Axial Preference of Methylthio Substituent in Dioxaphosphorinanyl Ring System

A. Okruszek and W. J. Stec*

Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, 90-362 Łódź, Bocznna 5, Poland

(Z. Naturforsch. 30b, 430-436 [1975]; received February 4, 1975)

2-Methylthio-1,3,2-dioxaphosphorinans, Synthesis, Spectral Characteristics, Conformation

The spatial disposition of a 2-methylthio group in the 4-methyl-1,3,2-dioxaphosphorinanyl ring system was studied by stereochemical correlation, \(^1\)H, \(^{13}\)C and \(^{31}\)P NMR. It has been established that a CH\(_3\)S-group prefers an axial orientation much more strongly than does a methoxy group.

There has been considerable interest recently in establishing the relationship between the stereochemistry at phosphorus and that of variously substituted carbon atoms in 1,3,2-dioxaphosphorinans. In a number of studies it has been shown that the stable isomers of 2-X-1,3,2-dioxaphosphorinans adopt a chair conformation and \(X\) substituents such as alkoxy, halogeno\(^1\), alkyl\(^2\), aryl\(^3\) or hydrogen\(^4\) prefer to occupy an axial position whereas a dialkylamino group prefers to be equatorial\(^5\). More detailed studies of several cyclic amides have shown that the spatial orientation of a 2-amino group depends upon the nature of the N-substituents\(^6,7\). This prompted us to investigate the axial-equatorial preference of other electronegative \(X\)-substituents at phosphorus in 2-X-1,3,2-dioxaphosphorinans.

In this communication we report the results of our studies on the spatial preference of thioalkyl groups in this system. As a model we chose 2-methylthio-4-methyl-1,3,2-dioxaphosphorinane (1). This model is specially suitable because it has a relatively simple \(^1\)H NMR spectrum. It was obtained by the reaction of 2-chloro-4-methyl-1,3,2-dioxaphosphorinane (2) with methanethiol in the presence of triethylamine. The \(^{31}\)P NMR spectrum of the distilled product revealed the presence of a compound absorbing at \(-179.5\) ppm (Fig. 1) accompanied with minute amounts (~2\%) of another one, \(\delta_{31P} = -182.0\) ppm. Mass spectrometry as well as elemental analysis were consistent with the formula C\(_4\)H\(_8\)O\(_2\)P-SCH\(_3\). Its \(^1\)H NMR spectra show (Table I) that 1b exists in a chair conformation with an equatorial 4-methyl group as follows\(^8\):

1) The magnitude of the coupling constant between the vicinal ring protons (\(J_{ad} = 13.0\) Hz) indicates their anti-disposition and \(a\) must therefore be axial and the ring methyl group equatorial.

2) Proton \(a\) must be axial (and the 4-methyl group therefore equatorial) because of the relatively small coupling between phosphorus and \(a\) (\(J_{Pa}\)  

<table>
<thead>
<tr>
<th>(\delta_H[ppm]) (TMS)</th>
<th>Ha</th>
<th>Hb</th>
<th>He</th>
<th>Hd</th>
<th>He</th>
<th>Hf</th>
<th>Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.53</td>
<td>4.41</td>
<td>3.75</td>
<td>1.88</td>
<td>1.14</td>
<td>1.06</td>
<td>2.05</td>
<td></td>
</tr>
</tbody>
</table>

Table I. \(^1\)H NMR spectral parameters for 1b (C\(_6\)H\(_6\)).
which is indicative of its gauche-relationship with respect to the endocyclic P-O bond.

3) The absence of coupling between the C₁ and the C₄₇-protons shows that only one of them (e) is equatorial and therefore the methyl group must be equatorial as well.

4) The absence of coupling between the 4-methyl group and the vicinal axial proton (d) confirms the equatorial disposition of the methyl group.

Further, the value of 10.0 Hz for Jₚₑ indicates that the lone pair on phosphorus is equatorially orientated. This conclusion is supported by the value of Jₚ₋ₐₓ (4.4 Hz, obtained from the ³¹C NMR spectrum). If the phosphorus lone pair had been axially orientated this value would have been about 10 Hz.

