

EUROPEAN QUALIFYING EXAMINATION 1992

**PAPER B
CHEMISTRY**

This paper comprises:

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92/B(C)/e

INSTRUCTIONS TO CANDIDATES

In this paper, you should assume that a European patent application for all the Contracting States comprising the appended documents* has been filed and that the European Patent Office has issued the annexed official communication.

You should accept the facts given in the paper and base your answers upon such facts. Whether and to what extent these facts are used is your responsibility.

You should not use any special knowledge you may have of the subject-matter of the invention, but are to assume that the prior art given is in fact exhaustive.

Your task is now to draft a full response to the official communication. The response should be a letter to the EPO, accompanied, if appropriate, by an amended set of claims. No amendments to the description should, however, be made, even if such amendments would be appropriate.

The claims should afford the maximum protection while meeting the requirements of the Convention. In your letter of response you should at least set out your arguments in support of the patentability of the independent claim(s).

If your response includes a proposal to make any part of the application the subject of divisional application(s), you should suggest a text for at least the independent claim(s) thereof and also include your arguments in support of the patentability of such claim(s).

In addition to your elaborated solution, you may - but this is not mandatory - give, on a separate sheet of paper, the reasons for your choice of solution, for example, why you selected a particular form of claim, a particular feature for an independent claim, a particular piece of prior art as starting point or why you rejected or preferred some piece of prior art. Any such statement should however be brief.

It is assumed that you have studied the examination paper in the language in which you have given your answer. If this is not so, please indicate on the front page of your answer in which language you have studied the examination paper. This always applies to candidates who - after having filed such a request when enrolling for the examination - give their answer in a language other than German, English or French.

Different sets of claims for those states which have made reservations under Article 167(2) EPC are not required.

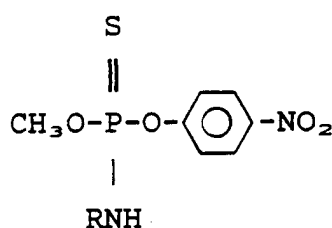
* These documents do not necessarily constitute the only or best solution to the task set in Paper A (Chemistry)

Description of the Application

The invention relates to amido thionophosphoric acid esters, their preparation and use. It also pertains to herbicides for use in crop plant cultivation. These herbicide compositions contain as an active ingredient an amido thionophosphoric acid ester of the formula given below.

It is already known from Document II that certain amido thionophosphoric acid esters of the general formula

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such as, for example, the compound O-methyl-N-isopropylamido-O-(4-nitrophenyl)-thionophosphoric acid ester, may be used as herbicidal agents. To be properly effective, the known herbicide compositions need to be used in relatively large quantities. However, the high concentration is frequently found to cause a certain phytotoxicity to useful plants.

The object of the invention is to make available agents for treating agricultural areas which can be effectively applied as a herbicide composition in small quantities without displaying the aforementioned disadvantages.

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To solve this problem compounds have unexpectedly been found which demonstrate a high herbicidal activity at lower concentrations compared to the known compounds. These compounds are amido thionophosphoric acid esters the nitro group of which is at the 2-position on the phenyl group and of which the phenyl group is further substituted with one or more methyl groups. The compounds according to the invention correspond to the formula



15 wherein R^1 is a C_3 - C_4 alkyl group, R^2 is a C_1 - C_4 alkyl group, X is a methyl group, and n is an integer from 0 to 3.

The compounds according to the invention display a surprisingly low phytotoxicity to crop plants and are moreover not toxic to mammals.

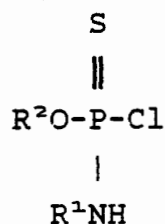
The invention therefore relates to herbicide compositions containing at least one amido thionophosphoric acid ester of the above formula as active ingredient, in addition to usual additives.

25 The literature to date mentions only one compound corresponding to this formula and that is O-ethyl-N-propylamido-O-(2-nitro-5-methylphenyl) thionophosphoric acid ester (Document III), used there to modify synthetic resins or as an additive in high-pressure oils.

