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Reactions of Dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetanes with Arsenic Derivatives Containing the As-O, As-S, and As-N Bonds

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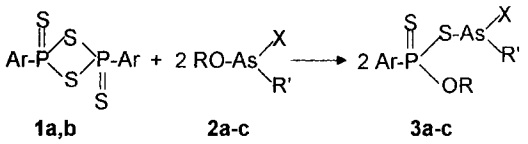
ABSTRACT: *S-Arsenic(III) and arsenic(V) derivatives of aryldithiophosphonic, aryltrithiophosphonite, and aryl(amido)dithiophosphonic acids* **3a–c, 5, 7,** *and* **9a–c** *were obtained by the reactions of 2,4-diaryl-1,3,2,4-dithiadiphosphetane-2,4-disulfides* **1a,b** *with O-isobutyl arsinite* **2a,** *O,O-dimethylphosphonites* **2b,c,** *O,O-dibutylarsonite* **4,** *thiobisarsine* **6,** *and aminoarsines* **8a,b.** © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10:670–675, 1999

INTRODUCTION

Arsenic esters of pentavalent phosphorus thioacids with the P(S)SAs central structural fragment are known to possess some properties of practical use [1,2]. The common methods of synthesizing arsenic(III) dithiophosphates are usually based on the reactions of corresponding dithiophosphoric acids or their salts with arsenic(III) halides or oxides [1–7]. We recently developed alternate methods for the synthesis of *S*-organoarsenic(III) esters of tetrathiophosphoric and trithiophosphonic acids directly from phosphorus sulfide (P_4S_{10}) and 1,3,2,4-dithiadiphosphetane-2,4-disulfides [8]. *S*-Isobutyl diethylthioarsenite was involved in these reactions [8]. We have now extended our approach to other arsenic(III) and arsenic(V) derivatives containing reactive As-O, As-S, and As-N bonds.

RESULTS AND DISCUSSION

We have now found that 1,3,2,4-dithiadiphosphetane-2,4-disulfides **1a,b** react with *O*-isobutyl diethylarsinite **2a** and *O,O′*-dimethyl-4-nitro- or 2-nitrophenylarsonites **2b,c** in anhydrous benzene at 20°C for 5 to 8 hours to give *S*-diethylarsenic(III) or *O*-methyl(aryl)arsenic(III) *O*-alkylaryldithiophosphonates **3a–c** (Reaction 1, Tables 1–5).



(1)

Ar = 4-MeOC$_6$H$_4$, R = Me, X = OMe, R' = 4-NO$_2$-C$_6$H$_4$ (**1b, 2b, 3b**);

The formation of **3a** was accompanied by an exothermic effect (up to +73°C). Products **3a–c** are yellow, oily liquids and were purified by the use of column chromatography (see Experimental section). It

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TABLE 1 Experimental Data and Yields of the Products Obtained

Initial Compounds Quantity [g (mmol)]	*Reaction of Conditions Temp [(°C)/Time (h)]*		*Product Yield [g(%)]*
1a 9.3 (15.5), **2a** 6.4 (31.1)	20/5	7 mL PhH	**3a** 12.0 (76)[a], 1.2[b]
1b 5.0 (12.3), **2b** 6.4 (24.7)	20/8	5 mL PhH	**3b** 6.8 (60)[a]/4.0 (35)[b]
1b 2.7 (6.7), **2c** 3.4 (13.5)	20/8	3 mL PhH	**3c** 1.24 (20)[a]/0.7 (11)[b]
1b 3.7 (9.2), **4** 5.8 (18.5)	20/3		**5** 8.6 (91)[a]/0.42 (5)[b]
1a 0.33 (0.8), **6** 0.8 (1.6)	20/5	5 mL PhMe	**7** 1.1 (∼99)[c]
1a 4.6 (11.4), **8a** 4.7 (22.9)	20/1.5	6 mL PhH	**9a** 4.1 (44)[b]
1b 4.1 (6.8), **8b** 2.8 (13.7)	20/1	4 mL PhH	**9b** 2.5 (36)[a]/1.1 (16)[d]
1b 4.0 (6.7), **9c** 3.5 (13.4)	20/3	7 mL PhH	**9c** 3.4 (45)[a]

[a]Yield of crude product.
[b]Yield of product isolated by column chromatography.
[c]Yield of crystalline product.
[d]Yield of product isolated by falling-film distillation.

