

Silicon-Containing Dimethylphosphoric Acid Amides

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Abstract— α -Silylmethylamines $\text{MeNHCH}_2\text{SiMe}_n(\text{OMe})_{3-n}$ ($n = 0, 2$) were involved into Todd–Atherton reaction with $(\text{MeO})_2\text{P}(\text{O})\text{H}$ giving *N*-methyl-*N*-trimethoxysilylmethyl- and *N*-methyl-*N*-dimethyl-(methoxy)silylmethylamides of dimethylphosphoric acid. A reaction of these compounds with $\text{BF}_3\cdot\text{Et}_2\text{O}$ led to the formation of the corresponding *N*-methyl-*N*-trifluoro- and *N*-methyl-*N*-(dimethyl)fluorosilylmethylamides of dimethylphosphoric acid. $(\text{MeO})_2\text{P}(\text{O})\text{N}(\text{Me})\text{CH}_2\text{SiF}_3$ existed as an (O–Si)-chelate with a pentacoordinate silicon due to the occurrence of a rare and unstudied intramolecular coordinating interaction $\text{P}=\text{O} \rightarrow \text{Si}$.

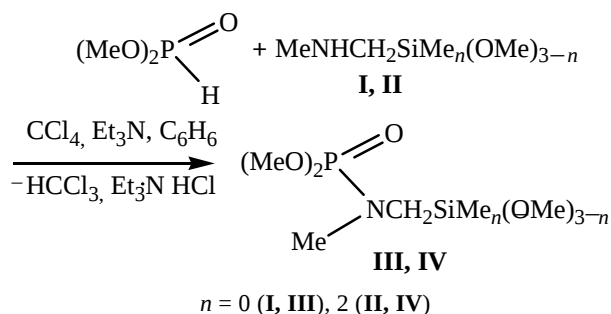
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A search for synthetic routes to polyheteroatomic structures with several reactive sites within a single molecule, the study of their structures and reactivity is among the most promising and extensively developing fields of the modern organoelemental chemistry. For instance, the chemistry of silicon-containing phosphorus compounds is effectively elaborated nowadays [1–9]. The introduction of a silyl group into the α -position with respect to a functional fragment in compounds XCH_2SiY_3 ($\text{X} = \text{Hlg, RO, RS, RR'N}$) causes a change in the physicochemical properties and reactivity of the functional group as compared with the carbon analogs XCH_2CY_3 [10–15]. This phenomenon originates from the intramolecular electronic interactions in the XCH_2Si moiety, but their nature remains unstudied up till now [16–20].

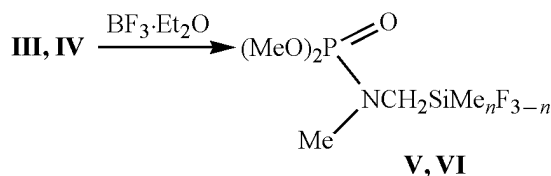
Compounds containing an O–P(O)–N fragment play an important part in the processes occurring in the living organisms and in the last time they are widely used as bidentate P,N-ligands in the metal complex catalysis [21–23]. We presume that a modification of amidoesters of phosphoric acids by introduction of a silyl group into the α -position with respect to the nitrogen may provide polyfunctional compounds with unique physicochemical characteristics. To this end we investigated the behavior of very reactive α -silylmethylamines $\text{R}_2\text{NCH}_2\text{SiX}_3$ [24–27] in the Todd–Atherton reaction. This reaction is a convenient and efficient method of oxidative phosphorylation of nucleophiles by the treatment with hydrophosphoryl compounds, CCl_4 , and bases [28–34].

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We report here the first results obtained in the study of reaction between α -silylmethylamine $\text{MeNHCH}_2\text{SiMe}_n(\text{OMe})_{3-n}$ and dimethylphosphite $(\text{MeO})_2\text{P}(\text{O})\text{H}$.



The reaction proceeded in benzene in the presence of equimolar amount of CCl_4 and excess Et_3N giving dimethylphosphoric acid *N*-methyl-*N*-trimethoxysilylmethyl- (**III**) or *N*-methyl-*N*-dimethyl(methoxy)silylmethylamide (**IV**). The use of an equimolar quantity of Et_3N resulted in the decrease of the yield of target products due to the formation of organosilicon amine hydrochloride. Compounds **III** and **IV** are oily high boiling fluids with a slight odor, they are well soluble in C_6H_6 , Et_2O , CHCl_3 , and CH_2Cl_2 . Their structure was confirmed by the data of multinuclear magnetic resonance spectroscopy. The reaction of compounds **III** and **IV** with boron trifluoride etherate led to the formation of the corresponding dimethylphosphoric acid *N*-methyl-*N*-fluorosilylmethylamides.



