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2,862,019

THIOPHOSPHORIC ACID ESTERS AND THEIR PRODUCTION

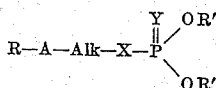
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Serial No. 644,463

Claims priority, application Germany March 12, 1956

5 Claims. (Cl. 260—461)

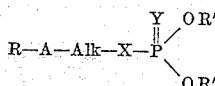
This invention relates to and has as its objects new and useful phosphoric acid esters, which correspond to the following formula:



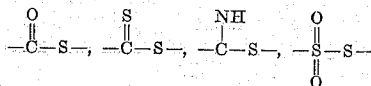
in which R—A stands for an acyl radical, Alk stands for a lower alkylene chain, X and Y stand for either oxygen or sulphur, and R' represents a lower alkyl radical, especially such ones having 1 to 4 carbon atoms.

Many thiophosphoric acid esters and related compounds have become known as very valuable insecticides or generally pesticides during the last years, and these compounds therefore have also become very useful plant-protecting agents. Intensive work has been done in finding more effective compounds especially such ones with better activities, lower toxicities and the like.

In accordance with the present invention a new class of valuable insecticides and plant-protecting agents has been found which corresponds to the above described formula; more particularly this invention is concerned with such compounds of the above formula

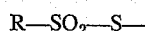


in which R stands for alkyl or aryl radicals (which may furthermore be substituted, e. g. by alkyl, halogen, nitro and the like) or for substituted primary or secondary amino radicals, A stands for one of the groups



Alk stands for a lower alkylene group having from 1 to 4 carbon atoms (which chain may be straight or branched) and R' stands for a lower alkyl radical such as methyl, ethyl, propyl or butyl.

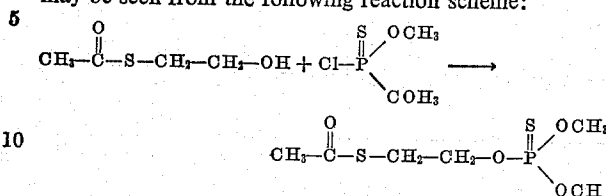
In accordance with the above said the acyl radical R—A may be the residue of thioalkanoic acids such as thioacetic acid, thiopropionic acid, thiobutyric acid, thiochloroacetic acid, thiodichloroacetic acid, thiotrichloroacetic acid, of aroyl-thio-acids such as thiobenzobac acid, thio-2,4-dichlorobenzobac acid, thionaphthoic acid, of heterocyclic-thio-acids such as thio- α -pyridinic acid, of thio- and dithiocarbamic acids such as dimethylthiocarbamic acid, dimethyldithiocarbamic acid, diethylthiocarbamic acid, diethyldithiocarbamic acid, pentamethylene thiocarbamic acid, 3-oxapentamethylene thiocarbamic acid, 3-azopentamethylene thiocarbamic acid and the corresponding dithiocarbamic acids of the afore mentioned compounds, of phenylthiocarbamic acid, phenyldithiocarbamic acid and the like. Furthermore the radical R—A may be one of the formula



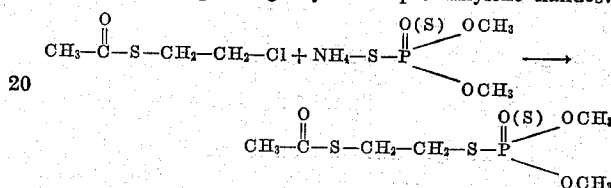
wherein R stands for methyl, ethyl, phenyl and the like.

