[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORIES, THE LUBRIZOL CORP.]

Novel Method for the Preparation of *O,O*-Dialkyl Phosphorochloridothionates[1]

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O,O-Dialkyl phosphorochloridothionates may be prepared by the reaction of *O,O*-dialkyl hydrogen phosphorodithioates with hydrogen chloride in the presence of hydrogen sulfide acceptors. Acetonitrile, benzonitrile, ethyl, phenyl and benzyl thiocyanates, and ethyl isothiocyanate function as the hydrogen sulfide acceptors in the reaction.

The preparation of *O,O*-dialkyl phosphorochloridothionates has received considerable study as evidenced by the literature reports and patents issued on the subject.[3–18] Three general methods have been used in the preparation of the *O,O*-dialkyl phosphorochloridithionates as shown in equations (1),[1–10,14] (2),[17] and (5).[3,5–7,11–13,15,16,18]

$$2ROH + PSCl_3 \longrightarrow (RO)_2PSCl + 2HCl \quad (1)$$

$$2ROH + PCl_3 + S \longrightarrow (RO)_2PSCl + 2HCl \quad (2)$$

$$2(RO)_2PSSH + 3Cl_2 \longrightarrow 2(RO)_2PSCl + S_2Cl_2 + 2HCl \quad (3)$$

A fourth method based upon the double decomposition of *O,O*-dialkyl hydrogen phosphorodithioates with hydrogen chloride appeared to be feasible for the preparation of the *O,O*-dialkyl phosphorochloridothionates, since this reaction was known to occur with diphenylphosphinodithioic acid,[19] as in equation (4). However, the elimination of hydrogen

$$(C_6H_5)_2PSSH + HCl \xrightarrow{150\text{–}200°} (C_6H_5)_2PSCl + H_2S \quad (4)$$

sulfide in this reaction takes place at temperatures in excess of 150°, which makes it impractical for use with the ester acid.

It has now been found that in the presence of a hydrogen sulfide acceptor,[20] the elimination of hydrogen sulfide in the double decomposition reaction between hydrogen chloride and *O,O*-dialkyl hydrogen phosphorodithioates takes place smoothly in ethyl ether at the reflux temperature. The hydrogen sulfide acceptors used in this study were acetonitrile, benzonitrile, ethyl, phenyl and benzyl thiocyanates, and ethyl isothiocyanate. In addition to the *O,O*-dialkyl phosphorochloridothionates, which were obtained in yields as high as 88%, there were also obtained the products which would be produced by the addition of hydrogen sulfide to the acceptor molecules in accordance with equations (5) and (6). Ethyl isothiocyanate did not function as a hydrogen sulfide acceptor in ethyl ether. In dioxane, at 100°, the reaction between *O,O*-diethyl hydrogen phosphorodithioate, hydrogen chloride, and ethyl isothiocyanate yielded 39% of *O,O*-diethyl phosphorochloridothionate and 83% of ethylamine hydrochloride. The amine salt was probably formed through decomposition of the intermediate dithiocarbamic acid, equations (7) and (8).

$$(RO)_2PSSH + R'CN + HCl \longrightarrow (RO)_2PSCl + R'CSNH_2 \quad (5)$$

$$(RO)_2PSSH + R'SCN + HCl \longrightarrow (RO)_2PSCl + R'SCSNH_2 \quad (6)$$

$$(C_2H_5O)_2PSSH + C_2H_5NCS + HCl \longrightarrow (C_2H_5O)_2PSCl + [C_2H_5NHCS_2H] \quad (7)$$

$$[C_2H_5NHCS_2H] + HCl \longrightarrow C_2H_5NH_3^+Cl^- + CS_2 \quad (8)$$

The yields of *O,O*-diethyl phosphorochloridothionate and the coproducts obtained with the hydrogen

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(1) Paper VI. Chemistry of the Aliphatic Esters of Phosphorodithioic Acids. For previous paper in this series see W. E. Bacon, N. A. Meinhardt, and W. M. LeSuer, *J. Org. Chem.*, in press.

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(16) A. D. F. Toy, U. S. Patent **2,715,136**, Aug. 9, 1955.

(17) W. T. Dye, Jr., U. S. Patent **2,730,541**, Jan. 10, 1956.

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sulfide acceptors used in this reaction are shown in Table I.

TABLE I

Yields of *O,O*-Diethyl Phosphorochloridothionate and Coproducts Obtained with Hydrogen Sulfide Acceptors

Acceptor	Yield of $(C_2H_5O)_2PSCl$, %	Coproduct	Yield, %
CH_3CN	74	CH_3CSNH_2	51
C_6H_5CN	74	$C_6H_5CSNH_2$	77
C_2H_5SCN	73	$C_2H_5SCSNH_2$	91
C_6H_5SCN	88	$C_6H_5SCSNH_2$	94
$C_6H_5CH_2SCN$	85	$C_6H_5CH_2SCSNH_2$	90

Phenyl isothiocyanate, potassium cyanide, and octene-1 did not serve as hydrogen sulfide acceptors in this reaction.

