Aluminium Triflate [$Al(OTf)_3$] as a Recyclable Catalyst for the Conversion of α-Hydroxyphosphonates, Alcohols and Phenols to Their Corresponding O-Silylated Products with Hexamethyldisilazane (HMDS)

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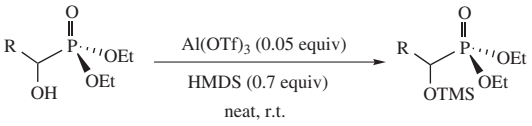
Abstract: $Al(OTf)_3$ as a recyclable catalyst conducts the efficient conversion of various types of α-hydroxyphosphonates to their corresponding α-trimethysilyloxyphosphonates with HMDS in the absence of solvent at room temperature. The general applicability of the catalyst under solvent-free conditions is demonstrated by applying it for the successful silylation of alcohols and phenols with HMDS in high yields.

Keywords: α-hydroxyphosphonates, solvent-free, aluminium triflate, α-acetyloxyphosphonates, alcohols, phenols

In conjunction with our interest in the development of synthetic methods for the preparation of phosphonate derivatives from α-hydroxyphosphonates, we have focused our attention to the preparation of α-trimethylsilyloxyphosphonates by direct silylation of α-hydroxyphosphonates with HMDS catalyzed by iodine, $Cu(OTf)_2$ and $Mg(OTf)_2$.[1] α-Trimethylsilyloxyphosphonates are attractive compounds from different views. They are potential synthons of masked acyl anions[2] which react with various ketones to produce the corresponding α-hydroxyketones.[3] Unsymmetrical ketones can be also produced by the reaction of α-lithiated α-trimethylsilyloxyphosphonates with alkylating agents.[4] α-Lithiated α-trimethylsilyloxyphosphonates can undergo acylation with a variety of acylating agents to produce the corresponding α-acylated products. These compounds in turn, can be easily transformed to α-hydroxyketones by the cleavage of Si-O bond and elimination of dialkyl phosphite in alkaline media.[2c,5]

The common methods for the preparation of α-trimethylsilyloxyphosphonates include reaction of aldehydes with either diethyl trimethylsilyloxyphosphite or the mixture of triethylphosphite and trimethylsilyl chloride.[2a,6] These protocols need harsh reaction conditions and long reaction times. The other method includes the reaction of trialkyl phosphate with silyl phenyl ketone, which requires a long reaction time (12 h) and also proceeds at a rather high temperature (80 °C).[7] Procedures for the preparation of α-trimethylsilyloxyphosphonates by direct silylation of α-hydroxyphosphonates[8] are limited to only a few reports.[1,9] Except in our reported methods in which HMDS has been used as a silylating agent at room temperature, in the only other available method, hexamethylsilathiane has been used as a silylating agent at 50–70 °C.[9] We now report $Al(OTf)_3$[10,11] as a reusable, efficient and easy to handle catalyst for the high yielding preparation of diethyl α-trimethylsilyloxyphosphonates **2a–o** by direct reaction of diethyl α-hydroxyphosphonates **1a–o** with HMDS at room temperature using neat conditions (Scheme 1, Table 1).



1a–o **2a–o**

Scheme 1

As shown in Table 1, various types of diethyl α-hydroxy(phenylmethyl)phosphonates (**1a–k**) were cleanly and efficiently converted into their corresponding diethyl α-trimethylsilyloxyphosphonates (**2a–k**) with HMDS in the presence of a catalytic amount of $Al(OTf)_3$ at room temperature under solvent-free conditions (yields = 90–97%). Diethyl α-hydroxy-2-naphthyl-, 3-pyridyl-, alkyl- and aryl-β,γ-unsaturated phosphonates (**1l–o**) are also silylated efficiently giving the corresponding diethyl α-trimethylsilyloxyphosphonates (**2l–o**) in 90–96% yields under similar reaction conditions.

