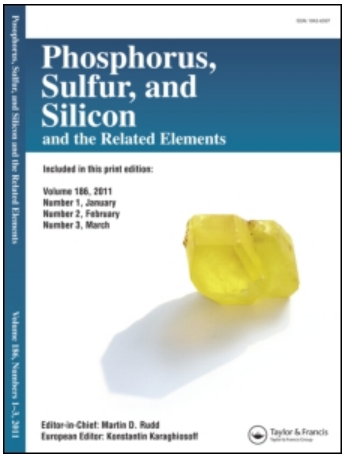

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

CHIRAL LIGANDS: SYNTHESIS AND CHARACTERIZATION OF CARBOHYDRATE DERIVATIVES OF SEVEN- AND EIGHT-MEMBERED CYCLIC PHOSPHITES

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To cite this Article Babiarz, Joseph E. and Pastor, Stephen D.(1994) 'CHIRAL LIGANDS: SYNTHESIS AND CHARACTERIZATION OF CARBOHYDRATE DERIVATIVES OF SEVEN- AND EIGHT-MEMBERED CYCLIC PHOSPHITES', Phosphorus, Sulfur, and Silicon and the Related Elements, 91: 1, 263 — 269
To link to this Article: DOI: 10.1080/10426509408021952
URL: http://dx.doi.org/10.1080/10426509408021952

Phosphorus, Sulfur, and Silicon, 1994, Vol. 91, pp. 263–269
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CHIRAL LIGANDS: SYNTHESIS AND CHARACTERIZATION OF CARBOHYDRATE DERIVATIVES OF SEVEN- AND EIGHT-MEMBERED CYCLIC PHOSPHITES

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(Received July 20, 1994)

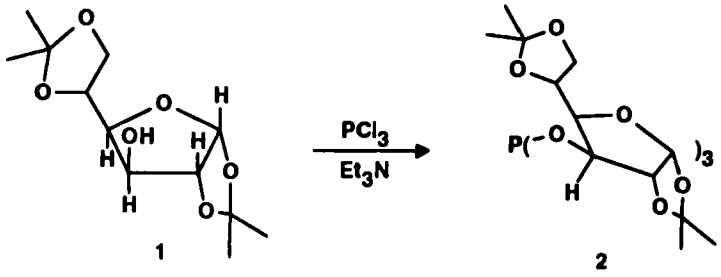
The synthesis and characterization of carbohydrate derivatives of the dibenzo[*d*,*f*][1,3,2]dioxaphosphepin and dibenzo[*d*,*g*][1,3,2]dioxaphosphocin ring system is described.

Key words: Dibenzo[*d*,*f*][1,3,2]dioxaphosphepin, dibenzo[*d*,*g*][1,3,2]dioxaphosphocin, carbohydrate derivative, stereoaxis, chiral ligand.

Chiral phosphorus ligands have played an important role in the design of chiral transition-metal catalysts for asymmetric synthesis.[1] Quite recently, studies have appeared on sterically congested ligands incorporating the dibenzo[*d*,*f*][1,3,2]dioxaphosphepin and dibenzo[*d*,*g*][1,3,2]dioxaphosphocin ring systems,[2–4] which are touted as superior ligands for transition-metal-catalyzed hydroformylation reactions.[5] Van Leeuwen *et al.* reported asymmetric rhodium-catalyzed hydroformylation reactions using chiral derivatives of the dibenzo[*d*,*f*][1,3,2]dioxaphosphepin ring system as ligands.[6] The utilization of carbohydrates from the chiral pool offers an attractive route for the preparation of chiral organophosphorus ligands.[7] The synthesis of chiral carbohydrate derivatives of the dibenzo[*d*,*f*][1,3,2]-dioxaphosphepin and dibenzo[*d*,*g*][1,3,2]dioxaphosphocin ring systems is reported herein.[8]

