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# Effect on Chair–Chair Equilibrium of 3-Substituted-1,3,2-Oxazaphosphorinanes of Replacement of $Me_2N$ Substituent on Phosphorus by $isoPr_2N$

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## ABSTRACT

*The chair–chair conformational equilibria (A ⇌ B) of a series of 1,3,2-dioxaphosphorinanes featuring three-coordinated phosphorus substituted with an $isoPr_2N$ group (1–6) have been studied by $^1H$ NMR spectroscopy. Substituents at N(3) included Ph, Me, and isoPr. Compared to the analogous series with an $Me_2N$ group on phosphorus, 1–6 populate the chair conformation B with $R_2N$ equatorial to a greater extent. This is interpreted to mean that conformer A is more destabilized by the greater steric size of $isoPr_2N$ than is conformer B. Thus, the repulsive interactions between equatorial $Me_2N$ and the substituent on N3, believed to be responsible for depopulation of B that results in an unexpectedly high population of A with $Me_2N$ on phosphorus, is overcome by destabilization of A by the axial $isoPr_2N$. The apparent size effect of substituents on N3 in destabilization of B follows the order Ph > isoPr > Me, as observed earlier for the series with a $Me_2N$ group on phosphorus.* © *1996 John Wiley & Sons, Inc.*

## *INTRODUCTION*

We have recently explored the steric and electronic effects of substituents Z and R on the equilibrium **A** ⇌ **B** [1]. Our interest was spurred by the report that, for compound **2′** (Table 3), the equilibrium favored chair conformer **A** [2]. This is in spite of the ≈1 kcal/mol preference of the $Me_2N$ for the equatorial position in the corresponding 1,3,2-dioxaphosphorinane ring system that predominantly populates **C** [3]. We indeed determined that the ratio **B/A** for 1,3,2-oxazaphosphorinane **2′** ($R^1 = R^2 = Me$; $R^3$ = isoPr; Z = $Me_2N$) is 23/77. As originally proposed by Nifant'ev [2], the major effect of introducing the $N(3)R^3$ in place of oxygen in such a ring appears to be to engender repulsive steric interactions between the $N(3)R^3$ and the *equatorial* $Me_2N$ substituent in **B** that are relieved in **A**. This factor evidently is more important than destabilization of **A** by 1,3-synaxial repulsions or interaction of $N(3)R^3$ with the *axial* $Me_2N$. These effects are opposite to the known dominant steric repulsions between an *axial* $Me_2N$ and N(3)Ph for 2-dimethylamino-2-oxo-3-phenyl-1,3,2-oxazaphosphorinanes that destabilize conformation **D** and lead to very predominant population of the $Me_2N$-equatorial form, **E** [4].

The ratio **B/A** for **1′** (Z = $Me_2N$, $R^1 = R^2 = Me$, $R^3$ = Ph) was found to be 13/87, a number somewhat greater than that determined **2′**. The net destabilization of **B** was, however, decreased in **3′** (Z = $Me_2N$, $R^1 = R^2 = Me$, $R^3 = Me$) by 1.3 kcal/mol such that **B/A** (58/42) favored conformer **B**. These measure-

Dedicated to Prof. Louis D. Quin on the occasion of his retirement from the Department of Chemistry of the University of Massachusetts at Amherst.

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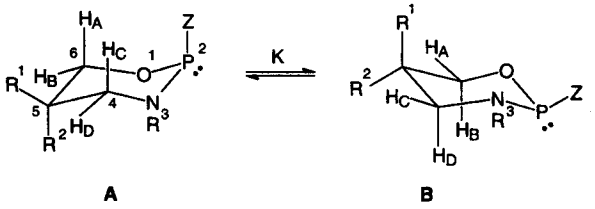
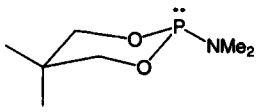
ments established for Z = $Me_2N$ an apparent steric order for substituents $R^3$ on N(3) of Ph > isoPr > Me [1].



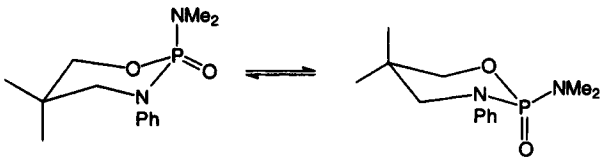
A B

1 $R^1$ = $R^2$ = Me; $R^3$ = $C_6H_5$; Z = $isoPr_2N$
2 $R^1$ = $R^2$ = Me; $R^3$ = isoPr; Z = $isoPr_2N$
3 $R^1$ = $R^2$ = Me; $R^3$ = Me; Z = $isoPr_2N$
4 $R^1$ = $H_x$, $R^2$ = $H_y$; $R^3$ = $C_6H_5$; Z = $isoPr_2N$
5 $R^1$ = $H_x$, $R^2$ = $H_y$; $R^3$ = isoPr; Z = $isoPr_2N$
6 $R^1$ = $H_x$, $R^2$ = $H_y$; $R^3$ = Me; Z = $isoPr_2N$



C

In the study reported here of 1,3,2-oxazaphosphorinanes **1–6**, the same N(3) substituents (Ph, isoPr, and Me) have been employed to probe the effect on the ratio **B/A** of a potentially larger substituent on phosphorus; i.e., Z = $isoPr_2N$. Indeed, Z = $isoPr_2N$ is observed to be more destabilizing of **A** than **B**, the net effect being a shift of the equilibrium toward **B** in all cases.



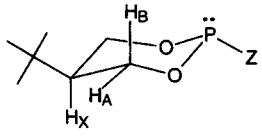
D E

## *RESULTS AND DISCUSSION*

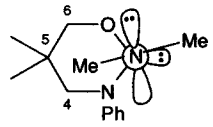
The 1,3,2-oxazaphosphorinanes **1–6** studied were prepared according to Scheme 1.

$^1$H NMR spectra were obtained at 300 MHz and ambient probe temperatures. These products were converted by *tert*-BuOOH to the corresponding 2-oxo derivatives (**1-O** through **6-O**) that were characterized by $^{31}$P, $^{13}$C, and $^1$H NMR analyses and quantitative elemental analyses. Listed in Tables 1 and 2 are pertinent coupling constants and chemical shifts for **1–6**. Second-order spectra were analyzed with the aid of the LAOCN5 spectral simulation program, as indicated.

Compounds **2**, **3**, **5**, and **6** display $J_{BP}$ (2.8–4.2 Hz) and $J_{AP}$ (19.7–21.9 Hz), values consistent with *essentially total population of conformer A*. This conclusion arises from comparisons with $J_{AP}$ values for *trans*-**7** (19.8 Hz in $C_6D_6$; 21.6 Hz in *o*-dichlorobenzene [3a]) and *trans*-**8** (20.2 Hz, $C_6D_6$ [5]), two molecules that have been judged to be entirely in the diequatorially substituted chair conformation shown. (The very large ≈20 Hz coupling constant is found generally for equatorial hydrogen on C6 of 1,3,2-oxazaphosphorinanes and C4 and C6 of 1,3,2-dioxaphosphorinanes when the lone pair on phosphorus is axial [6]). Moreover, for **5** and **6**, $J_{BX}$ (11.3, 11.8 Hz) and $J_{DX}$ (10.8, 12.0 Hz) and the other $J_{HH}$ values recorded support the conclusions based on $J_{HP}$ values. $^3J_{HCNP}$ couplings, e.g., $J_{CP}$ and $J_{DP}$, have not been shown to be reliable for assignment of conformation, especially when nitrogen is phenyl substituted. However, these coupling constants for **2**, **3**, **5**, and **6** are what one expects for population of **B** if a Karplus relationship like that for $^3J_{HCOP}$ holds true.

