## **Dimethylsulfonium Methylide in Methylation of Silylphosphines**

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**Abstract**—Selective monodesilylation of bissilylated alkyl- or arylphosphines under the action of dimethylsulfonium methylide and the subsequent methylation of the resulting silyl phosphides with the sulfonium salt offers a convenient route to difficultly accessible monosilylated secondary methylalkyl(aryl)phosphines.

We showed previously [1] that dimethylsulfonium methylide I methylates primary alkyl- and arylphosphines and some secondary phosphines whose acidity in THF does not exceeds 30–32 p $K_a$  units to give the corresponding methylphosphines in high yields. The reaction occurs in two stages: the initial deprotonation of phosphines with ylide I is followed by the nucleophilic cleavage of the sulfonium salt with the resulting phosphide. The second stage determines the overall reaction rate. As trimethylsilylphosphines  $R^1R^2PSi$ ·Me<sub>3</sub> II are fairly reactive synthetic precursors of phosphides, it seemed important to study the reaction of compounds II with trimethylsulfonium iodide, which could be a simpler route to methylphosphines III [1].

$$\mathbf{R}^{1}\mathbf{R}^{2}\mathbf{P}\mathbf{S}\mathbf{i}\mathbf{M}\mathbf{e}_{3} + \mathbf{M}\mathbf{e}_{3}\mathbf{S}\mathbf{\overline{I}} \xrightarrow[-\mathbf{M}\mathbf{e}_{3}\mathbf{S}\mathbf{i}\mathbf{I}] \xrightarrow[-\mathbf{M}\mathbf{e}_{2}\mathbf{S}] \mathbf{II} \xrightarrow[-\mathbf{M}\mathbf{e}_{2}\mathbf{S}] \mathbf{R}^{1}\mathbf{R}^{2}\mathbf{P}\mathbf{M}\mathbf{e}.$$
(1)

After prolonged keeping of equimolar mixtures of silvlphosphines IIa and IIb  $[R^1 = R^2 = Ph (a), R^1 =$  $R^2 = i$ -Pr (b)] with the salt Me<sub>3</sub>S<sup>+</sup>I<sup>-</sup> in benzene or THF in sealed ampules at 20°C, the <sup>31</sup>P NMR spectra of the resulting mixtures contained no signals other than those of the starting silvlphosphines **IIa** and **IIb**  $(\delta_{\rm P}$  –57 and –44 ppm, respectively). Even after 2 h of heating at 100°C in benzene, in the case of silvl phosphine IIa, the conversion of the starting compounds in reaction (1) did not exceed 10%. Along with phosphine IIIa ( $\delta_{\rm P}$  –27.9 ppm) and approximately the same amount of unchanged silylphosphine IIa, the major reaction product was diphenylphosphine ( $\delta$  –42 ppm), evidently arising from protodesilvlation of silvlphosphine **IIa** with the sulfonium salt. Heating of silylphosphines IIa and IIb with  $Me_3S^+I^-$  in THF for 2 h at 100°C results in complete disappearance of the signals of the starting silylphosphines IIa and IIb from the <sup>31</sup>P NMR spectra, but the

formed compounds with the downfield signals at  $\delta_{\mathbf{p}}$ 22 and 42 ppm are, evidently, phosphonium salts rather than the products of monomethylation of silylphosphines IIa and IIb. Special experiments showed that THF is not cleaved with silvlphosphines **II** in 2 h at 100°C. Thus, reaction (1) is of no promise as a route to methylphosphines III. Therefore, we studied the reaction of silvlphosphines **II** with dimethylsulfonium methylide  $Me_2S^+$ -C<sup>-</sup>H<sub>2</sub> I. This reaction can be of separate interest, because, due to the low energy of the P–Si bond (~50 kcal mol<sup>-1</sup> [2]), ylide I can be a nucleophilic agent capable of desilylation of silylphosphines **II** with the formation of phosphides and silvlated sulfonium salt. These compounds can further react according to scheme (2), and realization of pathway (2b), at least partial, would allow synthesis of compounds IV. These compounds are of high synthetic value due to the presence of the labile C–Si bond [3]. Analogous cleavage with sodium iodide of the sulfonium salt  $PhS^+(Me)CH_2RI^-$  prepared by alkylation of the corresponding sulfide with methyl iodide was described in [4]. It was shown that the reaction proceeds not by methyl group but by the more shielded groups. Corey and Jautelat [4] consider that this is the shortest pathway for conversion of methyl iodide to its homologs RCH<sub>2</sub>I.

