

United States Patent Office

2,961.457

Patented Nov. 22, 1960

1

2.961.457

NEW ESTERS OF O,O-DIALKYLPHOSPHORIC OR O,O-DIALKYLTHIONOPHOSPHORIC ACIDS

Heinz Pohlemann and Siegfried Winderl, Ludwigshafen (Rhine), Herbert Stummeyer, Mannheim, and Heinrich Adolphi, Limburgerhof, Pfalz, Germany, assignors to Badische Anilin- & Soda-Fabrik Aktiengesellschaft, Ludwigshafen (Rhine), Germany

No Drawing. Filed Dec. 30, 1958, Ser. No. 783,671

Claims priority, application Germany Jan. 2, 1958

12 Claims. (Cl. 260—461)

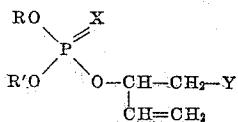
This invention relates to a process for the production of new esters of O,O-dialkylphosphoric or O,O-dialkylthionophosphoric acids, and to the new esters themselves. It relates in particular to the production of esters of O,O-dialkylphosphoric and O,O-dialkylthionophosphoric acids with substituted butenols, and to the esters themselves.

It is already known that triesters of phosphoric acids are obtained by reacting dialkoxyphosphoric acid mono-halides with alcohols or phenols. According to the process disclosed in U.S. patent specification No. 2,536,647, for example, the alkali salt of para-nitrophenol is allowed to act on the bis-(beta-chlorethyl)-thiophosphoryl chloride obtainable by the reaction of sulfur with chloro-bis-(beta-chlorethyl)-phosphite, whereby there is formed bis-(chlorethyl)-paranitrophenyl-thiophosphate. As alcohols for the reaction with phosphoric acid ester halides there have been used both saturated, unsaturated, linear or branched chain alcohols and also thioalcohols. For example by the reaction of methylalyl alcohol or its alkali salts with phosphoric acid ester halides, for example with O-mono- or O,O-di-alkylphosphoric acid halides, the corresponding methylalyl phosphates are obtained (cf. U.S. patent specification No. 2,176,416).

Many of the triesters of phosphoric acids already prepared in large numbers have considerable technical importance and are known as destructive agents for insects or rodents, or may be used as corrosion protective agents, flame protective agents, flotation agents, softeners or as additives for high pressure lubricants.

The primary object of the present invention consists in the discovery and production of new halogen-free esters of O.O-dialkylphosphoric acids and O.O-dialkylthionophosphoric acids which have both strong insecticidal and ovicidal properties but which on the contrary are less toxic for warm-blooded animals than the phosphoric acid esters hitherto known. A further object consists in the discovery of new insecticides which do not contain any halogen atoms, which can be used against pests of all kinds and which above all have a systematic action.

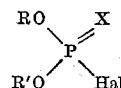
We have found that the above objects can be achieved and that new halogen-free O,O-dialkylphosphoric acid esters of substituted butenols of the general formula:



in which R and R' stand for lower aliphatic saturated hydrocarbon radicals, especially alkyl groups with 1 to 4 carbon atoms, X stands for an oxygen or sulfur atom, and Y stands for a radical from the group consisting of alkoxy, alkoxyloxy, phenoxy and nitrophenoxy groups containing 1 to 4 carbon atoms, mono- and di-alkylamino groups with 1 to 4 carbon atoms in the alkyl groups, cycloalkylamino, anilino, pyrrolidyl, alkylmercapto and alkylsulfonyl groups with 1 to 4 carbon atoms in the alkyl radicals and phenylmercapto and phenylsulfonyl groups, are obtained by reacting a O-O-dialkylphosphoric

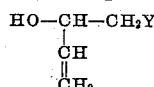
5

(or O,O-dialkylthionophosphoric) acid halide of the general formula:



in which R, R' and X have the meaning given above and Hal is a halogen atom, with a butene-(3)-ol-(2) substituted in 1-position and of the general formula:

10



in which Y has the meaning given above.