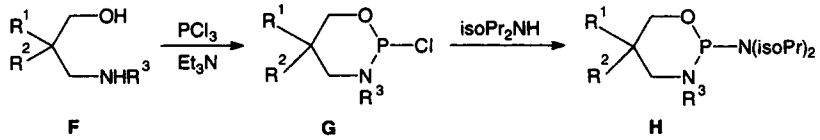


*trans*-**7** Z = t-Bu
*trans*-**8** Z = $Me_2N$



**9**

Only 1,3,2-oxazaphosphorinanes **1** and **4** show coupling constants reflective of sizeable populations of both **A** and **B**. The values of $^3J_{HCOP}$ for **1** and **4** can be used to obtain the mole fractions of **A** and **B** and the ratios of **B/A** found in Table 3. As shown in previous articles [1], the mole fraction of conformer **A**, *N*(**A**), can be calculated from the following equation, the measured coupling constant, $J_{AP}$(obsd), and assumed $J_{AP}$ values for conformers **A** and **B**. A completely analogous expression is available for $J_{BP}$.



F G H

**SCHEME 1**

**TABLE 1** Selected $^1$H NMR Coupling Constants (Hz) for **1–6**[a] in $C_6D_6$ at 300 MHz, 18°C

| Compd. | $^3J_{AP}$ | $^3J_{BP}$ | $^3J_{CP}$ | $^3J_{DP}$ | $^3J_{BD}$ | $^3J_{AC}$ | $^3J_{AY}$ | $^3J_{BY}$ | $^3J_{CY}$ | $^3J_{DY}$ | $^3J_{AX}$ | $^3J_{BX}$ | $^3J_{CX}$ | $^3J_{DX}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1**[b] | 12.7 | 9.2 | 4.6 | 5.8 | −1.3 | | | | | | | | | |
| **2**[c,d] | 20.4 | 2.4 | 16.6 | 2.5 | | −2.4 | | | | | | | | |
| **3**[b] | 21.4 | 4.2 | 17.1 | 2.4 | | −2.8 | | | | | | | | |
| **4**[c,e] | 13.3 | 8.2 | 3.3 | 5.8 | −0.6 | | 7.9 | 5.0 | 10.1 | 5.1 | 4.7 | 5.9 | 4.6 | 4.7 |
| **5**[c,e] | 19.7 | 3.7 | 15.0 | 2.9 | | −1.9 | 2.9 | 2.9 | 4.3 | 2.4 | 4.6 | 11.3 | 4.1 | 10.8 |
| **6**[c,e] | 21.9 | 3.4 | 16.8 | 2.4 | | −2.2 | 2.3 | 2.2 | 3.1 | 2.8 | 4.3 | 11.8 | 4.4 | 12.0 |

[a] $^2J_{AB}$ = −10.7 to −11.5; $^2J_{CD}$ = −11.6 to −12.1
[b] Spectrum partially simulated to confirm chemical shifts and coupling constants.
[c] From iterative spectral simulation by use of LAOCN5 program.
[d] RMS error 0.067; probable error in $\delta$, 0.014–0.052 Hz; $J$, 0.019–0.104 Hz.
[e] RMS error for **4**, 0.094 Hz; **5**, 0.073 Hz; **6**, 0.104 Hz. Probable error in $\delta$: **4**, 0.009–0.017 Hz; **5**, 0.007–0.014 Hz; **6**, 0.009–0.015 Hz. Probable error in $J$: **4**, 0.013–0.035 Hz; **5**, 0.010–0.030 Hz; **6**, 0.013–0.045 Hz.

**TABLE 2** Selected $^1$H Chemical Shifts for **1–6** in $C_6D_6$

| Compd. | $H_A$ | $H_B$ | $H_C$ | $H_D$ | $H_X$ | $H_Y$ |
|---|---|---|---|---|---|---|
| **1**[a] | 3.58 | 3.41 | 3.16 | 3.02 | | |
| **2**[b] | 3.53 | 3.56 | 2.51 | 2.60 | | |
| **3**[a] | 3.46 | 3.58 | 2.41 | 2.53 | | |
| **4**[a] | 3.75 | 3.69 | 3.36 | 3.24 | 1.53 | 1.42 |
| **5**[a] | 3.88 | 3.69 | 2.85 | 2.69 | *c* | 1.69 |
| **6**[a] | 4.01 | 3.85 | 2.93 | 2.80 | 1.16 | 1.96 |

[a] Partially simulated, not iterated.
[b] Iteratively simulated using LAOCN5 program. Probable error in $\delta$, 0.014–0.052 Hz. RMS error 0.067.
[c] Obscured by $isoPr_2N$ resonance.

$$N(\mathbf{A}) = \frac{J_{AP}(\text{obsd}) - J_{AP}(\mathbf{B})}{J_{AP}(\mathbf{A}) - J_{AP}(\mathbf{B})}$$

This approach is completely parallel to that used previously to obtain the same measures of equilibrium **A** ⇌ **B** for other 1,3,2-oxazaphosphorinanes featuring three-coordinated phosphorus [1]. The assumption of appropriate values for $J_{AP}$ and $J_{BP}$ for conformers **A** and **B** is essential.

In recent work from this laboratory [1b], $J_{AP}$ (5.8 Hz) and $J_{BP}$ (11.7 Hz) values were estimated for conformer **A** of the molecule analogous to **1**, but with $Me_2N$ in place of $isoPr_2N$. ($J_{BP}$ values ≈ 12 Hz are typical of conformers with the phosphorus lone pair equatorial [6]). These numbers were assumed for **A** in the calculation of the population of **A** for **1** and **4** by use of the foregoing equation. The coupling constant $J_{AP}$ = 21.9 Hz was assigned to **B** (*lone pair axial*). This is the value for **6** recorded in Table 1 and was chosen because $J_{AP}$ (21.9 Hz) observed for **6** is the largest in the series **2**, **3**, **5**, and **6**, all of which clearly populate **B** nearly exclusively. Since $J_{AP}$ should reach a maximum when **B** is totally populated, the value observed for **6** was deemed to be closely characteristic of that conformation. The value of $J_{BP}$ for **6** (3.4 Hz) was assigned to **B** as well. The ratio **B/A** ($K$) and the corresponding $\Delta G°$ thus estimated for **1** and **4** appear in Table 3. The **B/A** ratios are averages based on $J_{AP}$ and $J_{BP}$, for **1**, 43/57 and 30/70, respectively, and for **4**, 47/53 and 42/58, respectively. The greater population of **A** by **1** and **4**, relative to **2**, **3**, **5**, and **6**, also is seen in the larger values of $J_{AY}$ and $J_{CY}$ for **4**. (Indeed, the $J_{CY}$ value seems somewhat too large.) Lower limit values for $K$ and $\Delta G°$ for **2**, **3**, **5**, and **6**, based on the assumption that the ratio **B/A** is at least 95/5 (≥95/5), also are found in Table 3. The same data, obtained by the identical approach [1], for the analogs (**1′**, **2′**, etc.) with Z = $Me_2N$ instead of Z = $isoPr_2N$ are listed in Table 3 for comparison.

Several observations are readily made from the data of Table 3: (1) In all instances, the analog with Z = $isoPr_2N$ more greatly populates **B**. (2) When Z = $isoPr_2N$, only for $R^3$ = Ph is conformer **B** not essentially totally populated. (3) The population of **A** increases for the Z = $Me_2N$ analogs in the order $R^3$ = Me < isoPr < Ph. (4) For the Z = $isoPr_2N$ analogs, the same order is $R^3$ = Me,isoPr < Ph. (5) The effect on **B/A** of changing Z from $Me_2N$ to $isoPr_2N$ is much greater for $R^3$ = Me and isoPr than for $R^3$ = Ph.