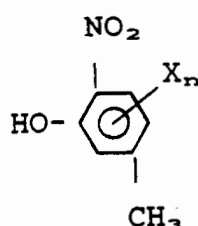
The invention also relates to compounds of the above formula other than the compound wherein R^1 is the propyl group, R^2 the ethyl group and n is 0.

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The invention relates further to a process for preparing the
aforementioned compounds in which a thionophosphoric acid chloride
of the formula



10 wherein R^1 and R^2 are the same as in the above formula, is reacted
with a nitrophenol of the formula



(X and n are as indicated above). The reaction is carried out in an
organic solvent in the presence of an acid-binding agent.

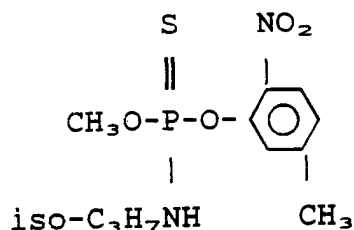
20 Many aliphatic or aromatic hydrocarbons or other polar aprotic
solvents such as benzene, toluene, dichloromethane and dioxane are
suitable as organic solvents. However, lower aliphatic nitriles,
preferably those with a boiling point of up to 100°C such as
25 acetonitrile and propionitrile, have been found to be particularly
satisfactory. As acid-binding agents both inorganic compounds, such
as potassium carbonate, and organic bases, such as triethylamine or
pyridine, may be used.

30 The reaction is normally carried out at a temperature ranging from
room temperature to 120°C, preferably at temperatures from 40-70°C.
Depending on the temperature chosen, the reaction takes approxi-
mately two to five hours. If one wants to obtain a product which is
to be solvent free, the solvent is removed by distillation under
35 reduced pressure once the reaction has been carried out. The
resulting crude product which is an oil can then be purified by
repeated washing, for example with benzene and with water and by
subjecting it to column chromatography using active
aluminium oxide.

Examples of amido thionophosphoric acid esters according to the invention, and represented by the above formula, which produced particularly good results when used as an active substance for controlling weeds, are

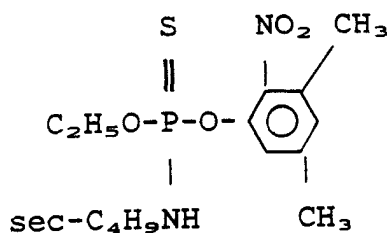
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(I)



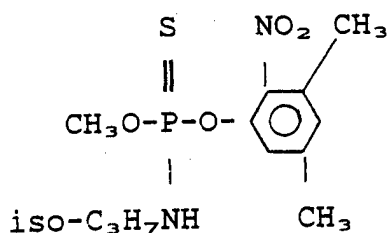
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(II)



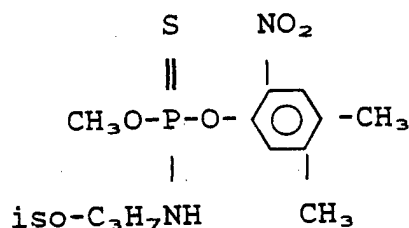
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(III)



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(IV)

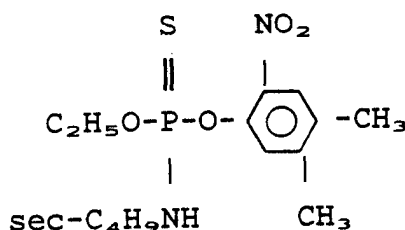


25

and

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(V)



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Of these compounds, compounds IV and V show a particularly high herbicidal activity.

A wide range of weeds can be controlled extremely effectively the compounds according to the invention.

Weed control is particularly effective when the herbicide composition is applied to the agricultural area before the emergence of the crop plants or before the emergence of the weeds. Amounts of as little as 0.5 to 5 kg/ha of the active ingredient are found to be effective.

