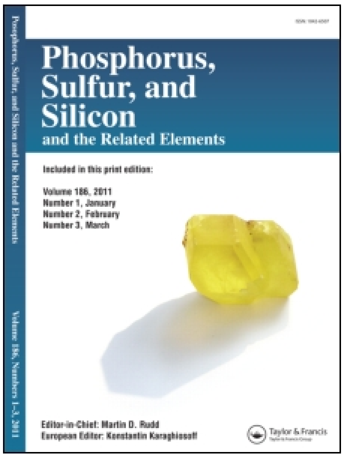

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Non-Metal Derivatives of the Bulkiest Known Tertiary Phosphine, Trimesitylphosphine

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NON-METAL DERIVATIVES OF THE BULKIEST KNOWN TERTIARY PHOSPHINE, TRIMESITYLPHOSPHINE[1]

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Trimesitylphosphine ($Pmes_3$) is the bulkiest known tertiary phosphine. The low yield synthesis of this known compound, its failure to form a carbon disulfide adduct or a selenide derivative, the relatively low values for ν(P—O), ν(P—S) and ν(P—H) in its oxide, sulfide and phosphonium salt respectively, and the high barriers to rotation about the P—C_{ipso} bond in $Pmes_3$, and its derivatives all attest to this fact. Nevertheless, $Pmes_3$, does show chemistry typical of most tertiary phosphines due to its relatively high basicity and the electronic character of even this most bulky phosphine must also be considered in any discussion of its chemistry.

Key words: Tertiary phosphine; triaryl phosphine; steric effect; electronic effect.

INTRODUCTION

Tertiary phosphine compounds have long been among the most important ligands in coordination chemistry. Their effective ligating ability is very dependent upon the availability of the phosphorus lone pair electrons for donation to a metal center. This is in turn dependent upon the nature of the substituents on phosphorus and their effect upon the overall steric and electronic properties of the phosphine. These latter properties are closely inter-related and very often extremely difficult to differentiate.

We have been working with trimesitylphosphine ($Pmes_3$), the bulkiest known tertiary phosphine,[2,3] in an attempt to isolate purely steric effects. It is now clear that the transition metal chemistry of $Pmes_3$ is dominated by steric over electronic effects[4] but this may not necessarily be true of its non-metal chemistry. The latter has been remarkably little studied since the initial preparation of this unique phosphine in 1901.[5]

In this paper, we briefly review what is known about $Pmes_3$ and present our own observations pertaining to non-metal $Pmes_3$ derivatives.

EXPERIMENTAL

Physical Methods. All melting point determinations were made on a Gallenkamp Melting Point Apparatus in unsealed capillary tubes and checked against appropriate standards. Elemental analyses were performed by MHW Laboratories, Phoenix, Arizona. Infrared spectra were recorded either as Nujol mulls between KBr plates or in chloroform solution between KBr windows on a Perkin–Elmer-180 grating spectrophotometer. NMR spectra (in $CDCl_3$) were recorded on a Bruker WH-400 spectrometer operating in the pulsed FT mode at 400.13, 100.61 and 161.98 MHz for the ^1H, ^{13}C and ^{31}P nuclei respectively. Chemical shifts are relative to internal TMS (^1H and ^{13}C) or external 80%

aqueous H_3PO_4 (^{31}P) standards and chemical shifts to low field (high frequency) are considered positive.

Synthesis. Trimesitylphosphine is available commercially (Organometallics, Inc., Route 111, East Hampstead, N.H. 03826) and used as received. The other compounds studied were prepared in purified solvents under dinitrogen atmospheres using standard Schlenk-line procedures. Details are given below.

