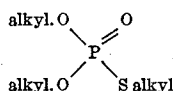


2,597,534

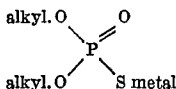
Gerhard Schrader, Opladen-Bruchhausen, Germany, assignor to Farbenfabriken Bayer, Leverkusen, Germany

4 Claims. (Cl. 260—461)

Hitherto the neutral esters of thiophosphoric acid of the formula:

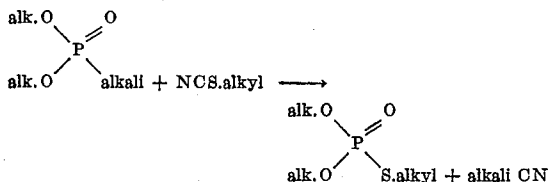


in particular the esters in which alkyl of the above formula is methyl, ethyl, propyl and isobutyl, were prepared by reacting salts of thiophosphoric acid of the formula:



with alkyl halides. In most cases, however, this reaction could successfully be carried through only when the salts of heavy metals, such as silver or lead salts, and as alkyl halides the iodides were used.

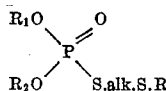
It has now been found that esters of the above type can easily be prepared by reacting alkyl thiocyanates with alkali salts of dialkyl phosphites. The dialkyl phosphites which are technically easily obtainable react hereby, as is known, in the tautomeric form. The reaction takes the following surprising course:



The reaction is most conveniently carried out in an inert solvent, e. g. in benzene or its homologues, chlorobenzene and also in ketones such as acetone, methyl ethyl ketone, methyl propyl ketone, and others. Slight heating, as a rule to about 40 to 60° C., is required. The alkyl radicals of the alkyl thiocyanates employed may belong to the lower or higher alkyls such as methyl, ethyl, propyl, butyl, hexyl, dodecyl. Also alkyl thiocyanates containing the SCN-group twice may be used in which case the reaction shown in the above equation will take place with two molecules of the alkali salts of dialkyl phosphites. Besides alkyl thiocyanates, also aralkyl thiocyanates may be used.

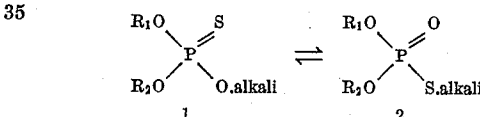
These neutral aliphatic esters of thiophosphoric acid are, as a rule, oily liquids of a high

It has further been found that neutral esters of thiolphosphoric acid of particular value and interest are obtained when in the above described new process instead of simple alkyl thiocyanates thiocyanates of the formula R. S. alk. SCN are used. R in this formula means alkyl, preferably methyl or ethyl, or aryl, in particular phenyl or substituted phenyl. The radical designated "alk" in this formula stands for a straight or branched alkylene chain. Compounds obtained by means of these thiocyanates correspond to the general formula:

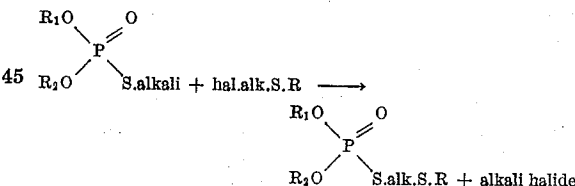


in which R₁ and R₂ are alkyl radicals which may be the same or different, and are preferably lower radicals such as methyl, ethyl, or propyl. These new esters of thiophosphoric acid are distinguished by very good insecticidal properties, in particular by their systemic insecticidal properties.

It has further been found that these valuable compounds can also be prepared by reacting alkali dialkyl thiophosphates with mercapto alkyl halides of the formula R. S. alk. hal. The alkali dialkyl thiophosphates react, as is known, e. g. from Journal of American Chemical Society 67 [1945], pp. 1662-1664 (T. W. Mastin, G. R. Norman and E. A. Weilmuenster) in their tautomeric form 2:



40 The reaction takes place according to the following equation:

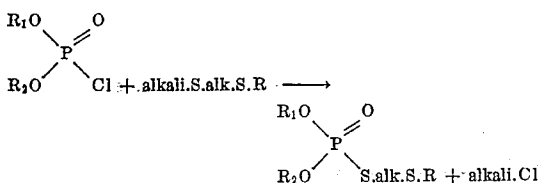


50 It is carried out in the presence of inert solvents of the kind mentioned above at elevated temperatures, usually at about 40 to about 100° C.

