

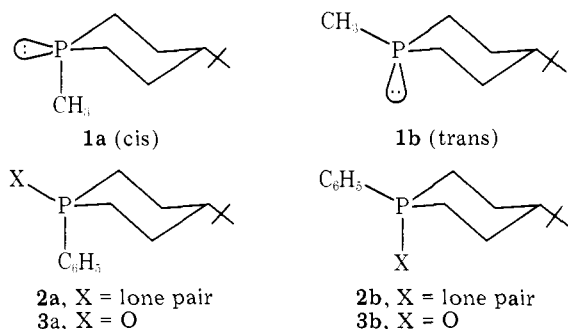
# Nuclear Magnetic Resonance Studies of Phosphorus Inversion in and Conformational Analysis of *cis*- and *trans*-4-*tert*-Butyl-1-phenylphosphorinane

G. D. Macdonell,<sup>1</sup> K. D. Berlin,\*<sup>1</sup> J. R. Baker,<sup>2</sup> S. E. Ealick,<sup>2</sup> Dick van der Helm,\*<sup>2</sup> and K. L. Marsi\*<sup>3</sup>

Contribution from the Departments of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74074, University of Oklahoma, Norman, Oklahoma 73019, and California State University, Long Beach, California 90840. Received November 21, 1977

**Abstract:** Pyramidal inversion at phosphorus in *cis*- and *trans*-4-*tert*-butyl-1-phenylphosphorinane has been investigated at 417, 437, and 454 K. Starting from either phosphine, the thermodynamic mixture at 417 K had a  $K_{\text{eq}}$  of 1.44 and a  $\Delta G^\circ = -0.30$  kcal/mol in favor of the *trans* phosphine [both the  $\text{C}_6\text{H}_5$  and  $(\text{CH}_3)_3\text{C}$  groups are equatorial]. The activation energy ( $\Delta G^\ddagger$ ) for the inversion process was determined to be 35.7 kcal/mol via NMR analysis of the reaction mixture over the above temperature range. This is the first example of P-inversion to be reported in the phosphorinane family. Isomerically pure *cis* and *trans* phosphines displayed  $^{31}\text{P}$  NMR signals at  $-32.92$  and  $-38.62$  ppm (upfield from 85%  $\text{H}_3\text{PO}_4$ ), respectively. Thus the isomer with the axial phenyl group had the  $^{31}\text{P}$  signal at the lower field strength. Oxidation of individual phosphines with  $\text{H}_2\text{O}_2$  gave individual oxides presumably of the same relative configurations as the phosphines.  $^{13}\text{C}$  NMR analysis of the phosphines and the corresponding oxides supports the structural assignments.  $^{13}\text{C}$  chemical shifts for C(3,5) in the *cis* phosphine occurred at 21.32 ppm, which was at higher field than that found for the *trans* phosphine (24.86 ppm), a fact which supports the axial  $\text{C}_6\text{H}_5$ -P arrangement in the former compound. A  $^2J_{\text{P-C}}$  of 5.1 Hz in the *trans* phosphine parallels that found in a previously reported system in which the  $\text{C}_6\text{H}_5$ -P and C(2)-C(3) bonds were antiperiplanar. An x-ray diffraction analysis of a single crystal of *trans*-4-*tert*-butyl-1-phenylphosphorinane 1-oxide revealed a space grouping  $P2_1/c$ . Assuming that oxidation of the *trans* phosphine was stereospecific to give *trans* oxide, the structure is confirmed also for the phosphine. A chair conformation for the solid *trans* oxide was found with the  $\text{C}_6\text{H}_5$  and  $(\text{CH}_3)_3\text{C}$  groups in equatorial positions. The  $\text{C}_6\text{H}_5$  group is rotated about  $20^\circ$  from a plane passing through P=O and C(4) of the phosphorinane ring as well as through the central carbon [C(7)] of the *tert*-butyl group and the carbon in the  $\text{C}_6\text{H}_5$  group which is attached to phosphorus. The rotation apparently minimizes H-H and H-O contact.

The chemistry of phosphorinanes is a very active area, and there recently appeared the preparation and tentative stereochemical assignment of *cis*- and *trans*-4-*tert*-butyl-1-methylphosphorinane (**1a** and **1b**, respectively) and *cis*- and *trans*-4-*tert*-butyl-1-phenylphosphorinane (**2a** and **2b**, re-



spectively).<sup>4</sup> We now wish to report on NMR studies which have provided thermodynamic data ( $\Delta G^\ddagger$  and  $\Delta G^\circ$ ) regarding the pyramidal inversion at phosphorus in **2a**  $\rightleftharpoons$  **2b**. In addition, analyses of the  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra of phosphines **2a** and **2b** and their corresponding oxides **3a** and **3b** have been recorded. All data support the original stereochemical assignments.<sup>4</sup> Also, herein, we report a single-crystal, x-ray crystallographic analysis of oxide **3b** which supports the original structural assignments for the phosphines **2a** and **2b**.

## Results and Discussion

As reported earlier,<sup>31</sup>P NMR may offer a powerful tool for conformational analysis of dynamic systems.<sup>5</sup> We have utilized a similar technique for the determination of the pyramidal inversion barrier ( $\Delta G^\ddagger$ ) at phosphorus in **2a**  $\rightleftharpoons$  **2b**.

When isomerically pure **2a** ( $^{31}\text{P}$   $-32.92$  ppm) or **2b** ( $^{31}\text{P}$   $-38.62$  ppm) (judged by the initial observation of only one  $^{31}\text{P}$  signal) was heated in solution (1,2-dichlorobenzene, ODCB)

at 144, 164, and 181  $^\circ\text{C}$ , a second signal in the  $^{31}\text{P}$  spectrum, corresponding to the other configurational isomer (either **2b** or **2a**), was detected with time. That this second signal was due only to the other configurational isomer was substantiated by oxidation of the mixture with  $\text{H}_2\text{O}_2$ <sup>6</sup> and isolation of *only* **3a** and **3b**. Rate and mixture composition data obtained for the three temperatures are reported in Tables I and II, respectively.

It was possible to isolate both **2a** and **2b** and to subject both isomers to thermal equilibration to obtain the kinetic data by approaching from both sides of the equilibrium. Thus, kinetic data were extracted from both compounds which, in our opinion, makes the resulting thermodynamic parameters more reliable. However, oxidation does begin to take place in the mixture of phosphines **2a** and **2b** after about 10–11 h (signals for the oxides **3a** and **3b** were well separated from those of the phosphines)<sup>4</sup> in spite of very careful degassing of the sample with  $\text{N}_2$  and the use of a sealed tube. Scavenging traces of oxygen by the phosphines becomes effective after 10–11 h as judged by  $^1\text{H}$  and  $^{31}\text{P}$  NMR analysis so the kinetic data were accumulated during the initial period. Nevertheless, small amounts of oxides could form and remain undetected at least for the first 2–3%. This could influence the rates of inversion slightly which in turn would not alter  $\Delta G^\ddagger$  very much but of course could affect  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  considerably since these data are obtained from the slope and intercept, respectively, of the Eyring equation. Thus, one can calculate  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  to be  $+15.03$  kcal/mol and  $-46.2$  cal/deg-mol, respectively, from the data in Table I. Consequently, these latter values may not be very meaningful in view of the complications discussed. The  $\Delta G^\ddagger$  value is very reliable and from our limitation analysis standard deviations are less than 2 kcal/mol.