10 Weeds which can be successfully controlled with the herbicide compositions according to the invention are grass family weeds such as barnyard grass (*Echinochloa crus-galli*), large crabgrass (*Digitaria sanguinalis*) and green foxtail (*Setaria viridis*), and also such broad-leaved weeds as common purslane (*Portulaca*
15 *oleracea*), common lambsquarter (*Chenopodium album*), monochoria and chickweed (*Stellaria media*).

Depending on the concentration applied, herbicide compositions containing at least one of the new compounds as an active
20 ingredient can control completely the growth of the weed species mentioned above without any significant phytotoxicity to crops such as rice, soy bean, pea or cotton. As already mentioned, the substances are most effective when applied before germination of the weeds.

25 The compounds according to the invention are preferably used in the form of a suitable preparation (formulation).

They may in particular be used as wettable powders, granulates, oil
30 sprays and emulsifiable concentrates. These preparations are formed by mixing the active substance with additives, such as solid carriers and/or solvents. Advantageously surface active agents,

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dispersants and emulsifiers are also used in addition. The solvents and carriers may, for example, be ground kaolin or fine-grained clay. Examples of solvents are benzene and toluene, and in particular cyclohexanone.

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Such preparations are, of course, adapted to the purpose and method of application. It is moreover possible to use the herbicidal active agent or a formulation containing such an agent in admixture with fungicides, insecticides and also fertilisers. Formulating the
10 herbicide as an emulsifiable concentrate, that can be diluted with water, has proved particularly advantageous.

Such an emulsifiable concentrate is prepared by dissolving the compounds in one of the aforementioned solvents and mixing them
15 with an emulsifier. Examples of such emulsifiers which can be added to the liquid mixture are polyethylene glycol ether or a mixture of polyethoxylated fatty acid and polyethoxylated alkylphenol.

The composition of an emulsifiable herbicidal concentrate, which
20 can be advantageously used as a liquid preparation, is as follows:

10 to 30% by weight of active ingredient in the form of a compound according to the aforementioned formula,
50 to 70% by weight of cyclohexanone as solvent and
25 10 to 20% by weight of polyethylene glycol ether as emulsifier.

To ensure that the active ingredient is properly dispersed it is advisable to add spreading agents to the preparation. As spreading agents fatty alcohols or fatty acid esters may be used. Isopropyl
30 myristate and isopropyl palmitate have been found to be particularly effective as spreading agents. They are preferably added in quantities of 5 to 10% by weight relative to the emulsifiable concentrate.

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In certain circumstances the presence of a significant amount of spreading agent in the preparation may, however, lead to stability problems, causing the preparations to decompose to a lesser or greater extent on storage. This can be avoided, preferably by adding a stabiliser such as methane sulphonic acid, benzene sulphonic acid, tetrapropylene benzene sulphonic acid, and in particular 2-nitrobenzoic acid. Where appropriate, 0.5 to 1% by weight of stabiliser is added to the emulsifiable concentrate.

Such a stabilised concentrate is particularly beneficial in weed control in crops of transplanted or wet-sown rice, since even an undiluted concentrate can be applied directly to the water surface.

The examples which follow illustrate the excellent herbicidal effect of compounds of formulae I to V set out above.

Example 1

Seeds of barnyard grass, large crabgrass, common purslane, monochoria and radish (*Raphanus sativus*) were individually sown in flower pots and covered with soil. The five test compounds of the above-mentioned formulae I to V were then applied to the soil. All the test compounds were used in the form of an aqueous dilution of an emulsifiable concentrate. The composition of the concentrate was as follows:

20 parts by weight of the test compound,
65 parts by weight of cyclohexanone and
15 parts by weight of a polyethylene glycol ether.

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The test plants were grown in a greenhouse for twenty days, at the end of which the results were evaluated according to the following scale:

- 5 0: no appreciable damage
- 1: very slight damage
- 2: minor damage
- 3: moderate damage
- 4: badly damaged
- 10 5: completely killed.

The results are set out in Table 1.