It should be recalled that, in the work by the Bentrude and Nifant'ev groups on **2′** [1b,2], the premise was set forth that the large population of **A** arose from depopulation of **B** as a result of destabilizing *equatorial–equatorial* interactions between the $isoPr_2N(3)$ and $Me_2NP$ substituents in **B** [1,2]. The substituent Z = $isoPr_2N$ is presumably sterically larger than Z = $Me_2N$ [7]. Evidently, this increase in steric size is felt more strongly in **A** than in **B**. That is, on replacement of $Me_2N$ by $isoPr_2N$, steric repulsions involving the *axial* $R_2N$ in **A** increase more than those accompanying the *equatorial* $R_2N$ in **B**, shifting the equilibrium in favor of **B**. Furthermore, this differential effect is emphasized with the $R^3$ substitu-

**TABLE 3** Estimated Equilibrium Constants (**B/A**) at 25°C

| *Compd.* | $R^1 = R^2$ | $R^3$ | *Z* | ***B/A***[a] | *K*[b] | *ΔG°* *(kcal/mol)* | *ΔΔG°* | *Ref.* |
|---|---|---|---|---|---|---|---|---|
| **1** | Me | Ph | $isoPr_2N$ | 36/64 | 0.56 | 0.33 | | This work |
| **1′** | Me | Ph | $Me_2N$ | 13/87 | 0.15 | 1.1 | 0.8 | [1b] |
| **2** | Me | isoPr | $isoPr_2N$ | >95/5 | >19 | <−1.7 | | This work |
| **2′** | Me | isoPr | $Me_2N$ | 23/77 | 0.30 | 0.69 | >2.4 | [1b] |
| **3** | Me | Me | $isoPr_2N$ | >95/5 | >19 | <−1.7 | | This work |
| **3′** | Me | Me | $Me_2N$ | 58/42 | 1.4 | −0.19 | >1.5 | [1a] |
| **4** | H | Ph | $isoPr_2N$ | 44/56 | 0.79 | 0.14 | | This work |
| **4′** | H | Ph | $Me_2N$ | 20/80 | 0.25 | 0.80 | 0.66 | [1b] |
| **5** | H | isoPr | $isoPr_2N$ | >95/5 | >19 | <−1.7 | | This work |
| **6** | H | Me | $isoPr_2N$ | >95/5 | >19 | <−1.7 | | This work |
| **6′** | H | Me | $Me_2N$ | 65/35 | 1.9 | −0.38 | >1.3 | [1a] |

[a]Average based on $J_{AB}$ and $J_{BP}$.
[b]$K$ = **B/A**.

ents isoPr and Me. These substituents show less evidence of equatorial–equatorial repulsions in **B** when Z = $Me_2N$ (compound **1′** vs. **2′** and **3′**; **4′** vs. **6′**). Thus, the depopulation of **B** in favor of **A** is greater for $R^3$ = Ph (compounds **1′** and **2′**) than for $R^3$ = Me or isoPr (compounds **2′**, **3′**, and **6′**). The greater incremental increase in the population of **B**, due to the change of Z from $Me_2N$ to $isoPr_2N$ when $R^3$ = Me or isoPr (compare **1** vs. **2** and **3**; **4** vs. **5** and **6**), is consistent with an increase in destabilization of **A** of similar magnitude in all three cases that is more greatly offset by increased repulsions in **B** by the substituent Ph that evidenced the greatest steric repulsions in **1′**–**4′** and **6′**.

The steric order isoPr > Me for $R^3$ was evident in the series **1′**–**4′** and **6′** (see Table 3). The size and similarities of the coupling constants for **2**, **3**, **5**, and **6** led us to postulate earlier in this paper that they all are essentially totally in conformation **B**, suggesting similar steric effects for isoPr and Me. Though one would hesitate to quantitate the differences, careful comparison of key coupling constants for **2** with those of **3** and, independently, those of **5** with coupling constants for **6** suggests that the analog with $R^3$ = Me in each case more greatly populates **B** than does its $R^3$ = isopropyl counterpart. Thus, for the $R^3$ = Me case (**3** and **6**) in both comparisons, $^3J_{AP}$ values are larger. Furthermore, for the **5** vs. **6** comparison, $^3J_{BZ}$ and $^3J_{DX}$ are somewhat larger for **6**. The same comparison is found for $^3J_{CP}$ and $^3J_{DP}$, although, as noted earlier, these couplings constants have not been generally utilized in conformational analysis of 1,3,2-oxazaphosphorinanes containing three-coordinated phosphorus. It appears likely, therefore, that the steric order isoPr > Me, and therefore the overall order Ph > isoPr > Me, applies to the series with Z = $isoPr_2N$ (**1**–**6**) as well as to that studied previously with Z = $Me_2N$.

That increased repulsive interactions in **A** when Z is changed from $Me_2N$ to $isoPr_2N$ so importantly influence **B/A** in **1**–**6** by destabilizing **A** may be understood in terms of features of the X-ray structure for **1′** depicted by **9** [1b]. Indeed, it was seen that repulsive interactions stemming from axial $Me_2N$ repulsions appear to be relieved by flexing of the ring so that the axial $Me_2N$ can be accommodated in the P-$NMe_2$ conformation shown in **9**. This conformation, in which the orientation of the phosphorus and nitrogen lone pairs is approximately orthogonal, is optimal energetically [8]. For an axial $isoPr_2N$, such a P–$NR_2$ conformation is likely too high in energy to be populated because of repulsions between axial ring hydrogens and the isoPr group (R = isoPr). The $R_2N$ group is, therefore, forced to rotate approximately 90° about the P–N bond so that the electron lone pair is oriented between the axial hydrogens at C4 and C6. The P–$NR_2$ bonding system then sacrifices the energy gained from the optimal orientation [8] of the substituents on the P–N bond shown in **9**, which, in turn, destabilizes conformation **A**.

## *EXPERIMENTAL*

### *Methods and Materials*

All glass apparatus were flame dried under argon before use. Commercial solvents were used as received unless otherwise noted. Ethyl ether and tetrahydrofuran were dried and distilled from sodium metal and benzophenone. Ethyl acetate and dichloromethane were dried over calcium hydride and freshly distilled before use. Triethylamine was dried over potassium hydroxide and distilled. Phosphorus trichlo-

ride was distilled before use. *tert*-Butyl hydroperoxide (3.0 M in toluene) was used as received from Fluka Chemical Company. Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected. $^1$H NMR spectra were obtained on Varian XL-300 and Unity 300 spectrometers. Proton assignments are given in structures **A** and **B**. Second-order spectra were analyzed with the aid of the LAOCN5 simulation program. $^{31}$P NMR spectra were obtained on a Varian XL-300 spectrometer at 121 MHz. $^{13}$C NMR spectra were recorded on a Varian XL-300 spectrometer at 75.4 MHz. $^{13}$C NMR $J$ values designate carbon–phosphorus couplings. $^1$H and $^{13}$C chemical shifts are in parts per million downfield from TMS as internal standard, while $^{31}$P chemical shifts are relative to external 85% $H_3PO_4$. $^{13}$C chemical shifts for phenyl ring carbons were assigned from their intensities and from empirical calculations using standard parameters [9]. Detailed coupling constant listings, given in the Results and Discussion, are not repeated here. Multiplicities in NMR spectra are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), ddd (doublet of doublet of doublets), m (multiplet). Unless otherwise indicated, $^{13}$C resonances are singlets. The purities of products were checked by capillary GC on a Varian 3300 instrument with flame ionization detection. GC/MS were obtained on a Finnigan MAT 95 mass spectrometer. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

*2-Chloro-3-phenyl-5,5-dimethyl-1,3,2-oxazaphosphorinane.* This compound was prepared according to the literature procedure [10] from N-phenyl-2-hydroxymethyl-2-methylpropylamine (13.8 g, 0.080 mol), triethylamine (15.6 g, 21.4 mL, 0.150 mol), and phosphorus trichloride (10.5 g, 6.69 mL, 0.080 mol). Crude, undistilled product was estimated to be 90% pure from its $^{31}$P NMR spectrum ($\delta$ $^{31}$P = 145.9) and was used directly in the next step.

