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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

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To cite this Article Scheide, Gary M. and Neilson, Robert H.(1989) 'Synthesis and NMR Characterization of Heteroarene Substituted N-Silylphosphoranimines', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 46: 3, 139 — 144

To link to this Article: DOI: 10.1080/10426508909412059

URL: <http://dx.doi.org/10.1080/10426508909412059>

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SYNTHESIS AND NMR CHARACTERIZATION OF HETEROARENE SUBSTITUTED N-SILYLPHOSPHORANIMINES

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(Received March 2, 1989; in final form March 22, 1989)

Several of the title compounds were prepared by application of the Peterson olefination reaction to the C-silylated phosphoranimine, $\text{Me}_3\text{SiN}=\text{P}(\text{OCH}_2\text{CF}_3)(\text{Me})\text{CH}_2\text{SiMe}_3$ (**1**). Deprotonation of **1** by treatment with *n*-BuLi, followed by addition of acetylenes or arene-carboxaldehydes, and quenching with Me_3SiCl , afforded the phosphoranimine derivatives, $\text{Me}_3\text{SiN}=\text{P}(\text{OCH}_2\text{CF}_3)(\text{Me})\text{CH}=\text{C}(\text{Ar})\text{R}$ [**3a**: Ar = 2- $\text{C}_4\text{H}_3\text{O}$, R = Me; **3b**: Ar = 2- $\text{C}_4\text{H}_3\text{S}$, R = H; **3c**: Ar = 2- $\text{C}_4\text{H}_3\text{S}$, R = Me; **3d**: Ar = 2- $\text{C}_5\text{H}_4\text{N}$, R = H; **3e**: Ar = 2- $\text{C}_5\text{H}_4\text{N}$, R = Me]. These new phosphoranimines (**3a–3e**), generally formed as mixtures of *cis* and *trans* isomers, were obtained as distillable liquids in yields of 60–75% and were fully characterized by NMR (^1H , ^{13}C , and ^{31}P) spectroscopy and elemental analyses.

Key words: Phosphazene; phosphoranimine; heteroarene; arene; N-silylphosphoranimine; N-silyl-P-trifluoroethoxyphosphoranimine.

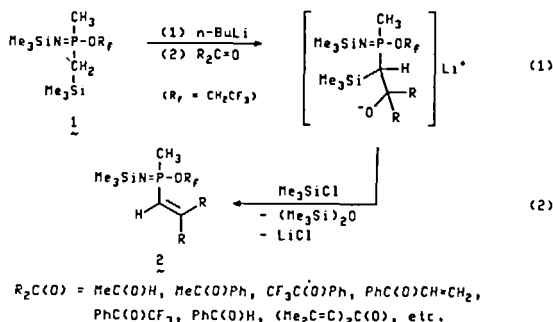
INTRODUCTION

Poly(alkyl/arylphosphazenes), $[\text{R}_2\text{PN}]_n$, a class of phosphazene polymers in which all of the substituents are attached via P—C bonds,^{1,2} are readily prepared by thermal condensation reactions of appropriate Si—N—P precursors such as $\text{Me}_3\text{SiN}=\text{P}(\text{OCH}_2\text{CF}_3)\text{Me}_2$. Because of their importance as phosphazene precursors, we are currently studying the derivative chemistry of these N-silylphosphoranimines. Two general modes of reactivity have been demonstrated: (1) Si—N bond cleavage (e.g., transsilylation³), and (2) deprotonation/substitution reactions of the pendant methyl groups. The latter process has afforded N-silylphosphoranimines bearing silyl,⁴ phosphinyl,⁵ and various organic functional groups.⁶ Moreover, Wisian-Neilson and coworkers⁷ have shown that many such deprotonation/substitution reactions can be successfully applied to the preformed poly(alkyl/arylphosphazenes).

