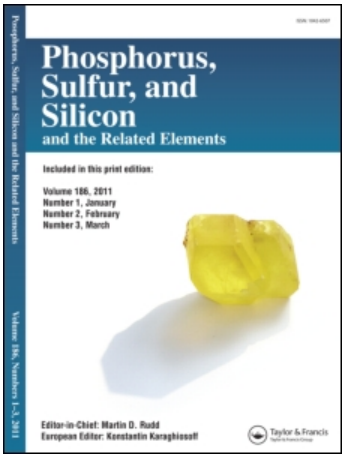

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PREPARATION OF S,S-DISUBSTITUTED PHOSPHONOTRITHIOATES: A CATALYTIC METHOD FOR REACTION OF PHOSPHONOTHIOIC DICHLORIDES AND MERCAPTANS

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PREPARATION OF S,S-DISUBSTITUTED PHOSPHONOTRITHIOATES: A CATALYTIC METHOD FOR REACTION OF PHOSPHONOTHIOIC DICHLORIDES AND MERCAPTANS

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S,S-Disubstituted phosphonotrithioates may be prepared by reaction of phosphonothioic dichlorides with mercaptans in the presence of a catalytic amount of solubilized halide anion.

Key words: Phosphonotrithioates; esterification; catalysis; phosphonothioic dichlorides; mercaptan

INTRODUCTION

During the course of our research on organophosphorus compounds, we became interested in the preparation of phosphonotrithioate esters from phosphonothioic dichlorides and mercaptans, and, specifically, the preparation of S,S-di-*t*-butyl esters of lower alkylphosphonotrithioic acids. Although numerous procedures have been reported for the preparation of these materials,[1–18] many methods have limited scope, make use of exotic or highly reactive phosphorus intermediates, or require a stoichiometric amount of base. We wish to report a catalytic procedure for the formation of S,S-dialkyl alkylphosphonotrithioates **2** from alkylphosphonothioic dichlorides **1** (Scheme I) which proceeds in high yield and allows convenient large scale preparation of these materials. This synthetic method appears to be equally applicable to the preparation of S-aryl esters and arylphosphonotrithioates, as well as to have utility for the preparation of the corresponding phosphonodithioic chlorides.

$$\underset{\mathbf{1}}{RP(S)Cl_2} + 2\ R'SH \xrightarrow{\text{catalyst}} \underset{\mathbf{2}}{RP(S)(SR')_2} + 2\ HCl$$

SCHEME I Catalytic formation of S,S-dialkyl alkylphosphonotrithioates **2** from alkylphosphonothioic dichlorides **1**.

RESULTS AND DISCUSSION

Initial attempts to catalyze the conversion of phosphonothioic dichloride **1** (R = CH_3—) to phosphonotrithioate **2** (R = CH_3—, R′ = —$C(CH_3)_3$) were carried out with methylphosphinous dichloride on the premise that methylphosphinous dichloride would be converted to the corresponding phosphinodithioic diester **3**, which

would undergo transsulfurization to afford phosphonotrithioate **2** (R = CH_3—, R′ = —$C(CH_3)_3$) and regenerated methylphosphinous dichloride (Scheme II).[4] Treatment of phosphonothioic dichloride **1** (R = CH_3—) with excess *t*-butyl mercaptan and 5 mole percent of methylphosphinous dichloride at 110°C for 9 hours afforded a 22% yield of phosphonotrithioate **2** (R = CH_3—; R′ = —$C(CH_3)_3$) and 71% yield of recovered starting material, while carrying out the reaction at 128°C gave a 33% yield of **2** but only 45% recovered starting material. Attempted catalysis with 5 mole percent of a more traditional catalyst, KI, gave no reaction after 0.75 hour at 110°C, but use of 5 mole percent of KI and 5 mole percent of 18-crown-6 gave conversion to 7% phosphonotrithioate **2** (R = CH_3—, R′ = —$C(CH_3)_3$) and 29% phosphonodithioic chloride **4** (R = CH_3—, R′ = —$C(CH_3)_3$) after 9 hours at 110°C. Substitution of tetra-*n*-butylammonium iodide for KI/18-crown-6 increased the yield of phosphonotrithioate **2** to 80%. Subsequent experiments with other tetrabutylammonium halides showed that iodide was not a prerequisite for catalytic activity.

$$CH_3PCl_2 + 2\,(CH_3)_3CSH \rightarrow \underset{\mathbf{3}}{CH_3P(SC(CH_3)_3)_2} + 2\,HCl$$

$$\underset{\mathbf{1}\ R = CH_3}{CH_3P(S)Cl_2} + CH_3P(SC(CH_3)_3)_2 \rightarrow \underset{\mathbf{2}\ R = CH_3,\ R' = -C(CH_3)_3}{CH_3P(S)(SC(CH_3)_3)_2} + CH_3PCl_2$$

$$\underset{\mathbf{4}}{RP(S)(SR')Cl}$$

SCHEME II Proposed mode of catalysis by methylphosphinous dichloride in the conversion of methylphosphonothioic dichloride **1** to S,S-Di-*t*-butyl methylphosphonotrithioate **2**.

