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Convenient Methods for the Synthesis of S-Organothioarsenic(III) Derivatives of Tetrathiophosphoric and Trithiophosphonic Acids

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ABSTRACT

S-*Organoarsenic(III) derivatives of tetrathiophosphoric and trithiophosphonic acids* **3a,b** *and* **7** *were easily obtained by the reactions of tetraphosphorus decasulfide* **1**, *the ethyl homologue of Davy's reagent* **5**, *and Lawesson's reagent* **6** *with S-isobutyldiethylarsenite* **2**. © 1997 John Wiley & Sons, Inc.

INTRODUCTION

Organoarsenic(III) derivatives of tetracoordinated phosphorus thioacids possess properties of practical use. Some of these compounds are used as pesticides [1], analytical reagents [2], and for regeneration of cracking catalysts [2]. Organoarsenic(III) dithiophosphates have been obtained by the reactions of dithiophosphoric acids or their salts with arsenic(III) halides and oxides [1–7]. These techniques, however, are multistep procedures. Thus, organothiophosphorus derivatives of arsenic(III) appear to have been limited to compounds containing dithiophosphato moieties [1–7]. On the other hand, organothiophosphorus derivatives of arsenic(III) containing tetrathiophosphato moieties and a P–C bond have remained unknown. In this article, convenient methods are presented for the synthesis **S**-triorganoarsenic(III) derivatives of tetrathiophosphoric and trithiophosphonic acids directly from tetraphosphorus decasulfide, **1**, and 1,3,2,4-dithiadiphosphetane-2,4-disulfides, **5** and **6**.

RESULTS AND DISCUSSION

For the synthesis of new organothiophosphorus derivatives of arsenic(III), we have now used tetraphosphorus decasulfide **1**, the ethyl homologue of Davy's reagent **5**, and Lawesson's reagent **6** as thiophosphorylating agents instead of dithiophosphoric acids. Dithiophosphoric acids have previously had to be synthesized by treatment of alcohols or diols with tetraphosphorus decasulfide [8]. We minimized the number of steps for the synthesis of **S**-organoarsenic(III) derivatives of tetrathiophosphoric and trithiophosphonic acids **3a,b** and **7** by using arsenic(III) alkylmercaptides instead of arsenic(III) halides and oxides.

We have now found that **1** reacts with **S**-isobutyldiethylarsenite **2** in anhydrous benzene at 20 °C for 2 hours to give **S**″-diethylarsenic(III) **S**, **S**′-diisobutyltetrathiophosphate **3a**, and bis(diethylarsenic)sulfide **4** (Reaction 1, Tables 1–4).

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TABLE 1 Yields, Physical, Analytical, and ^{31}P NMR Data of the Products Obtained

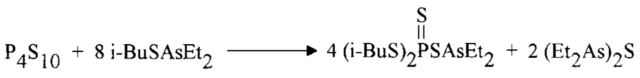
Prod.	*Yield (%)*	*Bp, °C (mm Hg)*[c]	n_D^{20}	*Molecular Formula (Mol. mass)*	*Found/Calc., %*		^{31}*P NMR* δ[d]
					P	*As*	
3a	52[b]	130 (0.07)	1.5901	$C_{12}H_{28}AsPS_4$	7.44	18.77	92.4
				(406.1)	7.63	18.45	
3b	83[a]		1.6249	$C_{10}H_{24}AsPS_4$	8.37	20.33	90.8
				(378.0)	8.19	19.82	
7	76[b]	140 (0.02)	1.5422	$C_{15}H_{26}AsOPS_3$	7.52	18.22	81.2
				(424.0)	7.30	17.67	

[a] Yield of crude product.
[b] Yield of isolated product.
[c] Temperature of thermal element of a falling-film distillation apparatus.
[d] IN C_6H_6.

