An improved process for preparing a phosphorodichlorothioate of formula (I), wherein R is: a C₁₋₃₀ alkyl group, optionally substituted with a C₁₋₁₀ alkyl group, a C₁₋₃₀ alkoxy group, a C₁₋₃₀ alkylthio group, or a halogen group; a C₃₋₆ cycloalkyl group; a C₆₋₁₅ aralkyl group, optionally substituted with up to three C₁₋₃₀ alkyl groups, C₁₋₃₀ alkoxy groups, halogen groups or nitro groups, C₆₋₁₅ aryl group, optionally substituted with up to three C₁₋₃₀ alkyl groups, C₁₋₃₀ alkoxy groups, halogen groups or nitro groups; which comprises reacting, at a temperature of from about -20 °C to about 20 °C, a mercaptan of the formula R-SH, wherein R is as previously defined, with at least one chlorinating agent, sulfur based acid and phosphorus trichloride. The compounds produced by this process are useful as intermediates in the preparation of O,S-disubstituted phosphorodichlorothioates, which are, in turn, useful in the preparation of organophosphorus pesticides.
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IMPROVED PROCESS FOR PREPARATION OF PHOSPHORODICHLOROTHIOATES

Background of the Invention

1. Field of the Invention

This invention relates to an improved process for the preparation of S-substituted phosphorodichlorothioates, which are useful as intermediates for the manufacture of insecticides.

2. Description of the Related Art

The compounds produced by this process are useful as intermediates in the preparation of O,S-disubstituted phosphorochloridothioates, which are, in turn, useful in the preparation of organophosphorus pesticides described in, for example, U.S. Patent Nos. 3,374,293, 3,784,654 and 3,839,509. The phosphorodichlorothioates of the present invention can be converted to O,S-disubstituted phosphorochlorothioates by reacting them with an alcohol in the presence of an acid scavenger (i.e., a tertiary amine).


U.S. Patent 4,056,581 describes the preparation of certain S-alkyl, -cycloalkyl, -aralkyl, and -aryl phosphorodichloridothioates by reacting a sulfenyl chloride, which can be prepared in situ, with phosphorus trichloride and a carboxylic acid or water. This reference utilizes either water or a carboxylic acid as an oxygen donor. In the referenced process, one equivalent of sulfuryl chloride is consumed and one equivalent of carboxylic acid chloride or hydrogen chloride is generated as a byproduct (which must be removed, neutralized and disposed of). The present invention, unlike the process disclosed in U.S. Patent 4,056,581, replaces half of the sulfuryl chloride with an inexpensive sulfur based acid which also serves as the full equivalent of the oxygen donor; therefore, no carboxylic acid chloride is generated, thereby obviating problems of its removal, neutralization and disposal.

**Brief Summary of The Invention**

Applicant’s invention relates to a process for preparing a phosphorodichlorothioate of the formula

\[ \text{RS} \vdash \text{Cl}_2 \]

wherein R is a \( C_1-C_{10} \) alkyl group, optionally substituted with
a C₁-C₄ alkoxy group, a C₁-C₄ alkylthio group or a halogen group; a C₃-C₆ cycloalkyl group; a C₇-C₁₀ aralkyl group, optionally substituted with up three C₁-C₅ alkyl groups, C₁-C₄ alkoxy groups, halogen groups or nitro groups; a C₆-C₁₀ aryl group, optionally substituted with up to three C₁-C₅ alkyl groups, C₁-C₄ alkoxy groups, halogen groups or nitro groups; which comprises reacting, at a temperature of from about -20°C to about 20°C, a mercaptan of the formula R-SH, wherein R is as previously defined, with at least one chlorinating agent, a sulfur based acid and phosphorus trichloride.