*2-Diisopropylamino-3-phenyl-5,5-dimethyl-1,3,2-oxazaphosphorinane* (**1**). The above chloridite (18.8 g, 0.080 mol) was dissolved in ether (200 mL) and added dropwise to stirred diisopropylamine (19.5 g, 27.0 mL, 0.190 mol) in ether (200 mL) at 0°C under argon. The reaction mixture was stirred for overnight at room temperature. The ammonium salt was removed by filtration, and the solvent was evaporated under reduced pressure. Distillation (bp 97°C/0.05 mmHg) yielded 10.0 g (53%) of pure **1**, an oil: $^{31}$P NMR ($C_6D_6$) $\delta$ 116.0. $^1$H NMR ($C_6D_6$) $\delta$ 0.82 (3 H, s, $(CH_3)C$), 0.85 (3 H, s, $(CH_3)C$), 0.93 (6 H, d, $(CH_3)_2CHNP$, $J$ = 6.6 Hz), 1.27 (6 H, d, $(CH_3)CHNP$, $J$ = 6.8 Hz), 3.06 (1 H, ddd, $CH_2N$), 3.20 (1 H, dd, $CH_2N$), 3.37 (2 H, m, $(CH_3)_2CHNP$), 3.47 (1 H, ddd, $CH_2O$), 3.62 (1 H, dd, $CH_2O$), 6.86 (1 H, m, $C_6H_5$), 7.20 (4 H, m, $C_6H_5$); $^{13}$C NMR ($C_6D_6$) $\delta$ 23.64 (d, $(CH_3)_2CHNP$, $J$ = 6.0 Hz), 23.97 ($(CH_3)C$), 24.77 ($(CH_3)C$), 25.07 (d, $(CH_3)_2CHNP$, $J$ = 9.2 Hz), 32.65 (s, $(CH_3)C$), 45.82 (d, $(CH_3)_2CHNP$, $J$ = 10.6 Hz), 60.28 ($CH_2N$), 73.23 ($CH_2O$), 120.81 (d, $o$-$C_6H_5$, $J$ = 12.4 Hz), 120.91 (d, $p$-$C_6H_5$, $J$ = 3.9 Hz), 128.87 ($m$-$C_6H_5$), 149.86 (d, $i$-$C_6H_5$, $J$ = 11.2 Hz); GC–MS (EI, 70 eV) $m/z$ (relative intensity) 308 ($M^+$, 32), 265 (4), 209 (12), 208 (100).

*2-Diisopropylamino-2-oxo-3-phenyl-5,5-dimethyl-1,3,2-oxazaphosphorinane* (**1-O**). *tert*-Butyl hydroperoxide in toluene (2.62 mL, 7.86 mmol) was slowly added to a stirred solution of **1** (2.42 g, 7.86 mmol) in $CH_2Cl_2$ (35 mL) at 0°C. The reaction mixture was stirred for 1 hour. Solvent was removed by rotary evaporation and then under high vacuum to give a pale-yellow solid, purified by Kugelrohr distillation (bp 60°C/0.06 mmHg) to yield 1.78 gm (70%) of colorless crystalline **1-O**: mp 139–140°C; $^{31}$P NMR ($C_6D_6$) $\delta$ 9.3; $^1$H NMR ($C_6D_6$) $\delta$ 0.44 (3 H, s, $(CH_3)C$), 0.92 (6 H, d, $(CH_3)_2CHNP$, $J$ = 6.6 Hz), 1.02 (3 H, s, $(CH_3)C$), 1.34 (6 H, d, $(CH_3)_2CHNP$, $J$ = 6.7 Hz), 2.75 (1 H, ddd, $CH_2N$), 3.34 (1 H, dd, $CH_2N$), 3.23–3.40 (2 H, m, $((CH_3)_2CH)_2NP$), 3.42 (1 H, ddd, $CH_2O$), 4.26 (1 H, dd, $CH_2O$), 6.94–7.59 (5 H, m, $C_6H_5$); $^{13}$C NMR ($C_6D_6$) $\delta$ 22.21 (d, $(CH_3)_2CHNP$, $J$ = 2.4 Hz), 22.65 ($(CH_3)_2CHNP$), 22.88 ($(CH_3)C$), 23.83 ($(CH_3)C$), 32.80 (d, $(CH_3)C$, $J$ = 2.2 Hz), 46.55 (d, $(CH_3)_2CHNP$, $J$ = 4.7 Hz), 64.36 (d, $CH_2N$, $J$ = 2.4 Hz), 75.07 (d, $CH_2O$, $J$ = 6.6 Hz), 124.92 ($o$-$C_6H_5$), 126.36 (d, $p$-$C_6H_5$, $J$ = 5.3 Hz), 128.02 ($m$-$C_6H_5$), 146.47 (d, $i$-$C_6H_5$, $J$ = 2.4 Hz). Anal. calcd for $C_{17}H_{29}N_2O_2P$: C, 62.94; H, 9.01; N, 8.64. Found: C, 62.91; H, 9.06; N, 8.59.

*3-(N-Phenyl)aminopropan-1-ol.* A solution of 3-bromo-1-propanol (12.7 g, 8.2 mL, 0.901 mol) and aniline (19.7 g, 19.2 mL, 0.201 mol) in THF (70 mL) was refluxed for 3 days. The salt was removed by filtration and washed with THF. Solvent removal by rotary evaporation, followed by short-path distillation, gave the desired product aminoalcohol (bp 120–121°C/0.14 mmHg; Ref. [11] bp 172–179°C/11 mmHg) as a colorless liquid (8.71 g, 64%): $^1$H NMR ($CDCl_3$) $\delta$ 1.77 (2 H, quintet, $CH_2CH_2CH_2$), 3.17 (2 H, t, $CH_2N$, $J$ = 6.5 Hz), 3.35 (2H, bs, OH, NH), 3.68 (2H, t, $CH_2O$, $J$ = 5.9 Hz), 6.65–7.15 (5 H, m, $C_6H_5$); $^{13}$C NMR ($CDCl_3$) $\delta$ 31.79 ($CH_2CH_2CH_2$), 41.68 ($CH_2N$), 61.19 ($CH_2O$), 112.97 ($m$-$C_6H_5$), 117.45 ($p$-$C_6H_5$), 129.07 ($o$-$C_6H_5$), 148.30 ($i$-$C_6H_5$).

*2-Chloro-3-phenyl-1,3,2-oxazaphosphorinane.* By a procedure [10] identical to that for the preparation of 2-chloro-3-phenyl-5,5-dimethyl-1,3,2-oxazaphosphorinane, reaction of 3-(N-phenyl)aminopropan-1-ol (8.71 g, 0.060 mol) and triethylamine (11.6 g, 0.110 mol) in ether (100 mL) with phosphorus trichloride (7.90 g, 0.060 mol) in ether (100 mL) gave 5.56 g (64%) of the product as a colorless liquid: $^{31}$P NMR (ether) $\delta$ 153.3 that was used without further purification.