TABLE 2 IR Data (cm^{-1}) of the Products Obtained

Prod.	*CH₃, CH₂*	*Ph*	δ[a] *CH₃ CH₂*	*P=S*	*P–S*	*As–S*
3a	2959		1453	680		378
	2926		1426 (S)		562	
	2869		1409 (As)		517	
			1386			
			1366			
3b	2960		1453	682	522	376
	2926		1425 (S)			
	2869		1413 (As)			
			1386			
			1366			
7	2957	1600	1454	724		392
	2927	1502	1425 (S)		565	
	2869	803	1410 (As)		551	
			1380			
			1366			

[a] Deformation vibrations.



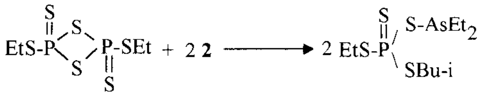
$$P_4S_{10} + 8\ \text{i-BuSAsEt}_2 \longrightarrow 4\ (\text{i-BuS})_2\overset{S}{\overset{\|}{P}}\text{SAsEt}_2 + 2\ (\text{Et}_2\text{As})_2\text{S}$$

1 2 3a 4

(1)

The tetrathiophosphate of diethylarsenic(III), **3a**, is a pale yellow, oily liquid, and it was purified by a falling-film distillation. It decomposed when common vacuum distillation was attempted. The product **3a** is a new type of organothiophosphorus derivative of arsenic(III) containing the $S_2P(S)SAs$ structural fragment. The structure of **3a** has been established by evaluation of IR (Table 2), ^{1}H (Table 3), ^{31}P NMR (Table 1), and mass spectra (Table 4) and by microanalyses (Table 1).

The formation of products of similar structure could be expected by the reaction of the ethyl homologue of Davy's reagent **5** with arsenic(III) mercaptides. In fact, **S**″-diethylarsenic(III) **S**-ethyl-**S**′-isobutyltetrathiophosphate **3b** resulted from the reaction of **5** with the thioarsinite **2** (Reaction 2, Tables 1–4).

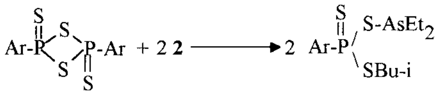


5 3b

(2)

Reaction 2 proceeded in anhydrous benzene at room temperature for 2 hours and resulted in the formation of **3b** in 83% yield.

This reaction may be extended to other 1,3,2,4-dithiadiphosphetane-2,4-disulfides, for example, the well-known Lawesson's reagent **6**. Thus, the reaction of the thioarsinite **2** with **6** at 20°C for 4 hours in anhydrous benzene yielded **S**′-diethylarsenic(III) **S**-isobutyl-4-methoxyphenyltrithiophosphonate **7** (Reaction 3, Tables 1–4).



6 7

(3)

Ar = 4-MeOC$_6$H$_4$

Product **7** was obtained in 76% yield. It is of interest that the thermal stability of **7** with its P–C bond is higher than that of **3a,b.**

It is also of interest to compare the ^{31}P NMR spectral data of corresponding isostructural dialkyltetrathiophosphates of main group IV and V elements. We have shown that the ^{31}P chemical shift values of dialkyl(trimethylgermyl)tetrathiophosphate (δ = 84.7–86.7 [9]) and **3a** and **3b** (δ = 92.4

