

PATENT SPECIFICATION

(11) 1276 277

NO DRAWINGS

1276 277

10



- (21) Application No. 22932/71 (22) Filed 19 April 1971
 (31) Convention Application No. P 20 10 119.3
 (32) Filed 4 March 1970 in
 (33) Germany (DT)
 (45) Complete Specification published 1 June 1972
 (51) International Classification C07F 9/44; A01N 5/00 // C07F 9/42
 (52) Index at acceptance
 C2P 1L1 2E11A 2E12B 2E18A 2E18B 2E18C 2E19D 2E23
 2E25A 2E26D 2J 2L11A 2L12B 2L18B 2L18C
 2L19F 2L25A 2L26D 3C12B 3C18A 3C18B 3C18C
 3C21
 C1B 3F1
 (72) Inventors WOLFGANG HOFER, REINHARD SCHLIEBS,
 ROBERT SCHMIDT and LUDWIG EUE

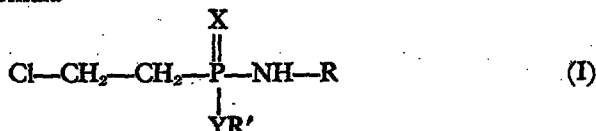
(54) 2-CHLOROETHANE-(THIONO)-PHOSPHONIC ACID AMIDO
 COMPOUNDS, PROCESSES FOR THEIR PREPARATION, AND
 THEIR USE FOR THE REGULATION OF PLANT GROWTH

(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:—

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

It is known (see Dutch Patent Specification 6 802 633) that 2-chloroethane-phosphonic acid exhibits plant-growth-regulating properties.

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



in which

X and Y, independently of each other, are oxygen or sulphur,

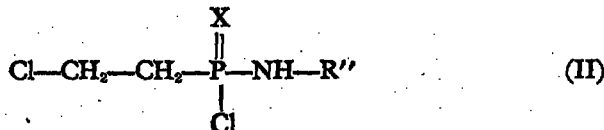
R is hydrogen or alkyl, and

R' is alkyl or, if R is hydrogen or Y is sulphur, R' may be phenyl which may be substituted by hydroxy, alkyl, halogen and/or nitro.

It has surprisingly been found that these compounds exhibit strong plant-growth-regulating properties.

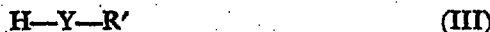
The present invention also provides a process for the production of a 2-chloroethane-(thiono)-phosphonic acid amido compound of the formula (I) in which

(a) a 2-chloroethane-(thiono)-phosphonic acid amide chloride of the general formula



in which

X has the meaning stated above, and R'' is alkyl is reacted with a compound of the general formula



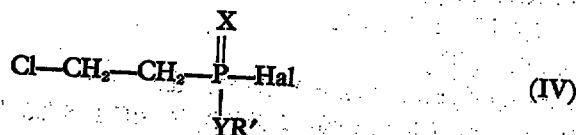
in which

Y and R' have the meanings stated above,
 (the compound of the formula (III) possibly being used in the form of its alkali metal

[Price 25p]

salt, alkaline earth metal salt or ammonium salt), optionally in the presence of an acid-binding agent and optionally in the presence of a solvent,

(b) a 2-chloroethane-(thiono)-phosphonic acid ester halide of the general formula



in which

X, Y and R' have the meaning stated above, and

Hal is halogen,

is reacted with a compound of the general formula



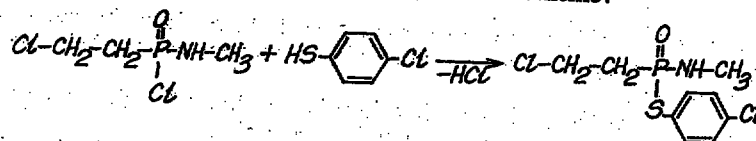
in which

R has the meaning stated above,

optionally in the presence of an acid-binding agent and optionally in the presence of a solvent.

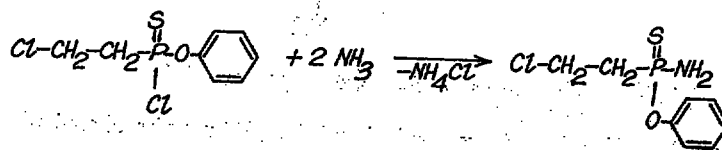
Surprisingly, the 2-chloroethane-(thiono)-phosphonic acid amido compounds according to the invention show a notably greater plant-growth-regulating activity than the 2-chloroethanephosphonic acid known from the prior art which is the chemically closest active compound of the same type of activity. The substances according to the invention therefore represent a valuable enrichment of the art.