Example 2 (application under waterlogged conditions)

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In further tests, flower pots were filled with paddy-field soil and rice seedlings were transplanted to them. Seeds of the two types of weed indicated in Table 2 were then sown in the pots, which were filled to the top with soil and placed in a water tank. On the
20 third day after sowing, undiluted emulsifiable concentrates of the same composition as in Example 1 were applied in the quantities shown in Table 2. After twenty five days the effect on the weeds and the phytotoxicity to the rice were evaluated in accordance with the scale given in Example 1. The results are set out in Table 2.

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As is clear from table 2, no phytotoxicity could be demonstrated for the compounds used according to the invention against rice with the result that they are particularly suitable for use in paddy-fields as well.

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Table 1

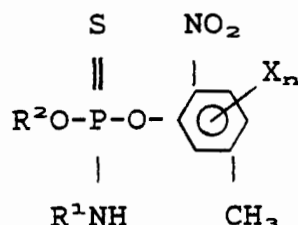
| Test compound | Amount of active ingredient (g/are) | Effect on | | | | |
|---------------|-------------------------------------|----------------|------------------|--------------------|------------|--------|
| | | barnyard grass | large crab-grass | portulaca oleracea | monochoria | radish |
| I | 50 | 5 | 5 | 5 | 5 | 0 |
| | 22 | 4 | 5 | 4 | 4 | 0 |
| | 8 | 3 | 3 | 4 | 3 | 0 |
| II | 50 | 5 | 4 | 5 | 5 | 0 |
| | 22 | 5 | 3 | 4 | 5 | 0 |
| | 8 | 4 | 3 | 3 | 3 | 0 |
| III | 50 | 5 | 5 | 5 | 5 | 0 |
| | 22 | 5 | 4 | 4 | 4 | 0 |
| | 8 | 3 | 3 | 3 | 3 | 0 |
| IV | 50 | 5 | 5 | 5 | 5 | 0 |
| | 22 | 5 | 5 | 5 | 5 | 0 |
| | 8 | 5 | 5 | 4 | 5 | 0 |
| V | 50 | 5 | 5 | 5 | 5 | 0 |
| | 22 | 5 | 5 | 5 | 5 | 0 |
| | 8 | 4 | 4 | 4 | 4 | 0 |

Table 2

| Test compound | Amount of active ingredient (g/are) | Effect on | | |
|---------------|-------------------------------------|----------------|--------------------|------|
| | | barnyard grass | portulaca oleracea | rice |
| I | 50 | 5 | 5 | 0 |
| | 25 | 4 | 4 | 0 |
| | 12 | 4 | 3 | 0 |
| II | 50 | 5 | 5 | 0 |
| | 25 | 5 | 4 | 0 |
| | 12 | 4 | 3 | 0 |
| III | 50 | 5 | 5 | 0 |
| | 25 | 4 | 4 | 0 |
| | 12 | 3 | 3 | 0 |
| IV | 50 | 5 | 5 | 0 |
| | 25 | 5 | 5 | 0 |
| | 12 | 5 | 5 | 0 |
| V | 50 | 5 | 5 | 0 |
| | 25 | 5 | 5 | 0 |
| | 12 | 5 | 4 | 0 |

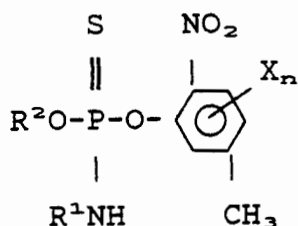
Claims

1. A herbicide composition characterised in that in addition to usual additives it contains as a herbicidally active compound at least one amido thionophosphoric acid ester of the formula



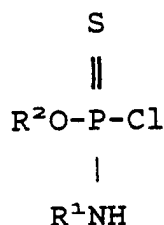
wherein R^1 is a C_3 - C_4 alkyl group, R^2 is a C_1 - C_4 alkyl group, X is a methyl group and n is an integer from 0 to 3.

