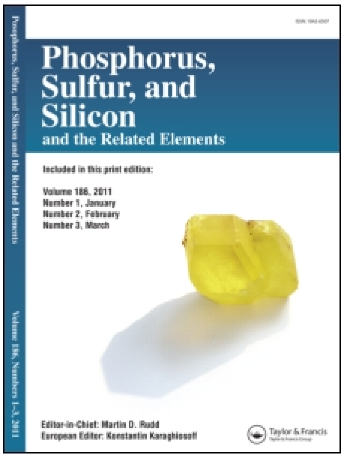

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PHOSPHONATE CHEMISTRY. A NOVEL PREPARATION OF PHOSPHONODITHIOIC HALIDES

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PHOSPHONATE CHEMISTRY. A NOVEL PREPARATION OF PHOSPHONODITHIOIC HALIDES

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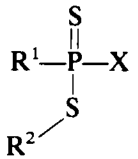
Phosphonodithioic halides can be obtained *via* a novel "one-flask" process by treatment of 2,4-bis(alkyl or aryl)-1,3-dithia-2,4-diphosphetane-2,4-disulfides with a lithium halide, an alkyl halide, and 15-crown-5.

INTRODUCTION

Phosphonodithioic halides (**1**) are important intermediates in the synthesis of pesticides.[1,2] We required the ready availability of S-alkyl alkylphosphonodithioic halides **1a** and **1b** as synthetic intermediates. The bromides were of particular interest due to their greater reactivity (over the chlorides). Most literature syntheses have dealt with the preparation of the chlorides with a few reported examples of the bromides.[1-3] Typically, the phosphonodithioic halides have been obtained in multi-step fashion *via* the precursor phosphonous di- and monohalides.[1] Recently, it was shown that phosphonothioic dichlorides could be selectively converted to the desired S-alkyl phosphonodithioic chlorides (**1b**) by addition of α-branched alkyl mercaptans in the presence of triethylamine.[2] However, S-(primary alkyl) phosphonodithioic chlorides (**1b**) cannot be cleanly obtained by this method. A synthesis of S-alkyl arylphosphonodithioic bromides (**1c**) has been reported.[3] The procedure involves treatment of a 2,4-bis(aryl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide with an alkyl halide in a sealed tube for 48 hours. We were unable to adapt this process to the preparation of the corresponding alkylphosphonodithioic bromides (**1a**). We now wish to report a novel "one-flash" approach to these bromides (**1a**). In addition, alkylphosphonodithioic chlorides (**1b**) and arylphosphonodithioic bromides (**1c**) are also amenable by this method.



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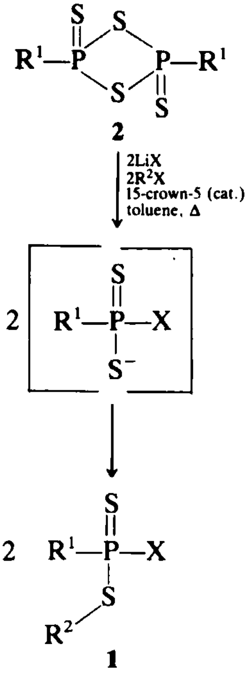
1a, R^1 = alkyl, R^2 = alkyl, X = Br
1b, R^1 = alkyl, R^2 = alkyl, X = Cl
1c, R^1 = aryl, R^2 = alkyl, X = Br

RESULTS AND DISCUSSION

Our approach required the cleavage of a bis(alkyl)dithiophosphetanedisulfide (**2**)[4] with bromide anion. The resulting intermediate, in the presence of an alkyl bromide, would undergo alkylation to yield the alkylphosphonodithioic bromide (**1a**). Generation of a soluble and sufficiently reactive bromide anion could be facilitated by the use of a crown ether (see Scheme 1).

Initially, treatment of 2,4-bis(ethyl)-1,3-dithio-2,4-diphosphetane-2,4-disulfide with lithium bromide, 1-bromopropane, and 12-crown-4[5] in refluxing toluene resulted in essentially no reaction. This was unusual in view of the reported suitability of 12-crown-4 for lithium complexation.[6] However, substitution of 12-crown-4 with 15-crown-5[5] effected reaction to provide S-*n*-propyl ethylphosphonodithioic bromide (**3**). Not surprisingly, use of alkyl halides of greater reactivity (e.g., allyl bromide or benzyl bromide) afforded higher yields of products (**4** and **5**). S-allyl 4-methoxyphenylphosphonodithioic bromide (**6**) was also successfully prepared by this process. Alternatively, the use of lithium chloride proceeded smoothly to yield S-allyl ethylphosphonodithioic chloride (**7**), demonstrating the applicability of this method to the preparation of the corresponding chlorides. All results are summarized in Table I.