Most published work with simple phosphines to date has treated this type of inversion as that of one static system being converted to another because of the high inversion barrier usually found. We have elected to use the general equation

Table I. Rate Data for **2a**  $\rightleftharpoons$  **2b**

Temp, K	$k \times 10^5, \text{s}^{-1}$	$\Delta G, \ddagger \text{ kcal/mol}^a$
417	0.87	34.3
437	2.37	35.2
454	4.11	36.0

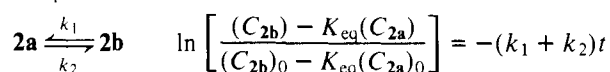
<sup>a</sup> Obtained from the Eyring equation:  $k = (k_B T/h) e^{-\Delta G^\ddagger/RT}$ .

Table II. Equilibrium Data for **2a**  $\rightleftharpoons$  **2b**

Temp, K	$K_{\text{eq}}^a$	$\Delta G^\circ, \text{kcal/mol}^b$
417	1.44	-0.30
437	1.38	-0.28
454	1.21	-0.17

<sup>a</sup>  $K_{\text{eq}}$  in favor of **2b**. <sup>b</sup> Obtained from  $-\Delta G^\circ = RT \ln K_{\text{eq}}$ .

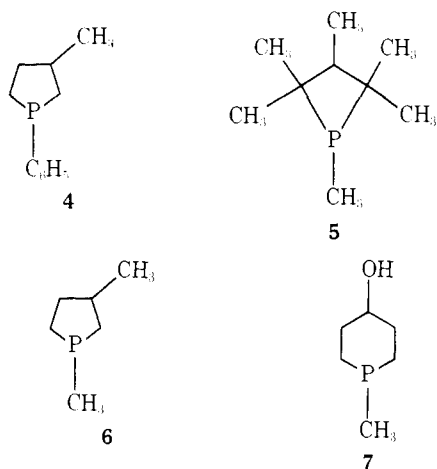
shown (found in standard kinetic texts) which is for a first-order reversible process. Values of  $k_1$  and  $k_2$  can be obtained via the well-known relationships  $k_1 + k_2 = k_{\text{obsd}}$  and  $k_1/k_2 = K_{\text{eq}}$ .



The values for  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  do not seem very defensible on the basis of an unusual effect on the inversion by ODCB. However, we could find no model reaction for comparison purposes. We have tentatively concluded that the rates ( $k_{\text{obsd}}$ ) are affected by oxidation as discussed above.

The  $\Delta G^\circ$  value was determined from the equilibrium mixtures as approached from both sides of the equilibrium as cited previously. Areas for the  $^1\text{H}$  NMR signals for the *tert*-butyl group in **2a** and **2b** were measured over several sweep widths for better accuracy.

The barrier to pyramidal inversion ( $\Delta G^\ddagger \approx 35.2 \text{ kcal/mol}$ , Table I) in **2a**  $\rightleftharpoons$  **2b** compares to the reported value of ca. 36 kcal/mol for 3-methyl-1-phenylphospholane (**4**)<sup>7</sup> and is ca. 4 kcal/mol higher than that for a number of dialkylphenylphosphines.<sup>8</sup> It is interesting to note that 1,2,2,3,4,4-hexamethylphosphetane (**5**),<sup>9</sup> 1,3-dimethylphospholane (**6**),<sup>10</sup> and



1-methyl-4-phosphorinanol (**7**)<sup>11</sup> failed to invert after heating at 162 °C for 4 days, 150 °C for 3 days, and 170 °C for 18 days, respectively. However, the *P*-phenyl and *P*-*tert*-butyl derivatives of **5** did invert over a temperature range similar to ours with barriers ( $\Delta G^\ddagger$ ) to pyramidal inversion of ca. 33.1 and ca. 31.5 kcal/mol, respectively.<sup>9</sup> It is interesting also that the *P*-phenyl substituted phosphetane had a higher barrier to pyramidal inversion compared to the *P*-*tert*-butyl compound. It seems reasonable that steric strain associated with the *P*-*tert*-butyl substituted system lowers the energy of the transition

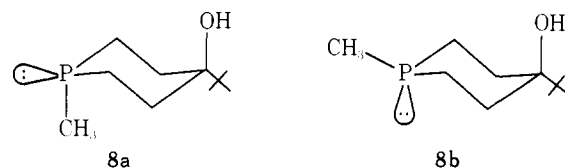
Table III.  $^{13}\text{C}$  NMR Parameters—Chemical Shifts<sup>a</sup> (Coupling Constants)<sup>b</sup>

Carbon <sup>c</sup>	Comps			
	<b>2a</b>	<b>2b</b>	<b>3a</b>	<b>3b</b>
2,6	21.55 (11.6)	25.55 (8.9)	27.58 (64.8)	28.69 (64.2)
3,5	21.32 (s)	24.86 (5.1)	25.03 (3.8)	22.37 (5.8)
4	47.98 (s)	48.48 (s)	48.06 (s)	49.03 (s)
7	31.82 (s)	31.93 (s)	32.72 (s)	33.03 (s)
8,9,10	26.17 (s)	26.70 (s)	27.64 (s)	27.48 (s)
11	137.34 (19.4)	140.60 (15.6)	130.06 (75.0)	133.31 (94.9)
12,16	128.82 (11.9)	129.40 (15.6)	129.63 (8.9)	129.94 (9.0)
13,15	126.99 (s)	126.98 (7.6)	128.79 (11.1)	128.35 (11.1)
14	124.98 (s)	126.64 (s)	129.45 (s)	131.42 (s)

<sup>a</sup> Shifts are  $\pm 0.03$  ppm downfield from internal  $\text{Me}_4\text{Si}$ . <sup>b</sup> Coupling constants are  $\pm 0.7$  Hz; s = singlet. <sup>c</sup> See Figure 2 for numbering of positions.

state more than possible stabilization from (p-p) $\pi$  overlap in the transition state of the *P*-phenyl phosphetane.<sup>9</sup> As pointed out previously,<sup>12</sup> the *gem*-dimethyl groups at C(2) and C(4) in the *P*-phenyl derivative of **5** may influence the lowering of the inversion barrier compared to the nonsubstituted compound. Although speculative, one might expect the inversion barrier in the C(2,6) tetrasubstituted derivatives of **2a,b** to be lower than that for **5** with the *P*-phenyl group because the assumed smaller CPC endocyclic bond angle in the *P*-phenyl derivative of **5** should stabilize the ground-state pyramid.

