stirred for 1.5 h at 0 °C. Workup was effected by addition of ether (10 mL), neutralization with aqueous sodium bicarbonate solution, and extraction. Concentration of the organic phase gave an oil (128 mg) which was purified by preparative TLC (Kiesel gel Merck PF_{254}, CH_2Cl_2, R_f 0.35–0.49) to afford **2a** (101 mg, 70% yield): bp 78–80 °C (0.04 Torr); IR (neat) 1716, 1646 cm^{-1}; ^1H NMR (CCl_4) δ 1.08 (s, 3 H), 6.37 (t, 1 H, $J = 3.6$ Hz); mass spectrum *m/e* 150 (M^+). Formation of the regioisomer of **2a** corresponding to **11** was <5% as revealed by GLC.

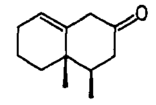
(8) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Verlag Chemie GmbH, Weinheim-Berchstr., Germany, 1970, p 58; T. S. Sorensen and A. Rauk in "Pericyclic Reactions", Vol 2, A. P. Marchand and R. E. Lehr, Eds., Academic Press, New York, 1977, p 31.

(9) **2b:** bp 105–113 °C (bath temperature) (0.07 Torr); IR (neat) 1723, 1653 cm^{-1}; ^1H NMR (CCl_4) δ 0.95 (s, 3 H), 1.07 (d, 3 H, $J = 6.0$ Hz), 6.37 (t, 1 H, $J = 3.0$ Hz); mass spectrum *m/e* 164 (M^+).

(10) Potassium hydroxide (6.80 g, 121 mmol) was dissolved in an aqueous 55% solution (Tokyo Kasei Kogyo Co.) of 1-butyn-3-ol (5.74 g, 45 mmol). To this solution was added 2-methylcyclohexanone (3.36 g, 30 mmol) over a period of 2 h at 40 °C. The resulting mixture was stirred for 24 h. Usual workup followed by purification of the crude product by short column chromatography on silica gel gave the adduct **1b** (two of the four possible racemic isomers were separable, but the mixture of the isomers was used for the next reaction): 4.59 g, 84% yield; IR (neat) 3344 cm^{-1}; ^1H NMR (CCl_4) δ 0.91 (d, 3 H, $J = 6.0$ Hz), 1.02 (d, 3 H, $J = 6.0$ Hz), 4.3–4.7 (m, 1 H).

(11) **4:** IR (neat) 1700, 1619 cm^{-1}; ^1H NMR (CCl_4) δ 1.23 (s, 3 H), 1.99 (d, 3 H, $J = 1.7$ Hz), 5.7–5.8 (m, 1 H); mass spectrum m/e 164 (M^+).

(12) Dibromomethyllithium addition (83% yield) followed by butyllithium treatment[13] gave i (41% yield; IR (neat) 1715 cm^{-1}; ^1H NMR (CCl_4) δ 0.94 (d, 3 H, $J = 6.0$ Hz), 1.10 (s, 3 H), 5.3–5.5 (m, 1 H); mass spectrum *m/e* 178 (M^+)) which was isomerized to **5** under acidic conditions (5% H_2SO_4–THF (1:1), room temperature, 2 h, 73%). The ^1H NMR spectrum ($CDCl_3$) of **5** showed a bridgehead methyl signal at δ 1.08 (s) identical with that of the authentic sample[14] and was clearly distinguished from that of the cis isomer.



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(13) H. Taguchi, H. Yamamoto, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, **50,** 1588, 1592 (1977).

(14) C. J. V. Scanio and R. M. Starrett, *J. Am. Chem. Soc.*, **93,** 1539 (1971).

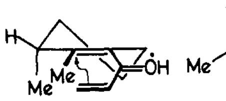
(15) Obtained in 89% yield. The two stereoisomers were separated chromatographically. Both gave **2c** equally well. The result in the text refers to that of the mixture.

(16) **2c:** IR (neat) 1718, 1654 cm^{-1}; ^1H NMR (CCl_4) δ 0.87 (d, 3 H, $J = 7.2$ Hz), 1.19 (s, 3 H), 6.46 (t, 1 H, $J = 3.6$ Hz); mass spectrum *m/e* 164 (M^+).