RESULTS AND DISCUSSION

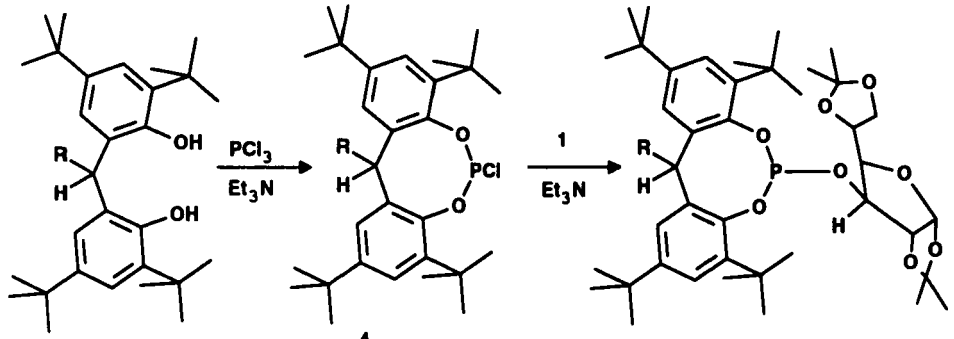
In 1965 Nifant'ev and Tuseev reported that the reaction of 1,2:5,6-bis-O-(1-methylethylidene)-D-glucofuranose **1** (commonly diacetoneglucose) with hexamethylphosphorous triamide (HMPA) gave phosphite **2**.[9] The synthesis of **2** was inves-



1 **2**

tigated using phosphorus(III) chloride in place of HMPA as a model for the synthesis of sugar derivatives from seven- and eight-membered phosphorochloridites.[2,8,10,11] The reaction of three equivalents of **1** with one equivalent of phosphorus(III) chloride using triethylamine as an acid acceptor gave **2** (70% column chromatographed). In the $^{31}P\{^1H\}$ NMR spectrum of **2**, a singlet was observed at δ 145.8, which is in the region expected for a tricoordinate P(III) ester.[12]

The chloridite **4a** was prepared *in situ* by the reaction of the bisphenol **3a** with phosphorus(III) chloride using triethylamine as an acid acceptor.[13] The reaction of **4a** with **1** afforded **5a** (50% recrystallized yield). In the $^{31}P\{^1H\}$ NMR spectrum of **5a** a singlet was observed at δ 132.9, which is in the region previously observed for analogous eight-membered ring phosphites.[10,11a,14] In the ^1H NMR spectrum of **5a**, the magnitude of the geminal coupling ($^2J_{HCH} = -12.6$ Hz) observed for the C(12) bridging methylene protons of the dioxaphosphocin ring is that expected for the boat-chair conformation (BC) commonly found for the trivalent phosphorus containing ring.[15-17] The downfield C(12) proton coupled to phosphorus, whose NMR signal overlapped with the proton signals in the carbohydrate substituent, has previously been shown to have a pseudoaxial ring orientation.[16]



3
a. R = H
b. R = CH_3

4
a. R = H
b. R = CH_3

5
a. R = H
b. R = CH_3

The corresponding C(12)-substituted dioxaphosphocin **5b** was prepared by the reaction of **1** with the chloridite **4b**. In the $^{31}P\{^1H\}$ NMR of the reaction product, a singlet was observed at δ 132.5 that was assigned to the tricoordinate P(III) atom of **5b**. A signal at δ 127.6 was observed in the $^{31}P\{^1H\}$ NMR for a minor phosphorus moiety that could not be isolated and fully characterized. Although attempts to separate the mixture were not completely successful, the concentration of **5b** in the mixture could be enriched by recrystallization from 2-butanone.

In the ^1H NMR spectrum of **5b**, the C(12) proton appears as a doublet of quartets at δ 5.46 with $^3J_{HCCH} = 7.5$ Hz and $^5J_{HP} = 2.1$ Hz.[10,18] The proton assignments were verified by 2D homonuclear ^1H-COSY NMR experiments (Figures 1 and 2). The observation of five-bond *J* coupling of the C(12)-methine proton to phosphorus is consistent with a BC conformation of the dioxaphosphocin ring with a pseudoaxial orientation for both the C(12) proton and the lone pair of electrons on phosphorus.[15,16] The signal for the C(12)-methyl protons of **5b** is observed at δ 1.57 in the COSY spectrum.[19]