Although they do not undergo condensation polymerization themselves, the C-silylated precursors (e.g., **1**),⁴ are particularly useful reagents for further derivative chemistry. For example, we have recently shown that, by application of the Peterson⁸ olefination process (Equations 1 and 2), they can easily be converted into a variety of vinyl substituted phosphazene precursors (**2**).⁹

As an extension of this general synthetic methodology, we report here the synthesis and NMR spectroscopic characterization of a series of N-silylphosphoranimines which contain heteroarene substituents. These compounds are of interest as potential phosphazene precursors and as small molecule models

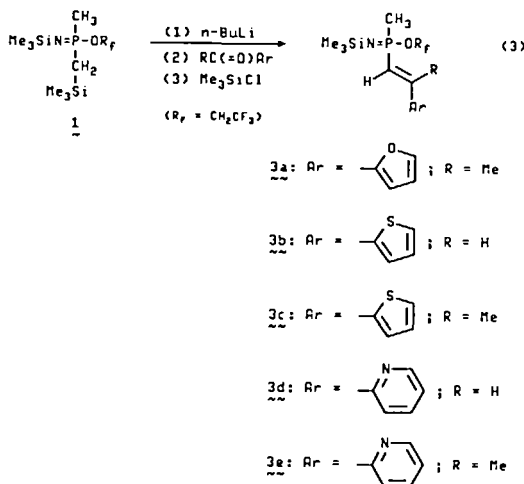
* Author to whom correspondence should be addressed.



for the synthesis of *poly*(alkyl/arylphosphazenes) bearing the same substituent groups. In this context, it is interesting to note that a thiophene derivative of $[\text{Ph}(\text{Me})\text{PN}]_n$ has been recently reported.^{7c}

RESULTS AND DISCUSSION

Treatment of an Et_2O solution of the carbanion derived from the C-silylated phosphoranimine **1** with 2-acetylfuran, followed by quenching with Me_3SiCl , gave the N-silylphosphoranimine **3a** (Equation 3) in which the furan moiety is attached to phosphorus through a $-\text{C}=\text{C}-$ spacer group.



Similar reactions involving thiophenecarboxaldehyde, acetylthiophene, pyridinecarboxaldehyde, and acetylpyridine were used to prepare compounds **3b–3e** (Equation 3). All of these new phosphoranimine derivatives were readily purified by fractional distillation under reduced pressure and were obtained in good yields (ca. 60–75%) as colorless, moisture sensitive liquids. They were fully characterized by NMR spectroscopy (Table I) and elemental analyses (Table II).

The ^1H , ^{13}C , and ^{31}P NMR spectral data, summarized in Table I, are completely consistent with the proposed structures of these vinyl substituted

