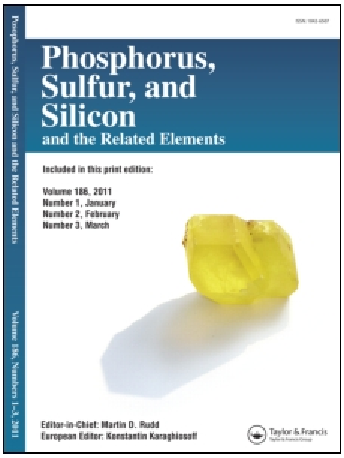

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# A FACILE SYNTHESIS OF TRIALKYLSILYLPHOSPHITES AND PHOSPHATES

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# A FACILE SYNTHESIS OF TRIALKYLSILYLPHOSPHITES AND PHOSPHATES

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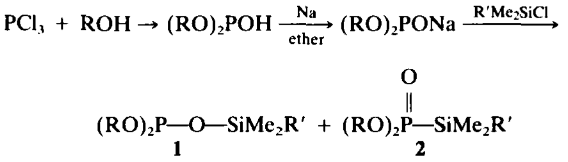
Trialkylsilylphosphites (**1a–1d**) and trialkylsilylphosphates (**2a–2d**) were synthesized in good yield by a facile method. The method could be easily used to prepare P—O—Si bond and P—Si bond compounds from dialkylphosphites and trialkylchlorosilanes.

*Key words:* Phosphates; trialkylsilylphosphites; trialkylchlorosilanes.

## INTRODUCTION

The special properties and uses of some organic compounds containing both phosphorus and silicon atoms have received increasing attention in recent years. A few papers have reported the synthesis, properties, and applications of this type of compound.[1-6] A number of phosphorated organosilicon compounds have proven to be useful reagents or intermediates in organic synthesis.[7-9]

In this paper we report a new method for the synthesis of trialkylsilylphosphites and trialkylsilylphosphates, which have obvious physiological activities and potential medical functions.[10] The synthetic route is indicated in Equation (1).



$$PCl_3 + ROH \rightarrow (RO)_2POH \xrightarrow[\text{ether}]{Na} (RO)_2PONa \xrightarrow{R'Me_2SiCl}$$

$$\underset{\mathbf{1}}{(RO)_2P{-}O{-}SiMe_2R'} + \underset{\mathbf{2}}{(RO)_2\overset{\overset{O}{\|}}{P}{-}SiMe_2R'} \qquad (1)$$

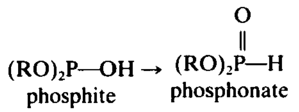
R, R′: **1a** = Me, Me; **1b** = Me, Et; **1c** = Et, Me; **1d** = Et, Et;
**2a** = Et, Me; **2b** = Et, Et; **2c** = Et, n-Pr; **2d** = Et, n-Bu.

The compounds with a P—O—Si bond and P—Si bond can be obtained by control of the reaction conditions. At room temperature, the main product is silylphosphite 1. By increasing the temperature, however, silylphosphate 2 is formed as the principle product. Eight silicon-phosphorus compounds (**1a–1d**, **2a–2d**) have been synthesized in this way.

## DISCUSSION

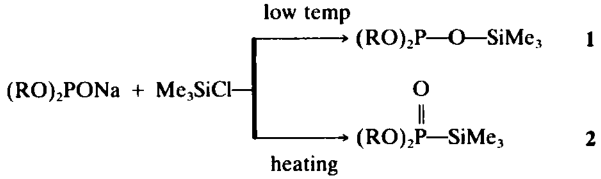
In the synthesis of diethyl trimethylsilylphosphite (**1c**, a commonly used silicon-phosphorus reagent), Bugerko suggested that diethyl phosphite is transformed into its sodium salt in the presence of sodium hydride in tetrahydrofuran, the salt solution then reacts with trimethylchlorosilane to form the product in a yield of 50–55%.[11] Metallic sodium was reacted with diethyl phosphite in ether, then trimethylchlorosilane was added dropwise to the metallic salt solution and **1c** was obtained in good yield (76%).