Another new process of preparing these compounds consists in reacting dialkyl phosphoric 55 chlorides with alkali salts of mercapto alkyl mer-

3

captans of the formula R. S. alk. SH. The reaction takes place according to the following equation:



Also here the reaction is carried through in the presence of an inert solvent of the mentioned kind at elevated temperatures, usually at about 40 to about 100° C.

Neutral aliphatic esters of thiophosphoric acid substituted in one ester group by the radical of an aliphatic or aromatic mercaptan obtainable by one of the forementioned processes are e. g.:

- O,O-diethyl S-β-ethylmercapto-ethyl thiolphosphate
- O,O-diethyl S-β-methylmercapto-ethyl thiolphosphate
- O,O-diethyl S-β-4-methylphenylmercapto-ethyl thiolphosphate
- O,O-diethyl S-ethylmercapto-methyl thiolphosphate
- O,O-diethyl S-4-methylphenylmercapto-methyl thiolphosphate
- O,O-di-isopropyl S-β-ethylmercapto-ethyl thiolphosphate

The present invention is illustrated by the following examples; it is, however, not restricted thereto:

Example 1

70 grams of diethyl phosphite are mixed with 2 cc. of absolute alcohol and diluted with 100 cc. of toluene. 12 grams of sodium are caused to act upon the solution thus obtained. When the sodium has dissolved, 37 grams of methyl thiocyanate are added drop by drop with stirring at 40° C. Stirring is continued at 40° C. for 2 hours. 15 cc. of water are then added to the reaction mixture and the precipitated salts are removed by filtering. 48 grams of O,O-dimethyl S-methyl thiolphosphate having a boiling point of 112–113° C. at 14 mm. pressure are obtained. The product is soluble in water.

Example 2

Sodium salt prepared from 12 grams of sodium and 70 grams of diethyl phosphite in benzene as described in Example 1 is heated to 45–50° C. with stirring. At this temperature 44 grams of ethyl thiocyanate are added drop by drop within 10 minutes controlling the temperature by cooling. The reaction mixture is then heated to 55° C. for one hour. After working up as usual 35 grams of O,O-diethyl S-ethyl thiolphosphate, boiling at 98° C. at 2 mm. pressure, are obtained. The new product is soluble in water to a limited degree.

Example 3

52 grams of n-propyl thiocyanate are reacted at 40° C. with the sodium salt prepared from 12 grams of sodium and 70 grams of diethyl phosphite in benzene as described in Example 1. The reaction mixture obtained is heated to 55° C. for one hour and then worked up as usual. 40 grams of O,O-diethyl S-propyl thiolphosphate, boiling at 103–105° C. at 1 mm. pressure, are obtained. The product is insoluble in water.

4

Example 4

57.5 grams of isobutyl thiocyanate are reacted at 40° C. with the sodium salt prepared from 12 grams of sodium and 70 grams of diethyl phosphite as described in Example 1. The reaction mixture thus obtained is heated to 55° C. for one hour and subsequently worked up as usual. 74 grams of O,O-diethyl S-isobutyl thiolphosphate, boiling at 105° C. at .5 mm. pressure, are obtained. The product is insoluble in water.

Example 5

65 grams of n-hexyl thiocyanate are reacted at 40° C. with the sodium salt prepared from 12 grams of sodium and 70 grams of diethyl phosphite as described in Example 1. The reaction mixture is heated to 55–60° C. for one hour and worked up as usual. 48 grams of O,O-diethyl S-hexyl thiolphosphate of the boiling point 125–130° C. at 1 mm. pressure are obtained.

Example 6

115 grams of dodecyl thiocyanate are reacted at 50° C. with the sodium salt prepared from 12 grams of sodium and 70 grams of diethyl phosphite as described in Example 1. The reaction mixture is heated to 55–60° C. for one hour and is then worked up as usual. 60 grams of O,O-diethyl S-dodecyl thiolphosphate, having a boiling point of 185–190° C. at .5 mm. pressure, are obtained.

Example 7

The sodium salt prepared from 12 grams of sodium and 70 grams of diethyl phosphite as described in Example 1 is heated to 45° C. At this temperature 76 grams of benzyl thiocyanate are added drop by drop with stirring. The reaction mixture is further heated to 40° C. for half an hour and is then worked up as usual. 70 grams of O,O-diethyl S-benzyl thiolphosphate with a boiling point of 165–170° C. at 2 mm. pressure are obtained.