If 2-chloroethanephosphonic acid N-monomethylamide chloride and *p*-chlorothiophenol are used as starting materials, the reaction course according to process variant (a) can be represented by the following formula scheme:



(VI)

If 2-chloroethanethionophosphonic acid phenyl ester chloride and ammonia are used as starting materials, the reaction course according to process variant (b) can be represented by the following formula scheme:



(VII)

The starting materials are defined generally by the formulae (II) to (V).

R is preferably hydrogen or alkyl with 1 to 4 carbon atoms, R' is preferably alkyl with 1 to 4 carbon atoms or, when R is hydrogen or Y is sulphur, a phenyl radical substituted by nitro, methyl, hydroxy and/or chlorine. Hal in Formula (IV) is preferably chlorine or bromine. R'' is preferably alkyl with 1 to 4 carbon atoms.

As examples of the amines of the formula (V), alcohols, mercaptans, phenols and thiophenols of the formula (III), there are mentioned in particular:

ammonia, methyl, ethyl, propyl and *n*-, *sec*-, *tert*- or *iso*-butyl amine, methanol, ethanol, propanol and *n*-, *sec*-, *tert*- or *iso*-butyl alcohol, methyl, ethyl, propyl, *iso*-propyl and butyl mercaptan, 2-, 3- and 4-chlorophenol, 2-, 3- and 4-nitrophenol, 2-, 3- and 4-methylphenol as well as resorcinol, catechol and hydroquinone, thiophenol, *o*-, *m*-, *p*-thiocresol and 2- and 4-chlorothiophenol.

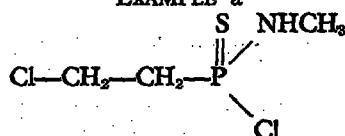
The amines, alcohols, mercaptans, phenols and thiophenols used as starting materials are known and can be prepared according to known methods.

The 2-chloroethane-(thiono)-phosphonic acid ester chlorides or amido chlorides of the formulae (IV) or (II), respectively, used as starting materials are not known but can be obtained in simple manner according to known methods by reaction of 2-chloro-

ethane-(thiono)-phosphonic acid dichloride with ammonia, amines, alcohols, mercaptans, phenols or thiophenols (the phenols and thiophenols possibly being used in the form of their alkali metal salts, alkaline earth metal salts or ammonium salts), optionally in the presence of an acid-binding agent and optionally, in the presence of a solvent, at temperatures from -10° to $+50^{\circ}\text{C}$.

Examples a to d stated below are intended to illustrate this process:

EXAMPLE a



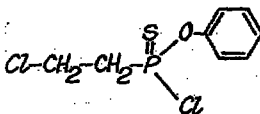
(1)

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 afterwards effected for one hour at room temperature; the salts are then filtered off with suction, washing with water and drying over sodium sulphate are effected, 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%) 2-chloroethanethionophosphonic acid N-monomethyl amide chloride, $n_D^{25}=1.5613$.

Analysis:

Calculated for $\text{C}_2\text{H}_5\text{Cl}_2\text{NPS}$: S 16.65 % N 7.30 %
Found: S 16.47 % N 7.35 %

EXAMPLE b



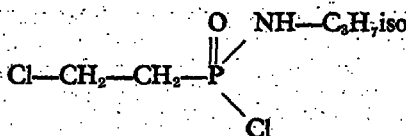
(2)

19 g (0.2 mole) phenol in 50 ml H_2O and 8 g (0.2 mole) sodium hydroxide are added to 39.5 g (0.2 mole) 2-chloroethanethionophosphonic acid dichloride at 20°C . Stirring for 2 hours at room temperature is afterwards effected, followed by taking up in methylene chloride, separation of the organic phase and washing with water. After drying over sodium sulphate has been carried out, the solvent is drawn off and slight distillation (1 mm Hg/ 60°C) is then effected. Yield: 39 g (77%) 2-chloroethanethionophosphonic acid phenyl ester chloride as colourless liquid, $n_D^{25}=1.5688$.

