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An Efficient Synthesis of Phosphenimidous Esters, RO—P=N—Ar

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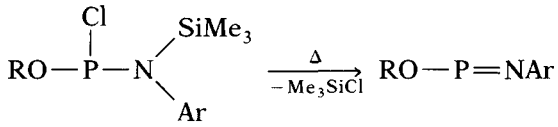
ABSTRACT

Trimethylsilyltrifluoromethane sulfonate is shown to be an efficient catalyst for the elimination of Me_3SiCl from N-trimethylsilyl-N-(2,4,6-tri-tert-butylphenyl)amidochlorophosphites **1a–f**, *leading to the phosphenimidous esters* **3a–f**. *The crystal structures of phosphites* **1a** *and* **1d** *provide a stereochemical explanation for the better thermal stability of* **1d**. *On the basis of these observations a convenient and general synthesis of phosphenimidous esters* **3a–f** *is presented.*

INTRODUCTION

For the synthesis of dicoordinated phosphorus compounds with a —P=N double bond, the thermal 1,2-elimination of chlorotrimethylsilane, from crowded N-trimethylsilylchlorophosphites **1** is the most suitable and the widely applicable method [1]. For example, the phosphenimidous ester **3a**, the first compound of the —O—P=N— type, stable at room temperature, has been previously prepared in such a way from the corresponding amidochlorophosphite **1a** [2, 3]



1a **3a**

R = 2,6-tert-butyl-4-methylphenyl
Ar = 2,4,6-tri-tert-butylphenyl

Unfortunately, attempts to extend this reaction to the other N-trimethylsilyl-N-(2,4,6-tri-tert-butylphenyl)amidochlorophosphites **1** were not successful. Phosphites **1** containing alkoxy or aryloxy substituents exhibit a high thermal stability and they do not split off chlorotrimethylsilane even under relatively harsh conditions. For example, the compounds **1b** (R = Me) and **1d** (R = Ph) remain unchanged after prolonged reflux (4 hr) in tetrahydrofuran or toluene. Alternatively, phosphenimidous esters **3** may be obtained by condensation of N-(2,4,6-tri-tert-butylphenyl)phosphenimidous chloride [4] with lithium salts of alcohols and phenols. It was found, however, that this method gives satisfactory results in the case of alkyl esters [5, 6], but it is not suitable for the synthesis of aryl esters due to the concomitant formation of 1,2-(PN)-addition products [6].

We report in this paper, a modified and highly efficient procedure for the conversion of N-trimethylsilylamidochlorophosphites **1** to phos-

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phenimidous esters **3**, based on the catalyzed 1,2 elimination of $ClSiMe_3$ from the —O—P—(Cl)—N($SiMe_3$) fragment, using Me_3SiOTf as catalyst.

RESULTS AND DISCUSSION

Our initial efforts were directed towards the generation of the phosphenium cation **2a** in the reaction of phosphite **1a** with Me_3SiOTf (Tf = CF_3SO_2). This procedure, in recent years, has been shown to be especially successful for the abstraction of chloride anion from bis(dialkylamido)chlorophosphites [7]. However, treatment of the phosphite **1a** with the stoichiometric amount of Me_3SiOTf at −30°C, in dichloromethane resulted in the fast and quantitative formation of the imidophosphenite **3a** (scheme 1).

It is likely that the reaction in the first step involves the alkoxyphosphenium cation **2a**, as an intermediate; but we were not able to detect it in solution by ^{31}P NMR spectroscopy even at −70°C.

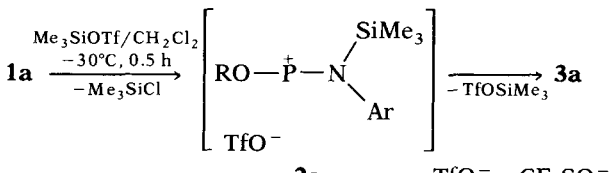
However, it is obvious, from scheme 1, that the conversion of **1a** into **3a** is a catalytic process, since the second step of the reaction includes the regeneration of Me_3SiOTf. Furthermore, we have shown that the phosphite **1a**, which is stable at room temperature in benzene solution, in the presence of 0.02 to 0.05 molar equivalent of Me_3SiOTf, eliminates Me_3SiCl, fairly fast (48 hr at 25°C) to give the corresponding imidophosphenite **3a**.