Description of Invention

The present invention relates to an improved process for preparing a phosphorodichlorothioate of the formula

```
\( \text{RS}\text{PCl}_2 \) (I)
```

wherein R is a C₁-C₁₀ alkyl group, optionally substituted with a C₁-C₄ alkoxy group, a C₁-C₄ alkylthio group, or a halogen group; a C₃-C₆ cycloalkyl group; a C₇-C₁₀ aralkyl group, optionally substituted with up to three C₁-C₅ alkyl groups, C₁-C₄ alkoxy groups, halogen groups or nitro groups; a C₆-C₁₀ aryl group, optionally substituted with up to three C₁-C₅ alkyl groups, C₁-C₄ alkoxy groups, halogen groups or nitro groups; which comprises reacting, at a temperature of from about -20°C to about 20°C, a mercaptan of the formula R-SH, wherein R is as previously defined, with at least one chlorinating agent, a sulfur based acid and phosphorus trichloride.

In a preferred embodiment of this invention, R is a (C₁-C₇) alkyl group, especially a (C₂-C₄) alkyl group. As used in the specification and claims, the terms alkyl, alkoxy, alkylthio, and aralkyl refer to groups having straight or branched chain spatial configuration.
The process of the present invention involves reacting a mercaptan of the formula:

\[ \text{R-SH} \]

wherein R is as defined for Formula I, with phosphorus trichloride, a chlorinating agent and sulfur based acid to give a compound of Formula I.

The present process can be represented by the following reaction Scheme (A), which is presented for illustrative purposes only:

\[
\begin{align*}
\text{(A) } \text{PCl}_3 + \text{SO}_2\text{Cl}_2 + \text{RSH} + \text{H}_2\text{SO}_4 & \rightarrow \text{RS-PCl}_2 + \text{HCl} + \text{SO}_2 \\
\end{align*}
\]

The process can be carried out neat or with a solvent. Suitable solvents include aromatic hydrocarbons such as benzene, toluene, and xylene; aromatic and aliphatic halogenated hydrocarbons such as chlorobenzene, chloroform, carbon tetrachloride, and perchloroethylene; carboxylic acid esters such as ethyl acetate and butyl acetate; and the like.

The reaction is normally conducted at a temperature range of about -20°C to about 20°C and preferably at about -10°C to about 0°C. Generally, a substantially equimolar ratio of reactants is preferred (except for the chlorinating agent and \( \text{H}_2\text{SO}_4 \), for which half molar quantities are preferred), though up to 100% molar excesses of any of the reactants can be employed.

The reaction products are obtained by fractional distillation at reduced pressures or by other conventional techniques. The products thus obtained can be used in additional syntheses without further purification.

The reactants can be combined in any order, provided that the chlorinating agent is added to the mercaptan.
before the phosphorus trichloride. A preferred sequence involves (a) combining the mercaptan and the chlorinating agent (b) adding the phosphorus trichloride and then (c) adding the sulfur based acid.

Reaction conditions such as choice of solvents and temperature correspond to the conditions described above for Scheme (A). Up to 100% molar excesses of any of the reagents can be employed, but the preferred molar ratios are as follows: about 1.0 \( \text{PCl}_3 \); about 0.5 \( \text{SO}_2\text{Cl}_2 \); about 1.0 propyl mercaptan; and about 0.5 \( \text{H}_2\text{SO}_4 \).

Representative chlorinating agents include chlorine, sulfonyl chloride, \( \text{N}-\text{chlorosuccinimide} \) and the like. Sulfonyl chloride is the most preferred.

Sulfur based acids are sulfur-containing organic and inorganic acids. Representative sulfur based acids include sulfuric acid, chlorosulfonic acid, methylsulfonic acid and the like. Sulfuric acid is the most preferred.

The reaction products can be obtained by fractional distillation at reduced pressures or by other conventional techniques. The products obtained can be used in additional syntheses without further purification.