C–P and Si–O bonds usually undergo cleavage and they are sensitive towards reaction conditions. The almost quantitative yields of the products strongly indicate that C–P and Si–O bonds tolerate these mild reaction conditions, which is an advantage of the method. Work-up of the reaction mixture is not a time-consuming process and the products are isolated in highly pure states and do not require further purification.

The spectral data of the known products (**2a, b, g, k, n** and **o**) are compared with those reported in the literature. The spectral data of the other known products (**2c**, **e**, **f**, **i** and **j**), which have not been reported before and the spectral data (^{1}H NMR, ^{13}C NMR, IR and MS) of the unknown products (**2d, h, l, m**) are presented in the experimental section.

In order to show the advantage and limitation of $Al(OTf)_3$, we have compared the catalytic activity of this catalyst with LiOTf,[15] $Ce(OTf)_4$,[16] $Hg(OTf)_2$,[17] $Cu(OTf)_2$,[18]

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Table 1 Silylation of Diethyl α-Hydroxyphosphonates (**1a–o**) to Diethyl α-Trimethylsilyloxyphosphonates (**2a–o**) with HMDS in the Presence of $Al(OTf)_3$ Under Solvent-Free Conditions at Room Temperature

Product **2**[ref]	R	Time (min)	Yield[a] (%)
a[2c,7]	C_6H_5	–[b]	97
b[12]	4-$CH_3C_6H_4$	–[b]	90
c	4-$CH_3OC_6H_4$	–[b]	92
d	2,4,6-$(CH_3)_3C_6H_2$	–[b]	90
e	2-ClC_6H_4	5	95
f	3-ClC_6H_4	10	96
g[13]	4-ClC_6H_4	5	95
h	2,6-$Cl_2C_6H_3$	–[b]	96
i	2-$O_2NC_6H_4$	10	90
j	3-$O_2NC_6H_4$	20	91
k[13]	4-$O_2NC_6H_4$	25	92
l	2-Naphthyl	10	92
m	3-Pyridyl	–[b]	96
n[14]	PhCH=CH	10	90
o[14]	MeCH=CH	25	90

[a] Yields of isolated products at r.t.
[b] Reaction occurred immediately.

$Mg(OTf)_2$,[19] and Lewis acids such as $AlCl_3$, $ZnCl_2$,[20a] $Zn(bipy)_3Cl_2$,[20b] $FeCl_3$, $Fe(bipy)Cl_3$,[20b] $CuCl_2$, $MgCl_2$, and $ZrOCl_2{\cdot}8H_2O$ for the silylation of **1a** as a model compound, with HMDS in the absence of solvent at room temperature in our laboratory. We found that $Al(OTf)_3$ was the most effective catalyst and is comparable with $Mg(OTf)_2$ among the other catalysts we have studied for this purpose (Table 2).

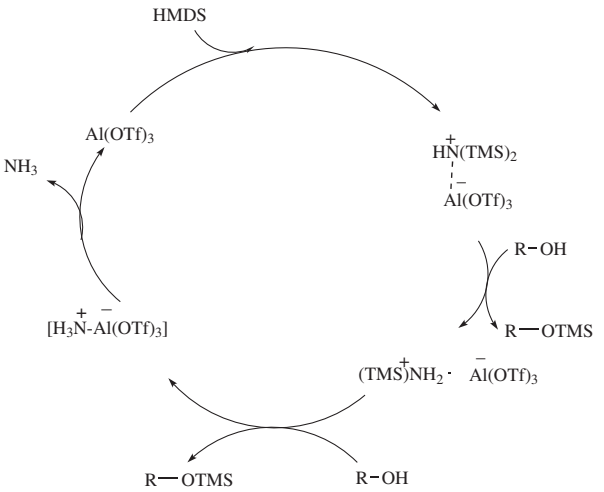
In the reactions we have studied, fast evolution of NH_3 was observed. We were also able to recover $Al(OTf)_3$ and reuse it without loss of its catalytic activity. Therefore, we have proposed a mechanism in which the generation of NH_3 and the catalytic role of $Al(OTf)_3$ in a catalytic cycle are clarified (Scheme 2).