In order to extend the application of this method, we have prepared five amidochlorophosphites (**1b–f**) and studied their behavior in thermal and catalytic induced elimination of Me_3SiCl.

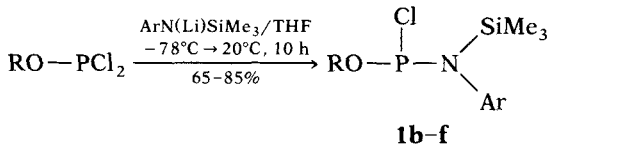
Thermal Stability of Amidochlorophosphites

The syntheses of amidochlorophosphites **1b–f** were achieved by reaction of the dichlorophosphites with lithium N-trimethylsilyl-N-(2,4,6-tri-tert-butylphenyl)amide (scheme 2)

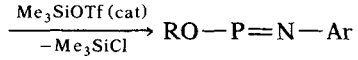
All of these new phosphites were isolated in good yields and characterized by ^1H and ^{31}P-NMR spectroscopy and by microanalysis (Tables 1 and 3). It is important to note that the phosphites **1b–f** are stable in boiling tetrahydrofuran or toluene over a long period (3 hr); in contrast, the phosphite **1a** easily splits off chlorotrimethylsilane under the same conditions. Such notable differences in the



SCHEME 1



1b–f



3b–f

	R
b	Me
c	1-adamantyl
d	Ph
e	2-MeC_6H_4
f	4-FC_6H_4

SCHEME 2

thermal stability of phosphites prompted us to study the molecular crystalline structures of compounds **1a** and **1d** by X-ray diffraction (Table 4).

A characteristic feature of the spatial structure of the thermally labile phosphite **1a** (Figure 1) turned out to be the cis-planar conformation of the Cl—P—N—Si skeleton (the corresponding torsional angle being −0.5°) (Table 4). In this conformation the trimethylsilyl group is eclipsed by the chlorine atom and the distance Si . . . Cl (3.33 Å) is shorter than the sum of the van der Walls radii of the Si and Cl atoms (3.60 Å).

Now, going from **1a** to the sterically less crowded phosphite **1d** we observe (Figure 2) a great change in the molecular conformation: the Cl—P—N—Si fragment is nonplanar with a torsional angle of 68.6°; accordingly, the intramolecular Si . . . Cl distance is considerably larger (3.93 Å). From the point of view of the solid state, it could be suggested that the thermal stability of the phosphites **1a** and **1d** is mainly dependent on the spatial orientations of the Me_3Si group and the Cl atom, the transformation of **1a** into **3a** occurring more easily than in the case of **1d**. However, this observation is not conclusive, since it is well known that spontaneous elimination reactions occur in sterically crowded precursor molecules.

Catalytic Me_3SiCl Elimination

The heating of phosphites **1b–f** under benzene reflux during 1 or 2 hours in the presence of 0.05 to 0.2 molecular equivalent of trimethylsilyl trifluoromethanesulfonate readily gives the corresponding estes **3b–f** in almost quantitative yields (63–98%) (scheme 2).

All compounds prepared gave satisfactory elemental analyses and were identified by their ^1H and ^{31}P NMR parameters (Tables 2 and 3). The structure of **3a** and **3e** were confirmed by X-ray crystallographic analysis [3–8]. Thus, the facile elimination of Me_3SiCl of the amidochlorophos-

TABLE 1 N-Trimethylsilyl-N(2,4,6-tri-tert-butylphenyl)amidochlorophosphites **1a–f**

