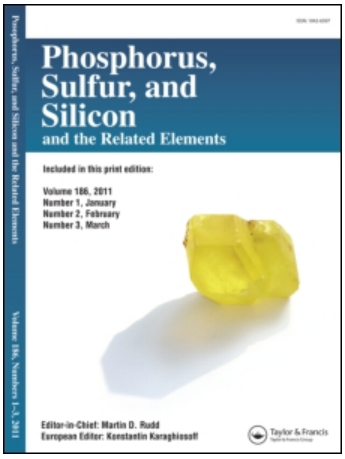

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BISARYLDITHIOPHOSPHONIC ACIDS: SYNTHESIS AND THEIR REACTIONS WITH ORGANYL CHLOROSILANES, GERMANES, STANNANES, AND PLUMBANES

Il'yas S. Nizamov,[1,2] Gulnara T. Gabdullina,[1,2] Ilnar D. Nizamov,[1,2] Yevgeniy N. Nikitin,[1,2] Lyubov A. Al'metkina,[3] and Rafael A. Cherkasov[3]

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A method of synthesizing arylbisdithiophosphonic acids was developed by the reaction of 2,4-diaryl 1,3,2,4-dithiadiphosphetane-2,4-disulfides with tri(ethylene glycol) and 1,4-butandiol in anhydrous benzene suspension under mild conditions. The arylbisdithiophosphonic acids thus obtained were transformed into the corresponding diammonium salts. New bis(triorganylgermyl), stannyl and plumbyl, and cyclic diphenylsilyl and diphenylplumbyl derivatives of arylbisdithiophosphonic acids were prepared from the reactions of diammonium salts of the corresponding acids with triorganylchlorogermane, chlorostannane, chloroplumbane, diphenyldichlorosilane, and diphenyl dichloroplumbane.

Keywords Bisdithiophosphonic acids; chlorogermanes; chloroplumbanes; chlorosilanes; chlorostannanes; 1,3,2,4-dithiadiphosphetane-2,4-disulfides; glycols

INTRODUCTION

There is a considerable interest in group 14 element derivatives of pentavalent phosphorus thioacids containing the P(S)S-E (E = Si, Ge, Sn, Pb) structural fragments due to their biological activity, because of their high reactivity and their use as synthetic intermediates in the preparation of new organothiophosphorus compounds.[1–19] *S*-Organosilyl and *S*-germyl dithiophosphates and heterocycles were obtained in the reactions of ammonium dithiophosphoric acids with organochlorosilanes and organogermanium mono- and dichlorides.[5–8] The common methods of synthesizing *S*-organotin dithiophosphates, dithiophosphinates, and tetrathiophosphates were usually based on the reactions of the corresponding pentavalent phosphorus thioacids or their salts with organotin halides (also in the presence of β-diketones), oxides, hydroxides, tetraalkyltin, and tributyltin isocyanates.[3,4,9–14] Bis(trimethylstannyl) *tert*-butyltrithiophosphonate

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Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

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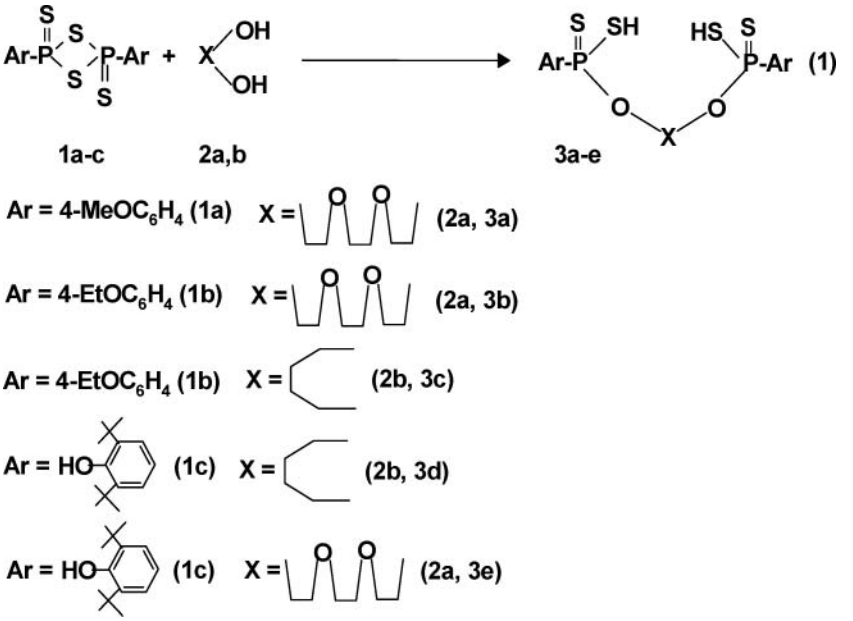
was obtained by the reaction of 2,4-bis(*tert*-butyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide with bis(trimethylstannyl)sulfide.[15] Triphenyl and diphenyllead(IV) *O,O*-alkylenedithiophosphates were prepared similarly in reactions of corresponding dithiophosphoric acids.[16–19]