Trimesitylphosphine Oxide (mes_3PO). A solution of $Pmes_3$ (0.720 g, 1.85 mmol) and hydrogen peroxide (0.4 cm^3 30% H_2O_2) in acetone (75.0 cm^3) was refluxed (4 h), cooled and reduced to dryness under reduced pressure. The resulting pale yellow residue was recrystallized from (i) ethanol/water and (ii) cyclohexane, yield 98.7% (0.74 g). Anal. calcd: C, 80.17; H, 8.22. Found: C, 79.78; H, 8.24; MP: 208–210°C.

Trimesitylphosphine Sulfide (mes_3PS). A solution of $Pmes_3$ (0.389 g, 1.00 mmol) and sulfur (S_8, 0.16 g, 5.00 mmol) in toluene (50.0 cm^3) was refluxed (124 h), cooled and concentrated under reduced pressure (to 4.0 cm^3). Excess sulfur was removed and the pale yellow filtrate was reduced to dryness, washed with diethyl ether and recrystallized from ethanol to give a cream-coloured solid, yield 89.1% (0.375 g). Anal. calcd.: C, 77.10; H, 7.91. Found: C, 76.08; H, 7.99. MP: 196–198°C.

Trimesitylphosphine Selenide (mes_3PSe). This compound could not be formed but a summary of attempts is given below. In each case, the final product was unreacted $Pmes_3$ as determined by MP, IR and ^{31}P NMR.

Method A[6]: $Pmes_3$ (0.194 g, 0.500 mmol) was reacted at room temperature with KSeCN (0.072 g, 0.500 mmol) in acetonitrile (190.0 cm^3) to the point of cloudiness (*ca.* 1.5 n), reduced to dryness and extracted with benzene. The benzene fractions were reduced to dryness and the residue was recrystallized from ethanol. This procedure was also repeated for excess KSeCN and with refluxing (6 h).

Method B[7]: $Pmes_3$ (1.00 mmol) and $(p\text{-}Cl—C_6H_4)_3PSe$ (1.00 mmol) were dissolved in toluene (80 0 cm^3), refluxed (18 h), concentrated (to 3.0 cm^3) and this solution was analyzed.

Method C[8]: Selenium powder (1.220 g, Alfa 325 mesh, m3N) was added to a solution of $Pmes_3$ (1.5 g, 4.00 mmol in 30.0 cm^3 CS_2) refluxed (168 h), filtered while hot through Celite, reduced to dryness, washed with diethyl ether and recrystallised from ethanol. This procedure was used to synthesize the $(p\text{-}Cl—C_6H_4)_3PSe$ used in Method B and was also repeated with different solvents.

Method D: $Pmes_3$ (1.00 g) and selenium powder were ground together and melted followed by extractions with chloroform, ethanol and acetone. These fractions were analyzed.

Methyltrimesitylphosphonium Iodide ($Pmes_3PCH_3I$). $Pmes_3$ (1.00 g, 2.57 mmol) was dissolved in methyl iodide (4.0 cm^3), stirred (1 h), and evapourated under a dinitrogen flow to give white crystalline solid. Yield: 97.3% (1.33 g). Anal. calcd: C, 63.40; H, 6.85. Found: 63.21; H, 6.97. MP: 313–316°C.

Trimesitylphosphonium chloride (mes_3PHCl). Hydrogen chloride gas was bubbled through concentrated sulfuric acid (for drying) and into a solution of $Pmes_3$ (1.00 g, 2.57 mmol in 5.0 cm^3 $CHCl_3$) for 3 min. The solvent was allowed to evaporate and the white crystalline residue was present in 100% yield (1.09 g). Anal. calcd: C, 76.31; H, 8.06. Found: C, 76.10; M, 8.13. MP: >330°C.

METHODS AND DISCUSSION

Michaelis[5] first prepared $Pmes_3$ by a stoichiometric Wurtz–Fittig type reaction. He characterized the product solely on the basis of colour and melting point and reported no percentage yield. The latter is assumed to have been very low since repetition of his procedure has led to low yields (4.4%; 6.0%[10]). Stepanov *et al.*[10] have also prepared $Pmes_3$ in higher yield (~29%) by the now standard Grignard methodology but this yield is still low relative to synthesis for other tertiary phosphines.