**$^{13}\text{C}$  NMR Assignments.**  $^{13}\text{C}$  NMR chemical shifts and  $^{13}\text{C}$ - $^{31}\text{P}$  coupling constants for phosphines **2a** and **2b** and corresponding oxides **3a** and **3b** are given in Table III. Shifts for C(2,6) in **2a** and **2b** reflect the greater deshielding of equatorially oriented P substituents (**2b**, 25.55 ppm vs. **2a**, 21.55 ppm).<sup>13,14</sup> The differences in chemical shifts for C(2,6) in **2a** and **2b** parallel the  $\Delta\delta$  found for **8a** and **8b** which have



the P substituent in a fixed arrangement and of known stereochemical configuration.<sup>14</sup> A decrease from 25.55 (**2b**) to 21.55 ppm (**2a**) was observed in interchanging the position of the lone pair of electrons on phosphorus with a phenyl group (group changed from equatorial to axial position with the resultant implying a greater deshielding due to the equatorial *P*-phenyl<sup>13,14</sup>). This  $\Delta\delta$  of -3.60 ppm is smaller than that found by interchanging the lone pair and a methyl group ( $\Delta\delta$  -5.8 ppm<sup>14</sup>) in **8a** to give **8b**. This could result from solvent differences. However, the difference (-3.6 vs -5.8 ppm) could be associated with  $\gamma$ -shielding,<sup>7</sup> possibly reducing the  $\beta$ -deshielding value. The coupling  $^1J_{\text{PC}}$  in **2a** (11.5 Hz) was essentially the same as in **8a** (12 Hz) as was also found for  $^1J_{\text{PC}}$  in **2b** (8.9 Hz) and **8b** (10 Hz) which indicated that the electronic factors affecting the  $^1J_{\text{PC}}$  values in these two compounds do not differ markedly.

Shifts for C(3,5) are apparently quite indicative of the orientation of the substituent on phosphorus in phosphines **8a** and **8b**.<sup>14</sup> The chemical shift for C(3,5) in **2a** (21.32 ppm) was at higher field as compared to that in **2b** (24.86 ppm) which could be the result of steric compression<sup>13</sup> from axial *P*-phenyl in **2a**. The  $^2J_{\text{PC}}$  values of 0 (**2a**) and 5.1 Hz (**2b**) are also similar to those reported for **8a** (0 Hz) and **8b** (7.5 Hz).<sup>14</sup> As cited for **8a** and **8b**,<sup>14</sup> these values are representative of the disposition of the substituent on phosphorus, i.e., the larger coupling constant ( $^2J_{\text{PC}}$ ) corresponds to the conformer where the dihedral angle between the lone pair on phosphorus and the C(3)

Table IV.  $^{31}\text{P}$  Chemical Shifts<sup>a</sup>

Compd	$\delta, ^b$ ppm	Compd	$\delta, ^b$ ppm
<b>2a</b>	-32.92	<b>3a</b>	+29.99
<b>2b</b>	-38.62	<b>3b</b>	+28.19

<sup>a</sup> Shifts are  $\pm 0.02$  ppm. Shifts determined on ca. 200-mg samples in 2 mL of 1,2-dichlorobenzene. <sup>b</sup> Chemical shifts relative to 85%  $\text{H}_3\text{PO}_4$ . Minus sign indicates shifts upfield from the external standard.

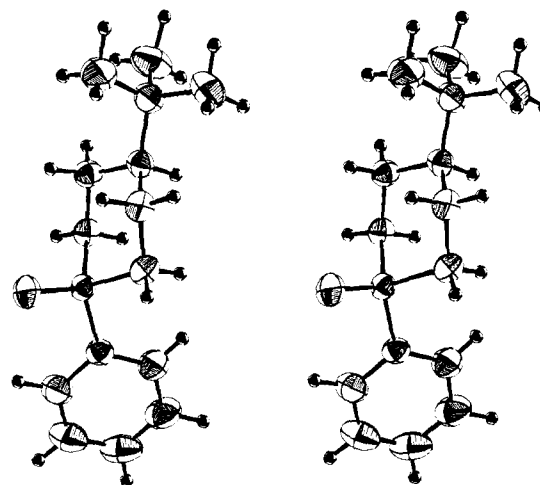
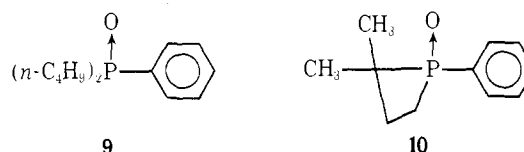
[or C(5)] atom is small [ $\text{C}_6\text{H}_5\text{-P-C}(2)\text{-C}(3)$  bonds are anti-periplanar]. Carbon atoms 4, 7, and 8 (also 9, 10) in both **2a** and **2b** had very similar chemical shifts, probably reflecting minor geometric differences around C(4) in solution.

The chemical shifts for carbon atoms in the phenyl group in **2a** and **2b** were suggestive of the position of that group. For example, in **2a** with axial  $\text{C}_6\text{H}_5\text{-P}$ , C(11) should be shielded compared to C(11) in **2b** with the equatorial phenyl group. This was indeed the case and C(11) in **2a** had a shift of 137.3 ppm compared to a value of 140.6 ppm for C(11) in **2b**. However, the signal for C(11) in **2b** was nearly the same (140.6 vs. 141.3 ppm) as that for the same carbon in 1-phenylphosphorinane.<sup>15</sup> This similarity could have arisen from a solvent-induced shift ( $\text{C}_6\text{D}_6$  vs.  $\text{DCCl}_3$  for **2b**) since the axial preference of several exocyclic P substituents in six-membered rings has been well documented.<sup>5b,16</sup> The  $^1J_{\text{PC}}$  value for C(11) in **2a** was 19.1 Hz compared to 15.6 Hz for C(11) in **2b**. This reduction in coupling constant for C(11) in **2b** (presumably becoming less negative<sup>15</sup>) may have been due to a relief in steric strain about phosphorus with equatorial phenyl as compared to **2a** with axial phenyl. The same observation was made for C(12,16) in **2b**, i.e.,  $^2J_{\text{PC}}$  increased with a decrease in strain at phosphorus [ $^2J_{\text{PC}}$  (**2b**) = 15.6 Hz vs.  $^2J_{\text{PC}}$  (**2a**) = 11.9 Hz]. The above conclusions were based on the assumption that  $^1J_{\text{PC}}$  was negative and  $^2J_{\text{PC}}$  was positive utilizing data reported for similar compounds.<sup>15</sup>