The above spectroscopic data clearly show that the thiomethyl group in the 1,3,2-dioxaphosphorinanyl ring system prefers an axial orientation. Since it is known that the chlorine atom in 2 exclusively occupies the axial position, the trans-geometry of the isolated 1b could be explained as follows:

Either 1) nucleophilic substitution at the PIII atom in the 1,3,2-dioxaphosphorinanyl ring system proceeds with retention of configuration, or, 2) the nucleophilic attack proceeds with inversion but the cis-isomer produced quickly isomerizes to the thermodynamically more stable trans-isomer.

In this series of experiments we were able to show that the second assumption was the correct one. Because the ³¹P NMR spectrum of crude 1, prepared at room temperature, reveals the presence of only 1b, we performed a condensation of 2 with methanethiol in ether at —20 °C in the presence of a 10% molar excess of triethylamine. The ³¹P NMR spectrum, recorded at this temperature immediately after the removal of amine hydrochloride, showed the presence of a mixture of two components with δ = —179.5 ppm and δ = —182.0 ppm in the ratio 30:70 respectively. The minor component (30%) was 1b. At room temperature the second component readily disappeared and there was a corresponding increase in the proportion of 1b.

It is suggested that second component (δₚ₃₃₉ = —182.0 ppm) was the cis-isomer (1a, see Scheme I).

This was additionally demonstrated by the direct oxidation of 1 with dinitrogen tetroxide. 1 was prepared at —20 °C and oxidized immediately at the same temperature. The oxidation product consists of a mixture of the known cis- and trans-2-methylthio-2-oxo-4-methyl-1,3,2-dioxaphosphorinans (3a and 3b) in the ratio 68:32, respectively, whereas dinitrogen tetroxide oxidation of distilled 1 gives 3 containing 95% of the trans-isomer (3b) (see Scheme I). Although the stereoselectivity observed for the dinitrogen tetroxide oxidation of trans-1 was lower than that observed in previous cases, retention of configuration was still strongly favoured. Thus, we could establish the cis-geometry of the kinetically controlled product of the condensation of 2 with methanethiol. Since 1a could not be isolated as a pure compound, its ¹H NMR spectrum could not be obtained. We cannot, therefore, describe its conformation. However, careful analysis of the ¹H NMR spectrum of crude 1, prepared at —20 °C, led us to assign some absorption bands to compound 1a (see Table II). The value of the coupling constant between C₄ and phosphorus (10.3 Hz) is characteristic for an axial orientation of the lone pair on phosphorus and confirms the cis-geometry of 1a. However, the γ effect (the upfield shift of a ring carbon atoms γ to the axial phosphorus substituent) noted lately in 1,3,2-dioxaphosphorinan series, is valid only for C₄ carbon.

The spectroscopic evidence demonstrating the trans-geometry of 1b was confirmed by chemical evidence. Addition of selenium to distilled 1 gave only one isomer of the 2-seleno compound (4b). Its treatment with hydrogen peroxide in nitromethane solution resulted in pure 3b in high yield (see Scheme II). Because the addition of selenium
and the oxidation of cyclic selenoesters with hydrogen peroxide\(^\text{11}\) are known to proceed with retention of configuration at phosphorus, these results strongly supported the trans-configuration of the thermodynamically stable isomer of 1. The same conclusion can be also drawn from the stereoselective oxidation of distilled 1 with trimethylamine N-oxide\(^\text{54}\) which results in pure trans-3. Additional proof that the thermodynamically stable 2-thiono-4-methyl-1,3,2-dioxaphosphorinane (1) has trans-geometry was obtained from the addition of phenyl azide to distilled 1. The 2-N-phenylimino compound (5b) was obtained, which, after treatment with carbon disulphide, gave the corresponding 2-methylthio-2-thiono-4-methyl-1,3,2-dioxaphosphorinane (6b). This compound was obtained by an independent route involving the addition of elemental sulphur to distilled 1. It is notable, that both the addition of sulphur and the addition of phenyl azide to P\(^\text{11}\) compounds, as well as the reaction of N-phenylimino compounds with CS\(_2\), are known to proceed with retention of configuration at phosphorus\(^\text{12}\).

The opposite isomers of 2-thiono- (6a) and 2-seleno-compounds (4a) were obtained as the preponderant products of the reaction between respectively, 2-thiono- (7) and 2-seleno-2-chloro-4-methyl-1,3,2-dioxaphosphorinane (8) with potassium methyl mercaptide (see Scheme II).

