ISSN 1070-3632, Russian Journal of General Chemistry, 2015, Vol. 85, No. 2, pp. 380–382. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © N.K. Gusarova, P.A. Volkov, N.I. Ivanova, K.O. Khrapova, B.A. Trofimov, 2015, published in Zhurnal Obshchei Khimii, 2015, Vol. 85, No. 2, pp. 206–208.

To the 80th Anniversary of B.I. Ionin

Chlorination of Secondary Phosphine Chalcogenides with Carbon Tetrachloride in the Absence of Bases

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Received December 18, 2014

Abstract—The interaction of bis(2-phenylethyl)phosphine sulfide, bis(2-phenylethyl)phosphine selenide and bis[2-(2-phenyl)propyl]phosphine selenide with carbon tetrachloride under heating (80°C, 8–20 h) leads to the formation of the corresponding chlorophosphine chalcogenides with the yield of 80–90%.

Keywords: secondary phosphine chalcogenide, carbon tetrachloride, chlorophosphine chalcogenide

DOI: 10.1134/S107036321502005X

Chlorophosphine chalcogenides $R_2P(X)Cl$ (X = S or Se) are used in phosphorus-containing organoelement compounds synthesis as active agents for formation of the P–C as well as P–heteroatom (N, O, or S) bonds. The resulting tertiary phosphine chalcogenides or amides, esters and thioesters of chalcogenophosphinic acids have been recognized as efficient ligands for synthesis of metal complexes for multipurpose applications [1–4], precursors for drug design [5–7], intermediates for preparation of nanosized metal chalcogenides with unique semiconductor and magneto-optical properties [8–10].

Chlorophosphine chalcogenides are usually obtained by oxidation of bisorganylchlorophosphines with elemental sulfur [11, 12] or selenium [13, 14]. A serious drawback of this method is using of poorly accessible and unstable (easily oxidized and hydrolyzed) bisorganylchlorophosphines as starting compounds.

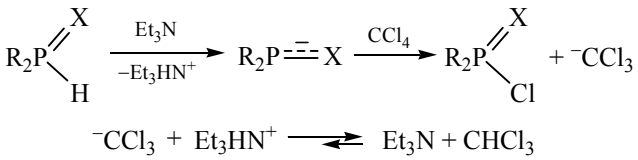
A more convenient method of chlorophosphine chalcogenides preparation has been proposed, consisting in chlorination of secondary phosphine chalcogenides with the CCl_4–Et_3N system (room temperature, the secondary phosphine chalcogenide : Et_3N molar ratio of 1 : 1) [15, 16]. Under such conditions the reaction does not proceed in the absence of triethylamine [16], the latter acting as a deprotonating agent [15, 16] (Scheme 1).

In this work, we present updated experimental data on the direct chlorination of secondary phosphine chalcogenides with carbon tetrachloride.

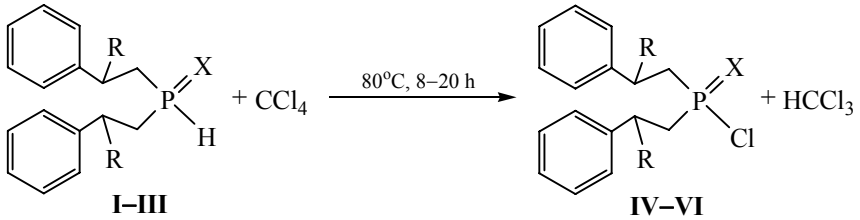
Bis(2-phenylethyl)phosphine sulfide (**I**), bis(2-phenylethyl)phosphine selenide (**II**), and bis-[2-(2-phenyl)propyl]phosphine selenide (**III**) reacted with carbon tetrachloride at heating (80°C, 8–20 h) to form chlorophosphine chalcogenides **IV–VI** with yield of 80–90%. Chloroform was qualitatively identified in the reaction mixtures (^{13}C NMR) (Scheme 2).