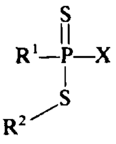
In conclusion, this method affords the ready synthesis of both phosphonodithioic bromides and chlorides, and also complements the literature[2] by allowing preparation of S-(primary alkyl) phosphonodithioic halides such as **3**.



Scheme 1

TABLE I

Phosphonodithioic halides



1

Compound	R^1	R^2	X	Reaction time (hrs)[a]	Yield (%)[b]
3	C_2H_5	n-C_3H_7	Br	26	31
4	C_2H_5	$H_2C{=}CH{-}CH_2$	Br	4	50
5	CH_3	$C_6H_5{-}CH_2$	Br	5	60
6	4-$CH_3O{-}C_6H_4$	$H_2C{=}CH{-}CH_2$	Br	8	25
7	C_2H_5	$H_2C{=}CH{-}CH_2$	Cl	4	51

[a] Reflux.

[b] Distilled.

EXPERIMENTAL

Boiling points are uncorrected. The 60-MHz ^{1}H-NMR spectra were determined on a Varian EM-360L spectrometer. IR spectra were determined on a Beckman 4250 infrared spectrophotometer. Low resolution mass spectra were obtained on a Finnegan 1020 mass spectrometer. High resolution mass spectra were obtained on a VG-7070E-HF mass spectrometer. Microanalyses were performed by the Analytical Laboratory, Department of Chemistry, University of California, Berkeley.

The following examples are typical of the preparation of the phosphonodithioic halides in Table I.

S-Benzyl methylphosphonodithioic bromide (**5**). To a slurry of 4.44 g (0.0202 mole) of 2,4-bis(methyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide[4] in 60 mL of toluene and under nitrogen was added 7.58 g (5.27 mL, 0.0444 mole) of benzyl bromide, 4.20 g (0.0484 mole) of lithium bromide, and 1.07 g (0.96 mL, 0.0048 mole) of 15-crown-5.[5] The mixture was refluxed for 5 hrs and stirred at room temperature overnight. The mixture was filtered, washed with water and saturated aqueous sodium chloride, dried with magnesium sulfate, and evaporated to a clear, mobile oil. Bulb-to-bulb distillation [oven temperature 105–120° (0.02 torr)] yielded 6.82 g (60%) of **5**, a clear oil: ^{1}H-NMR ($CDCl_3$) δ7.35–7.80 (m,5), 4.40 (d, 2, J = 17 Hz), 2.60 (d, 3, J = 13 Hz); IR (film) 1497, 1457, 900, 770, 700, 643 cm^{-1}; EIMS m/e 282, 280 (M^+), 201 ($M^+ - Br$), 123 ($C_7H_7S^+$), 92 ($C_7H_7^+$). High resolution EIMS M^+ 279.9145, 281.9124 ($C_8H_{10}BrPS_2$).

Anal. Calculated for C_8H_{10} $BrPS_2$: C, 34.18; H, 3.56. Found: C, 34.77; H, 3.61.

S-Allyl ethylphosphonodithioic chloride (**7**). The title compound was prepared from 5.0 g (0.0202 mole) of 2,4-bis(ethyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide,[4] 4.62 g (4.92 mL, 0.0605 mole) of allyl chloride, 2.05 g (0.0484 mole) of lithium chloride, 1.07 g (0.96 mL, 0.0048 mole) of 15-crown-5,[5] and 60 mL of toluene according to the procedure above for **5**. The mixture was refluxed for 4 hours. Bulb-to-bulb distillation [oven temperature 60–70° (0.2 torr)] yielded 4.13 g (51%) of **7**, a clear, mobile oil: ^{1}H-NMR ($CDCl_3$) δ5.10–6.30 (m, 3), 3.80 (dd, 2, J = 18, 6.5 Hz), 2.30–3.0 (m, 2), 1.45 (dt, 3, J = 28, 7 Hz); IR (film) 1640, 1455, 1425, 1400, 1235, 1035, 930, 768, 730, 630, 510 cm^{-1}; EIMS m/e 202, 200 (M^+), 172 (M^+-ethylene), 167 (M^+-SH), 165 (M^+-Cl), 128 (M^+-C_3H_5S), 73 ($C_3H_5S^+$).

Anal. Calculated for $C_5H_{10}ClPS_2$: C, 29.93; H, 4.99. Found: C, 30.14; H, 5.11.

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