteria.
- The invention therefore also provides a composition for the control of plant growth containing as active ingredient a compound according to the invention in admixture with a solid diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.
- The invention also provides a method for influencing plant growth which comprises applying to the growing plant or plant seed a compound according to the invention alone or in the form of a composition containing as active ingredient a compound according to the invention in admixture with a solid or liquid diluent or carrier.
- The invention is illustrated by the following Examples.
- 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.

- 5 Two batches each 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.
- 10 After three 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, the concentrations of the active compounds in ppm (=mg/kg) and results can be seen from Tables A1 and A2.

15

20

TABLE A1.
Growth inhibition/linseed

Active compound	% inhibition with 250 ppm	
	root	shoot
water (control)	0	0
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P} \begin{array}{l} \text{O} \quad \text{OH} \\ \parallel \quad / \\ \text{OH} \end{array}$ (1)	83	36
(known)		
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P} \begin{array}{l} \text{O} \quad \text{NH}-\text{C}_3\text{H}_7-i \\ \parallel \quad / \\ \text{Cl} \end{array}$ (2)	85	55

TABLE A2

Growth inhibition/linseed

Active compound	% inhibition of the shoot with	
	50 ppm	250 ppm
water (control)	0	0
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{O})(\text{OH})_2$ (known) (1)	15	36
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{S})(\text{NH}-\text{C}_3\text{H}_7)_2$ (3)	40	54
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{S})(\text{Cl})_2$ (4)	25	50

EXAMPLE B

Growth inhibition and defoliation/beans

Solvent: 40 parts by weight acetone

5 Emulsifier: 0.25 parts 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.

15 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.

20 The 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
2-chloroethane-phosphonic acid (known)		11.0	4
$\begin{array}{c} \text{S} \quad \text{NH-CH}_3 \\ \parallel \quad / \\ \text{Cl-CH}_2\text{-CH}_2\text{-P} \\ \quad \quad \backslash \\ \quad \quad \text{Cl} \end{array}$	(5)	11.0	3
$\begin{array}{c} \text{O} \quad \text{NH-C}_8\text{H}_7\text{-i} \\ \parallel \quad / \\ \text{Cl-CH}_2\text{-CH}_2\text{-P} \\ \quad \quad \backslash \\ \quad \quad \text{Cl} \end{array}$	(2)	11.0	3
$\begin{array}{c} \text{S} \quad \text{O-C}_6\text{H}_5 \\ \parallel \quad / \\ \text{Cl-CH}_2\text{-CH}_2\text{-P} \\ \quad \quad \backslash \\ \quad \quad \text{Cl} \end{array}$	(6)	11.5	0

EXAMPLE C

Growth inhibition/wheat

Solvent: 40 parts by weight acetone

- 5 Emulsifier: 0.25 parts 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.

Wheat plants of a size of 4 cm are sprayed with a preparation which contains 5000 ppm of active compound. After 10 days, the average length of the wheat is evaluated.

The results can be seen from Table C.

15

TABLE C

Growth inhibition/wheat

Active compound	Length in cm
water (control)	20.0
2-chloroethane-phosphonic acid (known)	6.5
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{S})(\text{NH}-\text{CH}_3)\text{Cl}$ (5)	6.0
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{S})(\text{O}-\text{C}_6\text{H}_5)\text{Cl}$ (6)	5.0

EXAMPLE D

Growth inhibition/beans (watering test)

Solvent: 40 parts by weight acetone

- 5 Emulsifier: 0.25 parts 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.

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 results can be seen from Table D.

TABLE D

Growth inhibition/beans (watering test)

Active compound	Length in cm
water (control)	25.0
2-chloroethane-phosphonic acid (known)	14.0
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{S})(\text{NH}-\text{CH}_3)\text{Cl}$ (5)	14.0
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{O})(\text{NH}-\text{C}_6\text{H}_7-\text{i})\text{Cl}$ (2)	11.5

EXAMPLE E

Growth inhibition/millet

Solvent: 40 parts by weight acetone

Emulsifier: 0.25 parts by weight alkylaryl polyglycol ether

5

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

10

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

Millet plants (*Panicum milliaceum*) 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.

15

The results can be seen from Table E.