TABLE 2 Physical, Analytical, and ^{31}P NMR Data of the Products Obtained

Prod.	*R_f (eluant)*	*n_D^{20}*	*Molecular Formula (Mol. Mass)*	*Found/Calc (%)*		*^{31}P NMR[a] δ (ratio)*
				As	*P*	
3a	0.86	1.5759	$C_{22}H_{40}AsO_2PS_2$	14.59	5.55	90.4[a]
	(Et_2O)		(506.2)	14.80	6.21	
3b	0.74	1.6656	$C_{15}H_{17}AsNO_5PS_2$	16.13	6.79	93.2[b] (1)[f]
	(CH_2Cl_2)		(461.0)	16.25	6.72	93.4[b] (0.2)[f]
3c	0.79	1.6668	$C_{15}H_{17}AsNO_5PS_2$	16.56	6.16	90.2[b] (1)[g]
	(CH_2Cl_2)		(461.0)	16.25	6.72	91.8[b] (0.4)[g]
5	0.77		$C_{21}H_{30}AsO_4PS_2$	14.02	6.35	90.1[b] (0.6)[g]
	(CH_2Cl_2)		(516.1)	14.52	6.00	89.5[b] (1)[g]
7	64–66[c]		$C_{31}H_{27}As_2PS_3$	14.17	4.34	69.0
			(676.0)	14.19	4.58	
9a	120 (0.04)[d]		$C_{15}H_{27}AsNOPS_2$	18.16	7.22	81.3
			(407.1)	18.40	7.61	
9b	0.86 (Et_2O)		$C_{22}H_{41}AsNOPS_2$	14.66	6.50	87.4
			(505.2)	14.83	6.13	
9c			$C_{26}H_{49}AsNOPS_2$	13.45	5.38	87.8
			(561.3)	13.35	5.52	

[a]Broad signal.
[b]The mixture of diastereoisomers.
[c]m.p.
[d]Temperature of thermal element of a falling-film distillation apparatus.
[e]In benzene solution.
[f]Ratio of diastereoisomers in crude reaction mixtures in $CDCl_3$ solution.
[g]Ratio of diastereoisomers in chromatography fractions.

is noteworthy that only one methoxy group of **2b,c** takes part in the reaction with **1b** at 20°C. The other methoxy group remained attached to the arsenic atom in **3b,c** as established by IR (Table 3) and ^{1}H spectra (Table 4). Thus, the bands in the region ν 618–640 cm^{-1} in the IR spectra (Table 3) of **3b,c** may be attributed to the As-OC valence vibrations. The bands of AsO-C are probably overlapping with ones of (P)O-C in the region ν 1030 cm^{-1} of **3b,c** as with dialkyldithiophosphate derivatives of 1,3,2-dioxarsolanes and 1,3,2-arsenanes [4]. The protons of the methoxy group at the arsenic atom $\underline{CH_3}OAs$ of **3b** appear as two singlets at δ = 3.70 and 3.76 (a mixture of diastereoisomers).

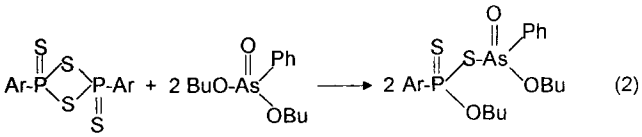
TABLE 3 IR Data of the Products Obtained

