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PREPARATION OF ORGANOTHIOPHOSPHORUS HALIDES

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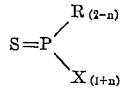
ABSTRACT OF THE DISCLOSURE

Process for the preparation of organophosphonothioic dihalides [$RP(S)X_2$] and diorganophosphinothioic halides [$R_2P(S)X$] which comprises reacting an organic sulfide [R_2S] with a phosphorus trihalide [PX_3] wherein R is hydrocarbyl of not more than 18 carbon atoms and X is halogen.

This invention relates to processes for the preparation of compounds of phosphorus and more particularly to processes for the preparation of organophosphonothioic dihalides and diorganophosphinothioic halides.

In accordance with this invention phosphorus compounds selected from the group consisting of compounds represented by the formula

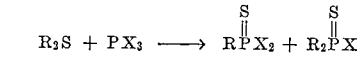


wherein each R, which can be the same or different, is hydrocarbyl of not more than 18 carbon atoms bonded to the phosphorus atom through a carbon-phosphorus bond, X is halogen (Cl, Br, F and I) and *n* is an integer from 0 to 1, and mixtures thereof are prepared by the process which comprises reacting an organic sulfide of the formula

$$R_2S$$

with a phosphorus trihalide of the formula PX_3 wherein each R is hydrocarbyl of not more than 18 carbon atoms and X is as defined above.

The reaction of this invention can be represented by the following non-stoichiometric expression



In accordance with the above represented reaction, the process of this invention results in the concomitant production of organophosphonothioic dihalides [$RP(S)X_2$] and diorganophosphinothioic halides [$R_2P(S)X$]. When substantially equimolar amounts of reactants are employed, the organophosphonothioic dihalides generally comprise a major amount of the product phosphorus compounds and the diorganophosphinothioic halides a minor amount of the product phosphorus compounds. However, the ratio of diorganophosphinothioic halide to organophosphonothioic dihalide in the product phosphorus compounds can be increased by using an excess of organic sulfide reactant.

Representative R hydrocarbon radicals of the compounds of the above formulae prepared by the process of this invention include by way of example alkyl (1 to 18 carbon atoms) such as methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, amyl, hexyl, heptyl, octyl, nonyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl and the various homologues and isomers of alkyl having from 1 to 18 carbon atoms, alkenyl (2 to 18 carbon atoms) such as vinyl, allyl, n-butenyl-1, n-butenyl-2, n-pentenyl-2, n-rexenyl-2, 2,3-dimethylbutenyl-2, n-heptenyl, n-decenyl, n-dodecenyl and the various homologues and isomers of alkenyl having 2 to 18 carbon atoms, alkynyl (3 to 18 carbon atoms) such as propargyl and the various homologues and isomers of alkynyl having from 3 to 18 carbon atoms, cycloalkyl and alkyl substituted cycloalkyl (3 to 18 carbon atoms) such as cyclopentenyl, cyclohexyl, mono- and polymethylcyclohexyl, mono- and polyethylcyclohexyl, cycloheptyl and the like, cycloalkenyl and alkyl substituted cycloalkenyl (3 to 18 carbon atoms) such as cycopentenyl, cyclohexenyl, cycloheptenyl, mono- and polyethylcyclohexenyl and the like, aryl (6 to 18 carbon atoms) such as phenyl, biphenyl, naphthyl and the like, aralkyl (7 to 18 carbon atoms) such as benzyl, phenylethyl, diphenylmethyl and the like and alkaryl (7 to 18 carbon atoms) such as tolyl, ethylphenyl, xylyl, butylphenyl, tert-butylphenyl, trimethylphenyl, diethylphenyl, methylpropylethylphenyl and the like.

The process of this invention is usually carried out with substantially equimolar amounts of organic sulfide and phosphorus trihalide, but an excess of either reactant can be employed. The reaction can be carried out in the liquid or vapor phase at temperatures from about 100° C. to 600° C. Preferably the liquid phase reaction is carried out at temperatures from about 250° C. to about 350° C. from the standpoint of optimum conversion in reasonable reaction periods. Reaction temperatures below about 250° C. can be used but reaction time is increased substantially at such lower temperatures. At temperatures above about 350° C. in the liquid phase some decomposition occurs and the yield of phosphonothioic and phosphinothioic compounds is substantially reduced. The vapor phase reaction is preferably carried out at temperatures from about 300° C. to 600° C. The reaction can be carried out at subatmospheric, atmospheric or superatmospheric pressure, the pressure not being critical. The exact reaction conditions, i.e. time, temperature and pressure will depend upon the specific organic sulfide employed. The reaction can be carried out in the presence of an inert organic medium or inert carrier gas. Suitable organic media include for example xylene, mesitylene, "Decalin," dichlorobenzene, benzene, toluene, "Tetralin" and chlorinated biphenyls. Suitable vapor phase inert carriers include for example nitrogen, helium, argon and methane.

The separation of the desired phosphorus compound from the product mixture is readily accomplished by conventional means well known in the art, e.g., fractional distillation under reduced pressure, selective extraction, fractional distillation using a carrier gas, film distillation, elution or any suitable combination of these methods.

The following examples will illustrate the invention. Parts and percent are by weight unless otherwise indicated.