TABLE E

Growth inhibition/millet

Active compound	Concentration in ppm	Growth increase in cm
water (control)	0	9.0
2-chloroethane-phosphonic acid	2000	2.0
(known)	1000	5.0
$\begin{array}{c} \text{S} \quad \text{NH}-\text{CH}_3 \\ \parallel \quad \diagup \\ \text{Cl}-\text{CH}_2-\text{CH}_2-\text{P} \\ \quad \quad \quad \diagdown \\ \quad \quad \quad \text{Cl} \end{array} \quad (5)$	2000	1.0
	1000	4.0

EXAMPLE F

Acceleration of fruit ripeness/tomato plants

Solvent: 40 parts by weight acetone

Emulsifier: 0.25 parts by weight alkylaryl polyglycol ether

25

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

30

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

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

35

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

40

TABLE F

Acceleration of fruit ripeness/tomato plants

Active compound	Acceleration of ripeness in days
water (control)	0
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P} \begin{array}{l} \text{O} \text{ OH} \\ \parallel \diagup \\ \text{OH} \end{array}$ (1)	12
(known)	
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P} \begin{array}{l} \text{S} \text{ NH}-\text{CH}_3 \\ \parallel \diagup \\ \text{Cl} \end{array}$ (5)	15
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P} \begin{array}{l} \text{O} \text{ NH}-\text{C}_3\text{H}_7-i \\ \parallel \diagup \\ \text{Cl} \end{array}$ (2)	17
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P} \begin{array}{l} \text{S} \text{ O}-\text{C}_6\text{H}_5 \\ \parallel \diagup \\ \text{Cl} \end{array}$ (6)	14
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P} \begin{array}{l} \text{S} \text{ NH}-\text{C}_3\text{H}_7-i \\ \parallel \diagup \\ \text{Cl} \end{array}$ (3)	15

EXAMPLE G

Growth inhibition/beans

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 di-

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

Beans (*Phaseolus*) 10 cm high are sprayed with preparations which contain 2500 ppm of active compound. After 6 days, the average length is determined and the inhibition of growth increase in comparison with the untreated control is expressed in %.

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

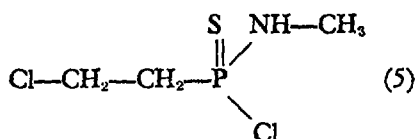
15

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TABLE G
Growth inhibition/beans

Active compound		% inhibition of the shoot with 2500 ppm
water (control)		0
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{O})(\text{OH})_2$	(1)	52
(known)		
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{O})(\text{NH}-\text{C}_2\text{H}_5)_2$	(8)	63
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{S})(\text{Cl})_2$	(9)	55
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{S})(\text{Cl})(\text{O}-\text{C}_6\text{H}_4\text{CH}_3)$	(10)	63
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{S})(\text{Cl})(\text{O}-\text{C}_6\text{H}_3\text{Cl}_2)$	(11)	68

EXAMPLE 1



5 15.5 g (0.5 mole) methylamine in 200 ml toluene are added to 49.5 g (0.25 mole) 2-chloroethanethionophosphonic acid dichloride

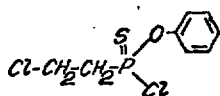
in 500 ml toluene. Stirring is effected for one hour at room temperature, then the salts are filtered off with suction; washing with water is effected, followed by drying over sodium sulphate, and the solvent is drawn off. After "slight distillation" at 0.01 mm Hg/80°C, a yellow oil remains behind.

Yield: 41 g (85%) of 2-chloroethanethionophosphonic acid mono - N - methylamide 15 chloride, $n_D^{25} = 1.5613$.

Analysis:

Calculated for $\text{C}_3\text{H}_8\text{Cl}_2\text{NPS}$: S 16.65 N 7.3%
Found: 16.47, 7.35

EXAMPLE 2



(6)

19 g (0.2 mole) phenol in 50 ml H₂O and
8 g (0.2 mole) sodium hydroxide are added
5 at 20°C to 39.5 g (0.2 mole) 2-chloroethane-

thionophosphonic acid dichloride. Stirring is
effected for 2 hours at room temperature;
taking up in methylene chloride is then
effected, followed by separation of the organic
phase and washing with water. After drying
over sodium sulphate, the solvent is drawn
off, and "slight distillation" is subsequently
effected (1 mm Hg/60°C).