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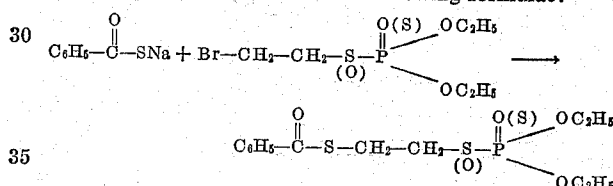
The preparation of these compounds may be accomplished by various ways. Thus, acyl mercapto alkanols may be reacted with thiophosphoric acid halides as it may be seen from the following reaction scheme:



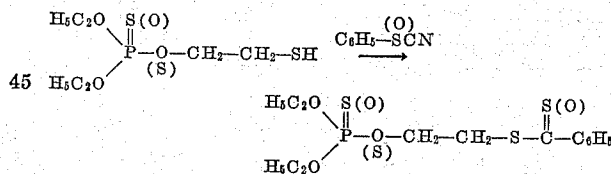
Another method for obtaining the thiolisomers or thiol-thiono analogs of the afore mentioned type consists in reacting salts of thio- or dithiophosphoric acid esters with the corresponding acyl mercapto alkylene halides:



A special method for preparing some compounds of the inventive type consists in reacting haloalkyl thio- or dithiophosphoric acid esters with salts of thiocarbonic acids as it may be seen from the following formulae:



Still another way for obtaining some classes of the inventive compounds consists in reacting mercapto alkyl thio- or dithiophosphoric acid esters with isocyanates or thioisocyanates as it may be seen from the following reaction scheme:



It has to be understood, however, that all these above mentioned reaction schemes and their formulae have been given only by way of illustration without limiting the present invention thereto.

The compounds of the present invention are generally valuable insecticides and plant-protecting agents. They kill pests such as aphids, flies and mites and exhibit a very remarkable systemic action. The application of these compounds should be carried out according to the use of other known phosphor insecticides, i. e. in dilution or solution with solid or liquid carriers such as chalk, talc, bentonite, water, alcohols, liquid hydrocarbons etc. The inventive compounds may further be used in combination with other known insecticides or pesticides, etc. Effective concentrations of 0.0001% to 1.0% kill pests effectively. The combinations of the compounds may be sprayed or dusted or otherwise brought in contact with pests or plants to be protected. They may also be used as aerosols.

As a special example for demonstrating the use of the inventive compounds those compounds of the formula shown below have been used for combating Colorado beetles, flies and mosquito larvae. The compounds were

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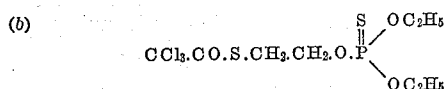
dissolved in a small amount of acetone (about 10 times its weight). Then the same amount of weight of an emulsifier, e. g. a benzyldiphenyloxypolyglycolate having 15 glycol residues is added. This solution then has been diluted with water to give dilutions of the concentration indicated in the list below. The activity is to be seen from the following table:

$(C_7H_5O)_2PS.S.CH_2.CH_2.S.COCH_3$	Colorado beetle, percent		flies, percent	
	0.001	100	0.001	90
$(C_2H_5O)_2PO.S.CH_2.CH_2.S.COCH_3$	Colorado beetle, percent		mosquito larvae, percent	
	0.001	100	0.0001	100

Example 1

(a) $CCl_3.CO.S.CH_2.CH_2.OH$

24 grams anhydrous hydroxyethyl mercaptan are dissolved in 450 millilitres anhydrous ether. 30 grams triethylamine are dropped into this solution while stirring. While cooling at 0° C. 55 grams trichloro-acetyl-chloride are added slowly. The reaction is completed within 2 hours, and the resulting solution is filtered with suction. The ether is removed in vacuo, and the residue is distilled at a pressure of 0.01 mm. Hg. It distills at 40° C. and is a colourless and water-insoluble oil.