Prod.	*ν, cm⁻¹*
3a	3625 ν (O-H); 3092, 3072, 3040 ν (=C-H, Ar); 2970, 2920, 2880 ν (CH_3 as, s; CH_2 as, s); 1585, 1480 ν (C=C, Ar); 1430 δ (CH_3 as; CH_2 s); 1395, 1370 δ [$(CH_3)_2$C gem s]; 1023 ν [(P)O-C]; 680 ν (P=S, PS_2 as); 510 ν (P-S, PS_2 s).
3b	3068, 3095, 3015 ν (=C-H, Ar); 2945, 2900, 2843, 2825 ν (CH_3 as); 1593, 1520, 1500 ν (C=C, Ar); 1030 ν [P-O(C)], ν (As-OC); 830, 805 ν [P-O(C)]; 685 ν (P=S, PS_2 as); 618 ν (As-OC); 535, 520, 475 ν (P-S, PS_2 s, As-C).
3c	3090, 3070, 3030, 3010 ν (=C-H, Ar); 2970, 2942, 2900, 2841 ν (CH_3 as, s); 1600, 1530, 1515, 1500 ν (C=C, Ar); 1030 ν [P-O(C)], ν (As-OC); 830 cp, 805 ν [P-O(C)], 685 ν (P=S, PS_2 as); 640 ν (As-OC); 535, 520, 475, 443 ν (P-S, PS_2 s, As-C).
5	3075, 3060 ν (=C-H, Ar); 2963, 2938, 2878, 2845 ν (CH_3 as, s; CH_2 as, s); 1600, 1508 ν (C=C, Ar); 1465 δ (CH_3 as), δ (CH_2); 1440 cp (Ph); 1410 δ (CH_3 s); 1303 β (=CH), ν (Ph); 1260 ν (=C-O); 1183 ρ (CH_3), β (=CH), 1120 ν (P-Ar); 1035 ν [P-O(C)], ν (As-OC); 988 ν (As=O); 840, 810 ν [P-O(C)], γ (=CH); 748 γ (=CH); 694 ν (P=S, X-P=S, PS_2 as), ν (Ph); 635 δ (Ph); 620 ν (As-OC); 555, 535 ν (P-S, PS_2 s, As-C); 466 δ [(S)PC=], δ (POC), δ (PhOC).
7[a]	3070, 3010 ν (=C-H, Ar); 1600, 1510 ν (C=C, Ar); 1480, 1462 δ (CH_3 as); 1430 ν (Ph); 1408 δ (CH_3 s), ν (Ph); 1380 δ (CH_3 s); 1300 β (=CH), ν (Ph); 1187 β (CH_3); 810 γ (=CH); 740 γ (=CH); 695 ν (P=S, PS_2 as), 535, 480 ν (P-S, PS_2 s, As-C); 460 δ (Ph).
9a	3075, 3050, 3020 ν (=C-H, Ar); 2980, 2933, 2910, 2848, 2842 ν (CH_3 as, s; CH_2 as, s); 1600, 1508 ν (C=C, Ar); 1465, 1412 ν (Ph); 1385 δ (CH_3 s); 1310, 1360 ν (=C-H), ν (Ph); 1260 ω, τ (CH_2); 1187 ν (C-N-C as); 1112 c ν (P-Ar); 1028 ν (P-N-C as); ν (As-C); 942 ν (NC-C); 705 ν (P=S, PS_2 as), ν (Ph-X); 675 ν (P-N-C s); 627 δ (Ph); 565, 537, 515 ν (P-S, PS_2 s, As-C_2).
9b	3620 ν (O-H); 3095, 3080, 3040 ν (=C-H, Ar); 2975, 2935, 2875, 2830 ν (CH_3 as, s CH_2 as, s); 1589, 1490 ν (C=C, Ar); 1490, 1460, 1432, 1415 ν (Ph); 1380 δ (CH_3 s); 1306, 1290 β (=CH), ν (Ph); 1255 ω, τ (CH_2); 1175 ρ (CH_3), β (=CH); 1113 ν (P-Ar); 1030, 1050 ν (C-N-C as), ν (As-C), ρ (CH_3); 950 ν (NC-C); 820 γ (=CH); 700, 682, 658 ν (P=S, PS_2 as), ν (Ph), ν (P-N-C s); 616 δ (Ph); 558, 520, 495 ν (P-S, PS_2 s, As-C_2)
9c	3640 ν (O-H); 3090, 3080, 3040, 3010 ν (=C-H, Ar); 2965, 2930, 2880, 2825 ν (CH_3 as, s; CH_2 as, s); 1590, 1482 ν (C=C, Ar); 1450 δ (CH_3 as, CH_2); 1435, 1412 ν (Ph); 1398, 1375 δ [$(CH_3)_2$C rem s]; 1330, β (=CH) (Ph); 1260 ω, τ (CH_2); 1212 ν (C-N-C as); 1170 ρ (CH_3), β (=CH); 1130 β (=CH); 1023 ν (P-N-C s); ρ (CH_3), ν (As-C); 970 ν (NC-C); 820 γ (=CH); 765, 740 ρ (CH_2), γ (=CH); 680, 655 ν (P-N-C s), ν (P=S, PS_2 s); ν (Ph); 620 δ (Ph); 560, 535, 495 ν (P-S, PS_2 as, As-C_2).