$Pmes_3$ has been since characterized by X-ray crystallography,[2] electronic spectroscopy,[9–10] IR[10] and ^{13}C NMR.[11–12] Some early studies have shown that in the ground state, the lone pair electrons are localized on phosphorus and that there is minimal conjugation with the mesityl rings.[11–13] This is a vital consideration since it means that the lone pair electrons will be available for donation to a suitable Lewis acid acceptor (see Introduction).

Triarylphosphines are propeller-like molecules which approach idealized C_{3V} symmetry. Thus one would expect the three mesityl rings of Pmes$_3$ to be chemically and magnetically equivalent. This is shown to be the case by ^{1}H NMR spectrometry (Table I, Figure 1). There is only one set of three resonances a, b and c which appear in the ratio 6:3:2. The aromatic c-resonance is a doublet due to four-bond coupling to phosphorus-31 and this coupling (~3.0 Hz) is higher than that observed for other triaryl phosphines (1–2 Hz)[14] and appears to be solvent dependent. The actual symmetry of Pmes$_3$ in the solid state however, is very close to C_3^2 implying that the two ortho and the two meta positions of the mesityl ring may not be equivalent. In the solution ^{1}H NMR, there is a broadening of the a-resonance with increasing field strength. This is most likely due to the corresponding increase in chemical shift dispersion but it does indicate that the two ortho-methyl groups are magnetically inequivalent. Low temperature spectra (223 K) show splitting of this resonance and the c resonance each into two signals while an increase in temperature leads to sharpened resonances. The b resonance is unaffected. Clearly, even in solution at ambient temperature, the two halves of the mesityl plane are not magnetically equivalent. This must be due to restricted rotation about the P—C_{ipso} bond since similar observations were not made for the analogous compound, Asmes.[3,15] The longer As—C_{ipso} bond is expected to allow for freer rotation. The ^{13}C {^{1}H} NMR spectrum for Pmes$_3$ corroborates our reasoning here. At 223 K, the resonances corresponding to the ortho-ring, ortho-methyl and meta-ring carbons (C(2), C(5) and C(3) respectively) are split into two resonances each.

The ^{31}P {^{1}H} NMR spectrum for Pmes$_3$ is a single narrow line ($\Delta v\frac{1}{2} \approx 10$ Hz) which does not change shape with temperature. The chemical shift (−35.77 ppm in CDCl$_3$) however, is temperature, solvent and field dependent but concentration independent. For any given set of conditions, the position of this resonance is very upfield relative to other triarylphosphines. This has been ascribed to the

TABLE I

Ambient temperature ^{1}H NMR data for Pmes$_3$

Spectral frequency (MHZ)	Solvent	δ(ppm) ($^4J(^{31}P—^1H)$Hz)[c,d]		
60.00[a]	CDCl$_3$	6.73 (3.00)	2.20	2.01
250.13[b]	CDCl$_3$	6.79 (3.03)	2.26	2.06
400.13	CDCl$_3$	6.78 (2.82)	2.25	2.04 (br)
400.13	C_6H_{12}	6.71 (2.71)	2.19	2.03 (br)
400.13	CCl$_4$	6.69 (br)	2.22	2.01 (br)

[a] Spectrum recorded on a Varian EM-360L spectrometer operating in the CW mode (298 K).

[b] Spectrum recorded on a Bruker AM-250 spectrometer operating in pulsed FT mode (297 K).

[c] Relative integration 2:3:6 (see Figure 1).

[d] br = broad.