Compound	Yield[a] (%)	mp (°C)[b] (hexane)	Molecular Formula[b] or Lit. mp (°C)	^1H NMR (solvent/TMS) δ, J (Hz)	^{31}P NMR δ (C_6D_6)
1a	85	148–150	148–150[3]	3	173
1b	65	112–114	$C_{22}H_{41}ClNOPSi$ (430.1)	$CDCl_3$: 0.30 (s, 9H, Me_3Si), 1.27 (s, 9H p-(t-Bu)), 1.54 (s, 9H, o-(t-Bu)), 1.72 (s, 9H, o-(t-Bu)), 3.34 (d, 3H, J = 13.2, MeO), 7,55m (s, 2H, C_6H_2)	193
1c	79	155–156	$C_{31}H_{53}ClNOPSi$ (550.3)	C_6D_6: 0.41 (s, 9H, Me_3Si), 1.29 (s, 9H, p-(t-Bu)), 1.42–2.24 (m, 15H, Ad) 1.62 (s, 9H, o-(t-Bu)), 1.79 (s, 9H, o-(t-Bu)), 7.59 (s, 2H, C_6H_2)	187
1d	73	123–124	$C_{27}H_{43}ClNOPSi$ (492.2)	C_6D_6: 0.39 (s, 9H, Me_3Si), 1.27 (s, 9H, p-(t-Bu)), 1.57 (s, 9H, o-(t-Bu)), 1.71 (s, 9H, o-(t-Bu)), 6.8–7.3 (m, 5H, C_6H_5) 7.56 (s, 2H, C_6H_2)	181
1e	67	120–121	$C_{28}H_{45}ClNOPSi$ (506.2)	C_6D_6; 0.41 (s, 9H, Me_3Si), 1.27 (s, 9H, p-(t-Bu)), 1.60 (s, 9H, o-(t-Bu)), 1.70 (s, 9H, o-(t-Bu)), 2.41 (s, 3H, Me), 6.8 7.2 (m, 4H, C_6H_4), 7.58 (s, 2H, C_6H_2)	180
1f	75	109–110	$C_{27}H_{42}ClFNOPSi$	$CDCl_3$: 0.26 (s, 9H, Me_3Si), 1.30 (s, 9H) 1.55 (s, 18H, o-(t-Bu)), 7.10 (d, 4H, J = 7.6, C_6H_4), 7.55 (s, 2H, C_6H_2)	181

[a] Yield of isolated pure products. Unoptimized.
[b] Satisfactory microanalysis obtained: C ± 0.21, H ± 0.15, Cl ± 0.19.

phites **1b, f**, indicates that the catalytic conversion of **1b, f** into **3b, f** is not particularly sensitive to the stereochemical features of the substrate. This remark should strengthen the fact that the reaction of amidochlorophosphites with Me_3SiOTf proceeds in the first step by chloride abstraction and the formation of the alkoxyphosphenium intermediates **2** (scheme 1).

TABLE 2 N-(2,4,6-Tri-tert-butylphenyl)phosphenimidous Esters **3a–f**

Compound	Yield[a] (%)	mp (°C)[b] (solvent) or bp(°C) / Torr	Molecular Formula[c] or Lit. mp (°C)	^1H NMR (C_6D_6 / TMS) δJ_{P-H} (Hz)	^{31}P NMR δ(THF)
3a	75	180–183 (DME)	180–182[3]	3	139
3b	63	171–172 (hexane)	$C_{19}H_{32}NOP$ (321.4)[d]	1.35 (s, 9H, p-(t-Bu)), 1.56 (s, 18H, o-(t-Bu)), 3.18 (d, 3H, J = 9.3, MeO), 7.49 (d, 2H, J = 1.8, C_6H_2)	156
3c	68	157–159 (DME)	$C_{28}H_{44}NOP$ (441.6)[d]	1.37 (s, 9H, p-(t-Bu)), 1.44–1.92 (m), 1.37 (s, 9H, p-(t-Bu)), 1.71 (s, 18H, o-(t-Bu)), 7.45 (s, 2H, C_6H_2)	179
3d	98	oil[e]	$C_{24}H_{34}NOP$ (383.5)	1.36 (s, 9H, p-(t-Bu)), 1.38–2.20 (m, 15H, Ad), 1.73 (s, 18H, o-(t-Bu)), 7.55 (d, 2H, J = 1.8, C_6H_2)	150
3e	65	96–98 (hexane)	$C_{25}H_{36}NOP$ (397.5)[d]	1.36 (s, 9H, p-(t-Bu)), 1.64 (s, 18H, o-(t-Bu)), 1.98 (s, 3H, Me), 6.85 (m, 4H, C_6H_4), 7.52 (s, 2H, C_6H_2)	148
3f	67	130–133 / 0.05	$C_{24}H_{33}FNOP$ (382.5)	1.35 (s, 9H, p-(t-Bu), 1.61 (s, 18H, o-(t-Bu)), 6.5–6.7 (m, 4H, C_6H_4), 7.52 (d, 2H, J = 1.6, C_6H_2)	148