Although the reverse stereochemistry was observed, when sodium alkoxides and mercaptides reacted with haloanhydrides such as 7 and 8\(^\text{13}\), the reactions we describe in Scheme III proceeded with preponderate inversion.

\[\text{Scheme III}\]

It should be noted that the absolute values of the spin-spin coupling constants between phosphorus and selenium\(^\text{14}\) in both isomers of 4 provide additional evidence for their configurations. As was shown in our previous paper\(^\text{15}\), magnetically active nuclei directly bonded to phosphorus in the 1,3,2-dioxaphosphorinanyl ring system have higher absolute values of \(J_{\text{P}\text{S}}\) when equatorially orientated than when axially orientated. The isomer obtained from the reaction of distilled 1 with selenium has a \(J_{\text{P}\text{S}}\) value (960 Hz) higher than that of the preponderant one from the reaction of 8 with potassium methyl mercaptide (895 Hz).

The reasons for the higher axial preference of the thiomethyl group relative to the methoxyl group deserve special attention. It is known that the product of the reaction of 2 with methanol in the presence of triethylamine (9a) has the cis configuration.
tion and can be isolated even by distillation at temperatures below 60 °C. Higher temperatures and/or acid catalysis cause its epimerisation into the thermodynamically more stable trans-2-methoxy-4-methyl-1,3,2-dioxaphosphorinane (9b). The axial orientation of the methoxy group in this compound is very well documented. It seems reasonable to consider the much more easy exchange process of 2-methylthio group of cis-1 with methyl-mercaptane in the presence of triethylamine leading to trans-1 than corresponding exchange of methoxy substituent of 9a with methanol, due to a better leaving-group properties of methylthio substituent.

The thermodynamic stability of 1b (trans) relative to 1a (cis) can be explained in terms of the gauche effect.

Our findings about axial preference of 2-methylthio group in 4-methyl-1,3,2-dioxaphosphorinanyl ring system fully agree with a very recent Denney's observation about anachimeric character of 2-phenylthio-4-methyl-1,3,2-dioxaphosphorinane and axial orientation of phenylthio-substituent.

Experimental

All m.ps and b.ps are uncorrected. Solvents and commercial reagents were distilled and dried by conventional methods before use.

1H NMR spectra were recorded at 60 MHz with a Jeol C-60H spectrometer, equipped with Hetero-Spin-Decoupler JNH-SD-HC, with TMS as an internal standard. 31P NMR spectra were obtained on the same instrument operating at 24.3 MHz with external H3PO4 or (PhO)3P as the reference. Negative chemical shift values are reported for compounds absorbing at lower fields than H3PO4.

13C NMR measurements were recorded on a Bruker-HX72 spectrometer using TMS as an internal standard.

Mass spectra were obtained on an LKB-9000S spectrometer at 70 eV ionizing energy. The chlorophosphite (2) was synthesized from butan-1,3-diol and PCl5 in CH2Cl2 according to Lucas' procedure.

1. Condensation of 2 with methyl mercaptane

a) Trans-2-methylthio-4-methyl-1,3,2-dioxaphosphorinane (1b)

To a solution of 2 (30.8 g, 0.2 m) in benzene (150 ml) was added dropwise at 10 °C, with vigorous stirring and cooling, a solution of methyl mercaptane (9.6 g, 0.2 m) and triethylamine (20.4 g, 0.2 m) in benzene (150 ml). Stirring at room temperature was continued for 15 min. Amine hydrochloride was filtered off and washed with benzene. The combined benzene solutions were evaporated and the residue was distilled under reduced pressure to give 1b (25 g, 75%) as a colourless liquid; b.p. 64 °C/2 mmHg; δCH3P = 1.5142, δ31P = -179.5 ppm (benzene).

Mass spectrum: m/e 55 (100%); 166 (21%) 119 (93%); 47 (20%).

C5H11O2PS (166.19)

Calcd C 36.05 H 6.68 P 18.64.