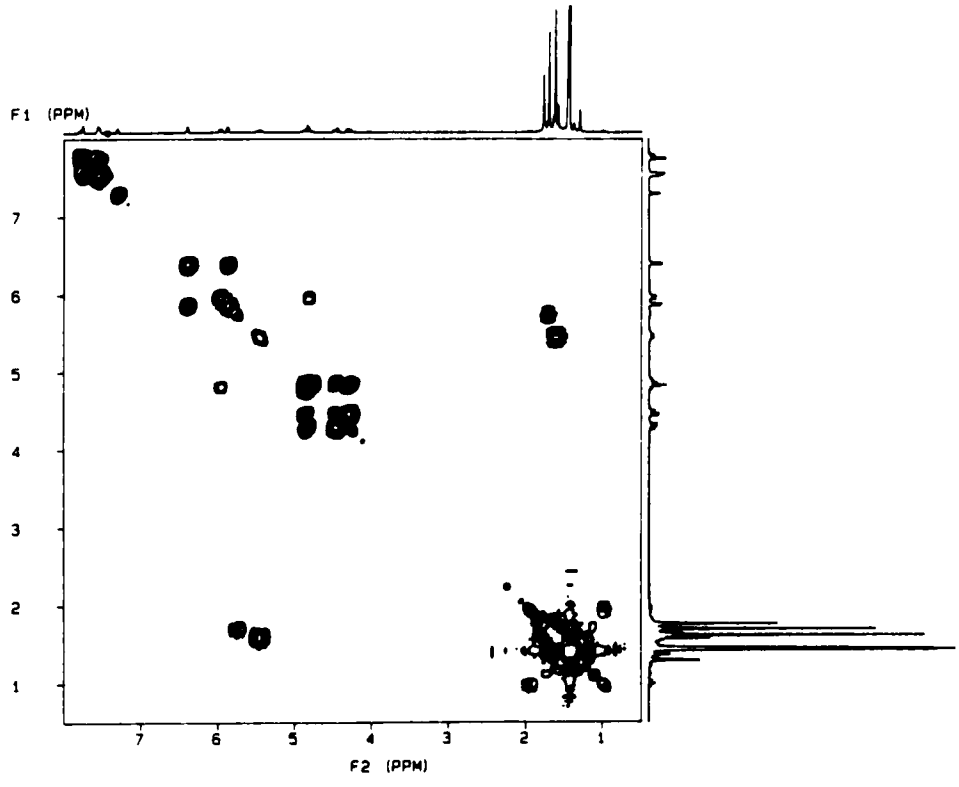


FIGURE 1 2D Homonuclear COSY ^{1}H NMR spectrum of **5b**.

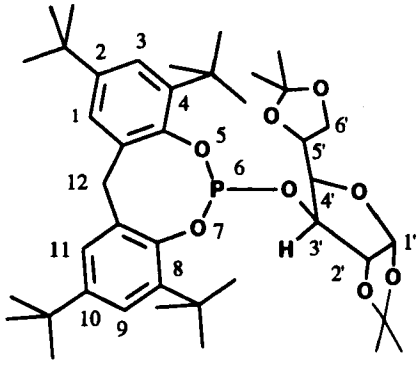
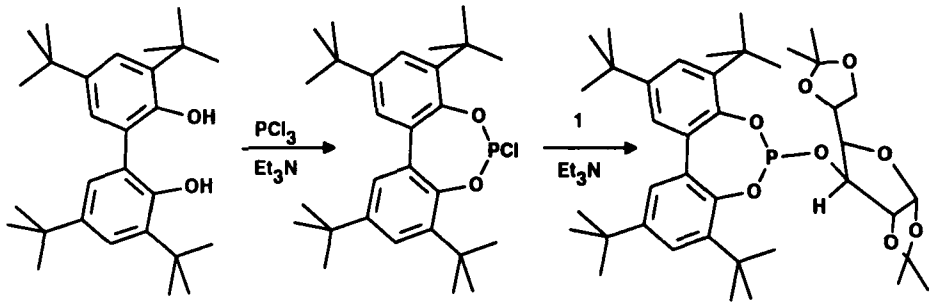


FIGURE 2 Atom numbering scheme.

