Introduction of Functional Silyl Groups into Tris(dialkylamino)phosphonium Methylides

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Starting from tris(dialkylamino)phosphonium methylides (R^3N)^3PCH=PR [1a: R = Me; 1b: R = Et] a series of silylated ylides with functional groups at the silicon substituents have been prepared (2 - 8). In the general formula X:Si=CH=P(NR)^3 the group SiX^3 represents examples for X = Me, Cl, Br, OMe, tPrO, NMe_2, but also for X_3 = PhH_2 etc. The compounds are prepared either via the transylation reaction of 1a, b with reaction components X:SiY [Y = Cl, OTf], or through action of a base on the corresponding silylated phosphonium salts, following methods of preparation for non-functional silylated ylides. Bis(ylides) (9 - 12) are available along the same sequence of reactions, but employing difunctional silanes X_2SiY_2. Products of the type X_3Si[CH=P(NR)^3]_3 were investigated with X = Me, OMe, OEt, and NMe_2. All ylides are thermally stable, distillable liquids, which have been identified via conventional spectroscopic methods. The ylides are versatile synthons in trans-silylation, trans-ylidation, and de-silylation reactions.

Introduction

Silylated phosphorus ylides of the type R_3Si-CH=PR’^3 are important versatile reagents [1 - 3]. In the past most of the pertinent studies had focused on standard ylides with alkyl or aryl substituents R at the phosphorus atom, and it is only recently that ylides with additional P-bound functional groups have been investigated [4, 5]. A change in the substitution pattern can lead to quite different chemical properties, and dialkylamino substituents are a good example in case. We therefore undertook a systematic study of simple Si-functional silylated ylides based on tris(dimethylamino)- and tris(diethylamino)phosphonium methylide (1a, b). The results of our investigations are summarized in this report and in an accompanying paper, where questions of the structural chemistry have also briefly been addressed [6]. Complementary experiments have been included in a series of other recent communications [7 - 9].

Preparative Results

There are two general pathways to monosilylated ylides [1 - 3]. The first one uses the trans-silylation reaction of functional silanes R’^3SiX or R’_2SiX_2 with two/four equivalents of the free ylide, half of which is introduced simply as an auxiliary base to trap the HX by-product. In standard cases with no or little steric hindrance and with less electronegative groups R and R’ the leaving group X can be a halide, but otherwise precursors with X = OTf (trifluoromethanesulfonate, “triflate”) give better results [10]. The second method employs stronger auxiliary bases for the deprotonation of the monosilylated phosphonium cation of the precursor salt. These salts, which are also the intermediates of the transylation reaction, are generally readily available from the free ylide and one equivalent of the functional silane.

The following equations give representative examples.

1a. Phosphonium salt formation:

(R_2N)^3PCH_2 + R’^3SiX → [(R_2N)^3PCH_2SiR’^3]^+ X^- + Base

1b. Deprotonation of the silylated cation of the salt:

[(R_2N)^3PCH_2SiR’^3]^+ X^- + Base → [(R_2N)^3PCHSiR’^3] + Base/HX

2. Transylation:

2(R_2N)^3PCH_2 + R’^3SiX → [(R_2N)^3PMe]^+ X^- + (R_2N)^3PCHSiR’^3

4. Reaction of transylated ylides with R’_2SiX_2:

[(R_2N)^3PMe]^+ X^- + R’_2Si[CHP(NR)^3]_2

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Using these methods (Experimental Part) the following new silylated ylides have been prepared in good yields and high purity. Halogen (4a, 5a), alkoxy (6a, 7a, 10a, 11b) and amino groups (8a, 12a) were chosen as the Si-bound substituents, and a few hydrido- (3a) and alkylsilyl compounds (2a, 9a) were also included.