15 in which Y has the meaning given above.

16 Suitable butene-(3)-ol-(2) compounds substituted in 1-position and in which Y is an oxygen atom combined with an alkyl radical are 1-alkoxybutene-(3)-ols-(2) with 1 to 4 carbon atoms in the alkoxy groups, such as 1-methoxybutene-(3)-ol-(2), 1-ethoxy-butene-(3)-ol-(2), and also 1-propyl- and 1-isopropyl-butene-(3)-ol-(2) and also the isomeric 1-butyl-butene-(3)-ols-(2). Further butene-(3)-ols-(2) substituted in 1-position by an oxygen-containing radical are 1-allyloxy-butene-(3)-ol-(2) and also 1-phenoxy-butene-(3)-ol-(2), and if desired the phenoxy group may be substituted by a nitro group. As representatives of butenols substituted in 1-position in the substituent contains a nitrogen atom through which the linkage with the butenol radical takes place there may be mentioned for example 1-methylamino-butene-(3)-ol-(2) and also the corresponding 1-ethylamino-, 1-propylamino- and 1-butylamino-butene-(3)-ols-(2), as well as 1-dimethyl-, 1-diethyl-, 1-dipropyl-, 1-dibutyl-, 1-methylethyl-, 1-methylpropyl-, 1-ethylpropyl- and 1-ethylbutyl-amino-butene-(3)-ols-(2). As initial butenols of this kind there may also be mentioned 1-anilino-butene-(3)-ol-(2) and also 1-substituted butenols in which the N-atom of the substituents is connected to a cycloalkane radical, for example cyclopentyl, cyclohexyl or cyclo-octyl, or is a constituent of a heterocyclic compound which contains no further unsaturated linkages and further hetero atoms. Such butenols are for example 1-cyclopentylamino-butene-(3)-ol-(2), 1-cyclooctylamino-butene-(3)-ol-(2), 1-pyrrolidylbutene-(3)-ol-(2) and 1-piperidino-butene-(3)-ol-(2).

45 Of the derivatives of butene-(3)-ol-(2) compounds substituted in 1-position, those are especially suitable initial materials of which the substituent is an alkyl mercapto group containing up to 4 carbon atoms or a phenyl-mercaptop group, and the sulfur atom may also be oxidized to a sulfonic acid group. There may be mentioned for example 1-methylmercapto-butene-(3)-ol-(2), 1-ethyl-mercapto-butene-(3)-ol-(2), 1-propyl- or 1-butyl-mercapto-butene-(3)-ol-(2) and also 1-methyl- or 1-ethyl-sulfonyl-butene-(3)-ol-(2), 1-propyl- or 1-butylsulfonyl-butene-(3)-ol-(2) and 1-phenylsulfonyl-butene-(3)-ol-(2).

55 Of the O.O-dialkylphosphoric or O.O-dialkylthiono-
phosphoric acid monohalides serving as the second reac-
tion component there may be mentioned the chlorides,
bromides and iodides of O.O-dialkylphosphoric and O.O-
60 dialkylthionophosphoric acids, the chlorides being the
preferred compounds. The alkyl groups may be identical
or different alkylradicals with 1 to 4 carbon atoms. These
monohalides of O.O-dialkylphosphoric or O.O-dialkyl-
thionophosphoric acids will hereinafter be referred to
65 briefly as O.O-dialkylphosphoric acid monohalides. They
are readily accessible known compounds which are ob-
tained for example by reaction of phosphorus oxychloride
or thionophosphoric acid trihalides with the calcu-
lated amount of an aliphatic monohydric alcohol. As
70 representative for these reaction components there may
be mentioned above all dimethoxyphosphoric acid mono-
chloride, dimethoxyphosphoric acid monobromide and
monoiodide, and also the corresponding halides of O.O-

diethyl-, O,O-dipropyl- and O,O-dibutyl-phosphoric acid, as well as the chlorides, bromides and iodides of O,O-dimethylthionophosphoric acid, O,O-diethylthionophosphoric acid, O,O-dipropylthionophosphoric acid and O,O-dibutylthionophosphoric acid.