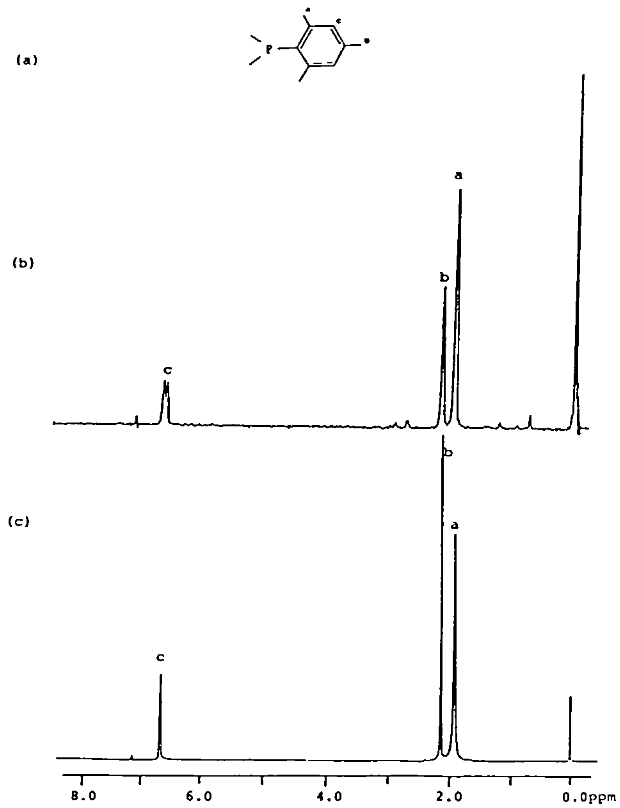


FIGURE 1 Ambient temperature ^{1}H NMR spectra for Pmes$_3$. (a) Labelling scheme showing three magnetic environments; (b) spectrum recorded at 60 00 MHz; (c) Spectrum recorded at 400.13 MHz.

proximity of the ortho-methyl groups gamma to the phosphorus lone pair electrons[16] and is considered a purely steric effect.[16]

To see what steric effects are active in the chemistry of Pmes$_3$, we investigated several non-metal reactions. Unlike most other tertiary phosphines, Pmes$_3$ forms neither a CS$_2$ adduct nor adducts with halogenated solvents. A large trimethoxy analogue however does form the salt, [(2,4,6--MeO)$_3$C$_6$H$_2$)$_3$PCH$_2$Cl]Cl, rapidly ($t_{\frac{1}{2}} < 15$ min) and at ambient temperatures in neat methylene chloride.[17]

Typically, Pmes$_3$ is very stable over long periods of time in solution although if left standing in a halogenated solvent (CHCl$_3$ or CH$_2$Cl$_2$), mes$_3$PO will form very slowly over a period of months. If Pmes$_3$ is refluxed in CHCl$_3$ (15–20 h) with or without the presence of oxygen, the oxide is not formed. Instead, the ^{31}P NMR (297 K) shows a new resonance (δ1.58 ppm) of low intensity relative to unaffected Pmes$_3$. Similarly, refluxing of Pmes$_3$ in CH$_3$OH/CHCl$_3$ solvent mixtures leads to a new resonance at a different position (δ3.03 ppm). The species corresponding to these chemical shifts are short-lived but might be [mes$_3$PCHCl$_2$]Cl and [mes$_3$PCH$_3$]OH respectively, based on their chemical shifts corresponding to the quarternary salts region (see Table II).

The oxide, mes$_3$PO, is easily identifiable by either IR or ^{31}P NMR. The IR

TABLE II

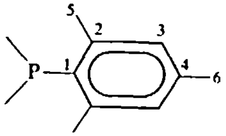
NMR parameters for Pmes$_3$ and Pmes$_3$ derivatives