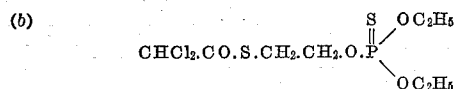


67 grams trichloro-acetyl- β -hydroxyethyl mercaptan which are obtained as described above are dissolved in 70 millilitres of pyridine. While stirring there are added at 40° C. slowly 57 grams diethylthionophosphoric acid monochloride. The reaction has been completed after 2 hours, wherein pyridine hydrochloride separates. The crude product is poured on ice-hydrochloric acid (200 grams ice/100 millilitres concentrated hydrochloric acid). The oil is taken up in chloroform, this solution is dried over anhydrous sodium sulphate, and the solvent then is removed by distillation. There are obtained 50 grams of the above shown thiophosphoric acid ester boiling at 0.01 mm. Hg at 110° C.

Example 2

(a) $CHCl_2.CO.S.CH_2.CH_2.OH$

As described in the foregoing example 24 grams anhydrous hydroxy-ethyl mercaptan are dissolved in 450 millilitres ether. 30 grams triethylamine are added and then while stirring and cooling at 0° C. 55 grams dichloroacetyl chloride dissolved in 150 millilitres ether are dropped in slowly. Working up the reaction mixture as described above there are obtained 45 grams of the above shown compound boiling at 2 mm. Hg at 72° C.



55 grams of the compound (a) are dissolved in 70 millilitres pyridine and while stirring and cooling at a temperature of 40° C. there are added slowly 57 grams diethylthionophosphoric acid monochloride. Working up the reaction mixture as described in Example 1 there are obtained 51 grams of the above shown ester boiling at 0.01 mm. Hg at 108° C.

Example 3

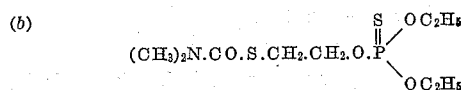
(a) $(CH_3)_2N.CO.S.CH_2.CH_2.OH$

63 grams hydroxyethyl mercaptan are dissolved in 250

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millilitres methylethyl ketone. 120 grams finely divided potassium carbonate are added and while stirring and cooling the temperature to 60° C. there are added 87 grams dimethylamino carbamic acid chloride. The temperature is kept at 60° C. for a further hour wherein the reaction is completed. The salts, which have been formed during the reaction are filtered with suction and

from the filtrate the solvent is removed by distillation. There are obtained 92 grams of the above shown alcohol boiling at 0.01 mm. Hg at 82° C.

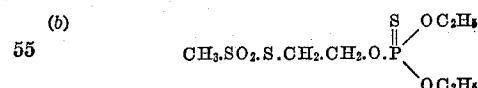


45 grams of the above mentioned alcohol (a) are dissolved in 35 grams pyridine. There are added at 40° C. 58 grams diethyl-thionophosphoric acid monochloride. Keeping the temperature for at least 3 hours at 40° C. the reaction product is poured in a diluted (5%) hydrochloric acid in a sufficient amount to give a Congo-red reaction. The oil which separates is taken up in chloroform and worked up in usual manner. There are obtained 45 grams of the above shown ester boiling at 0.01 mm. Hg at 127° C. and being a colourless water-insoluble oil.

Example 4

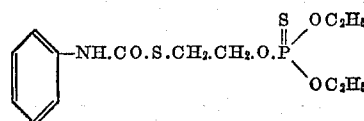
(a) $CH_3.SO_2.S.CH_2.CH_2.OH$

67 grams ($\frac{1}{2}$ mol) of the sodium salt of methylthiosulphonic acid are treated with 130 grams of bromohydrin for 20 minutes at a temperature at about 75° C. The reaction mixture is cooled and then taken up in 500 millilitres benzene. The precipitated sodium bromide is removed by filtration and the benzenic layer is dried over anhydrous sodium sulphate. After distilling off the solvent the residue is distilled in vacuo. There are obtained 60 grams of the above shown alcohol boiling at 0.01 mm. Hg at 105° C.



