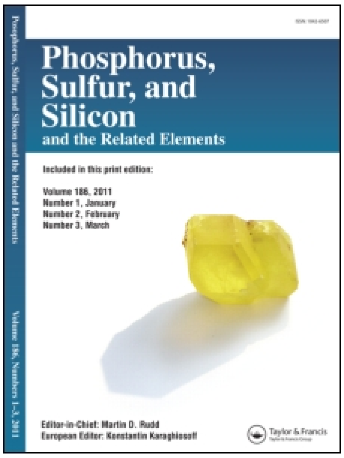

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CHLOROMETHYLATION AT SULFUR WITH METHYLENE CHLORIDE. PREPARATION OF S-CHLOROMETHYL O,O-DIETHYL PHOSPHORODITHIOATE.

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O,O-Diethyl phosphorodithioic acid salts can be S-chloromethylated in high yield using a large excess of methylene chloride at reflux. A small amount of a polar solvent, such as DMF (20–40% of the reaction volume), is required for reaction.

Chloromethylation of sulfur nucleophiles is commonly accomplished by the condensation of formaldehyde and hydrochloric acid with the nucleophile.[1,2] More recent reports[3,4] have indicated the usefulness of bromochloromethane in the chloromethylation of sulfur nucleophiles. Use of symmetrical methylene dihalides has generally led to double displacement reactions, giving the symmetrical methylene-bis compounds.[5-7]

S-Chloromethyl O,O-diethyl phosphorodithioate (chlormephos, **1**) is a good corn rootworm insecticide, as well as a useful intermediate for the preparation of other phosphate derivatives. It is prepared at present by reaction of a salt of O,O-diethyl phosphorodithioic acid with bromochloromethane.

The reported[4] procedure gives the product contaminated with 10–15% of the methylene-bis product, **2** (Eq. 1). Bromochloromethane is an expensive reagent, and a high percentage of its total weight is lost in the reaction as bromide ion. An alternative route to that of equation 1 is, therefore, desirable.

$$(EtO)_2PS_2^- + BrCH_2Cl \longrightarrow \underset{1\ (85\%)}{(EtO)_2PS_2CH_2Cl} + \underset{2\ (10\text{–}15\%)}{(EtO)_2PS_2CH_2SPS(OEt)_2} \qquad (1)$$

We have found that salts of O,O-diethyl phosphorodithioic acid can be chloromethylated in good yield using a large excess of methylene chloride, along with a polar co-solvent such as dimethylformamide (DMF), at reflux. No reaction occurs without the co-solvent. The best yields were realized using sodium carbonate to generate the salt from the dithio acid in the reaction mixture. No **2** was obtained under these conditions.

Ammonium O,O-diethyl phosphorodithioate could also be used in this reaction, but a somewhat lower yield of **1** resulted, and the product was found to contain small amounts of **2**.

It was found that smaller relative amounts of methylene chloride caused the formation of more **2**, and a lower yield of **1**. Likewise, the amount of DMF used in the reaction was found to be critical, passing through an optimum at about 20–40% of the reaction mixture. We have also shown that **1** is unstable under the reaction conditions at 100°C.

Polar solvents other than DMF gave similar results. The best alternative solvents seemed to be dimethylacetamide, dimethylsulfoxide (DMSO), *N*-methylpyrrolidinone, and hexamethylphosphoramide (HMPA). Many other polar solvents gave significant yields of chloromethyl ester. Pure methylene chloride (no co-solvent), or relatively non-polar co-solvents such as hexane or toluene gave no **1** under the reaction conditions studied.

EXPERIMENTAL

General Comments

NMR spectra were recorded on a Perkin-Elmer R 24B spectrometer using tetramethylsilane as an internal standard. **1** and **2** were well separated by TLC on silica gel, developed with 1:1 methylene chloride: hexane.

Ammonium O,O-diethyl phosphorodithioate was purchased from Aldrich Chemical Company as 95% pure. No attempt was made to identify or remove the contaminants from this material, but all calculations took purity of starting material into account. O,O-Diethyl phosphorodithioic acid was purchased from Aldrich Chemical Company and was distilled before use.

Preparation of **1** *from O,O-diethyl phosphorodithioic acid, methylene chloride, and sodium carbonate.*

To a stirred mixture of 5.3 g (.05 mol) of sodium carbonate, 350 ml (467.25 g, 5.5 mol) of methylene chloride, and 150 ml of DMF, was added over 15 minutes 9.31 g (.05 mol) of O,O-diethyl phosphorodithioic acid. The reaction mixture was then heated at reflux (48°C) for 22 hours. The resulting reaction mixture was concentrated, and the residue was stirred with 400 ml of water, and extracted three times with hexane. The combined hexane extract was washed twice with water, and then with saturated NaCl, dried ($MgSO_4$), and concentrated, leaving 13.0 g of a yellow oil. The product was distilled at 120–125°C/4.4 mm [Lit[4(a)]bp 113–115°C/2.5 mm] giving 8.17 g (70% of theory) of a colorless oil: ^1H NMR ($CDCl_3$): δ 1.3 (*t*, J = 7, 6H), 4.20 (*dq*, J_{PH} = 10, J_{HH} = 7, 4H), and 4.90 (*d*, J = 21, 2H).

Anal. Calcd. for $C_5H_{12}ClO_2PS_2$: C, 25.58; H, 5.16.
Found: C, 25.7; H, 5.2

Preparation of **1** *from ammonium O,O-diethyl phosphorodithioate in methylene chloride: DMF (80:20).*

A mixture of 10.15 g (.05 mol) of ammonium O,O-diethyl phosphorodithioate, 400 ml of methylene chloride, and 100 ml of DMF was heated at reflux (49°C) for 22 hours. It was then cooled and worked up as in the previous experiment. Distillation gave 8.03 g (68% of theory) of product, bp 121–126°C/4.5 mm.

Stability of **1** *at 100° under reaction conditions.*

A mixture of 1.0 g (.0043 mol) of **1**, 10 ml (13.2 g) of methylene chloride, and 10 ml of DMF was placed in a sealed tube and heated at 100° for 16 hours. The reaction mixture was then cooled and worked up in the same way as previous reactions to give 0.20 g (20% of theory) of a yellow liquid which NMR indicated to be 83% **1**. The calculated recovery of **1** was 17%.

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