Russian Journal of General Chemistry, Vol. 73, No. 3, 2003, pp. 492–493. Translated from Zhurnal Obshchei Khimii, Vol. 73, No. 3, 2003, pp. 525–526. Original Russian Text Copyright © 2003 by Prishchenko, Livantsov, Livantsova, Novikova, Nikolaev, Grigor'ev.

LETTERS TO THE EDITOR

Reaction of Bis(trimethylsiloxy)phosphine with Methyl(phenyl)divinylsilane

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Received May 7, 2002

Bis(trimethylsiloxy)phosphine is successfully used in various addition reactions to unsaturated synthons, leading to promising types of organophosphorus compounds [1]. We showed that the reaction of an excess of bis(trimethylsiloxy)phosphine with methyl-(phenyl)divinylsilane provides a mixture of phosphonite I and bisphosphonite II in equal amounts. Phosphonites I and II were isolated in high yield. The reaction was initiated with 2,2'-azobisisobutyronitrile (AIBN) under conditions of its thermolysis (100– 130°C).

$$n(Me_{3}SiO)_{2}PH + (CH_{2}=CH)_{2}Si(Me)Ph$$

$$\xrightarrow{R^{\circ}} (Me_{3}SiO)_{2}PCH_{2}CH_{2}SiCH=CH_{2}(Me)Ph$$

$$I$$

$$+ [(Me_{3}SiO)_{2}PCH_{2}CH_{2}]_{2}Si(Me)Ph,$$

$$II$$

$$R' = Me_2(NC)C'$$

Phosphonite I is easily aminomethylated with bis-(dialkylamino)methanes at 130°C in the presence of zinc chloride as catalyst to form phosphinates IIIa and IIIb in good yields.

$$I \xrightarrow{(R_2N)_2CH_2, ZnCl_2}_{-Me_3SiNR_2} \rightarrow Me_3SiOP \xrightarrow{CH_2CH_2SiCH=CH_2(Me)Ph}_{CH_2NR_2}$$

$$IIIa, IIIb$$

$$R_2N = Me_2N (a), \qquad N (b).$$

Treatment of phosphonites **I** and **II** and phosphinates **III** with dilute solutions of sodium methylate in methanol gives water-soluble sodium phosphonates **IV** and **V** and phosphinates **VI**, which contain stable organosilicon fragments.



Salts IV-VI are white hygroscopic crystals. The ¹H NMR spectra of compounds I-VI contain characteristic signals of the PC¹H₂C²H₂Si and PC³H₂NC⁴H_n fragments. Their parameters are listed below. In ¹H NMR spectra, the signals of these fragments partially or completely overlap. The vinyl and phenyl proton signals of these compounds are multiplets at 5.7–6.5 and 7.2–7.6 ppm, respectively.

Bis(trimethylsilyl) [2-[methyl(phenyl)(vinyl)silyl]ethyl]phosphonite (I) and bis[2-bis(trimethylsiloxy)phosphinoethyl]methyl(phenyl)silane (II). A mixture of 50 g of bis(trimethylsiloxy)phosphine, 12.7 g of methyl(phenyl)(divinyl)silane, and 0.4 g of AIBN was heated to 100°C and, within 1 h, to 130°C. After that the reaction mixture was distilled in a vacuum to give 13.5 g of phosphonite I and 19.6 g of bisphosphonite II. Phosphonite I, yield 48%, bp 133°C (1 mm). ¹³C NMR spectrum, δ_C , ppm: 34.01 d (C¹, ¹J_{PC} 25.7 Hz), 4.20 d (C², ²J_{PC} 6.8 Hz). ³¹P NMR spectrum, δ_P , ppm: 157.34 s. Phosphonite II, yield 45%, bp 178°C (1 mm). ¹³C NMR spectrum, $\delta_{\rm C}$, ppm: 33.58 d (C¹, ¹J_{PC} 26.0 Hz), 3.01 d (C², ²J_{PC} 10.8 Hz). ³¹P NMR spectrum, $\delta_{\rm P}$, ppm: 158.23 s.

Trimethylsilyl (dimethylaminomethyl)[2-[me**thyl(phenyl)(vinyl)silyl]ethyl]phosphinate (IIIa).** A mixture of 4 g of phosphonite **I**, 2.4 g of bis(dimethylamino)methane, and 0.1 g of zinc chloride was heated at 110–130°C for 1.5 h and then distilled to give 3 g of phosphinate **III**, yield 78%, bp 141°C (1 mm), n_D^{20} 1.5019. ¹H NMR spectrum, δ, ppm: 2.05 s (C⁴H₃). ¹³C NMR spectrum, δ_P, ppm: 21.81 d (C¹, ¹J_{PC} 91.5 Hz), 4.84 d (C², ²J_{PC} 7.2 Hz), 57.14 d (C³, ¹J_{PC} 111.9 Hz), 47.08 d (C⁴, ³J_{PC} 10.0 Hz). ³¹P NMR spectrum, δ_P, ppm: 42.99 s.