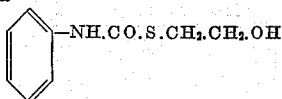
56 grams of the above shown S-methanthiosulphonic acid β -hydroxyethyl ester are dissolved in 42 grams pyridine and 80 grams diethylthionophosphoric acid chloride are dropped into this solution. Keeping the temperature at about 45° C. the reaction mixture is stirred for a further hour, and worked up as described in the foregoing examples. There are obtained 79 grams of the new ester of the above shown formula as a water-insoluble and slightly yellow coloured oil. This compound decomposes when distilled even in high vacuo.

Example 5



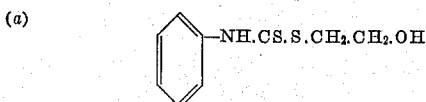
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43.5 grams phenylthiocarbamic-acid-hydroxyethyl ester of the formula

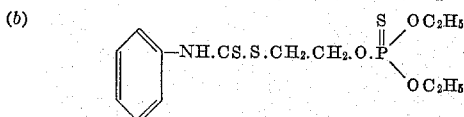


which may be obtained according to Journ. Chem. Soc. 119, 1861 (1921), are dissolved in 20 millilitres ether and this solution is added to a suspension of 70 grams sodium ethylate in 80 millilitres ether. The sodium compound of the above shown alcohol precipitates in the form of a thick jelly. After precipitation has completed there are added at a temperature of 35° C. 42 grams diethylthionophosphoric acid chloride. The temperature arises to about 48° C. and reaction is completed while warming the reaction mixture for a further period of about 5 hours at 45° C. The reaction product then is poured into water, the oily precipitation is taken up in 100 millilitres chloroform and the chloroformic solution washed with water and dried over anhydrous sodium sulphate. After the chloroform has been distilled off there are obtained 25 grams of the above shown new ester as a yellow and thick water-insoluble oil, which may not be distilled without decomposition even in high vacuo.

Example 6

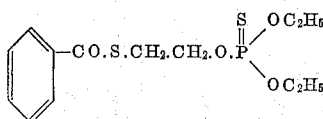


41 grams phenylisothiocyanate ($\frac{1}{10}$ mol) are brought together with the molecular amount (24 grams) hydroxyethylmercaptan and heated to a temperature of about 85° C. After a short period of time the reaction starts and the temperature arises to about 110° C. This temperature is kept for a further period of about 5 minutes, and then the reaction mixture may cool down. The alcohol of the above shown formula is pure enough for further reaction. The yield is almost quantitative.

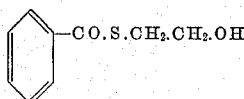


61 grams of the above alcohol are dissolved in 32 grams pyridine, and 56 grams diethylthionophosphoric acid chloride are added while stirring. The temperature is kept for 12 hours at 30 to 40° C. and the reaction product then is poured into water which has been made acidic by adding diluted hydrochloric acid so that the aqueous solution reacts Congo red. The oil which separates is taken up in chloroform and this solution is washed with water and dried over anhydrous sodium sulphate. The chloroform is distilled off, and the remainder consists of 53 grams of the thick water-insoluble and undistillable oil.

Example 7



46 grams thiobenzoic-acid- β -hydroxyethylester of the following formula

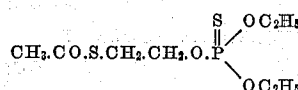


(boiling at 0.01 mm. Hg: 195° C.) which may be prepared from sodium thiobenzoate and glycol chlorohydrin according to known methods are dissolved in 25

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grams pyridine, while stirring there are added 48 grams O,O-diethylthiophosphoric acid chloride. The temperature is kept for 3 hours at 40° C. and the crude product is poured into water and acidified with diluted hydrochloric acid to give a Congo-red reaction. The oil which precipitates is taken up in chloroform, the chloroformic layer is washed with water and worked up in the usual manner as described in the foregoing examples. There are obtained 32 grams of the new ester of the above shown formula boiling at 0.04 mm. Hg at 160° C.