[a] Yields refer to purified products (exception **3d**).
[b] Melting point determinations were carried out in sealed tubes and are uncorrected.
[c] Satisfactory microanalysis obtained: C ± 0.25, H ± 0.14, P ± 0.23
[d] The monomeric structure is confirmed by cryoscopic molecular mass determination (in C_6H_6): 3b-321, 3c-428, 3e-397.
[e] The product is at least 95% pure, according to NMR spectra. Sample kept 10 hr at 20°C / 0.05 Torr prior analysis.

TABLE 3 Analytical data for compounds **1** and **3**[a]

Compound	Molecular Formula	%C		%H		% Cl (1) P (3)	
		Calc.	Found	Calc.	Found	Calc.	Found
1b	$C_{22}H_{41}ClNOPSi$	61.44	61.35	9.61	9.51	8.24	8.30
1c	$C_{31}H_{53}ClNOPSi$	67.66	67.45	9.71	9.74	6.44	6.49
1d	$C_{27}H_{43}ClNOPSi$	65.89	65.70	8.81	8.96	7.20	7.33
1e	$C_{27}H_{43}ClNOPSi$	66.44	66.61	8.96	8.80	7.00	7.19
1f	$C_{27}H_{43}ClNOPSi$	63.56	63.65	8.30	8.17		
3b	$C_{19}H_{32}NOP$	70.99	71.24	10.03	10.18	9.63	9.40
3c	$C_{28}H_{44}NOP$	76.15	76.33	10.04	10.09	7.01	6.89
3d	$C_{24}H_{34}NOP$	75.16	76.36	8.94	8.80	8.08	8.28
3e	$C_{25}H_{36}NOP$	75.53	75.41	9.13	9.07	7.79	7.85
3f	$C_{24}H_{33}FNOP$	75.36	75.30	8.70	8.81	8.10	8.14

[a] Products **1a** and **3a** are known compounds.

In conclusion, the method described here is a simple, practical procedure for the synthesis of phosphenimidous esters **3**. It is suitable for the preparation of both aliphatic and aromatic phosphenimidous esters and can be considered to be an essential improvement of the traditional method for the formation of a multiple $(p\text{-}p)_{\pi}$ phosphorus nitrogen bond based on the reactions of the thermal elimination of chlorotrimethylsilane.

EXPERIMENTAL SECTION

All manipulations were carried out under a purified argon atmosphere with use of deoxygenated solvents dried with appropriate reagents (THF from Na/benzophenone, dichloromethane and benzene from CaH_2). Trimethylsilyl trifluoromethanesulfonate was purchased from Fluka Chemical Co. and used without further purification. Dichlorophosphites were prepared by the literature procedure [9–10]. N-trimethylsilyl-2,4,6-tri-tert-butylaniline was obtained according to the procedure described earlier [11].

^1H NMR spectra were taken on a Gemini-200 spectrometer. ^{31}P NMR spectra were recorded at 80 MHz with a Bruker WP-200 spectrometer using 85% H_3PO_4 as external reference.