Phosphine oxides **3a** and **3b** gave quite interesting  $^{13}\text{C}$  NMR results, further delineating the geometric configuration about phosphorus. Shifts for C(2,6) in **3a** appeared upfield at 27.58 ppm ( $^1J_{\text{PC}} = 64.8$  Hz) compared to the same carbon atoms in **3b** (28.69 ppm,  $^1J_{\text{PC}} = 64.2$  Hz). This small shift difference most probably reflects  $\beta$ -deshielding associated with equatorial P-phenyl in **3b**.<sup>13,14</sup>

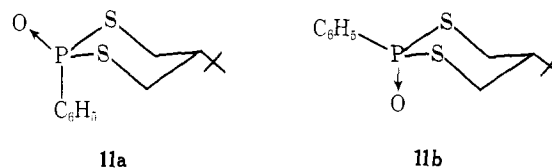
It was interesting to note that atoms C(3,5) in **3b** (equatorial  $\text{C}_6\text{H}_5\text{-P}$ ) were more shielded (22.37 vs. 25.03 ppm) than C(3,5) in **3a** (axial  $\text{C}_6\text{H}_5\text{-P}$ ). These data compared favorably to those reported earlier concerning increased shielding at the  $\gamma$  carbon (" $\gamma$ -shielding") accompanying sulfurization<sup>17</sup> of phosphines and a similar observation of  $\gamma$ -shielding in triethylphosphine  $\rightarrow$  triethylphosphine oxide.<sup>18</sup> Carbon atoms 4, 7, and 8 (9, 10 also) were quite similar in both **3a** and **3b**, suggesting that the geometric and electronic environments about these atoms were also comparable.

The striking feature found in the  $^{13}\text{C}$  resonances in the phenyl carbon atoms of oxides **3a** and **3b** was the dramatic difference at C(11) in terms of both chemical shift and coupling constant. The chemical shift of C(11) in **3b** (133.31 ppm) was close to the value for the comparable carbon in simple 1-phenylphosphorinane 1-oxide (134.29 ppm)<sup>15</sup> as was the  $^1J_{\text{PC}}$  value (94.9 Hz in **3b** vs. 92.6 Hz in 1-phenylphosphorinane 1-oxide) both in  $\text{DCCl}_3$ . This similarity was suggestive of preferential axial orientation of the oxygen atom in 1-phenylphosphorinane 1-oxide, an observation reported earlier with similarly substituted phosphorinane 1-sulfides.<sup>19</sup> However, the higher field signal for C(11) in **3a** (130.06 vs. 133.31 ppm in **3b**) and the smaller  $^1J_{\text{PC}}$  value of 75.0 Hz (vs. 94.9 Hz for **3b**) more nearly resembled the same parameters found for *di-n*-butylphenylphosphine oxide (**9**) and 2,2-dimethyl-

Figure 1. Stereoview of the *trans* oxide **3b**.<sup>39</sup>

phenylphosphetane 1-oxide (**10**).<sup>15</sup> Consequently, that the chemical shift for C(11) in **3a** and the corresponding  $^1J_{\text{PC}}$  value were only the result of steric factors seems questionable. Interestingly, a small upfield shift was observed for C(14) in **3a** compared to **3b** (129.45 vs. 131.42 ppm,  $\Delta\delta = -1.97$ ).

**$^{31}\text{P}$  NMR Assignments.**  $^{31}\text{P}$  NMR chemical shifts for **2** and **3** have been recorded in Table IV. The  $^{31}\text{P}$  NMR data revealed an unusual difference between phosphorinanes **2a** and **2b** and structurally similar phosphorinaneols **8a** and **8b** reported previously.<sup>11</sup> Chemical shifts of -32.92 and -38.62 ppm (upfield from external reference 85%  $\text{H}_3\text{PO}_4$ ) were observed for **2a** and **2b**, respectively, whereas  $^{31}\text{P}$  shifts of -67.3 and -57.7 ppm were recorded for **8a** and **8b**, respectively. That the  $^{31}\text{P}$  chemical shifts for **2a** and **2b** were assigned correctly was based on the  $^{13}\text{C}$  NMR data previously discussed as well as on a single-crystal x-ray analysis of oxide **3b** (discussion to follow), which, upon reduction with phenylsilane,<sup>20</sup> gave **2b**. A similar observation has been recently made for *cis*- and *trans*-2-phenyl-2-oxo-5-*tert*-butyl-1,3,2-dithiaphosphorinanes (**11a** and



**11b**), respectively.<sup>21</sup> These workers suggested that the reversal in  $^{31}\text{P}$  chemical shifts may be due to predominance of a twist conformer for **11a** in solution. Similarly, the small  $^{13}\text{C}$  shift differences [between C(2,6) and C(3,5)] of  $\Delta\delta = -0.23$  in **2a** and  $\Delta\delta = -2.55$  in **3a** may be the result of a distorted chair or twist conformation since the same atoms in **8a** with known absolute configuration displayed a chemical shift difference of  $\Delta\delta = +6.06$ .<sup>14</sup> We conclude that the anomalous  $^{31}\text{P}$  chemical shift data for **2a,b** and **3a,b** may result from a geometric deformation of a chair conformation in both **2a** and **3a**.<sup>22</sup> In support of this argument, molecular models (Courtauld) indicate a severe steric interaction between the  $\pi$  orbital system of the phenyl ring (or the ortho hydrogens) and the H(3,5) axial protons of the phosphorinane ring when phenyl was axial. This interaction could be relieved in part by a distorted chair or twist conformation for **2a** and **3a**. Therefore, we suggest that assignment

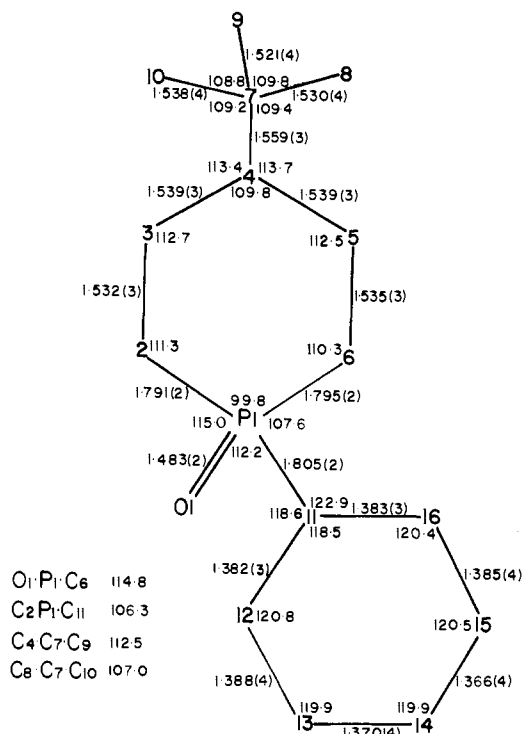


Figure 2. Bond angles and bond distances in the trans oxide **3b**.