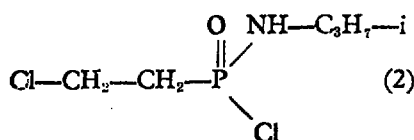
Yield 39 g (77%) of 2-chloroethane-thiono-
phosphonic acid phenyl ester chloride as
15 colourless liqued, $n_D^{25}=1.5688$.

Analysis:

Calculated for C ₈ H ₉ Cl ₂ OPS:	S 12.55	Cl 27.9%
Found	12.46	28.82

20

EXAMPLE 3



(2)

59 g (1 mole) i-propylamine are added at

0°C to 91 g (0.5 mole) 2-chloroethanephos-
phonic acid dichloride in 1500 ml toluene.
Stirring is effected for 1 hour at room tem-
perature, and the salts are filtered off with
suction; the solution is washed with a little
water, and the solvent is distilled off.

Yield 93 g (91%) of 2-chloroethanephos-
phonic acid mono-N-isopropylamide chloride;
30 $n_D^{25}=1.4854$.

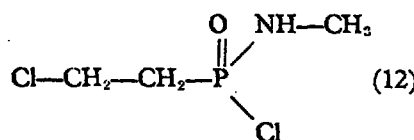
Analysis:

Calculated for C ₅ H ₁₂ Cl ₂ NOP:	N 6.85	Cl 34.8%
Found:	6.58	33.74

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EXAMPLE 4

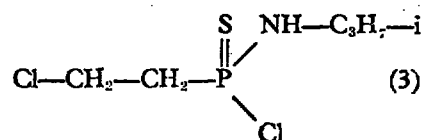
Analogously with Example 3, there is pre-
pared the compound of the formula:



(12)

40 Yield: 56% 2 - chloroethane - phosphonic
acid mono - N - methylamide chloride,
 $n_D^{25}=1.5019$

EXAMPLE 5



(3)

59 g (1 mole) i-propylamine are added,
with cooling, to 99 g (0.5 mole) 2-chloro-
ethanethionophosphonic acid dichloride in
1500 ml toluene. Stirring is effected for one
hour at room temperature, then the salts are
filtered off with suction; washing with water
is effected, followed by drying over sodium
sulphate, and the solvent is drawn off. After
"slight distillation", a pale oil remains behind.
Yield: 85 g=87% of the theory 2-chloro-
ethanethionophosphonic acid mono - N - iso-
propylamide chloride, $n_D^{25}: 1.5476$.

Analysis:

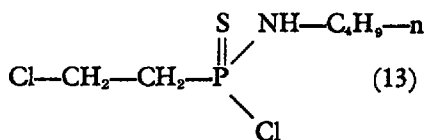
Calculated for C ₅ H ₁₂ Cl ₂ NPS:	32.15%	Cl 6.35%	N 14.55%	S
Found:	31.74%	Cl 5.85%	N 14.94%	S

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EXAMPLE 6

Analogously with Example 5, there is prepared the compound of the formula:



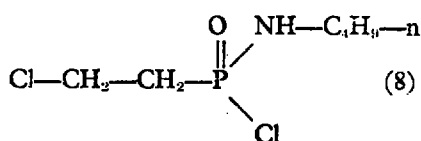
- 5 Yield: 91% 2-chloroethane-thiono-phosphonic acid mono-N-n-butylamide chloride, n_D^{25} : 1.5363.

Analysis:

25

Calculated for $\text{C}_8\text{H}_{10}\text{Cl}_2\text{NPS}$: 28.00% Cl 5.50% N 12.60% S
 Found: 28.00% Cl 5.32% N 12.62% S

EXAMPLE 8



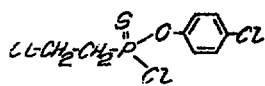
73 g (1 mole) n-butylamine are added, with cooling, to 91 g (0.5 mole) 2-chloroethane-

40

Analysis:

Calculated for $\text{C}_8\text{H}_{14}\text{Cl}_2\text{NOP}$: 32.60% Cl 6.42% N
 Found: 32.38% Cl 6.52% N