When the starting materials shown below in Column I are utilized in the preferred process of this invention, the corresponding products shown in Column II are obtained.
methyl mercaptan
ethyl mercaptan
n-propyl mercaptan
isopropyl mercaptan
n-butyl mercaptan
isobutyl mercaptan
sec-butyl mercaptan
n-amyl mercaptan
n-hexyl mercaptan
n-decyl mercaptan
2-(n-propanoxyethyl) mercaptan
2-methylthio-n-propyl mercaptan
2-chloroethyl mercaptan
cyclohexyl mercaptan
benzyl mercaptan
2-chlorophenethyl mercaptan
thiophenol
2-methyl thiophenol
4-ethyl thiophenol
3,5-dimethyl-4-methoxy thiophenol
4-ethoxy thiophenol
3-bromo thiophenol
4-chloro thiophenol
2,5-dichloro thiophenol
2,4,6-trichloro thiophenol
2,4-dichloro-6-methyl thiophenol
2-chloro-4-propoxy thiophenol
2-chloro-4-bromo thiophenol
4-fluoro thiophenol
4-nitro thiophenol
2-nitro-4-chloro thiophenol
2-nitro-4-methyl thiophenol
naphthyl mercaptan
3,5-dimethylnaphthyl mercaptan
3-chloronaphthyl mercaptan
II
S-methyl phosphorodichloridothiolate
S-ethyl phosphorodichloridothiolate
S-n-propyl phosphorodichloridothiolate
S-isopropyl phosphorodichloridothiolate
S-n-butyl phosphorodichloridothiolate
S-isobutyl phosphorodichloridothiolate
S-sec-butyl phosphorodichloridothiolate
S-n-decyl phosphorodichloridothiolate
S-n-amyl phosphorodichloridothiolate
S-n-hexyl phosphorodichloridothiolate
S-2-(n-prooxyethyl)phosphorodichloridothiolate
S-2-methylthio-n-propyl phosphorodichloridothiolate
S-2-chloroethyl phosphorodichloridothiolate
S-cyclohexyl phosphorodichloridothiolate
S-benzyl phosphorodichloridothiolate
S-2-chloro-phenethyl phosphorodichloridothiolate
S-phenyl phosphorodichloridothiolate
S-(2-methylphenyl) phosphorodichloridothiolate
S-(4-ethylphenyl) phosphorodichloridothiolate
S-(3,5-dimethyl-4-methoxyphenyl) phosphorodichloridothiolate
S-(4-ethoxyphenyl) phosphorodichloridothiolate
S-(3-bromophenyl) phosphorodichloridothiolate
S-(4-chlorophenyl) phosphorodichloridothiolate
S-(2,5-dichlorophenyl) phosphorodichloridothiolate
S-(2,4,6-trichlorophenyl) phosphorodichloridothiolate
S-(2,4-dichloro-6-methylphenyl) phosphorodichloridothiolate
S-(2-chloro-4-prooxyphenyl) phosphorodichloridothiolate
S-(2-chloro-4-bromophenyl) phosphorodichloridothiolate
S-(4-fluorophenyl) phosphorodichloridothiolate
S-(4-nitrophenyl) phosphorodichloridothiolate
S-(2-nitro-4-chlorophenyl) phosphorodichloridothiolate
S-(2-nitro-4-methylphenyl) phosphorodichloridothiolate
S-naphthyl phosphorodichloridothiolate
S-(3,5-dimethylnaphthyl) phosphorodichloridothiolate
S-(3-chloronaphthyl) phosphorodichloridothiolate
and the like.

All of the starting materials used in the preparation of the compounds of this invention are known compounds or are readily prepared by methods available to those skilled in the art.

The following example illustrates, without limitation of the scope of the present invention, a preferred process of this invention.

**EXAMPLE I**

A 3 L four-necked round-bottomed flask was equipped with a mechanical stirrer, an addition funnel topped by a nitrogen bubbler, a thermometer, and a cooling bath. The flask was charged with propanethiol (543 mL, 6.0 moles) and cooled to -10°C. Sulfuryl chloride (241 mL, 3.0 moles) was added over 60 min. while maintaining the temperature at -5 to -10°C (Caution: rapid evolution of HCl gas!). Phosphorous trichloride (524 mL, 6.0 moles) was added over 30 min. while maintaining the temperature at -13°C to -10°C (Caution: evolution of HCl gas!). Sulfuric acid (160 mL, 3.0 moles) was added over 25 min. while maintaining the temperature at -11°C (Caution: evolution of HCl gas!). The solution was allowed to warm to room temperature overnight (Caution: rapid evolution of HCl gas as the solution warms!). The solution was stripped to remove volatiles and obtain 1061 g of orange oil. A
portion of this material (101.3 g) was distilled collecting 83.9 g of colorless oil bp 113 - 114°C at 26 mmHg pressure. The product was identified as S-propyl phosphorodichloridothioate contaminated with dipropyl disulfide by GC/MS.
WHAT IS CLAIMED IS:

1. A process for preparing a phosphorodichlorothioate of the formula

\[ \text{RSFCl}_2 \]

wherein R is a \( \text{C}_1-\text{C}_{10} \) alkyl group, optionally substituted with a \( \text{C}_1-\text{C}_4 \) alkoxy group, a \( \text{C}_1-\text{C}_4 \) alkylthio group, or a halogen group; a \( \text{C}_3-\text{C}_6 \) cycloalkyl group; a \( \text{C}_7-\text{C}_{10} \) aralkyl group, optionally substituted with up to three \( \text{C}_1-\text{C}_5 \) alkyl groups, \( \text{C}_1-\text{C}_4 \) alkoxy groups, halogen groups or nitro groups; a \( \text{C}_6-\text{C}_{10} \) aryl group, optionally substituted with up to three \( \text{C}_1-\text{C}_5 \) alkyl groups, \( \text{C}_1-\text{C}_4 \) alkoxy groups, halogen groups or nitro groups; which comprises reacting, at a temperature of from about \(-20^\circ\text{C}\) to about \(20^\circ\text{C}\), a mercaptan of the formula \( \text{R-SH} \), wherein R is as previously defined, with at least one chlorinating agent, sulfur based acid and phosphorus trichloride.

2. A process according to Claim 1, wherein R is a \( \text{C}_1-\text{C}_{10} \) alkyl group optionally substituted with a \( \text{C}_1-\text{C}_4 \) alkoxy group, a \( \text{C}_1-\text{C}_4 \) alkylthio group, or a halogen group.

3. A process according to Claim 1, wherein R is a \( \text{C}_3-\text{C}_6 \) cycloalkyl group.

4. A process according to Claim 1, wherein R is a \( \text{C}_7-\text{C}_{10} \) aralkyl group optionally substituted with up to three \( \text{C}_1-\text{C}_5 \) alkyl groups, \( \text{C}_1-\text{C}_4 \) alkoxy groups, halogen groups or nitro groups.

5. A process according to Claim 1, wherein R is a \( \text{C}_6-\text{C}_{10} \) aryl group, optionally substituted with up to three \( \text{C}_1-\text{C}_5 \) alkyl groups, \( \text{C}_1-\text{C}_4 \) alkoxy groups, halogen groups or nitro groups.
6. A process according to Claim 1, wherein R is a C₁-C₆ alkyl group.

7. A process according to Claim 1, wherein R is an n-propyl group.

8. A process according to Claim 1, wherein said chlorinating agent is chlorine, sulfuryl chloride, or N-chlorosuccinimide.

9. A process according to Claim 1, wherein said chlorinating agent is sulfuryl chloride.

10. A process according to Claim 1, wherein R is a C₁-C₅ alkyl group, and said chlorinating agent is sulfuryl chloride.

11. A process according to Claim 1, wherein R is an n-propyl group, and said chlorinating agent is sulfuryl chloride.

12. A process according to Claim 1, wherein said temperature is from about -20°C to about 20°C.

13. A process according to Claim 1, wherein said temperature is from about -10°C to about 0°C.

14. A process according to Claim 1, wherein 1.0 equivalent of mercaptan is reacted with 0.5 to 1.0 equivalents of chlorinating agent, 0.5 to 1.0 equivalents of sulfur based acid and 1.0 equivalent of phosphorus trichloride.

15. A process according to Claim 1, wherein one equivalent of propyl mercaptan is reacted with one-half equivalent of sulfuryl chloride, one-half equivalent of sulfuric acid and one equivalent of phosphorus trichloride at a temperature from about -10°C to about 0°C.
16. A process according to Claim 1, wherein said sulfur based acid is a sulfur containing organic or inorganic acid.

17. A process according to Claim 1, wherein said sulfur based acid is a sulfuric acid, chlorosulfonic acid or methyl sulfonic acid.