Analysis:

Calculated for $\text{C}_8\text{H}_9\text{Cl}_2\text{OPS}$: S 12.55 % Cl 27.90 %
Found: S 12.46 % Cl 28.82 %

EXAMPLE c



(3)

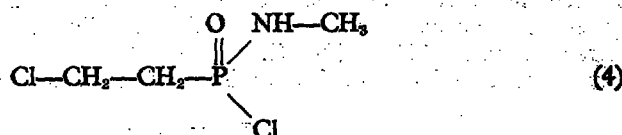
59 g (1 mole) iso-propylamine are added to 91 g (0.5 mole) 2-chloroethanephosphonic acid dichloride in 1.5 l of toluene at 0°C . Stirring is afterwards effected for one hour at room temperature, the salts are filtered off with suction, the solution is washed with a little water and the solvent is drawn off with suction; slight distillation is then effected (0.01 mm Hg/ 80°C). Yield: 93 g (91%) 2-chloroethanephosphonic acid N-monoisopropylamide chloride: $n_D^{25}=1.4854$.

Analysis:

Calculated for $\text{C}_6\text{H}_{12}\text{Cl}_2\text{NOP}$: N 6.85 % Cl 34.80 %
Found: N 6.58 % Cl 33.74 %

EXAMPLE d

Analogously with Example c, there is prepared:



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

As indicated above, either process variant according to the present invention may be carried out in the presence of a solvent (this term includes a mere diluent). The solvent may for example be water or an inert organic solvent. Such solvents include aliphatic and aromatic (possibly chlorinated) hydrocarbons such as benzene, toluene, xylene, benzine, methylene chloride, chloroform, carbon tetrachloride, chlorobenzene; ethers, such as diethyl ether, dibutyl ether, dioxan; ketones, such as acetone, methyl-ethyl ketone, methylisopropyl ketone, methylisobutyl ketone; and nitriles, such as aceto-

An acid-binding agent may be used, as mentioned above. All customary acid-binding agents are suitable. Particularly suitable are alkali metal carbonates and alcoholates, such as sodium and potassium carbonate and sodium and potassium methylate or ethylate; and aliphatic, aromatic or heterocyclic amines, such as triethylamine, dimethylaniline, dimethylbenzylamine and pyridine.

The reaction temperatures can be varied within a fairly wide range. In general, the work is carried out at from -20° to 100°C , preferably 0° to 60°C .

The reactions are generally carried out at normal pressure.

When carrying out the process variants according to the invention, approximately 1 mole of alcohol, mercaptan, phenol or thiophenol and approximately 1 mole of acid acceptor are used per mole of (thiono)phosphonic acid amide chloride; approximately 2 moles of primary amine or ammonia are used per mole of (thiono)phosphonic acid ester chloride. The reactions may be carried out in water or another suitable solvent, in most cases at room temperature. A slight excess of the compounds of formulae (III) and (V) is not detrimental.

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, by longer heating to moderately elevated temperatures under vacuum), be freed from the last volatile components and can in this way be purified. For their characterisation, the refractive index is especially useful. If the compounds are obtained in crystalline form, the melting point serves for their characterisation.

The 2-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 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 plants. Thus, with plant growth regulators the seed germination can either be inhibited or promoted, depending on the concentration applied. 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 may 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 for example 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.

An example of an economic application is the suppression of grass growth at roadsides and waysides. Further, the growth of lawns can be inhibited by growth regulators, 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 be multiplied by a chemical breaking of the apical dominance. This can be a valuable feature for example 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 tobacco plants in order to prevent the formation of side-shoots 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 time of the application, either a retarding or an acceleration of blossom formation. Under certain circumstances, a multiplication of blossom initiation can 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 plants are to be transplanted.

Fruit initiation can be promoted so that more, or seedless, fruits are formed (parthenocarp). Under 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, however, also be so exploited that the treatment is effected at the time of the harvest, whereby harvesting is facilitated.

By spraying unripe fruits with the compounds according to the invention, the ripening process can 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 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 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 from 0.01 to 0.5%, are used.

There are applied, in general, 0.1 to 100 kg, preferably 1 to 10 kg, of active compound per hectare of soil area.

As regards the application time, there is generally a preferred space of time for application, depending on the object to be achieved, and on the climatic and vegetative circumstances.

The invention is illustrated by the following Examples.

EXAMPLE A

Growth inhibition/linseeds

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.

Batches of 25 linseeds are laid out on 2 filter papers 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 three days, the length of the shoot 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 concentration of the active compound in ppm (=mg/kg) and results can be seen from Table A.