2. Herbicide composition according to Claim 1, characterised in that the composition is in the form of a wettable powder, a granulate, an oil spray or an emulsifiable concentrate.
3. Herbicide composition according to Claim 2, characterised in that the emulsifiable concentrate contains in addition to the herbicidally effective ingredient at least one surface active agent and a solvent.
4. Compound according to the general formula

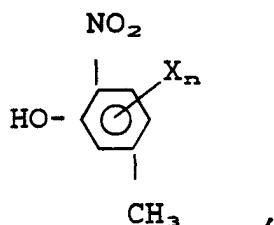


wherein R^1 is a C_3 - C_4 alkyl group, R^2 is a C_1 - C_4 alkyl group, X is a methyl group and n an integer from 0 to 3, other than the compound where R^1 is the propyl group, R^2 the ethyl group and n is 0.

5. Process for preparing an amido thionophosphoric acid ester according to the formula in Claim 1, characterised in that a thionophosphoric acid chloride of the formula



is reacted with a nitrophenol of the formula



wherein R^1 , R^2 , X and n are as defined above, in an organic solvent in the presence of an acid-binding agent.

6. Process according to Claim 5, characterised in that acetonitrile or propionitrile is used as the organic solvent.
7. Use of compounds according to the formula in Claim 1 to treat agricultural areas.

Communication

1. Document IV describes compositions used to control phytotoxic threadworms, especially in agriculture, which contain as an active ingredient a compound represented by the formula according to Claim 1. Whilst the present claim relates to a herbicide composition, the formulation of the composition as such is known from Document IV and therefore not novel. Under Articles 52(1) and 54(1) and (2) EPC, therefore, this claim cannot be allowed.
2. Since the use of the known composition in the form of an emulsifiable concentrate is also already known from Document IV, and in particular from the example, Claims 2 and 3 cannot be allowed either because they lack novelty as well.

Apart from Document IV, Document II also shows that the use of herbicidally active agents of this or a similar structure generally in formulations such as those claimed in Claim 2 is usual and common knowledge to the expert. That claim does not therefore meet the requirements of Articles 52(1) and 56 EPC either.

3. The example in Document IV specifically mentions the compounds represented by formulae (I) and (II) in the present description [formulations (A) and (B) in the example]. The compounds of formulae (IV) and (V) are explicitly disclosed in the experimental part of Document V. Claim 4 does not therefore meet the requirements of Articles 52(1) and 54(1) and (2) EPC.
4. The process according to Claims 5 and 6 is likewise known from Document V, and in particular from the experimental part. Because they too lack novelty these two claims cannot therefore be allowed either.

5. Document IV also describes the use of compounds, represented by the formula in Claim 1, for treating agricultural areas. Claim 1 cannot therefore be allowed because it lacks novelty (Articles 52(1) and 54(1) and (2) EPC).
6. If the applicant is able to see anything else patentable in what the present application discloses, he should file one or more claims corresponding thereto.
7. The reply should also indicate, on the one hand, the difference between the prior art and the essential feature or features of the application and, on the other, their significance so that the problem to be solved having regard to that prior art and its solution can be readily understood.

DOCUMENT IV (State of the Art)

The invention relates to a composition based on alkyl-substituted amido nitrophenyl thionophosphoric acid ester used in particular in agriculture to control phytotoxic threadworms (nematodes).

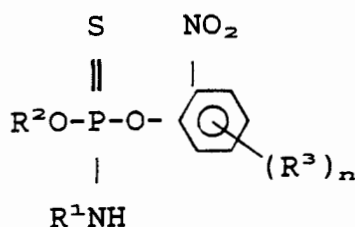
5 Such threadworms are generally present in the soil where crops are grown and are therefore controlled with nematocides, for example based on mixed alkyl and phenyl esters of amido thionophosphoric acid. Their general effectiveness, however, in both pre- and post-emergence treatment leaves something to be desired.

