Nucleophilic diaddition of secondary phosphine sulfides to acetylene and methylacetylene*

*N. K. Gusarova, S. F. Malysheva, N. A. Belogorlova, V. A. Kuimov, I. A. Ushakov, and B. A. Trofimov**

A. E. Favorsky Irkutsk Institute of Chemistry,
Siberian Branch of the Russian Academy of Sciences,
1 ul. Favorskogo, 664033 Irkutsk, Russian Federation.
Fax: +7 (395) 241 9346. E-mail: gusarova@irioch.irk.ru

Secondary phosphine sulfides react with acetylene and methylacetylene in the system KOH—DMSO (50 °C, 2—3 h) to form the corresponding tertiary bis-phosphine sulfides in high yield (up to 97%). Specific features of the NMR spectra (^{1}H, ^{13}C, and ^{31}P) of compounds obtained are discussed.

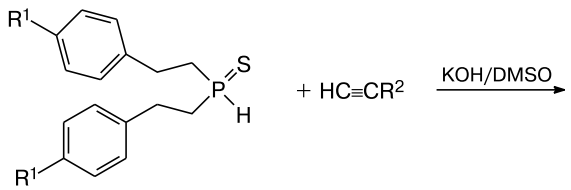
Key words: acetylene, methylacetylene, alkynes, phosphine sulfides.

Bis-phosphine sulfides are under intensive study as efficient polydentate ligands for the design of metal complex catalysts,[1—4] antipyrenes,[5] intermediate products for the development of fluorescent and electroluminescent sensors,[6] as well as promising solvents and intermediates for the preparation of semiconducting nanomaterials.[7] Bis-phosphine sulfides with chiral centers are of particular value.[8] Reduction of the latter leads to the corresponding optically active bis-phosphines,[9] which are widely used in the catalytic stereoselective synthesis.[10,11] At the same time, methods for the preparation of bis-phosphine sulfides, as a rule, are multistep and laborious and are based on toxic phosphorus halides and organometallic reagents.[12] One of the most convenient approaches to the synthesis of tertiary bis-phosphine chalcogenides is the reaction of nucleophilic addition of two molecules of secondary phosphine chalcogenide to acetylenes. This reaction is at the time under intensive study on the example of "activated" acetylenes with the triple bond bearing electron-withdrawing groups.[13—16] The reaction of acetylene and its first and the most available homolog (methylacetylene) with secondary phosphine sulfides has not been implemented so far. Moreover, it was reported[13] that diphenylphosphine sulfide does not react with electron-saturated acetylenes (hexyne, phenylacetylene) under nucleophilic conditions, for example, in the system KOH—H_2O—MeCN.

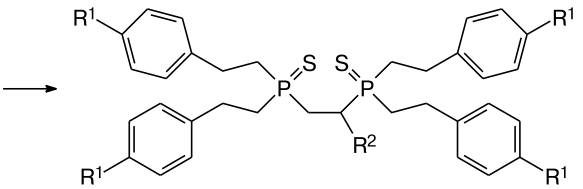
In the present work, in order to develop a straightforward method for the synthesis of new bis-phosphine sulfides, the reaction of nucleophilic addition of secondary phosphine sulfides **1a,b**, easily available from styrenes, red phosphorus, and elementary sulfur, to acetylene and methylacetylene has been studied.[17,18]

Experiments showed that virtually no reaction takes place in the system KOH—THF. At the same time, when superbasic catalytic system KOH—DMSO[19] was used, the nucleophilic addition of two molecules of secondary phosphine sulfide proceeds efficiently at mild temperatures (50 °C, 2—3 h) under pressure of acetylene (autoclave, the initial pressure of 14 atm) or in the channel system (in the case of methylacetylene) with the formation of bis-adducts **2a—c** in high yield (Scheme 1).

Scheme 1



1a,b



2a—c

$R^1 = R^2 = H$ (**a**); $R^1 = Bu^t$, $R^2 = H$ (**b**); $R^1 = H$, $R^2 = Me$ (**c**)