Over the past several years, we have been involved in the development of alternate methods of synthesizing organosilicon, germanium, tin, and lead derivatives of pentavalent phosphorus thioacids using tetraphosphorus decasulfide and 1,3,2,4-dithiadiphosphetane-2,4-disulfides. *S*-Trimethylsilyl, *S*-triphenyl, or trialkylgermyl esters of dialkyl dithiophosphoric and tetrathiophosphoric, 4-methoxyphenyldithiophosphonic, and trithiophosphonic acids were easily obtained in reactions of tetraphosphorus decasulfide or Lawes son's reagent with trimethyl (alkoxy) silanes or trimethyl(alkylthio)silanes, triphenyl or trialkyl(alkoxy) germanes, and with (alkylthio)germanes.[20,21] Reactions of tetraphosphorus decasulfide or Lawesson's reagent with trialkyl(alkoxy)stannanes, with (alkylthio) stannanes, and with bis(trialkylstannyl)sulfide result in the formation of *S*-trialkylstannyldialkyldithiophosphates, *S*-trialkylstanny-ltetrathiophosphates, tris(trial kylstannyl)tetrathiophosphates, *S*-trialkylstannyl-(4-methoxyphenyl)dithiophosphonates, and trithiophosphates, respectively.[22–29] Reactions of 2,4-diaryl-1,3,2,4-dithiadiphos phetane-2,4-disulfides with alkoxy or alkylthiotriorganylplumbanes yielded also the triorganolead derivatives of aryldithiophosphonic and trithiophosphonic acids.[28,30] In this article, a facile method of synthesizing new organosilicon, germanium, tin, and lead derivatives of bisaryldithiophosphonic acids is presented.

RESULTS AND DISCUSSION

We have previously prepared the first representatives of bisalkyldithiophosphonic acids from the reaction of 2,4-dimethyl-1,3,2,4-dithiadiphosphetane-2,4-disulfide with alkylene glycols in 1:1 molar ratio in diethyl ether suspension at room temperature.[31] In 1968, G. Schumacher studied a reaction of Lawesson's reagent with ethylene glycol in acetonitrile giving rise to *O*-(2-hydroxyethyl)-4-methoxyphenyldithiophosphonate and *O,O*-(1,2-ethylene)bis(4-methoxyphenyl)dithiophosphonic acids.[32] However, these compounds were not isolated in pure form. Meanwhile, it was reported that Lawesson's reagent and its 4-phenoxy homologue react with 1,2-ethanediol and its substituted derivatives and with 1,4-butanediol at 70–80°C for 10–12 h in acetonitrile as a solvent to give the mixture of 1,3,2-dioxaphosphorinane-2-sulfide, cyclic aryltrithiopyrophosphonate, and thioacetamide.[33,34] These compounds seem to be secondary products formed from arylbisdithiophosphonic acid as an initial product via the hydrogen sulfide elimination due to the effect of acetonitrile as sulfur acceptor. Indeed, we have previously shown that bisalkyldithiophosphonic acids react with acetonitrile to form cyclic alkyltrithiopyrophosphonates and thioacetamide.[35]

Taking into account the low solubility of Lawesson's reagent and other 2,4-diaryl-1,3,2,4-dithiadiphosphetane-2,4-disulfides in diethyl ether previously used as a solvent for synthesizing bisalkyldithiophosphonic acids[31] and the non-inert properties of acetonitrile toward pentavalent phosphorus thioacids,[35] we have tried to find an inert solvent appropriate for the preparation of bisaryldithiophosphonic acids. We also deemed it to be necessary to establish milder conditions and shorter time to prevent undesirable thermal destructions of an initial product. Anhydrous benzene seems to be the most appropriate inert solvent for successful synthesis of bisaryldithiophosphonic acids. The reaction of 2,4-diaryl-1,3,2,4-dithiadiphosphetane-2,4-disulfides **1a–c** with tris(ethylene glycol) **2a** and 1,4-butandiol **2b** in benzene suspension have been found to bring about



Scheme 1

the formation of alkylenoxy(bisaryl)dithiophosphonic acids **3a–e** at 50–60°C for 1-2 h (Scheme 1, Tables I–IV).

Bisaryldithiophosphonic acids **3a–e** were obtained with high yields. Compounds **3a–e** are colorless, viscous liquids, nonvolatile even under reduced pressure, and stable at room temperature in anhydrous inert atmosphere. Products **3a–e** tend to partially decompose at high temperature and when a falling-film distillation is used in attempted purification. Bisaryldithiophosphonic acids **3a–e** decomposed when water treatment was used.

