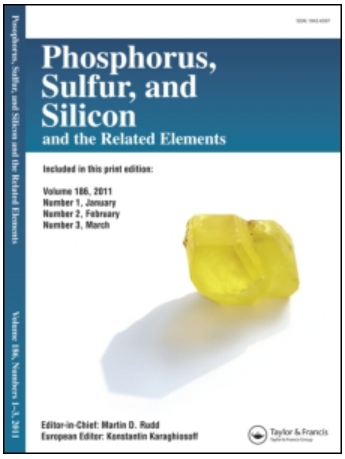

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REDUCTION OF TERMINAL ORGANYLCHALCOGENO PHOSPHONATES AS A WAY TO PREPARE PRIMARY ORGANYLCHALCOGENO PHOSPHINES

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REDUCTION OF TERMINAL ORGANYLCHALCOGENO PHOSPHONATES AS A WAY TO PREPARE PRIMARY ORGANYLCHALCOGENO PHOSPHINES

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2-Organylseleno(telluro)ethyl phosphines and 4-organylthio(seleno (telluro))butyl phosphines were prepared by reduction of diethyl 2-organylseleno(telluro)ethyl phosphonates and diethyl 4-organylthio(seleno(telluro)) butyl phosphonates with lithium aluminium hydride in diethyl ether. ^{1}H and ^{31}P NMR spectra as well as mass spectra of the resulting phosphines were considered. Their stability in regard to the oxidation by oxygen was discussed.

Keywords: Organylchalcogenoalkyl phosphines; organylchalcogeno alkyl phosphonates; reduction

Diethyl 2-organylchalcogenoethyl (**1**) and 4-organylchalcogenobutyl phosphonates (**2**) prepared earlier by us[1] represent prospective intermediates in the synthesis of hemilabile ligands of the type $RX(CH_2)_nPR'_2$ possessing, besides phosphorus, a chalcogen (S, Se, Te) in the molecule. One of the possible modifications of phosphonates **1**,**2** is reduction of the phosphoryl group to phosphine. It is known that the phosphoryl groups in alkyl phosphonates and phosphinates are reduced by lithium aluminium hydride to primary and secondary phosphines respectively.[3] However, in the case of terminal organylchalcogen-substituted alkyl phosphonates, the result was not evident since, at least with sulfides, lithium aluminium hydride could split the

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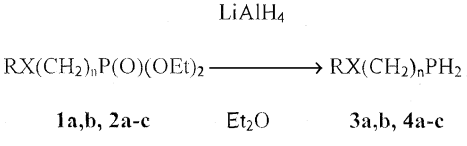
carbon-sulfur bond to yield a thiol and the corresponding protonated organic fragment.[4,5]

Earlier we reported that reduction to phosphine could be performed in the case of diethyl 2-phenylselenoethyl phosphonate **1a**.[6] This reaction has been examined in detail with different terminal organylchalcogen-substituted alkyl phosphonates **1a**,**b** and **2a–c**, and the results are reported in the present paper.

RESULTS AND DISCUSSION

We have found that treatment of diethyl 2-organylseleno(telluro)ethyl phosphonates **1a**,**b** and diethyl 4-organylthio(seleno(telluro)butyl phosphonates **2a–c** with $LiAlH_4$ in diethyl ether at room temperature leads to reduction of the phosphoryl function and to formation mostly of the corresponding primary phosphines **3a**,**b** and **4a–c** (Scheme 1, Table I).



1,**3**: n = 2, X = Se, R = Ph (**a**); X = Te, R = Me (**b**)

2,**4**: n = 4, X = S, R = Ph (**a**); X = Se, R = Me (**b**); X = Te, R = Me (**c**)

SCHEME 1

Formation of primary phosphines **3**,**4** is evidenced by ^1H and ^{31}P spectroscopy (Table II) and GC-MS (Table I). In the ^1H NMR spectra the primary phosphine group manifests itself as a doublet of triplets in the range 3.0–2.4 ppm with a characteristic splitting constant of $^1J_{PH}$ 194–196 Hz and $^3J_{HH}$ ~7 Hz (Table II). In the ^{31}P NMR spectrum without proton decoupling the primary phosphine group reveals itself as a triplet at $-125 \div -136$ ppm with the same splitting constant $^1J_{PH}$ (194–196 Hz) (Table II). Because of field inhomogeneity the methylene group adjacent to the chalcogen atom manifests itself as doublet of triplets.