TABLE A

Growth inhibition/linseeds

Active compound	% inhibition of the shoot with	
	50 ppm	250 ppm
water (control)	0	0
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P} \begin{array}{l} \text{O} \\ \parallel \\ \text{OH} \\ \text{OH} \end{array}$ (known) (5)	15	36
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P} \begin{array}{l} \text{O} \\ \parallel \\ \text{NH}-\text{C}_3\text{H}_7-\text{iso} \\ \text{S}-\text{C}_2\text{H}_5 \end{array}$ (6)	70	82
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P} \begin{array}{l} \text{O} \\ \parallel \\ \text{NH}-\text{C}_3\text{H}_7-\text{iso} \\ \text{S}-\text{C}_6\text{H}_5 \end{array}$ (7)	80	85

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 results can be seen from Table B.

TABLE B

Growth inhibition and defoliation/beans

16

Active compound	Length in cm	Number of leaves
	with 5000 ppm	
water (control)	17.0	6
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P} \begin{array}{l} \text{O} \text{ OH} \\ \parallel \diagup \\ \text{OH} \end{array}$	11.0	4
(known) (5)		
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P} \begin{array}{l} \text{S NH}_2 \\ \parallel \diagup \\ \text{O}-\text{C}_6\text{H}_4-\text{Cl} \end{array}$	10.5	0
(8)		

EXAMPLE C

Growth inhibition/tomato plants

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.

Tomato plants of a height of 10 cm are sprayed with a preparation which contains 500 ppm of active compound.

After 8 days, the percentage inhibition of the treated plants compared with the untreated control plant is determined. With 100% inhibition, no growth is present; with 0% inhibition, the growth corresponds to that of the control plant.

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

TABLE C

Growth inhibition/tomatoes

Active compound	% inhibition with 500 ppm
water (control)	0
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{O})(\text{OH})_2$ (known) (5)	43
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{O})(\text{NH}-\text{C}_2\text{H}_5-\text{iso})(\text{S}-\text{C}_2\text{H}_5)$ (6)	66
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{O})(\text{NH}-\text{C}_2\text{H}_5-\text{iso})(\text{S}-\text{C}_6\text{H}_5)$ (7)	48

EXAMPLE D

Growth inhibition/apple seedlings

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.

Apple seedlings are, at a height of about 2 cm, sprayed with a preparation which contains 500 ppm of active compound. After 7 days, the percentage inhibition of the treated plants compared with the untreated control plant is determined. With 100% inhibition, no growth is present; with 0% inhibition, the growth corresponds to that of the control plant.

Table D shows the results.

TABLE D

Growth inhibition/apple seedlings

Active compound	% inhibition with 500 ppm
water	0
(control)	
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{O})(\text{OH})_2$	25
(known) (5)	
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{O})(\text{NH}-\text{C}_3\text{H}_7\text{-iso})(\text{S}-\text{C}_6\text{H}_5)$	32
(7)	

EXAMPLE E

Growth inhibition/Cynosurus

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.

A grass planting (*Cynosurus cristatus*) is sprayed with a preparation (which contains 1000 ppm of active compound) in an applied amount of 25 kg/hectare. After 14 days, the retardation of grass growth is determined and expressed in % compared with the untreated control.

The results can be seen from Table E.

TABLE E

Growth inhibition/Cynosurus

Active compound	% inhibition
water	0
(control)	
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{O})(\text{OH})_2$	60
(known) (5)	
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{O})(\text{NH}-\text{C}_3\text{H}_7\text{-iso})(\text{O}-\text{C}_3\text{H}_7\text{-iso})$	68
(9)	

EXAMPLE F

Acceleration of fruit ripeness/tomato plants

Solvent: 40 parts by weight acetone

Emulsifier: 0.25 part 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 a disodium hydrogen phosphate-potassium dihydrogen phosphate buffer solution (pH 6) to the desired concentration.

10 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.

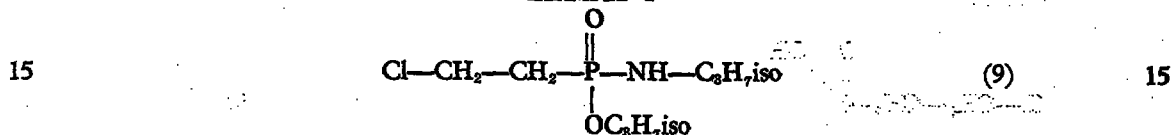
The result can be seen from Table F.