Compound	^1H $\delta(^4J(^{31}P—^1H))$int[a]		^{13}C $\delta(^4J(^{31}P—^{13}C))$		^{31}P δ
Pmes$_3$	6.78 (2.82)	2	C(1) 131.54 (17.4)	C(4) 137.47	−35.77
	2.25	3	C(2) 142.62 (16.1)	C(5) 22.74 (15.4)	
	2.04	6	C(3) 129.67	C(6) 20.93	
mes$_3$PO	6.88[b]	1	C(1) 130.85 (99.9)	C(4) 140.52[b]	27.81
	6.68 (3.32)	1	C(2) 144.73 (8.7)	C(5) 23.72 (3.8)	
	2.50	3	139.05 (11.7)	23.65 (5.7)	
	2.27	3	C(3) 131.13 (10.8)	C(6) 20.93	
	1.77	3	130.56 (10.9)		
mes$_3$PS	7.00[b]	1	C(1) 131.49 (89.0)	C(4) 140.46[b]	33.26
	6.75	1	C(2) 144.75 (11.4)	C(5) 25.62 (5.1)	
	2.61	3	139.60 (9.6)	24.83 (5.3)	
	2.28	3	C(3) 132.50 (10.8)	C(6) 20.93	
	1.91	3	130.87 (11.4)		
mes$_3$PCH$_3$I[d]	7.10 (3.06)	1	C(1) 119.38 (78.2)	C(4) 144.64	7.20
	6.90 (2.98)	1	C(2) 143.11 (11.2)	C(5) 23.69 (4.9)	
	2.29	3	142.69 (10.4)	22.31 (5.8)	
	2.27	3	C(3) 132.63 (11.1)	C(6) 26.24 (16.7)	
	1.86	3	132.42 (11.1)		
mes$_3$PHCl[e]	7.01	1	C(1) 110.46 (82.2)	C(4) 145.42[b]	−25.62
	6.88	1	C(2) 142.89 (5.0)	C(5) 22.01 (3.6)	
	2.64	3	142.69 (5.4)	21.19 (11.4)	
	2.25	3	C(3) 132.12 (11.3)	C(6) 20.89	
	1.88	3	130.78 (9.3)		

[a] int. = relative integration.

[b] spectra recorded at 223 K.

[c] ^{13}C assignments based on scheme:



[d] Alkly methyl protons, δ2.85 (ppm), $^2J(^{31}P—^1H) = 21.21$ Hz; Alkyl methyl carbon, δ26.24 ppm, $^1J(^{31}P—^{13}C) = 16.7$ Hz.

[e] Phosphonium hydrogen, δ8.92 ppm, $^1J(^{31}P—^1H) = 502.90$ Hz.

spectrum (Nujol) shows a very strong band at 1165 cm^{-1} which is at lower energy than ν(P—O) for other triarylphosphine oxides[18–19] (e.g. ν(P—O) = 1174 cm^{-1} for (o-xylyl)$_3$PO).[19] The lowering of ν(P—O) as (Ar=) Ph > p-tol > 2,4-xylyl > 2,6-xylxyl > mes, has been attributed to steric crowding leading to C—P—C bond angle opening with corresponding changes in P hybridization.[19] This explanation however is insufficient in view of the similar sizes of Ph and p-tol, o-tol and p-xylyl and of o-xylyl and mes substituents. Also, it should be noticed that the order of decreasing ν(P—O) is the same as order of increasing pKa.[11,20] Clearly, electronic effects are also active here.

On the other hand, the difficulties encountered during synthesis of mes$_3$PS and

mes_3PSe are more likely to be due to dominating steric effects. Most attempts at synthesis of the sulfide led to incomplete reaction or selectively to oxide formation if any oxygen was present. The selenide could not be formed at all even though each of the four methods attempted were successful (>80% yield) for synthesis of Ph_3PSe and (o-tol)$_3$PSe. It is worth noting, that the selenide for P(o-oxylyl)$_3$, although this phosphine is less basic than $Pmes_3$, could also not be formed (compare the oxide case, above). These observations are being investigated further.[21]

Once formed, mes_3PS is stable either as a solid or in oxygen-saturated solutions. Elemental mercury reacts rapidly with any unreacted sulfur which may be present but does not affect the sulfide. As in the oxide case, the IR bands for mes_3PS (635 cm^{-1} (s) and 680 cm^{-1} (m)) are at low energy relative to other tertiary phosphine sulfides (627–663 cm^{-1} (s) and 685–800 cm^{-1}).[18–19]