$$R^{1}R^{2}PSiMe_{3} + H_{2}\bar{C}-\bar{S}Me_{2} \longleftrightarrow [R^{1}R^{2}\bar{P}=Me_{3}SiCH_{2}\bar{S}Me_{2}]$$

$$IIa-IIe I$$

$$2a R^{1}R^{2}PMe + MeSCH_{2}SiMe_{3},$$

$$IIIa, IIId, IIIe (2)$$

$$2b R^{1}R^{2}PCH_{2}SiMe_{3} + Me_{2}S,$$

**II, III,**  $R^1 = R^2 = Ph$  (a);  $R^1 = R^2 = i$ -Pr (b);  $R^1 = t$ -Bu,  $R^2 = H$  (c);  $R^1 = t$ -Bu,  $R^2 = Me_3Si$  (d);  $R^1 = Ph$ ,  $R^2 = Me_3Si$  (e).

IV

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We found that highly nucleophilic ylide I even at low temperatures (from -70 to  $-10^{\circ}$ C) quantitatively desilylates silylphosphines IIa, IId, and IIe, but the only subsequent transformation is regioselective cleavage of the sulfonium salt by more sterically accessible methyl group with the formation of the corresponding methylphosphines IIIa, IIId, and IIIe (pathway 2a). The alternative pathway of formation of phosphines **III** involving the cleavage of the sulfonium salt not by phosphide, but by iodide, followed by alkylation of phosphide  $R^{1}R^{2}PLi$  with the arising methyl iodide, seems less probable, because it was shown [4] that dealkylation of sulfonium salts with iodide occurs only in refluxing DMF. In spite of the fact that in no case we detected spectroscopically compounds like IV (the use of the ylide  $Ph_2S^+-C^-H_2$ ) might be successful), this method appeared to be useful for preparing difficultly accessible monosilvlated secondary methylalkyl(aryl)phosphines from more accessible bis(silyl)alkyl(aryl)phosphines. Desilvlation of sterically overcrowded bis(silvl)phosphines **IId** and **IIe** occurs even at low temperature. In fact, for the preparative purposes, 1.1–1.2 equivalents of ylide I and not the equimolar amounts can be used, because the products of reaction (2), monosilylated secondary methylphosphines IIId and IIIe, practically do not react with ylide I. This result, as well as the fact that silvlphosphine **IIb** does not enter reaction (2), is evidently connected with the higher energy of dialkyl and even alkylphenylphosphides as compared to silvlphosphides formed from bis(silvl)phosphines **IId** and IIe. The Me<sub>3</sub>Si group of these phosphides can stabilize the anionic centers by its 3d orbitals [5]. The same reasons also explain the regiospecificity of the reaction of phosphine **IIc** with ylide **I** containing reactive P-Si and P-H bonds [1]. In this case, only the methylation of the P-H bond takes place.

$$t-BuP \begin{pmatrix} H \\ SiMe_{3} + H_{2}\bar{C}-\bar{S}Me_{2} \end{pmatrix}$$

$$IIc I$$

$$[t-Bu\bar{P}(SiMe_{3})//Me_{3}\bar{S}] \xrightarrow{-Me_{2}S} t-BuP(SiMe_{3})Me,$$

$$IIId (3)$$

$$\times [t-Bu\bar{P}H//Me_{3}SiCH_{2}\bar{S}Me_{2}] \xrightarrow{-Me_{3}S} t-Bu(Me)PH.$$

We attempted to perform the reactions similar to (2) with other classes of organophosphorus compounds of the R<sub>2</sub>P–E type having the low-energy P–E bond, in particular, with diphosphines in which the energy of the P–P bond, depending on the substituents, varies from 44 to 58 kcal mol<sup>-1</sup> [6]. However, on prolonged keeping of equimolar amounts of ylide **I** with tetraphenyl- ( $\delta_P$  –15.2 ppm) and 1,1-diisopropyl-

2,2-diethoxydiphosphines ( $\delta_{PPr-i}$  –12.4 ppm,  $\delta_{POEt}$  210.8 ppm,  ${}^{1}J_{PP}$  229 Hz) in THF, according to  ${}^{31}P$  NMR data, no changes were observed, in contrast to the reaction with silylphosphines **II**.