Table V. Torsion Angles for **3b**

Angle	$\phi$ , deg	Angle	$\phi$ , deg
P(1)C(2)C(3)C(4)	61.9	O(1)P(1)C(11)C(12)	19.8
C(2)C(3)C(4)C(5)	-62.4	C(2)P(1)C(11)C(12)	-106.7
C(3)C(4)C(5)C(6)	63.6	C(6)P(1)C(11)C(12)	147.0
C(4)C(5)C(6)P(1)	-63.8	O(1)P(1)C(11)C(16)	-161.6
C(5)C(6)P(1)C(2)	55.3	C(2)P(1)C(11)C(16)	71.9
C(6)P(1)C(2)C(3)	-54.7	C(6)P(1)C(11)C(16)	-34.4

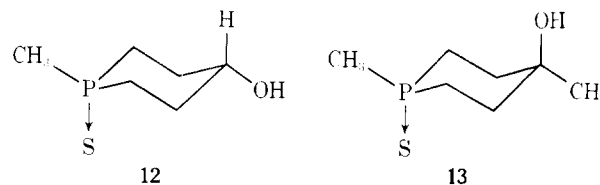
of configurations in phosphorinanes based on  $^{31}\text{P}$  NMR data alone must be done with marked caution.

**Single-Crystal Analysis of **3b**.** A stereoview of a single molecule of **3b** is shown in Figure 1, and the numbering scheme, bond distances, and bond angles are shown in Figure 2. The phosphorinane oxide **3b** exists in a chair conformation as can be seen from the torsion angles reported in Table V. The *tert*-butyl and phenyl groups are in equatorial positions with the *tert*-butyl group staggered with respect to its attachment to the phosphorinane ring. With the exception of the phenyl group, oxide **3b** possesses a pseudo-mirror plane passing through atoms P(1), C(4), C(7), C(9), C(11), and O(1). The dihedral angle between the pseudo-mirror plane and the plane defined by the atoms of the phenyl group is  $20.1^\circ$ . Alternately, this can be viewed as a rotation of the phenyl group about the P(1)-C(11) bond away from the pseudo-mirror plane resulting in a torsion angle O(1)-P(1)-C(11)-C(12) of  $19.8^\circ$ ; the related torsion angles are reported in Table V.

The rotation ( $\approx 20^\circ$ ) of the phenyl group is a result of two close intramolecular contacts. The rotation cannot easily be less than  $20^\circ$  because of a contact between O(1) and H[C(12)] of  $2.63 \text{ \AA}$  and cannot be greater than  $20^\circ$  because of a contact between H[C(6)] and H[C(16)] of  $2.19 \text{ \AA}$ . These contacts result in a high rotational barrier for the phenyl group, thus producing the observed conformation.

When the chair conformation in oxide **3b** was compared to the chair conformations in 1-phenyl-4-phosphorinane,<sup>23</sup> 4,4-dimethoxy-1-phenylphosphorinane,<sup>24</sup> *trans*-4-*tert*-butyl-1-methyl-4-phosphorinanol,<sup>25</sup> and 4-substituted epimeric

1-methyl-4-phosphorinanol 1-sulfides<sup>26</sup> (all with axially oriented alkyl or aryl substituents on phosphorus), it was observed that the magnitudes of all torsion angles were larger for the present structure **3b**. The difference is ca.  $10^\circ$  for the P(1)-C(2) type,  $5^\circ$  for the C(2)-C(3) type, and  $2^\circ$  for the C(3)-C(4) type indicating that the chair conformations for those phosphorinane structures are flattened with respect to the phosphorinane oxide ring in **3b**. However, the average torsion angles in equatorial substituted sulfides **12** and **13**<sup>26</sup> are only



slightly smaller than those in **3b**, which conceivably results from the presence of sulfur with a larger van der Waals radius of  $1.75 \text{ \AA}$  compared to oxygen with a radius of  $1.40 \text{ \AA}$ .<sup>27</sup> In addition, the average endocyclic bond angle at a ring C atom in **3b** was  $3^\circ$  smaller than the average of the previously reported values for the phosphorinane ring systems. Also the endocyclic bond angle at the P atom was  $2^\circ$  larger. These observations are accountable on the basis of an equatorial phenyl group and the hybridization at phosphorus. The hybridization change on P is probably the main factor for the resultant shortening of the P-C bond distances in **3b** by  $0.03\text{--}0.05 \text{ \AA}$  compared to the same bond in 4,4-dimethoxy-1-phenylphosphorinane<sup>25</sup> and 1-phenyl-4-phosphorinane.<sup>23</sup> The observation that the P(1)-C(11) ( $\text{sp}^2$ ) bond length of  $1.805(2) \text{ \AA}$  in **3b** was longer than two reported<sup>28,29</sup> P-C( $\text{sp}^3$ ) bond distances (average of  $1.793 \text{ \AA}$ ) was somewhat unusual. Comparison of the P(1)-C(11) bond length in **3b** with that in the salts reported<sup>28,29</sup> may not be entirely legitimate since the angles around P exhibit about 1% variation. Nevertheless, the  $\text{C}_6\text{H}_5\text{-P}$  distance compared well with the value of  $1.80 \text{ \AA}$  reported for the P-C( $\text{sp}^2$ ) bond length for the large number of compounds.<sup>30</sup> Many factors influence the P-C bond distance, e.g., hybridization, charge, valency, and steric factors, resulting in wide variations for these distances in P-C heterocycles; accordingly more observations seem necessary to correlate these factors with bond length.

The electronegativity of the substituents attached to phosphorus influences the P $\rightarrow$ O bond length. The value of  $1.483 \text{ \AA}$  in **3b** was considered normal and could be compared to a value of  $1.48 \text{ \AA}$  determined by electron diffraction for trimethylphosphine oxide.<sup>31</sup> The value of  $1.483 \text{ \AA}$  for the P $\rightarrow$ O bond length in **3b** was somewhat larger than the average value of  $1.462 \text{ \AA}$  reported<sup>30</sup> for many compounds having highly electronegative atoms attached to the phosphorus atom.

The average C-C (phenyl) bond length was  $1.379 \text{ \AA}$ , which is only an apparent shortening due to thermal motion, and could be correlated with the distance of the bonding atoms from the center of the molecule. A calculation of intermolecular distances based on final parameters for **3b** revealed no unusually short contacts (see Tables VI and VII).