The reaction takes place by introducing the two reaction components in an anhydrous medium and in general it is immaterial which component is introduced first. It is suitable to add the dialkylphosphoric acid monohalide to the substituted butenol. The initial materials are used in about equivalent amounts. Sometimes it may be advantageous however to use one or other initial material in slight excess, for example 1.2 to 1.5 times the theoretically calculated amount.

Working in the presence of inert organic diluents may be convenient. As diluents there may be used for example aromatic, aliphatic and cycloaliphatic hydrocarbons, such as benzene, toluene, xylene, gasolines and cyclohexane or aliphatic chlorohydrocarbons, as for example methylene chloride, chloroform, and also ethylene chloride and carbon tetrachloride. The use of solvents is especially recommended when one or both of the reactants is solid. It has been found to be advantageous to collect the hydrogen halide set free by means of substances which bind hydrogen halide for example by the addition of pyridine, aniline, methylaniline, triethylamine, tripropylamine or other amines of which the boiling point lies above the reaction temperature. Alkali carbonates or alkali bicarbonates may also be used for the purpose. The said substances effect the removal of the hydrogen halide from the sphere of the reaction as soon as it is formed by the reaction. This removal of the halogen hydrides set free may be described as base neutralization of halogen hydrides.

The reaction already takes place appreciably even in the cold, but it is preferable to work at room temperature or at higher temperatures, for example at about 10° to 130° C., advantageously at about 15° to 75° C., if necessary in closed vessels.

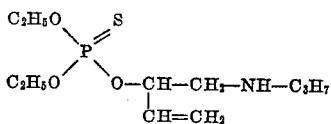
The following examples will further illustrate this invention but the invention is not restricted to these examples.

The parts specified in the examples are parts by weight.

Example 1

56.4 parts of diethoxythionophosphoric acid monochloride are allowed to react with a mixture of 37.7 parts of 1-propyl-amino-butene-(3)-ol-(2) and 23.7 parts of anhydrous pyridine slowly while stirring vigorously. The temperature thereby rises to 50° C. After the completion of the addition, the whole is stirred for another 4 to 5 hours at 45° to 50° C. to complete the reaction. The reaction product is cooled to room temperature, 20 parts of water and 100 parts of benzene are added thereto, stirred well and the aqueous layer separated from the non-aqueous layer in a separator. The latter is dried with sodium sulfate. After distilling off the solvent, 72 parts of a non-distillable oil remain.

The compound has the formula:

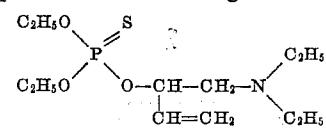


Example 2

56.4 parts of diethoxythionophosphoric acid monochloride are allowed to flow while stirring into a mixture of 42.9 parts of diethylaminobutene-(3)-ol-(2) and 23.7 parts of pyridine. After completion of the addition, the whole is stirred for another 5 hours at about 60° C. and then worked up as in Example 1. After separating into phases and distilling off the solvent from the organic phase, there remain as a residue 68 parts of an oil which cannot be distilled.

5

The compound has the following formula:

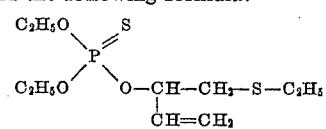


Example 3

10

56.4 parts of diethoxythionophosphoric acid monochloride are added to 39.6 parts of 1-ethylmercaptobutene-(3)-ol-(2) and 23.7 parts of anhydrous pyridine while stirring well. It is then stirred for another 5 hours at 40° to 45° C. The reaction mixture is cooled to room temperature, about 20 parts of water and 100 parts of benzene added, stirred well and the layers separated. The benzene solution is then washed with dilute hydrochloric acid and water and dried over sodium sulfate. The solvent is distilled off. The residue may be distilled with partial decomposition. At 0.5 mm. Hg pressure and 130° to 135° C. there are obtained 74 parts of the compound of the following formula:

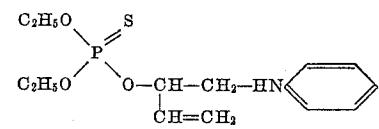
15



Example 4

37.6 parts of diethoxythionophosphoric acid monochloride are allowed to flow slowly with good stirring into a mixture of 32.6 parts of 1-anilino-butene-(3)-ol-(2) and 15.8 parts of anhydrous pyridine. The reaction temperature rises to 45° C. After completion of the addition the whole is stirred for another 5 hours at 55° to 60° C. and then worked up as in Example 1. After distilling off the solvent from the resultant organic phase, there remain 60 parts of the compound of the following formula as a non-distillable oil.

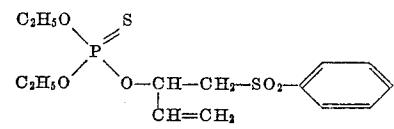
20



Example 5

42.4 parts of 1-phenylsulfonyl-butene-(3)-ol-(2) and 15.8 parts of pyridine are mixed and, while stirring well, 37.6 parts of diethoxythionophosphoric acid chloride are allowed to flow in. The whole is stirred for another 5 hours at 50° to 60° C., worked up as described in Example 1, and 60 parts of the new phosphoric acid ester are obtained as a non-distillable oil of the formula:

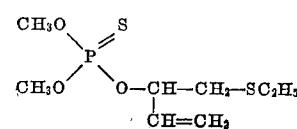
25



Example 6

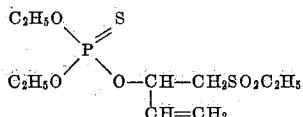
40 parts of 1-ethylmercaptobutene-(3)-ol-(2), 24 parts of anhydrous free pyridine and 50 parts of benzene are brought together and 48 parts of dimethoxythionophosphoric acid monochloride are allowed to flow in while stirring well. The reaction mixture is then further stirred for another 5 hours at 40° C. After cooling, a further 50 parts of benzene and 20 parts of water are added. The mixture is well shaken. The organic phase is separated and dried over sodium sulfate. After distilling off the solvent there remains a residue of 49 parts of a yellow oil of the formula:

75



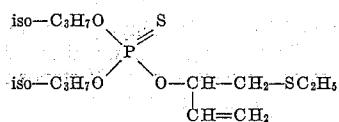
Example 7

68 parts of diethoxythionophosphoric acid monochloride are allowed to drip while stirring well into a mixture of 60 parts of 2-hydroxybutene-(3)-yl ethyl sulfone, 30 parts of anhydrous pyridine and 250 parts of benzene. After the addition had been completed, the whole is stirred for another 5 hours at 45° to 50° C. After the reaction material has been cooled it is washed with water and then the organic layer is dried over sodium sulfate. After distilling off the solvent there remain behind 91 parts of a pale brown readily mobile oil. The compound has the formula:



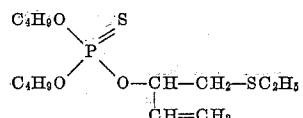
Example 8

432 parts of di-isopropoxythionophosphoric acid chloride are allowed to flow slowly into a mixture of 264 parts of 1-ethylmercaptobutene-(3)-ol-(2) and 160 parts of anhydrous pyridine heated to 30° C. while stirring powerfully. The whole is then stirred for another 5 hours at 45° to 50° C. to complete the reaction. After the reaction product has been cooled to room temperature, it is worked up in the manner described in Example 7 after the addition of 500 parts of benzene. After distilling off the solvent there are obtained 600 parts of a yellow-brown oil of the formula:



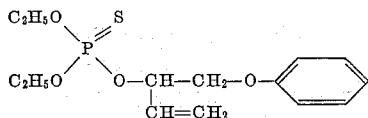
Example 9

73.2 parts of dibutoxythionophosphoric acid chloride are allowed to flow while stirring into a mixture, heated to 45° C., of 40 parts of 1-ethylmercaptobutene-(3)-ol-(2) and 23.7 parts of anhydrous pyridine. After the addition has been completed, the whole is stirred for another 5 hours at 50° C. and, after the addition of 50 parts of benzene, worked up as in Example 7. After distilling off the solvent, there remain 83.7 parts of a pale brown colored oil of the formula