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It has now been found that compounds of the aforementioned kind, in which the phenyl ester group is substituted in the 2-position by a nitro group and in addition by one or more short-chain alkyl groups (in particular one or two methyl and/or ethyl groups), one of which
15 occupies the 5-position in the phenyl group, display a considerably greater nematocidal effectiveness than the compounds known to date.

The compounds according to the invention, which have a particularly good nematocidal effect, are represented by the formula

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wherein R^1 and R^2 , independently of one another, are each C_1 - C_4 alkyl, R^3 is methyl or ethyl and $n = 1$ to 4.

30 The active ingredients are preferably compounds where R^1 is the isopropyl group and R^2 and R^3 are each a methyl group, or alternatively R^1 is the isopropyl group, R^2 the methyl and R^3 the ethyl group.

35 The active ingredients according to the invention are advantageously formulated as emulsifiable concentrates containing

(a) 10-40% by weight of active ingredient, (b) 40-60% by weight of a solvent, e.g. cyclohexanone, and (c) 15-40% by weight of emulsifier, in which components (a), (b) and (c) together always amount to 100%. Furthermore, small amounts of other customary additives such as spreading agents and stabilisers may also be added to the concentrate. In actual application such as concentrate can be readily diluted with water, whilst the high emulsifier content ensures that the soil particles are properly wetted. After dilution with water, the concentrate is applied to the soil and then worked into the earth. In general, 1 to 6 kg of active ingredient per hectare is sufficient for effective control of nematodes. The preparations can be used all year round.

Similarly good results are achieved with wettable powders, granulates and oil sprays, which contain the above compounds as active ingredient.

Example

Two formulations were produced in the form of emulsifiable concentrates. Thus 2.5 kg of active ingredient was dissolved in 4.5 kg of cyclohexanone and 3.0 kg of polyethylene glycol ether was then added to the solution. Prior to use, both formulations were diluted ten times with water and then sprayed on to the infested ground. In formulation (A) the active ingredient used was O-(2-nitro-5-methylphenyl)-O-methyl-N-isopropylamido thionophosphate. In formulation (B) O-(2-nitro-3,5-dimethylphenyl)-O-ethyl-N-sec-butylamido thionophosphate was used as an active ingredient. When used, 3.2 kg/ha of active ingredient according to formulation (A) and 3.6 kg/ha of active ingredient according to formulation (B) completely killed the nematodes. The infestation was found to be reduced by 80% with 1.8 and 2.1 kg/ha respectively.

DOCUMENT V (State of the Art)

In the course of our researches into organic sulphur-phosphorus compounds we have discovered a novel process for preparing substituted amido thionophosphoric acid esters, and in particular nitrophenyl esters of O-alkyl-N-alkylamido thionophosphoric acids.
5 The compounds are prepared by reacting an O-alkyl-N-alkylamido thionophosphoric acid halide of the formula



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with a substituted 2-nitrophenol. In the above formula, R^1 is an alkyl group having generally 1 - 8 carbon atoms, R^2 an alkyl group having generally 1 - 4 carbon atoms and Hal a halogen atom, in particular chlorine or bromine. The nitrophenol is substituted on the phenyl nucleus by one to three C_1 - C_4 alkyl groups (R^3). These symbols have the same meaning in the other formulae. In singly substituted 2-nitrophenols, the alkyl group R^3 - methyl in particular should be mentioned here - is normally bonded at the para
20 position, in other words at the 4-position on the phenol ring.

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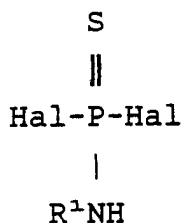
The phenol may be used as such or alternatively as an alkali or ammonium phenolate. When free phenol is used, an acid-binding agent, e.g. potassium carbonate, or an organic base, e.g. a

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tertiary amine such as pyridine, trimethylamine or triethylamine is added to the reaction mixture.