Further screening of potential catalysts consisted of a systematic evaluation of a variety of materials using methylphosphonothioic dichloride **1** (R = CH_3—) and *t*-butyl mercaptan as the test system. Weak bases, *e.g.*, tertiary amides and amines, were tested because of the potential for increasing the concentration of mercaptide anion. Soluble and solubilized metal halides, quaternary ammonium and phosphonium halides, and trivalent phosphorus compounds were included in the study because these materials had shown catalytic activity in preliminary experiments. Lewis acids were tested in the hope that they would increase the electrophilicity of the phosphonothioic dichloride. Transition metal halides were included because of the reported activity of cobalt(II) chloride in the reaction of mercaptans with carboxylic acid chlorides and anhydrides.[19] Activated carbon was tested because of its known catalytic effect in the reaction of mercaptans with phosgene.[20]

The results of the screening experiments indicated that, in general, yields obtained with the various classes of catalysts decreased in the following order: quaternary ammonium and phosphonium halides > amines and amine hydrochlorides ≥ soluble and solubilized alkali metal halides ≥ trivalent phosphorus compounds ≥ tertiary carboxylic acid amides > Lewis acids > miscellaneous. Higher yields were obtained with tetra-*n*-butylammonium and phosphonium halides (80–86%) than with either the longer chain quaternary ammonium halide, Aliquat 336 (58–68%), or with tetraethylammonium halides (68–71%). Still lower yields were obtained with tetra-*n*-butylammonium hydrogen sulfate as catalyst (45%). Tri-*n*-

butylamine (71%) exhibited better activity than either Alamine (60%) or triethylamine (46%), while aromatic amines (pyridine, 42%; 2,6-lutidine, 27%; 4-(N,N-dimethylamino)pyridine, 36%; N,N-dimethylaniline, 55%) showed moderate but variable activity. Lithium chloride showed essentially no catalytic activity, while cesium chloride afforded a 14% yield of phosphonotrithioate. Use of 18-crown-6 and potassium chloride, however, afforded a 52% yield of phosphonotrithioate. Potassium fluoride/18-crown-6 gave a 35% yield. Tri-*n*-butylphosphine and triphenylphosphine showed catalytic activity comparable to methylphosphinous dichloride while triphenyl phosphite showed essentially no activity. These latter materials differed from the other potential catalysts examined in that moderate to large amounts of unreacted phosphonothioic dichloride remained in the reaction mixture. In the majority of other cases, if any catalytic activity was noted, substantially all the starting phosphonothioic dichloride was consumed even if the desired product was not formed. DMF showed some activity, affording a 31% yield of phosphonotrithioate, while N-methylpyrrolidinone was essentially inactive. Lewis acids ($AlCl_3$, $SnCl_4$, $FeCl_3$, $MgCl_2$, $BF_3 \cdot Et_2O$) displayed little or no catalytic activity. Miscellaneous materials (*e.g.*, activated charcoal, silica gel, alumina, DMSO, triphenylphosphine oxide, triethylamine N-oxide, N-methylimidazole, imidazole, CuCl, $CoCl_2$) showed little or no activity with the exception of N-methylimidazole which afforded at 26% yield of phosphonotrithioate after 6.5 hours at 100–110°C.

A variety of phosphonotrithioates **2** were prepared from other mercaptans and phosphonothioic dichlorides **1** using tetra-*n*-butylphosphonium halides as catalyst (Table I). In general, the phosphonothioic dichloride and catalyst were heated,

TABLE I

Preparation of S,S-disubstituted phosphonotrithioates **2** from phosphonothioic dichlorides **1**