In this mechanism, we have suggested that a Lewis acid-base interaction between metal triflate and nitrogen in HMDS polarizes N–Si bond of HMDS to produce a reactive silylating agent, **3**. Both Mg^{2+} and Al^{3+} that are harder Lewis acids in comparison with Li^+, Cu^{2+}, Ce^{4+}, and Hg^{2+} interact more strongly with the nitrogen atom as a hard Lewis base in HMDS. Therefore, N–Si bond polarization effected by $Mg(OTf)_2$ and $Al(OTf)_3$ is more pronounced (Table 2) than those generated by LiOTf, $Cu(OTf)_2$, $Ce(OTf)_4$, and $Hg(OTf)_2$. This qualitative explanation justifies the higher activity of $Mg(OTf)_2$ and $Al(OTf)_3$ than the other triflates we have studied.

Table 2 Silylation of Diethyl α-Hydroxy(phenylmethyl)phosphonate (**1a**) with HMDS in the Presence of Various Lewis Acids in Neat Conditions at Room Temperature

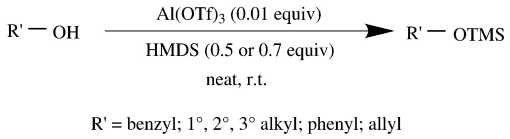
Entry	Lewis acid [a]	Time (h)	% Conversion based on ^1H NMR
1	$Al(OTf)_3$	–[b]	100
2	$Mg(OTf)_2$	–[b]	100
3	$Cu(OTf)_2$	4.5	60
4	$Ce(OTf)_4$	3	80
5	$Hg(OTf)_2$	10	60
6	LiOTf	1.5	100
7	$ZnCl_2$	1	100
8	$Zn(bipy)_3Cl_2$	24	20
9	$FeCl_3$	1.5	80
10	$Fe(bipy)Cl_3$	1.5	30
11	$ZrOCl_2.8H_2O$	1.5	30
12	$AlCl_3$	4.5	80
14	$CuCl_2$	10	20
15	$MgCl_2$	6.5	50

[a] The molar ratios of substrate–HMDS–catalyst are 1:0.7:0.1.
[b] Reaction occurred immediately.



Scheme 2

Silylation of alcohols are among the most frequently used processes in organic synthesis and provides cheap and efficient means for the protection of hydroxyl group during oxidation, peptide coupling and halogenation reactions.[21] In order to show general applicability of the presented method, we have also studied silylation of alcohols and phenols with HMDS in the presence of catalytic amounts of $Al(OTf)_3$ under solvent-free conditions at room temperature (Scheme 3).



Scheme 3

Treatment of several of alcohols with HMDS and the catalyst in the absence of solvent at room temperature produces the corresponding trimethylsilyl ethers in excellent yields (Table 3). Substituted benzylic alcohols containing electron-donating and electron-withdrawing groups, primary and allylic alcohols are also protected efficiently in short reaction times in high yields (Table 3, entries 1–14). Silylation of secondary and tertiary aliphatic alcohols requires longer reaction times under similar reaction conditions (Table 3, entries 16–23). We have also tried silylation of cholesterol under solvent-free conditions in the presence of this catalyst with HMDS. Our observation shows that this compound does not undergo silylation under such conditions and the starting material was isolated intact after 24 hours. However, we tried this reaction at room temperature in solution using CH_2Cl_2. The reaction proceeded well and the desired compound was isolated in 97% yield after 80 minutes (Table 3, entry 15). Silylation of phenolic hydroxyl group also proceeded smoothly by this method. Our studies show that *p*-cresol is silylated faster and in a higher yield than phenol and *p*-chlorophenol (Table 3, entries 24–26). Silylation of thiols and amines by this protocol failed; the starting materials were isolated from the mixture after 48 hours (Table 3, entries 27–29).

