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2,910,500

## PHENYL SULFOXY AND LOWER ALKYL SULFOXY O,O-DI (LOWER ALKYL) THIOPHOSPHATE ESTERS AND PROCESS FOR PREPARATION

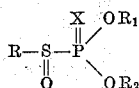
Gerhard Schrader, Wuppertal-Cronenberg, and Walter Lorenz, Wuppertal-Elberfeld, Germany, assignors to Farbenfabriken Bayer Aktiengesellschaft, Leverkusen, Germany, a corporation of Germany

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5 Claims. (Cl. 260-461)

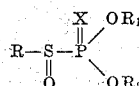
The present invention relates to and has as its objects new and useful phosphoric acid esters, which may be represented by the following formula



in which R stands for alkyl and aryl radicals, R<sub>1</sub> and R<sub>2</sub> stand for alkyl radicals especially lower alkyl radicals up to 4 carbon atoms, and X is oxygen or sulfur.

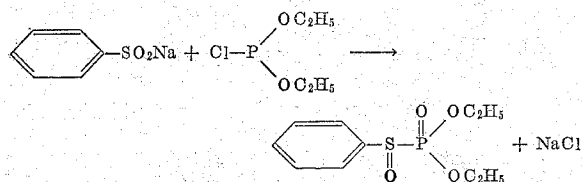
In the class of insecticides the phosphoric or thiophosphoric acid esters have become well known during the last years. These insecticides or generally pesticides are outstanding plant-protecting agents, and intensive studies have been done to find new phosphoric acid esters with special properties such as low toxicity or better activity against special classes of pests.

In accordance with the present invention it has now been found that new phosphoric acid esters with insecticidal properties and being useful in the field of plant protecting agents correspond to the above shown formula



in which more specifically R stands for alkyl radicals, such as methyl, ethyl, propyl (n-propyl or isopropyl), n-butyl, isobutyl, tert. butyl, or aryl radicals, such as phenyl, o-, m- or p-tolyl, o-, m- or p-chloro phenyl, nitrophenyl, methoxyphenyl, p-chloro-m-nitrophenyl, p-nitro-m-chloro phenyl, and the like.

These new esters of the above shown formula may be obtained by various methods. Thus, e.g. the phosphoric acid esters of the above shown formula, these are those esters in which X of the above shown formula stands for oxygen, may be obtained by reacting the corresponding aliphatic or aromatic sulfinic acids or their salts with O,O-dialkyl phosphorous acid halides. This reaction may be seen from the following scheme, using sodium benzene sulfinate and O,O-diethyl phosphorous acid chloride as reaction components:

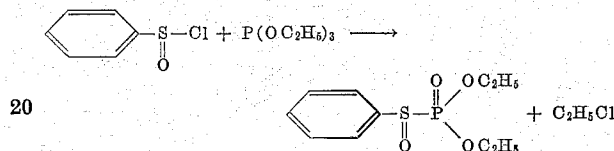


Instead of using the salts of the above said sulfinic acids also the free acids may be used in combination with suitable organic acid binding agents, such as tert. amines, e.g. pyridine. This reaction generally should be carried out in the presence of inert solvents, such as methanol,

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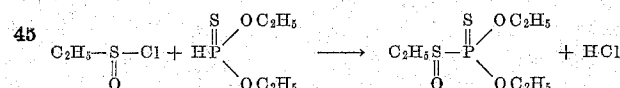
ethanol, methyl ethyl ketone, acetone, dimethyl formamide, benzene, toluene, and the like. The reaction furthermore may be carried out at temperatures from about 0 to 100° C., especially suitable are slightly elevated temperatures between 40 to 60° C.

It is also possible to prepare these compounds by an alternate way, starting from corresponding sulfinic acid halides, especially chlorides, and reacting these with secondary or tertiary alkyl phosphites. This way sometimes is very economical, since sulfinic acid chlorides recently became known as being very easily obtainable, see e.g. Chemical and Engineering News, volume 34, page 477 (1956). This reaction may be seen from the following scheme, using benzene sulfinic acid chloride and triethyl phosphite as reactants:



Instead of using trialkyl phosphites also dialkyl phosphites successfully may be used, whereby instead of an alkyl halide a hydrogen halide is splitted off. This reaction also should be carried out usually in the presence of inert organic solvents, such as especially benzene, toluene, lower saturated liquid hydrocarbons (benzine or ligroine) or chlorinated aliphatic hydrocarbons, such as methylene chloride, ethylene chloride, chloroform, and the like. This reaction may be carried out also between about 0 to 100° C., but especially suitable in this case are temperatures somewhat lower than room temperature, say between about 10 to 30° C.