TABLE F

Acceleration of fruit ripeness/tomatoes

Active compound	Acceleration of ripeness in days with 5 000 ppm
water	0
(control)	
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{O})(\text{OH})_2$ (known) (5)	12
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{O})(\text{NH}-\text{C}_3\text{H}_7\text{-iso})(\text{O}-\text{C}_3\text{H}_7\text{-iso})$ (9)	17
$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}(=\text{O})(\text{NH}-\text{C}_3\text{H}_7\text{-iso})(\text{S}-\text{C}_6\text{H}_5)$ (7)	15

EXAMPLE 1



20 24 g (0.4 mole) isopropanol and 33 g (0.33 mole) triethylamine are added to 67 g (0.33 mole) 2-chloroethanephosphonic acid N-monoisopropylamide chloride in 200 ml benzene at room temperature. Stirring is afterwards effected for 2 hours at 50°C, followed by suction filtration from precipitated salt, and the reaction solution is washed with water. After drying with sodium sulphate and drawing off of the solvent, slight

20

distillation is effected. There remains behind a colorless oil, $n_D^{22}=1.4686$, yield: 50 g (67%) 2-chloroethanephosphonic acid isopropyl ester N-monoisopropylamide.

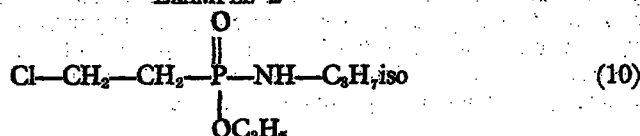
Analysis:

Calculated for $C_9H_{19}ClNO_2P$: 15.65 % Cl 6.15 % N

Found: 16.05 % Cl 6.36 % N

The 2-chloroethane-phosphonic acid N-mono-isopropylamide chloride used as starting product is prepared from 2-chloroethane-phosphonic acid dichloride and isopropylamine in toluene at 0°C. Yield: 91 % of the theory, $n_D^{20}=1.4854$.

EXAMPLE 2



87 ml (0.2 mole) ethanolic sodium ethylate solution are added to 41 g (0.2 mole) 2-chloroethanephosphonic acid N-monoisopropylamide chloride in 200 ml benzene at room temperature. Stirring is afterwards effected for 2 hours; the salts are then filtered off with suction, the reaction solution is washed with water, and drying with sodium sulphate is effected. After the solvent has been drawn off, slight distillation is carried out. There remains behind a colourless oil, $n_D^{20}=1.4580$, yield: 27 g (64%) 2-chloroethanephosphonic acid ethyl ester N-monoisopropylamide.

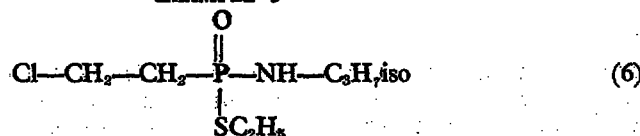
Analysis:

Calculated for $C_7H_{17}ClNO_2P$: 16.65 % Cl 6.60 % N

Found: 16.33 % Cl 6.56 % N

Starting product compare Example 1.

EXAMPLE 3



13 g (0.2 mole) ethylmercaptan and 20 g (0.2 mole) triethylamine are added to 41 g (0.2 mole) 2-chloroethanephosphonic acid N-monoisopropylamide chloride in 100 ml benzene. Stirring is afterwards effected for 2 hours at 40°C; the salts are then filtered off with suction, the reaction solution is washed with water, and drying with sodium sulphate is carried out. After the solvent has been drawn off, there remains behind a crystalline residue, m.p. 51°C, yield: 15 g (33%) 2-chloroethanethiophosphonic acid S-ethyl ester N-monoisopropylamide.

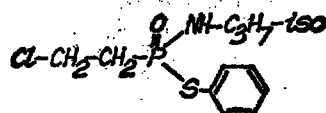
Analysis:

Calculated for $C_7H_{17}ClNOPS$: 15.45 % Cl 6.10 % N 13.95 % S

Found: 15.30 % Cl 6.80 % N 13.80 % S

Starting product compare Example 1.

EXAMPLE 4



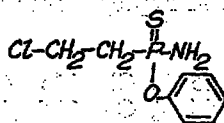
is prepared analogously with Example 3, m.p. 61°C, yield: 59 % 2-chloroethane-thiophosphonic acid S-phenyl ester N-monoisopropylamide.