(17) Birch reduction (Li–NH_3), followed by enolate trap with acetic anhydride, ozonization, and acetic acid–sodium acetate treatment, gave **6:** IR (CCl_4) 1758, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (d, 3 H, $J = 6.8$), 1.20 (s, 3 H), 5.30 (t, 1 H, $J = 7.0$ Hz); mass spectrum *m/e* 180 (M^+). The ^1H NMR data are completely consistent with those of the trans isomer and clearly different from those of the cis isomer of **6.**[18]

(18) E. Piers, R. W. Britton, and W. de Waal, *Can. J. Chem.*, **47,** 4307 (1969).

(19) A priori, four transition states (**3′c,** ii, iii, and iv) can lead to cyclopentenones. Transition state **3′c** or ii gives **2c** while iii or iv affords the cis isomer of **2c.** In the transition state iii or iv interaction of the two methyl groups grows severe as C–C bond formation develops, while in **3′c** or ii such Interaction is not crucial as the two methyl groups are more farther apart during the course of C–C bond formation. Of the two transition states (**3′c** and ii) we prefer **3′c** for the reason that the methyl group on the six-membered ring takes a pseudoequatorial position and C–C bond formation occurs from the antiperiplanar direction of C–H_a bond under orbital control.[20]



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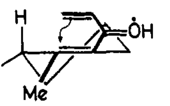

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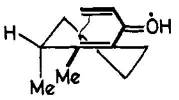

iv

(20) C. L. Liotta, *Tetrahedron Lett.*, 519 (1975).

(21) **1d:** IR (neat) 3346 cm^{-1}; ^1H NMR (CCl_4) δ 0.87 (d, 6 H, $J = 6.0$ Hz), 1.02 (d, 3 H, $J = 6.0$ Hz), 4.3–4.7 (m, 1 H); mass spectrum *m/e* 224 (M^+).

(22) The ratio was determined by ^1H NMR. The major product gave an olefinic proton signal at δ 6.53 (dd, $J = 7.7$, 3.0 Hz) and the minor component at δ 6.36 (t, $J = 3.3$ Hz); IR (neat) 1715, 1652 cm^{-1}; mass spectrum *m/e* 206 (M^+).

(23) Dibromomethyllithium addition (74% yield), butyllithium treatment (83% yield), and subsequent acidic isomerization (79% yield).

(24) **8–9:** IR (neat) 1663, 1627 cm^{-1}; ^1H NMR (CCl_4) of the major product δ 0.87 (d, $J = 6.0$ Hz), 0.97 (d, $J = 6.0$ Hz), 1.043 (s), 5.65 (br s, 0.82 H), and of the minor product gave peaks at δ 1.063 (s) and 5.59 (br s, 0.18 H); mass spectrum *m/e* 220 (M^+).

(25) An authentic specimen of 7-epinootkatone was prepared according to the literature: Y. Takagi, Y. Nakahara, and M. Matsui, *Tetrahedron*, **34,** 517 (1978). The sample was hydrogenated to **8** ($RhCl(PPh_3)_3$, H_2, benzene, room temperature, overnight): ^1H NMR (CCl_4) δ 1.046 (s), 5.65 (br s).

(26) Prepared according to the literature: H. C. Odom and A. R. Pinder, *J. Chem. Soc. Perkin Trans. 1*, 2193 (1972). We are indebted to Professor Pinder for his generous gift of a sample of (±)-nootkatone. ^1H NMR (CCl_4) spectra of dihydronootkatone gave peaks at δ 1.066 (s), 5.59 (br s).

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(28) This research was financially assisted by the Ministry of Education, Science and Culture, Japanese Government (Grant-in-aid No. 375462).