N-Trimethylsilyl-N-(2,4,6-tri-tert-butylphenyl) amidochlorophosphite **1**; *General Procedure*

To a stirred solution of $ROPCl_2$ (35 mmol) in diethyl ether (70 ml) at −30°C was added dropwise lithium N-trimethylsilyl-N-(2,4,6-tri-tert-butylphenyl)amide (35 mmol, generated *in situ* from $ArNHSiMe_3$ and BuLi) in anhydrous THF (100 ml). The solution was slowly warmed to r.t. and stirred for 12 hr. Then the mixture was filtered,

TABLE 4 Selected bond lengths (Å), bond angles and torsional angles (deg) for **1a** and **1d**

Atoms		
P—Cl	2.105(1)	2.1538(7)
P—O	1.664(2)	1.639(1)
P—N	1.702(3)	1.666(1)
N—Si	1.788(3)	1.793(1)
N—Cl	1.495(4)	1.474(3)
O—C_{22}	1.425(4)	1.413(2)
Cl—P—O	100.9(1)	94.48(5)
Cl—P—N	99.61(1)	107.52(5)
O—P—N	104.7(1)	96.80(6)
P—N—Si	132.0(2)	125.79(8)
P—N—C_1	104.8(2)	120.3(2)
Si—N—C_1	121.7(2)	113.5(1)
P—O—C_{22}	112.6(2)	118.5(2)
Cl—P—N—Si	−0.5(3)	68.6(2)
Cl—P—N—C_1	165.0(3)	−118.4(2)
Cl—P—O—C_{22}	−72.9(3)	72.1(2)
Si—N—P—O	103.5(3)	−28.3(2)
C_1—N—P—O	−91.0(3)	144.8(2)
N—P—O—C_{22}	−175.8(3)	−179.7(2)

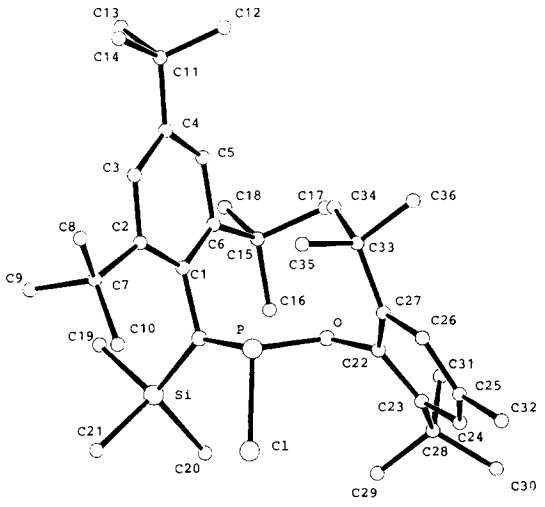


FIGURE 1 X-ray structure of the N-trimethylsilyl-N-(2,4,6-tri-tert-butylphenyl)amido-(2,6-di-tert-butyl-4-methyl)phenoxychlorophosphite **1a**.

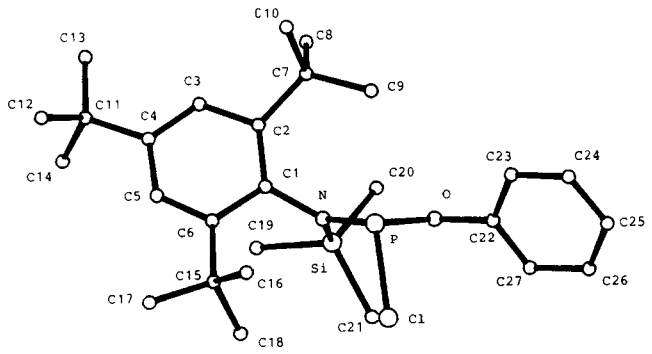


FIGURE 2 X-ray structure of the N-trimethylsilyl-N-(2,4,6-tri-tert-butylphenyl)amidophenoxychlorophosphite **1d**.

the filtrate evaporated under reduced pressure, and pentane (100 ml) added. Filtration, followed by solvent removal, and recrystallization of the residue from hexane afford **1** as a colourless crystalline solid (Table 1).