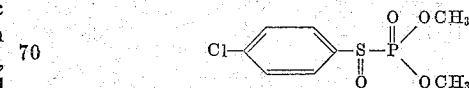
The aforementioned method also may successfully be used for the preparation of corresponding thiophosphoric acid esters. These are compounds of the above shown formula in which X is sulfur. In this case instead of trialkyl phosphites corresponding trialkyl monothiophosphites or dialkyl monothiophosphites may be used. This reaction may be shown by the following scheme, using ethyl sulfinic acid chloride and diethyl thiolphosphite as starting materials:



The reaction conditions in this case are the same as described in the preparation of corresponding phosphates.

The compounds of the present invention are generally valuable insecticides especially systematically active insecticides and kill effectively insects such as flies, aphids, mites and the like. A special advantage of the inventive compounds is their activity against sucking insects, such as caterpillars. Usually they are to be applied in the same manner as other well known phosphorus containing insecticides, i.e. in concentrations from about 0.0001 to about 1% in dilution with liquid or solid carriers. Examples of such liquid carriers are water, alcohols, liquid hydrocarbons, ketones and the like, and as examples of solid carriers there may be named talc, chalk, bentonite etc. Additional emulsifiers may be used, if necessary, and the new compounds may be dusted or sprayed e.g. as aerosols or brought in contact otherwise with living plants or insects.

As an example for the special utility of the above shown compounds the compound of the following formula



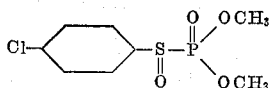
has been tested against black bean aphids, spider mites

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and caterpillars. Tests have been carried out against black bean aphids and spider mites on drip wet sprayed black beans and nasturtium plants and on drip wet sprayed cabbage respectively (using caterpillars of large garden whites). Black bean aphids and spider mites are killed effectively with 0.01% solutions and caterpillars are killed with 0.1% solutions. The solutions have been prepared by diluting the active ingredient with the same amount of dimethyl formamide, thereafter adding 20% by weight of active ingredient of benzyl hydroxy diphenyl polyglycol ether (commercial emulsifier) and diluting this pre-mixture with water to the above shown concentrations.

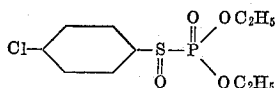
The following examples are given by way of illustration only without, however, limiting the present invention hereto:

## Example 1



110 grams of sodium-p-chloro-benzene sulfinate are added to 600 millilitres of dimethyl formamide. While stirring there is dropped into this solution at 50° C. 65 grams of dimethyl phosphorous acid monochloride dissolved in 80 millilitres of toluene. The reaction is completed at 60° C. within one hour, whereupon the reaction mixture is cooled at room temperature. Sodium chloride precipitates and is removed by filtration. The solvent is distilled off in vacuo, and the remaining oil is taken up in 200 millilitres of benzene. The benzenic solution is washed twice with 50 millilitres of water, whereupon the benzenic layer is dried over anhydrous sodium sulfate. The benzene is distilled off in vacuo. A small amount of impurities crystallizes and can be removed by freezing and filtration. The remaining oil is distilled in vacuo at 85 to 86° C. There are obtained 100 grams of the above shown ester as slightly yellowish colored water-unsoluble oil. LD<sub>50</sub> rat per os: 10 mg./kg.

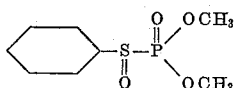
## Example 2



45 grams of p-chloro-benzene sulfonic acid are dissolved in 100 millilitres of methyl ethyl ketone. There are added while stirring 21 grams of pyridine and 40 grams of diethyl phosphorous acid monochloride are dropped into this solution at a temperature of 35° C. The temperature is kept at 40° C. for half an hour and the reaction mixture then is cooled to room temperature. The reaction mixture is poured into 200 millilitres of ice-water and the oil is taken up in 200 millilitres of benzene. The benzene layer is separated, washed twice with 50 millilitres of water and dried over sodium sulfate. After distilling off the solvent there are obtained 35 grams of the above ester boiling at 0.01 mm. at 108 to 110° C. 0.1% solutions exhibit complete systemic action on black bean aphids and spider mites and also kill caterpillars effectively.