Analysis of the mass spectra of the primary phosphines shows that, under electron impact, besides molecular ion formation, fragmentation occurs, mainly at the C–X and XCH_2–C bonds with formation of the

TABLE I Conditions of the Phosphonate **1**,**2** Reduction, Yields of Phosphines **3**,**4** and By-Products, MS Data for Phosphines **3**,**4**

Phosphonate, g (mM)	Reaction time, h	Method of product isolation[a]	Yield of phosphine, g (%)[b]	Product content in the mixture according to ^{31}P NMR data				GC-MS data for phosphine, RT, m/z (^{80}Se), (^{130}Te)
				Phosphine, %	Phosphine oxide, %	Phosphinic acid, %	Unidentified products, δ_P ppm (%)	
1a, 0.69 (2.15)	8	A	0.33 (70.0)	**3a**, 67.5	—	**7a**, 20	24.4 (8), 23.0 (4)	RT 13.25 min: $[M]^+$. 218; $[PhSePH_2]^+$. 190; $[PhSe]^+$ 157; $[M—Ph]^+$ 141; $[CH_2CH_2SeH]^+$ 109
1a 2.24 (7)	20	B	0.78 (51.5)	**3a**, 93	**5a**, 3	**7a**, 4	—	
1b, 1.03 (3.35)	1.5	B	0.50 (73.5)	**3b**, 77	**5b**, 12.5	**7b**, 4	−16.9 (3), 25.0, 27.5, 28.4 (3.5)	—
2a, 0.87 (2.9)	5	A	—	—	**6a**, 41.5	**8a**, 47	33.8 (11.5)	RT 14.39 min: $[M]^+$. 198, $[M—PH_2]^+$ 165, $[PhSPH_2]^+$. 142, $[PhSCH=CH]^+$ 135, $[M— Ph]^+$ 121, $[PhSCH_2]^+$ 123, $[PhS]^+$ 109
2a, 2.09 (6.91)	4.5	B	0.72 (64.0)	**4a**, 62	**6a**, 38	—	—	
2b, 1.19 (4.14)	3	B	0.70 (92.0)	**4b**, 35	**6b**, 65	—	—	RT 10.48 min: $[M]^+$. 184 (trace), $[M—Me]^+$ 169, $[MeSeCH_2]^+$ 109, $[MeSePH]^+$ 127, $[MeSe]^+$ 95, $[CH=Se]^+$ 93
2c, 1.66 (4.94)	6	A	—	—	**6c**, 28	**8c**, 35.5	39.1 (12.5), 35.2 (10), 33.9 (7), 31.8 (7)	RT 11.38 min: $[M]^+$. 234, $[M—Me]^+$ 219, $[M—Me—PH_2]^+$ 185, $[MeTePH_2]^+$. 178, $[MeTe]^+$ 145
2c, 1.10 (3.28)	2	B	0.65 (87.0)	**4c**, 72	—	—	−19.8 (14), −19.1 (14)	

[a]A—Reaction mixture is treated with water and extracted with Et_2O; B—Et_20 is evaporated from the reaction mixture, the residue is extracted with $CHCl_3$ and the precipitate filtered off.

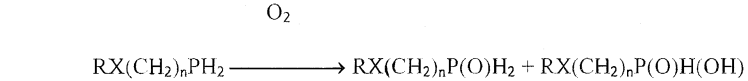
[b]Based on the content in the reaction mixture.

