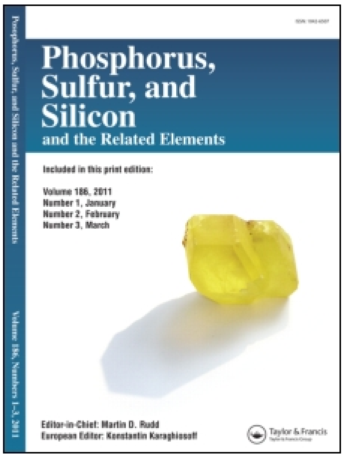

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REACTIONS OF LAWESSON'S REAGENT WITH ARSENIC (III) ALKOXIDES

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REACTIONS OF LAWESSON'S REAGENT WITH ARSENIC (III) ALKOXIDES

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New arsenic (III) derivatives of 4-methoxyphenyldithio- and trithiophosphonic acids were obtained in the reactions of Lawesson's reagent with arsenic (III) alkoxides.

Keywords: Lawesson's reagent; arsenic alkoxides; organothiophosphorus compounds

INTRODUCTION

Organic derivatives of main group V elements of phosphorus (IV) thioacids with structural fragment P(S)SE (E = As, Sb, Bi) are necessary for developing a series of fundamental and practical problems. In this case a series of fundamental problems could be solved such as chemical reactivity, electronic structure, influence of heteroatoms in the fragment P(S)SE, conjugation, tautomerism, complexation, stereochemistry etc. Different modes of bonding of dithiophosphato moieties (e.g. monodentate, bridging/chelating, bidentate) in the complex formation with arsenic, antimonium and bismuth have been elucidated by physico-chemical tecniques.[1-8] They are used as pesticides,[2-3] analytical reagents[3] and for regeneration of cracking catalysts.[3]

Although a large number of arsenic (III) derivatives of phosphorus (IV) thioacids have been synthesized[2-8] these compounds appear to be limited to the dithiophosphato moieties. The common methods of synthesizing arsenic (III) dithiophosphates are usually based on the interactions of corresponding dithio-

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phosphoric acids or their salts with arsenic (III) halides or oxides.[2-8] However, these techniques are multi-step procedures as the initial dithiophosphoric acids had to be synthesized by treatment of alcohols or diols with tetraphosphorus decasulfide with evolution of toxic gaseous hydrogen sulfide.[9] The shortcoming of these synthesis also involve heating of the reaction mixture and formation of by-products.

On the other hand, organothiophosphorus derivatives of arsenic (III) containing P-C bond remained unknown. In this article facile and efficient methods are presented for the synthesis of 4-methoxyphenyldithio- and trithiophosphonates of arsenic (III) directly from Lawesson's reagent.

RESULTS AND DISCUSSION

Over the past few years we have been involved in developing new synthetic routes for organoelement derivatives of phosphorus (IV) thioacids. We have recently developed convenient methods for the synthesis of organosilicon, germanium and tin derivatives of phosphorus (IV) thioacids with the P(S)SE (E = Si, Ge, Sn) structural fragment on the basis of the reactions of phosphorus sulfide (P_4S_{10}) and 1,3,2,4-dithiadiphosphetane-2,4-disulfides.[10-23] We have extended this approach to organic derivatives of main V group elements. We assumed that the use of the organoarsenic (III) protecting groups in protonodonating reagents as alcohols and phenol may lead to organoarsenic (III) derivatives of dithiophosphonic acids directly from Lawesson's reagent. As we expected, the reaction of Lawesson's reagent **1** with alkyl and phenyl ethers of arsinious acids **2a-c** has been found to bring about S-diorganylarsenic (III) O-organyl-4-methoxyphenyldithiophosphonates **3a-c** under mild conditions (20°C, 2-5 h, anhydrous benzene) (Equation (1), Table I).

(1)

1

2a, R^1 = Me, R^2 = Ph, R^3 = Ph

b, R^1 = Et, R^2 = Et, R^3 = Ph

c, R^1 = Ph, R^2 = Et, R^3 = Et

3a, R^1 = Me, R^2 = Ph, R^3 = Ph

b, R^1 = Et, R^2 = Et, R^3 = Ph

c, R^1 = Ph, R^2 = Et, R^3 = Et

Ar = 4-$MeOC_6H_4$

It should be noted that this preparative method (Equation 1) is characterized by minimum of steps, simple operation, mild conditions, high yields of products and