In order to explain the oxidative chlorination of secondary phosphine chalcogenides with carbon tetrachloride in the absence of triethylamine we suggested the following scheme: tautomers (**A**) of P,X-ambident bisorganylphosphine chalcogenides (containing a tricoordinated phosphorus atom) reacted with carbon tetrachloride at the first stage to form phosphonium salts (**B**) in equilibrium with phosphorane (**C**). The subsequent cleavage of the P–C and X–H bonds in

Scheme 1.



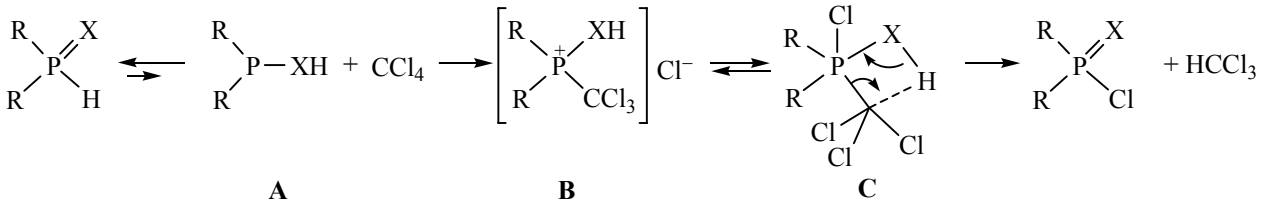
Scheme 2.



I–III **IV–VI**

R = H, X = S (**I, IV**); R = H, X = Se (**II, V**); R = Me (**III, VI**).

Scheme 3.



A **B** **C**

X = S, Se; R = $Ph(CH_2)_2$, $PhCH(Me)CH_2$.

intermediate (**C**) led to formation of chlorophosphine chalcogenides and chloroform (Scheme 3).

To conclude, the direct chlorination of secondary phosphine chalcogenides with carbon tetrachloride makes a fundamental contribution to the chemistry chalcogen-containing phosphine compounds being a convenient practical method for synthesis of highly demanded chlorophosphine sulfides and chlorophosphine selenides.

EXPERIMENTAL

IR spectra were recorded with a Bruker Vertex 70 spectrometer (thin film). ^{1}H, ^{13}C, ^{31} P, and ^{77}Se spectra of the solutions in $CDCl_3$ were recorded using a Bruker DPX-400 spectrometer operating at 400.13, 101.61, 161.98, and 76.31 MHz, respectively, internal references being HMDS (^{1}H and ^{13}C) or Me_2Se (^{77}Se), external reference being 85% H_3PO_4 (^{31}P).

All operations were performed in argon atmosphere. The reaction course was monitored with ^{31}P NMR.

Chlorophosphine chalcogenides IV–VI (general procedure). A solution of phosphine chalcogenide **I–III** (1 mmol) in 4 mL of CCl_4 was purged with argon and stirred at 80°C during 20 (**I**), 8 (**II**), or 10 h (**III**). Formation of chloroform in the reaction mixture was detected by ^{13}C NMR. The solvent was removed under reduced pressure, 0.3 mL of hexane was added to the residue obtained, and the hexane solution was removed by decantation. The procedure was repeated 8–10 times. Hexane extracts were combined and evaporated under reduced pressure; the residue was dried in vacuum to yield chlorophosphine chalcogenides **IV–VI**.

Bis(2-phenylethyl)thiophosphorylchloride (IV). Yield 80%, viscous liquid. IR spectrum, ν, cm^{-1}: 638, 624 (P=S). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.45–2.64 (4H, CH_2P), 2.97–3.18 m (4H, CH_2Ph), 7.17–7.31 m (10H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 29.10 d ($PhCH_2$, $^2J_{CP}$ 3.0 Hz), 42.28 d (CH_2P, $^1J_{CP}$ 52.6 Hz), 126.89 (C^p), 128.42 (C^o), 128.92 (C^m), 139.66 d (C^{ipso}, $^3J_{CP}$ 17.2 Hz). ^{31}P NMR spectrum: δ_P 100.9 ppm. Found, %: C 62.20; H 5.87; Cl 11.37; P 9.95; S 10.21. $C_{16}H_{18}ClPS$. Calculated, %: C 62.23; H 5.88; Cl 11.48; P 10.03; S 10.38.

