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Reaction of Bis(Trimethylsiloxy)phosphine with Trimethylsilane

M. G. Voronkov, A. E. Pestunovich, A. I. Albanov, and V. A. Kukhareva

Favorskii Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences,
ul. Favorskogo 1, Irkutsk, 664033 Russia
e-mail: voronkov@irioch.irk.ru

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Abstract—Bis(trimethylsilyl) [3-(trimethylsilyl)propyl]phosphonate and trimethylsilyl [3-(trimethylsilyl)propyl]-phosphinate are obtained by the reaction of bis(trimethylsiloxy)phosphine with trimethylallylsilane and converted into [3-(trimethylsilyl)propyl]phosphinic and [3-(trimethylsilyl)propyl]phosphonic acid, respectively, by the reaction with methanol.

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Bis(trimethylsiloxy)phosphine $(Me_3SiO)_2PH$ was first synthesized by the reaction of ammonium hypophosphite with trimethyl(diethylamino)silane or hexamethyldisilazane [1]. It was found that bis(trimethylsiloxy)phosphine is readily oxidized to bis(trimethylsilyl)phosphonate $(Me_3SiO)_2P(O)H$ and is self-ignited in air.

Addition of bis(trimethylsiloxy)phosphine to the C=C and C=O bonds was first realized in [1, 2]. Later on, the reactions of addition of bis(trimethylsiloxy)phosphine to double bonds attracted great interest since they lead to the earlier unknown or hardly accessible organophosphorus compounds. Addition of bis(trimethylsiloxy)phosphine to the C=C bond proceeds without a catalyst or in the presence of azoisobutyronitrile (AIBN) [1–5]. It was reported that bis(trimethylsiloxy)phosphine is readily added to *N,N*-diethyl(vinyl)sulfonamide in the absence of a catalyst to give the adduct in 78% yield. Along with this, a side product of addition of trimethylsilylhypophosphite to two molecules of *N,N*-diethyl(vinyl)sulfonamide was isolated in 12% yield [3]. The addition of bis(trimethylsiloxy)phosphine to the derivatives of vinylsilanes $(CH_2{=}CH)_nSiX_{4-n}$ (X = Alk, AlkO, n = 1, 2) is thoroughly studied [1, 2, 5]. However, its reaction with Si-substituted allylsilanes $CH_2{=}CHCH_2SiX_3$ proceeds with difficulty and, hence, is poorly studied [2].

We have studied the possibility of addition of bis(trimethylsiloxy)phosphine to trimethylallylsilane in the molar ratio of 1:1 in the presence of AIBN (0.03 mol %) without solvent in the argon atmosphere. After reflux of the reaction mixture during 7 h, 70% of the starting trimethylallylsilane remained intact; therefore, the reaction is sluggish under the studied conditions. Further operations in the contact with air and investigation of the reaction mixture led to substantial changes of the composition of the reaction mixture due to interaction with the atmospheric oxygen and moisture. The methods of ^1H, ^{13}C, ^{29}Si, ^{31}P NMR and IR spectroscopy revealed the presence of unreacted bis(trimethylsiloxy)phosphine, trimethylsilylhypophosphite (**I**), bis(trimethylsilyl) phosphonate (**II**), bis(trimethylsilyl) [3-(trimethylsilyl)propyl]phosphonate (**III**), trimethylsilyl [3-(trimethylsilyl)propyl]phosphonite (**IV**), tris(trimethylsilyl) phosphate (**V**). The expected product of addition of bis(trimethylsiloxy)phosphine to trimethylallylsilane, bis(trimethylsilyl) [3-(trimethylsilyl)propyl]phosphonite was not detected. The formation of the above products is the result of the following reactions.

$$(Me_3SiO)_2PH + H_2O \rightarrow \underset{\textbf{I}}{Me_3SiOP({=}O)H_2} + Me_3SiOH,$$

$$(Me_3SiO)_2PH \xrightarrow{+\,0.5\,O_2} \underset{\textbf{II}}{(Me_3SiO)_2P({=}O)H},$$

$$(Me_3SiO)_2PH + CH_2{=}CHCH_2SiMe_3$$

$$\rightarrow [(Me_3SiO)_2PCH_2CH_2CH_2SiMe_3]$$

$$\xrightarrow{+\,0.5\,O_2} \underset{\textbf{III}}{(Me_3SiO)_2P({=}O)CH_2CH_2CH_2SiMe_3},$$