[a]In vaseline oil.

The ^{31}P NMR spectra of **3a–c** reveal signals in the region δ = 90.2–93.4 (Table 2). These resonances are within the common region attributed for other arsenic(III) dithiophosphates [4–7,9]. Products **3b,c** were formed as a mixture of diastreoisomers; their ^{31}P NMR spectra showed two singlets at δ = 93.4 and 93.2 (in ratio 5:1 for **3b**) and δ = 90.2 and 91.8 (in ratio 1:0.4 for **3c**). However, we have not managed to separate the diastreoisomers of **3c** by use of column chromatography. The large intensity signal at δ = 1.28 was observed in the ^{1}H NMR spectrum of **3a** and may be assigned to the methyl protons of $(CH_3)_3$C groups.

It is considered of interest to compare the reactivity of arsenic(III) and arsenic(V) alkoxides toward 1,3,2,4-dithiadiphosphetane-2,4-disulfides. We have shown that *O,O′*-dibutyl(phenyl)arsonate **4** is more reactive than *O,O′*-dimethyl-4-nitro- or 2-nitrophenylarsonites **2b,c** toward **1b**. The reaction of **1b** with arsonate **4** is exothermic and occurs at room temperature resulting in the formation of *O*-butyl(phenyl)arsonic(V) *O*-butyl-4-methoxyphenyldithiophosphonates **5** (Reaction 2, Tables 1–5).



1b **4** **5**

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

Arsonate **4** takes part in Reaction 2 via the cleavage of only one As-O bond as well as with arsenic(III) dialkoxides **2**. The electron impact mass spectra of **5** (Table 5) exhibit the mass peak *m/e* 516 that may be attributed to its molecular ion. The formation of **5** as a mixture of diastreoisomers was confirmed by spectral methods. Thus, the ^{31}P NMR spectrum of **5** in anhydrous benzene indicates the existence of two singlets of δ = 90.1 and 89.5 in a ratio 2:3. The ^{1}H NMR spectrum of **5** in $CDCl_3$ solution (Table 4) reveals two singlets (δ_1 = 3.88 and δ_2 = 3.85) of the methoxy protons of the 4-MeOC$_6$H$_4$ group. It should be noted that the As=O bond remains present in the molecule of **5**. This was confirmed by the presence