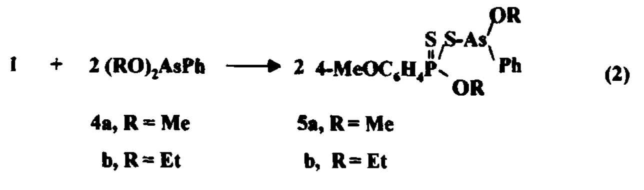
TABLE I Yields, physical, analytical and the ^{31}P NMR data of the products obtained

Prod.	*Yield (%)*	*B.P., °C (mm Hg)*[c]	n_D^{20}	*Molecular Formula (Mol. mass)*	*Found/Calc., %*		^{31}P *NMR δ, ppm*[d]
					P	*As*	
3a	71[a]/23[b]	170-185 (0.03)	1.6818	$C_{20}H_{20}AsO_2PS_2$ (462.0)	6.60 6.70	16.68 16.22	95.4
3b	43[a]	120 (0.05)	1.4680	$C_{17}H_{22}AsO_2PS_2$ (428.0)	7.31 7.23	17.22 17.50	96.7
3c	80[b]	100 (0.03)	1.6212	$C_{17}H_{22}AsO_2PS_2$ (428.0)	7.06 7.23	17.88 17.50	97.0
5a	93[a]/24[b]	160-165 (0.02)	1.6389	$C_{15}H_{18}AsO_3PS_2$ (416.0)	7.81 7.44	18.50 18.01	93.8
5b	55[b]	180-190 (0.02)	1.6330	$C_{17}H_{22}AsO_3PS_2$ (444.0)	6.67 6.97	16.40 16.87	91.9
7	48[a]/17[b]	130-140 (0.02)	1.6802	$C_{10}H_{16}AsO_4PS_2$ (370.0)	8.10 8.37	20.55 20.25	94.1

[a] Yield of crude product.
[b] Yield of isolated product.
[c] Temperature of thermal element of a thin layer distillation apparatus.
[d] In C_6H_6.

formation of no by-products. Our approach allowed to obtain new type of organothiophosphorus derivatives of arsenic (III) with the CP(S)(OC)SAS structural fragment. They are pale yellow liquids. Products **3a-c** are rather stable compounds and do not decompose in the course of vacuum thin layer distillation. All these compounds are soluble in common organic solvents. It should be emphasized that formally **3a-c** are the products of the insertion of the monomeric unit, 4-MeOC$_6$H$_4$PS$_2$, of **1** into the O-As bond of **2a-c**. The structures of **3a-c** were confirmed by IR (Table II), ^{1}H (Table III) and ^{31}P NMR (Table I), mass spectral data (Table IV) as well as elemental analyses (Table I).

We have tried to find the boundary of this method. It is considered of interest to study chemical behaviour of **1** with arsenic (III) derivatives containing two or three functional groups. Thus, arsenic (III) dialkoxides were also involved in the reaction with **1**. We have shown that the reaction of **1** with O,O-dialkyl(phenyl)arsonites **4a,b** gives S-(O-alkyl)phenylarsenic (III) O-alkyl-4-methoxyphenyldithiophosphonates **5a,b** (Equation (2), Tables I-IV).



(2)

TABLE II IR spectral data (cm^1) of the products obtained

Prod.	*:CH* *Ar*	*CH_3,* *CH_2*	*C=C* *Ar*	*PhO-C* *AsO-C*	*PO-C*	*P-OC* *$Ph_{1,4}$*	*P=S, Ph* *As-OC*	*P-S* *As-C*	*As-S*
3a	3069	2940	1595	1258	1026	830	738	532	390
	3052	2840	1501			802	692		
							618		
3b	3053	2963	1594	1258	1023	830	738	577	385
		2867	1500			802	691	531	377
		2840					618	516	
3c	3070	2961	1595	1260	1025	830	689	565	391
	3040	2930	1500			812		529	
		2910						511	
		2869							
		2855							
5a	3069	2941	1596	1259	1026	830	740	530	381
	3002	2837	1501			802	690		
							615		
5b	3069	2977	1595	1258	1024	782	739	530	381
		2934	1501			803	688	514	
		2838				782	617		
7	3068	2942	1593		1029	830	681	531	373
	3005	2838	1501			822	614	516	347