Analysis:

Calculated for $C_{11}H_{17}ClNOPS$: 5.50 % N 11.50 % S

Found: 5.55 % N 11.95 % S

EXAMPLE 5



(11)

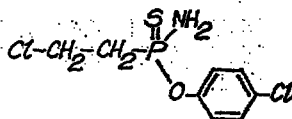
To 51 g (0.2 mole) 2-chloroethanethionophosphonic acid phenyl ester chloride, emulsified in 100 ml of water, there are added, at room temperature, 30 g (0.42 mole) of aqueous ammonia solution. Stirring is afterwards effected for 2 hours; the organic phase is then taken up in methylene chloride, washing with water is effected and, after drying with sodium sulphate has been carried out, the solvent is drawn off. After slight distillation, there remains behind a pale oil, $n_D^{27} = 1.5848$, yield: 32 g (68%) 2-chloroethanethionophosphonic acid phenyl ester amide.

Analysis:

Calculated for $C_8H_{11}ClNOPS$: 15.05 % Cl 5.95 % N 12.60 % S
 Found: 14.82 % Cl 5.21 % N 12.42 % S

The starting product used is prepared from 2-chloroethanethiono-phosphonic acid dichloride and sodium phenolate in water, $n_D^{28} = 1.5688$, yield: 77 % 2-chloroethanethionophosphonic acid phenyl ester chloride.

EXAMPLE 6



(8)

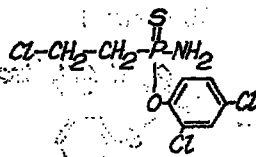
87 g (0.3 mole) 2-chloroethanethionophosphonic acid 4'-chlorophenyl ester chloride in 500 ml benzene are treated with gaseous ammonia at room temperature until the solution is saturated with ammonia. Stirring is afterwards effected for one hour; the salt is then filtered off with suction, and the reaction solution is washed with water. After drying with sodium sulphate, the solvent is drawn off. After slight distillation, there remains behind a colourless oil, $n_D^{24} = 1.5945$, yield: 62 g (76%) 2-chloroethanethionophosphonic acid 4'-chlorophenyl ester amide.

Analysis:

Calculated for $C_9H_{10}Cl_2NOPS$: 26.15 % Cl 5.17 % N 11.85 % S
 Found: 26.23 % Cl 4.83 % N 11.65 % S

The starting product is prepared analogously with the starting product of Example 5, $n_D^{28} = 1.5856$, yield: 59 % 2-chloroethanethiono-phosphonic acid 4'-chloro-phenyl ester chloride.

EXAMPLE 7



(12)

is prepared analogously with Example 6, $n_D^{24} = 1.6020$, yield: 86 % 2-chloroethanethiono-phosphonic acid 2',4'-dichlorophenyl ester amide.

Analysis:

Calculated for $C_9H_{11}Cl_3NOPS$: 35.00 % Cl 10.5 % S
 Found: 35.54 % Cl 10.1 % S

The starting product is prepared analogously with the starting product of Example 5, $n_D^{20}=1.5962$, yield: 60 % 2-chloroethane-thiono-phosphonic acid 2',4'-dichloro-phenyl ester chloride.

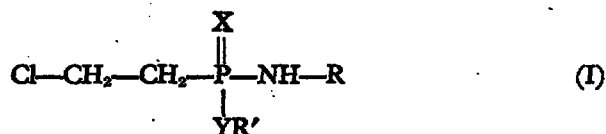
It will be seen from the above description that the invention also provides a plant growth regulating composition containing as active ingredient a compound according to the invention in admixture with a solid diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.

The invention also provides a method of regulating plant growth which comprises applying to a plant a compound according to the invention alone or in the form of a composition according to the invention in admixture with a solid or liquid diluent or carrier.

The invention also provides plants where growth has been regulated by their being grown in areas in which, immediately prior to and/or during the time of the growing, a compound according to the invention was applied alone or in admixture with a solid or liquid diluent or carrier.

WHAT WE CLAIM IS:—

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



in which

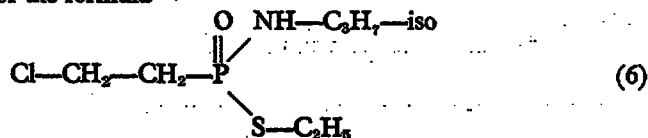
X and Y, independently of each other, are oxygen or sulphur,

R is hydrogen or alkyl, and

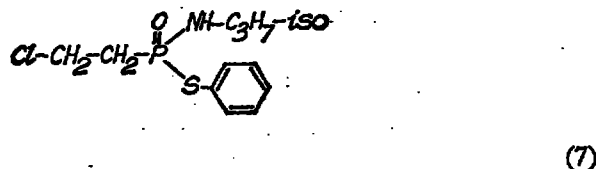
R' is alkyl or, if R is hydrogen or Y is sulphur, R' may be phenyl which may be substituted by hydroxy, alkyl, halogen and/or nitro.