TABLE 4 ^{1}H NMR Data of the Products Obtained

Prod.	*δ, J [Hz], in $CDCl_3$*
3a	0.75 (d, 6H, $\underline{CH_3}CHCH_2O$, $^3J_{HH}$ 7.0); 1.12 (t, 6H, $\underline{CH_3}CH_2As$, $^3J_{HH}$ 6.1); 1.28 (s, 18H, $(\underline{CH_3})_3C$); 1.52–1.68 (m, 1H, $CH_3\underline{CH}CH_2OP$); 1.82 (q, 4H, $CH_3\underline{CH_2}As$, $^3J_{HH}$ 6.1); 3.50 (d. d, 2H, $CH_3CH\underline{CH_2}OP$, $^3J_{HH}$ 7.0, $^3J_{PH}$ 13.0); 6.06 (m, 1H, $\underline{HO}$); 7.45 (d, 2H, 2,6-$\underline{H_2}C_6$, $^3J_{PH}$ 11.4).
3b[a]	δ_1 3.48 (d, 3H, $\underline{CH_3}OP$, $^3J_{PH}$ 11.2); δ_2 3.49 (d, 3H, $\underline{CH_3}OP$, $^3J_{PH}$ 10.0); δ_1 3.70 (s, 3H, $\underline{CH_3}OAs$); δ_2 3.76 (s, 3H, $\underline{CH_3}Oas$); δ_1 3.89 (s, 3H, $\underline{CH_3}OC_6H_4$); δ_2 3.90 (s, 3H, $\underline{CH_3}OC_6H_4$); 6.81 (m, 2H, 3,5-$H_2C_6\underline{H_2}As$), 6.93 (m, 2H, 2,6-$\underline{H}'_2C_6H'_2P$); 7.58 (m, 2H, 2,6-$\underline{H_2}C_6H_2As$); 7.83–8.13 (m, 2H, 2,6-$\underline{H}'_2C_6H'_2As$).
3c[a]	δ_1 3.57 (d, 3H, $\underline{CH_3}OP$, $^3J_{PH}$ 13.7); δ_2 3.58 (d, 3H, $\underline{CH_3}OP$, $^3J_{PH}$ 13.7); δ_1 3.81 (s, 3H, $\underline{CH_3}Oas$); δ_2 3.82 (s, 3H, $\underline{CH_3}Oas$); δ_1 3.83 (s, 3H, $\underline{CH_3}OC_6H_4$); δ_2 (s, 3H, $\underline{CH_3}OC_6H_4$); 6.74–6.94 (m, 2H, 3,5-$\underline{H_2}C_6H_2$); 7.31–8.35 (m, 2H, 2,6-$H_2C_6\underline{H_2}P$ + 6H, C_6H_4As).
5[a]	1.19–1.51 and 2.06–2.11 (two m, 18H, $\underline{CH_3CH_2CH_2}CH_2O$); δ_1 3.88 (s, 3H, $\underline{CH_3}OC_6H_4$); δ_2 3.85 (s, 3H, $\underline{CH_3}OC_6H_4$); δ_1 4.13 (q, 2H, $CH_3CH_2CH_2\underline{CH_2}OAs$, $^3J_{HH}$ 7.0); δ_2 4.25 (q, 2H, $CH_3CH_2CH_2\underline{CH_2}OAs$, $^3J_{HH}$ 7.1); δ_1 4.98 (d. q, 2H, $CH_3CH_2CH_2\underline{CH_2}OP$, $^3J_{HH}$ 7.0, $^3J_{PH}$ 18.7); δ_2 5.08–5.25 (m, 2H, $CH_3CH_2CH_2\underline{CH_2}OP$); 6.92–7.00 (m, 2H, 3,5-$H_2C_6\underline{H_2}$); δ_1 7.80 (d. d, 2H, 2,6-$\underline{H_2}C_6H_2$, $^3J_{HH}$ 8.5, $^3J_{PH}$ 15.8); δ_2 7.95 (d. d, 2H, 2,6-$\underline{H_2}C_6H_2$, $^3J_{HH}$ 8.9, $^3J_{PH}$ 15.6).
7[b]	3.31 (s, 3H, $\underline{CH_3}OC_6H_4$); 6.83 (d. d, 2H, 3,5-$H_2C_6\underline{H_2}$, $^3J_{HH}$ 9.0, $^4J_{PH}$ 3.0); 7.10–7.28 and 7.56–7.77 (two m, 20H, $C_6\underline{H_5}$); 8.07 (d. d, 2H, 2,6-$\underline{H_2}C_6H_2$, $^3J_{HH}$ 9.0, $^3J_{PH}$ 13.0).
9a	1.21 (t, 6H, $\underline{CH_3}CH_2As$, $^3J_{HH}$ 6.5); 1.34 (t, 6H $\underline{CH_3}CH_2NP$, $^3J_{HH}$ 6.5); 1.85 (q, 4H, $CH_3\underline{CH_2}As$, $^3J_{HH}$ 6.5); 3.30 (d. q, 4H, $CH_3\underline{CH_2}NP$, $^3J_{HH}$ 6.5; $^3J_{PH}$ 13.0); 3.92 (s, 3H, $\underline{CH_3}OC_6H_4$); 6.94 (d. d, 2H, 3,5-$H_2C_6\underline{H_2}$, $^3J_{HH}$ 9.0, $^4H_{PH}$ 3.0); 7.97 (d. d, 2H, 2,6-$\underline{H_2}C_6H_2$, $^3J_{HH}$ 9.0, $^3J_{PH}$ 13.0).
9b	0.91 (t, 6H, $\underline{CH_3}CH_2As$, $^3J_{HH}$ 7.0); 1.17 (6, 6H, $\underline{CH_3}CH_2NP$, $^3J_{HH}$ 7.0); 1.42 (s, 18H, $(\underline{CH_3})_3C$); 1.82 (q, 4H, $CH_3\underline{CH_2}As$, $^3J_{HH}$ 7.0); 3.24 (d. q, 4H, $CH_3\underline{CH_2}NP$, $^3J_{HH}$ 7.0, $^3J_{PH}$ 13.0); 5.47 (m, 1H, $\underline{OH}$); 7.61 (d. d, 2H, 2,6-$\underline{H_2}C_6$, $^4J_{HH}$ 4.0, $^3J_{PH}$ 16.0).
9c	0.75 (d, 12H, $\underline{CH_3}CHCH_2NP$, $^3J_{HH}$ 6.0); 1.16 (t, 6H, $\underline{CH_3}CH_2As$, $^3J_{HH}$ 7.0); 1.42 (s, 18H, $(\underline{CH_3})_3C$); 1.27–1.70 (m, 2H, $CH_3\underline{CH}CH_2NP$); 1.82 (q, 4H, $CH_3\underline{CH_2}As$, $^3J_{HH}$ 7.0); 2.82 (d. d, 4H, $CH_3CH\underline{CH_2}NP$, $^3J_{HH}$ 6.0, $^3J_{PH}$ 12.4); 5.46 (m, 1H, $\underline{OH}$); 7.81 (d. d, 2H, $C_6\underline{H_2}\underline{H_6}$, $^4J_{HH}$ 4.0, $^3J_{PH}$ 16.0).