Tamejiro Hiyama,* Masaki Shinoda, Hitosi Nozaki
Department of Industrial Chemistry, Kyoto University
Yoshida, Kyoto 606, Japan

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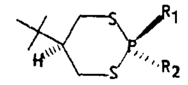
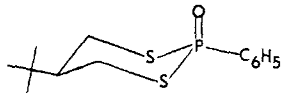
Nonchair Conformations in Phosphorus-Containing Cyclohexanes. Crystal and Molecular Structures of *cis*- and *trans*-2-Phenyl-2-oxo-5-*tert*-butyl-1,3,2-dithiaphosphorinanes and *cis*-2-Phenyl-5-*tert*-butyl-1,3,2-dithiaphosphorinane

Sir:

Saturated homocyclic and heterocyclic six-membered rings generally exhibit a strong preference for the chair conformation over nonchair forms ($\Delta H° = \sim 3$–8 kcal/mol).[1] Although special ring modifications or severe steric biasing influences afford a predisposition for the twist or other nonchair structures, molecules that inherently favor a twist conformation in unstrained situations are rare.[1a,2] In a recent ^1H NMR study on the stereochemical properties of **1a** and **1b** in solution, we found that, although **1b** assumes predominantly a chair conformation (**2**), **1a** populates considerably a twist form (**3**).[3]



1a; $R_1 = C_6H_5$; $R_2 = O$
b; $R_1 = O$; $R_2 = C_6H_5$
c; $R_1 = C_6H_5$; R_2 = lone pair



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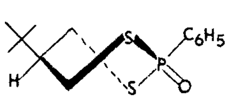

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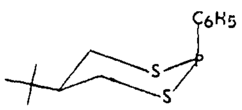

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Since the free-energy difference between the chair and twist forms was estimated to be as low as 0.5 kcal/mol,[3] the 1,3,2-dithiaphosphorinane ring system appeared to be a good candidate for obtaining unconstrained twist structures. To find out whether the twist conformation for **1a** would be manifested in the solid state, X-ray crystallographic analyses were performed on **1a** and, for comparison, on **1b** and **1c.** Surprisingly, *both* **1a** *and* **1b** *adopt a twist conformation* in the solid state, which represents an unusual case where two configurational isomers of a six-membered ring assume twist forms.

Crystals of **1a, 1b,** and **1c** all belong to the monoclinic system, space group $P2_1/c$. All three crystal structures were solved by direct methods using MULTAN.[4] Atomic positional[5] and thermal parameters (anisotropic C, O, P, S; isotropic H) were refined by full-matrix least-squares calculations to R = 0.054 (**1a**), 0.050 (**1b**), and 0.040 (**1c**) over 2433, 1876, and 1270, respectively, statistically significant ($I > 2.0\sigma(I)$) reflections measured on an Enraf-Nonius CAD-3 automated diffractometer (Ni-filtered Cu Kα radiation, $\lambda = 1.5418$ Å; θ-2θ scans).

Views of the solid-state conformations for **1a**[6] and **1b** are shown in Figures 1 and 2;[5a] endocyclic torsion angles defining the heterocyclic ring shapes of **1a–c** are in Table I. Although the endocyclic torsion angles for **1a** and **1b** depart significantly from ideal symmetry-related values characterizing a twist (D_2) form, it is quite apparent that the six-membered rings in each

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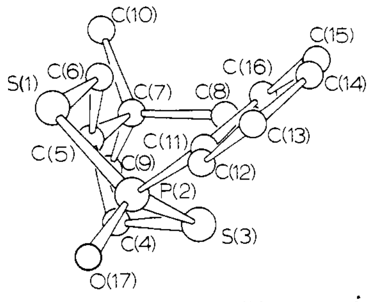


Figure 1. Atom numbering scheme and solid-state conformation of **1a**.

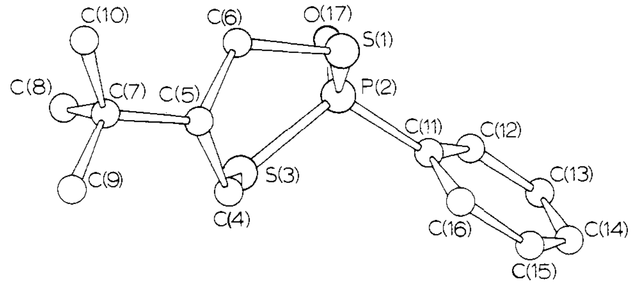


Figure 2. Atom numbering scheme and solid-state conformation of **1b**.