\[
\begin{align*}
\text{Me}_2\text{Si-CH=P(NMe}_2\text{)}_3 & \quad (2a); \\
\text{PhH}_2\text{Si-CH=P(NMe}_2\text{)}_3 & \quad (3a); \\
\text{Cl}_2\text{Si-CH=P(NMe}_2\text{)}_3 & \quad (4a); \\
\text{Br}_2\text{Si-CH=P(NMe}_2\text{)}_3 & \quad (5a); \\
\text{(MeO)}_3\text{Si-CH=P(NMe}_2\text{)}_3 & \quad (6a); \\
\text{(iPrO)}_3\text{Si-CH=P(NMe}_2\text{)}_3 & \quad (7a); \\
\text{(iPrO)}_3\text{Si-CH=P(NEt}_2\text{)}_3 & \quad (7b); \\
\text{(Me}_2\text{N})_2\text{Si-CH=P(NMe}_2\text{)}_3 & \quad (8a); \\
\text{Me}_2\text{Si-CH=P(NMe}_2\text{)}_3 & \quad (9a); \\
\text{(MeO)}_2\text{Si-CH=P(NMe}_2\text{)}_3 & \quad (10a); \\
\text{(EtO)}_2\text{Si-CH=P(NEt}_2\text{)}_3 & \quad (11b); \\
\text{(Me}_2\text{N})_2\text{Si-CH=P(NMe}_2\text{)}_3 & \quad (12a).
\end{align*}
\]

A few of the corresponding phosphonium salts have been isolated as precursors (2a', 6a'), which can be treated with base to generate the ylides. Reprotonation of the corresponding ylides (where available) is of course another alternative (13a', 13b'). The spectroscopic data of these salts can serve as reference values for the characterization of the target ylide molecules.

\[
\begin{align*}
&[\text{Me}_2\text{Si-CH}_2\text{P(NMe}_2\text{)}_3]\text{OTf}^- (2a'); \\
&[\text{(MeO)}_3\text{Si-CH}_2\text{P(NMe}_2\text{)}_3]\text{OTf}^- (6a'); \\
&[\text{Cl(iPrO)}_2\text{Si-CH}_2\text{P(NMe}_2\text{)}_3]\text{Cl}^- (13a'); \\
&[\text{Cl(iPrO)}_2\text{Si-CH}_2\text{P(NEt}_2\text{)}_3]\text{Cl}^- (13b').
\end{align*}
\]

All ylides 2 - 12, except for compounds 4a and 5a, are colourless, oily liquids, which can be purified by distillation in a vacuum. The compounds are soluble in (or miscible with) common aprotic organic solvents, preferably aliphatic and aromatic hydrocarbons and ethers, but they are also stable to di- and trichloromethane at ambient temperature. Their composition has been confirmed in selected cases by elemental analysis and otherwise by mass spectrometry, while NMR spectroscopy served as a means to further determine the molecular structures. The nuclei \(^1\text{H}, \ ^{13}\text{C}, \ ^{15}\text{N}, \ ^{17}\text{O}, \ ^{29}\text{Si}, \text{ and }^{31}\text{P}\) were used as probes for local connectivities, where appropriate. Assignments of the resonance patterns as first order spin systems were generally straightforward. The spectra were not temperature-dependent within the common range between -50 and +50°C, and showed no anomalies in chemical shifts and coupling constants. (Details are given in the Experimental Part.)

General trends of chemical shifts and coupling constants of silylated ylides were discussed in a previous paper [7]. It should be pointed out that the range of chemical shifts \(\delta^{(15}\text{N})\) is extremely limited (less than 2 ppm), while \(\delta^{(17}\text{O})\) shows much greater sensitivity to changes in the molecular environment. Variations of \(J^{(31}\text{P-15}\text{N})\) are much larger rendering this parameter much more useful for the tracing of electronic effects.

Regarding the constitution of the ylides it should be noted that the molecular structure of the imine molecule \(\text{Me}_2\text{Si-N=P(NMe}_2\text{)}_3\), which is an isoelectronic analogue of 2a, has very recently been determined in the solid state [11]. The imine features local mirror symmetry for the tris(dimethylamino)phosphonium group resembling very closely the structure of the free phosphine \(\text{P(NMe}_2\text{)}_3\) [12]. It therefore appears that this conformation is the preferred arrangement of the substituents at this end of the molecules and should also be valid for most of the ylides 2 - 12.

The crystal structure of \((\text{iPrO})_2\text{Si}[(\text{CH=P(NMe}_2\text{)}_3)]_{2}\), the di(isopropoxy) homologue of the bis(ylides) 10a and 11b, has also been determined [7]. The molecular geometry of the two ylidylic groups is close to that of the corresponding units in \((\text{Me}_2\text{N})_3\text{P=NSiMe}_3\) (above). Intrinsic structural characteristics of phosphorus ylides were the subject of a detailed study in 1989, the results of which also apply to silylated ylides [13].