*2-Diisopropylamino-3-phenyl-1,3,2-oxazaphosphorinane* (**4**). To a stirred solution of 2-chloro-3-phenyl-1,3,2-oxazaphosphorinane (12.4 g, 0.060 mol) in dry ether (200 mL) was added dropwise at 0°C under argon atmosphere over a 30 minute period a solution of diisopropylamine (12.8 g, 17.8 mL, 0.130 mol) in ether (200 mL). The solution was stirred overnight at room temperature. The salts were removed by filtration. Solvent removal and short-path distillation of the residue yielded **4** (bp 110–111°C/0.05 mmHg) as a colorless liquid (4.47 g, 36%): $^{31}$P NMR ($C_6D_6$) $\delta$ 119.0; $^1$H NMR ($C_6D_6$) $\delta$ 0.96 (6 H, d, $(CH_3)_2$CHNP, $J$ = 4.2 Hz), 1.26 (6 H, d, $(CH_3)_2$CHNP, $J$ = 4.2 Hz), 1.42 (1 H, m, $CH_2CH_2CH_2$), 1.53 (1 H, m, $CH_2CH_2CH_2$), 3.24 (1 H, m, $CH_2N$), 3.37 (1 H, m, $CH_2N$), 3.66–3.79 (2 H, m, $(CH_3)_2CH_2NP$), 3.69 (1 H, dddd, $CH_2O$), 3.75 (1 H, dddd, $CH_2O$); $^{13}$C NMR ($C_6D_6$) $\delta$ 23.61 (d, $(CH_3)_2$CHNP, $J$ = 6.0 Hz), 25.11 (d, $(CH_3)_2$CHNP, $J$ = 9.2 Hz), 27.01 (d, $CH_2CH_2CH_2$, $J$ = 0.9 Hz), 45.80 (d, $(CH_3)_2$CHNP, $J$ = 10.6 Hz), 46.81 ($CH_2N$), 61.21 ($CH_2O$), 119.68 (d, *o*-$C_6H_5$, $J$ = 12.8 Hz), 120.58 (d, *p*-$C_6H_5$, $J$ = 2.6 Hz), 128.83 (*m*-$C_6H_5$), 149.68 (d, *i*-$C_6H_5$, $J$ = 12.8 Hz). GC–MS (EI, 70 eV) *m/z* (relative intensity) 280 ($M^+$, 63), 237 (12), 181 (38), 180 (100), 152 (67), 104 (21), 77 (15).

*2-Diisopropylamino-2-oxo-3-phenyl-1,3,2-oxazaphosphorinane* (**4-O**). This compound was prepared from **4** (3.14 g, 12.7 mmol) by oxidation with *tert*-butyl hydroperoxide (4.25 mL, 12.7 mmol) in $CH_2Cl_2$ (38 mL) by the procedure described for **1**. Purification by Kugelrohr distillation (bp 68°C/0.07 mmHg) gave crystalline **4-O** (2.67 g, 85%): mp 68–70°C; $^{31}$P NMR ($C_6D_6$) $\delta$ 8.72; $^1$H NMR ($C_6D_6$) $\delta$ 0.92 (6 H, d, $(CH_3)_2$CHNP, $J$ = 6.6 Hz), 1.31 (6 H, d, $(CH_3)_2$CHNP, $J$ = 6.9 Hz), 2.06 (1 H, m, $CH_2CH_2CH_2$), 2.12 (1 H, m, $CH_2CH_2CH_2$), 3.31–3.41 (2 H, m, $(CH_3)_2CH_2NP$), 3.56 (1H, m, $CH_2N$), 3.64 (1 H, m, $CH_2N$), 4.18 (1 H, m, $CH_2O$), 4.35 (1 H, m, $CH_2O$); $^{13}$C NMR ($C_6D_6$) $\delta$ 22.28 (d, $(CH_3)_2$CHNP, $J$ = 2.3 Hz), 22.61 ($(CH_3)_2$CHNP), 27.01 (d, $CH_2CH_2CH_2$, $J$ = 5.2 Hz), 46.49 (d, $(CH_3)_2$CHNP, $J$ = 4.8 Hz), 50.93 (d, $CH_2N$, $J$ = 2.6 Hz), 65.26 (d, $CH_2O$, $J$ = 7.3 Hz), 124.02 (d, *o*-$C_6H_5$, $J$ = 11.4 Hz), 124.13 (d, *p*-$C_6H_5$, $J$ = 4.8 Hz), 128.81 (*m*-$C_6H_5$), 146.24 (d, *i*-$C_6H_5$, $J$ = 3.5 Hz). Anal. calcd for $C_{15}H_{25}N_2O_2P$: C, 60.79; H, 8.50; N, 9.45. Found: C, 60.85; H, 8.54; N, 9.35.

*2-Diisopropylamino-3,5,5-trimethyl-1,3,2-oxazaphosphorinane* (**3**). To a solution of the chloridite [10] (17.8 g, 0.097 mol) in dry ether (200 mL) a solution of diisopropylamine (21.7 g, 30.0 mL, 0.214 mol) in dry ether (200 mL) was added dropwise at 0°C under an argon atmosphere over a 1 hour period. The reaction solution was stirred for 24 hours at room temperature. Removal of the ammonium salt by filtration and ether from the filtrate by distillation, and distillation of the residue yielded **3** (bp 54°C/0.06 mmHg) as a colorless liquid, 14.96 g (62%): $^{31}$P ($C_6D_6$) $\delta$ 144.2; $^1$H NMR ($C_6D_6$) $\delta$ 0.55 (3 H, s, $(CH_3)C$), 1.14 (6 H, d, $(CH_3)_2$CHNP, $J$ = 6.8 Hz) 1.20 (3 H, s, $(CH_3)C$), 1.30 (6 H, d, $(CH_3)_2$CHNP, $J$ = 6.8 Hz), 2.18 (3 H, d, $CH_3N$, $J$ = 12.0 Hz), 2.41 (1 H, ddd, $CH_2N$), 2.53 (1 H, dd, $CH_2N$), 3.46 (1 H, ddd, $CH_2O$), 3.58 (1 H, dd, $CH_2O$), 3.77–3.89 (2 H, m, $(CH_3)_2CH)_2NP$); $^{13}$C NMR ($C_6D_6$) $\delta$ 23.94 ($(CH_3)C$), 24.51 (d, $(CH_3)_2$CHNP, $J$ = 5.5 Hz), 24.69 (d, $(CH_3)C$, $J$ = 1.5 Hz), 25.17 (d, $(CH_3)_2$CHNP, $J$ = 9.8 Hz), 33.19 (d, $(CH_3)C$, $J$ = 4.6 Hz), 37.52 (d, $CH_3N$, $J$ = 20.2 Hz), 44.09 (d, $(CH_3)_2$CHNP, $J$ = 10.7 Hz), 65.15 (d, $CH_2N$, $J$ = 14.1 Hz), 74.19 (d, $CH_2O$, $J$ = 5.8 Hz). GC–MS (EI, 70 eV) *m/z* (relative intensity) 246 ($M^+$, 60), 203 (10), 147 (19), 146 (100), 128 (6), 90 (14).

*2-Diisopropylamino-2-oxo-3,5,5-trimethyl-1,3,2-oxazaphosphorinane* (**3-O**). As described for the preparation of **1-O**, reaction of **3** (2.01 g, 8.33 mmol) in $CH_2Cl_2$ (30 mL) with *tert*-butyl hydroperoxide (2.77 mL, 8.33 mmol) gave **3-O** (1.33 g, 61%) on distillation (bp 90–91°C/0.25 mm of Hg) as a white solid: mp 72–74°C; $^{31}$P NMR ($C_6D_6$) $\delta$ 16.5; $^1$H NMR ($C_6D_6$) $\delta$ 0.34 (3 H, s, $(CH_3)C$), 1.00 (3 H, s, $(CH_3)C$), 1.22 (6 H, d, $(CH_3)_2$CHNP, $J$ = 6.0 Hz), 1.35 (6 H, d, $(CH_3)_2$CHNP, $J$ = 6.0 Hz), 2.09 (1 H, ddd, $CH_2N$), 2.28 (1 H, dd, $CH_2N$), 3.31 (1 H, ddd, $CH_2O$), 3.37–3.52 (m, 2H, $(CH_3)_2CH)_2NP$), 4.17 (1 H, dd, $CH_2O$); $^{13}$C NMR ($C_6D_6$) $\delta$ 22.68 (d, $(CH_3)_2$CHNP, $J$ = 2.2 Hz), 22.71 (d, $(CH_3)_2$CHNP, $J$ = 2.3 Hz), 23.0 ($(CH_3)C$), 23.78 ($(CH_3)C$), 32.42 (d, $(CH_3)C$, $J$ = 2.5 Hz), 36.60 ($NCH_3$), 46.37 (d, $(CH_3)_2$CHNP, $J$ = 4.7 Hz), 62.50 ($CH_2N$), 74.72 (d, $CH_2O$, $J$ = 6.0 Hz). Anal. calcd for $C_{12}H_{27}N_2O_2P$: C, 54.90; H, 10.37; N, 10.68. Found: C, 54.82; H, 10.40; N, 10.61.