Calc. for mol-weight 296.5: Cl=11.8%, P=10.4%, S=10.7%. Found: Cl=11.1%, P=9.9%, S=11.0%.

## Example 3



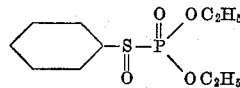
55 grams of a crude sodium benzene sulfinate (containing 67% of benzene sulfonic acid salt and 33% of sodium chloride) are mixed with 150 millilitres of dimethyl formamide. At a temperature of 50° C. there are added while stirring 33 grams of dimethyl phosphorous acid monochloride in the form of a solution in 40

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millilitres of toluene. The reaction is completed within 1 hour at a temperature of 60° C. After cooling to room temperature and filtration the ester is worked up as described in the foregoing examples. There are obtained 32 grams of the above ester, which distills at 0.01 mm. at 105° C. This ester is slightly yellowish colored and a water-unsoluble oil.

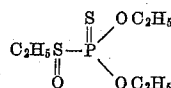
Calc. for mol-weight 262: S=12.2%, P=11.8%. Found: S=13.2%, P=11.9%. LD<sub>50</sub> rat per os: 25 mg./kg.

## Example 4



36 grams of benzene sulfonic acid are dissolved in 100 millilitres of methyl ethyl ketone; 21 grams of pyridine are added. While stirring there are dropped into this solution at 50° C. 43 grams of diethyl phosphorous acid monochloride dissolved in 44 millilitres of toluene. The reaction mixture is kept at 65° C. for 1 further hour, and worked up as described in the foregoing examples. There are obtained 30 grams of the new ester of the above shown formula.

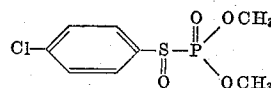
## Example 5



34 grams of ethyl sulfonic acid chloride are dissolved in 150 millilitres of methylene chloride and while stirring and cooling this solution to 25 to 30° C. there are dropped into this solution 55 grams (0.36 mole) of O,O-diethyl thiophosphite. The reaction mixture is stirred for a few minutes after the addition is completed, and then the solvent is distilled off. The remaining oily residue is treated with 160 millilitres of water and neutralized with sodium hydrocarbonate. The remaining oil is taken up in benzene. The benzenic solution is washed twice with a small amount of water and then dried over sodium sulfate. The solvent is distilled off. There are obtained 42 grams of the above ester as a colorless oil, which boils at 0.01 mm. at 45° C. Yield: 91% of the theoretical. The ester is water-unsoluble.

0.1% solutions kill black bean aphids and spider mites effectively, also caterpillars are killed with such solutions. The product is highly systemic active.

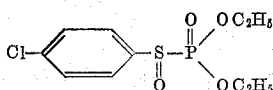
## Example 6



36 grams (0.85 mole) of p-chloro-benzene sulfonic acid chloride are dissolved in 50 millilitres of benzene, and treated dropwise while cooling at 15 to 25° C. into a solution of 46 grams (0.37 mole) of trimethyl phosphite in 150 millilitres of benzene. After the addition has been completed the mixture is stirred for a short period of time and the solvent then is removed by distillation. The remaining oily residue is stirred half an hour with water, and the aqueous layer is neutralized with diluted potassium carbonate solution. Now the oil is taken up in benzene, the benzenic solution is washed twice with a small amount of water, then dried over sodium sulfate and the organic solvent at last is distilled off. The above shown new ester boils at 0.01 mm. at 85 to 86° C. There are obtained 31 grams i.e. 62.5% of the theoretical of a slightly yellowish water-unsoluble oil. Spider mites and black bean aphids are killed effectively with 0.01% solutions of this ester. 0.1% solutions are systemic and kill also sucking insects as for instance caterpillars.