In ylide 8a the unit \((\text{Me}_2\text{N})_3\text{P}=\) is associated with the isoelectronic group \(-\text{Si(NMe}_2\text{)}_3\) in the same molecule. For a series of compounds of the type \(\text{X-Si(NMe}_2\text{)}_3\), a number of structures have recently also been determined [14]. In agreement with the results of theoretical calculations it was found that the tris(dimethylamino)silane/phosphine groups are conformationally extremely flexible. Even minor influences from the remainder substituent \(\text{X}\) or from packing forces can induce significant changes in the conformation, because the energy profile of inversion, rotation and angle distortion of the amino groups are very flat. Therefore a very flexible structure is also expected for the present family of ylides. The low melting points of most compounds are indicative of this flexibility which is generally characteristic of siloxanes, silazanes and related compounds in the phosphorus series [15].
Chemical reactions of the new ylides will be the subject of future reports. Silylated ylides are readily de-silylated using nucleophiles with an affinity for silicon, or can undergo trans-silylation reactions with other Si-functional substrates [1 - 3], and all these transformations also apply to the present compounds. The bis(ylides) 9 - 12 are known to be precursors for cyclic compounds. Ring closure is readily accomplished e.g. by condensation with R₂SiX₂ molecules [16 - 17]. The phosphonium salts 13a,b give the same type of disilacyclobutane heterocycle upon dehydrohalogenation [16].

Experimental Part

**General:** Standard equipment and instrumentation was used throughout, and all experiments were routinely carried out in an atmosphere of dry, pure nitrogen. Starting materials were obtained either commercially or following published procedures: (Me₂N)₂PCH₂ and (Et₂N)₂PCH₂ [18]; Me₃SiOTf, Me₂PhSiOTf and (MeO)₃SiOTf [18]; Me₃SiOTf, Me₂PhSiOTf and (MeO)₃SiOTf [8].

**Compound 1a/b:** [18]; compound 2a [16].

**Compound 2a’** (for the chloride see ref. [16]): The trflate is prepared from Me₃SiOTf (3.5 ml, 18 mmol) in a mixture of PhH₂SiBr (2.5 ml, 18 mmol) in 20 ml of the same solvent at 20°C with stirring. The reaction mixture is refluxed for 1 h and filtered. The solvent is removed from the filtrate and condensed in a vacuum and the residue is distilled at 125°C/0.01 Torr. Yield 3.4 g (67%). - MS (El): m/z = 281 [M⁺-Me], NMR (CDCl₃, 20°C), 1H: -0.64 (d, J = 10.4, 1H, PCH), 1.23 (d, J = 5.5, 5.5, 1H, PC), 2.35 (d, J = 10.1, 18H, NMe), 5.17 (dd, J = 7.9 and 4.9, 4H, SiH₂), 7.19-7.28 (m, 5H, Ph); 13C (1H): -8.98 (dd, J = 161.8, 1H, PC), 37.68 (dd, J = 2.8, NMe), 127.77, 128.48, 135.15, and 141.04 (s, s, s, d, J = 6.4, 4H, Ph); 13C (29Si): -92.02 (d, ddt, J = 161.8, 137.4 and 7.4), 37.66 (quint, J = 136.0, 4.1, and 4.1); 15N: -363.05 (d, J = 10.3); ²⁹Si: -42.61 (ddqm, J = 183.4, 19.2, 5.9 and 5.9); ³¹P: 68.96, s.

**Compound 4a:** Ylide 1a (6 ml, 30 mmol) and SiCl₄ (2.50 g, 15 mmol) are each dissolved in 30 ml of pentane and dropped simultaneously into 100 ml of the same solvent at 20°C with stirring. The reaction mixture is refluxed for 1 h and filtered. The solvent is removed from the filtrate in a vacuum and the residue is sublimed at 105°C/0.01 Torr, yield 1.96 g (27%), m.p. 164°C. MS (EI): m/z = 309 [M⁺]. NMR (CDCl₃, 20°C), 1H: 0.80 (d, J = 9.2, 1H, PCH), 2.24 (d, J = 9.8, 18H, NMe); 13C: 13.92 (dd, d, J = 177.0 and 139.3, PC), 37.16 (quint, J = 136.1, 4.1 and 4.1, NMe); 15N: -363.79 (d, J = 15.8); ²⁹Si: -8.43 (dd, J = 36.7 and 5.3); ³¹P: 62.11, s.