In conclusion, Al(OTf)$_3$ is a mild and efficient catalyst for the preparation of varieties of diethyl α-trimethylsilyloxyphosphonates by direct silylation of diethyl α-hydroxyphosphonates with HMDS. Cleavages of C–P or Si–O bonds are not observed in the process of the reactions. High yields, solvent-free, mild reaction conditions, short reaction times, reusability of the catalyst and easy work-up are the strong points of the protocol for the preparation of α-trimethylsilyloxyphosphonate compounds. The protocol is applicable to the efficient silylation of alcohols and phenols in high yields.

Chemicals were purchased from Merck and Fluka. The products were characterized by comparison of their physical data with those of known samples or by their spectral data. IR spectra were run on a Shimadzu model 8300 FT-IR spectrophotometer. NMR spectra were recorded on a Bruker Avance DPX-250 spectrometer at 250 MHz for ^{1}H NMR and at 62.5 MHz for ^{13}C NMR. Mass spectra were recorded on a Shimadzu GCMS-QP 1000 EX spectrometer. The purity of the products and the progress of the reactions were accomplished by TLC on silica gel polygram SILG/UV$_{254}$ plates.

Preparation of Diethyl α-Trimethylsilyloxyphosphonates (2); General Procedure

Al(OTf)$_3$ (0.05 mmol, 0.024 g) was added to a stirring mixture of **1** (1 mmol, 0.218–0.342 g) and HMDS (0.7 mmol, 0.113 g) at r.t. The reaction progress was monitored by TLC. After completion of the reaction, Et_2O (10 mL) was added to the reaction mixture, which

Table 3 Silylation of Alcohols and Phenols with HMDS in the Presence of Al(OTf)$_3$ at Room Temperature

Entry	Substrate	Time (min)	Yield[a] (%)
1	$C_6H_5CH_2OH$	–[e]	95[b]
2	4-$CH_3C_6H_4CH_2OH$	–[e]	93[b]
3	4-$CH_3OC_6H_4CH_2OH$	–[e]	95[b]
4	4-$ClC_6H_4CH_2OH$	–[e]	90[b]
5	2-$O_2NC_6H_4CH_2OH$	–[e]	90[b]
6	$PhCH(CH_3)OH$	–[e]	92[b]
7	Anthracene-9-methanol	–[e]	95[c]
8	$(Ph)_2CHOH$	–[e]	95[b]
9	$CH_2=CHCH_2OH$	–[e]	95[b]
10	$(CH_3)_2C=CHCH_2OH$	–[e]	90[b]
11	$CH_3(CH_2)_5CH(CH=CH_2)OH$	10	94[b]
12	$PhCH_2CH_2OH$	15	90[c]
13	$Ph(CH_2)_2CH_2OH$	10	92[c]
14	$CH_3(CH_2)_6CH_2OH$	10	90[c]
15	Cholesterol	24 h	–[c,f]
16	Nopol	35	90[c]
17	Cyclohexanol	24	92[c]
18	2-Octanol	20	96[c]
19	Terpineol	50	92[c]
20	Adamantan-1-ol	60	93[c]
21	*t*-Amyl alcohol	67	95[c]
22	5-Methyl-5-decanol	55	95[c]
23	*t*-BuOH	90	90[c]
24	4-$CH_3C_6H_4OH$	65	90[c]
25	C_6H_5OH	140	70[c]
26	4-ClC_6H_4OH	120	70[c]
27	C_6H_5SH	48 h	–[f]
28	$C_6H_5NH_2$	48 h	–[f]
29	Cyclohexyl amine	48 h	–[f]

[a] Yields of isolated products.
[b] The molar ratio of substrate–HMDS–Al(OTf)$_3$ was 1:0.5:0.01.
[c] The molar ratio of substrate–HMDS–Al(OTf)$_3$ was 1:0.7:0.01.
[d] CH_2Cl_2 was used as solvent.
[e] Immediate reaction occurred.
[f] Reaction did not occur.

was then washed with H_2O (3 × 10 mL). The aqueous layer was separated and evaporated under reduced pressure to afford the catalyst. The organic layer was dried over anhyd Na_2SO_4. After evaporation of the solvent, the pure product (**2**) was isolated without requiring further purification in 90–97% yields (Table 1).

