The First Synthesis and Isolation of 'Bis(aryloxy)phosphorothioylsulfenyl Iodides' (= Bis(aryloxy)phosphinesulfenyl Iodide *P*-Sulfides) from the Reaction of *S,S'*-(Diphenylstannylene) *O,O,O',O'*-Tetraaryl Bis[phosphorodithioates] (= [(Diphenylstannylene)bis(thio)]bis[bis(aryloxy)phosphine *P*-Sulfides]) with *N*-Iodosuccinimide

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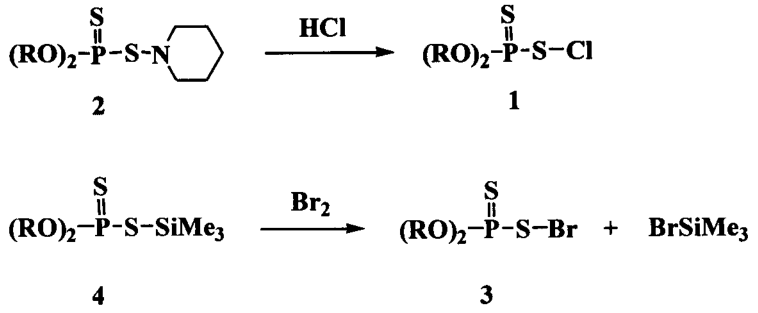
Dedicated to Professor *Shinji Kato* on the occasion of his retirement

S,S'-(Diphenylstannylene) *O,O,O',O'*-tetraaryl bis[phosphorodithioates] (= [(diphenylstannylene)bis(thio)]bis[bis(aryloxy)phosphine *P*-sulfides]) **5** react with *N*-iodosuccinimide (NIS) in CH_2Cl_2 at −30° under A to give 'bis(aryloxy)phosphorothioylsulfenyl iodides' (= bis(aryloxy)phosphinesulfenyl iodide *P*-sulfides) **6** (*Scheme 3*), which can readily react *in situ* with 4-methylbenzenecarbodithioic acid, thiol, and cyclohexene to afford the corresponding unsymmetrical disulfides and the adduct in good yields as the novel electrophilic dithiophosphorylating reagents (*Schemes 4* and *5*). By adding hexane into the solution at −30° after reaction of **5** with NIS, the 'phosphorothioylsulfenyl iodides' **6** can be isolated as yellow solids in good yields (see *Table*).

Introduction. – Phosphorodithioic acid derivatives such as $(RO)_2P(=S)SR'$ and $[(RO)_2P(=S)]_2S_x$ ($x = 1, 2, 3, 4$ *etc.*) are of great importance because of their wide application as pesticides [1] and lubricating additives, *etc.* [2][3]. For dithiophosphorylation, the nucleophilic reagents such as alkali-metal phosphorodithioates $(RO)_2P(=S)SNa$ [4] and ammonium phosphorodithioates $(RO)_2P(=S)S(NH_2R'_2)$ [4] have been widely employed. In contrast, 'phosphorothioylsulfenyl halides (= phosphinesulfenyl halide *P*-sulfides) $(RO)_2PS(=S)X$ ($X = Cl, Br, I$), which are potential electrophilic dithiophosphorylating reagents, have rarely been investigated due to their thermal instability and difficult synthesis.

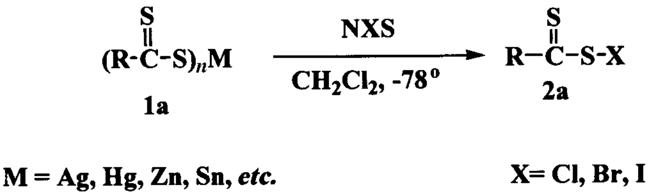
To the best of our knowledge, only *Almasi* and co-workers [5–8] reported in 1962 that 'bis(alkyloxy)phosphorothioylsulfenyl chlorides' **1** can be obtained by the reaction of 'bis(alkyloxy)phosphorothioylsulfenamides' (= bis(alkyloxy)phosphinesulfenamide *P*-sulfides) **2** with hydrochloric acid (*Scheme 1*). Moreover, in 1982, *Michlaski et al.* indicated that 'bis(alkyloxy)phosphorothioylsulfenyl bromides' **3** can be isolated from the reaction of phosphorodithioic acid *O*,*O*-dialkyl *S*-(trimethylsilyl) esters **4** with bromine (*Scheme 1*). Very recently, further details of this reaction have been disclosed [10]. These methods, however, suffer from two main drawbacks: *i*) the starting materials are not readily available, and *ii*) the starting compounds **3** are very prone to hydrolysis. In addition, the compounds **2** and **4** synthesized according to these procedures are oily substances, so their purification is very difficult.