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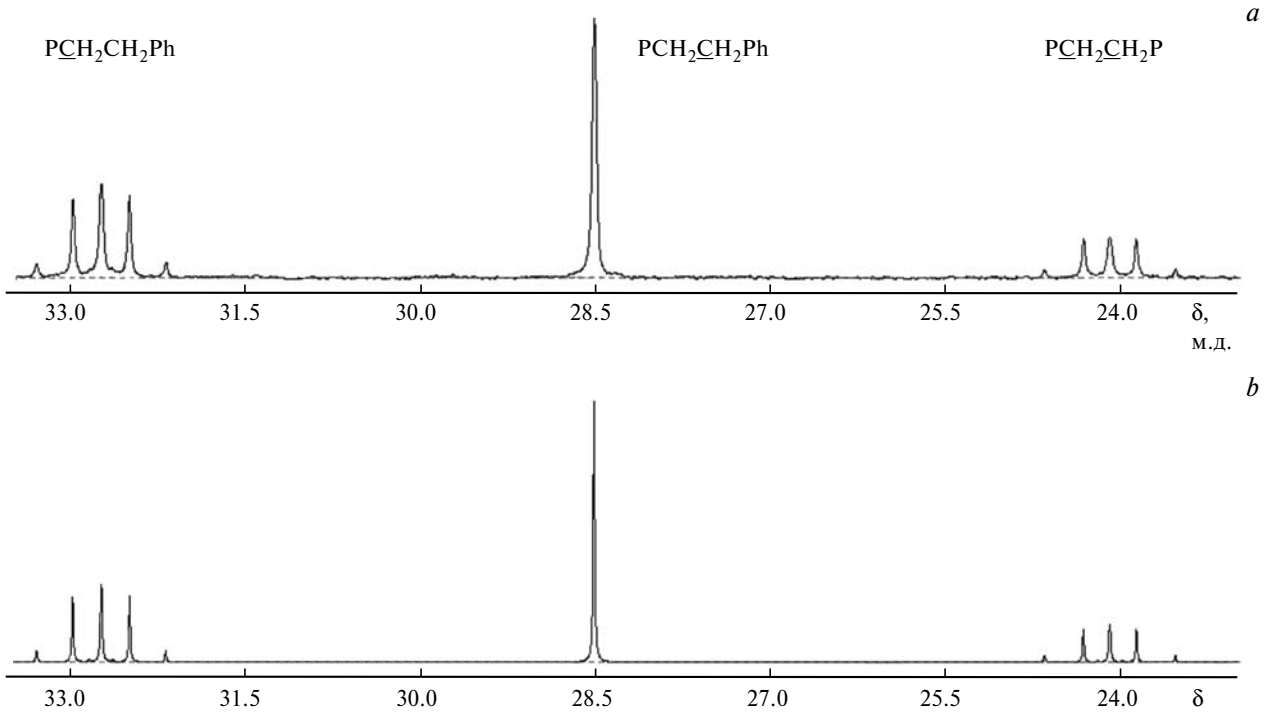

Fig. 1. Fragments of experimental (*a*) and simulated (*b*) ^{13}C NMR spectra of compound **2a**.

Certain specific features are observed in the NMR spectra (^{1}H, ^{13}C, and ^{31}P) of compounds obtained.

Thus, in the ^{1}H NMR spectra of compounds **2a,b**, the signals of the bridged CH_2 groups for the methylene protons in the fragment (S)PCH_2CH_2P(S) are present as a broad singlet in the region 2.0 ppm, that, probably, results from the retarded rotation around the C—C bond. The signals for the protons of the CH_2 group of the phenylethyl fragment are represented by two multiplets at 2.0—2.2 ppm ((S)PCH_2) and 2.8—3.0 ppm (CH_2Ph).

In the ^{13}C NMR spectra of **2a,b**, the signals of the $PhCH_2\underline{C}H_2P$(S) and (S)$P\underline{C}H_2\underline{C}H_2P$(S) groups are represented by complex multiplets (Fig. 1, *a*). Earlier, in Ref. 20 dealt with the study of polyphosphines with the ethylene bridge, it has been reported that the signals for the ^{13}C carbon atoms of the PCH_2CH_2P group are triplets and this was the basis for the suggestion on the equivalence of the $^{1}J_{C,P}$ and $^{2}J_{C,P}$ spin-spin coupling constant values in such a fragment. Taking into account the complex character of the multiplets observed in the ^{13}C NMR spectra, we simulated the ^{13}C NMR spectrum using the gNMR 5.0 program, which allows one to perform the iteration selection of spectral parameters (Fig. 1, *b*). The calculations result in determination of precise $^{1}J_{C,P}$, $^{2}J_{C,P}$, and $^{3}J_{P,P}$ spin-spin coupling constant values, which differ from those measured directly from the spectrum and agree with the values observed by us earlier for phosphine sulfide series.[21] A decrease in the intensity of central component in the ^{13}C NMR spectra results from the isotopic shift of the ^{31}P NMR signal for the phosphorus atom bonded to the ^{13}C carbon atoms in the system AA´XX´ under consideration. Assignment of the ^{1}H and ^{13}C signals was made using 2D-heteronuclear NMR spectroscopy methods HSQC and HMBC, which confirm structures of the compounds.

