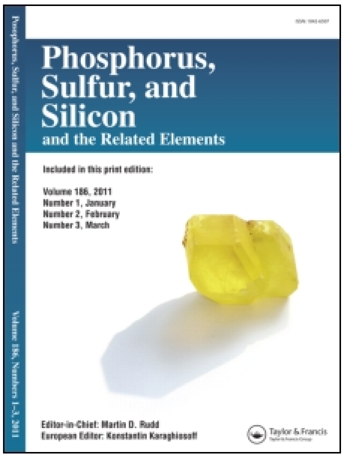

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Brand, William W. , Gullo, James M. and Carr, Michael C.(1981) 'REACTION OF O,O-DIETHYL PHOSPHOROTHIOITE WITH CHLOROMETHYLSULFENYL SPECIES Preparation of S-Chloromethyl O,O-Diethyl Phosphorodithioate', Phosphorus, Sulfur, and Silicon and the Related Elements, 10: 2, 183 — 184

To link to this Article: DOI: 10.1080/03086648108077503

URL: http://dx.doi.org/10.1080/03086648108077503

Phosphorus and Sulfur, 1981, Vol. 10, pp. 183–184
0308-664X/81/1002-0183$06.50/0

REACTION OF O,O-DIETHYL PHOSPHOROTHIOITE WITH CHLOROMETHYLSULFENYL SPECIES

Preparation of S-Chloromethyl O,O-Diethyl Phosphorodithioate

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(*Received June 28, 1980; in final form September 22, 1980*)

S-Chloromethyl O,O-diethyl phosphorodithioate can be prepared in high yield from O,O-diethyl phosphorothioite and an appropriate chloromethylsulfenyl species. Chloromethyl thiocyanate requires the presence of a stoichiometric amount of a base, such as sodium carbonate, for the reaction to proceed. Chloromethylsulfenyl chloride, however, gives better yields in the absence of any base.

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 presently prepared by the condensation of O,O-diethyl phosphorodithioic acid and bromochloromethane.[1] We have recently shown[2] that under certain special conditions, methylene chloride can also serve as an effective S-chloromethylating reagent in this reaction.

Reports of phosphorodithioate ester formation from the reaction of a phosphorothioite with a sulfenyl chloride[3] or thiocyanate[4] suggest the alternative route to the preparation of **1** outlined in Eq. 1.

$$(EtO)_2PSH + ClCH_2SX \longrightarrow \underset{\mathbf{1}}{(EtO)_2PS_2CH_2Cl} \qquad (1)$$

$$X = Cl, CN$$

For this approach to be successful, however, would require that the X (Eq. 1) be more readily displaced than the Cl alpha to sulfur or than the SCN group, both of which have been displaced from chloromethyl thiocyanate.[5] The successful application of Eq. 1 is the subject of this paper. O,O-Diethyl phosphorothioite was obtained by the literature[6] procedure. Reaction of the phosphorothioite with chloromethyl thiocyanate under the reported[4] conditions resulted in a low yield of **1**. We have found that reaction of the phosphorothioite with chloromethyl thiocyanate can be made to give **1** in high yield under a variety of conditions, with no evidence for the displacement of either the chlorine or the SCN group. A full equivalent of base is required for the reaction. Contrary to literature[4] reports, base strength was not a critical factor. Sodium carbonate was commonly used with success. The identity of the solvent[4] was also not critical, although the reaction rate appeared to be increased in more polar reaction mixtures. Phase transfer conditions employing aqueous potassium hydroxide were also demonstrated to work. Use of acetone as the reaction solvent allowed trapping of the by-product hydrogen cyanide as acetone cyanohydrin.

The use of chloromethylsulfenyl chloride in this reaction required a different set of conditions for a high yield of **1**. Chloromethylsulfenyl chloride was prepared by controlled chlorination of dimethyl disulfide.[7] Reaction of O,O-diethyl phosphorothioite with chloromethyl sulfenyl chloride in refluxing methylene chloride and one equivalent of pyridine gave a very low yield of **1**. However, when the reagents were allowed to react, without any base or solvent present, the reaction went exothermally to give a good yield of **1**. When mediated by the presence of ether as a solvent, the reaction went more slowly, but a quantitative yield of **1** was obtained.

EXPERIMENTAL

General Comments

NMR spectra were recorded on a Perkin–Elmer R 24B spectrometer using tetramethylsilane as an internal standard. Infrared spectra were recorded on a Perkin–Elmer Infracord. Diethyl phosphorochloridite (Eastman Organic Chemicals), chloromethyl thiocyanate (Aldrich Chemical Company), and dimethyl disulfide (Aldrich Chemical Company) were used without purification.

O,O-Diethyl phosphorothioite[6]

A stirred mixture of 108 g (0.69 mol) of O,O-diethyl phosphorochloridite, 54.6 g (0.69 mol) of pyridine, and 225 mL of ether was cooled to 3°C. Into this mixture was passed 23.5 g (0.69 mol) of hydrogen sulfide while the temperature was kept below 10°C. The reaction mixture was allowed to warm to room temperature and held for 20 minutes, after which it was filtered, and the ether evaporated at reduced pressure. The residual oil was vacuum distilled at 75°–78°/15 mm [Lit.[8] bp 73–74°/15 mm] giving 88.2 g (83% of theory) of the product as a yellow oil. NMR ($CDCl_3$): δ 1.35 (t, J = 7, 6H), 4.18 (dq, $J_{HH} = 7$, $J_{PH} = 11$, 4H), 7.81 (d, J = 650). IR showed a broad peak at 4.2–4.3 μ (PH).

