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THIOPHOSPHOROSULFENYL BROMIDES AND IODIDES —— SYNTHESIS AND CHARACTERIZATION

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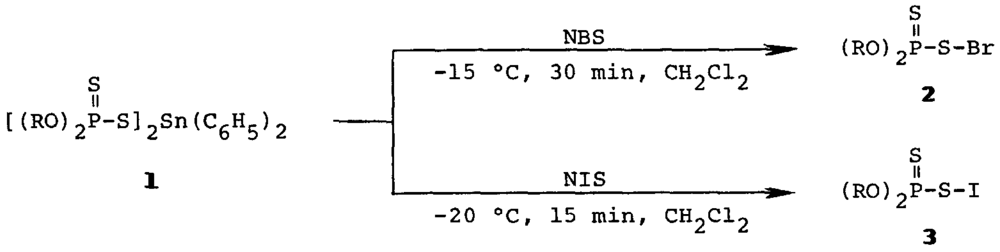
Summary: The reaction of diphenyltin bis(dithiophosphates) with N-bromo- and N-iodosuccinimides afforded corresponding thiophosphorosulfenyl bromides and iodides, which reacted with a variety of nucleophiles such as thiol, dithiocarboxylic acid, amine, and olefin to give novel unsymmetrical disulfides, sulfenamides, and dithiophosphoric acid esters.

Dithiophosphoric acid derivatives are of great importance, because of their wide application as pesticizers, and lubricating additives, etc. For dithiophosphorylation, nucleophilic alkali metal and ammonium salts have been employed widely. In contrast, due to instability and synthetic difficulty, electrophilic dithiophosphorylating reagents have been limited to a few of thiophosphorosulfenyl chlorides[1] and bromides,[2] despite their considerable synthetic utility. Recently, we have developed the convenient synthetic methods of acylsulfenyl bromides and iodides.[3] Now we wish to report the synthesis and characterization of thiophosphorosulfenyl bromides **2** and iodides **3** from the reaction of diphenyltin bis(dithiophosphates) **1** with N-bromo-(NBS) and N-iodosuccinimides (NIS).

When three equivalents NBS in dichloromethane were added to diphenyltin bis[O,O-di(*p*-tolyl)dithiophosphate] **1b** in the same solvent at -15 °C, the reaction mixture gradually changed from colourless to yellow. After stirring for 30 min, removal of the solvent in vacuo, extraction of the residue with *n*-hexane, and then cooling of the extracts at -70 °C gave 80% of O,O-di(*p*-tolyl)thiophosphorosulfenyl bromide **2b** as yellow crystals. Similarly, bromination of the tin esters (**1a**, **c**, **d**, **e**) yielded corresponding sulfenyl bromides (**2a**, **c**, **d**, **e**) in moderate isolated yields (Table 1). This is the first example of crystalline thiophosphorosulfenyl halides.



$$[(RO)_2\overset{\overset{S}{\|}}{P}-S]_2Sn(C_6H_5)_2 \xrightarrow[-15\ °C,\ 30\ min,\ CH_2Cl_2]{NBS} (RO)_2\overset{\overset{S}{\|}}{P}-S-Br$$

$$[(RO)_2\overset{\overset{S}{\|}}{P}-S]_2Sn(C_6H_5)_2 \xrightarrow[-20\ °C,\ 15\ min,\ CH_2Cl_2]{NIS} (RO)_2\overset{\overset{S}{\|}}{P}-S-I$$

Table 1. Yields and physical properties of thiophosphorosulfenyl bromides **2**

No.	$(RO)_2P(S)SBr$ R	Yield [%]	mp[a] [°C]	IR (KBr) ν_{S-Br}	mass[b] m/z$[M^+]$	$^{31}P(CH_2Cl_2)$[c] δ
2a	C_6H_5	60	88-92	451	360, 362	+71.9
2b	*p*-$CH_3C_6H_4$	80	86-89	458	388, 390	+73.2
2c	*p*-$CH_3OC_6H_4$	72	85-87	452	420, 422	+71.8
2d	*p*-ClC_6H_4	50	85-88	452	428, 430, 432,434	
2e	*cyclo*-C_6H_{11}	81	64-67	450	372, 374	+72.1(t)[d]

[a] Decomposition; [b] 20 eV, 60 °C; [c] H_3PO_4 as external standard; [d] J_{P-O-CH}= 12.2 Hz.

The structures of **2** were confirmed by spectral data and microanalyses. For example, in the mass spectrum **2b** shows molecular ions at m/z 389, 392. The ^{31}P NMR spectrum shows a singlet peak at δ= +70.1. In the IR spectrum, a characteristic absorption band at 450 cm^{-1} due to νS-Br is observed.[4] In addition, the result of microanalyses supports the structure of **2b**.[5]

Analogous reactions of **1** with NIS produced the expected thiophosphorosulfenyl iodides **3**. A number of attempts to isolate them and to measure their IR, NMR, and electron spectra faild. Therefore, constitutions were established by conversion into the thioacyl phosphorothioyl disulfides **4**.[6]

The obtained sulfenyl bromides **2** and iodides **3** readily react with thiols and dithiocarboxylic acids at -10 °C to give the novel unsymmetrical disulfides $[(RO)_2P(S)SSR']$.[6] In addition, similar reactions with sodium seleno- and tellurophenolates, primary and secodary amines, and olefins led to the corresponding chalcogeno derivatives $[(RO)_2P(S)SEPh$, E= Se, Te$]$, sulfenamides $[(RO)_2P(S)SNR'_2]$, and addition products $[(RO)_2P(S)S\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-}X$, X= Br, I$]$.

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5. **2b**: Found: C, 43.32; H, 3.63; Calcd for $C_{14}H_{14}O_2PS_2Br$: C, 43.20, H, 3.63.
6. For example, *p*-tolyl derivative **3b** reacted with *p*-(methoxy)dithiobenzoic acid at -10 °C to give O,O-di(*p*-tolyl)phosphorothioyl *p*-(methoxy)thiobenzoyl disulfide **4b** as oil: UV/Vis (CH_2Cl_2) 347, 518 nm; ^{13}C-NMR ($CDCl_3$) δ218.9 (CS); ^1H NMR ($CDCl_3$) δ2.32 (s, 3H, CH_3), 3.86 (s, 3H, CH_3O), 6.8-8.3 (m, 12H, Ar).

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