In the ^{31}P NMR spectra of compounds **2a,b**, the phosphorus atoms resonate as singlets with chemical shifts characteristic of tertiary phosphine sulfides.[21]

For unsymmetric compound **2c**, four lines are observed in the ^{31}P NMR spectrum and additional signals appear in the ^{13}C NMR spectrum.

In conclusion, the use of superbasic system KOH—DMSO allowed us to accomplish for the first time the reaction of nucleophilic addition of two molecules of secondary phosphine sulfides to acetylene and methyl-acetylene and to obtain the corresponding bis-phosphine sulfides in high yields.

Experimental

IR spectra were recorded on a Specord IR-75 spectrometer in KBr pellets. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker DPX 400 spectrometer (400, 100, and 161.98 MHz, respectively) in $CDCl_3$ with HMDS as the internal standard. To assign signals in the ^{1}H and ^{13}C NMR spectra, two-dimensional homo- and heteronuclear methods of NMR spectroscopy

(NOESY, HSQC) were used. Analysis of the cross-sections in the 2D-spectrum HSQC allowed us to determine positions of the resonance signals for the aliphatic protons, which are complex overlapping multiplets resulted from the homonuclear ^1H-^1H and heteronuclear ^1H-^{31}P spin-spin interactions. The nonequivalence of the protons in the fragments $CH_2P{=}S$ results from their diastereotopy.

Experiments with acetylene were carried out in a 0.25-L autoclave under pressure of acetylene (the initial pressure at room temperature was ~14 bar, the residual pressure, ~11 bar).

1,2-Bis[bis(2-phenylethyl)thiophosphoryl]ethane (2a). A suspension of bis(2-phenylethyl)phosphine sulfide (**1a**) (0.3 g, 1.1 mmol), KOH (1.04 g, 18.6 mmol) in DMSO (35 mL) was saturated with acetylene, stirred for 3 h at 50 °C, cooled, diluted with water, and extracted with benzene. The benzene extracts were washed with water and dried with K_2CO_3, benzene was evaporated, the residue was dried *in vacuo* to obtain compound **2a** (0.3 g, 97%), white powder, m.p. 166—168 °C (hexane). ^1H NMR ($CDCl_3$), δ: 1.94 (br.s, 4 H, PCH_2CH_2P), 2.04—2.06 (m, 8 H, PCH_2), 2.90—2.92 (m, 8 H, $PhCH_2$), 7.17—7.27 (m, 20 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 24.07 (m, $P\underline{C}H_2\underline{C}H_2P$, $^1J_{P,C}$ = 56.1 Hz), 28.49 (m, $Ph\underline{C}H_2CH_2P$), 32.55 (m, $P\underline{C}H_2CH_2Ph$, $^1J_{P,C}$ = 48.9 Hz), 126.71 (*p*-C_{Ph}), 128.44 (*o*-C_{Ph}), 128.87 (*m*-C_{Ph}), 140.24 (m, *ipso*-C_{Ph}, $^3J_{P,C}$ = 12.8 Hz). ^{31}P NMR ($CDCl_3$): δ_P 51.32. IR (KBr), ν/cm^{-1}: 3100, 3079, 3063, 3025, 3000 (=CH ring); 2895, 2864, 2851 (CH); 1601, 1583, 1494 (C=C ring); 1452, 1436, 1401 δ(CH_2); 1189, 1180, 1141, 952, 858; δ(CH ring); 780 δ(CH_2); 759 (P—C); 746, 702 δ(CH ring); 545 (P=S); 503 δ (CPC). Found (%): C, 70.65; H, 7.58; P, 10.89, S, 11.03. $C_{34}H_{40}P_2S_2$. Calculated (%): C, 71.05; H, 7.01; P, 10.78; S, 11.16.