*2-Diisopropylamino-3-methyl-1,3,2-oxazaphosphorinane* (**6**). This compound was prepared according to the procedure described for **3**. Reactants were: 2-chloro-3-methyl-1,3,2-oxazaphosphorinane

[1a] (11.4 g, 0.074 mol), N,N diisopropylamine (17.3 g, 0.171 mol), each in ether (200 mL). Product distillation (bp 41°C/0.06 mm of Hg) afforded 10.2 g (66%) of **6**, a colorless liquid: $^{31}$P NMR ($C_6D_6$) $\delta$ 141.5; $^1$H NMR ($C_6D_6$) $\delta$ 1.14 (6 H, d, $(CH_3)_2$CHNP, $J$ = 6.6 Hz), 1.31 (6 H, d, $(CH_3)_2$CHNP, $J$ = 6.6 Hz), 2.23 (3 H, d, $CH_3N$, $J$ = 12.1 Hz), 1.16 (1 H, dtt, $CH_2CH_2CH_2$), 1.96 (1 H, dtt, $CH_2CH_2CH_2$), 2.93 (1 H, ddddd, $CH_2N$), 2.80 (1 H, dddd, $CH_2N$), 3.85 (1 H, ddddd, $CH_2O$), 4.01 (1 H, dddd, $CH_2O$); $^{13}$C NMR ($C_6D_6$) $\delta$ 24.52 (d, $(CH_3)_2$CHNP, $J$ = 5.4 Hz), 25.11 (d, $(CH_3)_2$CHNP, $J$ = 9.5 Hz), 28.63 (d, $CH_2CH_2CH_2$, $J$ = 6.4 Hz), 37.55 (d, $NCH_3$, $J$ = 21.7 Hz), 43.93 (d, $(CH_3)_2$CHNP, $J$ = 11.1 Hz), 52.97 (d, $CH_2N$, $J$ = 13.1 Hz), 64.80 (d, $CH_2O$, $J$ = 5.0 Hz); GC–MS (EI, 70 eV) *m/z* (relative intensity) 218 ($M^+$, 14), 175 (13), 118 (100), 90 (43), 70 (11), 42 (15).

*2-Diisopropylamino-2-oxo-3-methyl-1,3,2-oxazaphosphorinane* (**6-O**). By the procedure that was used to obtain **1-O**, **6** (1.83 g, 7.01 mmol) in $CH_2Cl_2$ (30 mL) and *tert*-butyl hydroperoxide (2.55 mL, 7.01 mmol) gave, on Kugelrohr distillation (bp 60°C/0.05 mm of Hg), product **6-O** (1.32 g, 72%) as a white crystalline solid: mp 89–90°C. $^{31}$P NMR ($C_6D_6$) $\delta$ 16.0; $^1$H NMR ($C_6D_6$) $\delta$ 0.88 (1 H, dtt, $CH_2CH_2CH_2$), 1.58 (1 H, dtt, $CH_2CH_2CH_2$), 1.22 (d, 6H, $(CH_3)_2$CHNP, $J$ = 6.0 Hz), 1.33 (d, 6H, $(CH_3)_2$CHNP, $J$ = 6.9 Hz), 2.40 (1 H, ddddd, $CH_2N$), 2.41 (3 H, d, $CH_3N$, $J$ = 11.7 Hz), 2.84 (1 H, dddd, $CH_2N$), 3.39 (2H, m, $((CH_3)_2CH)_2$NP), 3.64 (1 H, ddddd, $CH_2O$), 4.14 (1 H, dddd, $CH_2O$); $^{13}$C ($C_6D_6$) $\delta$ 22.69 (d, $(CH_3)_2$CHNP, $J$ = 1.9 Hz), 22.74 ($(CH_3)_2$CHNP), 26.82 (d, $CH_2CH_2CH_2$, $J$ = 3.2 Hz), 36.49 ($NCH_3$), 46.28 (d, $(CH_3)_2$CHNP, $J$ = 4.9 Hz), 50.53 ($CH_2N$), 65.87 (d, $CH_2O$, $J$ = 6.5 Hz); Anal. calcd for $C_{10}H_{23}N_2O_2P$: C, 51.27; H, 9.89; N, 11.96. Found: C, 51.18; H, 9.95; N, 11.90.

*N-Isopropyl-2-carboethoxy-2-methylpropionamide.* A mixture of 2-carboethoxy-2-methylpropionic acid [12] (27.3 g, 0.171 mol) and thionyl chloride (30.4 g, 18.6 mL, 0.261 mol) was heated for 24 hours at 60°C. Excess thionyl chloride was removed first by water aspirator and then by a vacuum pump, protected by liquid nitrogen and base traps. The residual liquid was dissolved in ether (100 mL) and slowly added to a stirred solution of isopropylamine (85.9 g, 124 mL, 1.45 mol) in ether (250 mL) at room temperature. The reaction mixture was stirred for 2 days. The salts were filtered off and washed with ether. The filtrate was concentrated. Pentane (30 mL) was added, and the solution was kept in the refrigerator for 2 days. The colorless crystalline product, after being washed with cold pentane, melted to a colorless liquid (23.3 g, 68%) on standing at room temperature: $^1$H NMR ($CDCl_3$) $\delta$ 1.14 (6 H, d, $(CH_3)_2$CHN, $J$ = 6.5 Hz), 1.27 (3 H, t, $CH_3CH_2O$, $J$ = 7.1 Hz), 1.43 (6 H, s, $(CH_3)_2C$), 4.04 (1 H, septet, $(CH_3)_2CHN$, $J$ = 6.5 Hz), 4.18 (2 H, q, $CH_3CH_2O$, $J$ = 7.1 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 13.62 ($CH_3CH_2O$), 22.02 ($(CH_3)_2$CHN), 23.09 ($(CH_3)_2C$), 41.17 ($(CH_3)_2$CHN), 49.36 ($(CH_3)_2C$), 60.92 ($CH_3CH_2O$), 170.42 (CONH), 174.31 ($COCH_2CH_3$). Anal. calcd for $C_{10}H_{19}NO_3$: C, 59.68; H, 9.51; N, 6.96. Found: C, 59.59; H, 9.47; N, 6.94.