Clearly, in descending the Group 16 family, steric effects become more important in terms of Ar_3PX ($X = 0$, S, Se) formation and stability. The NMR data for the oxide and sulfide (Table 2) show that restricted rotation about the P—C_{ipso} bond is dramatically increased relative to free $Pmes_3$. That is, the ^1H and $^{13}C\{^1H\}$ NMR spectra can only be fully resolved at low temperatures ($\leqq$223 K). The ^{31}P $\{^1H\}$ NMR spectrum for either compound however, shows only one resonance at ambient temperatures having line width comparable to that of the $Pmes_3$ resonance. The resonance for the sulfide (33.26 ppm) appears downfield of that for the oxide (27.81 ppm) as expected[18] and the peak shapes are not affected by changes in temperature, solvent or field strength.

The mes_3PCH_3I salt is readily formed and observed to show IR bands at 1340 cm^{-1} (m) and 1100 cm^{-1} (s, broad) consistent with literature values for comparable compounds.[18] The ^1H and $^{13}C\{^1H\}$ NMR spectra are fully resolved at ambient temperatures showing non-equivalence of the two ortho and the two meta positions. The alkyl-methyl protons are more deshielded than expected (1.12–2.65 ppm)[18] but show reasonable coupling to phosphorus-31 (3–20 Hz).[18] This compound is much more stable than the mes_3PHCl salt which can decompose to $Pmes_3$ in the solid state over a period of weeks or if in solution by addition of water or dimethylsulfoxide.

The solution IR spectrum for mes_3PHCl shows a strong ν(P—H) band at 2252 cm^{-1}, lower than expected (2328–2358 cm^{-1}).[18] The ^1H and $^{13}C\{^1H\}$ NMR spectra require low temperature for resolution but the $^1J(^{31}P—^1H)$ value of 501 Hz measured from the ambient temperature coupled ^{31}P NMR spectrum is quite reasonable (i.e., 436–548 Hz for Ar_3PHX).[18,20] Synthesis of mes_3PHCl was also effected by reaction of $Pmes_3$ with concentrated HCl in refluxing acetone. This procedure was extended to the related compounds, mes_3PHX($X = F$, BF_4, ClO_4 etc.) with high yields (97–99%). The latter species have been characterized spectroscopically and both $^1J(^{31}P—^1H)$ and ν(P—H) values appear to be dependent upon the nature of X. This is receiving further attention.[21]

All the observations discussed in this paper indicate that $Pmes_3$ is at least approaching the upper limit to tertiary phosphine steric bulk. Nevertheless, as has been pointed out above, the steric effects are somewhat offset by electronic effects. Generally, the basicity of a given triarylphosphine is determined by the functional groups present on the aromatic moieties. Electron-donating groups, such as the methyl group, in the ortho and/or para positions increase the overall pKa thereby increasing the nucleophilicity of the phosphine. This latter property however, is expected to be very sensitive to steric effects.[22] Thus, it seems that steric and electronic effects cannot ever be completely separated for tertiary phosphine ligands.