2,6-Di-tert-butyl-4-methylphenyl Ester of N-(2,4,6-Tri-tert-butylphenyl)phosphenimidous Acid **3a**; *Synthesis by Reaction of* **1a** *with* $TfOSiMe_3$

To a stirred solution of **1a** (2.48 g, 4 mmol) in anhydrous CH_2Cl_2 (15 ml), cooled to −78°C, under Ar, $TfOSiMe_3$ (0.89 g, 0.73 ml, 4 mmol) was added by means of a syringe. The mixture was warmed to r.t. and stirred for 1 hr. Removal of the solvent and volatile products in vacuo led to an oil which gave a crystalline compound upon dissolution in 1,2-dimethoxyethane (10 ml) and storage at 4°C for 5 hr. Recrystallization from dimethoxyethane yielded pure **3a**. Yield: 1.39 g (68%), mp 180–183°C. (Lit. mp 180–182°C)

^1H NMR (C_6D_6/TMS): δ = 1.35 (s, 9H, p-(t-Bu)), 1.57 (s, 18H, o-(t-Bu)), 1.70 (s, 18H, o-(t-Bu)), 2.21 (s, 3H, Me), 7.18 (s, 2H, C_6H_2), 7.60 (s, 2H, C_6H_2).

N-(2,4,6-Tri-tert-butylphenyl)phosphenimidous Esters **3**; *General Procedure*

To a solution of **1b–f** (10 mmol) in dry benzene (40 ml) $TfOSiMe_3$ (0.045 g, 0.036 ml, 0.2 mmol) was added. The solution was refluxed for 2 hr. In all cases the formation of **3** was demonstrated by the development of a yellow coloration. The solvent and volatile products were removed under reduced pressure yielding a residue that contained the expected product having more than 95% purity (^{31}P NMR). Compounds **3b, c, e** could be purified by recrystallization from hexane. Compound **3f** was purified by vacuum distillation (Table 3).

Single Crystal X-ray Diffraction Analyses [12] of Compounds **1a** *and* **1d**

Data were collected on an Enraf Nonius CAD-4 diffractometer at r.t., using graphite monochromated MoK_α radiation (λ = 0.71073 Å) for **1a** and CuK_α radiation (λ = 1.54184 Å) for **1d**. Intensity data were collected by using the $\omega/1.2\ \theta$ scan mode in the range $1° < \theta < 22°$ for **1a** and $1° < \theta < 60°$ for **1d**. Both structures were solved by direct methods and refined by full-matrix least squares. About 80% of the hydrogen atoms of **1a** and 95% of **1d** were located in the difference Fourier maps; the positions of the remaining atoms were calculated.

All H atoms were included in the final refinement with the fixed positional and thermal (B_{iso} = 5 Å^2) parameters. Corrections for Lorentz and polarization effects but not for absorption were applied.

Crystallographic Data for **1a**

$C_{36}H_{61}ClNOPSi$, M = 618.4, triclinic, a = 10.425(2), b = 10.734(5), c = 19.369(5), Å, α = 75.11(3), β = 82.86(2), γ = 89.22(3), V = 2078.1 Å^3, Z = 2, d_c = 0.99 g/cm^3, space group $P\bar{1}$, μ = 1.8 cm^{-1}. Number of unique reflection 4956, reflection with $I > 3\sigma(I)$3020; R = 0.064, R_w = 0.084. Number of refined parameters 370.

Crystallographic data for **1d**

$C_{27}H_{43}ClNOPSi$, M = 492.2, monoclinic, a = 10.157(3), b = 28.654(10), c = 10.222(4) Å, β = 105.13(3)°, V = 2871.9 Å^3, Z = 4, d_c = 1.14 g/cm^3, space groupe $P2_1/c$, μ = 22.6 cm^{-1}. Number of unique reflection 4250, reflection with $I > 3\sigma(I)$ 3367; R = 0.058, R_w = 0.078. Number of refined parameters 289.

ACKNOWLEDGMENTS

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