TABLE II ^{1}H and ^{31}P NMR Data for Phosphines **3** and **4**

	Phosphine			^{1}H NMR data, δ, ppm.				^{31}P NMR data	
Compound	n	X	R	R	X-CH_2	$(CH_2)_{n-1}P$	PH_2	δ_P, PH_2, ppm	$^{1}J_{PH}$, Hz
3a	2	Se	Ph	7.59–7.42 m 7.28–7.23 m	3.05 t ($^{3}J_{HH}$ 8 Hz), 3.03 t ($^{3}J_{HH}$ 8 Hz)	1.89–1.79 m	2.98 t ($^{3}J_{HH}$ 7.4 Hz), 2.49 t ($^{3}J_{HH}$ 7.4 Hz) ($^{1}J_{PH}$ 195 Hz)	−133.4 (t)	195.2
3b	2	Te	Me	1.93 s	2.82 t ($^{3}J_{HH}$ 8.2 Hz), 2.80 t ($^{3}J_{HH}$8.1 Hz)	2.01–1.94 m	3.01 br, 2.51 br ($^{1}J_{PH}$ 196 Hz)	−125.6 (t)	192.7
4a	4	S	Ph	7.31–7.24 m 7.18–7.07 m	2.89 t ($^{3}J_{HH}$ 7.2 Hz), 2.92 t ($^{3}J_{HH}$ 6.4 Hz)	1.77–1.58 m, 1.52–1.40 m	2.90 t ($^{3}J_{HH}$ 7.3 Hz), 2.41 t ($^{3}J_{HH}$ 7.5 Hz) ($^{1}J_{PH}$ 194 Hz)	−136.8 (t)	195.2
4b	4	Se	Me	1.97 s	2.56 t ($^{3}J_{HH}$ 7.5 Hz), 2.53 t ($^{3}J_{HH}$ 7.3 Hz)	1.85–1.68 m, 1.66–1.58 m, 1.56–1.47 m	2.93 t ($^{3}J_{HH}$ 7 Hz), 2.44 t ($^{3}J_{HH}$ 7 Hz) ($^{1}J_{PH}$ 194.4 Hz)	−136.8 (t)	194.8
4c	4	Te	Me	1.89 s	2.61 t ($^{3}J_{HH}$ 7.52 Hz) 2.63 t ($^{3}J_{HH}$ 7.70 Hz) 2.64 t ($^{3}J_{HH}$ 6.91 Hz)	1.86–1.78 m, 1.67–1.46 m	2.93 t ($^{3}J_{HH}$ 7.3 Hz) 2.44 t ($^{3}J_{HH}$ 7.3 Hz) ($^{1}J_{PH}$ 194.5 Hz)	−136.9 (t)	195.2

ions $[RX]^+$, $[M - R]^{+\cdot}$ and $[RXCH_2]^+$, as well as the rearranged ion $[RXPH_2]^{+\cdot}$ probably at the expense of PH_2-group abstraction (Table I).

We have found that the final results of the reaction depend on the method of separation of the products obtained (Table I). Excess of $LiAlH_4$ as well as lithium and aluminium hydroxides formed in the course of the reaction were removed from the reaction mixture by treatment with water (Method A), significant oxidation of primary phosphines being noticed in the process (Scheme 2). In the ^1H and ^{31}P NMR spectra of the products obtained on reduction of phosphonates **2a**,**c**, we observed only the signals of the oxidized derivatives: phenylthiobutyl phosphine oxide $PhS(CH_2)_4P(O)H_2$ **6a**, methyltellurobutyl phosphine oxide $MeTe(CH_2)_4P(O)H_2$ **6c**, phenylthiobutyl phosphinic acid $PhS(CH_2)_4P(O)H(OH)$ **8a** and methyltellurobutyl phosphinic acid $MeTe(CH_2)_4P(O)H(OH)$ **8c**.



3,5,7: n = 2, X = Se, R = Ph (**a**); X = Te, R = Me (**b**)

4,6,8: n = 4, X = S, R = Ph (**a**); X = Se, R = Me (**b**); X = Te, R = Me (**c**)

SCHEME 2

Only from phosphonate **1a** under these conditions was it possible to prepare the corresponding phosphine **3a**, but its content in the mixture was only 67.5% along with the corresponding phosphinic acid $PhSe(CH_2)_2PH(O)OH$ **7a** (20%) and a number of unidentified products.

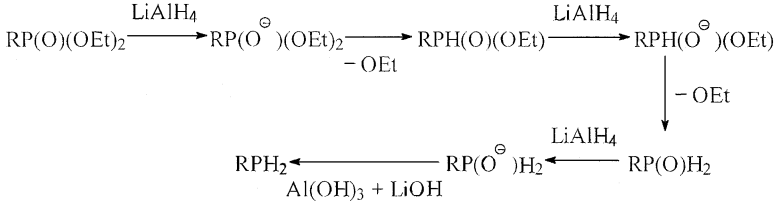
The best results were obtained with separation of the phosphine by a non-aqueous work-up procedure (Table I, Method B). Treatment of the reaction mixture with chloroform after removal of ether and consequent separation of the solution obtained from insoluble LiOH, $Al(OH)_3$ and excess of $LiAlH_4$ led to a mixture of products containing up to 93% (in the case of phosphine **3a**) of the main product. The lowest yields were obtained for phosphines **4a** (62%) and **4b** (35%) for which the only oxidized products were phenylthiobutyl phosphine oxide **6a** and methylselenobutyl phosphine oxide **6b** respectively. In the case of methyltelluroethyl phosphine **3b**, besides phosphine oxide $MeTe(CH_2)_2P(O)H_2$ **5b**, a trace amount of the phosphinic acid $PhTe(CH_2)_2PH(O)OH$ **7b** was detected along with a number of products characterized in ^{31}P

NMR spectra by signals at 25–28 ppm. In the case of reduction of the methyltelluro-substituted alkyl phosphonates **1b** and **2c**, the ^{31}P NMR spectra of the products exhibited high-field doublet signals at −16.9 ppm (phosphonate **1b**) and −19.1 and −19.8 ppm (phosphonate **2c**) with $^{1}J_{PH}$ constant 207 Hz. Absence of these signals in the spectra of the reduction products of other phosphonates indicates that these are tellurium-containing products but their nature is not yet clear. It is suggested that they may have PH(O)TeMe or PH(Te)OEt moieties in their structure.