Example 10

28.2 parts of diethoxythionophosphoric acid chloride are added to a mixture, heated to 70° C., of 24.6 parts of 1-phenoxybutene-(3)-ol-(2) and 20.7 parts of finely powdered potassium carbonate while stirring well. The whole is then stirred for another 5 hours at 75° C. After adding 50 parts of benzene, it is worked up as in Example 7. After distilling off the solvent, there are obtained 33 parts of an almost colorless oil. The compound has the formula:

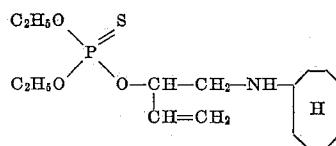


Example 11

37.6 parts of diethoxythionophosphoric acid chloride are allowed to flow into a mixture of 40 parts of 1-cyclooctylaminobutene-(3)-ol-(2) and 16 parts of anhydrous pyridine while stirring well. Stirring is then continued for another 5 hours at 50° C. and the whole worked up as in Example 7 after the addition of 100 parts of benzene.

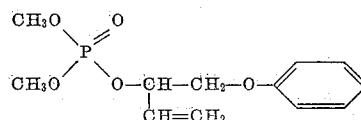
75

After distilling off the solvent, there remain 46 parts of a viscous red-brown oil of the formula:



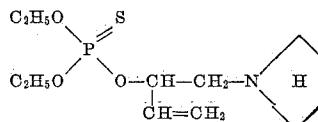
Example 12

49.2 parts of 1-phenoxybutene-(3)-ol-(2) and 24 parts of anhydrous pyridine are mixed and while stirring well 43.2 parts of dimethoxyphosphoric acid chloride are allowed to flow in. The whole is stirred for another 5 hours at 40° to 50° C. and then worked up as in Example 6. 44 parts of a colorless oil are obtained. The compound has the formula:



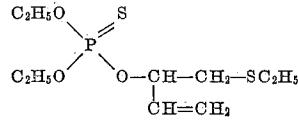
Example 13

37.6 parts of diethoxythionophosphoric acid chloride are allowed to flow slowly while stirring well into a mixture of 28.2 parts of 1-pyrrolidinobutene-(3)-ol-(2), 50 parts of carbon tetrachloride and 16 parts of anhydrous pyridine. The temperature thereby rises to 40° C. After all has been added, the whole is stirred for another 6 hours at 50° C. to complete the reaction. The reaction product is cooled to room temperature and worked up as in Example 7. After distilling off the solvent, 18 parts of a dark brown liquid remain behind having the formula:



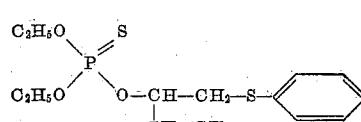
Example 14

36.6 parts of diethoxythionophosphoric acid monochloride are added while stirring well to 26.4 parts of 1-ethylmercaptobutene-(3)-ol-(2), 50 parts of toluene and 21.2 parts of finely powdered sodium carbonate. The whole is then stirred for another 5 hours at 70° to 75° C. The reaction mixture is cooled to room temperature and worked up as in Example 7. After distilling off the solvent, 30.7 parts of a brownish liquid are obtained having the formula:



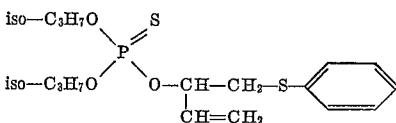
Example 15

28.2 parts of diethoxythionophosphoric acid monochloride are allowed to flow while stirring well into a mixture of 27 parts of 1-phenylmercaptobutene-(3)-ol-(2) and 12 parts of anhydrous pyridine. When the addition is completed, the whole is stirred for another 5 hours at 50° C. Then it is cooled to room temperature. 50 parts of benzene are added and the product worked up as in Example 7. After distilling off the solvent there remain 40 parts of a golden yellow oil. The compound has the formula:



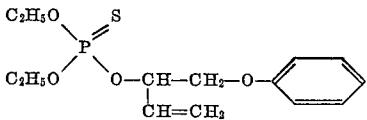
Example 16

32.4 parts of di-isopropoxythionophosphoric acid chloride are allowed to flow while stirring into a mixture of 27 parts of 1-phenylmercaptobutene-(3)-ol-(2), 50 parts of methylene chloride and 12 parts of anhydrous pyridine. The whole is stirred for another 5 hours at 40° C., then cooled to room temperature and worked up as in Example 7. After distilling off the solvent there remain 43.3 parts of a yellowish oil of the formula:



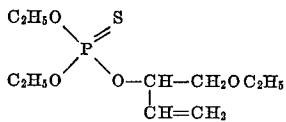
Example 17

37.6 parts of diethoxythionophosphoric acid chloride are allowed to flow slowly into a mixture of 32.8 parts of 1-phenoxybutene-(3)-ol-(2) and 16 parts of anhydrous pyridine while stirring well. Then the whole is stirred for another 5 hours at 50° C. After adding 50 parts of benzene, it is worked up as in Example 7. The solvent is distilled off. There remains a residue of 49.8 parts of a yellow oil of the formula:



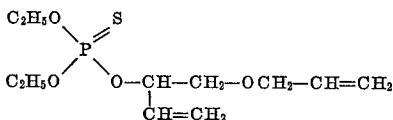
Example 18

37.6 parts of diethoxythionophosphoric acid monochloride are allowed to flow slowly while stirring into a mixture of 22 parts of 1-ethoxybutene-(3)-ol-(2) and 16 parts of anhydrous pyridine. When all has been added, the whole is stirred for another 5 hours at 50° C. It is then cooled to room temperature, 50 parts of benzene added and the product worked up as in Example 7. After distilling off the solvent there remain 21 parts of an almost colorless liquid. The compound has the formula:



Example 19

37.6 parts of diethoxythionophosphoric acid monochloride are added while stirring well to 25.6 parts of 1-allyloxybutene-(3)-ol-(2) and 16 parts of anhydrous pyridine. The whole is then stirred for another 5 hours at 50° C. The reaction mixture is cooled to room temperature, 50 parts of benzene are added and the product worked up as in Example 7. After distilling off the solvent, there are obtained 46.8 parts of an almost colorless liquid of the formula:

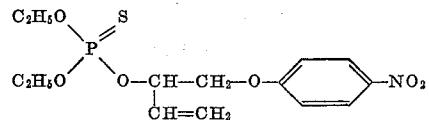


Example 20

37.6 parts of diethoxythionophosphoric acid monochloride are allowed to flow while stirring into a mixture of 42 parts of 1-(para-nitrophenoxy)-butene-(3)-ol-(2) and 16 parts of anhydrous pyridine. The whole is stirred for another 5 hours at 50° C., then cooled to room temperature and 50 parts of benzene added. It is worked up as in Example 7. After distilling off the solvent, there re-

75

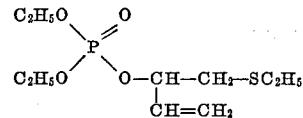
mains as a residue 25 parts of a red-brown oil of the formula:



Example 21

10 68.8 parts of diethoxyphosphoric acid monochloride are allowed to flow slowly while stirring well into a mixture of 52.8 parts of 1-ethylmercaptobutene-(3)-ol-(2) and 32 parts of anhydrous pyridine. When the addition is completed, the whole is stirred for another 3 hours at 50° C. It is then cooled to room temperature, 50 parts of benzene are added and the whole worked up as in Example 7. After distilling off the solvent there remain 36 parts of a colorless oil of the formula:

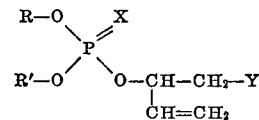
20



We claim:

1. Any compound of the general formula:

30

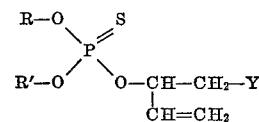


in which R and R' stand for alkyl groups having 1 to 4 carbon atoms, X stands for a member of the group consisting of oxygen and sulfur and Y stands for a radical

35 from the group consisting of alkoxy with 1 to 4 carbon atoms, allyloxy, phenoxy, nitrophenoxy, mono- and di-alkylamino with 1 to 4 carbon atoms in the alkyl groups, cycloalkylamino, anilino, pyrrolidyl, alkylmercapto and alkylsulfonyl with 1 to 4 carbon atoms in the alkyl groups, phenylmercapto and phenylsulfonyl.

40 2. Any compound of the general formula:

45

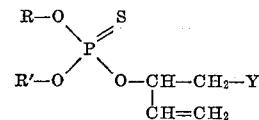


in which R and R' are alkyl groups with 1 to 4 carbon atoms and Y stands for an alkylmercapto radical containing 1 to 4 carbon atoms.

50

3. Any compound of the general formula:

55

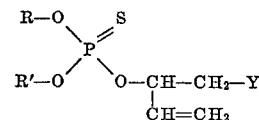


in which R and R' stand for alkyl groups with 1 to 4 carbon atoms and Y for an alkylsulfonyl group which contains 1 to 4 carbon atoms in the alkyl radical.

60

4. Any compound of the general formula:

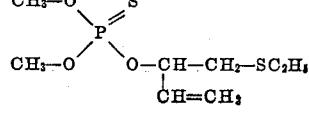
65



in which R and R' stand for alkyl groups with 1 to 4 carbon atoms and Y for a monoalkylamino group containing 1 to 4 carbon atoms in the alkyl radical.

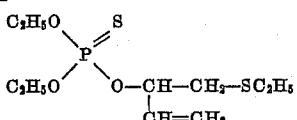
70

5. The compound of the formula:

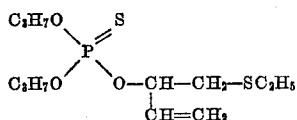


9

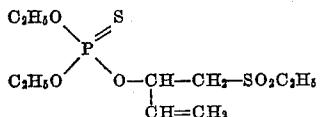
6. The compound of the formula:



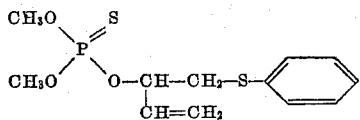
7. The compound of the formula:



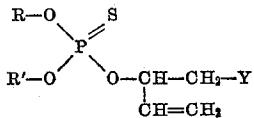
8. The compound of the formula:



9. The compound of the formula:



10. A compound having the general formula:

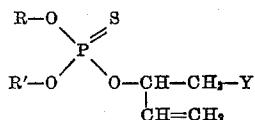


10

in which R and R' stand for alkyl groups with 1 to 4 carbon atoms and Y stands for a dialkylamino group containing from 1 to 4 carbon atoms in the alkyl radicals.

11. A compound of the general formula:

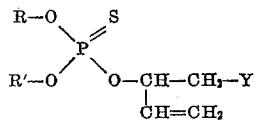
5



10 in which R and R' stand for alkyl groups with 1 to 4 carbon atoms and Y stands for phenylmercapto.

12. A compound of the general formula:

15



in which R and R' stand for alkyl groups with 1 to 4 carbon atoms and Y stands for phenoxy.

References Cited in the file of this patent

UNITED STATES PATENTS

25	2,736,726	Gaetzi et al. -----	Feb. 28, 1956
	2,777,792	Lutz et al. -----	Jan. 15, 1957
	2,852,513	Schrader et al. -----	Sept. 16, 1958
	2,865,801	Baker et al. -----	Dec. 23, 1958

80

FOREIGN PATENTS

789,122	Great Britain -----	Jan. 15, 1958
795,340	Great Britain -----	Mar. 21, 1958