## **EXPERIMENTAL**

The <sup>31</sup>P NMR spectra were recorded on a Varian FT-80A spectrometer (32.2 MHz), and <sup>1</sup>H NMR spectra, on a Varian VXR-400 spectrometer against external 85% phosphoric acid (<sup>31</sup>P) and internal TMS (<sup>1</sup>H). All the manipulations were carried out in

Methyldiphenylphosphine IIIa. To a suspension of 6.4 mmol of trimethylsulfonium iodide in 10 ml of THF, cooled to -70°C, we added dropwise with stirring a solution of 6.4 mmol of butyllithium in hexane. Ten minutes later, 6.4 ml of diphenyl(trimethylsilyl)phosphine in 5 ml of THF was slowly added at the same temperature. The reaction mixture turned orange. Then the mixture was warmed up to room temperature over a period of 30 min, the solvent was removed in a water-jet-pump vacuum, and 10 ml of pentane was added to the residue. The precipitate was removed on a centrifuge, the organic phase was concentrated in a vacuum, and the residue was distilled to give 1.1 g (88%) of phosphine IIIa, bp 148–150°C (8 mm),  $\delta_P$  –27.9 ppm. Published data [7]: bp 148°C (8 mm),  $\delta_P$  –28 ppm.

**Methyl**(*tert*-**butyl**)(**trimethylsilyl**)**phosphine IIId.** *a*. The target compound was prepared similarly to **IIIa** from 2.75 g of Si<sub>3</sub>SI, equimolar amount of BuLi, and 2.34 g of *tert*-butylbis(trimethylsilyl)phosphine. After heating the reaction mixture to 20°C and keeping it at this temperature for 2 h, 1.41 g (80%) of **IIId** was obtained; bp 51–52°C (8 mm). <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 0.02 d (9H, Me<sub>3</sub>Si, <sup>3</sup>J<sub>HP</sub> 4.0 Hz), 0.86 d (3H, Me, <sup>2</sup>J<sub>HH</sub> 3.0 Hz), 0.98 d (9H, *t*-Bu, <sup>3</sup>J<sub>HP</sub> 11.6 Hz). <sup>31</sup>P NMR spectrum:  $\delta_{\rm P}$ -68.5 ppm. Found, %: C 54.92; H 12.22. C<sub>8</sub>H<sub>21</sub>PSi. Calculated, %: C 54.50; H 12.00.

*b*. To a suspension of 5.0 g of trimethylsulfonium iodide in 15 ml of THF, cooled to  $-70^{\circ}$ C, we added dropwise with stirring a solution of an equimolar amount of butyllithium in hexane. Ten minutes later, a solution of 4.0 g of *tert*-butyl(trimethylsilyl)phosphine in 10 ml of THF was added at the same temperature. The resulting mixture was warmed up to room temperature over a period of 30 min, the solvent was removed in a vacuum, and the residue was treated with 20 ml of pentane. The precipitate was removed

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on a centrifuge, the organic phase was concentrated in a vacuum, and the residue was distilled to give 3.7 g (90%) of phosphine **IIId**. Its constants and spectral data were similar to those of the sample prepared by procedure *a*.

## Methyl(phenyl)(trimethylsilyl)phosphine IIIe

was prepared similarly to **IIId** by procedure *a* from 3.0 g of trimethylsulfonium iodide, an equimolar amount of butyllithium, and 3.0 g of phenylbis(trimethylsilyl)phosphine. After keeping the reaction mixture for 3 h at 20°C, 2.05 g (85%) of phosphine **IIId** was obtained, bp 72–76°C (1 mm),  $\delta_{\rm P}$  –102.0 ppm. Published data [8]: bp 78–80°C (1.2 mm),  $\delta_{\rm P}$  –102.3 ppm.

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