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REFERENCES AND NOTES

1. Presented in part at the X International Conference on Phosphorus Chemistry, Bonn (FRG), August 31-September 6, 1986, paper A-59 and at the 194th American Chemical Society National Meeting, New Orleans, La., U.S.A., August 30-September 4, 1987, paper INOR 241.
2. J. F. Blount, C. A. Maryanoff and K. Mislow, *Tetrahedron Lett.*, **11**, 913 (1975).
3. C. A. Tolman, *Chem. Rev.*, **77**, 313 (1977).
4. (a) E. C. Alyea, S. A. Dias, G. Ferguson and M. Parvez, *Inorg. Chim. Acta*, **37**, 45 (1977); (b) S. A. Dias and E. C. Alyea, *Trans. Met. Chem.*, **4**, 205 (1979); (c) E. C. Alyea, S. A. Dias and S. Stevens, *Inorg. Chim. Acta Lett.* **44**, 207 (1980); (d) E. C. Alyea, G. Ferguson and A. Somogyvari, *Inorg. Chem.*, **21**, 1396 (1982); (e) E. C. Alyea, S. A. Dias, G. Ferguson and P. Y. Siew, *Croat. Chem. Acta*, **57**, 457 (1984); (f) E. C. Alyea, G. Ferguson, J. Malito and B. L. Ruhl, *Inorg. Chem.*, **24**, 3719 (1985); (g) E. C. Alyea and J. Malito, *J. Organometal. Chem.*, **340**, 119 (1988).
5. A. Michaelis, *Liebigs. Ann. Chem.*, **315**, 102 (1901).
6. Adapted from D. W. Meek and P. Nicpon, *Inorg. Synth.*, **10**, 157 (1967).
7. Adapted from D. H. Brown, R. J. Cross and R. Keat, *J. Chem. Soc. Chem. Comm.*, 708 (1977).
8. Adapted from R. F. DeKetelaere, G. P. van der Kellen and Z. Eeckhart, *Phosphorus*, **5**, 43 (1974).
9. E. J. Halpern and K. Mislow, *J. Am. Chem. Soc.*, **89**, 5224 (1967).
10. B. I. Stepanov, E. N. Karpova and A. Bokonov, *Zh. Obshch. Khim*, **39**, 1544 (1969).
11. B. I. Stepanov, A. I. Bokonov and V. I. Svergun, *ibid*, **41**, 533 (1971).
12. A. J. Bellamy, R. O. Gould and M. D. Walkinshaw, *J. Chem. Soc., Perkins II*, 1099 (1981).
13. (a) W. R. Cullen, B. R. Green and R. M. Hochstrasser, *J. Inorg. Nucl. Chem.*, **27**, 641 (1965); (b) G. V. Ratovskii, A. M. Panov, O. A. Yakutina, Yu, I. Sukhorukov and E. N. Tsvetkov, *Zh. Obsch. Khim*, **48**, 1520 (1978); (c) N. A. Rozanel'skaya, A. I. Bokonov, B. M. Uzhinov and B. I. Stepanov, *ibid*, **45**, 277 (1975).
14. D. J. H. Smith in D. Barton and W. D. Ollis (Editors), *Comprehensive Organic Chemistry*, Pergamon Press, Oxford (1979).
15. E. C. Alyea, G. Ferguson, J. Malito and B. L. Ruhl, *Can. J. Chem.*, **66**, 3162 (1988).
16. S. O. Grim and A. W. Yankowsky, *Phosphorus and Sulfur*, **3**, 191 (1977) and references therein.
17. (a) M. Wada and S. Higashizaki, *J. Chem. Soc., Chem. Comm.*, 482 (1984); (b) M. Wada, S. Higashizaki and A. Tsuboi, *J. Chem. Res.* (*s*), 38 (1985).
18. (a) L. C. Thomas, *The Identification of Functional Groups in Organophosphorus Compounds*, Academic Press, London (1974); (b) L. C. Thomas, *intrepretation of the Infrared Spectra of Organophosphorus Compounds*, Heyden, London (1974).
19. R. R. Shifrinka, I. P. Romm, E. N. Gur'yanova and N. A. Rozanel'skaya, *Zh. Prikl. Spectrosk.*, **34**, 111 (1981).
20. T. Allman and R. G. Goel, *Can. J. Chem.* **60**, 716 (1982).
21. Unpublished observations and work in progress.
22. (a) H. Goetz and A. Sidhu, *Liebigs. Ann. Chem.* **682**, 71 (1965); (b) W. A. Henderson, Jr. and S. A. Buckler, *J. Am. Chem. Soc.*, **82**, 5794 (1980).