## Conclusion

Kinetic data for the pyramidal inversion at phosphorus in **2a** and **2b** gave  $\Delta G^\ddagger = \text{ca. } 35 \text{ kcal/mol}$ , in agreement with the pyramidal inversion barrier in other C-P heterocycles, *although none have heretofore been reported for phosphorinanes*. Furthermore, equilibration of **2a** and **2b** gave  $\Delta G^\circ_{164} = -0.28 \text{ kcal/mol}$  in favor of **2b** with equatorial phenyl. A similar value ( $\Delta G^\circ_{100} = -0.275 \text{ kcal/mol}$ ) has been determined for 4-*tert*-butyl-1-methylthianium perchlorate in which again there was a preference for the equatorial substituent.<sup>32</sup>

The low values for  $\Delta G^\circ$  at the higher temperatures indicate

**Table VI.** Positional Parameters ( $\times 10^4$ ) and Anisotropic Temperature Factors ( $\times 10^4$ ) for P, C, and O Atoms<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>
P(1)	668.1 (4)	1095.8 (9)	1329.9 (3)	421 (2)	332 (2)	384 (2)	-21 (2)	86 (2)	14 (3)
O(1)	488 (1)	-1387 (2)	1288 (1)	626 (9)	352 (8)	671 (11)	-56 (7)	123 (8)	3 (8)
C(2)	44 (2)	2635 (4)	546 (1)	477 (11)	456 (12)	386 (11)	-2 (9)	117 (8)	20 (9)
C(3)	-1178 (2)	2629 (4)	422 (1)	462 (11)	501 (13)	393 (11)	1 (10)	72 (8)	7 (9)
C(4)	-1562 (2)	3787 (4)	1023 (1)	432 (10)	374 (11)	484 (11)	-14 (9)	113 (8)	16 (10)
C(5)	-1135 (2)	2490 (4)	1719 (1)	515 (12)	479 (13)	429 (11)	-35 (10)	164 (9)	12 (9)
C(6)	93 (2)	2533 (4)	1960 (1)	496 (11)	506 (13)	373 (11)	-42 (10)	105 (9)	32 (9)
C(7)	-2795 (2)	4201 (4)	844 (1)	485 (12)	493 (13)	652 (14)	36 (10)	149 (10)	-6 (12)
C(8)	-3125 (2)	5610 (5)	167 (2)	724 (17)	970 (23)	754 (18)	327 (17)	132 (14)	189 (17)
C(9)	-3432 (2)	2007 (5)	756 (2)	482 (13)	659 (17)	1259 (27)	-84 (13)	138 (15)	-121 (19)
C(10)	-3076 (2)	5598 (5)	1440 (2)	674 (16)	725 (18)	832 (20)	144 (14)	293 (14)	-53 (15)
C(11)	2074 (2)	1809 (4)	1527 (1)	449 (10)	437 (11)	404 (11)	4 (9)	61 (8)	48 (9)
C(12)	2790 (2)	207 (4)	1403 (1)	531 (13)	588 (15)	690 (14)	63 (11)	129 (11)	38 (13)
C(13)	3876 (2)	688 (5)	1536 (2)	496 (13)	865 (21)	973 (22)	134 (14)	188 (14)	120 (18)
C(14)	4252 (2)	2757 (5)	1803 (2)	446 (13)	913 (21)	883 (20)	-72 (14)	34 (13)	251 (17)
C(15)	3552 (2)	4358 (5)	1926 (2)	567 (14)	696 (18)	886 (20)	-157 (13)	16 (13)	26 (16)
C(16)	2465 (2)	3905 (4)	1784 (1)	522 (13)	545 (14)	723 (16)	-58 (12)	99 (11)	-23 (13)

<sup>a</sup> Anisotropic thermal factors are of the form  $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^{*}b^{*} + 2U_{13}hla^{*}c^{*} + 2U_{23}klb^{*}c^{*})]$ . Estimated standard deviations for the last digit are given in parentheses.

a preferred diequatorial arrangement of the *P*-phenyl and C(4)-C(CH<sub>3</sub>)<sub>3</sub> groups. Consequently, although the phosphorinane ring is flattened and the C-P bonds (in the ring) are long, some steric interactions (presumably of the 1,3,5 type) may promote a preference of equatorial *P*-phenyl in the system studied. Obviously, as the temperature is raised, this preference of the *P*-phenyl group is sharply reduced.

<sup>13</sup>C NMR data for **2a,b** and **3a,b** supported the original assignments;<sup>4</sup> however, the <sup>31</sup>P NMR signals for **2a** and **3a** were at lower field than those of **2b** and **3b**, suggestive of a conformation different from that of a presumed flattened chair for **2a** and **3a**.<sup>22</sup> All phosphorinanes to date have exhibited a flattened chair in single-crystal analysis.<sup>23,25</sup> Finally a single-crystal x-ray analysis of conformer **3b** strongly supports the <sup>1</sup>H and <sup>13</sup>C NMR assignments for **2a,b** and **3a,b**. Moreover, we conclude that <sup>31</sup>P NMR assignments for axial-equatorial P substituents should be made cautiously for phosphorinanes.

### Experimental Section

**General.** The method of preparation and physical as well as <sup>1</sup>H NMR spectral data of all compounds studied have been described elsewhere.<sup>4</sup> <sup>13</sup>C and <sup>31</sup>P NMR data were obtained on a Varian XL-100(15) NMR spectrometer with a TT-100 PFT accessory operating at 25.2 MHz with Me<sub>4</sub>Si as internal standard for <sup>13</sup>C NMR and operating at 40.5 MHz with 85% H<sub>3</sub>PO<sub>4</sub> as external standard for <sup>31</sup>P NMR. All transfers and manipulations of phosphines were conducted either in a Vacuum/Atmospheres inert atmosphere box under N<sub>2</sub> or in standard taper glassware under a steady stream of N<sub>2</sub>.

**<sup>31</sup>P NMR Spectral Measurements.** Freshly distilled phosphorinanes **2a** or **2b**<sup>4</sup> were dissolved in degassed 1,2-dichlorobenzene and transferred under N<sub>2</sub> to a coaxial vessel equipped with a septum inlet to the inner chamber and a ground glass joint to which was attached a condenser and N<sub>2</sub> inlet. In the outer vessel were placed an appropriate solvent (1,1,2,2-tetrachloroethane, bp 144 °C; 1,3,5-trimethylbenzene, bp 164 °C; or 1,2-dichlorobenzene, bp 181 °C) and a condenser. The solvents were maintained at their boiling point which was monitored throughout the kinetic and equilibration experiments. At periodic intervals, a 1.5-mL aliquot was withdrawn and placed in the inner tube of a Wilmad 12-mm coaxial NMR tube along with a 1-mm sealed capillary of 85% H<sub>3</sub>PO<sub>4</sub>. In the outer portion of the NMR tube was placed D<sub>2</sub>O as the lock source. <sup>31</sup>P spectra were obtained using gated, broad band, proton decoupling with a 40-s delay between pulses to minimize effects of a nuclear Overhauser enhancement and unequal relaxation times. The composition of the mixture was then determined by several integrations of the <sup>31</sup>P signals which were then averaged.