TABLE I
NMR spectroscopic data^{a,b}

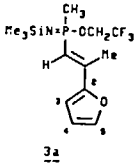
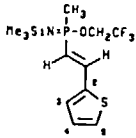
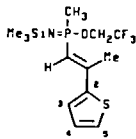
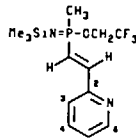
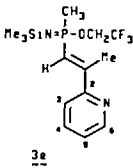
| Compound | Signal | ¹ H NMR | | ¹³ C NMR | | ³¹ P NMR |
|---|---------------------------------|----------------------|---------------------|----------------------|----------------------|---------------------|
| | | δ | J _{PH} | δ | J _{PC} | |
|  3a | Me ₃ Si | 0.05 | | 3.34 | 3.9 | 20.5 |
| | Me ₃ Si ^c | 0.06 | | 3.51 | 3.7 | 22.0 ^c |
| | MeP | 1.64 | 14.7 | 19.06 | 101.5 | |
| | MeP ^c | 1.58 | 14.2 | 19.86 | 97.4 | |
| | C—Me | 2.16 | | 15.51 | 7.0 | |
| | C—Me ^c | 2.33 | 2.6 | 23.75 | 18.0 | |
| | P—CH | 5.61 | 10.3 | 115.38 | 138.4 | |
| | P—CH ^c | 6.13 | 17.5 | 119.65 | 126.2 | |
| | =CMe | | | 142.18 | 7.6 | |
| | =CMe ^c | | | 140.10 | 3.4 | |
| | C ² | | | 154.47 | 21.1 | |
| | C ^{2c} | | | 152.50 | 7.1 | |
| | CH ^{3,4} | 6.4–7.4 ^d | | 110.113 ^d | | |
| | CH ⁵ | 6.4–7.4 ^d | | 143.57 | | |
| | CH ^{5c} | 6.4–7.4 ^d | | 143.79 | | |
|  3b | Me ₃ Si | 0.11 | | 3.72 | 3.6 | 21.8 |
| | MeP | 1.57 | 14.4 | 18.44 | 97.4 | |
| | P—CH | 6.10 | 21.5 | 119.46 | 135.5 | |
| | PCH=CH | 7.44 | (16.9) ^c | 139.39 | 6.3 | |
| | | | (16.8) ^c | | | |
| | C ² | | | 140.91 | 23.0 | |
| | CH ³⁻⁵ | 7.0–7.3 ^d | | 127–129 ^d | | |
|  3c | Me ₃ Si | 0.05 | | 3.46 | 3.3 | 19.9 |
| | Me ₃ Si ^c | 0.07 | | 3.50 | 3.3 | 21.0 ^c |
| | MeP | 1.29 | 14.3 | 17.67 | 97.6 | |
| | MeP ^c | 1.60 | 14.2 | 19.87 | 97.4 | |
| | C—Me | 2.25 | | 18.27 | 7.0 | |
| | C—Me ^c | 2.47 | (1.6) ^c | 29.15 | 18.6 | |
| | OCH ₂ | 4.0–4.4 ^d | | 59.45 | 4.5 | |
| | | | | | (36.9) ^f | |
| | P—CH | 6.00 | 15.8 | 117.48 | 136.5 | |
| | P—CH ^c | 5.79 | 12.0 | 122.56 | 131.3 | |
| | | | (1.3) ^c | | | |
| | =CMe | | | 146.64 | 3.5 | |
| | =CMe ^c | | | 147.56 | 22.3 | |
| | C ² | | | 146.17 | 22.3 | |
| | C ^{2c} | | | 141.78 | 7.7 | |
| | CF ₃ | | | 123.84 | 9.8 | |
| | | | | | (277.6) ^f | |
| | CH ³⁻⁵ | 7.0–7.6 ^d | | 125–129 ^d | | |
| | | | | | | |
|  3d | Me ₃ Si | −0.14 | | 3.17 | 3.8 | 21.8 |
| | Me ₃ Si ^c | 0.07 | | 3.69 | 3.5 | 22.4 ^c |
| | MeP | 1.58 | 14.4 | 18.37 | 99.2 | |
| | MeP ^c | 1.78 | 15.3 | 19.71 | 102.8 | |
| | P—CH | 6.90 | 23.4 | 125.45 | 131.1 | |
| | | | (16.8) ^c | | | |
| | P—CH ^c | 6.07 | 13.7 | 128.89 | 122.5 | |
| | | | (12.0) ^c | | | |
| | PCH=CH | 7.1–7.2 ^c | | 143.12 | | |
| | C ² | | | 153.40 | 26.9 | |
| | C ^{2c} | | | 145.55 | 5.8 | |
| | CH ⁶ | 8.60 | | 150.47 | | |
| | CH ³⁻⁵ | 7.3–7.5 ^d | | 123–137 ^d | | |

TABLE I (Continued)

| Compound | Signal | ¹ H NMR | | ¹³ C NMR | | ³¹ P NMR |
|--|---------------------------------|----------------------|-----------------|----------------------|-----------------|---------------------|
| | | δ | J _{PH} | δ | J _{PC} | δ |
|  ^{3e} | Me ₃ Si | -0.17 | | 3.27 | 3.7 | 20.4 |
| | Me ₃ Si ^c | 0.04 | | 3.44 | 3.8 | 21.5 ^c |
| | MeP | 1.59 | 14.2 | 19.54 | 97.0 | |
| | MeP ^c | 1.45 | 14.9 | 19.70 | 98.5 | |
| | C—Me | 2.49 | | 16.85 | 7.0 | |
| | C—Me ^c | 2.22 | | 25.76 | 17.9 | |
| | P—CH | 5.89 | 14.3 | 124.74 | 132.1 | |
| | P—CH ^c | 6.58 | 18.3 | 122.60 | 133.7 | |
| | =CMe | | | 149.25 | | |
| | =CMe ^c | | | 148.76 | | |
| | C ² | | | 157.76 | 20.7 | |
| | C ^{2c} | | | 153.06 | 6.7 | |
| | CH ⁶ | 8.6 | | 153.29 | | |
| | CH ³⁻⁵ | 7.2–7.7 ^d | | 120–136 ^d | | |