Reports on the synthesis and stereochemistry of the seven-membered dibenzo-[*d*,*f*][1,3,2]dioxaphosphepin ring system have appeared only recently.[2,3,15,20–23] Crystallographic, variable-temperature NMR, and modelling studies all suggest that the dibenzo[*d*,*f*][1,3,2]dioxaphosphepin ring has a rapidly equilibrating nonplanar twisted conformation in solution. A free energy of activation for ring inversion of 10.2 kcal/mol was determined by variable-temperature NMR spectroscopy for a tetra-*tert*-butyl-substituted dibenzo[*d*,*f*][1,3,2]dioxaphosphepin ring.[2,3b]



7 8 6

The phosphorochloridite **8** was prepared *in situ*,[11] as previously reported, by the reaction of bisphenol **7** with phosphorus(III) trichloride using triethylamine as an acid acceptor.[24,25] The reaction of **8** with **1** in the presence of triethylamine gave the carbohydrate derivative **6** as a white solid (71% recrystallized). In the $^{31}P\{^1H\}$ NMR spectrum of **6**, a singlet was observed at δ 144.7 for the phosphorus atom of the dibenzo[*d*,*f*][1,3,2]dioxaphosphepin ring. The observed optical rotation of **6** ($[\alpha]_D^{25}$ = +86.22 [c = 0.9522; CH_2Cl_2] is significantly larger than that reported for **1** ($[\alpha]_D^{25}$ = −18.5 [c = 5, H_2O],[26] which may reasonably be attributed to the contribution of the stereoaxis (the single bond connecting the two aryl rings) to the optical rotation.[27–29]

EXPERIMENTAL

All melting points were determined in open capillary tubes with a Thomas-Hoover melting point apparatus and are uncorrected. ^1H NMR and ^{31}P NMR spectra were taken on a Varian Model XL-200 or Bruker 300 FT NMR spectrometer. All ^1H chemical shifts are reported in ppm relative to tetramethylsilane, where a positive sign is downfield from the standard. All ^{31}P chemical shifts are reported in ppm relative to 85% phosphoric acid (external), where a positive sign is downfield from the standard. Significant ^1H NMR data are tabulated in the following order: multiplicity (m, multiplet; s, singlet; d, doublet; t, triplet; dd, doublet of doublets; dq, doublet of quartets; dt, doublet of triplets), atom assignments, coupling constants in Hertz, and number of protons. Merck silica gel 60 (70–230 mesh) was used for column chromatography. Merck precoated (0.25 mm) silica gel F-254 plates were used for TLC. Reagents were purchased from commercial laboratory supply houses. Solvents were dried prior to use when necessary with appropriate drying agents. Reactions were carried out in flame-dried apparatus under a dry inert atmosphere of either nitrogen or argon. Elemental analyses were performed by the Analytical Research Department, Ciba-Geigy Corporation.

Tris(1,2:5,6-bis(1-methylethylidene)-α-D-glucofuranosyl) phosphite, (**2**). To a solution of 1.38 g (10 mmol) of phosphorus(III) chloride in 100 mL of diethyl ether cooled with an ice-water bath was added 7.81 g (30 mmol) of **1** followed immediately by a solution of 3.18 g (32 mmol) of triethylamine in 20 mL of diethyl ether. The resultant reaction mixture was stirred for 20 h at rt and then the precipitate of triethylamine hydrochloride was removed by filtration. The solvent was removed *in vacuo* and the residue purified by column chromatography (180 g SiO_2; 9:1 dichloromethane:diethyl ether eluent) to give 5.70 g (70%) of a viscous liquid that crystallized upon standing, mp 54–57°C (lit[9] 54–57°C). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 145.8; ^1H NMR ($CDCl_3$) (300 MHz) δ 1.30 (s, 9 H), 1.35 (s, 9 H), 1.44 (s, 9 H), 1.50 (s, 9 H), 4.09 (overlapping m, 9 H), 4.29 (m, 3 H), 4.64 (d, 3 H), 4.76 (dd, 3 H), 5.93 (9, 3 H); $[\alpha]_D^{22}$ = −20.27 [c = 0.967; $CHCl_3$]. Anal. Calcd for $C_{36}H_{57}O_{18}P$: C, 53.5; H, 7.1; P, 3.8. Found: C, 53.5, H, 7.1, P, 3.8.