*N-Isopropyl-2-hydroxymethyl-2-methylpropylamine.* A solution of the above propionamide (10.1 g, 0.0508 mol) in anhydrous THF (100 mL) was slowly added to a rapidly stirred suspension of $LiAlH_4$ in THF (150 mL) at 0°C. The reaction mixture was refluxed for 5 days and then cooled to 0°C, the reaction quenched by addition of saturated sodium potassium tartrate solution (75 mL), and the mixture stirred for 10 hours. Filtration gave a gray cream that was washed with ethyl acetate. The organic extract was dried over $MgSO_4$. Solvent removal and distillation under water aspiration (bp 80°C/15 mmHg) gave the desired product, 6.16 g (86%), a colorless liquid: $^1$H NMR ($CDCl_3$) $\delta$ 0.82 (6 H, s, $(CH_3)_2C$), 0.98 (6 H, d, $(CH_3)_2$CHN, $J$ = 6.3 Hz), 2.52 (2 H, s, $CH_2NH$), 2.63 (1 H, septet, $(CH_3)_2CHN$, $J$ = 6.3 Hz), 3.41 (2 H, s, $CH_2OH$), 6.10 (2 H, bs, NH, OH); $^{13}$C NMR ($CDCl_3$) $\delta$ 22.76 ($(CH_3)_2C$), 23.08 ($(CH_3)_2$CHN), 34.63 ($(CH_3)_2C$), 49.25 ($(CH_3)_2$CHN), 50.12 ($CH_2NH$), 74.58 ($CH_2OH$). Anal. calcd for $C_8H_{19}NO$: C, 66.16; H, 13.18; N, 9.64. Found: C, 66.26; H, 13.17; N, 9.68.

*2-Chloro-3-isopropyl-5,5-dimethyl-1,3,2-oxazaphosphorinane.* This compound was prepared via the procedure [10] used to obtain 2-chloro-3-phenyl-5,5-dimethyl-1,3,2-oxazaphosphorinane. Reactants were the aforementioned aminoalcohol (6.18 g, 0.041 mol), phosphorus trichloride (6.08 g, 3.85 mL, 0.041 mol), and triethylamine (9.95 g, 13.7 mL, 0.981 mol), each in THF (300 mL). The solvent was removed by distillation to give 5.90 g (66%) of product chloride as a colorless liquid. $^{31}$P NMR ($Et_2O$) $\delta$ 150.7.

*2-Diisopropylamino-3-isopropyl-5,5-dimethyl-1,3,2,-oxazaphosphorinane* (**2**). This was prepared by the procedure described for **1**, except that THF was used instead of ether, and the reaction mixture was heated under reflux for 4 days. Reactants were the foregoing chloridite (5.90 g, 0.0282 mol), N,N-diisopropylamine (8.57 g, 11.9 mL, 0.081 mol), each in THF (400 mL). Distillation (bp 80°C/0.12 mmHg) gave 4.63 g (60%) of **2**, a colorless liquid: $^{31}$P NMR ($C_6D_6$) $\delta$ 137.0; $^1$H NMR ($C_6D_6$) $\delta$ 0.63 (3H, s, $(CH_3)C$),

1.01 (3 H, d, $(CH_3)_2CHN(3)P$, $J$ = 6.7 Hz), 1.04 (3 H, d, $(CH_3)_2CHN(3)P$, $J$ = 6.7 Hz), 1.12 (3 H, s, $(CH_3)C$), 1.16 (6 H, d, $(CH_3)_2CHNP$, $J$ = 6.7 Hz), 1.35 (6 H, d, $(CH_3)_2CHNP$, $J$ = 6.7 Hz), 2.51 (1 H, ddd, $CH_2N$), 2.60 (1 H, dd, $CH_2N$), 3.53 (1H, ddd, $CH_2O$), 3.60 (1 H, dd, $CH_2O$); $^{13}C$ ($C_6D_6$) $\delta$ 18.78 (d, $(CH_3)_2CHN(3)P$, $J$ = 3.2 Hz), 20.88 (d, $(CH_3)_2CHN(3)P$, $J$ = 1.5 Hz), 24.09 (d, $(CH_3)C$, $J$ = 1.7 Hz), 24.11 (d, $(CH_3)C$, $J$ = 3.2 Hz), 24.20 (d, $(CH_3)_2CHNP$, $J$ = 5.6 Hz), 25.20 (d, $(CH_3)_2CHNP$, $J$ = 10.1 Hz), 32.73 (d, $(CH_3)C$, $J$ = 4.2 Hz), 44.19 (d, $(CH_3)_2CHNP$, $J$ = 10.9 Hz), 45.37 (d, $(CH_3)_2CHN$, $J$ = 15.7 Hz), 52.52 (d, $CH_2N$, $J$ = 14.2 Hz), 73.89 (d, $CH_2O$, $J$ = 3.3 Hz); GC–MS (EI, 70 eV) $m/z$ (relative intensity) 274 ($M^+$, 34), 174 (100), 136 (10), 94 (15), 40 (17).

*2-Diisopropylamino-2-oxo-3-isopropyl-5,5-dimethyl-1,3,2-oxazaphosphorinane* (**2-O**). The procedure was similar to that described for **1**. Reactants were **2** (2.11 g, 7.70 mmol) and *tert*-butyl hydroperoxide (2.57 mL, 7.71 mmol) in $CH_2Cl_2$ (35 mL). Product **2-O** was purified by Kugelrohr distillation (bp 55°C/0.05 mmHg) to give 1.65 g (78%) of a white solid: mp 70–72°C; $^{31}P$ ($C_6D_6$) $\delta$ 15.3; $^1H$ NMR ($C_6D_6$) $\delta$ 0.41 (3 H, s, $(CH_3)C$), 0.89 (3 H, d, $(CH_3)_2CHN(3)P$, $J$ = 6.7 Hz), 0.97 (3 H, s, $(CH_3)C$), 1.23 (6 H, d, $(CH_3)_2CHNP$, $J$ = 6.7 Hz), 1.26 (3 H, d, $(CH_3)_2CHN(3)P$, $J$ = 6.9 Hz), 1.38 (6 H, d, $(CH_3)_2CHNP$, $J$ = 6.9 Hz), 2.23 (1 H, ddd, $CH_2N$), 2.90 (1 H, dd, $CH_2N$), 3.34 (1 H, ddd, $CH_2O$), 3.38–3.50 (2 H, m, $(CH_3)_2CHNP$), 3.73–3.86 (1 H, m, $(CH_3)CHN$), 4.17 (1 H, dd, $CH_2O$); $^{13}C$ NMR ($C_6D_6$) $\delta$ 19.1 ($(CH_3)_2CHN(3)P$), 20.40 (d, $(CH_3)_2CHN(3)P$, $J$ = 10.2 Hz), 22.49 (d, $(CH_3)_2CHNP$, $J$ = 2.1 Hz), 22.62 ($(CH_3)_2CHNP$), 23.22 ($(CH_3)C$), 23.31 (d, $(CH_3)C$, $J$ = 0.6 Hz), 31.85 (d, $(CH_3)C$, $J$ = 2.4 Hz), 45.54 (d, $(CH_3)CHN$, $J$ = 2.0 Hz), 46.35 (d, $(CH_3)_2CHNP$, $J$ = 4.7 Hz), 50.69 (d, $CH_2N$, $J$ = 1.2 Hz), 74.74 (d, $CH_2O$, $J$ = 6.3 Hz); Anal. calcd for $C_{14}H_{32}N_2O_2P$: C, 57.91; H, 10.72; N, 9.65. Found: C, 57.65; H, 10.72; N, 9.49.

*Ethyl (3-N-Isopropylamino)propionate.* A solution of ethyl acrylate (15.1 g, 16.3 mL, 150 mmol) and isopropylamine (13.4 g, 19.3 mL, 225 mmol) in benzene (150 mL) was refluxed for 24 hours. Solvent removal and distillation at aspirator pressure (bp 80°C/15 mmHg) yielded 17 g (71%) of a colorless liquid: $^1H$ NMR ($C_6D_6$) $\delta$ 1.03 (6 H, d, $(CH_3)_2CHNH$, $J$ = 6.3 Hz), 1.24 (3 H, t, $CH_3CH_2O$, $J$ = 7.1 Hz), 2.48 (2 H, t, $CH_2NH$, $J$ = 6.5 Hz), 2.78 (1 H, septet, $(CH_3)_2CHNH$, $J$ = 6.3 Hz), 2.85 (2 H, t, $CH_2CH_2CO_2$, $J$ = 6.6 Hz), 4.12 (2 H, q, $CH_3CH_2O$, $J$ = 7.1 Hz); $^{13}C$ NMR ($C_6D_6$) $\delta$ 13.94 ($CH_3CH_2O$), 22.64 ($(CH_3)_2CHNH$), 34.71 ($CH_2CH_2NH$), 42.30 ($CH_2CH_2CO_2$), 48.15 ($(CH_3)_2CHNH$), 60.04 ($CH_3CH_2O$), 172.53 (CO). Anal. calcd for $C_8H_{17}O_2N$: C, 60.35; H, 10.76; N, 8.80. Found: C, 60.47; H, 10.76; N, 8.73.