On the basis of the ^{31}P NMR spectra, it was established that bisaryldithiophosphonic acids **3a–e** were formed as major phosphorus-containing products with chemical shifts at δ = 87–89 ppm. Alongside the signals of **3a–e**, the ^{31}P NMR spectra of the crude reaction mixtures also reveal the minor singlet signals at δ = 84.1–83.1 ppm with integral intensity ratio 13:1. It is noteworthy to study the influence of acetonitrile on the stability of bisaryldithiophosphonic acids **3**. We have found that the ^{31}P NMR spectrum of the chloroform solution of **3e** after addition of acetonitrile and storing at room temperature for 24 h reveals two signals at δ = 88.9 and 84.1 ppm in ratio 1:1.6. It was assumed that compound with chemical shift at δ = 84.1 ppm is a secondary product.

The structures of **3a–e** were confirmed by IR (Table III), ^{1}H (Table IV), and ^{31}P NMR (Table II), as well as by elemental analyses (Table II). ^{1}H NMR spectrum of **3c** in $CDCl_3$ solution (Table IV) exhibits a triplet due to the methyl protons of two fragments $\underline{CH_3}CH_2O$-Ar at δ = 1.44 ppm ($^3J_{HH}$ = 7.0 Hz), and a quartet at δ = 4.08 ppm is assigned to the methylene protons of two $CH_3\underline{CH_2}O$-Ar substituents. The protons of the methoxy group of two $\underline{CH_3}OAr$ fragments of **3a** resonate as a singlet at δ = 3.78 ppm, whereas the protons of the *tert*-butyl group of two 3,5-di-*tert*-butyl-4-hydroxyphenyl substituents of **3e** appear as a inventive singlet at δ = 1.48 ppm. The ^{1}H NMR spectra of **3a**, **3b**, and **3e** also show characteristic resonances due to the presence of $OCH_2O\underline{CH_2}\underline{CH_2}OCH_2O$ substituent. Thus, a singlet situated at δ = 3.72 ppm was assigned to the four protons of

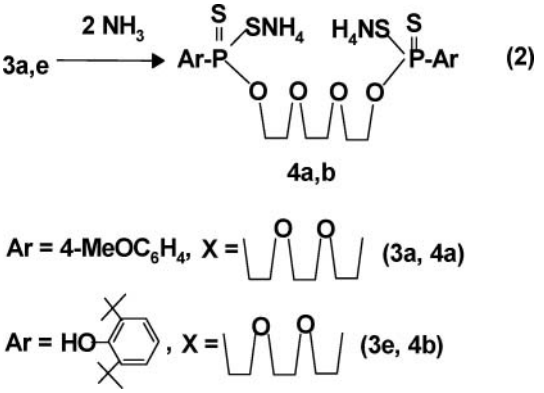
Table I Experimental data and yields of the products obtained

Starting compounds quantity [g (mmol)]	Reaction conditions temp.(°C), time (h), volume of C_6H_6	Product yield [g (%)]
1a 12.0 (29.7)/**2a** 4.4 (29.7)	50/1 20 mL	**3a** 10.0 (61)[a]
1b 8.0 (18.5)/**2a** 2.7 (18.2)	50/1 20 mL	**3b** 4.5 (42)[a]
1b 8.0 (18.5)/**2b** 1.7 (18.9)	50–55/2 20 mL	**3c** 6.8 (70)[a]
1c 5.0 (8.3)/**2b** 0.8 (8.9)	50/1 15 mL	**3d** 4.1 (71)[a]
1c 5.0 (8.3)/**2a** 1.2 (8.1)	50/1.5 15 mL	**3e** 4.8 (77)[a]
3a 7.1 (12.8)/NH_3 excess	20/1 20 mL	**4a** 6.6 (88)[b]
3e 1.2 (1.6)/NH_3 excess	20/1 20 mL	**4b** 1.2 (96)[b]
4b 2.0 (2.5)/**5a** 1.7 (5.0)	80/2 50 mL	**6a** 2.5 (68)[a]
4b 2.0 (2.5)/**5b** 1.0 (5.0)	80/2 50 mL	**6b** 1.4 (52)[a]
4b 2.0 (2.5)/**5c** 2.4 (5.1)	80/2 50 mL	**6c** 3.0 (72)[b]
4b 2.0 (2.5)/**7a** 0.65 (2.6)	80/1 40 mL	**8a** 1.7 (71)[a]
4b 2.0 (2.5)/**7b** 1.1 (2.5)	80/2 60 mL	**8b** 1.9 (68)[b]

[a] Yield of crude product.
[b] Yield of solid product.

two central methylene groups $CO\underline{CH_2}\underline{CH_2}OC$ of **3e**. The methylene protons connected to the phosphorus atom through the methylene bridge $O\underline{CH_2}CH_2OP$ appear as a triplet at $\delta = 3.84$ ppm ($^3J_{HH} = 4.7$ Hz) of **3e**. A doublet of triplets observed at $\delta = 4.39$ ppm in the ^1H NMR spectrum of **3e** has been assigned to the protons of the methylene group linked with the phosphorus atom via the oxygen atom $CH_2\underline{CH_2}OP$ ($^3J_{HH} = 4.7$ Hz, $^3J_{PH} = 10.0$ Hz). Bands in the region ν 2551–2649 and 2475–2396 cm^{-1} in the IR spectra of **3a–d** (Table III) are due to the valence vibrations of the S—H bonds-free and bonded ones, respectively. The electron impact mass spectrum of **3c** exhibits the mass peaks m/e 522 due to its molecular ion $[M]^{+\cdot}$ (calculated molecular mass M of **3c** is 522.1).