2,4,8,10-Tetrakis(1,1-dimethylethyl)-6-[1,2:5,6-bis(1-methylethylidene)-α-D-glucofuranosyl]-12H-dibenzo[d,g][1,3,2]dioxaphosphocin, (**5a**). To a solution of 8.9 g (65 mmol) of phosphorus(III) chloride in 100 mL of toluene at 0°C was added dropwise over 1 h a solution of 25.0 g (59 mmol) of 2,2'-

methylenebis(4,6-di-*tert*-butylphenol), **3a**, and 16.2 g (136 mmol) of triethylamine in 300 mL of toluene. The reaction mixture was stirred at rt overnight and then to the cooled reaction mixture was added 6.0 g (59 mmol) of triethylamine followed by portionwise addition of 15.4 g (59 mmol) of **1**. The reaction mixture was stirred at room temperature for 48 h and then the precipitate of triethylamine hydrochloride was removed by filtration. The solvent was removed *in vacuo* and the residue recrystallized from acetonitrile to give 21 g (50%) of a white solid, mp 173–176°C. $^{31}P\{^1H\}$ NMR (benzene-d_6) δ 132.9; ^1H NMR (benzene-d_6) (200 MHz) δ 1.1–1.6 (overlapping m, 48 H), 3.45 (d, C(12)-H, $^2J_{HCH}$ = 12.6 Hz, 1 H), 4.16 (m, 2 H), 4.3–4.6 (overlapping m, 3 H), 5.45 (overlapping m, 2 H), 6.00 (d, 1 H), 7.2–7.4 (overlapping m, 4 H). Anal. Calcd for $C_{41}H_{61}O_8P$: C, 69.1; H, 8.6. Found: C, 69.2; H; 9.0.

2,4,8,10-Tetrakis(1,1-dimethylethyl)-12-methyl-6-[1,2:5,6-bis(1-methylethylidene)-α-D-glucofuranosyl]12H-dibenzo[d,g][1,3,2]dioxaphosphocin, (**5b**). To a solution of 4.12 g (30 mmol) of phosphorus trichloride in 100 mL of toluene cooled with an ice-water bath was added dropwise a solution of 13.16 g (30 mmol) of **3b** and 6.07 g (60 mmol) of triethylamine. The reaction mixture was stirred at rt for 48 h. The reaction mixture was cooled with an ice-water bath and then a solution of 7.81 g (30 mmol) of **1** and 3.04 g (30 mmol) of triethylamine in 60 mL of toluene (mixture was warmed to effect complete solution) was added dropwise. The resultant reaction mixture was stirred for 48 h at rt and then the precipitate of triethylamine hydrochloride was removed by filtration. The solvent was removed *in vacuo* and the residue was recrystallized from 2-butanone to give 11.36 g (52%) of a white solid. The analytical sample[30] was prepared by recrystallization twice from a mixture of heptane and toluene, mp 244–247°C. $^{31}P\{^1H\}$ NMR (benzene-d_6) δ 132.5. ^1H NMR (benzene-d_6) (200 MHz) δ 1.20–1.80 (overlapping m, 51 H), 4.30 (dd, C(6′)-H(a), $^2J_{H(a)H(b)}$ = 8.5 Hz, $^3J_{H(a)C(6')C(5')H}$ = 5.7 Hz, 1 H), 4.48 (dd, C(6′)-H(b), $^2J_{H(a)H(b)}$ = 8.5 Hz, $^3J_{H(b)C(6')C(5')H}$ = 4.4 Hz, 1 H), 4.85 (overlapping m, C(4′)-H and C(5′)-H, 2 H), 5.46 (dq, C(12)-H, $^5J_{HP}$ = 2.1 Hz, $^3J_{HCCH}$ = 7.5 Hz, 1 H), 5.88 (d, C(2′)-H, $^3J_{HC(2')C(1')H}$ = 3.5 Hz, 1 H), 5.97 (dd, C(3′)-H, $^3J_{HC(3')C(4')H}$ = 2.3 Hz, $^3J_{HC(3')OP}$ = 6.4 Hz, 1 H), 6.40 (d, C(1′), $^3J_{HC(1')C(2')H}$ = 3.5 Hz, 1 H), 7.55 (d, ArH, 2 H), 7.75 (d, ArH, 1 H). Anal. Calcd for $C_{42}H_{63}O_8P$: C, 69.4; H, 8.7. Found: C, 69.5; H, 8.8.[31]