Dichloride R	Mercaptan R' (mole %)	Catalyst (mole %)	Time (h)	Temp (°C)	Solvent	Yield(%)
Me	Me (570)[b]	$Bu_4P^+Br^-$ (5)	8.8	100-110	none	82[a]
Me	t-Bu (326)[b]	$Bu_4P^+Br^-$ (4.9)	13.6	100-110	none	78[c]
Me	Ph (304)[b]	$Bu_4P^+Br^-$ (4)	12.7	107-128	toluene	56
Et	n-Bu (290)[b]	$Bu_4P^+Cl^-$ (5.8)	11.5	128-140	none	90[a]
Et	t-Bu (600)[b]	$Bu_4P^+Br^-$ (5)	13.0	104-113	none	74[c]
Ph	t-Bu (410)[b]	$Bu_4P^+Br^-$ (4)	8.1	100-110	none	91[d]
Ph	$-CH_2CH_2-$(101)[e]	$Bu_4P^+Br^-$ (5.3)	6.8	89- 92	benzene	93

a) Isolated by Kugelrohr distillation b) Added throughout course of reaction c) Corrected yield by quantitative GLPC *vs.* a reference standard. d) mp 58.0-60.5 (ether). Satisfactory analysis for C,H,P, and S. e) All mercaptan added during the first 1.2 h.

TABLE II

^{31}P and ^{1}H Data for S,S-disubstituted phosphonotrithioates **2** chemical shifts $\delta(J_{PH})$

		Chemical Shifts δ (J_{PH})								
		R					R'			
R	R'	CHCHCHCHP	CHCHCHP	CHCHP	CHP	P	SCH	SCHCH	SCHCHCH	SCHCHCHCH
Me	Me	-	-	-	2.25	83.1	2.36	-	-	-
		-	-	-	(13.5)		(16.5)	-	-	-
Me	t-Bu	-	-	-	2.32	64.9	-	1.63	-	-
		-	-	-	(12.8)		-	(0.9)	-	-
Me	Ph	-	-	-	2.11	80.3	-	7.55-7.60	7.30-7.50	
		-	-	-	(12.5)		-	b	b	b
Et	n-Bu	-	-	1.31	2.32	94.0	2.92	1.68	1.43	0.93
		-	-	(24.6)	(11.1)		(13.7)	a	a	a
Et	t-Bu	-	-	1.30	2.35	78.6	-	1.62	-	-
		-	-	(24.5)	(11.2)		-	(0.9)	-	-
Ph	t-Bu	7.44-7.53		8.17	-	64.1	-	1.51	-	-
		b	b	(16.3)	-		-	(0.8)	-	-
Ph	$-CH_2CH_2-$	7.45-7.73		8.10	-	94.2[c]	3.76-3.96	-	-	-
		b	b	(16.0)	-		b	-	-	-

a) none detected b) not determined c) Ref. 26 reports a value of 96.8.

and mercaptan was added at such a rate as to maintain reflux at the chosen reaction temperature. All reactions were carried out at reflux to promote disengagement of by-product hydrogen chloride since preliminary experiments showed phosphonotrithioate **2** to be unstable in the presence of dissolved hydrogen chloride. High boiling mercaptans were added early in the reaction period, and a solvent of the appropriate boiling point used. Since there have been few data reported on through sulfur ^{31}P-^{1}H coupling, ^{31}P-^{1}H coupling data for phosphonotrithioates prepared are listed in Table II.

Displacement of chloride from phosphonothioic dichloride **1** was found to proceed in a stepwise manner with only slow formation of phosphonotrithioate **2** at temperatures less than *ca.* 110°C. Surprisingly, this temperature effect was sufficient to afford a useful method of preparing phosphonodithioic chlorides **4** from phos-

phonothioic dichlorides **1**. Treatment of **1** (R = CH_3CH_2—) with excess *n*-butyl mercaptan and tetra-*n*-butylphosphonium chloride at 100–110°C for 4.5 hours afforded phosphonodithioic chlorides **4** (R = CH_3CH_2—, R′ = —$(CH_2)_3CH_3$) in 78% yield. Attempts to then add a second mole of mercaptide to afford mixed esters were unsuccessful: reaction of **4** (R = CH_3CH_2—, R′ = —$(CH_2)_3CH_3$) with *n*-propyl mercaptan in the presence of tetra-*n*-butylphosphonium chloride at 125–132°C for 1.5 hours gave a mixture of all possible monoester monochlorides and diesters.

Attempts to extend this method to the corresponding oxo analogs were unsuccessful. Treatment of ethylphosphonic dichloride with excess *n*-butyl mercaptan and tetra-*n*-butylphosphonium bromide at 122–134°C afforded not the expected phosphonodithioic ester but the phosphonotrithioic ester in 29% yield. Reaction of phenylphosphonic dichloride with ethanedithiol and tetra-*n*-butylphosphonium bromide at 90–118°C also gave the corresponding phosphonotrithioate as the major product in low yield. Only traces of product were noted in the absence of catalyst.