O,O-Di-*n*-propyl, *O,O*-diisopropyl, *O,O*-di-*n*-butyl, and *O,O*-di-*sec*-butyl phosphorochloridothionates were also prepared by this method, using benzyl thiocyanate as the coreactant. The yields and physical constants of these materials are shown in Table II.

Other materials used were commercially available reagents.

Preparation of O,O-dialkyl phosphorochloridothionates. Hydrogen chloride was bubbled through a solution of the *O,O*-dialkyl hydrogen phosphorodithioate (0.5 mole) and the hydrogen sulfide acceptor (0.5 mole) in 200 ml. of ethyl ether at the reflux temperature for 2 hr. The ether was removed by distillation at reduced pressure. The solid residue was extracted with 250-ml. portions of petroleum ether (b.p. 30–60°) four times. The combined extracts were dried over anhydrous sodium carbonate. The sodium carbonate was removed by filtration and the filtrate was distilled under reduced pressure over calcium carbonate chips.

The yields of *O,O*-diethyl phosphorochloridothionate obtained are shown in Table I. Typical analyses for this compound, as obtained, are: b.p. 34–35° at 0.5 mm.; n_D^{25} 1.4688 (reported 1.4685[3]).

Anal. Calcd. for $C_4H_{10}PSCl$: Cl, 18.8; P, 16.4; S, 17.0. Found: Cl, 19.2; P, 16.2; S, 16.9.

The yields of the other *O,O*-dialkyl phosphorochloridothionates prepared are shown in Table II.

The solid residue from the petroleum ether extractions was recrystallized to obtain the coproduct of the reaction. The yields are shown in Table I. The products were identified as follows:

Thioacetamide was recrystallized from isopropyl ether, m.p. 113–116° (reported[22] m.p. 115–116°), a mixed melting point with an authentic sample of thioacetamide showed no depression.

TABLE II

O,O-Dialkyl Phosphorochloridothionates from the Reaction of *O,O*-Dialkyl Hydrogen Phosphorodithioates with Hydrogen Chloride and Benzyl Thiocyanate

$$(RO)_2PSSH + C_6H_5CH_2SCN + HCl \longrightarrow (RO)_2PSCl + C_6H_5CH_2SCSNH_2{}^{a}$$

R	Yield, %	B.P.	Mm.	n_D^{25}	Phosphorus, % Found	Phosphorus, % Calcd.	Sulfur, % Found	Sulfur, % Calcd.	Chlorine, % Found	Chlorine, % Calcd.
n-C_3H_7	75.5	72	2	1.4701[b]	14.17	14.34	14.46	14.77	16.45	16.39
i-C_3H_7	81.0	61	3	1.4612[c]	14.32	14.34	15.05	14.77	16.30	16.39
n-C_4H_9	81.0	76	0.5	1.4697[d]	12.66	12.68	13.16	13.08	14.42	14.50
sec-C_4H_9	86.0	54	0.1	1.4692	12.65	12.68	13.30	13.08	14.55	14.50

[a] Yields of 85–95% of benzyl dithiocarbamate were obtained. [b] Reported[5] 1.4672. [c] Reported[5] 1.4601. [d] Reported[5] 1.4670.

The reaction sequence suggested for this reaction is shown in equation (9). The intermediate imino-ester hydrochloride postulated here is similar to

$$\begin{array}{l} (RO)_2PSSH + R'CN + HCl \longrightarrow \\ \qquad\qquad [(RO)_2PSSC(NH)R'\cdot HCl] \quad (9) \\ \qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad (RO)_2PSCl + R'CSNH_2 \end{array}$$

the imino-thioether hydrochloride isolated from the reaction of mercaptans with nitriles and hydrogen chloride.[21] The intermediate imino-thioester hydrochloride formed in the present reaction is apparently too unstable to be isolated, and breaks down immediately into the reaction products isolated.

EXPERIMENTAL

O,O-Dialkyl hydrogen phosphorodithioates were prepared by a previously described method.[4] The crude acids were purified by distillation at reduced pressure and then were 98% to 99% pure by titration.

Thiobenzamide was recrystallized from ether-petroleum ether (b.p. 30–60°), m.p. 114–116° (reported[22] m.p. 115–116°), a mixed melting point with an authentic sample showed no melting point depression.

Benzyl dithiocarbamate was recrystallized, successively, from ethyl acetate, isopropyl alcohol, and chloroform, m.p. 87–88°.

Anal. Calcd. for $C_8H_9NS_2$: S, 34.95; N, 7.66. Found: S, 35.19; N, 7.69.

Phenyl dithiocarbamate was recrystallized twice from chloroform, m.p. 109–110.5°.

Anal. Calcd. for $C_7H_7NS_2$: S, 37.88; N, 8.27. Found: S, 37.98; N, 8.30.

Ethyl dithiocarbamate was recrystallized from petroleum ether (b.p. 30–60°) m.p. 41.5–43° (reported[23] m.p. 42°).

Anal. Calcd. for $C_3H_7S_2N$: N, 11.58. Found: N, 11.65.

Ethylamine hydrochloride was recrystallized from isopropyl alcohol, m.p. 107–109°. A mixed melting point with an authentic sample of ethylamine hydrochloride showed no melting point depression.

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