EXAMPLE 9

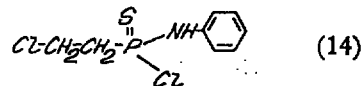


- 45 A solution of 65 g (0.5 mole) 4-chlorophenol and 20 g (0.5 mole) sodium hydroxide in 200 ml of water is added at 20°C, with vigorous stirring, to 99 g (0.5 mole) 2-chloro-

Analysis:

Calculated for $\text{C}_8\text{H}_8\text{Cl}_3\text{OPS}$: 36.80% Cl 11.05% S
 Found: 35.83% Cl 10.64% S

EXAMPLE 7



93 g (1 mole) aniline are added at 0°C, with cooling, to 99 g (0.5 mole) 2-chloroethanethionophosphonic acid dichloride in 1000 ml acetonitrile. Stirring is effected for two hours at room temperature, then the solvent is drawn off; taking up in benzene is effected, followed by separation of the salts and washing with 1N hydrochloric acid. After drying with sodium sulphate, the solvent is drawn off and the residue is "slightly distilled". Yield: 101 g (79% of the theory) of 2-chloroethanethionophosphonic acid anilide chloride, n_D^{25} : 1.6145.

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phosphonic acid dichloride in 1500 ml toluene. Stirring is effected for two hours at room temperature. then 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: 75 g (69% of the theory) of 2-chloroethanephosphonic acid mono-N-n-butylamide chloride, n_D^{25} : 1.4962.

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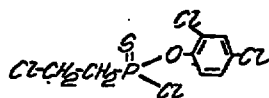
55

60

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Analogously with Example 9, there are prepared the compounds of the following Examples 10—16.

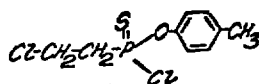
EXAMPLE 10



(16)

Yield: 60% 2 - chloroethane - thiono - phosphonic acid 2',4'-dichlorophenyl ester chloride, n_D^{20} : 1.5962.

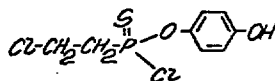
EXAMPLE 11



(9)

Yield: 64% 2 - chloroethane - thiono - phosphonic acid 4' - methylphenyl ester chloride, n_D^{21} : 1.5686.

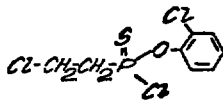
EXAMPLE 12



(17)

Yield: 58% 2 - chloroethane - thiono - phosphonic acid 4' - hydroxyphenyl ester chloride, n_D^{24} : 1.6031.

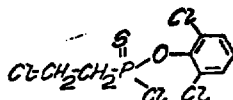
EXAMPLE 13



(10)

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

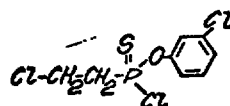
EXAMPLE 14



(11)

Yield: 53% 2 - chloroethane - thiono - phosphonic acid 2',6' - dichlorophenyl ester chloride, n_D^{24} : 1.5944.

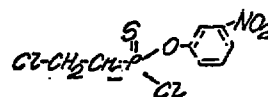
EXAMPLE 15



(4)

Yield: 73% 2 - chloroethane - thiono - phosphonic acid 3' - chlorophenyl ester chloride, n_D^{24} : 1.5851.

EXAMPLE 16

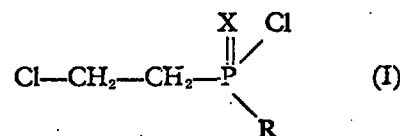


(18)

Yield: 34% 2 - chloroethane - thiono - phosphonic acid 3' - nitrophenyl ester chloride, n_D^{23} : 1.5985.

WHAT WE CLAIM IS:—

1. 2 - chloroethane - (thiono) - phosphonic acid derivatives of the general formula



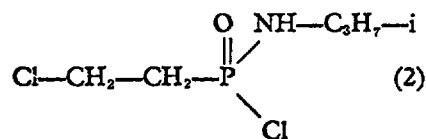
in which

X stands for oxygen or sulphur,

R stands for an aryloxy radical which may be substituted by alkyl, halogen, hydroxy or nitro groups, or for a mono-arylamino radical or a mono-alkylamino radical with 1 to 6 carbon atoms.