Trimethylsilylation of Alcohols and Phenols with HMDS Using $Al(OTf)_3$ in Neat Conditions; General Procedure

$Al(OTf)_3$ (0.01 mmol, 0.005 g) was added to a stirring mixture of alcohol or phenol (1 mmol) and HMDS (0.5–0.7 mmol, 0.08–0.113 g) at r.t. The reaction progress was monitored by TLC or GC. After completion of the reaction, Et_2O (10 mL) was added to this reaction mixture, which was then washed with H_2O (3 × 10 mL). The aqueous layer was separated and evaporated under reduced pressure to afford the catalyst. The organic layer was dried over anhyd Na_2SO_4. After evaporation of the solvent, almost pure trimethylsilyl ether was obtained. Pure product was obtained by column chromatography in 70–97% yields (Table 2).

Spectral Data and the Elemental Analysis of Unknown Diethyl α-Trimethylsilyloxyphosphonates

Diethyl α-Trimethylsilyloxy-2,4,6-trimethylbenzylphosphonate (2d)

IR (neat): OH Peak was absent.

^{1}H NMR ($CDCl_3$): δ = –0.04 [s, 9 H, $Si(CH_3)_3$], 1.02 (t, $^2J_{HH}$ = 7 Hz, 3 H, 2-OCH_2CH_3), 1.22 (t, $^2J_{HH}$ = 7 Hz, 3 H, 2-OCH_2CH_3), 2.12 (s, 3 H, CH_3), 2.25 (s, 3 H, CH_3), 2.51 (s, 3 H, CH_3), 3.58–3.68 (m, 1 H, 2-OCH_2CH_3), 3.81–3.90 (m, 1 H, 2-OCH_2CH_3), 3.98–4.10 (m, 2 H, 2-OCH_2CH_3), 5.28 (d, $^1J_{PH}$ = 18.3 Hz, 1 H, CH), 6.66 (s, 1 H, C_6H_2), 6.72 (s, 1 H, C_6H_2).

^{13}C NMR ($CDCl_3$): δ = 0.00 [$Si(CH_3)_3$], 16.56 (d, $^3J_{CP}$ = 5.9 Hz, 2-OCH_2CH_3), 16.87 (d, $^3J_{CP}$ = 5.9 Hz, 2-OCH_2CH_3), 21.16, 21.67, 21.69 (CH_3), 62.70 (d, $^2J_{CP}$ = 7.1 Hz, 2-OCH_2CH_3), 62.92 (d, $^2J_{CP}$ = 7.1 Hz, 2-OCH_2CH_3), 69.60 (d, $^1J_{CP}$ = 177.2 Hz, CH), 129.05 (d, J_{CP} = 2 Hz, C_6H_2), 130.25 (C_6H_2), 131.57 (d, J_{CP} = 3.3 Hz, C_6H_2), 136.08 (d, J_{CP} = 8.1 Hz, C_6H_2), 137.41 (d, J_{CP} = 3.4 Hz, C_6H_2), 139.88 (d, J_{CP} = 4.2 Hz, C_6H_2).

MS (70 eV): *m/z* (%) = 431 (19.3) [M + $Si(CH_3)_3$], 358 (3.2) [M^+], 221 (100) [M – $P(O)(OEt)_2$], 147 (12) [221 – $Si(CH_3)_3$], 73 (44.3) [$Si(CH_3)_3$].

Anal. Calcd for $C_{17}H_{31}O_4PSi$: C, 56.98; H, 8.66. Found: C, 56.90; H, 8.70.

Diethyl α-Trimethylsilyloxy-2,6-dichlorobenzylphosphonate (2h)

IR (neat): OH Peak was absent.