Taking into account the rather high thermal stability of the ammonium salts of pentavalent phosphorus thioacids,[3] we decided to prepare the corresponding ammonium salts using bisaryldithiophosphonic acids **3**. The formation of these ammonium salts as crystalline solids could be expected. In fact, the corresponding ammonium salts **4a**,**b** as white powders with sharp melting points were obtained by passing anhydrous gaseous ammonia via the benzene solutions of **3a**,**e** at room temperature (Scheme 2, Tables I–IV).



Scheme 2

Table II Physical, analytical, and ^{31}P NMR dataof the products obtained

	Mp,°C	Molecular formula	Found/(calc.), %					^{31}P NMR, δ(ppm) (C_6H_6)
			C	H	P	S	E	
3a[f]		$C_{20}H_{28}O_6P_2S_4$ (554.1)	43.24 43.31	5.15 5.10	11.35 11.18	23.29 23.08		87.2
3b		$C_{22}H_{32}O_6P_2S_4$ (582.1)	44.89 45.35	5.93 5.55	11.02 10.64	22.33 21.97		87.2
3c		$C_{20}H_{28}O_4P_2S_4$ (522.1)	45.54 45.97	5.05 5.42	11.65 11.86	23.94 24.49		86.1
3d		$C_{32}H_{52}O_4P_2S_4$ (690.3)	55.14 55.63	7.33 7.61	9.37 8.97	17.98 18.52		88.1
3e		$C_{34}H_{56}O_6P_2S_4$ (750.4)	54.18 54.37	7.63 7.52	8.06 8.25	17.11 17.08		88.9
4a	198–199	$C_{20}H_{34}N_2O_6P_2S_4$ (558.2)	41.09 40.81	5.53 5.84	10.75 10.53	21.50 21.74	4.40[a] 4.76[a]	107.0
4b	202–203	$C_{34}H_{58}N_2O_6P_2S_4$ (780.4)	52.68 52.28	7.38 7.48	8.04 7.93	16.35 16.42	3.30[a] 3.57[a]	109.7
6a		$C_{70}H_{84}O_6P_2S_4Ge_2$ (1355.8)	61.66 61.96	6.59 6.24	4.65 4.57	9.54 9.45	10.54[b] 10.70[b]	93.5
6b		$C_{40}H_{72}O_6P_2S_4Sn_2$ (1075.9)	44.73 44.62	6.45 6.74	5.35 5.75	12.06 11.91	22.27[c] 22.05[c]	97.7
6c	64	$C_{70}H_{84}O_6P_2Pb_2S_4$ (1625.1)	51.94 51.49	5.50 5.21	3.50 3.81	8.12 7.89	25.01[d] 25.49[d]	98.7
8a		$C_{46}H_{64}O_6P_2S_4Si$ (930.4)	59.24 59.33	6.90 6.93	6.77 6.65	13.78 13.77	3.12[e] 3.02[e]	91.0
8b	60–61	$C_{46}H_{64}O_6P_2PbS_4$ (1109.6)	49.51 49.76	5.90 5.81	5.29 5.58	11.13 11.55	19.00[d] 18.66[d]	100.1

[a] N.
[b] Ge.
[c] Sn.
[d] Pb.
[e] Si.
[f] n_D^{20} 1.5989.

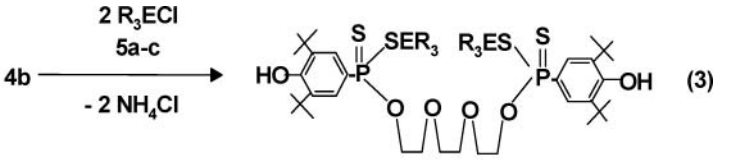
Table III IR Spectroscopic data of the products obtained