Example 8

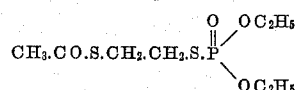


120 grams (1 mol) thioacetic-acid- β -hydroxyethylester boiling at 100° C. 10 mm. Hg which may be obtained by known methods (from sodium thioacetate and glycol chlorohydrin, see Journ. Chem. Soc. 121, 2145 [1922]) of the following formula



are dissolved in 164 grams pyridine. While stirring there are added 188 grams O,O-diethylthiophosphoric acid chloride. The temperature is kept for further 5 hours at 40° C. and the reaction mixture then is worked up as described in the foregoing examples. There are obtained 180 grams of the new ester boiling at 2 mm. Hg at 135° C. (or at 0.01 mm. Hg at 95° C.).

Example 9

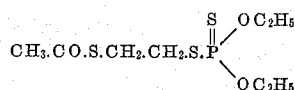


140 grams thioacetic-acid- β -chloroethylester of the following formula



(see Journ. Chem. Soc. 121, 2145 [1922]) are dropped into a solution of 185 grams of the ammonium salt of O,O-diethylthiophosphoric acid in 250 millilitres of methylethyl ketone. The reaction is completed by heating the mixture for a period of 5 hours to 60° C. The salt which precipitates is filtered with suction and the methylethyl ketone is distilled off in vacuo. The residue is taken up in benzene. The benzenic solution is washed with water and finally dried over anhydrous sodium sulphate. After distilling off the benzene the new ester of the above formula is distilled in vacuo: boiling at 0.01 mm. Hg 101° C.

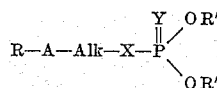
By the same way but using instead of 185 grams of the ammonium salt of O,O-diethylthiophosphoric acid, 205 grams of the ammonium salt of the corresponding thiolthionoanalogue there is obtained the ester of the following formula



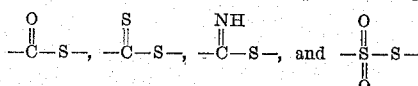
boiling at 0.01 mm. Hg at 90° C.

I claim:

1. A compound of the general formula



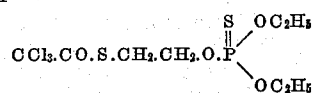
in which R stands for a member selected from the group consisting of lower alkyl, halo-substituted lower alkyl, phenyl, anilino, and lower alkylamino radicals; A stands for a radical selected from the group consisting of



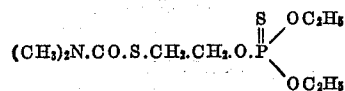
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Alk stands for a lower alkylene chain having from 1 to 4 carbon atoms; X and Y each stand for a member selected from the group consisting of oxygen and sulfur, one of them being sulfur; and R' is a lower alkyl radical having 1 to 4 carbon atoms.

2. A compound of the formula

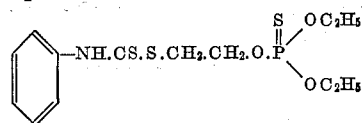


3. A compound of the formula

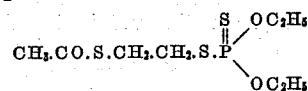


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4. A compound of the formula



5. A compound of the formula



No references cited.

UNITED STATES PATENT OFFICE
Certificate of Correction

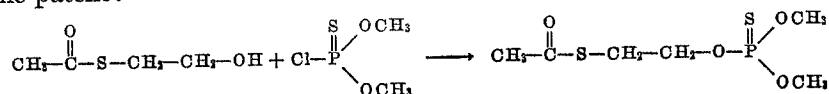
Patent No. 2,862,019

November 25, 1958

Gerhard Schrader

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, lines 5 to 12, the reaction scheme should appear as shown below instead of as in the patent:



Signed and sealed this 14th day of April 1959.

[SEAL]

Attest:

KARL H. AXLINE,
Attesting Officer.

ROBERT C. WATSON,
Commissioner of Patents.