The preparation methods may be varied by first reacting a substituted alkylaminophosphorus sulphide dihalide of the formula



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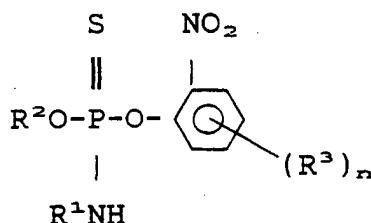
with approximately stoichiometric amounts of the nitrophenol described above and then reacting the reaction product with an alkali metal alkoxide $\text{M}'\text{O}-\text{R}^2$.

Both reactions are best carried out in an inert organic solvent. Examples are, in particular, aliphatic and aromatic halogenated hydrocarbons such as dichloromethane, chloroform and chlorobenzene, and also acetonitrile.

A particularly favourable temperature range for the above reactions has been found to be, for example, $40-70^\circ\text{C}$. Below this range reaction times become longer and the conversion decreases, whilst above this range precautions need to be taken to prevent evaporation of some components of the reaction mixture. Moisture must be excluded under any circumstances during the reaction process.

The products thus obtained, which are best purified by means of column chromatography, have the following structure

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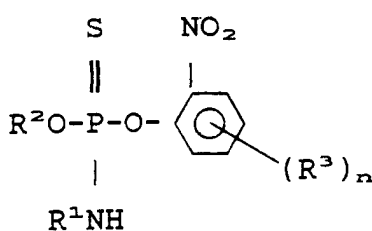


(wherein $n = 1$ to 3).

Experimental part

I. To a solution of 76g of 2-nitro-4-methylphenol (0.5 mole) dissolved in 400ml of acetonitrile was added 8g of anhydrous potassium carbonate. Then 101g of O-ethyl-N-isopropylamido thionophosphoric acid chloride (0.5 mole) was added under vigorous stirring and heating to 60°C. The reaction mixture was maintained at that temperature for three hours and then cooled to room temperature and poured into ice water. The separated oily substance was subsequently dissolved in benzene, separated from the aqueous phase, washed with water and dried. The benzene was then removed by vacuum distillation. In this way 127g of O-(2-nitro-4-methylphenyl)-O-ethyl-N-isopropylamido thionophosphate (I), which was identified by nucleus resonance spectroscopy, was obtained.

II. In the same way, similar yields of O-(2-nitro-4,5-dimethylphenyl)-O-methyl-N-isopropylamido thionophosphate (II), O-(2-nitro-4,6-dimethylphenyl)-O-methyl-N-isopropylamido thionophosphate (III) and O-(2-nitro-4,5-dimethylphenyl)-O-ethyl-N-sec-butylamido thionophosphate (IV) were obtained, the acid-binding agents used being trimethylamine, triethylamine or pyridine.

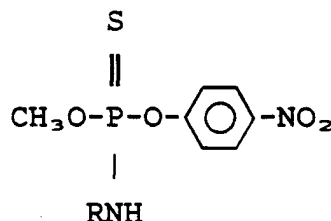


| | R ¹ | R ² | R ³ | n | Position on the phenyl ring |
|-----|---------------------------------|-------------------------------|-----------------|---|-----------------------------|
| I | i-C ₃ H ₇ | C ₂ H ₅ | CH ₃ | 1 | 4 |
| II | i-C ₃ H ₇ | CH ₃ | CH ₃ | 2 | 4, 5 |
| III | i-C ₃ H ₇ | CH ₃ | CH ₃ | 2 | 4, 6 |
| IV | s-C ₄ H ₉ | C ₂ H ₅ | CH ₃ | 2 | 4, 5 |

DOCUMENT II (State of the Art)

(identical to corresponding document in Paper A)

The invention relates to the preparation of new herbicides containing as an active ingredient a compound of the following structural formula



wherein R is a C₁-C₄ alkyl.

15 These derivatives of amido thionophosphoric acid with a nitro group as the substituent on the phenyl group have a broader spectrum of activity as herbicides than similar known compounds.