$$\mathrm{Me_3SiOP(=O)H_2 + CH_2{=}CHCH_2SiMe_3}$$

I

$$\rightarrow \mathrm{(Me_3SiO)HP(=O)CH_2CH_2CH_2SiMe_3},$$

IV

$$\mathrm{(Me_3SiO)_2PH + Me_3SiOH} \rightarrow \mathrm{[(Me_3SiO)_3P]}$$

$$\xrightarrow{+\,0.5\,\mathrm{O_2}} \mathrm{(Me_3SiO)_3P{=}O}.$$

V

Bis(trimethylsilyl) [3-(trimethylsilyl)propyl]phosphonate $\mathrm{(Me_3SiO)_2P(=O)(CH_2)_3SiMe_3}$ (**III**) and trimethylsilyl [3-(trimethylsilyl)propyl]phosphonite $\mathrm{(Me_3SiO)HP\cdot(=O)CH_2CH_2CH_2SiMe_3}$ (**IV**) were not known so far. Their yields were 1 and 6%, respectively, calculated to the starting bis(trimethylsiloxy)phosphine. In the IR spectrum of phosphinate **IV** the bands at 2380 (P–H), 1240 (P=O), 850 ($\mathrm{SiMe_3}$), 1050 (Si–O–P) $\mathrm{cm^{-1}}$ are present.

By the reaction with methanol, compounds **IV** and **III** were converted into the liquid 3-(trimethylsilylpropyl)-phosphinic **VI** and crystalline 3-(trimethylsilyl)propyl)-phosphonic **VII** acids.

$$\mathrm{(Me_3SiO)HP(=O)(CH_2)_3SiMe_3 + MeOH}$$

IV

$$\rightarrow \mathrm{(HO)HP(=O)(CH_2)_3SiMe_3 + Me_3SiOMe},$$

VI

$$\mathrm{(Me_3SiO)_2P(=O)(CH_2)_3SiMe_3 + 2\,MeO}$$

III

$$\rightarrow \mathrm{(HO)_2P(=O)(CH_2)_3SiMe_3 + 2\,Me_3SiOMe}.$$

VII

The ionization constant pK_1 of 3-(trimethylsilyl)propyl)phosphinic acid $\mathrm{(HO)HP(=O)(CH_2)_3SiMe_3}$ (**VI**) determined by the method of potentiometric titration in water is 3.85. Hence, it is weaker than the acids of general formula $\mathrm{(HO)_2P(=O)(CH_2)_\mathit{n}SiMe_3}$, $n = 1–3$ [6].

Compounds **III** and **IV** were isolated as a binary mixture and investigated by the methods of multinuclear NMR and IR spectroscopy. The structure of the hitherto unknown acid **VI** was proved by the method of multinuclear NMR.

EXPERIMENTAL

IR spectra were recorded in thin layer on a Specord IR-75 spectrophotometer.

NMR spectra of 5–10% solutions of compounds in $\mathrm{C_6D_6}$ and $\mathrm{CDCl_3}$ were obtained on a Bruker DPX 400 spectrometer using HMDS as an internal standard.