	ν, cm^{-1}
3a	3050 ν (=C–H, Ar); 2941, 2884 ν (CH_3 as, s; CH_2 as, s); 2500 (S–H, free), 2475 (S–H, bonded), 1595, 1569, 1501 ν (C=C, Ar), 1026 ν [(P)O–C]; 961 ν (C–O), ν (C–O–C), 681, 663 ν (P=S), 620 ν (C–S), 534 ν (P–S).
3b	3065 ν (=C–H, Ar); 2979, 2935, 2879 ν (CH_3 as, s; CH_2 as, s); 2550 ν (S–H, free); 2430 ν (SH, bonded); 1596, 1501 ν (C=C, Ar); 1041 ν [(P)O–C]; 956 ν (OC–C); 830 ν (P–OC); 695 ν (P=S); 537 ν (P–S).
3c	3089 ν (=C–H, Ar); 2979, 2938, 2887 ν (CH_3 as, s; CH_2 as, s); 2551 ν (SH, free); 1596, 1501, 1475 ν (C=C, Ar); 1041 ν [(P)O–C]; 971 ν (OC–C); 828 ν [P–OC]; 694 ν (P=S); 537 ν (P–S).
3d	3622 ν (OH); 3161, 3089 ν (=C–H, Ar); 2954, 2924, 2872 ν (CH_3 as, s; CH_2 as, s); 2549 ν (S–H, free); 2396 ν (S–H, bonded); 1583, 1467 ν (C=C, Ar); 1050 ν [(P)O–C]; 898 ν (P–OC); 655 ν (P=S); 505 ν (P–S).
3e	3619 ν (O–H); 2958, 2873 ν (CH_3 as, s; CH_2 as, s); 2478 ν (S–H free); 1582, 1480 ν (C=C, Ar); 1429 δ (CH_3 as); 1036 ν [(P)O–C]; 957 ν (OC–C); 656 ν (P=S); 504 ν (P–S).
4a[a]	3222 ν (N^+H_4); 1595, 1497 ν (C=C, Ar); 1067 ν [(P)O–C]; 952 ν (OC–C); 676 ν (P=S); 529 ν (P–S).
4b[a]	3634 ν (O–H); 3230 ν (N^+H_4); 1581, 1459 ν (C=C, Ar); 1427 δ (CH_3 as, s); 1068, 1044 ν [(P)O–C]; 949 ν (OC–C); 683 ν (P=S); 507 ν (P–S).
6a	3622 ν (O–H); 3068, 3087 ν (=C–H, Ar); 2959, 2873 ν (CH_3 as, s; CH_2 as, s); 1582, 1481 ν (C=C, Ar); 1431 δ (CH_3 as); 1036 ν [(P)O–C]; 953 ν (OC–C); 680, 687 ν (P=S); 504 ν (P–S); 461 ν ($GePh_3$ as); 409 ν (Ge-S).
6b	3622 ν (O–H); 3090, 3070, 3034 ν (=C–H, Ar); 2959, 2912, 2874 ν (CH_3 as, s; CH_2 as, s); 1581, 1479 ν (C=C, Ar); 1429 δ (CH_3 as); 1039 ν [(P)O–C]; 951 ν (OC–C); 680, 656 ν (P=S); 557, 538, 504 ν (Sn-C as, P–S).
6c[a]	3622 ν (O–H); 3088, 3061, 3036 ν (=C–H, Ar); 2958, 2873 ν (CH_3 as, s; CH_2 as, s); 1570, 1476 ν (C=C, Ar); 1430 δ (CH_3 as); 1036 ν [(P)O–C]; 951 ν (OC–C); 692, 680 ν (P=S); 558, 508 ν (P–S); 442 ν (Pb–C, $PbPh_3$ as).
8a	3618 ν (O–H); 3089, 3070, 3049, 3002 ν (=C–H, Ar); 2958, 2874 ν (CH_3 as, s; CH_2 as, s); 1590, 1479 ν (C=C, Ar); 1429 δ (CH_3 as); 1035 ν [(P)O–C]; 994 ν (OC–C); 680 ν (P=S); 511 ν (P–S, S–Si).
8b[a]	3613 ν (O–H); 3030 ν (=C–H); 2923, 2854 ν (CH_3 as, s; CH_2 as, s); 1572, 1462 ν (C=C, Ar); 1035 ν [(P)O–C]; 952 ν (OC–C); 654 ν (P=S); 564, 523 ν (P–S); 478 ν (Pb–C, $PbPh_2$).

[a] In baseline suspension.

The ^{31}P NMR spectra of salts **4a**,**b** in water solution reveal singlet signals at $\delta = 107.0$ and 109.7 ppm, respectively. The strong broad bands of the valence vibrations of the NH_4^+ bonds appeared in the range of ν 3222–3220 cm^{-1} in the IR spectra of **4a**,**b** in baseline suspension. Bands in the region ν 663–683 and 534–507 cm^{-1} are due to the valence vibrations of the P=S and P–S bonds of **4a**,**b**, respectively. A signal of the S–H proton of the initial acids **3a**,**e** at $\delta = 2.6$ ppm is absent in the ^1H NMR spectra of salts **4a**,**b**. The protons of the HO and NH_4 groups of **4b** display singlets at $\delta = 5.43$ and 5.45 ppm, respectively. A mass peak m/e 780.6 was observed in the electron impact mass spectrum of **4b**, which is attributed to its molecular ion $[M]^{+\cdot}$ (calculated molecular mass M of **4b** is 780.4).

The diammonium salts of bisaryldithiophosphonic acids seem to be efficient intermediates for synthesizing their organoelement derivatives by substitution reactions with appropriate organoelement halides. For this purpose, the chlorides of main IV group elements were used in the reaction with salt **4b**. We have found that **4b** reacts with triphenyl chlorogermane **5a**, trimethyl chlorostannane **5b**, and triphenyl chloroplumbane **5c** in benzene at 80°C for 2 h to give 1,8-bistriorganylgermyl, stannyl, and plumbyl derivatives of 1,8-triethyleneoxybis(3,5-di-*tert*-butyl-4-hydroxyphenyldithiophosphonic) acids **6a–c** (Scheme 3, Tables I–IV).