Phosphinate IIIb was obtained analogously.

Trimethylsilyl [2-[methyl(phenyl)(vinyl)silyl]ethyl](*N*-piperidinomethyl)phosphinate (IIIb). Yield 72%, bp 189°C (2 mm), n_D^{20} 1.5085. ¹³C NMR spectrum, δ_C , ppm: 21.60 d (C¹, ¹J_{PC} 91.2 Hz), 4.78 d (C², ²J_{PC} 6.7 Hz), 56.31 d (C³, ¹J_{PC} 117.7 Hz), 55.68 d (C⁴, ³J_{PC} 8.3 Hz). ³¹P NMR spectrum, δ_P , ppm: 43.32 s.

Sodium [2-[methyl(phenyl)(vinyl)silyl]ethyl]phosphonite (IV). To a solution of 1.62 g of sodium methylate in 50 ml of methanol, a solution of 11.5 g of phosphonite in 10 ml of diethyl ether was added with stirring at 10°C. The resulting mixture was heated to boil, the solvent was removed, and the residue was kept in a vacuum (1 mm) for 1 h to obtain 7.6 g (96%) of salt **IV**. ¹H NMR spectrum, δ , ppm: 6.84 d.t (PH, ¹*J*_{PH} 495.6, ³*J*_{HH} 1.6 Hz). ¹³C NMR spectrum, $\delta_{\rm C}$, ppm: 25.84 d (C¹, ¹*J*_{PC} 88.3 Hz), 5.23 d (C², ²*J*_{PC} 5.2 Hz). ³¹P NMR spectrum, $\delta_{\rm P}$, ppm: 30.93 s. Found, %: C 50.26; H 6.09. C₁₁H₁₆NaO₂PSi. Calculated, %: C 50.37; H 6.15.

Salts V and VI were obtained analogously.

Disodium 3-[methyl(phenyl)sila]pentane-1,5-diphosphonate (V). Yield 94%. ¹H NMR spectrum, δ, ppm: 6.83 d.t (PH, ${}^{1}J_{PH}$ 499.2, ${}^{3}J_{HH}$ 1.8 Hz). ${}^{13}C$ NMR spectrum, δ_{C} , ppm: 25.46 d (C¹, ${}^{1}J_{PC}$ 88.0 Hz), 4.33 d (C², ${}^{2}J_{PC}$ 5.4 Hz). ${}^{31}P$ NMR spectrum, δ_{P} , ppm: 31.06 s. Found, %: C 37.59; H 5.10. C₁₁H₁₈Na₂O₄ · P₂Si. Calculated, %: C 37.72; H 5.18.

Sodium dimethylaminomethyl[2-[methyl-(phenyl)vinylsilyl]ethyl]phosphinate (VIa). Yield 95%. ¹H NMR spectrum, δ, ppm: 2.49 d ($C^{3}H_{2}$, ²J_{PH} 9.2 Hz), 2.23 s ($C^{4}H_{3}$). ¹³C NMR spectrum, δ_C, ppm: 24.30 d (C^{1} , ¹J_{PC} 89.7 Hz), 6.27 d (C^{2} , ²J_{PC} 6.4 Hz), 58.06 d (C^{3} , ¹J_{PC} 99.4 Hz), 47.27 d (C^{4} , ³J_{PC} 7.9 Hz). ³¹P NMR spectrum, δ_P, ppm: 37.95 s. Found, %: C 52.57; H 7.12. C₁₄H₂₃NNaO₂PSi. Calculated, %: C 52.65; H 7.26.

Sodium [2-[methyl(phenyl)(vinyl)silyl]ethyl](*N*piperidinomethyl)phosphinate (VIb). Yield 93%. ¹H NMR spectrum, δ, ppm: 2.50 d ($C^{3}H_{2}$, ${}^{2}J_{PH}$ 9.2 Hz), 2.42 t ($C^{4}H_{2}$, ${}^{3}J_{HH}$ 5.2 Hz). ¹³C NMR spectrum, δ_{C} , ppm: 25.01 d (C^{1} , ${}^{1}J_{PC}$ 88.5 Hz), 6.57 d (C^{2} , ${}^{2}J_{PC}$ 6.6 Hz), 57.83 d (C^{3} , ${}^{1}J_{PC}$ 98.6 Hz), 56.19 d (C^{4} , ${}^{3}J_{PC}$ 7.0 Hz). ³¹P NMR spectrum, δ_{P} , ppm: 38.66. Found, %: C 56.64; H 7.49. C₁₇H₂₇NNaO₂PSi. Calculated, %: C 56.80; H 7.57.

The NMR spectra were obtained on a Varian VXR-400 spectrometer in CDCl₃ or D₂O (salts IV-VI) against TMS (¹H, ¹³C) and 85% H₃PO₄ in D₂O (³¹P).

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