1,2-Bis{bis[2-(4-*tert*-butylphenyl)ethyl]thiophosphoryl}ethane (2b). Compound **2b** (0.21 g, 68%) was synthesized under conditions for compound **2a** from bis[2-(4-*tert*-butylphenyl)-ethyl]phosphine sulfide (**1b**) (0.3 g, 0.78 mmol), white powder, m.p. 242 °C (hexane). ^1H NMR ($CDCl_3$), δ: 1.25 (s, 36 H, CH_3), 2.01—2.07 (br.s, 12 H, $CH_2PCH_2CH_2$), 2.85—2.88 (m, 8 H, $CH_2C_6H_4$), 7.09—7.27 (m, 16 H, C_6H_4). ^{13}C NMR ($CDCl_3$), δ: 23.94 (m, PCH_2CH_2P, $^1J_{P,C}$ = 45.0 Hz). 28.04 ($PCH_2\underline{C}H_2C_6H_4$), 31.38 ($\underline{C}H_3$), 32.76 (m, $P\underline{C}H_2CH_2C_6H_4$, $^1J_{P,C}$ = 48.0 Hz), 34.44 [$\underline{C}(CH_3)$], 125.68 (*o*-$C_{C_6H_4}$), 127.96 (*m*-$C_{C_6H_4}$), 137.15 (m, *ipso*-$C_{C_6H_4}$, $^3J_{P,C}$ = 13.3 Hz), 149.63 (*p*-$C_{C_6H_4}$). ^{31}P NMR ($CDCl_3$): δ_P 51.45. IR (KBr), ν/cm^{-1}: 3094, 3055, 3024 (=CH ring); 2962, 2933, 2902, 2866 (CH); 1516 (C=C ring); 1474, 1463, 1446 δ(CH_2); 1410, 1394, 1363, 1269 δ(CH_3); 811 δ(CH ring); 561, 552 (P=S). Found (%): C, 75.09; H, 9.06; P, 7.15, S, 8.24. $C_{50}H_{72}P_2S_2$. Calculated (%): C, 75.14; H, 9.08; P, 7.75; S, 8.02.

1,2-Bis[bis(2-phenylethyl)thiophosphoryl]propane (2c). A suspension of KOH (1.04 g, 18.6 mmol) in DMSO (10 mL) was saturated with methylacetylene and a solution of phosphine sulfide **1a** (0.26 g, 1.0 mmol) in DMSO (5 mL) was added dropwise for 0.5 h at 50 °C with simultaneous bubbling of methylacetylene. The reaction mixture was stirred for additional 0.5 h followed by addition of another portion of phosphine sulfide **1a** (0.07 g) in DMSO (1 mL), the mixture was stirred for 1 h at 50 °C, cooled, diluted with water, and extracted with benzene. The benzene extracts were washed with water and dried with K_2CO_3, benzene was evaporated, the residue was dried *in vacuo* to obtain compound **2c** (0.3 g, 94%), colorless clear crystals, m.p. 106 °C (hexane). ^1H NMR ($CDCl_3$), δ: 1.37 (dd, 3 H, Me, $^3J_{H,H}$ = 7.1 Hz, $^3J_{H,P}$ = 17.6 Hz); 1.54—1.58 (m, 1 H, CH_2); 2.01—2.03 (m, 1 H, PCH); 2.15—2.17 (m, 8 H, PCH_2), 2.48—2.64 (m, 1 H, CH_2), 2.79—2.98 (m, 8 H, $PhCH_2$), 7.19—7.28 (m, 20 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 15.42 (Me), 28.66 (d, CH_2Ph, $^2J_{P,C}$ = 2.9 Hz), 29.79 (d, CHP, $^1J_{P,C}$ = 45.7 Hz), 30.03 (d, CH_2P, $^1J_{P,C}$ = 46.4 Hz), 30.40 and 30.57 (d, Me, $^1J_{P,C}$ = 45.7 Hz), 33.76 and 34.68 (d, CH_2P, $^1J_{P,C}$ = 47.9 Hz), 126.31 (*p*-C_{Ph}), 127.96 (*o*-C_{Ph}), 128.42 (*m*-C_{Ph}), 140.11 (d, *ipso*-C_{Ph}, $^3J_{P,C}$ = 12.8 Hz). ^{31}P NMR ($CDCl_3$), δ: 50.43 (d, $^3J_{P,P}$ = 26.9 Hz) and 60.41 (d, $^3J_{P,P}$ = 26.9 Hz). IR (KBr), ν/cm^{-1}: 3103, 3083, 3062, 3024, 3000 (=CH ring); 2970, 2949, 2928, 2900, 2864 (C—H); 1601, 1583, 1495, 1452 (C=C ring); 744, 698 δ(CH ring); 560, 545 (P=S). Found (%): C, 71.45; H, 7.17; P, 10.89, S, 10.59. $C_{35}H_{42}P_2S_2$. Calculated (%): C, 71.40; H, 7.19; P, 10.52; S, 10.89. The ^1H-^1H COSY two-dimensional homonuclear NMR procedure with decoupling on the ^{31}P nucleus was used to assign signals in the ^1H NMR spectra.

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