6a-c

E = Ge, R = Ph (5a, 6a)

E = Sn, R = Me (5b, 6b)

E = Pb, R = Ph (5c, 6c)

(3)

Scheme 3

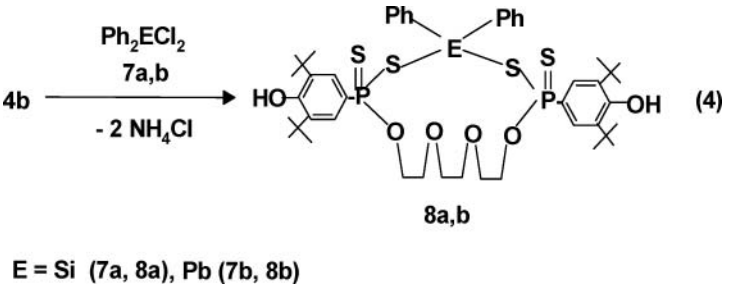
Reaction 3 was accompanied by the formation of a powder precipitate of ammonium chloride, which was removed from the reaction mixture by filtration. Products **6a–c** were obtained with yields of 52–73%. They are viscous under high vacuum nonvolatile oils. The ^{31}P NMR spectra of **6a–c** in benzene solutions display singlets in the region of $\delta = 93.5$–98.7 ppm. These resonances are shifted to low field compared to that of the starting acid