The dialkylphosphites are neutral substances which do not react with aqueous bases to form metallic salt solutions.[12] In the IR spectra, they exhibit a strong absorption at about 1250 $cm^{-1}$ (the characteristic frequency for the P═O groups). The chemical shifts in $^{31}P$ NMR are found in the range of 3 to 15 ppm. The resonance peak is split into a doublet, which shows one hydrogen proton is attached directly to phosphorus. The constant $J_{P—H}$ is 660–760 Hz. All the facts demonstrate that the dialkylphosphites exist mainly in the phosphonate form.



$$\underset{\text{phosphite}}{(RO)_2P{-}OH} \rightarrow \underset{\text{phosphonate}}{(RO)_2\overset{\overset{\displaystyle O}{\|}}{P}{-}H} \qquad (2)$$

It is of interest to note that while the metallic salt solution of dialkylphosphonate exhibits a strong absorption at 1050 $cm^{-1}$ for $P{-}O^-$ and P—O—R groups, there is a complete absence of the P═O bond. (The slight absorption found in a few cases could be attributed to hydrolysis by atmospheric moisture during transfer of the sample). This indicates the metallic sodium has transformed dialkylphosphonate into $(RO)_2P{-}O^-Na^+$, which then reacted with $Me_3SiCl$ at room temperature to form the P—O—Si bond compound **1**. Compound **1c**, for example, has been prepared by the action of trimethylchlorosilane on di-ethyl sodiophosphonate at 0°C for 2 hours. The chemical shift of **1c** in the $^{31}P$ NMR spectrum is 127 ppm. It is trivalent phosphorus. On heating the reaction mixture, the P—Si bond compounds **2** are formed. With the temperature over 80°C, trimethylchlorosilane is reacted with di-ethyl sodiophosphonate for 5 hours, and **2a** is produced almost without **1c**. The chemical shift of **2a** in the $^{31}P$ NMR spectrum is 25 ppm. It belongs to pentavalent phosphorus. The reaction may be indicated as follows:



$$(RO)_2PONa + Me_3SiCl \begin{cases} \xrightarrow{\text{low temp}} (RO)_2P{-}O{-}SiMe_3 & \mathbf{1} \\ \xrightarrow[\text{heating}]{} (RO)_2\overset{\overset{\displaystyle O}{\|}}{P}{-}SiMe_3 & \mathbf{2} \end{cases}$$

On heating to over 80°C, in the absence of air, compound **1** converts to **2**. It is known that the P—Si bond compounds are very unstable and difficult to form in most situations, but here a stronger P═O bond forming may be the driving force for the transformation. The $Me_3Si$-group behaves in a manner analogous to a proton in Equation (2). In general, many organic compounds in which the hydrogen proton is replaced by $Me_3Si$-group have common features. But the P—O—Si bond is more stable than the P—O—H bond.[10] Compound **2** is reactive, it shows high sensitivity to nucleophilic attacks by water, alcohol, phenol and so on.

Compounds **2a–2d** exhibit a strong P=O absorption near 1250 $cm^{-1}$ like the corresponding phosphonates in IR spectroscopy. The P—Si stretch in these compounds fall at 450 $cm^{-1}$, where there is very little interference from other bands. The resonances of alkyl carbon atoms adjacent to silicon are detected as easily as their attached protons by the unusually shielded position in the $^{13}C$ NMR spectrum. The resonances of Si—$CH_3$ carbon atoms in **2** occur 18.5 ppm relative to TMS, for example, and is more shielded than the analogous carbon in the C—$CH_3$ analog. There are differences in the trends of the chemical shifts observed for these carbons relative to the trends observed in the proton NMR of Si—$CH_3$ groups. The chemical shifts for **2** in $^{31}P$ NMR are 23–25 ppm, in the range of pentavalent phosphorus, which is a little lower field than the analogous phosphonates owing to the deshielding of the silicon attached directly to phosphorus.

## EXPERIMENTAL

The reactions were carried out under a nitrogen atmosphere with the exclusion of oxygen and moisture. All reagents were freshly distilled before use.

Infrared spectra were recorded on a Perkin-Elmer Model 983 spectrophotometer. Nuclear magnetic resonance spectra were measured on a Varian Associates Model XL-200 spectrometer, chemical shifts were reported in ppm on the scale relative to tetramethylsilane internal standard ($^1H$) or 85% phosphoric acid external standard ($^{31}P$). Mass spectra were obtained with a HP5988 GC-MS spectrometer.

Dimethyl trimethylsilyl phosphite (**1a**): 48 g (1.5 mol) of methanol and 100 ml of petroleum ether (30–60°C) was cooled to 0°C, then 68.7 g (0.5 mol) of phosphorus trichloride in 50 ml of petroleum ether was added dropwise with stirring at 50°C for 1 h. Distillation at atmospheric pressure removed solvent and vacuum distillation gave a 90% yield of dimethyl phosphite, bp. 55–58°C (10 mm).

5.5 g (50 mmol) of dimethyl phosphite was added to a suspension of metallic sodium (1.2 g, 50 mmol) in 50 ml of anhydrous ether and stirred until the metallic sodium disappearance. To the mixture, 5.4 g (50 mmol) of trimethylchlorosilane was added at 0°C, then stirred for 1.5 h at room temperature. The filtrate was separated from the residue by centrifuging. The solvent was removed and the residual liquid was distilled under reduced pressure to give 6.5 g of **1a** (72%). bp. 62–64°C (17 mm). IR: 1060 (Si—O), 1030 (P—O—C); $^1H$ NMR ($CDCl_3$): 0.1 (s, 9H, 3 × $SiCH_3$), 3.5 (d, 6H, 2 × $OCH_3$), $^{31}P$ NMR: 127.8.