The mechanism of the catalytic effect of soluble halide in the conversion of phosphonothioic dichlorides to phosphonotrithioates is not known, but is thought to entail generation of mercaptide by basic halide anion. By-product hydrogen halide formed exits from the system, and the mercaptide generated reacts with phosphonothioic dichloride to regenerate chloride anion completing the catalytic cycle. Alkanethiols are known to have substantially less hydrogen bonding behavior than water or alcohol[21]; thus it is not unreasonable to expect a reaction mixture composed of phosphonothioic dichloride **1**, phosphonotrithioate **2**, and unreacted mercaptan to behave as a polar aprotic solvent. Hydrogen chloride has been reported to have a pK_a of *ca.* 9 in acetronitrile,[22] and, although no specific data are available on the basicity of mercaptide in polar aprotic solvents, more solubilized anions are known to exhibit lower basicities in such solvents.[23] This would support the premise that the relative acidities of hydrogen chloride and mercaptan in the reaction solvent are such that a significant concentration of reactive mercaptide is present under the reaction conditions.

EXPERIMENTAL

^1H NMR spectra were obtained at ambient temperature in $CDCl_3$ solvent at either 300 MHz on a General Electric QE-300 or at 60 MHz on a Varian Associates T-60A. TMS was added as an internal reference. Spectra acquired at 300 MHz used the following conditions: 21.8 ppm spectral width, 1.25 second acquisition time, 1 second predelay, 3 microsecond pulse width (30 degree tip angle), and 16K of data points. The data were zero filled to 32K and a line broadening of 0.3 Hz was applied to the free induction decay before transformation. Spectra acquired on the T-60A used the following conditions: 500 Hz sweep width, 250 second sweep time and 0.03 to 0.05 mG RF power.

^{31}P NMR spectra were obtained at ambient temperature in $CDCl_3$ solvent at 81.0 MHz on a Varian Associates XL-200. Neat 85% phosphoric acid was used as external reference. The following are typical conditions: 493.8 ppm spectral width, 0.375 second acquisition time, 0.7 second predelay, 4.0 microsecond pulse width (26 degree tip angle), 30K of data points and double precision acquisition. The raw data were zero filled to 64K and a line broadening of 1 Hz was applied to the free induction decay before transformation.

The following examples are typical of the preparation of the phosphonotrithioates **2** in Table I.

S,S-Di-n-Butyl Ethylphosphonotrithioate **2** *(R = CH_3CH_2—, R′ = —$(CH_2)_3CH_3$).* A 50 mL 3-neck flask fitted with a thermometer, N_2 sweep, and a condenser vented to a base and hypochlorite scrubber was charged with 8.97 g (0.055 mole) ethylphosphonothioic dichloride, 5 mL (0.05 mole) *n*-butyl

mercaptan and 0.95 g (0.0032 mole) tetra-*n*-butylphosphonium chloride. The resulting mixture was heated to 128°C, and an additional 12 mL (0.11 mole) *n*-butyl mercaptan was added over 6 h at such a rate as to maintain the reaction temperature between 128–140°C. The reaction mixture was heated an additional 5.5 h at 130–135°C until *ca.* one area percent intermediate phosphonodithioic chloride remained by GLPC. The reaction mixture was concentrated *in vacuo* finally at 40°C/20 mm Hg to afford 16.1 g of an oil which was distilled bulb to bulb using a Kugelrohr distillation apparatus to give 13.3 g (89.6%) of phosphonotrithioate **2** (R = CH_3CH_2—, R′ = —$(CH_2)_3CH_3$) as a colorless oil: bp 127–132°C/0.075 mm Hg (Literature[24] bp 106–108°C/0.02 mm Hg). ^{1}H NMR (TMS, δ): 2.92, dt (4H, J_{PH} = 13.7 Hz, J_{HH} = 7.5 Hz S—C<u>H</u>$_2$—), 2.32, dq (2H, J_{PH} = 11.1 Hz, J_{HH} = 7.5 Hz —C<u>H</u>$_2$P—), 1.68, pentet (4H, J_{HH} = 7.5 Hz S—CH_2C<u>H</u>$_2$—), 1.43, hextet (4H, J_{HH} = 7.5 Hz S—CH_2CH_2C<u>H</u>$_2$—), 1.31, dt (3H, J_{PH} = 24.6 Hz, J_{HH} = 7.5 Hz C<u>H</u>$_3CH_2$P—), 0.93, t (6H, J_{HH} = 7.4 Hz, —$CH_2CH_2CH_2$C<u>H</u>$_3$).