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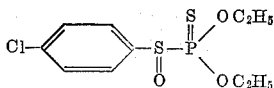
## Example 7



A solution of 48.5 grams (0.25 mole) of p-chloro-benzene sulfinic acid chloride in 50 millilitres of benzene is added dropwise while cooling to 10 to 20° C. to a solution of 49.8 grams (0.3 mole) of triethyl phosphite in 75 millilitres of benzene. After the addition has been completed the reaction mixture is stirred for further half an hour. The solvent then is distilled off and the remainder is washed with water and neutralized with a diluted potassium carbonate solution. The remaining oil is taken up in benzene, washed twice with water, dried over sodium sulfate and at last the benzene is distilled off. There are obtained 34 grams of the above ester as a slightly yellowish oil distilling at 0.01 mm. at 91 to 92° C. Yield: 45.8% of the theoretical. 0.1% solutions kill black bean aphids and are systemic active. Spider mites are killed with 0.01% solutions and caterpillars with 0.1% solutions of the above shown ester.

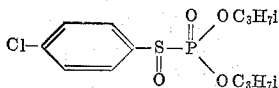
The same ester may be obtained by using 42 grams of diethyl phosphite instead of 49.8 grams of triethyl phosphite. The working up procedure is the same as shown above. The yield is slightly higher, it amounts up to about 56% of the theoretical.

## Example 8



39 grams of p-chloro-benzene sulfinic acid chloride are dissolved in 200 millilitres of petrol ether (boiling point about 60° C.). At a temperature of 20 to 25° C. this solution is added dropwise while cooling to 47 grams (0.3 mole) of diethyl thiophosphite. After the addition has been completed the reaction mixture is stirred for further 10 minutes. 100 millilitres of water are added. The layers are separated again and this procedure is continued, until the organic layer reacts neutrally. Now the organic layer is dried over anhydrous sodium sulfate and after evaporating the petrol ether and distilling the crude phosphoric acid ester there are obtained 44 grams of the above shown ester in the form of a light yellowish water-insoluble oil, which distills at 0.01 mm. at 94° C. Yield 71.4% of the theoretical. Black bean aphids and spider mites are killed completely with 0.01% solutions. 0.1% solutions are systemic and also kill caterpillars.

## Example 9



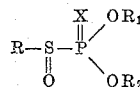
49.5 grams (0.25 mole) of p-chloro-benzene sulfinic acid chloride are dissolved in 50 millilitres of benzene, and this solution is dropped while cooling at 10 to 20° C. into a solution of 63 grams (0.3 mole) of triisopropyl phosphite in 200 millilitres of benzene. After the reac-

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tion has been completed the mixture is stirred for further half an hour and the solvent then is distilled off. The remaining oil is washed with water and neutralized with sodium hydrocarbonate. Then the oil is taken up in benzene, and the benzenic solution is washed with water, dried over anhydrous sodium sulfate and distilled. There are obtained 40 grams of the above ester as a slightly yellowish oil distilling at 0.01 mm. at 86° C. Yield: 49% of the theoretical. The ester is water-insoluble. Black bean aphids are killed with 0.1% solutions and spider mites with such solutions of 0.01% concentrations. The compound is slightly systemic.

We claim:

1. Phosphoric acid esters of the following formula



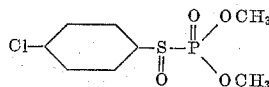
in which R stands for a member selected from the group consisting of lower alkyl, phenyl, lower alkyl phenyl, chlorophenyl, nitrophenyl and lower alkoxy phenyl radicals, R<sub>1</sub> and R<sub>2</sub> stand for lower alkyl radicals, and X stands for a member selected from the group consisting of oxygen and sulfur.

2. A process for the production of phosphoric acid esters, which comprises reacting a compound corresponding to the general formula

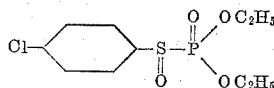


wherein R is a member selected from the group consisting of lower alkyl phenyl, chlorophenyl, nitrophenyl and lower alkoxy phenyl and X is a member selected from the group consisting of an alkali metal and a pyridine radical with O,O-dialkyl phosphorous acid chlorides.

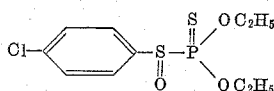
3. The phosphoric acid ester of the following formula



4. The phosphoric acid ester of the following formula



5. The phosphoric acid ester of the following formula



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