The other compounds were synthesized in the same way as **1a** and so only their physical data were given.

Dimethyl dimethylethylsilyl phosphite (**1b**): bp. 65–67°C (15 mm), 64% yield. IR: 1150 (Si—O), 1030 (P—O—C); $^1H$ NMR ($CDCl_3$): 0.1 (d, 6H, 2 × $OCH_3$), 0.8–1.2 (m, 5H, $SiCH_2CH_3$), 3.5 (d, 9H, 3 × $SiCH_3$); $^{31}P$ NMR: 128.1. Exact mass (75 eV) m/e calcd. for $C_8H_{17}O_3PSi$: 197. Found: 197.

Diethyl trimethylsilyl phosphite (**1c**): bp. 60–63°C (10 mm), 76% yield. IR: 1166 (Si—O), 1040 (P—O—C); $^1H$ NMR ($CDCl_3$): 0.1 (s, 9H, 3 × $SiCH_3$), 1.2 (t, 6H, 2 × $CH_3$), 4.1 (q, 4H, 2 × $OCH_2$); $^{31}P$ NMR: 126.9.

Diethyl dimethylethylsilyl phosphite (**1d**): bp. 65–68°C (12 mm), 61% yield. IR: 1165 (Si—O), 1040 (P—O—C); $^1H$ NMR ($CDCl_3$): 0.1 (s, 6H, 2 × $SiCH_3$), 0.8–1.2 (m, 5H, $SiCH_2CH_3$), 1.2 (t, 6H, 2 × $CH_3$), 4.1 (q, 4H, 2 × $OCH_3$); $^{31}P$ NMR: 127.2. Exact mass (75 eV) m/e calcd. for $C_8H_{21}O_3PSi$: 224.1, Found: 223.8.

*Diethyl trimethylsilyl phosphate* (**2a**), *was prepared in the similar way as* **1c**, *but the reaction was* performed at 70–80°C for 5 h. bp. 93–95°C (12 mm), 74% yield. IR: 1258 (P=O), 1038 (P—O—C). $^1H$ NMR ($CDCl_3$): 0.1 (s, 9H, 3 × $SiCH_3$), 1.2 (t, 6H, 2 × $CH_3$), 4.1 (q, 4H, 2 × $CH_2$); $^{13}C$ NMR: 18.5 (SiCH) 16.5 (—$CH_3$), 63.4 ($OCH_2$); $^{31}P$ NMR: 25.0; Anal. $C_7H_{19}O_3PSi$: C, 40.58; H, 8.74 (calcd. C, 39.81; H, 9.0).

Diethyl dimethylethylsilyl phosphate (**2b**): bp. 84–86°C (5 mm), 58% yield. IR: 1255 (P=O), 1045 (P—O—C). $^1H$ NMR ($CDCl_3$): 0.1 (s, 6H, 2 × $SiCH_3$), 0.9–1.2 (m, 5H, $SiCH_2CH_3$), 1.2 (t, 6H, 2 × $CH_3$), 4.1 (q, 4H, 2 × $OCH_2$); $^{31}P$ NMR: 24.3; Anal. $C_8H_{21}O_3PSi$: C, 42.15; H, 9.81 (calcd. C, 42.67; H, 9.33).

Diethyl dimethylpropylsilyl phosphate (**2c**): bp. 92–94°C (5 mm). 54% yield. IR: 1255 (P=O), 1040 (P—O—C). $^1H$ NMR ($CDCl_3$): 0.1 (s, 6H, 2 × $SiCH_3$), 0.5–1.0 (m, 4H, $CH_2CH_2$), 1.2–1.5 (m, 9H, 3 × $CH_3$), 4.1 (q, 4H, 2 × $OCH_2$); $^{31}P$ NMR: 24.2; Anal. $C_9H_{23}O_3PSi$: C, 45.18; H, 9.62 (calcd. C, 45.62; H, 9.84).

Diethyl dimethylbutylsilyl phosphate (**2d**): bp. 106–108°C (5 mm). 56% yield. IR: 1255 (P=O), 1045 (P—O—C). $^1$H NMR (CDCl$_3$): 0.1 (s, 6H, 2 × SiCH$_3$), 0.6–1.0 (m, 6H, 3 × CH$_2$), 1.2–1.5 (m, 9H, 3 × CH$_3$), 4.1 (q, 4H, 2 × OCH$_2$); $^{31}$P NMR: 23.8. Anal. $C_{10}H_{25}O_3PSi$: C, 47.43; H, 9.88 (calcd. C, 47.82; H, 9.35).

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