*3-(N-Isopropyl)aminopropan-1-ol.* By the procedure described for N-isopropyl-2-hydroxymethyl-2-methylpropylamine, the foregoing propionate (5.01 g, 31.5 mmol) and $LiAlH_4$ (2.03 g, 53.5 mmol), each in THF (150 mL), were combined and then refluxed for 3 days. Distilled at aspirator pressure (bp 85–88°C/15 mm Hg) yielded 2.42 g (66%) of a colorless liquid. $^1H$ NMR ($CDCl_3$) $\delta$ 1.04 (6 H, d, $(CH_3)_2CHN$, $J$ = 6.3 Hz), 1.66 (2 H, quintet, $CH_2CH_2CH_2$, $J$ = 5.7 Hz), 2.75 (1 H, septet, $(CH_3)_2CHN$, $J$ = 6.3 Hz), 2.84 (2 H, t, $CH_2N$, $J$ = 5.4 Hz), 3.78 (2 H, t, $CH_2O$, $J$ = 5.3 Hz); $^{13}C$ NMR ($CDCl_3$) $\delta$ 22.72 ($(CH_3)_2CH$), 31.41 ($CH_2CH_2CH_2$), 46.83 ($CH_2N$), 48.73 ($(CH_3)_2CH$), 63.58 ($CH_2O$). Anal. calcd for $C_6H_{15}NO$: C, 61.49; H, 12.90; N, 11.95. Found: C, 61.21; H, 12.61; N, 11.58.

*2-Chloro-3-isopropyl-1,3,2-oxazaphosphorinane.* This was obtained by the reported [10] procedure for the preparation of 2-chloro-3-phenyl-5,5-dimethyl-1,3,2-oxazaphosphorinane. Reactants were the above-mentioned aminoalcohol (10.1 g, 0.086 mol) and triethylamine (19.3 g, 26.5 mL, 0.190 mol) in 400 mL of THF and phosphorus trichloride (11.9 g, 8.70 mL, 0.086 mol), also in THF (400 mL). The solvent was removed by distillation to give approximately 10 g (64%) of the desired product. $^{31}P$ NMR (THF) $\delta$ 157.8.

*2-Diisopropylamino-3-isopropyl-1,3,2-oxazaphosphorinane* (**5**). This was prepared by the procedure used to obtain **2**. Reactants were the above-mentioned chloridite (6.88 g, 38.1 mmol) and N,N-diisopropylamine (11.5 g, 15.9 mL, 114 mmol), each in THF (400 mL). A 2-day reflux was required. Distillation (bp 58°C/0.07 mmHg) yielded 6.0 g (64%) of colorless liquid **5**. $^{31}P$ NMR ($C_6D_6$) $\delta$ 137.1; $^1H$ NMR ($C_6D_6$) $\delta$ 1.03 (3 H, d, $(CH_3)_2CHN(3)P$, $J$ = 6.7 Hz), 1.07 (3 H, d, $(CH_3)_2CHN(3)P$, $J$ = 6.7 Hz), 1.15 (6 H, d, $(CH_3)_2CHNP$, $J$ = 6.9 Hz), 1.33 (6 H, d, $(CH_3)_2CHNP$, $J$ = 6.7 Hz), obscured by $i$-$Pr_2N$ (1 H, m, $CH_2CH_2CH_2$), 1.69 (1 H, dtt, $CH_2CH_2CH_2$), 2.69 (1H, ddddd, $CH_2N$), 2.85 (1 H, dddd, $CH_2N$), 3.69 (1 H, ddddd, $CH_2O$), 3.89 (1 H, dddd, $CH_2O$); $^{13}C$ ($C_6D_6$) $\delta$ 18.86 (d, $(CH_3)_2CHN(3)P$, $J$ = 3.7 Hz), 21.08 (d, $(CH_3)_2CHN(3)P$, $J$ = 1.8 Hz), 24.33 (d, $(CH_3)_2)CHNP$, $J$ = 5.7 Hz), 25.22 (d, $(CH_3)_2CHNP$, $J$ = 9.7 Hz), 28.89 (d, $CH_2CH_2CH_2$, $J$ = 6.4 Hz), 40.34 (d, $CH_2N$, $J$ = 18.4 Hz), 43.86 (d, $(CH_3)CHNP$, $J$ = 11.3 Hz), 45.76 (d, $(CH_3)CHN$, $J$ = 12.2 Hz), 64.24 (d, $CH_2O$, $J$ = 3.1 Hz); GC–MS (EI, 70 eV) $m/z$ (relative inten-

sity): 246 ($M^+$, 37), 231 (81), 203 (71), 189 (74), 146 (100), 104 (36), 100 (69).

*2-Diisopropylamino-2-oxo-3-isopropyl-1,3,2-oxazaphosphorinane* (**5-O**). This was prepared via the procedure for **1**. Reactants were **5** (3.14 g, 12.8 mmol), *tert*-butyl hydroperoxide (4.25 mL, 12.8 mmol) in $CH_2Cl_2$ (40 mL). Kugelrohr distillation gave 2.34 g (70%) of **5-O** as a colorless oil (bp 68°C/0.07 mmHg): $^{31}P$ NMR ($C_6D_6$) $\delta$ 14.5; $^1H$ NMR ($C_6D_6$) $\delta$ 0.87 (3 H, d, $(CH_3)_2CHN(3)P$, $J$ = 6.9 Hz), 1.21 (6 H, d, $(CH_3)_2)CHNP$, $J$ = 6.6 Hz), 1.26 (3 H, d, $(CH_3)_2CHN(3)P$, $J$ = 6.7 Hz), 1.35 (6 H, d, $(CH_3)_2CHNP$, $J$ = 6.7 Hz), 1.39–1.57 (2 H, m, $CH_2CH_2CH_2$), 2.49 (1 H, ddddd, $CH_2N$), 2.80 (1 H, dddd, $CH_2N$), 3.27–3.45 (2 H, m, $(CH_3)_2CHNP$), 3.65 (1 H, ddddd, $CH_2O$), 3.75–3.85 (1 H, m, $(CH_3)_2CHN$), 4.13 (1 H, dddd, $CH_2O$); $^{13}C$ NMR ($C_6D_6$) $\delta$ 19.28 ($(CH_3)_2CHN(3)P$), 20.62 (d, $(CH_3)_2CHN(3)P$, $J$ = 9.5 Hz), 22.65 (d, $(CH_3)_2CHNP$, $J$ = 2.2 Hz), 22.72 ($(CH_3)_2CHNP$), 27.04 (d, $CH_2CH_2CH_2$, $J$ = 4.0 Hz), 38.93 ($CH_2N$), 45.74 (d, $(CH_3)CHN$, $J$ = 2.6 Hz), 46.25 (d, $(CH_3)_2CHN(3)P$, $J$ = 5.0 Hz), 65.74 (d, $CH_2O$, $J$ = 6.8 Hz); Anal. calcd for $C_{12}H_{27}O_2N_2P$: C, 54.94; H, 10.37; N, 10.68. Found: C, 54.69; H, 10.40; N, 10.59.

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