Scheme 1



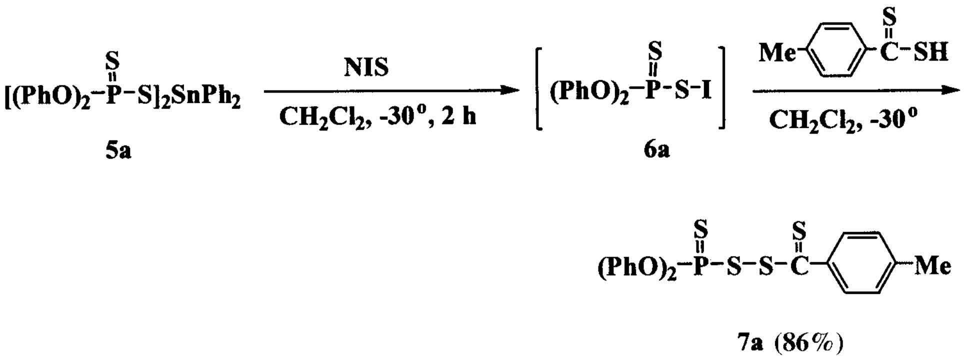
On the other hand, in our laboratory, the synthetic methods to furnish 'acylsulfenyl halides' RC(=O)SX (X = Cl, Br, I), which are also potential electrophilic thiocarboxylating reagents, have been developed. Thus, the 'acylsulfenyl halides' **2a** were readily obtained from the reaction of silver [11], mercury [12], zinc [13], and tin carbothiolates **1a** [14][15] with halogen or *N*-halosuccinimides (NXS, X = Cl, Br, I) (*Scheme 2*). These results suggest that 'phosphorothioylsulfenyl halides' might be synthesized by the reaction of phosphorodithioic acid metal salts with *N*-halosuccinimide or halogens. In fact, we have synthesized the 'phosphorothioylsulfenyl bromides' **3** from the reaction of *S,S'*-(diphenylstannylene) *O,O,O',O'*-tetraalkyl or *O,O,O',O'*-tetraarylbis-[phosphorodithioates] **5** with *N*-bromosuccinimide (NBS) in CH_2Cl_2 [16]. But we could not isolate the 'bis(aryloxy)phosphorothioylsulfenyl iodides' **6**. In this paper, we wish to report the synthesis and isolation of bis(aryloxy)phosphorothioylsulfenyl iodides **6** from the reaction of *S,S'*-(diphenylstannylene) *O,O,O',O'*-tetraaryl bis-[phosphorodithioates] (= [diphenylstannylenebis(thio)]bis[bis(aryloxy)phosphine *P*-sulfides]) **5** with *N*-iodosuccinimide (NIS).

Scheme 2

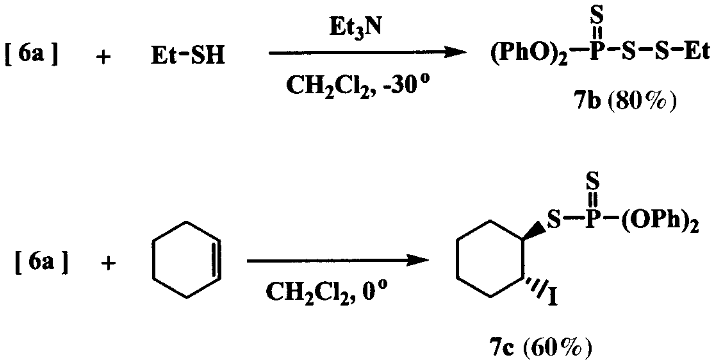


Results and Discussion. – Bis(aryloxy)phosphorothioylsulfenyl iodides **6** are unknown compounds because they are very labile, and their isolation from reaction mixtures is very difficult. So far, no successful isolation of this kind of compound has been reported. During our own investigation on the synthesis and isolation of **6**, we confirmed that, at low temperature (– 30°), diphenoxyphosphorothioylsulfenyl iodide **6a** was indeed formed by trapping reagents such as a carbodithioic acid, ethanethiol, or cyclohexene. In a typical trapping experiment, **5a** was treated with NIS in CH_2Cl_2 at – 30° for 2 h, and, then, the carbodithioic acid was added and the mixture stirred at

Scheme 3



Scheme 4



$-30°$ for 8 h (*Scheme 4*). After evaporation, the crude product was purified by column chromatography (silica gel) to give **7a** as a red oily product in high yield (86%). Its structure was established on the basis of spectroscopic data.