20 The application of a moderately large dose of the active ingredient - approximately 6 to 8 kg/ha - utilising the herbicide composition according to the invention will severely restrict the growth of many broad-leaved weeds and grass species, without any damage to crop plants such as rice, soy bean, pulses and cotton being observed. Approximately 10 to 15 kg/ha of active ingredient needs to be used to control completely the growth of weed species and
25 eradicate every single weed. Since this may give rise to some phytotoxicity to useful plants it is preferable to apply such a relatively concentrated dosage at the pre-emergence stage.

30 The herbicide compositions according to the invention are generally

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most effective when applied before the weed germinates. The germination of the weed seeds is then prevented.

The active ingredient represented by the above formula may be applied in the form of dusts, granulates or in aqueous form, and as a solution or dispersion.

Example 1

20 parts by weight of the compound according to the invention, O-methyl-N-isopropylamido-O-(4-nitrophenyl)-thionophosphoric acid ester, were mixed and ground together with 75 parts by weight of bentonite and 5 parts by weight of sodium alkylbenzene sulphonate to obtain a wettable powder, which is mixed with water and then applied.

Example 2

200g of the same compound as in Example 1 were dissolved with heating in xylene. The solution was then sprayed onto clay granules to obtain a granulate with 10% active ingredient.

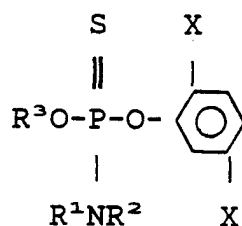
Example 3

Greenhouse experiments were conducted with the herbicide composition prepared in accordance with Examples 1 and 2. Using a dose of 6 to 7 kg/ha of active ingredient, the growth of weeds such as spring wild-oat (*avena fatua*), white mustard (*sinapsis alba*) - and to a somewhat lesser extent millet - was found to be significantly inhibited whilst the crop plants maize and soy bean were undamaged.

DOCUMENT III (State of the Art)

(identical to corresponding document in Paper A)

The invention relates to derivatives of amido thionophosphoric acid of the general structural formula



10 wherein R^1 is hydrogen or a methyl group, R^2 a C_1 - C_3 alkyl group, R^3 a C_1 - C_4 alkyl group and one of the groups X is a nitro group and the other group X is hydrogen or a methyl group.

15 The compounds according to the invention are prepared by reacting a phenol substituted in the 2 or 5 position by a nitro group and, where appropriate, additionally substituted by a methyl group in the 2 or 5 position not occupied by the nitro group with a phosphorus thiochloride. The intermediate product obtained is reacted
20 in two successive stages, first with a low aliphatic alcohol and then with a primary or secondary amine.

The compounds thus obtained are used in particular to modify synthetic resins and as an additive to high-pressure oils.

25 It was found, furthermore, that compounds of the above general

30

35

formula carrying a methyl group in the 5-position on the phenyl group are less suitable for the above uses.

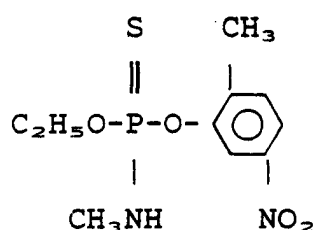
Example 1

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1 mole of 2-methyl-5-nitrophenol was reacted with 1 mole of phosphorus thiochloride to give O-(2-methyl-5-nitrophenyl)-thionophosphoric dichloride, which was then esterified with two moles of ethanol before being amidised with one mole of methylamine to give

10 the product of the following formula:

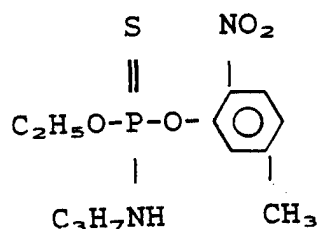
15



Example 2

20 Example 1 was repeated with the difference that 2-nitro-5-methylphenol was substituted for the phenol and propylamine was substituted for methylamine. The product thus obtained had the following formula

25



30 Example 3

Example 1 was repeated with the difference that 2-nitrophenol was used as the starting compound. The product thus obtained had the following formula

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