Bis(trimethylsilyl) [3-(trimethylsilyl)propyl]phosphonate (III) and trimethylsilyl [3-(trimethylsilyl)-propyl]phosphinate (IV). Mixture of 6.2 g of bis-(trimethylsiloxy)phosphine, 4.6 g of trimethylallylsilane and 0.05 g AIBN was refluxed during 7 h. After vacuum distillation, 3.3 g of unreacted trimethylallylsilane was isolated and 2.7 g of a fraction with bp 53–80°C (10 mm Hg), consisting of bis(trimethylsiloxy) phosphine, trimethylsilylhypophosphite **I** and bis-(trimethylsilyl) phosphonate **II**. Trimethylsilyl hypophosphite **I** has the structure corresponding to formula $\mathrm{Me_3SiOP(=O)PH_2}$ trimethylsilyl phosphonite rather than $\mathrm{Me_3SiOPHOH}$. This is unequivocally proved by splitting of the phosphorus signal (δ_P –2.0 ppm) into a triplet on two hydrogen atoms with $J_{P–H}$ 552.37 Hz. A higher-boiling fraction with bp 85–90°C (5 mm Hg) contains, from the ^{31}P NMR data, 0.35 g of bis(trimethylsilyl) phosphonate **II** and 0.1 g of tris(trimethylsilyl) phosphate **V**. ^{31}P NMR of **V**, δ_P, ppm: –25.36. The high-boiling fraction with bp 108–111°C (4 mm Hg) contains, from the ^{31}P NMR data, 0.12 g of *O,O*-bis(trimethylsilyl) [3-(trimethyl)silylpropyl]phosphonate **III** and 0.45 g of trimethylsilyl [3-(trimethyl)silylpropyl]phosphinate **IV**. Bis(trimethylsilyl) [3-(trimethyl)-silylpropyl]phosphonate **III**, ^{1}H NMR, δ, ppm: 0.67 ($\mathrm{CH_2Si}$), 1.61–1.80 ($\mathrm{CH_2CH_2P}$), 0.36 ($\mathrm{Me_3SiO}$), 0.00 ($\mathrm{Me_3SiCH_2}$). ^{13}C NMR, δ_C, ppm: 17.60 ($\mathrm{CH_2Si}$), 32.08 ($\mathrm{CH_2P}$, $^1J_{C–P}$ 142 Hz), 0.05 ($\mathrm{Me_3SiO}$), –2.32 ($\mathrm{Me_3Si}$). ^{31}P NMR, δ_P, ppm: 13.45. ^{29}Si NMR, δ_{Si}, ppm: 18.7. Trimethylsilyl [3-(trimethylsilyl)propyl]phosphinate **IV**, ^{1}H NMR, δ, ppm: 0.67 ($\mathrm{CH_2Si}$), 1.61–1.80 ($\mathrm{CH_2CH_2P}$), 0.36 ($\mathrm{Me_3SiO}$), 0.00 ($\mathrm{Me_3Si}$), 7.1 (P–H). ^{13}C NMR, δ_C, ppm: 17.50 ($\mathrm{CH_2Si}$), 15.34 ($\mathrm{CH_2}$), 34.1 ($\mathrm{CH_2P}$, $^1J_{C–P}$ 92.8 Hz), 0.41 ($\mathrm{Me_3SiO}$), –2.32 ($\mathrm{Me_3Si}$). ^{31}P NMR, δ_P, ppm: 26.6, J_{PH} 535 Hz. ^{29}Si NMR, δ_{Si}, ppm: 22.05 ($\mathrm{Me_3SiO}$), 0.24 ($\mathrm{Me_3SiCH_2}$), $^2J_{Si–P}$ 5.83 Hz.

Trimethylsilylpropylphosphinic acid (VI). Mixture of 0.3 g of phosphonate **III**, phosphinate **IV**, 2 ml of methanol, 2 ml of methylene chloride was heated to reflux for 1.5 h. Low-boiling compounds were removed under vacuum, the residue dried for 1 h at 3 mm Hg. The mixture of liquid trimethylsilylpropylphosphinic acid **VI** and crystalline phosphonic acid **VII** was isolated. Trimethylsilylpropylphosphinic acid **VI**, ^{1}H NMR, δ, ppm: 0.66 ($\mathrm{CH_2Si}$), 1.67 (C–$\mathrm{CH_2}$–C), 1.86 (P–$\mathrm{CH_2}$), 0.04 ($\mathrm{Me_3Si}$), 10.82 (OH), 7.15 (P–H). ^{13}C NMR, δ_C, ppm: 18.12 ($\mathrm{CH_2Si}$, $^3J_{C–P}$ 14.19 Hz), 15.58 (C–$\mathrm{CH_2}$–C), 32.68 ($\mathrm{CH_2P}$, $^1J_{C–P}$ 92.4 Hz), –1.7 ($\mathrm{SiMe_3}$). ^{31}P NMR, δ_P, ppm: 39.11, $J_{P–H}$ 543.6 Hz. ^{29}Si NMR, δ_{Si}, ppm: 0.89. Found, %: P

17.19. $C_6H_{17}PO_2Si$. Calculated, %: P 17.10. The structure of the earlier described crystalline trimethylsilylpropylphosphonic acid **VII** [2] was proved by multinuclear NMR. Trimethylsilylpropylphosphonic acid **VII**, ^1H NMR, ppm: 6.88 (P–H). ^{13}C NMR, δ_C, ppm: 18.30 (CH_2Si), 17.16 (C–CH_2–C), 30.13 (CH_2P). ^{31}P NMR, δ_P, ppm: 35.32. ^{29}Si NMR, δ_{Si}, ppm: 0.88.

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