$n = 0$ (**V**), 2 (**VI**)

Compounds obtained are viscous yellowish opalescent fluids which do not crystallize even at prolonged storage; they decompose at heating. Their structure was investigated by multinuclear magnetic resonance spectroscopy. Some features of NMR spectra of dimethylphosphoric acid *N*-methyl-*N*-(trifluorosilylmethyl)amide (**V**) are worth mentioning: 1) The shielding of silicon atom (δ –107.22 ppm) is larger by 36 ppm compared to the model compound $\text{ClCH}_2\text{SiF}_3$ (δ –71 ppm); 2) $^1J(^{29}\text{Si}-^{19}\text{F})$ 221.1 Hz is less by 46 Hz than $^1J(^{29}\text{Si}-^{19}\text{F})$ 267 Hz in $\text{ClCH}_2\text{SiF}_3$; 3) the shielding of ^{19}F (δ –131.29 ppm) decreases by 13 ppm with respect to $\text{ClCH}_2\text{SiF}_3$ (δ –143.99 ppm); 4) the shielding of ^{31}P (δ 20.19 ppm) decreases by 5.5 ppm with respect to ^{31}P in compound **III** (δ 14.57 ppm).

Similar features of NMR spectra are characteristic of the spectra of pentacoordinate silicon compounds with an intramolecular coordination bond $\text{C}=\text{O} \rightarrow \text{Si}$; carboxylic acids *N*-methyl-*N*-trifluorosilylmethylamides [35] and aroyloxymethyltrifluorosilanes [36, 37]. Our results unambiguously show that compound **V** exists as an (O–Si)-chelate with an intramolecular coordinating interaction $\text{P}=\text{O} \rightarrow \text{Si}$. However according to the data of multinuclear magnetic resonance spectroscopy the silicon atom in compound **VI** is tetracoordinate. This difference in the structure of compounds **V** and **VI** is presumably due to an essential change in the silicon acceptor ability. The extent of the donor-acceptor interaction in the silane complexes with amines grows with the number of fluorine atoms attached to silicon [38].

Although the $\text{P}=\text{O}$ group in phosphorus compounds possesses a high donor capacity [39, 40] and a large number of complexes is known involving it, only some examples of compounds are described containing an intramolecular coordination bond $\text{P}=\text{O} \rightarrow \text{M}$ ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$) [41–46]. Compound **V** is the first instance of (O–Si)-chelate with an intramolecular coordination bond $\text{P}=\text{O} \rightarrow \text{Si}$ in the series of dialkylphosphoric acids amides. To our regret the limited number of findings do not permit the analysis of the effect of the valence surrounding of

the silyl and phosphoryl groups on the degree of $\text{P}=\text{O} \rightarrow \text{Si}$ coordination.

EXPERIMENTAL

NMR spectra were registered from 20% solutions of compounds in CDCl_3 on a spectrometer Bruker DPX-400 using TMS or cyclohexane as internal reference. Organosilicon amines **I** and **II** were prepared by procedures developed for amination of $\text{ClCH}_2\text{SiMe}_n(\text{OAlk})_{3-n}$ [47]. The solvents were purified as described in [48]. All the syntheses were carried out in the atmosphere of dry argon.

Dimethylphosphoric acid *N*-methyl-*N*-(trifluoromethoxy)silylmethylamide (III). To a mixture of 0.01 mol of dimethyl phosphite, 0.01 mol of amine **I**, and 0.15 mol of Et_3N in 75 ml of anhydrous benzene was slowly added dropwise maintaining the reaction temperature below 20°C 0.01 mol of CCl_4 in 10 ml of anhydrous benzene. The reaction mixture was stored at room temperature for 12 h, the separated precipitate was filtered off and washed with anhydrous ethyl ether (2×10 ml). The ether washings were combined with filtrate, the solvent was removed in a vacuum, and the residue was subjected to distillation. Yield 75%, bp $140\text{--}142^\circ\text{C}$ (3 mm Hg), n_D^{20} 1.4273. ^1H NMR spectrum, δ , ppm: 2.62 d (2H, NCH_2Si , 3J 7.7 Hz), 2.71 d (3H, NMe, 3J 10.51 Hz), 3.60 s (9H, SiOMe), 3.67 d (6H, POMe, 3J 10.88 Hz). ^{13}C NMR spectrum, δ , ppm: 32.12 s (NCH_2Si), 35.51 d (NMe, 2J 2.95 Hz), 50.34 s (SiOMe), 52.60 (POMe). ^{29}Si NMR spectrum, δ , ppm: –50.32 d (3J 13.61 Hz). ^{31}P NMR spectrum, δ , ppm: 14.57. Found, %: C 30.53; H 7.21; N 5.04. $\text{C}_7\text{H}_{20}\text{NO}_6\text{PSi}$. Calculated, %: C 30.76; H 7.38; N 5.13.

