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THIONOPHOSPHINIC ACID ESTERS AND PROCESS FOR THEIR PRODUCTION

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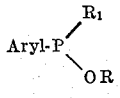
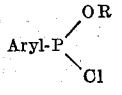
5 Claims. (Cl. 260—461)

The present invention relates to and has as its objects new and useful insecticidal thiophosphinic acid esters and processes for their production. Generally the new compounds of this invention may be represented by the following general formula



in which Aryl stands for an aryl radical, R_1 for an arbitrarily substituted alkyl radical and R for preferably low molecular weight alkyl radicals.

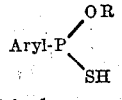
Ester chlorides of arylphosphonous acids having the following constitution (I)



(I)

are known in the literature.

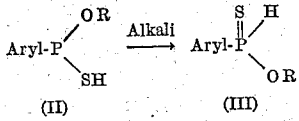
From these ester chlorides, aryl-thiolphosphonites of the following constitution (II)



(II)

can be easily obtained in known manner with hydrogen sulfide.

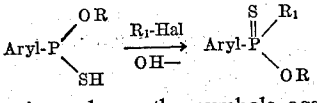
These aryl-thiophosphonites react with alkali with the formation of the isomeric compounds of the following constitution (III)



(II) (III)

In the foregoing formulae the symbols have the same significance as given in the above said first formula.

In accordance with the present invention it has now been found that the aforementioned aryl-thiolphosphonites, when reacted with alkyl halides in the presence of acid-binding agents, easily form aryl-alkyl-thionophosphinic acid esters of the following general formulae:

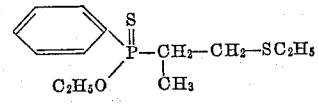


In this reaction scheme the symbols again have the same significance as given in the above said first formula. More specifically the radical R may be a lower alkyl radical up to 4 carbon atoms, whereas the radical R_1 stands for lower alkylene radicals also up to 4 carbon atoms and substituted by alkyl mercapto groups and carboxylic lower alkyl ester groups.

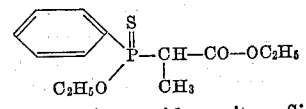
The compounds obtainable according to the present process and not yet described in literature are distinguished by a good insecticidal action and are intended to be used chiefly for plant protection. They are applied in a manner known in principle, i.e. in combination with suitable solid or liquid extenders or diluents, if desired with the use of other solvents or emulsifiers.

As examples for the special utility of the inventive compounds the esters of the following formulae

(I)



(II)



have been tested against spider mites, flies and caterpillars. Aqueous solutions of the aforementioned compounds have been prepared by admixing them with the same amount of an auxiliary solvent (acetone). A commercial emulsifier (benzyl hydroxy diphenyl polyglycol ether) is added in an amount of 20% referred to active ingredient. This premixture then is diluted with water to the desired concentration. The tests have been carried out as follows:

(*a*) Against spider mites (contact-insecticidal action): bean plants (*Phaseolus vulgaris*) of about 15 inches height were sprayed drip wet with solutions as prepared above in a concentration as shown below. The bean plants have been infested heavily with the two-spotted spider (species *Tetranychus telarius*). Evaluation has been carried out after 24 hours, 48 hours and 8 days. The following results have been obtained:

Compound	Aqueous concentration (in percent active ingredient/water	Killing rate (in percent)
(I)	0.01	100
(II)		

(*b*) Against flies (*Musca domestica*). About 50 flies are placed under covered petri dishes in which drip wet filter paper has been placed which is sprayed with an insecticidal solution of a concentration as shown below. The living status of the flies has been determined after 24 hours. The following results have been obtained:

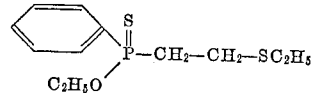
Compound	Aqueous concentration (in percent active ingredient/water	Killing rate (in percent)
(I)	0.001	100
(II)		

(*c*) Against caterpillars of the type diamond black moth (*Plutella maculipennis*): white cabbage has been sprayed drip wet with aqueous emulsions as prepared above in a concentration as shown below. Caterpillars (10 each) have been placed on the sprayed leaves of the white cabbage. The living status has been determined after 24 and 48 hours. The following results have been obtained:

Compound	Aqueous concentration (in percent active ingredient/water	Killing rate (in percent)
(I)	0.1	100
(II)		

The following examples are given for the purpose of illustrating the present invention.

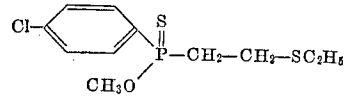
Example 1

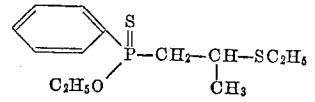


47 grams (0.25 mol) of phenyl-ethyl-thiolphosphonite (B.P. 105° C./1 mm. Hg.) are dissolved in 50 ml. of anhydrous alcohol. A sodium ethylate solution containing 0.25 mol of dissolved sodium is added thereto while stirring. Subsequently 32 grams of β-chloroethyl-thioethyl ether are added at 75° C. while stirring is continued. The mixture is further heated to 80° C. for an hour, then cooled to room temperature and the reaction product is poured into 300 ml. of icewater. The precipitated oil is taken up with 200 ml. of benzene, washed with water until neutral and then dried over sodium sulfate. Upon fractionating 41 grams of the new ester of B.P. 82° C./0.01 mm. Hg are obtained as a water-insoluble colorless oil. Yield: 60% of the theoretical. Caterpillars are killed completely with 0.1% solutions. Systematic action on spider mites with 0.1% solutions=100%.