Example 8

29 grams of ethylene dithiocyanate dissolved in 250 cc. of benzene are added drop by drop to the sodium salt prepared from 10 grams of sodium, 75 cc. of benzene and 56 grams of diethyl phosphite in the presence of 2 cc. of absolute alcohol as described in Example 1. The mixture obtained is heated to 60° C. for one hour and is then worked up in the usual manner. 15 grams of O,O,O,O-tetraethyl S,S-ethylene di-thiolphosphate with a boiling point of 190° C. at .5 mm. pressure are obtained. The product is insoluble in water.

Example 9

7 grams of sodium are suspended in 150 cc. of toluene. 42 grams of diethyl phosphite are added and the mixture is stirred at 40–50° C., until all sodium is dissolved. With stirring 44 grams of β-ethylmercapto-ethyl thiocyanate (boiling at 90° C. at 1 mm. pressure) are added drop by drop at a temperature of 40° C. The mixture is kept for one hour at 50° C. and is then worked up in the usual manner. Thus 28 grams of (C₂H₅O)₂PO.S.C₂H₄.S.C₂H₅ boiling at 137–141° C. at 1 mm. pressure are obtained. The product is a light-yellow oil which is insoluble in water.

Example 10

40 grams of β-methylmercapto-ethyl thiocyanate are added drop by drop with stirring at 40°

5

C. to the sodium salt solution obtained according to Example 9. The temperature is kept for one hour at 50° C. and is then worked up in the usual manner. Thus 34 grams of

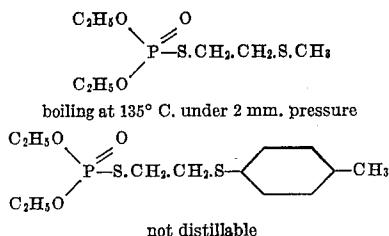


boiling at 134–138° C. at 2 mm. pressure are obtained.

Example 11

63 grams of β -mercapto-ethyl ethyl sulfide $C_2H_5.S.C_2H_4.SH$ (described in *Annalen der Chemie* 240, p. 311) are added to 12 grams of finely dispersed sodium in 170 cc. of toluene drop by drop, while stirring. The temperature is raised to 60° C. and then kept for half an hour. The sodium will then be dissolved. Thereafter the finely dispersed sodium salt of the mercaptan is cooled to 20° C. Thereto under constant outside cooling 87 grams of diethyl phosphoric monochloride, dissolved in 100 cc. of toluene, are added drop by drop within 20 minutes, while stirring. After adding the chloride the reaction product is kept at room temperature for a further hour. By adding 20 cc. of water the salts are then turned into a filterable form. After distilling off the toluene the remaining oil distills at a boiling point of 136° C. under 1 mm. pressure. 93 grams of O,O-diethyl S- β -ethylmercapto-ethyl thiophosphate, a slightly yellow oil, insoluble in water are obtained. Yield: 72 per cent of theory.

In a similar way can be obtained:



Example 12

7 grams of finely pulverized sodium are suspended in 100 cc. of toluene. 43 grams of diethyl phosphite are added thereto at a temperature of 40° C. The temperature of 40° C. is kept for half an hour. Then the sodium will be dissolved. Thereafter, 10 grams of sulfur are added to the reaction product at a temperature of 60° C., and it is then heated for another hour to 105° C. The sodium diethyl thiophosphate being now finely dispersed is reacted with 34 grams of chloromethyl ethyl sulfide $C_2H_5.S.CH_2.Cl$ (cf. *Berichte der Deutschen Chemischen Gesellschaft* 69 [1936], p. 1612) at a temperature of 55° C. The temperature of the reaction mixture is kept for another hour at 55° C., then 8 cc. of water are added, the toluene layer is removed and fractionated. 40 grams of O,O-diethyl S-ethylmercapto-methyl thiophosphate of a boiling point of 129–130° C. at 1.5 mm. pressure are obtained. The yield corresponds to 60 per cent of theory. The new thio-ester is insoluble in water.