18. A process according to Claim 1, wherein said sulfur based acid is sulfuric acid.
AMENDED CLAIMS

[received by the International Bureau on 11 December 1991(11.12.91);
original claims 1-18 replaced by amended claims 1-15 (3 pages)]

1. A process for preparing a phosphorodichlorothioate
of the formula

\[ \text{O} \quad \text{RSPCl}_2 \]

wherein R is a \(\text{C}_{1-10}\) alkyl group, optionally substituted with a
\(\text{C}_{1-4}\) alkoxy group, a \(\text{C}_{1-4}\) alkylthio group, or a halogen group;
a \(\text{C}_{3-6}\) cycloalkyl group; a \(\text{C}_{7-10}\) aralkyl group, optionally
substituted with up to three \(\text{C}_{1-5}\) alkyl groups, \(\text{C}_{1-4}\) alkoxy
groups, halogen groups or nitro groups; a \(\text{C}_{6-10}\) aryl group,
optionally substituted with up to three \(\text{C}_{1-5}\) alkyl groups, \(\text{C}_{1-4}\)
alkoxy groups, halogen groups or nitro groups; which comprises
reacting, at a temperature of from about -20°C to about 20°C, a
mercaptan of the formula R-SH, wherein R is as previously
defined, with at least one chlorinating agent, sulfuric acid and
phosphorus trichloride.

2. A process according to Claim 1, wherein R is a
\(\text{C}_{1-10}\) alkyl group optionally substituted with a \(\text{C}_{1-4}\) alkoxy
group, a \(\text{C}_{1-4}\) alkylthio group, or a halogen group.

3. A process according to Claim 1, wherein R is a
\(\text{C}_{3-6}\) cycloalkyl group.

4. A process according to Claim 1, wherein R is a
\(\text{C}_{7-10}\) aralkyl group optionally substituted with up to three
\(\text{C}_{1-5}\) alkyl groups, \(\text{C}_{1-4}\) alkoxy groups, halogen groups or nitro
groups.
5. A process according to Claim 1, wherein R is a C₆₋C₁₀ aryl group, optionally substituted with up to three C₁₋C₅ alkyl groups, C₁₋C₄ alkoxy groups, halogen groups or nitro groups.

6. A process according to Claim 1, wherein R is a C₁₋C₆ alkyl group.

7. A process according to Claim 1, wherein R is an n-propyl group.

8. A process according to Claim 1, wherein said chlorinating agent is chlorine, sulfuryl chloride, or N-chlorosuccinimide.

9. A process according to Claim 1, wherein said chlorinating agent is sulfuryl chloride.

10. A process according to Claim 1, wherein R is a C₁₋C₅ alkyl group, and said chlorinating agent is sulfuryl chloride.

11. A process according to Claim 1, wherein R is an n-propyl group, and said chlorinating agent is sulfuryl chloride.

12. A process according to Claim 1, wherein said temperature is from about -20°C to about 20°C.

13. A process according to Claim 1, wherein said temperature is from about -10°C to about 0°C.
14. A process according to Claim 1, wherein 1.0 equivalent of mercaptan is reacted with 0.5 to 1.0 equivalents of chlorinating agent, 0.5 to 1.0 equivalents of sulfuric acid and 1.0 equivalent of phosphorus trichloride.

15. A process according to Claim 1, wherein one equivalent of propyl mercaptan is reacted with one-half equivalent of sulfuryl chloride, one-half equivalent of sulfuric acid and one equivalent of phosphorus trichloride at a temperature from about -10°C to about 0°C.
INTERNATIONAL SEARCH REPORT
International Application No. PCT/US 91/05545

I. CLASSIFICATION OF SUBJECT MATTER
(if several classification symbols apply, indicate all)َ

According to International Patent Classification (IPC) or to both National Classification and IPC
Int.Cl. 5 C07F9/20

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IV. CERTIFICATION

Date of the Actual Completion of the International Search: 12 NOVEMBER 1991

Date of Mailing of this International Search Report: 21.11.91

International Searching Authority:

EUROPEAN PATENT OFFICE

Signature of Authorized Officer: BESLIER L.M.
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