filtrate and the collected mycelium were combined and evaporated to dryness to afford a metabolite mixture (700 mg). The mixture was dissolved in 200 mL of benzene under reflux and allowed to stand at room temperature to deposit an insoluble material which was collected by filtration to afford 150 mg (37.5% yield) of the *cis*-diol **19**.

The benzene-soluble part was chromatographed on alumina (20 g), and elution with benzene (320 mL) gave 85 mg (21% yield) of the (+)-ketol **18**: mp 194–195 °C; $[\alpha]^{30}_D$ +780° (*c* 0.13, $CHCl_3$); optical purity 92%.

Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.49; H, 6.01.

Further elution with benzene–$CHCl_3$ (1:1, 160 mL) gave 120 mg (30% yield) of the (−)-*cis*-diol **19**: mp 239–240 °C; $[\alpha]^{30}_D$ −274.9° (*c* 0.24, MeOH); optical purity 90%.

Anal. Calcd for $C_{18}H_{18}O_2$:C, 81.17; H, 6.81. Found: C, 81.22; H, 6.78.

(c) (−)-Diacetate 20. The benzene-insoluble *cis*-diol **19** (150 mg) was acetylated with acetic anhydride and pyridine to afford 195 mg of diacetate **20**: mp 169–169.5 °C; $[\alpha]^{30}_D$ −6.2° (*c* 0.41, $CHCl_3$); optical purity 2.2%.

Anal. Calcd for $C_{22}H_{22}O_4$: C, 75.41; H, 6.33. Found: C, 75.39; H, 6.37.

The benzene-soluble (−)-*cis*-diol **19** (30 mg, $[\alpha]^{30}_D$ −274.9°) was acetylated in the same way to afford 38 mg of the (−)-diacetate **20**: mp 184.5–185.5 °C; $[\alpha]^{28}_D$ −254° (*c* 0.3, $CHCl_3$); optical purity 90%.

Anal. Calcd for $C_{22}H_{22}O_4$: C, 75.41; H, 6.33. Found: C, 75.21; H, 6.31.

Acknowledgment. This research was partially supported by grants from the Ministry of Education, Japan (449015), the Yamada Science Foundation, and the Suntory Institute for Bioorganic Research to which the authors' thanks are due.

Registry No. 6, 39751-07-0; (±)-**7**, 76250-82-3; (+)-**7**, 76318-61-1; (−)-**7**, 76318-62-2; **8**, 700-58-3; **10**, 67092-78-8; (−)-**11**, 76250-83-4; (−)-**12**, 76250-84-5; (−)-**13**, 76250-85-6; (+)-**16**, 63902-07-8; (+)-**17**, 76250-86-7; (±)-**18**, 76250-87-8; (+)-**18**, 76318-63-3; (±)-**19**, 76250-88-9; (−)-**19**, 76318-64-4; (−)-**20**, 76250-89-0; (−)-**21**, 76318-65-5; (−)-**21** diacetate, 76318-66-6; *p*-(dimethylamino)benzoyl chloride, 4755-50-4.

Carbon–Phosphorus Heterocycles. Conformational Analysis of Substituted 1-Phenyl-4-phosphorinanones and Derivatives. Single-Crystal, X-ray Diffraction Analysis of 1-*r*,*cis*-2(a),*trans*-6(e)-Triphenyl-4-phosphorinanone 1-Sulfide

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A series of substituted 1,2,6-triphenyl-4-phosphorinanones has been prepared, and a conformational analysis was performed on these systems. Condensation of phenylphosphine or bis(hydroxymethyl)phenylphosphine with appropriately substituted 1,4-pentadien-3-ones gave the final products. For example, 1-phenyl-2,2,6,6-tetramethyl-4-phosphorinanone was obtained which could be oxidized, sulfurized, or alkylated to give the corresponding oxide, sulfide, or phosphonium salt. 1,2,6-Triphenyl-4-phosphorinanone was also obtained and was oxidized and sulfurized by standard procedures. ^1H, ^{13}C, and ^{31}P NMR analysis on all of the compounds indicated that flattened chairs were the major conformation in all cases. Two isomers of 1,2,6-triphenyl-4-phosphorinanone were obtained from the original condensation as indicated by ^{31}P NMR analysis, but only one isomer could be isolated in pure form. Oxidation and sulfurization of this phosphine gave only one oxide and sulfide, respectively. The NMR data are most supportive of an axial C(2)–C_6H_5 bond and an equatorial C(6)–C_6H_5 bond in the phosphine, the oxide, and the sulfide. The ^{13}C NMR chemical shift for the C(6) atom is suggested to be at higher field than that for the C(2) atom from normal compression effects. A single-crystal, X-ray diffraction analysis of 1-*r*,-*cis*-2(a),*trans*-6(e)-triphenyl-4-phosphorinanone 1-sulfide was completed. The crystal is triclinic, the space group is $P\bar{1}$, and unit cell dimensions (at −135 °C) are a = 9.600 (5) Å, b = 10.219 (7) Å, c = 10.490 (4) Å, α = 103.02 (3)°, β = 109.77 (2)°, and γ = 76.29 (3)°, and Z = 2. Reduction of the ketone group in the tetramethyl-substituted series was accomplished smoothly and gave solid alcohols in the case of the corresponding *P*-oxide, *P*-sulfide, and *P*-$CH_2C_6H_5$ phosphonium salts. A conformational study was made on these systems, and a model compound, 1-phenyl-2,2,6,6-tetramethyl-4-*tert*-butyl-4-phosphorinanol 1-oxide, was also synthesized for the sake of comparison of spectral properties. These examples are the first highly substituted phosphorinanones and phosphorinanols to be examined by ^{13}C NMR analysis in which the phosphorus atom is highly hindered by large groups at C(2) and at C(6).