[a]The mixture of diastereoisomers.
[b]In C_6D_6.

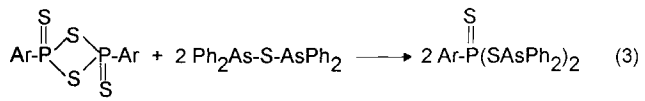
TABLE 5 Mass Spectral Data of the Products Obtained

Prod.	*i-C_4H_{10}, m/e (I_{rel}, %)*
3a[a]	388 [M-S-Bu-i-Et]$^+$ (10), 371 [M-OBu-i-S-Et]$^+$ (2) 359 [M-S-Bu-i-2Et]$^+$ (3), 343 [M-S-OBu-i-2Et]$^+$ (2).
3a[b]	375 [M + 2H-$AsEt_2$]$^+$ (5).
3b[b]	387 [M + 2H-NO_2-2Me]$^+$ (12), 309 [M + OMe-$C_6H_4NO_2$]$^+$ (12).
3c[a]	233 [M-As $C_6H_4NO_2$-OMe]$^+$ (94), 308 [M-OMe-$C_6H_4NO_2$]$^+$ (10).
3c[b]	386 [M + H-NO_2-2Me]$^+$ (10), 309 [M + H-OMe-$C_6H_4NO_2$]$^+$ (10).
5[a]	516 [M]$^+$ (21), 484 [M-S]$^+$ (7), 439 [M-Ph]$^+$ (3), 407 [M-S-Ph]$^+$ (2).
5[b]	408 [M + H-S-Ph]$^+$ (3).
7[a]	490 [M-2Ph-S]$^+$ (27), 306 [M-Me-2S-$AsPh_2$-Ph]$^+$ (23), 261 [M-S-$AsPh_2$-4-MeO C_6H_4PS]$^+$ (44).
9a[a]	407 [M]$^+$ (4), 378 [M-Et]$^+$ (1), 375 [M-S]$^+$ (6), 331 [M-Et-S-Me]$^+$ (4).
9a[b]	347 [M + H-S-Et]$^+$ (4).
9b[a]	314 [M-2Et-$AsEt_2$]$^+$ (2).
9b[b]	449 [M + 2H-2Et]$^+$ (6); 390 [M + H-4Et]$^+$ (2); 374 [M + 2H-$AsEt_2$]$^+$ (2).
9c[b]	562 [M + H]$^+$ (2); 535 [M + 3H-Et]$^+$ (16).

[a]Electron impact, 70 eV.
[b]Chemical ionization, 100 eV.

in the IR spectrum of **5** of a broad band of large intensity in the region ν 988 cm^{-1} (cf. ν(As=O) 988 cm^{-1} [10]). The presence of the As=O group in the molecule of **4** is likely to influence the reactivity enhancement of **4** in Reaction 2.