Ethylene Phenylphosphonotrithioate **2** *(R = C_6H_5—, R′, R′ = —CH_2CH_2—).* A 100 mL 3-neck flask fitted with a thermocouple probe, N_2 sweep, addition funnel, and reflux condenser vented to a base scrubber was charged with 1.81 g (0.0053 mole) tetra-*n*-butylphosphonium bromide, 1.32 g *n*-octadecane (internal standard for GLPC), 15.8 mL (21.5 g, 0.0986 mole) of 97 percent phenylphosphonothioic dichloride, and 50 mL of benzene. The contents of the flask were heated to reflux, and a solution of 1.7 mL (1.9 g, 0.020 mole) of 96% 1,2-ethanedithiol in 10 mL of benzene was added over 0.2 h at reflux (90°C). Analysis by GLPC indicated that reaction had begun and then slowed appreciably after 0.9 h at reflux. Another 7.0 mL (7.9 g, 0.08 mole) of 1,2-ethanedithiol was then added over 0.1 h at reflux, and the resulting solution heated at reflux (89–92°C) for an additional 5.6 h. Analysis by GLPC then indicated greater than 99 percent conversion of phenylphosphonothioic dichloride. The cooled reaction mixture was washed with water (2 × 100 mL), dried over Na_2SO_4, and concentrated *in vacuo* finally at 40°C/0.1 mm Hg for 1.0 h to give 22.8 g (93% yield after correction for the internal standard) of an oil that crystallized on storage in a freezer. Recrystallization of the crude product from ether gave 12.5 g (54%) of colorless prisms, mp 67–71°C (Literature[25] mp 66–68°C). ^{1}H and ^{31}P NMR data were in agreement with literature data.[26]

The following example is typical of the preparation of phosphonodithioic chlorides **4**.

S-n-Butyl Ethylphosphonodithioic Chloride **4** *(R = CH_3CH_2—, R′ = —$(CH_2)_3CH_3$).* A 50 mL 3-neck flask fitted with a thermometer and condenser vented to a base and hypochlorite scrubber was charged with 8.97 g (0.055 mole) ethylphosphonothioic dichloride, 8.42 g (0.093 mole) *n*-butyl mercaptan and 0.8 g (0.003 mole) tetra-*n*-butylphosphonium chloride. The resulting mixture was heated to 100°C and an additional 12.6 g (0.14 mole) *n*-butyl mercaptan was added. The reaction mixture was heated at 100–110°C for 4.5 h and then concentrated *in vacuo* finally at 40°C/2 mm Hg to afford 13.0 g of an oil. This oil was taken up in 100 mL ether, washed with 5% aq. Na_2CO_3 (2 × 20 mL) and water (1 × 25 mL), dried over $MgSO_4$, and concentrated *in vacuo* to give 11.2 g (93.8%) of technical S-*n*-butyl ethylphosphonodithioic chloride containing traces of ethylphosphonothioic dichloride and S,S-di-*n*-butyl ethylphosphonotrithioate. Distillation afforded 8.81 g (78.0%) of **4** (R = CH_3CH_2—, R′ = —$(CH_2)_3CH_3$) as a colorless oil: bp 61–64°C/0.02–0.025 mm Hg (Literature[27] bp 71–72°C/0.025 mm Hg). ^{1}H NMR (TMS, δ): 3.06, ddt (1H, J_{PH} = 19.0 Hz, J_{HH} = 12.6 Hz, J_{HH} = 7.4 Hz S—C<u>H</u>—), 3.18, ddt (1H, J_{PH} = 14.9 Hz, J_{HH} = 12.6 Hz, J_{HH} = 7.4 Hz S—C<u>H</u>—), 2.54, ddq (1H, J_{PH} = 11.0 Hz, J_{HH} = 14.6 Hz, J_{HH} = 7.4 Hz —C<u>H</u>P—), 2.64, ddq (1H, J_{PH} = 12.2 Hz, J_{HH} = 14.6 Hz, J_{HH} = 7.4 Hz —C<u>H</u>P—), 1.74 pentet (2H, J_{HH} = 7.4 Hz S—CH_2C<u>H</u>$_2$—), 1.46, hextet (2H, J_{HH} = 7.4 Hz S—CH_2CH_2C<u>H</u>$_2$—), 1.39, dt (3H, J_{PH} = 27.6 Hz, J_{HH} = 7.4 Hz C<u>H</u>$_3CH_2$P—), 0.95, t (3H, J_{HH} = 7.3 Hz, —$CH_2CH_2CH_2$C<u>H</u>$_3$); ^{31}P NMR (H_3PO_4, δ): 107.8.

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