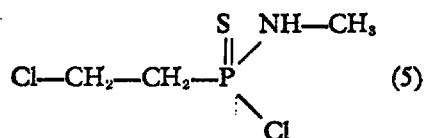
2. Compounds according to claim 1 in which R stands for a phenyloxy radical which may be substituted by nitro, methyl, hydroxyl and/or chlorine, for a monophenylamino radical or for a monoalkylamino radical with 1 to 4 carbon atoms.

3. The compound of the formula



(2)

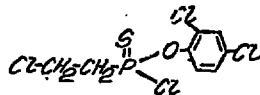
4. The compound of the formula



(5)

Analogously with Example 9, there are prepared the compounds of the following Examples 10—16.

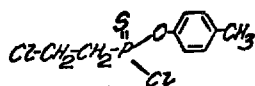
EXAMPLE 10



(16)

Yield: 60% 2 - chloroethane - thiono - phosphonic acid 2',4'-dichlorophenyl ester chloride, n_D^{20} : 1.5962.

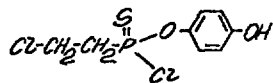
EXAMPLE 11



(9)

Yield: 64% 2 - chloroethane - thiono - phosphonic acid 4' - methylphenyl ester chloride, n_D^{21} : 1.5686.

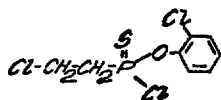
EXAMPLE 12



(17)

Yield: 58% 2 - chloroethane - thiono - phosphonic acid 4' - hydroxyphenyl ester chloride, n_D^{24} : 1.6031.

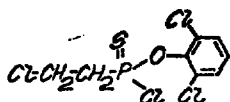
EXAMPLE 13



(10)

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

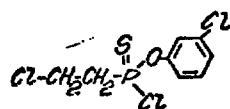
EXAMPLE 14



(11)

Yield: 53% 2 - chloroethane - thiono - phosphonic acid 2',6' - dichlorophenyl ester chloride, n_D^{24} : 1.5944.

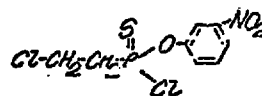
EXAMPLE 15



(4)

Yield: 73% 2 - chloroethane - thiono - phosphonic acid 3' - chlorophenyl ester chloride, n_D^{24} : 1.5851.

EXAMPLE 16

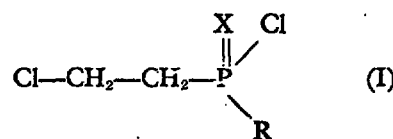


(18)

Yield: 34% 2 - chloroethane - thiono - phosphonic acid 3' - nitrophenyl ester chloride, n_D^{23} : 1.5985.

WHAT WE CLAIM IS:—

1. 2 - chloroethane - (thiono) - phosphonic acid derivatives of the general formula



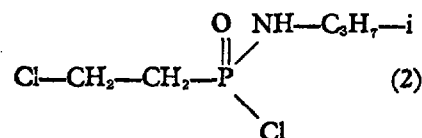
in which

X stands for oxygen or sulphur,

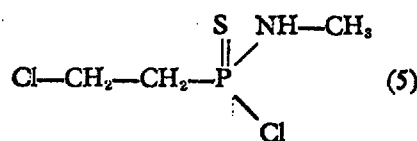
R stands for an aryloxy radical which may be substituted by alkyl, halogen, hydroxy or nitro groups, or for a mono-arylamino radical or a mono-alkylamino radical with 1 to 5 carbon atoms.

2. Compounds according to claim 1 in which R stands for a phenyloxy radical which may be substituted by nitro, methyl, hydroxyl and/or chlorine, for a monophenylamino radical or for a monoalkylamino radical with 1 to 4 carbon atoms.

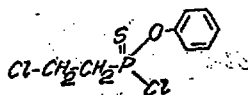
3. The compound of the formula



4. The compound of the formula

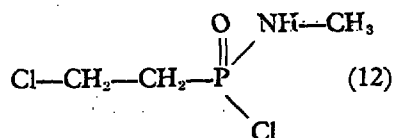


5. The compound of the formula



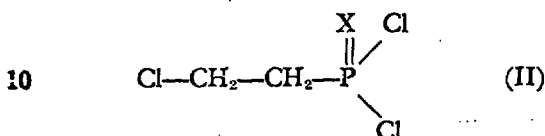
(6)

6. The compound of the formula



(12)

7. A process for the preparation of a 2-chloroethane - (thiono) - phosphonic acid derivative according to any of claims 1—6 in which a 2 - chloro - ethane - (thiono) - phosphonic acid dichloride of the formula



in which

X has the meaning stated in Claim 1 is reacted with a phenol or primary amine of the formula



in which

R has the meaning stated in Claim 1 (if desired being used in the form of its alkali metal, alkaline earth metal or ammonium salt).

