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A NEW CONVENIENT SYNTHESIS OF PHOSPHORO(-NO)CHLORIDOTHIONATES

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ABSTRACT: A general procedure for synthesis of phosphoro(-no)chlorides, particularly unsymmetrical ones, has been developed. The method involves the dealkylation of O,O-dialkyl phosphoro(-no)thionates **1** with dimethylamine and the chlorination of O-alkyl ammonium phosphoro(-no)thioates **2** using phosphorus oxychloride as a chlorinating agent.

Generally, the chlorination of organic phosphorothioic acid with phosphorus pentachloride occurs smoothly and gives the corresponding phosphorochloridothionate. As early as 1966, Michalski reported that the reaction of O-ethyl ethylphosphonothioic acid with pentachloride gave O-ethyl ethylphosphonochloridothionate[1]. Later in our laboratory the chlorination of chiral (+)-O-ethyl O-phenyl phosphorothioic acid with phosphorus pentachloride was investigated and gave (-)-O-ethyl O-phenyl phosphorochloridothionate stereospecifically[2]. Recently Liu reported that several O,S-dialkyl ammonium phosphorodithioates can also react with phosphorus pentachloride to afford the corresponding chlorinating products phosphorochloridodithioates[3, 4]. Among these products, O-ethyl S-propyl phosphorochloridodithioate is frequently used as a key intermediate for synthesis of unsymmetrical phosphorodithioates insecticides, e.g. Sulprofos and Prothiofos.

In this paper, it is reported that phosphorus oxychloride as chlorinating agent can also react with a variety of O-alkyl ammonium phosphoro(-no)thioates **2** to give the corresponding O-alkyl phosphoro(-no)chloridothionates **3**. The ammonium salt **2** can be conveniently

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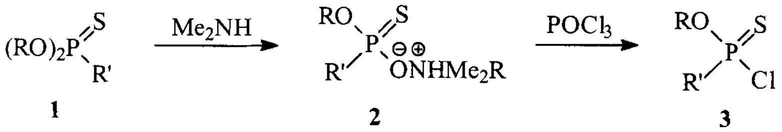
To whom correspondence should be addressed obtained from the dealkylation of O,O-dialkyl phosphoro(-no)thionate **1** with aqueous dimethylamine. Thus, this constitutes a new convenient method for preparation of various O-alkyl phosphoro(-no)chloridothionates, especially chiral ones.



EXPERIMENTAL

^{1}H NMR spectra were recorded on a JEOL FX-90Q instrument at 90 MHz, using TMS as an internal standard and $CDCl_3$ as the solvent. Quantitative elemental analyses were measured on a Yanaco MT-3 apparatus.

Column chromatography was performed on Qingdao silica gel (200~300 mesh) using petroleum ether (bp 60~90 ℃) / EtOAc as eluant. Phosphorus oxychloride was redistilled. Other reagents are commercial.

O-Alkyl N,N,N-alkyldimethyl ammonium phosphoro(-no)thioate 2 (General Procedure):

The mixture of **1** (0.1 mol) and 33% aqueous dimethylamine (0.4 mol) was refluxed vigorously at 50~60 ℃ for 6~30 h with stirring until **1** disappeared (TLC control, solvent system: petroleum ether / Et_2O, 10:1 (v/v), iodine as detecting agent). The excess aqueous dimethylamine was removed by rotary evaporation under reduced pressure to give the crude ammonium salt **2** as a viscous oil in an excellent yield (Table 1). The ammonium salt **2** can be used directly without purification.

Table 1. The Dealkylation of Phosphoro(-no)thionates **1** with Aqueous Dimethylamine

1	R	R'	Reaction Time (h)	Yield (%) of **2**
a	Me	PrS	8	87
b	Et	PrS	16	95
c	Me	PhO	17	89
d	Et	PhO	24	100
e	Me	NMe_2	12	97
f	Et	NMe_2	18	88
g	Et	EtS	15	88
h	Me	$PhCH_2S$	14	87
i	Et	$4\text{-}MeSC_6H_4O$	31	93
j	Me	Me	6	87
k	Me	Ph	15	100

O-Alkyl phosphoro(-no)chloridothionate 3 (General Procedure):

To a solution of phosphorus oxychloride (0.02 mol) and toluene (20 ml.) was added dropwise a suspension of the crude ammonium salt **2** (0.02 mol) and toluene (10 ml.) at room temperature with rapid stirring. After addition, the reaction mixture was stirred at 40 ℃ for

Table 2. Data of Compounds **3** Prepared

3	n_D^{25}	Yield*	^{1}H NMR ($CDCl_3$ / TMS) δ, J_{PH}(Hz)	Ref.
a	1.5411	82.9	1.04(t,3H), 1.80(m,2H), 3.06(dt,2H,J=16.4), 3.88(d,3H,J=16.2)	6
b	1.5328	73.8	1.02(t,3H), 1.40(t,3H), 1.80(m,2H), 3.00(dt,2H,J=16.4), 4.32(dq,2H,J=14.4)	7
c	1.5505	56.2	3.98(d,3H,J=10.8), 7.22(m,5H)	8
d	1.5385	62.3	1.44(t,3H), 4.40(dq,2H,J=14.4), 7.28(m,5H)	2
e	1.4980	58.2	2.85(d,6H,J=16.2), 3.85(d,3H,J=16.2)	9
f	1.4940	48.6	1.36(t,3H), 2.78(d,6H,J=15.8), 4.16(m,2H)	9
g	1.5372	75.8	1.36(t,6H), 3.20(dq,2H,J=19.4), 4.20(dq,2H,J=12.6)	10
h**	1.6041	67.3	3.70(d,3H,J=16.2), 4.20(d,2H,J=16.9), 7.22(bs,5H)	
i**	1.5771	46.4	1.45(t,3H), 2.44(s,3H), 4.36(dq,2H,J=11.2)	
j	1.4882	69.5	2.32(d,3H,J=14.8), 3.86(d,3H,J=16.6)	11
k	1.5828	65.1	3.96(d,3H,J=15.5), 7.84(m,5H)	12

*Two-step total yield based on **1**

**Satisfactory microanalyses obtained: C ± 0.26, H ± 0.11

additional 4~5 h, then cooled to room temperature, and poured into cold water (40 ml). The organic layer was separated and dried ($MgSO_4$). After removal of the solvent toluene under redued pressure, the crude product **3** was purified by column chromatography on silica gel to give the title compound **3** in a moderate isolated yield (Table 2).

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