Preparation of **1** *from chloromethyl thiocyanate and O,O-diethyl phosphorothioite in DMF.*

A mixture of 4.63 g (0.03 mol) of diethyl phosphorothioite, 3.23 g (0.03 mol) of chloromethyl thiocyanate, 3.18 g (0.03 mol) of sodium carbonate, and 50 mL of dimethylformamide (DMF) was stirred at room temperature. A small exotherm was noted after about 5 minutes. After 30 minutes, the reaction mixture was partitioned between 400 mL of water and 400 mL of hexane, then the aqueous layer was extracted with 100 mL of hexane. The combined hexane solution was washed three times with water, and then with saturated sodium chloride, dried over $MgSO_4$, and concentrated at reduced pressure, leaving 6.79 g of a colorless liquid (96% of theory). ^1H NMR spectroscopy and TLC indicated 91% purity. Distillation gave 0.88 g of a forerun, bp 65–69.5°C/0.14 mm (NMR indicated 95% pure product), followed by 5.56 g (79% of theory) of the product as a colorless liquid boiling at 69–69.5°C/0.14 mm [Lit.[1(a)] bp 113–115°C/2.5 mm]. NMR ($CDCl_3$): δ 1.37 (t, J = 7, 6H), 4.20 (dq, $J_{HH} = 7$, $J_{PH} = 10$, 4H), and 4.92 (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 chloromethyl thiocyanate and O,O-diethyl phosphorothioite in acetone.*

A mixture of 4.63 g (0.03 mol) of diethyl phosphorothioite, 3.23 g (0.03 mol) of chloromethyl thiocyanate, 3.18 g (0.03 mol) of sodium carbonate, and 50 mL of acetone was stirred at room temperature overnight. Work up as in the DMF reaction gave 6.88 g (98% of theory) of the crude product as a colorless oil. ^1H NMR of this product indicated >90% purity.

As an alternative work up procedure, distillation of the reaction mixture gave acetone, followed by an 82% yield of acetone cyanohydrin, bp 84–90°/10 mm [Lit.[9] bp 82°/22 mm]. The pot residue was then worked up as above to give the isolated product.

Preparation of **1** *from chloromethyl thiocyanate and O,O-diethyl phosphorothioite in water.*

A mixture of 0.47 g (0.003 mol) of diethyl phosphorothioite, 0.24 mL (0.003 mol) of chloromethyl thiocyanate, 0.25 mL (0.006 mol) of 50% aqueous potassium hydroxide, and a few crystals of benzyltriethylammonium chloride was stirred for thirty minutes during which time a mild exotherm was noted. The resulting brown reaction mixture was worked up as described in previous experiments giving 0.39 g of a light yellow liquid (56% of theory). ^1H NMR spectroscopy indicated only **1** to be present.

Preparation of **1** *from chloromethylsulfenyl chloride and O,O-diethyl phosphorothioite in ether.*

To a stirred solution of 2.5 g (0.016 mol) of O,O-diethyl phosphorothioite in 40 mL of ether was slowly added a solution of 1.9 g (0.016 mol) of chloromethylsulfenyl chloride[8] in 10 mL of ether. After standing overnight, the reaction mixture was concentrated leaving 5.4 g of a yellow oil. ^1H NMR analysis indicated 75% **1**, giving a quantitative calculated yield.

REFERENCES AND NOTES

1. (a) M. Pianka, U.S. Patent 3,896,219 (1975); (b) M. Pianka, German Patent 1,925,468 (1970) [*Chem. Abstr.*, **72**, 100883 (1970)]; (c) O. Scherer, *et al.*, U.S. Patent 3,020,304 (1962).
2. W. W. Brand, U.S. Patent 4,238,424 (1980).
3. W. Gerrard and H. R. Hudson in *Organic Phosphorus Compounds*, Vol. 5, G. M. Kosolapoff and L. Maier, Ed., John Wiley and Sons, New York, NY, 1973, p. 111.
4. W. Lorenz and G. Schrader, German Patent 1,087,591 (1960) [*Chem. Abstr.*, **55**, 17499 (1961)]; R. F. W. Raetz and A. D. Bliss, U.S. Patent 3,340,330 (1967).
5. S. A. Greenfield, U.S. Patent 3,772,331 (1973) and U.S. Patent 3,846,448 (1974).
6. R. Sallmann, U.S. Patent 2,805,241 (1957).
7. H. Brintzinger, *et al.*, *Chem. Ber.*, **83**, 87 (1950).
8. I. V. Murav'ev, N. I. Zemlyanskii, and E. P. Panov, *Zh. Obshch. Khim*, **38**, 133 (1968) [*Chem. Abstr.*, **69**, 58789 (1968)].
9. "The 1977–1978 Aldrich Catalog/Handbook of Organic and Biochemicals," p. 6.