^a Chemical Shifts relative to Me₄Si for ¹H and ¹³C NMR spectra and to H₃PO₄ for ³¹P NMR spectra; coupling constants in Hz; Solvents: CDCl₃ or CH₂Cl₂. ^b The ¹H and ¹³C NMR data for the CF₃CH₂O groups showed very little variation throughout this series of compounds. The complete data is given for **3c** as a representative example. ^c Signals due to the minor isomer. ^d Complex multiplet. ^e J_{HH} values in parentheses. ^f J_{FC} values in parentheses.

compounds. With the exception of the thiophenecarboxaldehyde product **3b**, the compounds exhibited two signals in their ³¹P NMR spectra due to the presence of *cis* and *trans* isomers. These isomers were not separable by fractional distillation and, typically, isomeric mixtures with compositions of ca. 1.5:1 to 3:1 were present even after one or more redistillations through a 10-cm column. In the case of **3b**, however, the proportion of the minor isomer was only about 5% after a single distillation.

Assignment of the structure of **3b** as the *trans* isomer was confirmed by the observation of a large spin-spin coupling (³J_{HH} ≈ 17 Hz) between the two vinylic protons and by the relatively large coupling (³J_{PC} = 23 Hz) between phosphorus

TABLE II
Preparative and analytical data

| Compound | % yield | bp °C/mm Hg | Analyses ^a | |
|-----------|---------|----------------|-----------------------|----------------|
| | | | %C | %H |
| 3a | 70 | 86/0.02 | 45.99 (46.01) | 6.41 (6.41) |
| 3b | 62 | 81–90/0.15 | 42.30 (42.22) | 5.74 (5.61) |
| 3c | 65 | 71/0.01 | 43.71 (43.92) | 6.76 (5.96) |
| 3d | 71 | 83–89/0.15 | 46.67 (46.42) | 6.33 (5.99) |
| 3e | 65 | 85–89/0.02 | 47.44 (47.99) | 6.48 (6.32) |

^a Calculated values in parentheses.

and C-2 of the thiophene ring.¹⁰ The use of similar arguments permits assignment of the major isomer of the other four compounds to the *trans* structure. In the case of the acetylfuran derivatives (**3a**, **3c**, and **3e**), the ¹³C NMR signals of the C-Me group provided additional structural evidence. In these compounds, two distinct doublets are observed in the C-Me region of the ¹³C NMR spectrum: one with a small coupling (³J_{PC} ≈ 7 Hz), assigned to the major isomer in which the C-Me group is *cis* to the phosphorus, and another with a large *trans* coupling (³J_{PC} ≈ 22 Hz), assigned to the minor isomer. Thus, in all cases, the major isomer is that in which the sterically most demanding substituents (i.e., the phosphoranimine and heteroarene moieties) are in a *trans* configuration.

In summary, this work has shown that a variety of heteroarene substituents can be easily incorporated into potential phosphazene precursors via Peterson olefination reactions on C-silylated phosphoranimines. The possibility of preparing alkyl/arylphosphazene polymers or copolymers containing these substituents is currently being investigated.

EXPERIMENTAL SECTION

Materials and General Procedures. The following reagents were obtained from commercial sources and used without further purification: *n*-BuLi, Me₃SiCl, acetylfuran, acetylthiophene, acetylpyridine, thiophenecarboxaldehyde, and pyridinecarboxaldehyde. The starting C-silyl-N-silylphosphoranimine (**1**) was prepared according to the published procedure.⁴ Hexane and ether were distilled from CaH₂ prior to use. Proton and ¹³C{¹H} NMR spectra were recorded on a Varian XL-300 spectrometer; ³¹P{¹H} NMR spectra were obtained on a JEOL FX-60 instrument. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. All reactions and other manipulations were carried out under an atmosphere of dry nitrogen or under vacuum. The following procedure is representative of those used for the synthesis of the new compounds prepared in this study.