Similarly, the trapping experiments with ethanethiol and cyclohexene gave the corresponding product **7b** and **7c**, respectively, in moderate yields (80 and 60%, resp.) (*Scheme 4*). All these results suggest that the bis(aryloxy)phosphorothioylsulfenyl iodides **6** were unambiguously formed at $-30°$.

We then attempted to isolate compounds **6** from the reaction mixture, although it is very difficult because evaporation of the mixture after reaction at room temperature, bis(aryloxy)phosphorothioylsulfenyl iodides **6** immediately decomposed to precipitate iodine (I_2), and the reaction solution turned from yellow-orange to dark red. After tremendous efforts, we finally found that 'bis(aryloxy)phosphorothioylsulfenyl iodides' **6a** – **d** could be precipitated from the reaction mixture at $-30°$ by adding hexane. Quick filtration of the resulting solid allowed us to isolate **6a** – **d** in good yield (see *Table*). Repeated recrystallization from CH_2Cl_2/hexane at $-30°$ finally gave **6** in quite pure form. The structure of the 'bis(aryloxy)phosphorothioylsulfenyl iodides' **6** were established by spectroscopic data (see *Table*) and microanalyses. This is the first report on the isolation of bis(aryloxy)phosphorothioylsulfenyl iodides **6**.

Table. *Yields, Spectral Data, and Physical Properties of* $(ArO)_2P(=S)SI$ (**6a** – **d**)

	Ar of $(ArO)_2P(=S)SI$	Yield[a]) [%]	M.p. [°]	IR (KBr): $\tilde{\nu}(P=S)$ [cm^{-1}]	^{31}P-NMR[b]) [δ]
6a	C_6H_5	74	85 – 86	635, 845	67.7
6b	4-MeC_6H_4	80	87 – 88	635, 845	68.2
6c	4-$MeOC_6H_4$	60	104 – 105	635, 845	70.0
6d	4-ClC_6H_4	50	95 – 96	635, 845	69.2

[a]) Isolated yield. [b]) External standard: 85% H_3PO_4.

Conclusions. – We found that bis(aryloxy)phosphorothioylsulfenyl iodides **6** can be isolated from the reaction mixture as yellow precipitates after addition of hexane at low temperature (– 30°). Efforts are underway to elucidate the mechanistic details of this reaction and to identify systems enabling similar syntheses of other substrates and subsequent transformations thereof.

Experimental Part

General. Organic solvents were dried by standard methods when necessary. Commercially available reagents were used without further purification. TLC Monitoring: *Huanghai-GF*$_{254}$ silica-gel-coated plates. Flash column chromatography (FC): silica gel, 200 – 300 mesh. M.p.: *Yanagimoto* micro-melting-point apparatus; uncorrected. ^1H-NMR Spectra: *Bruker AM-300* spectrometer; in $CDCl_3$ with $SiMe_4$ as internal standard; δ in ppm, *J* in Hz. Mass spectra: *Hewlett-Packard 5989* instrument; for high resolution, *Finnigan MA* + spectrometer. Some of the solid compounds reported in this paper gave satisfactory CHN microanalyses with *Carlo-Erba 1106* analyzer.

Reaction of S,S′-*(Diphenylstannylene)* O,O,O′,O′-*Tetraaryl Bis[phosphorodithioates] with NIS: General Procedure.* To *S,S′*-(diphenylstannylene) *O,O,O′,O′*-tetraphenyl bis[phosphorodithioate] (=([diphenylstannylene)bis(thio)]bis[diphenoxyphosphine *P*-sulfide]; **5a**; 835 mg, 1.0 mmol) in CH_2Cl_2 (20 ml), *N*-iodosuccinimide (NIS) (270 mg, 1.2 mmol) was added at – 30° under Ar (→ immediately orange soln). The mixture was stirred at – 30° for 2 h. Anh. hexane (16 ml) was added to the mixture to give a yellow precipitate. After filtration, the obtained solid was recrystallized from CH_2Cl_2 (8 ml)/hexane (20 ml): 301 mg (74%) of *diphenoxyphosphorothioylsulfenyl iodide* (= *diphenoxyphosphinesulfenyl iodide* P-*sulfide*; **6a**). Yellow solid. M.p. 85 – 86°. IR ($CHCl_3$): 635, 845 (P=S). ^1H-NMR ($CDCl_3$): 7.13 – 7.38 (*m*, Ph). ^{31}P-NMR (121 MHz, $CDCl_3$, 85% H_3PO_4): 67.7. EI-MS: 408 ($M^{+\bullet}$). Anal. calc. for $C_{12}H_{10}IO_2PS_2$: C 35.31, H 2.47; found: C 35.27, H 2.33%.

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