TABLE III ^1H NMR data of the products obtained

Prod.	*δ, ppm, J, Гu, C_6D_6*
3a	3.02 (s, 3H, $\underline{CH_3}0C_6H_4$); 3.40 (d, 3H, $\underline{CH_3}OP$, $^3J_{P-H}$ 15.0); 6.40 (d.d, 2H, 3,5-$H_2C_6\underline{H_2}$, $^3J_{H-H}$ 9.0, $^4J_{P-H}$ 4. 0); 6.68-7.43 (m, 10H, $C_6\underline{H_5}$); 7.79 (d.d, 2H, 2,6-$\underline{H_2}C_6H_2$, $^3J_{H-H}$ 9.0, $^3J_{P-H}$ 14.0).
3b	0.83 (t, 3H, $\underline{CH_3}CH_2O$, $^3J_{H-H}$ 7.0); 0.95 (t, 3H, $\underline{CH_3}CH_2As$, $^3J_{H-H}$ 7.0); 1.51-1.98 (m, 2H, $CH_3\underline{CH_2}As$); 3.02 (s, 3H, $\underline{CH_3}O$); 3.67-4.17 (m, 2H, $CH_3\underline{CH_2}OP$); 6.47 (d.d, 2H, 3,5-$H_2C_6\underline{H_2}$ $^3J_{H-H}$9.0, $^4J_{P-H}$ 3. 0); 6,.74-7.30 (m, 5H, C_6H_5 + C_6H_6-d_6); 7.91 (d.d, 2H, 2,6-$\underline{H_2}C_6H_2$, $^3J_{H-H}$ 9.0, $^3J_{p-H}$ 14.0).
3c	0.87 (t, 6H, $\underline{CH_3}CH_2As$, $^3J_{H-H}$ 7.0); 1.47 (q, 4H, $\underline{CH_3}CH_2As$, $^3J_{H-H}$ 7.0) ; 3.15 (s, 3H, $\underline{CH_3}O$); 6.57 (d.d, 2H, 3,5-$H_2C_6H_2$, $^3J_{H-H}$ 9.0, $^4J_{P-H}$ 3.5); 6.70-7.80 (m, 5H, $C_6\underline{H_5}$); 8.03 (d.d, 2H, 2,6-$\underline{H_2}C_6H_2$, $^3J_{H-H}$ 9.0, $^3J_{P-H}$ 13.0) .
5a[a]	3.40 (wide s, 3H, $\underline{CH_3}OP$, $^3J_{P-H}$ 14.5); 3.42 3.40 (wide s, 3H, $\underline{CH_3}OAs$); 3.62 (wide s, 3H, $\underline{CH_3}OC_6H_4$); 6.55-6.7 (m, 2H, 3,5-$H_2C_6\underline{H_2}$); 7.07-7.23 (m, 5H, $C_6\underline{H_5}$); 7.33-7.67 (m, 2H, 2,6-$\underline{H_2}C_6H_2$).
7[a]	3.70 (wide s, 3H, $\underline{CH_3}OC_6H_4$ + wide s, 6H, $\underline{CH_3}OP$, $^3J_{P-H}$ 28.5); 6.78 (d.d, 2H, 3,5-$H_2C_6\underline{H_2}$, $^3J_{H-H}$ 9.0, $^4J_{P-H}$ 3.0); 7.75 (d.d, 2H, 2,6-$\underline{H_2}C_6H_2$, $^3J_{H-H}$ 9.0, $^3J_{P-H}$14. 0).

[a] In CCl_4.

TABLE IV Mass Spectral data of the products obtained

Prod.	*m/e*(I_{rel}, %)
3a[a]	462 $[M]^{+\cdot}$(23); 385 $[M - Ph]^{+\cdot}$ (10); 353 $[M - Ph - S]^{+\cdot}$(5); 308 $[M - Ph - Ph]^{+\cdot}$ (10); 201 $[M - S - AsPh_2]^{+\cdot}$ (100); 154 $[M - S - SAsPh_2]^{+\cdot}$ (45).
3a[b]	108 $[M + .H - MeOPS - SAsPh_2]^+$ (15).
5a[a]	385 $[M - MeO]^{+\cdot}$(12); 308 $[M - MeO - Ph]^{+\cdot}$(5) ; 202 $[M - MeO - PhAsOMe]^{+\cdot}$ (100).
5a[b]	418 $[M + 2H]^+$(15); 248 $[M + 2H - MeO - MeO - MeOPh]^+$ (20); 139 $[M + H - PhAsOMe - 2S - MeO]^+$(40); 108 $[M + H - PhAsOMe - PS_2 - OMe]^+$(15).
5b[a]	322 $[M - Ph - OEt]^{+\cdot}$ (44) ; 154 $[M - S - Et - SAsPh(Et)]^{+\cdot}$ (100); 107 $[M - PS - OEt - SAsPh(Et)]^{+\cdot}$ (25).
7[a]	324 $[M - MeO - Me]^{+\cdot}$(10); 201 $[M - SAs(Me0)_2]^{+\cdot}$(100); 169 $[M - S - SAs(OMe)_2]^{+\cdot}$ (25) .
7[b]	139 $[M + H - MeO - S - SAs(OMe)_2]^+$ (35) ; 108 $[M + H - MeOPS - SAs(OMe)_2]^+$ (12).