Dimethylphosphoric acid *N*-methyl-*N*-(methoxy)-dimethylsilylmethylamide (IV) was similarly prepared from amine **II**. Yield 82%, bp $110\text{--}112^\circ\text{C}$ (3 mm Hg), n_D^{20} 1.4359. ^1H NMR spectrum, δ , ppm: 0.20 s (6H, SiMe_2), 2.58 d (2H, NCH_2Si , 3J 7.95 Hz), 2.71 d (NMe, 3J 10.39 Hz), 3.46 s (SiOMe), 3.67 d (6H, POMe, 3J 10.88 Hz). ^{13}C NMR spectrum, δ , ppm: –3.13 (SiMe_2), 38.24 (NCH_2Si), 35.92 d (NMe, 2J 3.69 Hz), 50.09 s (SiOMe), 52.66 (POMe). ^{29}Si NMR spectrum, δ , ppm: 16.5 d (3J 9.23 Hz). ^{31}P NMR spectrum, δ , ppm: 14.78. Found, %: C 34.54; H 8.03; N 5.91. $\text{C}_7\text{H}_{20}\text{NO}_4\text{PSi}$. Calculated, %: C 34.84; H 8.35; N 5.80.

Dimethylphosphoric acid *N*-methyl-*N*-(trifluorosilylmethyl)amide (V). To a solution of 0.005 mol of compound **III** in 15 ml of anhydrous ether was added

dropwise at stirring an equimolar amount of freshly distilled boron trifluoride etherate in 15 ml of ether. The reaction mixture was maintained for 2 h at room temperature. The ether was removed in a vacuum, the residue was maintained in a vacuum of an oil pump for 2 h at room temperature. We obtained a viscous substance decomposing at heating. ^1H NMR spectrum, δ , ppm: 2.57 d (3H, NMe, 3J 9.86 Hz), 2.72 d (2H, NCH_2Si , 3J 10.3 Hz), 3.69 d (6H, MeO, 3J 11.79 Hz). ^{13}C NMR spectrum, δ , ppm: 32.64 d (NMe, 2J 3.07 Hz), 40.15 q.d (NCH_2Si , 2J 27.22, 2J 9.2 Hz), 54.43 d (OMe, 2J 5.37 Hz). ^{29}Si NMR spectrum, δ , ppm: -107.22 q.d (1J 221.1, 3J 23.33 Hz). ^{19}F NMR spectrum, δ , ppm: -131.29 d (4J 13.5 Hz). ^{31}P NMR spectrum, δ , ppm: 20.19 q. Found, %: C 20.51; H 4.73; N 6.11. $\text{C}_4\text{H}_{11}\text{F}_3\text{NO}_3\text{PSi}$. Calculated, %: C 20.26; H 4.67; N 5.91.

Dimethylphosphoric acid *N*-methyl-*N*-(fluorodimethylsilylmethyl)amide (VI) was prepared similarly from compound IV. ^1H NMR spectrum, δ , ppm: 0.32 d (6H, SiMe_2 , 3J 7.58 Hz), 2.63 d.d (2H, NCH_2Si , $^3J_{\text{H-F}}$ 6.36, $^3J_{\text{H-P}}$ 8.93 Hz), 2.69 d (3H, NMe, $^3J_{\text{H-P}}$ 10.51 Hz), 3.67 d (6H, POMe, $^3J_{\text{H-P}}$ 11.0 Hz). ^{13}C NMR spectrum, δ , ppm: -1.84 d (SiMe_2 , $^2J_{\text{C-F}}$ 14.48 Hz), 39.64 d (NCH_2Si , 2J 17.66 Hz), 36.44 d (NMe, 2J 2.12 Hz), 52.96 d (POMe, 2J 6.0 Hz). ^{29}Si NMR spectrum, δ , ppm: 29.3 d.d (1J 283.8, 3J 8.26 Hz). ^{31}P NMR spectrum, δ , ppm: 14.35. Found, %: C 31.03; H 7.23; N 6.02. $\text{C}_6\text{H}_{17}\text{FNO}_3\text{PSi}$. Calculated, %: C 31.43; H 7.47; N 6.11.

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