Bis(2-phenylethyl)selenophosphorylchloride (V). Yield 85%, viscous liquid. IR spectrum, ν, cm^{-1}: 490 (P=Se). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.56–2.66 m and 2.69–2.80 m (4H, CH_2P), 2.96–3.06 and 3.08–3.19 m (4H, CH_2Ph), 7.17–7.23 and 7.27–7.31 m (10H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 29.24 d (CH_2Ph, $^2J_{CP}$ 2.6 Hz), 42.46 d (CH_2P, $^1J_{CP}$ 42.7 Hz), 126.46 (C^p), 128.01 (C^o), 128.46 (C^m), 138.94 d (C^{ipso}, $^3J_{CP}$ 17.2 Hz). ^{31}P NMR spectrum: δ_P 90.18 ppm (+ doublet of satellites, $^1J_{PSe}$ 830.6 Hz). ^{77}Se NMR spectrum: δ_{Se} –117.69 ppm (d, $^1J_{PSe}$ 830.6 Hz). Found, %: C 54.10; H 5.11; Cl 9.91; P 8.65; Se 22.05.

$C_{16}H_{18}ClPSe$. Calculated, %: 54.03; H 5.10; Cl 9.97; P 8.71; Se 22.20.

Bis[2-(2-phenyl)propyl]selenophosphorylchloride (VI). Yield 90%, viscous liquid. IR spectrum, ν, cm^{-1}: 510 (P=Se). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.27 d and 1.33 (3H, MeCH, $^3J_{HP}$ 7.0, $^3J_{HP}$ 6.6 Hz), 1.35 d and 1.39 d (3H, MeCH, $^3J_{HP}$ 6.7, $^3J_{HP}$ 7.0 Hz); 2.24–2.31 m, 2.38–2.47 m, and 2.51–2.57 m (4H, CH_2P), 3.31–3.55 m (2H, PhCH), 7.07–7.27 m (10H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 22.88 d (MeCH, $^3J_{CP}$ 11.2 Hz), 23.30 d (MeCH, $^3J_{CP}$ 12.5 Hz), 23.85 d (MeCH, $^3J_{CP}$ 12.1 Hz), 23.99 d (MeCH, $^3J_{CP}$ 11.2 Hz), 35.85 d (PhCH, $^2J_{CP}$ 4.3 Hz), 36.11 (PhCH, $^2J_{CP}$ 1.7 Hz), 36.32 d (PhCH, $^2J_{CP}$ 3.5 Hz), 35.41 d (PhCH, $^2J_{CP}$ 2.4 Hz), 49.15d (CH_2P, $^1J_{CP}$ 41.4 Hz), 49.57 d (CH_2P, $^1J_{CP}$ 41.4 Hz), 49.74 d (CH_2P, $^1J_{PC}$ 41.8 Hz), 50.06 d (CH_2P, $^1J_{CP}$ 43.1 Hz), 126.71–127.24 m and 128.58–128.73 m (C^o, C^m, C^p), 145.50–145.80 m (C^{ipso}). ^{31}P NMR spectrum, δ_P, ppm: 88.37 (+ doublet of satellites, $^1J_{PSe}$ 822.2 Hz), 89.72 (+ doublet of satellites, $^1J_{PSe}$ 825.9 Hz), 91.07 (+ doublet of satellites, $^1J_{PSe}$ 825.9 Hz). ^{77}Se NMR spectrum, δ_{Se}, ppm: –78.9 d ($^1J_{PSe}$ 822.2 Hz), –100.2 d ($^1J_{PSe}$ 825.9 Hz), –116.3 d ($^1J_{PSe}$ 825.9 Hz). Found, %: C 56.71; H 5.70; Cl 9.27; P 8.02; Se 20.49. $C_{18}H_{22}ClPSe$. Calculated, %: C 56.34; H 5.78; Cl 9.24; P 8.07; Se 20.58.

ACKNOWLEDGMENTS

This work financially supported from Council on grants of President of Russian Federation for state support of leading scientific schools (project NSH-156.2014.3).

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