Table I. Endocyclic Torsion Angles (Degrees) for **1a**, **1b**, and **1c**[a]

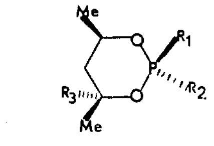
angle	**1a**[b]	**1b**	C_6H_{12}[c]	**1c**[d]
S(1)-P(2)-S(3)-C(4)	−39.5 (−41.7)	−19.5	−33.2	47.6
P(2)-S(3)-C(4)-C(5)	79.1 (79.9)	69.8	70.6	−62.8
S(3)-C(4)-C(5)-C(6)	−34.5 (−34.4)	−40.6	−33.2	74.7
C(4)-C(5)-C(6)-S(1)	−49.2 (−47.7)	−42.1	−33.2	−74.3
C(5)-C(6)-S(1)-P(2)	73.4 (70.3)	81.0	70.6	62.0
C(6)-S(1)-P(2)-S(3)	−17.8 (−14.9)	−37.5	−33.2	−47.4

[a] The torsion angle A-B-C-D is defined as positive if, when viewed along the B-C bond, atom A must be rotated clockwise to eclipse atom D. [b] Unprimed molecule; values for the primed molecule are in parentheses. [c] D_2 twist cyclohexane values were taken from J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961). [d] Atom numbering scheme is the same as in **1a** and **1b**.

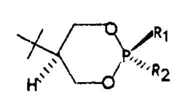
of these compounds do approximate such a form. In contrast to this conformational preference, the corresponding ring of **1c**, the tricoordinate analogue of **1a**, has a chair form (**4**), slightly flattened at phosphorus, with axial 2-phenyl and equatorial 5-*tert*-butyl groups.[7,8] It is noteworthy, especially in relation to a diminished $\Delta G°$ (chair–twist) for dithiaphosphorinanes, that *both* **1a** and **1b** adopt twist forms.

Other nonchair conformations have been observed for the related 1,3,2-dioxaphosphorinanes under conditions of moderate steric stress. Thus, **5** possesses a twist conformation in the solid state,[10] presumably to escape severe 1,3 syn-axial interactions present in both possible chair forms, **6** adopts a highly flattened ("chaise lounge") conformation in the solid state,[11a] and **7a**[12] was assigned a boat conformation in solution on the basis of ^1H NMR data.[11b] X-ray diffraction data for **7b**[12,14] indicated a slightly distorted chair conformation with equatorial 5-*tert*-butyl and axial 2-methyl groups,[15] and data for **8**[12] showed a flattened chair conformation with *axial 5-tert-butyl* and axial 2-methoxy groups.[16] Thus, the 1,3,2-dioxaphosphorinane ring has a lower propensity to assume a twist disposition, and this has been borne out in a solution study of **7c**,[12] the oxygen isostere of **1a**.[17] X-ray analysis of the carbon isostere of **1b** showed a chair conformation with equatorial 4-*tert*-butyl and 1-phenyl substituents.[18]

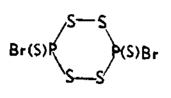
Replacement of methylene groups of cyclohexane by sulfur



5 R_1 = Se, R_2 = NH-t-C_4H_9
6 R_1 = O, R_2 = $C(C_6H_5)_3$
R_3 = H



7a R_1 = t-C_4H_9, R_2 = O
7b R_1 = CH_3, R_2 = O
7c R_1 = C_6H_5, R_2 = O
8 R_1 = O, R_2 = OCH_3



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atoms can lower the chair–twist energy difference. For example, while cyclohexane has a $\Delta H°$ (chair–twist) of ~5.3–6.0 kcal/mol,[1b,d] the value for 1,3-dithiane drops to ~3.4–4.0 kcal/mol.[1b,19,20] Furthermore, an entropy term ($\Delta S°_{ct}$) favoring the twist form lowers the free-energy difference such that $\Delta G°_{ct}$ (298 K) for 1,3-dithiane is only ~1.7–2.6 kcal/mol.[1b,19] Likewise, $\Delta G°_{ct}$ for the 1,2,4,5-tetrathiane ring system is lowered to such an extent that the twist form can be preferred,[1c,22] and this is supported by empirical force-field calculations.[1c] Although the relatively small $\Delta G°_{ct}$ for the 2-oxo-1,3,2-dithiaphosphorinane system is probably imparted by the 1,3 sulfur atoms, analogous to 1,3-dithiane, the presence of a phosphorus atom could further diminished $\Delta G°_{ct}$.[23] Interestingly, molecules of **9**[25] and 3,3,6,6-tetramethyl-1,2,4,5-tetrathiane[1c] exhibit a twist conformation in the solid state.