EXAMPLE 1

A pressure vessel is charged with 9 parts of methyl sulfide and 20 parts of phosphorus trichloride. The vessel is sealed and the reactants are heated at 275° C. for 12 hours. At the end of this time the vessel is cooled to room temperature, opened and the liquid product mixture removed. Gas chromatographic analysis shows 8.3 wt. percent of the product mixture is methylphosphonothioic dichloride and 1.5 wt. percent of the product mixture is dimethylphosphinothioic chloride. The liquid product is fractionated and the methylphosphonothioic dichloride is recovered at 60–70° C., 50 mm. of mercury, and the dimethylphosphinothioic chloride is recovered at 100–103° C.. 50 mm. of mercury.

EXAMPLE 2

A pressure vessel is charged with 62.8 parts of methyl sulfide and 137.4 parts of phosphorus trichloride. The vessel is sealed and the reactants heated at 290° C. for 12 hours. At the end of this time the vessel is cooled and the product mixture removed. Nuclear magnetic resonance spectrum analysis indicates that 47.0 mole per-

cent of the phosphorus compound content of the product mixture is methylphosphonothioic dichloride and 17.5 mole percent of the phosphorus compound content of the product mixture is dimethylphosphinothioic chloride. The product mixture is fractionated and the methylphosphonothioic dichloride is recovered at 60°–70° C., 50 mm. of mercury, and the dimethylphosphinothioic chloride is recovered at 100° C.–103° C., 50 mm. of mercury.

EXAMPLE 3

A reaction mixture comprising 62.8 parts of methyl sulfide and 137.4 parts of phosphorus trichloride is admitted into a U-tube immersed in a bath containing a heat transfer agent at a temperature of about 500° C. at the rate of about 4 parts per minute. A stream of dry nitrogen flowing at the rate of about 100 parts per minute is also admitted to the U-tube. The average residence time is about 10 seconds. The gas stream emerging from the U-tube is led into an ice-cooled receiver. Yields of dimethylphosphinothioic chloride and methylphosphonothioic dichloride comparable to those of Example II above are obtained.

Following the procedures of the foregoing examples and using the appropriate reactants, the following organophosphonothioic dihalides are prepared.

Examples:

4 ethylphosphonothioic dichloride
5 methylphosphonothioic dibromide
6 propylphosphonothioic dibromide
7 sec-butylphosphonothioic dichloride
8 amylphosphonothioic dichloride
9 heptylphosphonothioic dichloride
10 decylphosphonothioic dichloride
11 octadecylphosphonothioic dichloride
12 hexylphosphonothioic diiodide
13 methylphosphonothioic diiodide
14 allylphosphonothioic dichloride
15 propenylphosphonothioic dichloride
16 octenylphosphonothioic difluoride
17 butenylphosphonothioic dichloride
18 cycloheptylphosphonothioic dichloride
19 cycloheptenylphosphonothioic difluoride
20 cyclohexylphosphonothioic dichloride
21 cyclohexenylphosphonothioic dichloride
22 phenylphosphonothioic dichloride
23 benzylphosphonothioic dichloride
24 phenylethylphosphonothioic difluoride
25 tolylphosphonothioic dichloride
26 ethylphenylphosphonothioic dichloride
27 xylylphosphonothioic dichloride
28 trimethylphenylphosphonothioic dichloride
29 diethylphenylphosphonothioic dichloride
30 diethylphenylphosphonothioic difluoride

The phosphorus compounds prepared by the process of this invention and numerous uses therefor are well known in the art. These compounds are useful as fire retardants and rust inhibitors, and as chemical intermediates in the preparation of petroleum additives, agricultural chemicals, organophosphorus polymers and other products of commercial interest. For example, valuable lubricity additives for lubricating oils can be prepared by reacting the phosphorus compounds prepared by the process of this invention with phenol at temperatures from about 80° C. to about 150° C. in the presence of an acid acceptor in accordance with the following equations

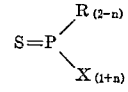
$$RP(S)X_2+2C_6H_5OH\rightarrow RP(S)(OC_6H_5)_2+2HX$$

$$R_2P(S)X+C_6H_5OH\rightarrow R_2P(S)OC_6H_5+HX$$

wherein R and X are as defined above.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. Process for the preparation of phosphorus compounds selected from the group consisting of compounds of the formula



wherein

R is hydrocarbon radical of not more than 18 carbon atoms selected from the group consisting of alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl, aralkyl and alkaryl,

X is selected from the group consisting of Cl, Br, F and I, and *n* is an integer from 0 to 1, and

mixtures thereof which comprise reacting an organic sulfide of the formula

$$R_2S$$

with a phosphorus trihalide of the formula PX_3 at a temperature from about 100° C. to about 600° C. wherein R and X are as defined above.

2. Process of claim **1** wherein the reaction is carried out in the liquid phase at a temperature above about 250° C.

3. Process of claim **1** wherein the reaction is carried out in the vapor phase at a temperature above about 300° C.

4. Process of claim **1** wherein the organic sulfide is an alkyl sulfide.

5. Process of claim **1** wherein the organic sulfide is an aryl sulfide.

6. Process of claim **1** wherein the phosphorus trihalide is phosphorus trichloride.

7. Process of claim **4** wherein the alkyl sulfide is methyl sulfide.

8. Process of claim **5** wherein the aryl sulfide is phenyl sulfide.

9. Process of claim **1** wherein the phosphorus trihalide is phosphorus trichloride and the organic sulfide is an alkyl sulfide.

10. Process of claim **9** wherein the alkyl sulfide is methyl sulfide.

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