Our conclusion concerning the formation on oxidation of phosphines **3**,**4** of corresponding phosphine oxides **5**,**6** was made on the basis of the presence in the ^{31}P NMR spectra of doublets at 5.8–9.2 ppm with $^{1}J_{PH}$ = 458–472 Hz in the product mixtures analyzed. In the ^{1}H NMR spectra doublets at 7.02–7.13 ppm with a similar $^{1}J_{PH}$ constant correspond to these signals. Similarly, the presence in the product mixtures of compounds with the $CH_2P(O)H(OH)$ function was evidenced by the presence in the ^{31}P NMR spectrum of doublets of triplets in the range 34.8–38.0 ppm with a $^{1}J_{PH}$ of 535–553 Hz and a $^{2}J_{PH}$ of 11.5–13 Hz. In the ^{1}H NMR spectra this group is characterized by a singlet low-field signal at δ 8.4–10.7 ppm and a doublet at δ 7.07–7.08 ppm with a $^{1}J_{PH}$ of 535–553 Hz.

The phosphines prepared are fairly stable in chloroform solution. Thus, a mixture of phenylthiobutyl phosphine **4a** and phosphine oxide **6a** (62:38) practically did not change during 2 days (60.5:39.5) and only after 8 days in this mixture had phosphinic acid **8a** (8%) appeared. A mixture of phosphine **3a** and phosphinic acid **7a** containing initially 68% of phosphine completely changed during 4 months into phosphinic acid.

Based on the accepted mechanism for reduction of carbonic esters with lithium aluminium hydride, the following mechanism of phosphonate reduction may be envisaged (Scheme 3).



R = R'X$(CH_2)_n$; R' = Me, Ph; X = S, Se, Te; n = 2.4

SCHEME 3

In accordance with this scheme, phosphine oxides could be intermediate products of the reduction, but GC data of the reaction mixtures indicating the presence of only one target product suggest that the formation of the oxidized products occurs only during separation of the phosphine. The most stable products toward oxidation appeared to be the ethyl phosphines which, judging from the values of the phosphorus chemical shifts (Table II), were the most sensitive to the influence of β-substituents.

EXPERIMENTAL

^{1}H and ^{31}P NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400 MHz (^{1}H) (solvent $CDCl_3$, HMDS as internal standard, δ in ppm) and 162 MHz (^{31}P) (80% H_3PO_4 as external standard, δ_P in ppm). GC-MS spectra were recorded on a HP 5971A spectrometer with electron energy 70eV, chromatograph HP-5890, capillary column 20 m Ultra-2 (5% phenyl methyl silicone), injection temperature 250°C, column temperature 70–280°C, temperature gradient 20°C/min. GLC analyses were carried out on chromatograph Chrom 5, glass columns 2.5 m, chromaton NAW (0.200–0.250 mm) with 5% silicon SE-30 using a thermal conductivity detector, column program: 6 min at 70°C, temperature rise to 140°C with gradient 6°/min, 6 min at 140°C, temperature rise to 220°C with gradient 7°C/min, 10 min at 220°C.

Preparation of ω-Organylchalcogenoalkyl Phosphines

To a stirred solution of diethyl 2-organylseleno(telluro)ethyl or diethyl 4-organylthio (seleno(telluro)butyl phosphonates in diethyl ether at room temperature under argon was added in small portions excess of $LiAlH_4$ until termination of the vigorous reaction. Stirring was continued for 2–3 h till complete reduction of phosphonate, the reaction being monitored by GC. To remove excess of $LiAlH_4$ and LiOH and $Al(OH)_3$ formed in a course of the reaction, the reaction mixture was treated with water. After separation of the ether layer, the aqueous layer was extracted with diethyl ether and chloroform, and the combined organic extracts were then dried over anhydrous $MgSO_4$. According to method B, ether was stripped off from the reaction mixture, the residue was treated with chloroform and the precipitate filtered off. After evacuation of solvents in vacuum the product obtained was analyzed by ^{1}H and ^{31}P NMR spectroscopy and GC-MS. Preparation conditions, yields of products and GC-MS data are presented in Table I. ^{1}H and ^{31}P NMR data for the phosphines prepared are presented in Table II.

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