8. A process according to Claim 7 in which when the amine or free phenol is used the reaction is carried out in the presence of an acid-binding agent.

9. A process according to claim 8 in which when the amine is reacted an excess of the amine of the general formula (III) is used as the acid-binding agent.

10. A process according to any of claims 7—9 in which the reaction is carried out in the presence of a solvent.

11. A process according to any of claims 7—10 in which the reaction is carried out at 0 to 20°C or at room temperature.

12. A process for the production of a compound according to claim 1, substantially as hereinbefore described in any of Examples 1—4.

13. Compounds according to claim 1 whenever prepared by a process according to any of claims 7—12.

14. A composition for the control of plant growth containing as active ingredient a compound according to any of claims 1—6 or 13 in admixture with a solid diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.

15. A composition according to claim 14 containing from 0.1 to 95% of the active compound, by weight.

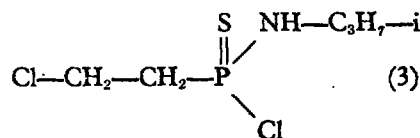
16. A method for influencing plant growth which comprises applying to the growing plant or plant seed a compound according to any of claims 1—6 or 13 alone or in the form of a composition containing as active ingredient a compound according to any of claims 1—6 or 13 in admixture with a solid or liquid diluent or carrier.

17. A method according to claim 16 in which a composition is used containing from 0.0005 to 2% of the active compound by weight.

18. A method according to claim 16 or 17 in which 0.1 to 100 kg of the active compound are applied per hectare.

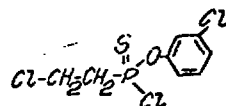
19. A method according to claim 16 substantially as hereinbefore described.

20. The compound of the formula



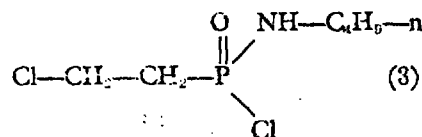
(3)

21. A compound of the formula



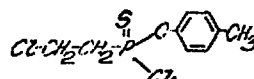
(4)

22. The compound of the formula



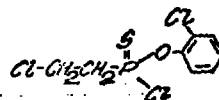
(3)

23. The compound of the formula



(9)

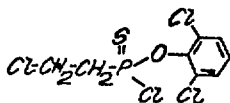
24. The compound of the formula



(10)

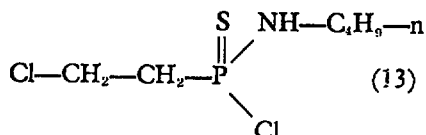


25. The compound of the formula



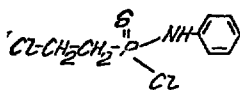
(11)

26. The compound of the formula



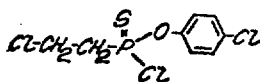
(13)

27. The compound of the formula



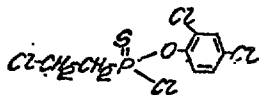
(14)

28. The compound of the formula



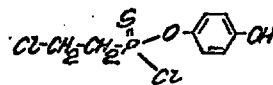
(15)

29. The compound of the formula



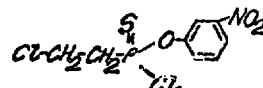
(16)

30. The compound of the formula



(17)

31. The compound of the formula



(18)

32. A process according to any of claims 7—11 for the production of a compound according to any of claims 20—31.

33. A process for the production of a compound according to claim 1, substantially as hereinbefore described in any of Examples 5—16.

34. Compounds according to claim 1 whenever prepared by a process according to claim 32 or 33.

35. A composition according to claim 14 or 15 in which the active compound is one according to any of claims 20—31 or 34.

36. A method according to any of claims 16—19 in which the active compound is one according to any of claims 20—31 or 34.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1972.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