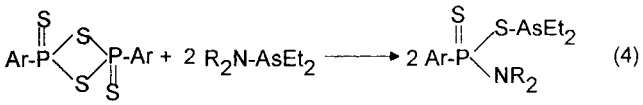
The rather high reactivity of compounds containing the As-S bond was also shown with the behavior of *S*-isobutyl diethylthioarsenite toward 1,3,2,4-dithiadiphosphetane-2,4-disulfides [8]. This insertion reaction may be extended to other arsenic compounds containing two As-S bonds such as in thiobisarsines. Indeed, the reaction of thiobis(diphenylarsine) **6** with **1b** at 20°C for ~20 hours in anhydrous toluene yielded crystalline *S,S′*-bis(diphenylarsine) 4-methoxyphenyltrithiophosphonate **7** (Reaction 3, Tables 1–5).



Ar = 4-MeOC_6H_4

It is noteworthy that the reactivity of thiobisarsines like **6** is higher than that of the corresponding silicon derivatives, such as bis(trimethylsilyl)sulfide, toward 2,4-diaryl-1,3,2,4-dithiadiphosphetane-2,4-disulfides [11]. The ^{31}P NMR spectrum of **7** in benzene solution shows a singlet at δ = 69.0 (Table 2). The ^{31}P NMR spectrum of the corresponding $PhP(S)(SSiMe_3)_2$ is reported to resonate in practically the same region (δ = 62.0–63.1) [11,12]. In the ^1H NMR spectrum of **7** in a C_6D_6 solution, the $\underline{CH_3}O$ protons appear as a singlet at δ = 3.31. The rupture of the As-C and As-S bonds under the condition of the recording of mass spectra was confirmed by the electron-impact mass-spectral analysis of **7** indicating the mass peak *m/e* 490 $[M - 2Ph - S]^{+\cdot}$ and 306 $[M - Me - 2S - AsPh_2 - Ph]^{+\cdot}$ (Table 5).

In a continuation of the comparison of the chemical behavior of silicon and arsenic derivatives containing reactive E-X bonds (E = Si, As; X = O, S, N) toward 1,3,2,4-dithiadiphosphetane-2,4-disulfides, we have tried to extend these reactions to compounds that have an As-N bond. *S*-Trimethylsilyl phenyl-*N,N*-dimethylamidodithiophosphonate was previously obtained by the reaction of 2,4-diphenyl-1,3,2,4-dithiadiphosphetane-2,4-disulfide with trimethyl(dimethylamino)silane in refluxing methylene chloride [11]. The formation of products of similar structure could be expected by use of aminoarsines. In fact, we have now found that reaction of **1a,b** with *N,N*-dialkylaminodiethylarsines **8a,b** give *S*-diethylarsenic(III) aryl-*N,N*-dialkylamidodithiophosphonates **9a–c** (Reaction 4, Tables 1–5).



Ar = 4-$MeOC_6H_4$, R = Et (**1b, 8a, 9a**);

Ar = HO-C$_6$H$_4$- , R = Et (**1a, 8b, 9b**);

Ar = HO-C$_6$H$_4$- , R = Bu-i (**1b, 8c, 9c**)

Reaction 4 is exothermic and occurs at room temperature in anhydrous benzene within 1 to 1.5 hours. Thus, as we can see, the reactivity of aminoarsines is higher than that of aminosilanes in the reactions with 1,3,2,4-dithiadiphosphetane-2,4-disulfides. Compounds **9a** and **9b** are a yellow liquid and a green-yellow oily liquid, respectively, whereas **9c** is a viscous oil. Product **9a** was isolated by use of a falling-film distillation, and **9b** was purified by column chromatography (see Experimental section). However, **9c** tends to decompose at high temperatures and when purification is attempted by column chromatography. The attachment of the dialkylamino group to the phosphorus atom and the formation of the P-N bond in **9a–c** were confirmed by their IR, ^1H NMR, and mass spectra. In the ^1H NMR spectrum of **9a,** the methylene protons of the two ethyl groups at the nitrogen atom $CH_3\underline{CH_2}NP$ appear as a doublet of quartets at δ = 3.30 ($^3J_{HH}$ = 6.5 and $^3J_{PH}$ = 13.0). A similar set of resonances was observed in the case of **9b** (δ = 3.24 for $\underline{CH_2}$ protons of $CH_3\underline{CH_2}NP$ group, $^3J_{HH}$ = 7.0 and $^3J_{PH}$ = 13.0). A typical doublet of doublets at δ = 2.82 was found in the ^1H NMR spectrum of **9c** that can be attributed to methylene protons of two isobutyl groups at the nitrogen atom $(CH_3)_2CH\underline{CH_2}NP$ ($^3J_{HH}$ = 6.0 and $^3J_{PH}$ = 12.4).