**Compound 5a:** As described for 4a from ylide 1a and SiBr₃: Yield 2.8 g (42%), m.p. 187°C (decomp.), subl. 125°C/0.01 Torr. MS (Cl): m/z = 441 [M⁺]; NMR (CDCl₃, 20°C), 1H: 1.33 (d, J = 8.2, 1H, PCH), 2.20 (d, J = 9.8, 18H, NMe₂); 13C: 21.52 (dd, J = 175.6 and 139.7, PC), 37.15 (quint, J = 137.0, 3.7 and 3.7, NMe₂); ²⁹Si: -50.60 (dd, J = 32.7 and 3.5); ³¹P: 60.80, s.

C₇H₉Br₃N₅PSi (444.02)
Calcd C 18.9 H 4.3 N 9.5%.
Found C 18.1 H 4.3 N 8.7%.

**Compound 6a:** Ylide 1a (25 mmol) is dissolved in 100 ml of pentane and treated with a solution of (MeO)₂SiCl (12.5 mmol) in 40 ml of the same solvent at 0°C with stirring. The reaction mixture is stirred for 12 h at 20°C and filtered. The solvent is evaporated from the filtrate and the residue distilled in a vacuum, b.p. 120°C/0.01 Torr, yield 68%. MS (EI): m/z = 281 [M⁺-Me]. NMR (CDCl₃, 20°C), 1H: -0.59 (d, J = 11.0, 1H, PCH), 2.42 (d, J = 9.8, 18H, NMe), 3.51 (s, J = 9.0, OMe); 13C: -7.81 (d, J = 166.4, PC), 37.74 (d, J = 4.2, NMe), 50.06 (s, OMe), 15N: -363.47 (d, J = 11.7); ¹⁷O: -10.6; ²⁹Si: -39.34 (dddec, J = 33.6, 7.7 and 3.8); ³¹P: 68.13, s.

**Compounds 7a/b:** As described for 6a, from ylides 1a,1b and (iPrO)₂SiCl; yields 78/92%, b.p. 120/130°C at 0.01 Torr. MS (Cl): m/z = 381/465 [M⁺]. NMR (CDCl₃, 20°C), 7a, 1H: 0.64 (d, J = 10.4, 1H, PCH), 1.23 (d, J = 6.1, 18H, CMe), 2.46 (d, J = 9.8, 18H, NMe), 4.36 (sept, J = 6.1, 3H, OCH); 13C: -6.75 (dd, J = 163.2 and 130.5, PC), 26.19 (qq, J = 124.6 and 4.6, CMe), 37.79 (quint, J = 135.1, 4.2 and 4.2, NMe) 63.95 (sept, J = 140.2 and 4.6, OCH); 15N: -363.64 (d, J = 11.0); ¹⁷O: 57.0, s; ²⁹Si: -46.48 (ddq, J = 30.7, 6.7 and 2.9); ³¹P: 69.03, s; 7b, 1H: -0.58 (d, J = 11.6, PCH), 0.99 (t, J = 7.3, 18H, NCMe), 1.26 (d, J = 6.1, 18H, OCMe), 3.03 (dq, J = 9.8 and 7.3, 12H, NCH₂), 4.39 (sept, J = 6.1, OCH); 13C: -1.34 (d, J = 172.4, PC), 14.39 (d, J = 3.2, NCH₂), 26.17 (s, OCMe), 40.23 (d, J = 5.1, NCH₂), 50.06 (s, OCH), 15N: -363.75, s; ¹⁷O: 56.0, s; ²⁹Si: -47.04 (ddq, J = 31.8, 7.7 and 2.7); ³¹P: 67.31, s.

**Compound 8a:** From (Me₂N)₂PST (19 mmol) and ylide 1a (38 mmol) in a total of 40 ml of diethylether as described for 6. The phosphonium salt is precipitated by addition of 25 ml of pentane; distillation of the filtrate gives a yield of 68%, b.p. 85°C/0.01 Torr. MS (Cl): m/z = 336 [M⁺]. NMR (CDCl₃, 20°C), 1H: -0.59 (d, J = 11.0,
Compounds 9a: A solution of 16 ml (80 mmol) of ylide 1a (27.4 mmol) and (MeO)2Si(OH)2 (6.85 mmol) in hexane/toluene. b.p. 210°C/0.01 Torr, yield 69%. MS (Cl): m/z = 442 [M+]. NMR (CD2Cl2, 20°C), 1H: 0.24 (AXX; N = 10.8, 2H, 6CH; 2.60 (d, J = 9.6, 18H, NMe), 3.78 (s, 6H, OMe); 13C: -0.85 (dd, J = 154.4, 130.1 and 8.3, PC), 37.86 (quint, J = 123.4 and 3.7, NMe), 49.67 (q, J = 138.8, OMe). 15N: -362.84 (d, N = 8.5); 17O: -1s; 31Si: -12.93 (t, J = 24.9); 31P: 67.04, s.