2. Compounds according to claim 1 in which R is hydrogen or alkyl with 1 to 4 carbon atoms and R' is alkyl with 1 to 4 carbon atoms or, when R is hydrogen or Y is sulphur, is phenyl which may be substituted by nitro, methyl, hydroxy and/or chlorine.

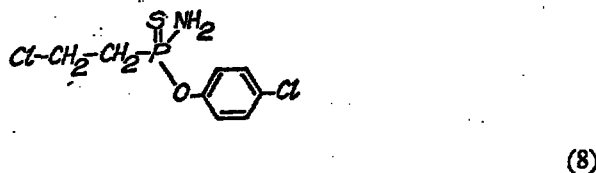
3. The compound of the formula



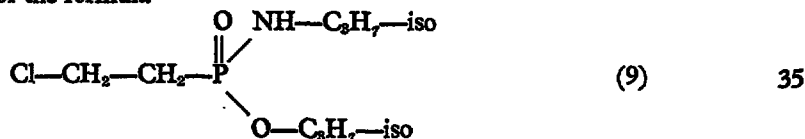
4. The compound of the formula



5. The compound of the formula



6. The compound of the formula



The starting product is prepared analogously with the starting product of Example 5, $n_D^{20}=1.5962$, yield: 60 % 2-chloroethane-thiono-phosphonic acid 2',4'-dichloro-phenyl ester chloride.

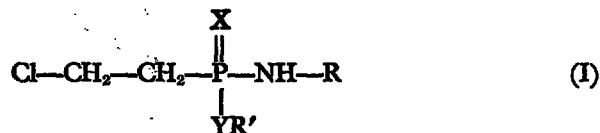
It will be seen from the above description that the invention also provides a plant growth regulating composition containing as active ingredient a compound according to the invention in admixture with a solid diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.

The invention also provides a method of regulating plant growth which comprises applying to a plant a compound according to the invention alone or in the form of a composition according to the invention in admixture with a solid or liquid diluent or carrier.

The invention also provides plants where growth has been regulated by their being grown in areas in which, immediately prior to and/or during the time of the growing, a compound according to the invention was applied alone or in admixture with a solid or liquid diluent or carrier.

WHAT WE CLAIM IS:—

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



in which

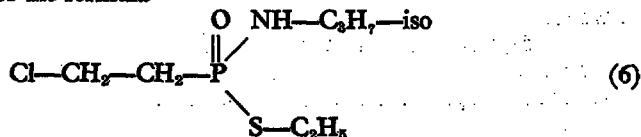
X and Y, independently of each other, are oxygen or sulphur,

R is hydrogen or alkyl, and

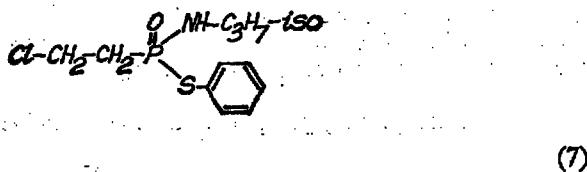
R' is alkyl or, if R is hydrogen or Y is sulphur, R' may be phenyl which may be substituted by hydroxy, alkyl, halogen and/or nitro.

2. Compounds according to claim 1 in which R is hydrogen or alkyl with 1 to 4 carbon atoms and R' is alkyl with 1 to 4 carbon atoms or, when R is hydrogen or Y is sulphur, is phenyl which may be substituted by nitro, methyl, hydroxy and/or chlorine.