TABLE 3 ^{1}H NMR Data of the Products Obtained

Prod.	*δ, J [Hz], C_6D_6*
3a	0.80 (d, 12 H, $\underline{CH_3}CHCH_2S$, $^3J_{H\text{-}H}$ 7.0); 1.02 (t, 6 H, $\underline{CH_3}CH_2As$, $^3J_{H\text{-}H}$ 7.0); 1.58 (q, 4H, $CH_3\underline{CH_2}S$, $^3J_{H\text{-}H}$ 7.0); 1.68–2.10 (m, 2H, $CH_3\underline{CH}CH_2S$); 2.84 (d. d, 4H, $CH_3CH\underline{CH_2}S$, $^3J_{H\text{-}H}$ 7.0), $^3J_{P\text{-}H}$15.0).
3b	0.68 (t, 3H, $\underline{CH_3}CH_2SP$, $^3J_{H\text{-}H}$ 7.0); 0.79 (d, 6H, $\underline{CH_3}CHCH_2S$, $^3J_{H\text{-}H}$ 7.0); 1.03 (t, 6H, $\underline{CH_3}CH_2As$, $^3J_{H\text{-}H}$ 7.0); 1.57 (q, 4H, $CH_3\underline{CH_2}As$, $^3J_{H\text{-}H}$ 7.0); 1.67–2.14 (m, 1H, $CH_3\underline{CH}CH_2S$); 2.40–3.14 (m, 2H, $CH_3\underline{CH_2}SP$); 2.87 (d. d, 2H, $CH_3CH\underline{CH_2}S$, $^3J_{H\text{-}H}$ 7.0, $^3J_{P\text{-}H}$ 16.0).
7	0.87 (d, 6H, $\underline{CH_3}CHCH_2S$, $^3J_{H\text{-}H}$ 6.0); 1.09 (t, 6H, $\underline{CH_3}CH_2As$, $^3J_{H\text{-}H}$ 6.0); 1.51 (q, 4H, $CH_3\underline{CH_2}As$, $^3J_{H\text{-}H}$ 6.0); 1.68–2.10 (m, 1H, $CH_3\underline{CH}CH_2S$); 2.85 (d. d, 2H, $CH_3CH\underline{CH_2}S$, $^3J_{H\text{-}H}$ 6.0, $^3J_{P\text{-}H}$ 15.0); 3.10 (s, 3H, $\underline{CH_3}O$); 6.53 (d. d, 2H, 3.5-$H_2C_6\underline{H_2}$, $^3J_{H\text{-}H}$ 9.0, $^4J_{P\text{-}H}$ 3.5) 8.09 (d. d, 2H, 2,6-$\underline{H_2}C_6H_2$, $^3J_{H\text{-}H}$ 9.0, $^3J_{P\text{-}H}$ 13.0).

TABLE 4 Mass Spectral Data of the Products Obtained

Prod.	*m/e (I_{rel}, %)*
3a[a]	406 $[M]^{+\cdot}$ (10); 241 $[M - AsEt_2]^{+\cdot}$ (56); 152 $[M - Bu - S - SasEt_2]^{+\cdot}$ (100).
3b[b]	269 $[M + H - 2\ Et]^{+\cdot}$(91); 185 $[M + H - Bu - SAsEt_2]^{+}$ (31).
3b[b]	378 $[M]^{+\cdot}$ (10).
3b[b]	350 $[M + H - Et]^{+}$(10); 246 $[M - H - AsEt]^{+}$ (42).

[a] Electron impact, 100 eV.

[b] Chemical ionization, 70 eV.

and 90.8, respectively) are shifted down field when passing from derivatives of the main group IV to V elements.

EXPERIMENTAL

General Data

The ^{31}P NMR spectra were recorded with a Bruker CXP-100 (36.5 MHz) instrument in C_6H_6 with 85% H_3PO_4 as an external reference. The ^{1}H NMR spectra were run on a Varian T-60 (60 MHz) spectrometer in C_6D_6 or CCl_4 with $(Me_3Si)_2O$ as an internal reference. The IR spectra were obtained in KBr pellets with a UR-20 infrared spectrophotometer and a Bruker IFS 113v infrared spectrometer. Mass spectra (EI, 70 eV; CI, 100 eV) were determined on an M 80 B Hitachi chromatomass spectrometer.

S″-Diethylarsenic(III) S,S′-diisobutyltetrathiophosphate **3a**. Typical Procedure

Compound **1** [1.2 g, (2.7 mmol)] was added portionwise with stirring at 20°C to 4.8 g (21.6 mmol) of **2** in 5 mL of anhydrous benzene, and stirring was continued for 2 hours at 20°C. The mixture was evaporated at reduced pressure (0.06 mm Hg) at 40–50°C for 2 hours. Product **3a** (2.3 g, 52%) was isolated from the residue by use of a falling-film distillation (see Tables 1–4). Products **3b** and **7** were obtained similarly (see Tables 1–4). Product **3b** was identified only in crude form.

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