Bands in the region ν 1215–1187, 1050–1023, 970–942, and 682–6675 cm^{-1} in the IR spectra of **9a–c** (Table 3) are due to the C-N-C as, P-N-C as, NC-C, and P-N-C s valence vibrations like other organophosphorus compounds containing the P-N bond [13]. The mass peaks *m/e* 407 and 562 observed in the mass spectra of **9a** and **9c,** respectively, are due to their molecular ions $[M]^{+\cdot}$ and $[M + H]^+$ (Table 5). The Et, Me, and S fragments are split out from molecules of **9a–c** under the conditions of recording of mass spectra. The chemical ionization mass spectrum of **9b** shows that the ion $[AsEt_2]^{+\cdot}$ (*m/e* 374) is due to the cleavage of the As-S bond.

Thus, the various derivatives of arsenic(III) such as alkoxides and alkylmercaptides of arsenic(III) and aminoarsines were involved in the reactions with 1,3,2,4-dithiadiphosphetane-2,4-disulfides. The reactivity of aminoarsines containing the As-N bond is higher than that of arsenic(III) alkoxides and alkylmercaptides with the As-O and As-S bonds, respectively.

EXPERIMENTAL

General Data

The ^{31}P NMR spectra were recorded with a Bruker MSL 400 (162 MHz) instrument in C_6H_6 with 85% H_3PO_4 as an external reference. The ^1H NMR spectra were taken on a Bruker MSL-400 (400 MHz) spectrometer and a Varian T-60 (60 MHz) spectrometer in C_6D_6 or $CDCl_3$ with $(Me_3Si)_2O$ as an internal reference. The IR spectra were obtained in KBr pellets with an UR-20 infrared spectrophotometer and a Bruker IFS 113v spectrometer. Mass spectra (EI, 70 eV; CI, 100 eV) were determined on an M 80 B Hitachi chromatomass spectrometer.

S-Diethylarsenic(*III*) *O-isobutyl-3,5-ditert.-butyl-4-hydroxyphenyldithiophosphonate* **3a.** Compound **1a** (9.3 g, 15.5 mmol) was added portionwise under dry argon with stirring at 20°C to a solution of 6.4 g (31.1 mmol) of **2a** in 7 mL of anhydrous benzene. After the exothermic period of the reaction was completed, the stirring of the reaction mixture was continued for 5 hours at 20°C. The mixture was filtered, and the filtrate was evaporated at reduced pressure (0.06 mm Hg) at 40°C for 2 hours to give 12.0 g (76%) of crude **3a**. Chromatography was performed on part (3.0 g) of crude **3a** on an silica gel column with Et_2O as eluant to yield 1.2 g of pure **3a** (see Tables 1–5). The products **3b, 3c, 5,** and **9b** were obtained similarly (see Tables 1–5).

S,S′-Bis(*diphenylarsine*)*-4-methoxyphenyltrithiophosphonate* **7.** Compound **1b** (0.33 g, 0.8 mmol) was added portionwise under dry argon with stirring at 20°C to a solution of 0.8 g (1.6 mmol) of **6** in 5 mL of anhydrous benzene, and stirring was continued for 4 hours at 20°C. The mixture was evaporated at reduced pressure (0.05 mm Hg) at 40–50°C for 2 hours. The crystalline precipitate of **7** (1.1 g, ~ 99%) that had formed was filtered off, washed with anhydrous Et_2O, and dried under vacuum (0.05 mm Hg) for 2 hours (see Tables 1–5).

S-Diethylarsenic(*III*) *4-methoxyphenyl-N,N-dialkylamidodithiophosphonate* **9a.** Compound **1b** (4.6 g, 11.1 mmol) was added portionwise under dry argon with stirring at 20°C to 4.7 g (22.9 mmol) of **8a**. After an exothermic period of the reaction was completed, the stirring of the reaction mixture was continued for 1.5 hours at 20°C. The mixture was filtered, and the filtrate was evaporated at reduced pressure (0.05 mm Hg) at 40°C for 2 hours. Product **9a** (4.1 g, 44%) was isolated from the residue by means of a falling-film distillation (see Tables 1–5). The product **9c** was obtained in crude form similarly (see Tables 1–5).

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