Table IV ^{1}H NMR spectral data of the products obtained

	$CDCl_3$, δ, ppm, J, Hz
3a	2.63 m (2H, PSH), 3.70 (s, 4H, COCH$_2$CH$_2$OC), 3.78 (s, 6H, CH$_3$OAr), 3.82 (t, $^3J_{HH}$7.8, 4H, OCH$_2$CH$_2$OP), 3.85 (dt, $^3J_{HH}$7.8, $^3J_{PH}$ 11.2, 4H, OCH$_2$CH$_2$OP), 6.98 (dd, $^3J_{HH}$9.2, $^4J_{PH}$3.1, 4H, 3,5-H$_2$C$_6$H$_2$), 7.93 (dd, $^3J_{HH}$9.2, $^3J_{PH}$15.9, 4H, 2,6-H$_2$C$_6$H$_2$).
3b	1.40 (t, $^3J_{HH}$7.0, 6H, CH$_3$CH$_2$OAr); 3.67 (s, 4H, COCH$_2$CH$_2$OC); 3.79 (t, $^3J_{HH}$4.9, 4H, OCH$_2$CH$_2$OP), 4.05 (q, $^3J_{HH}$7.0, 4H, CH$_3$CH$_2$OAr,); 4.33 (dt, $^3J_{HH}$4.9, $^3J_{PH}$14.6, 4H, POCH$_2$CHO$_2$); 6.92 (dd, $^3J_{HH}$8.6, $^4J_{PH}$3.4, 4H, 3,5-H$_2$C$_6$H$_2$); 7.90 (dd, $^3J_{HH}$8.6, $^3J_{HH}$14.6, 4H, 2,6-H$_2$C$_6$H$_2$).
3c	1.44 (t, $^3J_{HH}$7.0, 6H, CH$_3$CH$_2$OAr); 3.69 (m, 4H, OCCH$_2$CH$_2$CO); 4.08 (q, $^3J_{HH}$7.0, 4H, CH$_3$CH$_2$OAr); 4.21–4.30 (m, $^3J_{HH}$6.8, 4H, POCH$_2$CCCH$_2$OP); 6.97 (dd, $^3J_{HH}$8.6, $^4J_{PH}$3.9, 4H, 3,5-H$_2$C$_6$H$_2$); 7.91 (dd, $^3J_{HH}$8.6, $^3J_{HH}$14.6, 4H, 2,6-H$_2$C$_6$H$_2$).
3e	1.48 [s, 36H, (CH$_3$)$_3$C]; 2.37 and 2.64 (m, 2H, S—H); 3.72 (s, 4H, COCH$_2$CH$_2$OC); 3.84 (t, $^3J_{HH}$ 4.7, 4H, POCH$_2$CH$_2$O); 4.39 (dt, $^3J_{HH}$ 4.7, $^3J_{PH}$ 10.0, 4H, POCH$_2$CH$_2$O); 5.69 (m, 2H, O—H); 7.82 (d, $^3J_{PH}$ 16.2, 2H, C$_6$H$_2$P).
4b	1.47 [s, 36H, (CH$_3$)$_3$C]; 3.59 (t, $^3J_{HH}$ 4.1, 4H, POCH$_2$CH$_2$O); 3.65 (s, 2H, COCH$_2$CH$_2$OC); 3.82 (m, $^3J_{HH}$ 4.4, 4H, POCH$_2$CH$_2$); 5.43 and 5.45 (s, 8H, NH_4^+; 2H, OH); 7.94 (d, $^3J_{PH}$ 15.1, 2H, C$_6$H$_2$P); 7.96 (d, $^3J_{PH}$ 15.4, 2H, C$_6$H$_2$P).
6a	1.51 [s, 36H, (CH$_3$)$_3$C]; 3.76 (s, 4H, COCH$_2$CH$_2$OC); 3.88 (t, 4H, POCH$_2$CH$_2$O); 4.27 (m, 4H, POCH$_2$CH$_2$); 5.65 (m, 2H, O—H); 7.50 and 7.73 [m, 30H, (C$_6$H$_5$)$_3$Ge]; 7.93 (d, $^3J_{PH}$ 15.5, 4H, C$_6$H$_2$P).
6b	0.66 [s, d, $^2J_{^{118}Sn-Me}$56.4, 18H, (CH$_3$)$_3$Sn]; 1.49 [s, 36H, (CH$_3$)$_3$C]; 3.69 (s, 4H, COCH$_2$CH$_2$OC); 3.79 (t, $^3J_{HH}$ 5.0, 4H, POCH$_2$CH$_2$O); 4.22 (dt, $^3J_{HH}$ 5.2, $^3J_{PH}$ 9.5, 4H, POCH$_2$CH$_2$,); 5.63 (m, 2H, O—H); 7.87 (d, $^3J_{PH}$ 15.9, 2H, C$_6$H$_2$P).
6c	1.49 [s, 36H, (CH$_3$)$_3$C]; 3.64 (m, 4H, POCH$_2$CH$_2$O); 4.07 (m, $^3J_{HH}$ 4,5, 4H, POCH$_2$CH$_2$O); 5.61 (m, 2H, O—H); 7.55, 7.73 and 7.86 [m, 30H, (C$_6$H$_5$)$_3$Pb]; 7.86 (d, $^3J_{PH}$ 20.4, 4H, C$_6$H$_2$P).
8a	1.49 [s, 36H, (CH$_3$)$_3$C]; 3.74 (s, 4H, COCH$_2$CH$_2$OC); 3.85 (t, $^3J_{HH}$ 5.2, 4H, POCH$_2$CH$_2$O); 4.40 (dt, $^3J_{HH}$ 5.2, $^3J_{PH}$ 10.5, 4H, POCH$_2$CH$_2$O); 5.69 (m, 2H, OH); 7.41–7.43 and 7.64–7.80 [m, 10H, (C$_6$H$_5$)$_2$Si)]; 7.85 (d, $^3J_{PH}$ = 16.2, 4H, C$_6$H$_2$P).
8b	1.48 [s, 36H, (CH$_3$)$_3$C]; 3.76 (s, 4H, COCH$_2$CH$_2$OC); 3.92 (t, $^3J_{HH}$ 5.2, 4H, POCH$_2$CH$_2$O); 4.47 (dt, $^3J_{HH}$ 5.2, $^3J_{PH}$ 11.4, 4H, POCH$_2$CH$_2$O); 5.58 (m, 2H, O—H); 7.43, 7.56 and 7.75 [m, 10H, (C$_6$H$_5$)$_2$Pb]; 7.86 (d, $^3J_{PH}$ 16.2, 4H, C$_6$H$_2$P).

3e ($\delta = 88.9$ ppm). This effect indicates a bidentate coordination of the bisaryldithiophosphonic ligands to the tin and lead atoms similar to the chelating properties of dithiophosphato ligands toward tin and lead atoms.[36–38] The IR spectra of **6a–c** confirmed the absence of the bands of the valence vibrations of the NH_4^+ bonds attributed to salt **4b**. The IR spectrum of the lead-containing derivate **6c** exhibits a strong band at ν 442 cm^{-1} due to the valence vibrations of the bonds in the $PbPh_3$ group. This band appears in practically the same region as that for the valence vibrations of the bonds in the $GePh_3$ group of the germanium compound **6a** (ν 461 cm^{-1}). Bands of the valence vibrations of the Sn-C bonds are mixed with those of the P—S bonds and appeared in the range of ν 504 cm^{-1} in the case of the tin product **6b**. The protons of two trimethylstannyl groups $(\underline{CH_3})_3Sn$ in the ^1H NMR spectrum in $CDCl_3$ solution of **6b** appear as an intense singlet at $\delta = 0.66$ ppm as well as a doublet satellite signal with small intensity and with coupling constant $^2J_{^{119}Sn-Me} = 56.4$ Hz. The singlet with double intensity at $\delta = 1.48$ ppm was assigned to the protons of four *tert*-butyl groups of aryl substituents. The aromatic protons of two 3,5-di-*tert*-butyl-4-hydroxyphenyl substituents of **6b** give the typical doublet at $\delta = 7.87$ ppm ($^3J_{PH} = 15.9$ Hz).