Preparation of the Acetylfuran Derivative (3a). A 250-mL, 3-necked flask, equipped with a magnetic stirrer, N₂ inlet, and a rubber septum, was charged with Me₃SiN=P(OCH₂CF₃)(Me)(CH₂SiMe₃) (**1**) (12.8 g, 40 mmol) and Et₂O (100 mL). The solution was cooled to -78°C, stirred for 30 minutes, and then *n*-BuLi (16.0 mL, of 2.5 M hexane solution, 40 mmol) was added via syringe. After the mixture was stirred for 1 hour, 2-acetylfuran (4.4 g, 40 mmol) was added via syringe and the mixture was stirred for ca. 3 hours at -78°C before being quenched with chlorotrimethylsilane (5.1 mL, 40 mmol). The solution was allowed to warm to room temperature and the salts were allowed to settle. The supernatant solution was transferred by cannula to a 1-neck flask and the salts were washed with hexane. The ether-hexane solvent mixture was removed under reduced pressure. Distillation through a 10 cm column afforded **3a** as a colorless liquid (Tables I and II). Compounds **3b-3e** were prepared according to the same procedure by using the appropriate aldehyde or ketone in place of 2-acetylfuran.

ACKNOWLEDGMENT

We thank the U.S. Army Research Office and the Robert A. Welch Foundation for generous financial support of this research.

REFERENCES AND NOTES

1. See for example: (a) R. H. Neilson, P. Wisian-Neilson, *Chem. Rev.* **1988**, 88, 541. (b) R. H. Neilson, R. Hani, P. Wisian-Neilson, J. J. Meister, A. K. Roy, G. L. Hagnauer, *Macromolecules*, **1987**, 20, 910. (c) R. H. Neilson, R. R. Ford, R. Hani, A. K. Roy, G. M. Scheide, U. G. Wettermark, P. Wisian-Neilson, *ACS Symposium Series* **1988**, 360, 283.

2. For more general reviews of phosphazene chemistry, see: (a) H. R. Allcock, "Phosphorus-Nitrogen Compounds"; Academic Press: New York, 1972. (b) H. R. Allcock, *Chem. Eng. News* **1985**, 63(11), 22. (c) H. R. Allcock, *Angew. Chem., Int. Ed. Engl.* **1977**, 16, 147.
3. U. G. Wettermark, R. H. Neilson, *Inorg. Chem.* **1987**, 26, 929.
4. U. G. Wettermark, P. Wisian-Neilson, G. M. Scheide, R. H. Neilson, *Organometallics*, **1987**, 6, 959. For earlier, related work, see: H. Schmidbaur, G. Jonas, *Chem. Ber.* **1967**, 100, 1120.
5. A. K. Roy, R. Hani, R. H. Neilson, P. Wisian-Neilson, *Organometallics* **1987**, 6, 378.
6. A. K. Roy, U. G. Wettermark, G. M. Scheide, P. Wisian-Neilson, R. H. Neilson, *Phosphorus and Sulfur* **1987**, 33, 147.
7. (a) P. Wisian-Neilson, R. R. Ford, R. H. Neilson, A. K. Roy, *Macromolecules* **1986**, 19, 2089. (b) P. Wisian-Neilson, R. R. Ford, *Organometallics* **1987**, 6, 2258. (c) P. Wisian-Neilson, R. R. Ford, *Macromolecules* **1989**, 22, 72.
8. See for example: (a) D. J. Peterson, *J. Org. Chem.* **1968**, 33, 780. (b) G. G. Eberhardt, W. A. Butte, *J. Org. Chem.* **1964**, 29, 2928. (c) D. J. Peterson, *J. Org. Chem.* **1967**, 32, 1717. (d) D. J. Peterson, *J. Organomet. Chem.* **1967**, 8, 199. (e) F. A. Carey, A. S. Court, *J. Org. Chem.* **1972**, 37, 939.
9. (a) G. M. Scheide, Ph.D. Dissertation, Texas Christian University, Fort Worth, TX, 1988. (b) G. M. Scheide, R. H. Neilson, *Organometallics*, submitted for publication.
10. L. D. Quin, in *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; J. G. Verkade, L. D. Quin, Eds VCH: Deerfield Beach, FL, 1987; Chapter 12.