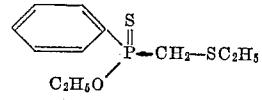
Calculated for mol 274: S, 23.2%; P, 11.3%. Found: S, 22.5%; P, 10.86%.

By exactly the same way there may be obtained the following compounds:



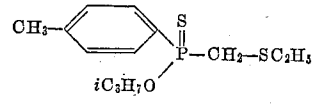


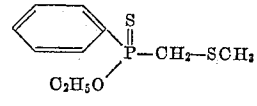
Example 2



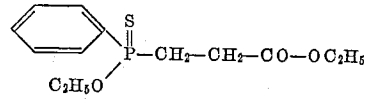
47 grams (0.25 mol) of phenyl-ethyl-thiolphosphonite are dissolved in 50 ml. of anhydrous alcohol. A sodium ethylate solution containing 0.25 mol of dissolved sodium is added thereto at 20° C. Subsequently 28 grams of α-chloro-methyl-thioethyl ether are added dropwise while stirring is continued. The mixture is heated to 60° C. for an hour and worked up as described in Example 1. 33 grams of the new ester of B.P. 76° C./0.01 mm. Hg are thus obtained as a colorless water-insoluble oil. Yield: 51% of the theoretical. Aphids and spider mites are killed completely with 0.01% solutions. Systemic action on spider mites with 0.1% solutions=100%.

By the same way there may be obtained the compounds of the following formulae:





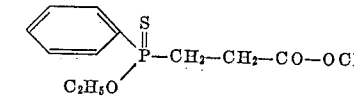
Example 3



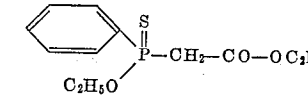
47 grams (0.25 mol) of phenyl-ethyl-thiolphosphonite are dissolved in 50 ml. of anhydrous alcohol. A sodium ethylate solution containing 0.25 mol of dissolved sodium is added thereto at 20° C. while stirring. Subsequently 46 grams of β-chloro-propionic acid ethyl ester are added dropwise at 50° C. while stirring is continued. The mixture is further heated to 70–75° for an hour and then worked up as described in Example 1. 55 grams of the new ester of B.P. 85° C./0.01 mm. Hg are thus obtained as a colorless water-insoluble oil. Yield: 77% of the theoretical. Spider mites are killed completely with 0.1% solutions.

Calculated for mol 286: S, 11.2%; P, 10.8%. Found: S, 10.9%; P, 10.8%.

By the same way there may be obtained the following compound:



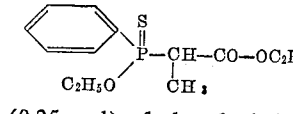
Example 4



47 grams (0.25 mol) of phenyl-ethyl-thiolphosphonite are dissolved in 50 ml. of anhydrous alcohol. A sodium ethylate solution containing 0.25 mol of dissolved sodium is added thereto at 20° C. while stirring. Subsequently 32 grams of chloro-acetic acid ethyl ester are added dropwise at 40° C. The mixture is further heated to 60° C. for an hour and then worked up as described in Example 1. 52 grams of the new ester of B.P. 78° C./0.01 mm. Hg are thus obtained as a water-insoluble colorless oil. Yield: 76% of the theoretical. Spider mites are killed completely with 0.1% solutions.

Calculated for mol 272: S, 11.8%; P, 11.4%. Found: S, 11.7%; P, 11.3%.

Example 5

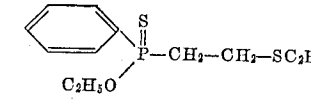


47 grams (0.25 mol) of phenyl-ethyl-thiolphosphonite are dissolved in 50 ml. of methanol. A sodium methylate solution containing 0.25 mol of dissolved sodium is added thereto at 20° C. Subsequently 46 grams of α-bromo-propionic acid ethyl ester are added dropwise at 40° C. while stirring is continued. The mixture is heated to 60° C. for another hour and then worked up as described in Example 1. 35 grams of the new ester of B.P. 78° C./0.01 mm. Hg are thus obtained as a colorless water-insoluble oil. Yield: 49% of the theoretical.

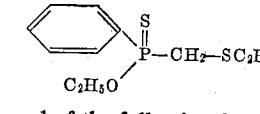
Calculated for mol 286: S, 11.2%; P, 10.9%. Found: S, 12.1%; P, 11.7%.

I claim:

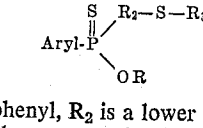
1. The compound of the following formula



2. The compound of the following formula

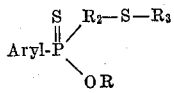


3. A compound of the following formula



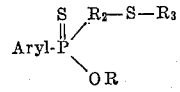
wherein aryl is phenyl, R_2 is a lower alkylene radical having up to 4 carbon atoms, R_3 is a lower alkyl radical and R is a lower alkyl radical having up to 4 carbon atoms.

4. A compound of the following formula



wherein aryl is chloro-substituted phenyl, R_2 is a lower alkylene radical having up to 4 carbon atoms, R_3 is a lower alkyl radical and R is a lower alkyl radical having up to 4 carbon atoms.

5. A compound of the following formula



wherein aryl is lower alkyl-substituted phenyl, R_2 is a lower alkylene radical having up to 4 carbon atoms, R_3 is a lower alkyl radical and R is a lower alkyl radical having up to 4 carbon atoms.

References Cited in the file of this patent

Kamai et al.: Zhur. Obshchei Khim, 28, 939–941 (1958), cited in Chem. Abs. 52, 17162 (1958).

Pudovik et al.: Bull. Acad. Sci. U.S.S.R. Div. Chem. Sci., English translation, 1952, 803–806.