**Structure Determination of 4-*tert*-Butyl-1-phenylphosphorinane 1-oxide (3b).** Crystals of **3b** were obtained by slow evaporation of a

**Table VII.** Positional Parameters ( $\times 10^3$ ) and Isotropic Temperature Factor ( $\text{\AA}^2$ ) for Hydrogen Atoms<sup>a</sup>

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>iso</sub>
H(C2)1	29 (1)	417 (3)	64 (1)	3.6 (4)
H(C2)2	28 (1)	204 (3)	12 (1)	3.9 (5)
H(C3)1	-149 (2)	340 (4)	-4 (1)	4.9 (5)
H(C3)2	-144 (1)	95 (3)	37 (1)	3.9 (4)
H(C4)1	-119 (2)	533 (3)	109 (1)	3.7 (5)
H(C5)1	-144 (2)	312 (4)	211 (1)	4.6 (5)
H(C5)2	-140 (2)	87 (4)	166 (1)	5.1 (5)
H(C6)1	36 (2)	415 (4)	199 (1)	4.6 (5)
H(C6)2	32 (2)	179 (4)	243 (1)	5.3 (6)
H(C8)1	-395 (2)	618 (5)	6 (2)	8.6 (8)
H(C8)2	-310 (2)	475 (4)	-24 (2)	7.8 (7)
H(C8)3	-269 (3)	704 (6)	19 (2)	12.0 (10)
H(C9)1	-332 (2)	117 (4)	36 (1)	7.7 (7)
H(C9)2	-330 (2)	106 (5)	120 (2)	9.1 (8)
H(C9)3	-426 (2)	230 (4)	63 (1)	6.9 (7)
H(C10)1	-387 (2)	594 (4)	130 (1)	7.2 (7)
H(C10)2	-299 (2)	467 (4)	188 (2)	7.5 (7)
H(C10)3	-264 (2)	712 (5)	154 (1)	7.8 (7)
H(C12)	251 (2)	-134 (4)	124 (1)	5.2 (5)
H(C13)	435 (2)	-37 (5)	141 (2)	8.3 (8)
H(C14)	499 (2)	306 (4)	188 (1)	6.5 (6)
H(C15)	380 (2)	589 (5)	214 (2)	9.3 (8)
H(C16)	195 (2)	498 (4)	186 (1)	6.0 (6)

<sup>a</sup> Estimated standard deviation for the last digit is given in parentheses.

refrigerated solution of acetone and water in a 2:1 ratio. The crystal selected for data collection was clear and blocky, having dimensions of 0.138  $\times$  0.121  $\times$  0.242 mm. The crystal data follow: C<sub>15</sub>H<sub>23</sub>PO; mol wt 250.31; monoclinic; space group *P*2<sub>1</sub>/*c*; *a* = 12.8680 (7) Å; *b* = 5.9065 (3) Å; *c* = 10.5011 (9) Å;  $\beta$  = 104.102 (4)°; *V* = 1437.51 Å<sup>3</sup>; *Z* = 4;  $\rho_{\text{calcd}}$  = 1.156,  $\rho_{\text{obsd}}$  = 1.152 g/cm<sup>3</sup>; nickel-filtered Cu K $\alpha$  radiation;  $\lambda$  = 1.540 51 Å for 2 $\theta$  data and  $\lambda$  = 1.541 78 Å for intensity data; all data collected at room temperature, using a Nonius CAD-4 automatic diffractometer. The least-square cell parameters were determined from the +2 $\theta$  and -2 $\theta$  values of 52 reflections distributed throughout reciprocal space. The observed density was measured by the flotation method using a mixture of toluene and carbon tetrachloride.

The intensities of all 2960 unique reflections with  $\theta$  less than 75° were measured using the  $\theta$ -2 $\theta$  scan technique. The scan width used was calculated for each reflection by the formula  $\Delta\theta = (0.9 + (0.09 \tan \theta))$ . A horizontal receiving aperture with variable width (width (mm) = 5 + (0.5) tan  $\theta$ ) and fixed height of 6 mm was positioned 173 mm from the crystal. The maximum scan time used was 60 s with  $\frac{1}{3}$

of the time used for scanning the peak ( $P$ ), and  $1/6$  each for each of the low  $\theta$  (LH) and high  $\theta$  (RH) backgrounds. A standard reflection was monitored every 25 reflections, and over the period of data collection, its intensity decreased by 3%. The monitor reflection was used to bring all intensities to a common relative scale. Three reflections were used to check the orientation of the crystal every 100 reflections, and a new orientation matrix was calculated when a deviation larger than  $0.1^\circ$  was observed.

There were 677 reflections whose intensities could not be distinguished from the background. All reflections meeting this criterion ( $I < 2(T)^{1/2}$  where  $T = P + 2(\text{RH} + \text{LH})$ ) were assigned intensities of  $T^{1/2}$  for further data analysis. Lorentz, polarization, and absorption corrections ( $\mu = 15.331 \text{ cm}^{-1}$ ) were applied to the data. A Gaussian integration was employed to correct for absorption,<sup>33</sup> using 216 sampling points.

The structure was solved by the combined use of MULTAN<sup>34</sup> and a sharpened Patterson synthesis. The structure was refined using block-diagonal least-squares calculations. After several cycles of refinement a difference Fourier synthesis revealed the positions of all hydrogen atoms, which were included in the refinement procedure. The refinement was considered completed when all shifts were less than  $1/2$  their standard deviations. The final  $R$  value ( $= \sum |kF_o| - |F_c| / \sum |kF_o|$ ) for all 2960 reflections was 0.067. Each structure amplitude was assigned an individual weight.<sup>35</sup> The mean values of  $w_F \Delta F^2$  calculated for various ranges of  $|F_o|$  were constant, thus validating the weighing scheme used.<sup>36</sup> A final difference Fourier map showed negative peaks of  $-0.33$  and  $-0.28 \text{ e } \text{Å}^{-3}$  corresponding to the P1 and O1 positions, respectively. The largest positive peak in the map was  $0.20 \text{ e } \text{Å}^{-3}$  at approximately halfway between P1 and C10. Atomic scattering factors for P, O, and C atoms were taken from the International Tables for X-Ray Crystallography<sup>37</sup> while those for H atoms were taken from Stewart, Davidson, and Simpson.<sup>38</sup>

**Acknowledgments.** Partial support of this work by the USPHS, National Cancer Institute, Grant CA 11967-13 (K.D.B.), Grant CA 17562 (D.v.d.H.), and the National Science Foundation, Grant GP 38756X (K.L.M.) is gratefully acknowledged. We (K.D.B.) also gratefully acknowledge grants to the Department by the National Science Foundation to purchase the XL-100(15) spectrometer (GP 17651) and Fourier transform accessory (CHE 76-09571).