Example 13

Sodium diethyl thiophosphate finely dispersed is prepared from the same quantities as in Example 1. 52 grams of chloromethyl 4-methylphenyl sulfide $CH_3.C_6H_4.S.CH_2.Cl$ (cf. *Berichte der Deutschen Chemischen Gesellschaft* 69 [1936], p. 1612) are added to this suspension. The reaction mixture is heated for 4 hours to 105°

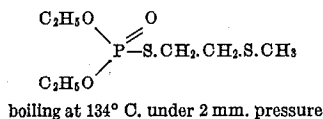
6

C.; the formed salts are then brought into a filterable form by adding 10 cc. of water, the toluene layer is separated and fractionated. 60 grams of O,O-diethyl S-4-methylphenylmercapto-methyl thiophosphate with a boiling point of 178° C. under .5 mm. pressure are obtained, corresponding to a yield of 65 per cent. The new substance is a colorless oil insoluble in water.

Example 14

Sodium diethyl thiophosphate is prepared from the same quantities as in Example 1. To this salt 37 grams of β -chloroethyl ethyl sulfide $C_2H_5.S.C_2H_4.Cl$ (cf. *Annalen der Chemie* 240 [1887], p. 310) are added at a temperature of 70° C., while stirring. The reaction mixture is then heated for another two hours to 105° C., and the salts are removed by means of water as in the preceding examples. By fractionating the toluene layer 54 grams of O,O-diethyl S- β -ethylmercapto-ethyl thiophosphate are obtained, corresponding to a yield of 70 per cent; colorless oil insoluble in water having a boiling point of 136° C. under 1 mm. pressure.

In a similar way e. g. the following compound can be produced:

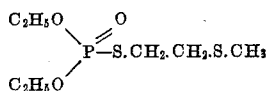


Example 15

7 grams of sodium powder are suspended in 100 cc. of toluene and heated with 42 grams of diisopropyl phosphite to 50° C., until the sodium is dissolved. Thereafter 9 grams of sulfur are added and the mixture is heated for another hour to 90–95° C. It is then cooled to 50° C., and at this temperature 37 grams of β -chloroethyl ethyl sulfide are added drop by drop. The reaction mixture is kept for further 4 hours at 90–95° C., while stirring. By adding 5 cc. of water the salts formed are thereupon brought into a filterable form. After sucking off the salts the solvent is removed from the toluene solution. The remaining crude product is now kept for 10 minutes at an inside temperature of 120° C. under a vacuum of 2 mm. to remove the last traces of the volatile solvent. O,O-diisopropyl S- β -ethylmercapto-ethyl thiophosphate thus obtained is a brown-yellow oil insoluble in water (60 grams). At a pressure of 2 mm. the ester can only be distilled with strong decomposition.

Example 16

Young peach trees infested with peach-aphides are sprayed with an aqueous solution containing 0.005 per cent of the following compound:

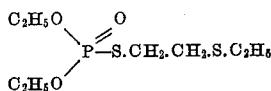


After some hours all aphides are killed.

This aqueous solution may also be used in the presence of alkaline reacting agents for simultaneously combating fungi.

Example 17

Talc is ground with the following substance:



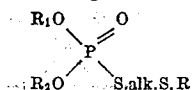
7

so that a 5-per-cent dust is obtained. This dust is applied to branches with caterpillars (*Mala-cosoma neustria*). The caterpillars are killed after a short time.

This application is a continuation-in-part of my copending earlier application Serial No. 94,721, filed May 21, 1949.

I claim:

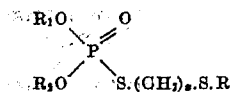
1. As new compounds neutral esters of thiol-phosphoric acid of the general formula:



wherein R_1 and R_2 stand for lower alkyl radicals, alk stands for a lower alkylene chain, and R stands for one of the group consisting of lower alkyl radicals, phenyl radicals and lower alkyl substituted phenyl radicals.

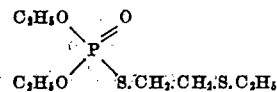
2. As new compounds neutral esters of thiol-phosphoric acid of the general formula:

8



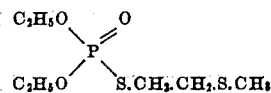
5. wherein R , R_1 and R_2 stand for lower alkyl radicals, and X is one of the integers 1 and 2.

3. As new compound the neutral ester of thiol-phosphoric acid of the formula:



10

4. As new compound the neutral ester of thiol-phosphoric acid of the formula:



15

GERHARD SCHRADER.

No references cited.

20