^{1}H NMR ($CDCl_3$): δ = 0.00 [s, 9 H, $Si(CH_3)_3$], 1.07–1.24 (m, 6 H, 2-OCH_2CH_3), 3.89–4.15 (m, 4 H, 2-OCH_2CH_3), 5.81 (d, $^1J_{PH}$ = 19.3 Hz, 1 H, CH), 7.03–7.10 (m, 1 H, C_6H_3), 7.20–7.25 (m, 1 H, C_6H_3).

^{13}C NMR ($CDCl_3$): δ = 0.00 [$Si(CH_3)_3$], 16.86 (d, $^3J_{CP}$ = 6.8 Hz, 2-OCH_2CH_3), 16.96 (d, $^3J_{CP}$ = 6.8 Hz, 2-OCH_2CH_3), 63.35 (d, $^2J_{CP}$ = 7.1 Hz, 2-OCH_2CH_3), 63.60 (d, $^2J_{CP}$ = 7.1 Hz, 2-OCH_2CH_3), 70.02 (d, $^1J_{CP}$ = 179.8 Hz, CH), 128.60 (d, J_{CP} = 2.0 Hz, C_6H_3), 129.99 (d, J_{CP} = 2.9 Hz, C_6H_3), 131.31 (d, J_{CP} = 2.8 Hz, C_6H_3), 135.73 (d, J_{CP} = 8.2 Hz, C_6H_3), 136.87 (d, J_{CP} = 4.9 Hz, C_6H_3).

MS (70 eV): *m/z* (%) = 457 (100) [M + $Si(CH_3)_3$], 389 (2.3) [M + 4], 387 (10.8) [M + 2], 385 (14) [M^+], 247 (52.2) [M – $P(O)(OEt)_2$], 173 (2.4) [247 – $Si(CH_3)_3$], 73 (93.5) [$Si(CH_3)_3$].

Anal. Calcd for $C_{14}H_{23}Cl_2O_4PSi$: C, 43.64; H, 5.97. Found: C, 43.60; H, 5.91.

Diethyl α-Trimethylsilyloxy-2-naphthylphosphonate (2l)

IR (neat): OH Peak was absent.

^{1}H NMR ($CDCl_3$): δ = 0.00 [s, 9 H, $Si(CH_3)_3$], 1.10 (t, $^2J_{HH}$ = 7.1 Hz, 6 H, 2-OCH_2CH_3), 3.79–3.99 (m, 4 H, 2-OCH_2CH_3), 5.03 (d, $^1J_{PH}$ = 14.5 Hz, 1 H, CH), 7.33–7.37 (m, 2 H, $C_{10}H_7$), 7.49–7.52 (m, 1 H, $C_{10}H_7$), 7.69–7.84 (m, 4 H, $C_{10}H_7$).

^{13}C NMR ($CDCl_3$): δ = 0.00 [$Si(CH_3)_3$], 16.39 (d, $^3J_{CP}$ = 5.6 Hz, 2-OCH_2CH_3), 16.48 (d, $^3J_{CP}$ = 5.6 Hz, 2-OCH_2CH_3), 62.77 (d, $^2J_{CP}$ = 7.3 Hz, 2-OCH_2CH_3), 63.22 (d, $^2J_{CP}$ = 7.3 Hz, 2-OCH_2CH_3), 72.13 (d, $^1J_{CP}$ = 174.4 Hz, CH), 125.23–126.44, 127.61–128.06, 133.07–133.21, 134.94–135.48 ($C_{10}H_7$).

MS (70 eV): *m/z* (%) = 439 (16.2) [M + $Si(CH_3)_3$], 366 (4.8) [M^+], 229 (100) [M – $P(O)(OEt)_2$], 155 (18.8) [229 – $Si(CH_3)_3$], 73 (87.5) [$Si(CH_3)_3$].

Anal. Calcd for $C_{18}H_{27}O_4PSi$: C, 59.02; H, 7.38. Found: C, 59.04; H, 7.35.