The formation of cyclic products could be expected in the case of 14 group element dichlorides in the reactions with bisaryldithiophosphonic acids or their salts. Indeed, cyclic diphenylsilyl and diphenylplumbyl derivatives of 1,8-triethyleneoxybis(3,5-di-*tert*-butyl-4-hydroxyphenyldithiophosphonic) acids **8a**,**b** were formed in the reaction of **4b** with diphenyl dichlorosilane **7a** and diphenyl dichloroplumbane **7b** at 80°C for 1–2 h in benzene with the precipitation of ammonium chloride (Scheme 4, Tables I–IV).



Scheme 4

The silylated product **8a** is an oily liquid, whereas the lead compound **8b** is formed as a colorless crystalline solid with sharp melting point. The ^{31}P NMR spectrum of the silicon containing product **8a** in benzene solution (Table II) displays a singlet at $\delta = 91.0$ ppm. As we can see, the ^{31}P NMR spectral signal of **8a** shows no significant change compared to that of the starting acid **3e** ($\delta = 88.9$ ppm). In the case of plumbyl derivative **8b**, its ^{31}P signal in benzene solution is shifted to lower field ($\delta = 100.1$ ppm) in comparison with that of acid **3e** and its silicon analogue. Thus, the observed tendency for a low field shift of the ^{31}P resonances of the isostructural arylbisdithiophosphonic derivatives of the group 14 elements increases when passing from the top to the bottom of this group. Moreover, isostructural arylbisdithiophosphonic derivatives of the silane **8a** and the plumbane **8b** have similar signal pattern in the ^1H NMR spectra (Table IV); the resonances of the plumbane **8b** are shifted to low field in comparison to those of the corresponding silane **8a**, however. The band at ν 654 cm^{-1} in the IR spectrum of plumbane **8b** (Table III) is assigned to the P=S valence vibrations showing a shift to lower frequency with respect to silane **8a** (ν P=S

680 cm^{-1}) that also suggests a chelating behavior of the arylbisdithiophosphonic ligands in the case of tin and lead derivatives.

Thus, the above substitution reactions of diammonium salts of arylbisdithiophosphonic acids with organyl chlorosilanes, germanes, stannanes, and plumbanes have a fundamental significance as they lead to new types of silicon, germanium, tin, and lead derivatives of pentavalent phosphorus thioacids containing the P(S)S-E (E = Si, Ge, Sn, Pb) structural fragments. Moreover, the reactions studied are of interest from the point of view of preparative organophosphorus chemistry.

EXPERIMENTAL

^{31}P NMR spectra were recorded with a Bruker CXP-100 (36.47 MHz) instrument in C_6H_6 with 85% H_3PO_4 as an external reference. The ^1H NMR spectra were obtained with a Bruker Avance-600 spectrometer (600 MHz) in $CDCl_3$. The IR spectra were obtained in KBr pellets with a Bruker Vector-22 infrared spectrophotometer. Mass spectra (EI, 60 eV) were measured with a Finnigan MAT-212 mass-spectrometer.

1,8-Triethyleneoxybis(4-methoxyphenylphosphonic) Acid 3a

A suspension of **1a** (12.0 g, 29.7 mmol) and **2a** (4.4 g, 29.7 mmol) in 20 mL of anhydrous benzene was stirred for 1 h at 50°C. The mixture was filtered. The precipitate was washed by 5 mL of benzene. The filtrate was evacuated (0.5 mm Hg) at 40°C for 1 h and then kept under vacuum (0.02 mm Hg) at 40°C for 1 h to yield 10.0 g (61%) of crude **3a** (see Tables I–IV).

Products **3b–e** were obtained similarly (see Tables I–IV).

Diammonium Salt of 1,8-Triethyleneoxybis (4-methoxyphenylphosphonic) Acid 4a

Excess of anhydrous gaseous ammonium was passed through the solution of **3a** (7.1 g, 12.8 mmol) in 20 mL of anhydrous benzene for 1 h. The mixture was stored at ~20°C for ~12 h and filtered. The precipitate was washed by 20 mL of benzene and dried under reduced pressure (0.02 mm Hg) at 40°C for 2 h to give 6.6 g (88 %) of **4a** (see Tables I–IV).

Compound **4b** was obtained similarly (see Tables I–IV).

1,8-Bis(triphenylgermyl) Ester of 1,8-Triethyleneoxybis (4-methoxyphenylphosphonic) Acid 6a

Compound **5a** (1.7 g, 5.0 mmol) was added in portions under dry argon with stirring at 20°C to the suspension of 2.0 g (2.5 mmol) of **4b** in 50 mL of anhydrous benzene, and stirring was continued for 2 h at 80°C. The mixture was filtered. The filtrate was evaporated under vacuum (0.5 mm Hg) at 40°C for 1 h and then under vacuum (0.02 mm Hg) at 40°C for 1 h to give 2.5 g (68%) of **6a** (see Tables I–IV).

Compounds **6a**, **6b**, **8a**, and **8b** were obtained similarly (see Tables I–IV).

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