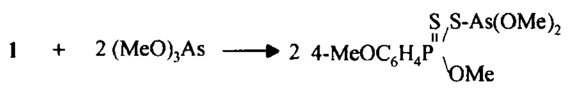
[a] Electron impact, 100 eV.

[b] Chemical ionization, 70 eV.

The reaction (2) proceeds at room temperature for 4-10 h. The formation of **5a,b** is carried out with no solvent. It is noteworthy that only one alkoxy group of **4a,b** takes part in the reaction with **1** under mild conditions. The other alkoxy group remained attached to the arsenic atom in **5a,b.** This feature of structure of **5a,b** was established by their ^1H and ^{31}P NMR and mass spectral data. Thus, the chemical ionization mass spectrum of **5a** exibits the mass peak m/e 418 which may be attributed to the molecular ion [M + 2H]. There are no mass peaks with large values m/e which may indicate the arsenic (III) bis(dithiophosphonate) structure for the products of the reaction (1). Besides, these arsenic (III) bis(dithiophosphonates) may be excluded as we do not observe multipletes in the ^{31}P NMR spectra of **5a,b** due to ^{31}P $\{^{31}P\}$ spin coupling constants. On the other hand, these arsenic (III) bis(dithiophosphonates) may be formed if we carry out the reaction (2) under severe conditions an if a large excess of **1** is used. In this case both alkoxy groups can take part in the interactions with **1** to form arsenic (III) bis(dithiophosphonates).

When using arsenic (III) alkoxides and dialkoxides **2b** and **4a,b** with different substituents we obtained **3b** and **5a,b** as mixtures of diastereomers, there being two asymmetrical centres (phosphorus and arsenic atoms).

In continuation of our approach taking into account the results of the reaction (2) we expected the similar chemical behaviour in the case of arsenic (III) derivatives containing three functional groups. Thus, we have found that **1** reacts with trimethylarsenite **6** under mild conditions (20°C, 1 h) to form S-dimethoxyarsenic (III) O-methyl-4-methoxyphenyldithiophosphonate **7** (Equation (3), Tables I-IV).



$$\mathbf{1} \;+\; 2\,(MeO)_3As \longrightarrow 2\;4\text{-}MeOC_6H_4P(=S)(S\text{-}As(OMe)_2)(OMe) \qquad (3)$$

6 **7**

The strong bands present in the region v 1029-1024 and 830-803 cm^{-1} in the IR spectra of **5a,b** and 7 containing both As-O-C and P-O-C bonds may be attributed to PO-C, AsO-C and P-OC valence vibrations. The bands of PO-C are probably overlapping with $Ph_{1,4}(\gamma:CH)$ vibrations.[5]

The reaction (3) is exothermic. We have observed that the reactivity of arsenic (III) alkoxides toward **1** increases in the series: mono-, di- and trialkoxides. It is considered of interest to compare the ^{31}P NMR spectral data of the corresponding isostructural aryldithiophosphonates of main IV and V group elements of the periodic table. We have shown that the ^{31}P chemical shift values of O-ethyl-S-triphenylgermyl-4-methoxyphenyldithiophosphonate (δ 89.3 ppm [20]) and of **3a-c, 5a,b** and **7** (δ 91.9-97.0 ppm) are shifted towards low field when passing from the main IV to V group element derivatives.

Thus, we have developed a facile method of synthesis of new types of S-organoarsenic (III) aryldithiophosphonates. These reactions are of interest from the point of view of preparative organoelement chemistry.

EXPERIMENTAL

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

S-Diphenylarsenic (III) O-Methyl-4-methoxyphenyldithiophosphonate 3a. Typical Procedure

Compound **1** (5.2 g, 12.9) was added portionwise with stirring at 20°C to **2a** (6.7 g, 25.8 mmol) in 5 mL of anhydrous benzene, and stirring was continued for 5 h at 20°C. The mixture was filtered and evaporated at reduced pressure (0.02 mm Hg) at 40°C for 2 h and gave crude **3a** (8.5 g, 71%). Pure **3a** (6.0 g, 50%) was isolated from the residue by means of vacuum thin layer distillation (See Tables I-IV).

The products **3b,c, 5a,b** and **7** were obtained similarly (See Tables I-IV) with no solvent.

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