**Supplementary Material Available:** Table VIII, a listing of observed and calculated structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

## References and Notes

- Oklahoma State University.
- University of Oklahoma.
- California State University, Long Beach.
- K. L. Marsi, J. L. Jasperse, F. M. Llort, and D. G. Kanne, *J. Org. Chem.*, **42**, 1306 (1977).
- (a) S. I. Featherman and L. D. Quin, *J. Am. Chem. Soc.*, **95**, 1699 (1973); (b) *ibid.*, **97**, 4349 (1975).
- Oxidation of tertiary phosphines with  $\text{H}_2\text{O}_2$  proceeds with retention of configuration. H. R. Hays and D. J. Peterson in "Organic Phosphorus Compounds", Vol. 3, G. M. Kosolapoff and L. Maier, Ed., Wiley, New York, N.Y., 1972, Chapter 6, and references cited therein.
- W. Egan, R. Tang, G. Zon, and K. Mislow, *J. Am. Chem. Soc.*, **92**, 1442 (1970).
- R. Baechler and K. Mislow, *J. Am. Chem. Soc.*, **92**, 3090 (1970).
- S. E. Cremer, R. J. Chorvat, C. H. Chang, and D. W. Davis, *Tetrahedron Lett.*, 5799 (1968).
- K. L. Marsi, *Chem. Commun.*, 846 (1968). The mixture of isomers used might have been coincidentally a thermodynamic mixture in which case no net isomerization would be observed.
- L. D. Quin and J. H. Somers, *J. Org. Chem.*, **37**, 1217 (1972).
- For a review on pyramidal inversion see J. B. Lambert, *Top. Stereochem.*, **6**, 19 (1971); A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem., Int. Ed. Engl.*, **9**, 400 (1970); K. Mislow, *Trans. N.Y. Acad. Sci., Ser. 11*, **35**, 227 (1973).
- K. K. Dalling and D. M. Grant, *J. Am. Chem. Soc.*, **89**, 6612 (1967).
- S. I. Featherman and L. D. Quin, *Tetrahedron Lett.*, 1955 (1973).
- G. A. Gray, S. E. Cremer, and K. L. Marsi, *J. Am. Chem. Soc.*, **98**, 2109 (1976).
- J. B. Lambert and S. I. Featherman, *Chem. Rev.*, **75**, 611 (1975).
- L. D. Quin, M. D. Gordon, and S. O. Lee, *Org. Magn. Reson.*, **6**, 503 (1974).
- G. A. Gray and S. E. Cremer, *J. Org. Chem.*, **37**, 3458 (1972).
- S. I. Featherman, S. O. See, and L. D. Quin, *J. Org. Chem.*, **39**, 2899 (1974).
- Reduction of phosphine oxides with phenylsilane proceeds stereospecifically to yield the corresponding phosphine with retention of configuration. K. L. Marsi, *J. Org. Chem.*, **39**, 265 (1974).
- B. E. Maryanoff and R. O. Hutchins, *J. Org. Chem.*, **42**, 1022 (1977).
- As pointed out by a reviewer, if **2a** and **3a** existed in a twist conformation in solution, the magnitude of coupling between the proton at C(4) and the protons at C(3,5) should be markedly different compared to that in **2b** and **3b**, which has been assumed to be in a chair conformation in solution. Lanthanide-induced shift (LIS) experiments and  $^1\text{H}\{^31\text{P}\}$  double resonance work revealed significant differences in the chemical shift and coupling pattern for the proton at C(4) in **3a** and **3b**. In  $\text{C}_6\text{D}_6$  ( $[\text{3a}]/[\text{Eu}(\text{fod})_3] = 1.59$ ), **3a** exhibited a single broad line centered at  $\delta$  2.50 for the proton at C(4). In contrast, **3b** ( $[\text{3b}]/[\text{Eu}(\text{fod})_3] = 1.43$ ) in  $\text{C}_6\text{D}_6$  exhibited a broadened multiplet centered at  $\delta$  2.26 for the proton at C(4). Also, the protons at C(3,5) gave signals which reduced to a broad single resonance (with  $^31\text{P}$  decoupling) for **3a**, whereas a broadened doublet of doublets (upfield portion,  $\delta$  2.34; downfield portion,  $\delta$  3.12) was observed for those same protons in **3b**. Therefore, albeit not strictly conclusive, the differences in chemical shift and coupling pattern for the protons at C(4) in **3a** and **3b** and the apparent single resonance for the protons at C(3,5) in **3a** seem to support a distorted chair or twist conformation for **3a** in  $\text{C}_6\text{D}_6$  (and  $\text{DCCl}_3$ ).<sup>21</sup> [It has been also observed that *cis*-4-*tert*-butyl-1-phenylcyclohexane may exist as a mixture of chair and twist forms; see E. W. Garbisch, Jr., and D. B. Patterson, *J. Am. Chem. Soc.*, **85**, 3228 (1963)].
- A. T. McPhail, J. J. Breen, and L. D. Quin, *J. Am. Chem. Soc.*, **93**, 2574 (1971).
- A. T. McPhail, J. J. Breen, J. H. Somers, J. C. H. Steele, Jr., and L. D. Quin, *Chem. Commun.*, 1020 (1971).
- A. T. McPhail, P. A. Luhan, S. I. Featherman, and L. D. Quin, *J. Am. Chem. Soc.*, **94**, 2126 (1972).
- L. D. Quin, A. T. McPhail, S. O. Lee, and K. D. Onan, *Tetrahedron Lett.*, 3473 (1974).
- L. Pauling, "The Nature of the Chemical Bond", 3rd ed. Cornell University Press, Ithaca, N.Y., 1960, p 260; D. van der Helm, A. E. Lessor, Jr., and L. L. Merritt, Jr., *Acta Crystallogr.*, **15**, 1227 (1962).
- S. R. Holbrook, M. Poling, D. van der Helm, R. W. Chesnut, P. R. Martin, N. N. Durham, M. L. Higgins, K. D. Berlin, and W. R. Purdum, *Phosphorus*, **6**, 15 (1975).
- K. K. Wu and D. van der Helm, *Cryst. Struct. Commun.*, **6**, 143 (1977).
- D. E. C. Corbridge, "The Structural Chemistry of Phosphorus", American Elsevier, New York, N.Y., 1974, pp 215-217, 395-396, and references cited therein.
- H. K. Wang, *Forsvarets-forsking Intern. Rapport (Norway)*, I.R.-K-225 (1960).
- E. L. Eliel, R. L. Willer, A. T. McPhail, and K. D. Onan, *J. Am. Chem. Soc.*, **96**, 3021 (1974).
- P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Crystallogr.*, **18**, 1305 (1965).
- G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **27**, 368 (1971).
- D. van der Helm and M. Poling, *J. Am. Chem. Soc.*, **98**, 82 (1976).
- For information concerning final  $F_o$ ,  $F_c$  tables, see paragraph at end of paper regarding supplementary material.
- "International Tables for X-Ray Crystallography", Vol III, Kynoch Press, Birmingham, England, 1962, p 202.
- R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
- C. K. Johnson, ORTEP Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.