Diethyl α-Trimethylsilyloxy-3-pyridylphosphonate (2m)

IR (neat): OH Peak was absent.

^{1}H NMR ($CDCl_3$): δ = 0.00 [s, 9 H, $Si(CH_3)_3$], 1.13 (t, $^2J_{HH}$ = 7.0 Hz, 6 H, 2-OCH_2CH_3), 3.91–3.99 (m, 4 H, 2-OCH_2CH_3), 4.89 (d, $^1J_{PH}$ = 14.5 Hz, 1 H, CH), 7.15–7.21 (m, 1 H, C_5H_4N), 7.74 (d, J_{PH} = 7.3 Hz, 1 H, C_5H_4N), 8.43 (d, J_{PH} = 4.1 Hz, 1 H, C_5H_4N), 8.54 (s, 1 H, C_5H_4N).

^{13}C NMR ($CDCl_3$): δ = 0.00 [$Si(CH_3)_3$], 16.51 (d, $^3J_{CP}$ = 5.1 Hz, 2-OCH_2CH_3), 16.58 (d, $^3J_{CP}$ = 5.1 Hz, 2-OCH_2CH_3), 63.06 (d, $^2J_{CP}$ = 7.3 Hz, 2-OCH_2CH_3), 63.43 (d, $^2J_{CP}$ = 7.3 Hz, 2-OCH_2CH_3), 69.88 (d, $^1J_{CP}$ = 175.8 Hz, CH), 123.31 (d, J_{CP} = 2.6 Hz, C_5H_4N), 133.53 (C_5H_4N), 135.14 (d, J_{CP} = 4.9 Hz, C_5H_4N), 148.69 (d, J_{CP} = 6.7 Hz, C_5H_4N), 149.43 (d, J_{CP} = 3.3 Hz, C_5H_4N).

MS (70 eV): *m/z* (%relative intensity) = 390 (62.1) [M + $Si(CH_3)_3$], 317 (1.2) [M^+], 180 (86.2) [M – $P(O)(OEt)_2$], 108 (48.8) [180 – $Si(CH_3)_3$], 73 (100) [$Si(CH_3)_3$].

Anal. Calcd for $C_{13}H_{24}NO_4PSi$: C, 49.21; H, 7.57. Found: C, 49.18; H, 7.51.

Spectral Data of Known α-Trimethylsilyloxyphosphonates Not Reported in the Literature

Diethyl α-Trimethylsilyloxy-4-methoxybenzylphosphonate (2c)

IR (neat): OH Peak was absent.

^{1}H NMR ($CDCl_3$): δ = 0.00 [s, 9 H, $Si(CH_3)_3$], 1.11–1.19 (m, 6 H, 2-OCH_2CH_3), 3.71 (s, 3 H, 4-OCH_3), 3.81–3.99 (m, 4 H, 2-OCH_2CH_3), 4.83 (d, $^1J_{PH}$ = 13.4 Hz, 1 H, CH), 7.79 (d, $^2J_{HH}$ = 8.4 Hz, 2 H, C_6H_4), 7.30 (d, $^2J_{HH}$ = 6.9 Hz, 2 H, C_6H_4).

^{13}C NMR ($CDCl_3$): δ = 0.00 [$Si(CH_3)_3$], 16.38–16.59 (2-OCH_2CH_3), 55.20 (4-OCH_3), 62.65–63.21 (2-CH_2CH_3), 71.50 (d, $^1J_{CP}$ = 173.7 Hz, CH), 113.58–113.62, 128.49–129.30, 159.47–159.51 (C_6H_4).

Diethyl α-Trimethylsilyloxy-2-chlorobenzylphosphonate (2e)

IR (neat): OH Peak was absent.