The fact that the twist form is adopted by **1a** and **1b** in the solid state suggests that $\Delta G°_{ct}$ may be very low (<1 kcal/mol), but the influence of crystal-packing forces cannot be accurately estimated.[26,28] Future solution studies on derivatives not biased by carbon substitution should help to define $\Delta G°_{ct}$.

The X-ray analysis of **1c** represents the first determination of molecular structure for a tricoordinate 1,3,2-dithiaphosphorinane and, more importantly, one of the few determinations for a tricoordinate phosphorus-containing cyclohexane.[13] The result for **1c** not only confirms the stereochemistry arrived at earlier,[3,9] but, coupled with the results for **1a** and **1b**, also establishes that peroxide oxidation of tricoordinate phosphorus in this system occurs with retention of configuration.

Acknowledgement. Crystallographic calculations were supported by a grant of computer time from Duke University.

Supplementary Material Available: Crystal data, exocyclic torsion angles, and table of atomic coordinates for **1a**, **1b**, and **1c** and Figure 3 showing atom numbering scheme and solid-state conformation of **1c** (9 pages). Ordering information is given on any current masthead page.

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(2) Introduction into cyclohexane of (1) sp^2-hybridized atoms, (2) substituents imposing severe strain (e.g.: axial *tert*-butyl or 1,3-diaxial substitutents) in the chair form, which can be relieved in the twist form, (3) constraint by chemical bonding (e.g., twistane), or (4) alternate pairs of disulfide linkages can lower the chair/twist energy difference to a point where the twist form predominates.[1a]

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(5) (a) See paragraph at end of paper regarding supplementary material. (b) Complete details of the crystallographic work will be reported elsewhere.

(6) Crystals of **1a** contain two crystallographically independent molecules which possess only minor conformational differences.

(7) A view of the solid-state conformation of **1c** is available in the supplementary materials.[5a]

(8) The X-ray results for **1c** confirm the previous assignment.[9]

(9) (a) R. O. Hutchins and B. E. Maryanoff, *J. Am. Chem. Soc.*, **94** 3266 (1972); (b) B. E. Maryanoff, Ph.D. Dissertation, Drexel University, 1972.

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(12) Expected to be the less stable isomer.[13]

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(14) This is the nearest analogue of **1a** for which an X-ray analysis has been performed.

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(20) Oxygen atoms, on the other hand tend to elevate ΔH°_{ct}, which for 1,3-dioxane is ~8 kcal/mol.[1b,21]

(21) R. M. Clay, G. M. Kellie, and F. G. Riddell, *J. Am. Chem. Soc.*, **95**, 4632 (1973).

(22) (a) M. F. Guimon, C. Guimon, F. Metras, and G. Pfister-Guillouzo, *J. Am. Chem. Soc.*, **98**, 2078 (1976). (b) It should be noted that in the compounds studied by Bushweller the pairs of *gem*-alkyl substituents exert a strong influence toward increasing the population of the twist conformer.[1c,e]

(23) For **7a**, ΔG°_{ct} may be as low as 1 kcal/mol,[11b] and ΔG°_{ct} for *trans*-2-methoxy-5-*tert*-butyl-1,3,2-dioxaphosphorinane was suggested to be 1.5-2 kcal/mol.[24]

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Robert O. Hutchins*
Department of Chemistry, Drexel University,
Philadelphia, Pennsylvania 19104

Bruce E. Maryanoff*
Chemical Research Department, McNeil Laboratories
Fort Washington, Pennsylvania 19034

Mario J. Castillo, Karl D. Hargrave
Andrew T. McPhail*
Paul M. Gross Chemical Laboratory
Duke University, Durham, North Carolina 27706