Found C 36.00 H 6.69 P 19.25.

b) cis-2-methylthio-4-methyl-1,3,2-dioxaphosphorinane (1a)

A solution of methyl mercaptane (2.4 g, 0.05 m) and triethylamine (5.6 g, 0.055 m) in ether (50 ml) was added dropwise with vigorous stirring and cooling at -20 °C (acetone/CO2 bath) to a solution of 2 (7.7 g, 0.05 m) in ether (100 ml). Stirring at this temperature was continued for 30 min and amine hydrochloride was filtered off and washed with cold ether. The filtrate was carefully evaporated under reduced pressure to a volume 50 ml. It was stored at -70 °C for further examination. The 31P NMR spectrum (ether, -20 °C) showed the presence of two isomers: 1a, δ = -182.0 ppm (70%) and 1b, δ = -179.5 ppm (30%). The 1H NMR spectrum obtained in benzene solution (after complete removing of ether) was too complex for the first-order analysis. However, we were able to draw out the spectral parameters for both methyl groups of the less stable isomer (1a):

δCH3 = 1.31 ppm, JHCH3 = 6.2 Hz; δCH3 = 2.06 ppm, JPSCH = 11.2 Hz. The close overlap of the signals of C4 and C5 protons (m, δ ~ 4.3 ppm) suggests the conformational mobility of 1a at ambient temperature.

When the sample of ethereal solution prepared above was warmed to room temperature an isomerisation took place and after one hour 31P NMR analysis showed the presence of a mixture containing 20% of 1a and 80% of 1b. Overnight storage resulted in complete isomerization to 1b.

2. Oxidation of 1 with dinitrogen tetroxide

a) To a solution of distilled 1 (3.3 g, 0.02 m) in CH2Cl2 (20 ml) was added dropwise at -20 °C, with stirring and cooling, the methylene chloride solution of dinitrogen tetroxide (10% w/v). The vigorous reaction accompanied with pale-pink color of the mixture was observed. Addition of N2O4/CH2Cl2 was stopped when the solution became rapidly pale-green. Resulting mixture was washed with NaHCO3 solution, dried over MgSO4 and evaporated. The residue was crystallized from ether yielding 3.0 g (61%) of 3b, m.p. 76-7 °C. The 31P NMR spectrum of crude product showed the presence of 3a (5%, δ = -23.5 ppm) and 3b (95%, δ = -19.5 ppm). Lit.: 3a, δ31P = -22.8 ppm; 3b, m.p. 77-77.5 °C, δ31P = -18.1 ppm.

b) To the ethereal solution of 1 (0.02 m), prepared as described in section 1b, was added at -20 °C,
dropwise, with vigorous stirring and external cooling, the methylene chloride solution of dinitrogen tetroxide (10% w/v) to the point, when pink color of the reaction mixture changed to pale-green. The resulting solution was worked-up as described in section 2a. The residue, after evaporation of solvent, was distilled under reduced pressure giving 3 (2.5 g, 70%) as a colorless liquid, b.p. 110-115 °C/0.2 mmHg, n_D = 1.4965. The 31P NMR analysis of distillate revealed the presence of 3a (81%, δ = —23.5 ppm) and 3b (19%, δ = —19.5 ppm), whereas crude product contained 68% of 3a and 32% of 3b.

3. Oxidation of 1b with trimethylamine N-oxide

A solution of trimethylamine N-oxide (1.5 g, 0.02 m) in acetone (30 ml) was added dropwise at 20 °C, with stirring and occasional cooling, to a solution of distilled 1 (3.3 g, 0.02 m) in acetone (30 ml). Stirring at room temperature was continued for 15 min and the resulting solution was evaporated under reduced pressure. The residue was crystallized from ether yielding 3.1 g (71.5%) of 3a, m.p. 77-8 °C, δ = 16.5 Hz; J_HCC = 6.0 Hz; J_OCH = 1.6 Hz. Mass spectrum: m/e 55 (100%); 198 (52%); 151 (8.4%); 119 (21%); 47 (19%).

C_{14}H_{11}O_{2}PSeCl (233.51)


4. Trans-2-methylthio-2-seleno-4-methyl-1,3,2-dioxaphosphorinane (4b)

Elemental selenium (1.58 g, 0.02 m) was added in small portions to the stirred solution of distilled 1 (3.22 g, 0.02 m) in benzene (20 ml). An exothermic reaction accompanied with disappearence of selenium was observed. Stirring at 50 °C was continued for 30 min and the unreacted selenium was filtered off and the filtrate was evaporated. The residue was distilled under reduced pressure yielding 28 g (80%) of 4b. Pale-red liquid, b.p. 90-92 °C/0.05 mmHg, n_D = 1.5955, had crystallized during the storage in refrigerator and was recrystallized from EtOAc/hexane, m.p. 50-1 °C, δ = —54.2 ppm (benzene). 3J_HCC = 1045 Hz. 31P NMR (benzene): δ = 0.975 ppm, δ = —59.0 ppm (lit.19: 5P = —59.0 ppm). Obtained product contained 5% of the cis-isomer (7a), δ = —59.0 ppm (lit.19: δ = —56.0 ppm).