^{1}H NMR ($CDCl_3$): δ = 0.00 [s, 9 H, $Si(CH_3)_3$], 1.08–1.24 (m, 6 H, 2-OCH_2CH_3), 3.79–4.10 (m, 4 H, 2-OCH_2CH_3), 5.50 (d, $^1J_{PH}$ = 12.3 Hz, 1 H, CH), 7.11–7.27 (m, 3 H, C_6H_4), 7.65–7.73 (m, 1 H, C_6H_4).

^{13}C NMR ($CDCl_3$): δ = 0.47 [$Si(CH_3)_3$], 16.47–16.73 (2-OCH_2CH_3), 63.20–63.69 (2-CH_2CH_3), 67.89 (d, $^1J_{CP}$ = 175.8 Hz, CH), 127.08–135.80 (C_6H_4).

Diethyl α-Trimethylsilyloxy-3-chlorobenzylphosphonate (2f)

IR (neat): OH Peak was absent.

^{1}H NMR ($CDCl_3$): δ = 0.00 [s, 9 H, $Si(CH_3)_3$], 1.09–1.17 (m, 6 H, 2-OCH_2CH_3), 3.90–4.01 (m, 4 H, 2-OCH_2CH_3), 4.83 (d, $^1J_{PH}$ = 14.5 Hz, 1 H, CH), 7.14–7.41 (m, 4 H, C_6H_4).

^{13}C NMR ($CDCl_3$): δ = 0.47 [$Si(CH_3)_3$], 16.44–16.59 (2-OCH_2CH_3), 62.94–63.50 (2-CH_2CH_3), 71.43 (d, $^1J_{CP}$ = 171.6 Hz, CH), 125.47–139.73 (C_6H_4).

Diethyl α-Trimethylsilyloxy-2-nitrobenzylphosphonate (2i)
IR (neat): OH Peak was absent.

^1H NMR ($CDCl_3$): δ = 0.00 [s, 9 H, $Si(CH_3)_3$], 1.01–1.11 (m, 6 H, 2-OCH_2CH_3), 3.83–3.97 (m, 4 H, 2-OCH_2CH_3), 6.02 (d, $^1J_{PH}$ = 15.9 Hz, 1 H, CH), 7.28 (t, $^2J_{HH}$ = 7.3 Hz, 1 H, C_6H_4), 7.48 (t, $^2J_{HH}$ = 7.3 Hz, 1 H, C_6H_4), 7.72–7.80 (m, 2 H, C_6H_4).

^{13}C NMR ($CDCl_3$): δ = 0.46 [$Si(CH_3)_3$], 16.41–16.60 (2-OCH_2CH_3), 63.26–63.62 (2-CH_2CH_3), 66.40 (d, $^1J_{CP}$ = 172.0 Hz, CH), 124.70–134.02, 147.94–148.04 (C_6H_4).

Diethyl α-Trimethylsilyloxy-3-nitrobenzylphosphonate (2j)
IR (neat): OH Peak was absent.

^1H NMR ($CDCl_3$): δ = 0.00 [s, 9 H, $Si(CH_3)_3$], 1.08–1.17 (m, 6 H, 2-OCH_2CH_3), 3.91–3.99 (m, 4 H, 2-OCH_2CH_3), 4.96 (d, $^1J_{PH}$ = 14.8 Hz, 1 H, CH), 7.41 (t, $^2J_{HH}$ = 7.8 Hz, 1 H, C_6H_4), 7.70 (d, $^2J_{HH}$ = 7.4 Hz, 1 H, C_6H_4), 8.01 (d, $^2J_{HH}$ = 7.9 Hz, 1 H, C_6H_4), 8.19 (s, 1 H, C_6H_4).

^{13}C NMR ($CDCl_3$): δ = 0.47 [$Si(CH_3)_3$], 16.50–16.63 (2-OCH_2CH_3), 63.20–63.75 (2-CH_2CH_3), 71.16 (d, $^1J_{CP}$ = 171.5 Hz, CH), 122.11–123.07, 129.12–129.33, 133.32–133.40, 140.23, 148.28–148.33 (C_6H_4).

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