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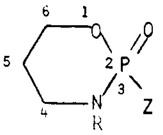
X-ray and NMR Studies of a Cyclophosphamide-like Molecule, *cis*-2-Oxo-2-dimethylamino-3-phenyl-5-*tert*-butyl-1,3,2-oxazaphosphorinane. Twist Conformation in Both Solid Phase and in Solution

Sir:

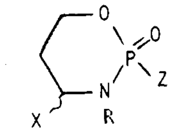
The 1,3,2-oxazaphosphorinanes cyclophosphamide (**1**), isophosphamide (**2**), and trophosphamide (**3**) are clinically useful anticancer drugs.[1] In vivo oxidation activates these molecules and gives the 4-hydroxy derivatives (**4**) in which the OH and Z may be related either cis or trans. Because of the expected relationship of molecular configuration and conformation to ease of oxidative microsomal potentiation and subsequent efficacy, X-ray studies of a number of such systems have been completed. These include **1**,[2] **2**,[3] and **3**;[4] 4-peroxy-**1**;[5] the 4-hydroperoxy derivatives of **1**[6] and **2**;[4b] and 4-keto-**1**.[7] In addition the enantiomers of **1** have recently been resolved[8] and their absolute configurations assigned by X-ray anomalous dispersion techniques.[9] Indeed, important differences in efficacies and rates of metabolism in humans and mice were ascribed to the two enantiomers.[10] Currently, investigations of the in vivo activities of the *cis*- and *trans*-4-methylcyclophosphamides (**5**) are being pursued.[11]



1 $R = H;\ Z = N(CH_2CH_2Cl)_2$

2 $R = CH_2CH_2Cl;\ Z = NHCH_2CH_2Cl$

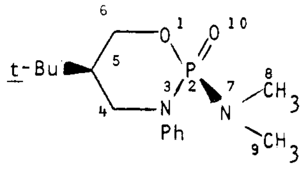
3 $R = CH_2CH_2Cl;\ Z = N(CH_2CH_2Cl)_2$



4 $X = OH$; R, Z based on **1**-**3**

5 $X = Me;\ R = H;\ Z = N(CH_2CH_2Cl)_2$

All of the above systems studied by X-ray crystallographic techniques were shown to possess chair-form conformations. It has been suggested that in solution both cyclophosphamide itself[12] and *trans*-**5** (Me and $N(CH_2CH_2Cl)_2$ trans)[11a] populate more than one conformation. We report here that closely related 1,3,2-oxazaphosphorinane **6** is in a *twist conformation* both in solid state and in solution. Thus, twist forms should receive important consideration in conformational equilibra involving **1-5**.



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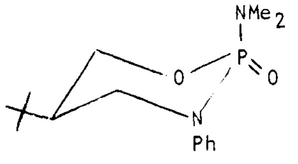

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A mixture of diastereomeric 2-dimethylamino-2-oxo-3-phenyl-5-*tert*-butyl-1,3,2-oxazaphosphorinanes was synthesized by the N_2O_4 oxidation of the corresponding trivalent phosphorus precursor. The latter was prepared by condensation of the required amino alcohol with $(Me_2N)_3P$ in a refluxing 50:50 mixture of ethyl acetate and toluene as solvent (6 h). The mixture of oxides was separated by column chromatography on silica gel eluted with anhydrous ether. Recrystallization of the cis isomer (**6**) from benzene gave white crystals, mp 165-166 °C (uncorrected). C, H, and P analyses within ±0.3 of calculated values were obtained.

Crystals of **6** belong to space group $P\bar{1}$ with $Z = 2$ ($\rho_{calcd} = 1.206$, $\rho_{measd} = 1.213$ g/cm^3) and cell dimensions $a = 6.143$ (2), $b = 11.273$ (4), $c = 12.423$ (3) Å; $\alpha = 102.3$ (1), $\beta = 95.3$ (1), $\gamma = 102.3$ (1)°. Data were collected on an Enraf-Nonius CAD-4 diffractometer using Mo K$\bar{\alpha}$ X-radiation with a graphite monochromator and ω-2θ scan technique. The structure was solved by direct methods with the use of MULTAN[1] and refined to $R = 0.046$ ($R_w = 0.035$) by full-matrix least squares using the 1754 unique nonzero diffraction maxima. All hydrogen atoms were located and refined isotropically.

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