Compounds 10b: Following a similar procedure (10a) from (EtO)2SiCl2 and ylide 1b in the molar ratio 1:4 in hexane; b.p. 245°C/0.01 Torr, m.p. 12°C, yield 59%. MS (El): m/z = 638 [M+]. NMR (CD2Cl2, 20°C), 1H: 0.49 (AXX; N = 11.2, 2H, 6CH; 1.04 (t, J = 7.0, 36H, NCMe), 1.29 (t, J = 7.0, 6H, OMe); 3.14 (dq, J = 10.1 and 7.0, 24H, NCH2), 3.95 (dq, J = 7.0, 4H, OCH2); 13C: 3.80 (dd, J = 154.9 and 6.4, PC), 14.62 (d, J = 3.2, NCMe), 19.35 (d, J = 9.0, OCH2), 40.43 (d, J = 5.1, NCH2), 56.97 (s, OMe); 15N: -336.08 (d, J = 8.7); 17O: 40.0, s; 31Si: -17.87 (t, J = 25.4); 31P: 66.52, s.

Compounds 12a: From ylide 1a and (Me3N)2Si(OTf)2 (molar ratio 4:1, in diethyl ether) at 0°C, b.p. 140°C/0.01 Torr, 58% yield. MS (Cl); m/z = 468 [M+]. NMR (CD2Cl2, 20°C), 1H: 0.25 (AXX; N = 12.7, 2H, CH2), 2.52 (d, J = 9.5, 36H, NMe), 2.92 (s, 12H, SiNMe); 13C: -2.55 (dd, J = 155.3 and 6.0, PC), 38.13 (AXX; N = 6.0, NMe), 40.03 (s, SiNMe); 15N: -362.18 (d, J = 7.3); 31Si: -11.3 (d, J = 23.5); 31P: 66.16, s.

Phosphonium salt 6la': A solution of ylide 1a (8 ml, 41 mmol) in 40 ml of diethyl ether is added slowly with stirring at 0°C to a solution of (MeO)2SiOTf (11.8 g, 43.7 mmol) in 20 ml of the same solvent. After 30 min the product is filtered and crystallized from toluene, yield 11.9 g (65%), m.p. 143°C (decomp.). NMR (CD2Cl2, 20°C), 1H: 1.91 (d, J = 20.4, CH2), 2.72 (d, J = 10.4, 18H, NMe), 3.63 (s, 9H, OMe); 13C: 6.26 (d, J = 101.1, PC), 36.98 (d, J = 4.1, NMe), 51.38 (s, OMe); 15N: -365.11 (d, J = 16.9); 31Si: -53.73 (d, dec, J = 3.9, 3.9 and 1.2); 31P: 58.94, s. (Anion resonances omitted.)

Phosphonium salts 13a', 13b': These compounds were prepared from the corresponding ylides [7,16] using a solution of dry HCl in diethyl ether (yields 70/56%, m.p. 173/202°C, decomp.). NMR (CDCl3, 20°C), 13a': 1H: 1.19 and 1.22 (d, J = 6.1, 6H each, diastereotopic ChMe); 2.75 (d, J = 10.1, 18H, NMe), 2.90 (d, J = 19.8, 2H, PCH2), 4.35 (sept, J = 6.1, 2H, OCH); 13C: 10.23 (d, J = 100.7, PCH2), 25.46 and 25.65 (d, diastereotopic ChMe2), 37.38 (d, J = 4.6, NMe), 66.71 (s, OMe). 13b': 1H: 1.15 (t, J = 7.0, 18H, NCMe), 1.22 and 1.24 (d, J = 5.8, 6H each, OMe); 2.68 (d, J = 20.5, 2H, PCH2), 3.17 (dq, J = 10.7 and 7.0, 12H, NCH2), 4.36 (sept, J = 6.1, 2H, OCH2); 13C: 11.66 (d, J = 111.0, PC), 13.44 (d, J = 2.5, NCMe), 25.15 and 25.38 (s, diastereotopic OMe); 39.47 (d, J = 4.7, NCH2), 66.64, s; 31Si: -67.64, s; 31P: 58.20, s.

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