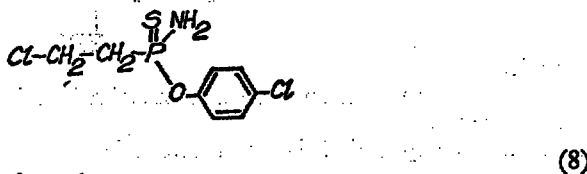
3. The compound of the formula



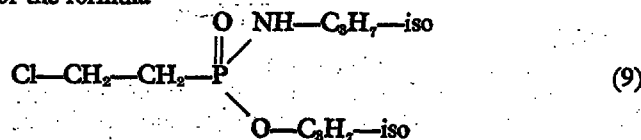
4. The compound of the formula



5. The compound of the formula

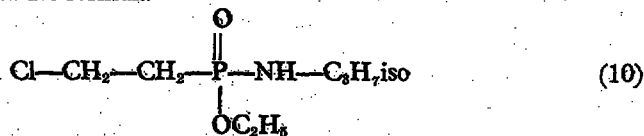


6. The compound of the formula





7. The compound of the formula

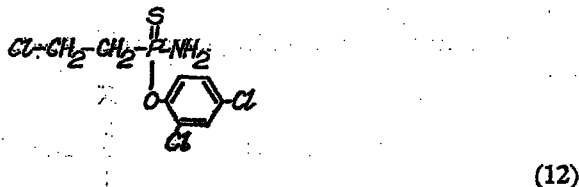


8. The compound of the formula



5

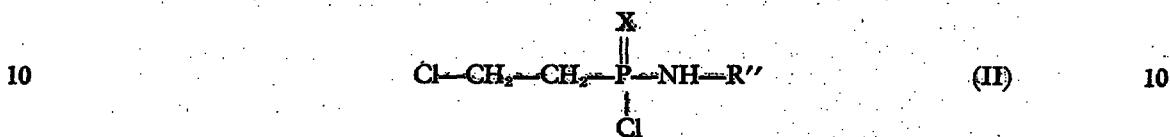
9. The compound of the formula



5

10. A process for the production of a 2-chloroethane-(thiono)-phosphonic acid amido compound according to any of claims 1—9 in which

(a) a 2-chloroethane-(thiono)-phosphonic acid amide chloride of the general formula



in which

X has the meaning stated in claim 1, and

R'' is alkyl

is reacted with a compound of the general formula



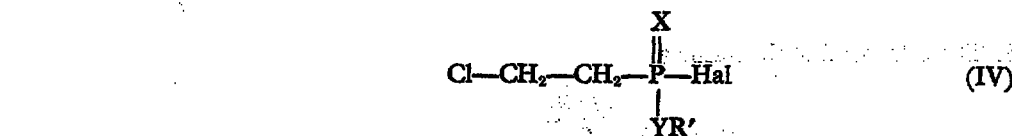
in which

Y and R' have the meanings stated in claim 1,

(the compound of the formula (III) possibly being used in the form of its alkali metal salt, alkaline earth metal salt or ammonium salt),

or

(b) a 2-chloroethane-(thiono)-phosphonic acid ester halide of the general formula

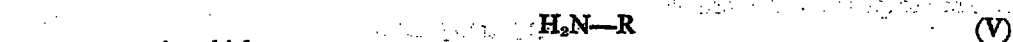


in which

X, Y and R' have the meanings stated in claim 1, and

Hal is halogen,

is reacted with a compound of the general formula



in which

R has the meaning stated in claim 1.

11. A process according to claim 10 in which the compound of formulae (III) or (V) is any of those hereinbefore specifically mentioned for the purpose.

12. A process according to claim 10 or 11 in which the reaction is carried out in the presence of a solvent.

13. A process according to any of claims 10—12 in which the reaction is carried out in the presence of an acid-binding agent.

14. A process according to any of claims 10—13 in which the reaction is carried out at -20 to 100°C .
15. A process according to claim 14 in which the reaction is carried out at 0 to 60°C .
- 5 16. A process for the production of a compound according to claim 1 substantially as hereinbefore described in any of Examples 1—7. 5
17. Compounds according to claim 1 whenever prepared by a process according to any of claims 10—16.
- 10 18. A plant growth regulating composition containing as active ingredient a compound according to any of claims 1—9 or 17 in admixture with a solid diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent. 10
19. A composition according to claim 18 containing from 0.1 to 95% of the active compound by weight.
- 15 20. A method of regulating plant growth which comprises applying to a plant a compound according to any of claims 1—9 or 17 alone or in the form of a composition containing as active ingredient a compound according to any of claims 1—9 or 17 in admixture with a solid or liquid diluent or carrier. 15
21. A method according to claim 20 in which a composition is used containing from 0.0005 to 2% of the active compound, by weight.
- 20 22. A method according to claim 20 in which the active compound is applied to an area of agriculture in an amount of 0.1 to 100 kg per hectare. 20
23. Plants where growth has been regulated by their being grown in areas in which, immediately prior to and/or during the time of the growing, a compound according to any of claims 1—9 or 17 was applied alone or in admixture with a solid or liquid diluent or carrier. 25

For the Applicant,
CARPMAELS & RANSFORD,
Chartered Patent Agents,
24, Southampton Buildings,
Chancery Lane, London, W.C.2.

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.



* C L M S *