2,4,8,10-Tetrakis(1,1-dimethylethyl)-6-[1,2:5,6-bis(1-methylethylidene)-α-D-glucofuranosyl]-dibenzo[d,f][1,3,2]dioxaphosphepin, (**6**). By the procedure used to prepare compound **5b**, compound **7** was prepared from 12.32 g (30 mmol) of **7**, 4.12 g (30 mmol) of phosphorus(III) chloride, 7.81 g (30 mmol) of **1**, and 9.11 g (90 mmol) of triethylamine in 200 mL toluene. The residue was recrystallized from a mixture of toluene (10 mL) and acetonitrile (90 mL) to give 15.02 g (71%) of a white solid. The analytical sample was prepared by recrystallization twice from acetone, mp 170°C. $^{31}P\{^1H\}$ NMR (benzene-d_6) δ 144.7, ^1H NMR (benzene-d_6) (200 MHz) δ 1.41–1.70 (overlapping s, 48 H), 4.10 (dd, C(6′)-H(a), $^2J_{H(a)H(b)}$ = 8.5 Hz, $^3J_{H(a)C(6)C(5)H}$ = 5.3 Hz, 1 H), 4.22 (dd, C(6′)-H(b), $^2J_{H(a)H(b)}$ = 8.5 Hz, $^3J_{H(b)C(6')C(5')H}$ = 5.3 Hz, 1 H), 4.48 (d, 1 H), 4.58 (d, 1 H), 4.71 (dt, 1 H), 5.31 (dd, 1 H), 5.97 (d, 1 H), 7.48 (d, 1 H), 7.51 (d, 1 H), 7.72 (d, 1 H), 7.74 (d, 1 H); $[\alpha]_D^{25}$ = +86.22 [c = 0.9522; CH_2Cl_2]. Anal. Calcd for $C_{40}H_{59}O_8P$: C, 68.7; H, 8.5. Found: C, 68.6; H, 8.5.

ACKNOWLEDGEMENTS

The authors wish to thank Giba-Geigy Corp. for permission to publish this paper and support of this work. S. D. P. thanks Mr. Rudolf Kesselring (Ciba-Geigy Central Research Laboratories, Basel, Switzerland) for the preparation of the tris(gluco)phosphite, and Dr. R. K. Rodebaugh for the 2D COSY experiments.

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26. S. Budavari, Ed., "The Merck Index," 11th ed., Merck & Co., Inc., Rahway, 1989, p. 468.
27. Compare to the optical rotation observed for **2** and the mixture **5b**, $[\alpha]_D^{25} = -11.94$ [c = 0.9113; CH_2Cl_2], which contains no additional chiral elements.
28. Rapid equilibration of diastereomers observed on the NMR time scale due to rapid ring inversion about the stereoaxis of **7** is not expected with the high frequencies associated with optical measurements. The observed optical rotation would be expected to be that of a mixture of diastereomers making the reasonable assumption that one diastereomer is not formed exclusively. For a discussion on time scales for spectral measurements, see F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press: New York, 1969, pp. 183–184.
29. For related work on dioxaphosphepins with P(V) oxidation state, see (a) L. V. Verizhnikov and P. A. Kirpichnikov, *Zh. Obshch. Khim. (Engl. Transl.)*, **37,** 1281 (1966); (b) M. S. R. Naidu and C. Nagaraju, *Indian J. Chem.*, **24b,** 1164 (1985); (c) B.-F. Hu, Q.-F. Sheng and Z.-M. Li, *Phosphorus Sulfur Silicon Relat. Elem.*, **35,** 371 (1988); (d) K. Sivakumar, K. Subramaanian, S. Natarajan, M. Krishnaiah and L. Ramamurthy, *Acta Cryst.*, **C45,** 806 (1989).
30. The ^{31}P and ^1H NMR spectra displayed signals corresponding to the unidentified phosphorus moiety discussed in the text and Reference 19. Integration of the phosphorus signals the ^{31}P NMR spectrum suggests that the sample is at least 75% of the desired **5b**. Caution, however, must be exercised in interpretation of integrated phosphorus signals, see A. B. Shortt, L. J. Durham and H. S. Mosher, *J. Org. Chem.*, **48,** 3125 (1983).
31. The correct elemental analysis obtained suggests that the unidentified phosphorus compound may be an isomer of **5b**.