C_{14}H_{13}O_{2}PSCl (319.51)


7. Trans-2-chloro-2-thiono-4-methyl-1,3,2-dioxaphosphorinane (7b)

The procedure described in section 6 was carried out with sulphur in place of selenium gave 90% of 7 as a colorless liquid, b.p. 115 °C/1.5 mmHg, n_D = 1.5222, δ = —60.0 ppm (benzene). Lit.19: b.p. 86-91 °C/0.05 mmHg, δ = —58 ppm). Obtained product contained 5% of the cis-isomer (7a), δ = —59.0 ppm (lit.19: δ = —56.0 ppm).

8. Reaction of 8 with potassium methyl mercaptide.

Cis-2-methylthio-2-seleno-4-methyl-1,3,2-dioxaphosphorinane (4a)

To a suspension of potassium methyl mercaptide (0.025 m, prepared from elemental potassium and methyl mercaptane) in benzene (20 ml) was added with stirring a solution of 8b (4.66 g, 0.02 m) in acetonitrile (30 ml). An exothermic reaction took place and temperature arose to 60 °C. The suspension was stirred under reflux for 2 hrs and cooled. The white precipitate was filtered off, washed with benzene, and the resulting solution was evaporated. The residue was distilled under reduced pressure yielding 3.5 g (71.5%) of 4, b.p. 115-20 °C/0.5 mmHg, n_D = 1.5875. The 31P NMR spectrum of distilled sample showed the presence of 4a (83%, δ = —94.0 ppm) and 4b (17%, δ = —85.5 ppm) whereas that one of the crude product revealed the presence of both isomers (4a and 4b) in the ratio 68:32, respectively. Further twice distillation of
obtained product gave pure 4a, b.p. 95 °C/0.01 mmHg, \( n^\circ = 1.5905, \delta_{15}^\text{D} = 94.0 \text{ ppm (benzene)} \). J_{31}^\text{PSCH} = 2.38 ppm, \( J_{PSCH} = 18.0 \text{ Hz; } \delta_{31}^\text{H} = 1.39 \text{ ppm; } \delta_{31}^\text{HCCCH} = 6.2 \text{ Hz, } J_{POCCCH} = 2.0 \text{ Hz.}

Mass spectrum: m/e (100%); 246 (46%); 166 (6.2%); 119 (30%); 47 (20%).

C\(_6\)H\(_{11}\)O\(_2\)PHSe (245.15)

Found C 24.92 H 5.00 P 12.21.

9. Reaction of 7 with potassium methyl mercaptide.

Cis 2-methylthio-2-thiono-4-methyl-1,3,2-dioxaphosphorinane (6a)

Reaction was performed in the same manner as in the section 8 with 7 (containing 5% of 7a and 95% of 7b) in place of 8. The \( ^{31} \text{P} \) NMR spectrum showed the presence of 6a (65%, \( \delta = -95.5 \text{ ppm} \)) and 6b (35%, \( \delta = -88.5 \text{ ppm} \)) of 6b (\( \delta_{31}^\text{PSCH} = -95.5 \text{ ppm} \)) and 22% of 6b (\( \delta_{31}^\text{PSCH} = -88.5 \text{ ppm} \)). Pure 6a was obtained by two-fold distillation of resulting product, b.p. 110 °C/0.3 mmHg, \( n^\circ = 1.5552, \delta_{15}^\text{D} = -95.5 \text{ ppm (benzene).} \)

\( ^1 \text{H} \) NMR (CC\(_4\)l): \( \delta_{31}^\text{H} = 2.38 \text{ ppm, } \delta_{31}^\text{HCCH} = 6.2 \text{ Hz, } J_{POCCCH} = 2.0 \text{ Hz.}

Mass spectrum: m/e (50%); 198 (62%); 151 (12.5%); 119 (21%); 47 (20%).

C\(_6\)H\(_{11}\)O\(_2\)PS (198.25)

Found C 30.68 H 5.95 P 16.20.

10. Oxidation of 4 with hydrogen peroxide

a) The concentrated (about 90%) H\(_2\)O\(_2\) solution was added at 30 °C, drop wise, to a solution of 4b (5.8 g, 0.02 m) in nitromethane (30 ml) at 36 °C. N\(_2\) was evolved. Stirring and reflux were continued for next hour and solvent was evaporated. The solid residue was crystallized from ether/hexane yielding 4.6 g (89%) of pure 5b, m.p. 71-2 °C, \( \delta_{15}^\text{D} = -9.5 \text{ ppm (benzene).} \)

\( ^1 \text{H} \) NMR (CC\(_4\)l): \( \delta_{31}^\text{H} = 2.06 \text{ ppm, } \delta_{31}^\text{HCCH} = 14.0 \text{ Hz; } \delta_{31}^\text{HCCCH} = 1.29 \text{ ppm, } J_{POCCCH} = 2.2 \text{ Hz.}

Mass spectrum: m/e 155 (100%); 227 (58.5%); 155 (87%); 93 (24%); 65 (22%); 55 (12.5%); lack of the molecular ion.

C\(_6\)H\(_{11}\)O\(_2\)NPS (257.29)

Caled C 51.25 H 6.26 P 12.02 N 5.43, Found C 51.32 H 6.36 P 12.46 N 5.54.

12. Reaction of 5b with carbon disulphide

A solution of 5b (5.14 g, 0.02 m) in carbon disulphide (20 ml) was heated under reflux for 10 hrs and left overnight. Carbon disulphide was removed under reduced pressure and the residue was crystallized from ether yielding 3.2 g (81%) of 6b, m.p. 62-3 °C, \( \delta_{15}^\text{D} = -88.5 \text{ ppm.} \)

The \( ^{31} \text{P} \) NMR spectrum of the crude product did not show the presence of 6a. The mother liquors were evaporated and the residue was distilled giving 2.1 g (76%) of phenyl isothiocyanate, b.p. 50-3 °C/1 mmHg, \( n^\circ = 1.6431. \)

13. Reaction of phenyl azide with 1b. Cis-2-methylthio-2-phenylimino-4-methyl-1,3,2-dioxaphosphorinane (5a)

Phenyl azide (2.4 g, 0.02 m) was added at 0 °C to the ethereal solution of 1b (0.02 m) prepared as described in section 1b. The solution was stirred magnetically for 3 hrs at this temperature (N\(_2\) was evolved) and solvent was evaporated. The \( ^{31} \text{P} \) NMR spectrum of the crude product revealed the presence of 5a (60%, \( \delta = -17.5 \text{ ppm) and 5b (40%, } \delta = -9.5 \text{ ppm.} \)

From \( ^1 \text{H} \) NMR spectrum we were able to draw out the spectral parameter for both methyl groups of 5a: \( \delta_{31}^\text{H} = 2.13 \text{ ppm, } J_{PSCH} = 14.6 \text{ Hz; } \delta_{31}^\text{HCCCH} = 1.29 \text{ ppm, } J_{POCCCH} = 6.2 \text{ Hz, } J_{POCCCH} = 2.2 \text{ Hz.}

Obtained mixture of 2-phenylimino compounds (5) was allowed to react with carbon disulphide as described in section 12. The \( ^{31} \text{P} \) NMR analysis of the crude reaction product revealed the presence of 6a (68%, \( \delta = -95.5 \text{ ppm) and 6b (40%, } \delta = -88.5 \text{ ppm.} \)

The distillation gave 2.7 g (68%) of 6b, m.p. 105-10 °C/0.2 mmHg, \( n^\circ = 1.5542 \) containing 75% of 6a and 25% of 6b.

Authors are indebted to Prof. J. Michalski for his interest in this work and to Dr. P. Simpson for reading of the manuscript.
2 W. G. Bentruđe and J. H. Hargis, ibid. 92, 7136 [1970].
6 b) W. G. Bentruđe and Han Wan Tan, ibid. 94, 8222 [1972]; 94, 4666 [1973].
12 b) R. Kinas and W. J. Stec, unpublished results.
14 a) M. Mikolajczyk and B. Ziernicka, unpublished results.
15 b) W. J. Stec and B. Uznański, unpublished results.
26 B. D. Denney and M. A. Moskal, Phosphorus 4, 77 [1974].