The chemistry and conformational analysis of six-membered heterocycles containing phosphorus as the heteroatom are an area of active interest.[2-4] Herein we report the syntheses of new derivatives of **1a** and **2a** as well as a conformational analysis, via ^1H, ^{13}C, and ^{31}P NMR examination, with regard to configurational preferences of groups attached to phosphorus and those located at C(2,6)

(1) (a) Postdoctorate, 1979–1980. (b) Predoctoral candidate, 1976–1978, Conoco Fellow, January–June 1976, and Dow Fellow, summers of 1975 and 1977. (c) Postdoctorate, 1979.

(2) J. B. Lambert and S. I. Featherman, *Chem. Rev.*, **75**, 611 (1975).

(3) S. D. Venkataramu, G. D. Macdonell, W. R. Purdum, M. El-Deek, and K. D. Berlin, *Chem. Rev.*, **77**, 121 (1977).

(4) D. E. C. Corbridge, "The Structural Chemistry of Phosphorus", Elsevier, Amsterdam, The Netherlands, 1974, p 394.

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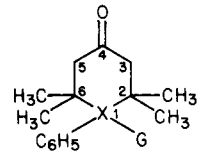
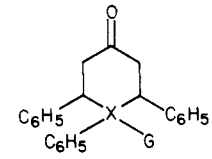




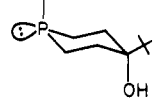
1a, X = P; G = lone pair
b, X = P; G = O
c, X = P; G = S
d, X = P^+; G = CH_3, I^-
e, X = P^+; G = C_2H_5, I^-
f, X = P^+; G = $C_6H_5CH_2$, Br^-

2a, X = P; G = lone pair
b, X = P; G = O
c, X = P; G = S

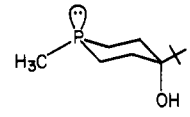
and C(4) in all systems. A few of the compounds to be discussed have previously been synthesized, although there were essentially no definitive conclusions about the geometry of these systems in solution.[5-8] A single-crystal, X-ray diffraction analysis of **2c** is reported also.

Modified procedures[5,6,8] gave **1a-d** and two isomers of **2a**, neither of which was previously identified although we believe the previous authors[5] had a mixture.[5] The syntheses of previously unknown **1e,f** and **2b,c** were accomplished via techniques of a similar nature but with significant alternations.

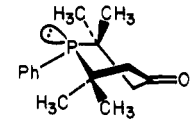
^{13}C NMR Parameters. Quite novel ^{13}C chemical shifts and ^{31}P-^{13}C coupling values (Table I) were recorded for **1a-f** and **2a-c** with full decoupling and without any decoupling. Of particular importance were the ^{13}C chemical shifts for C(3,5) (and the related ^{31}P-^{13}C coupling constants) and the ^{13}C shifts associated with the exocyclic methyl groups located at C(2,6) in **1a-f**. (Table I). It has been stated that the magnitude of $^2J_{PC(3,5)}$ for several six-membered, phosphorus-containing heterocycles can be employed for the determination of the configuration at phosphorus.[9-11] For example, the $^2J_{PC(3,5)}$ value in *trans*-4-*tert*-butyl-1-methyl-4-phosphorinanol was 0 Hz,



trans isomer

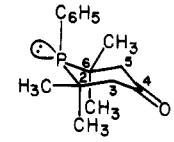


cis isomer

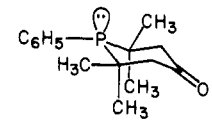


3

and in *cis*-4-*tert*-butyl-1-methyl-4-phosphorinanol it was 7.5 Hz.[9] For **1a** in $DCCl_3$, a $^2J_{PC(3,5)}$ of 2.53 Hz was recorded while a $^2J_{PC(3,5)}$ value of 2.82 Hz was found in C_6D_6 and 3.49 Hz in pyridine-d_5. Therefore, it could be argued that an equilibrium exists between the conformers and that there is a high population of one conformer of **1a** with the P-C_6H_5 group predominately in an *axial orientation*. The $^2J_{PC}$ values for the *exocyclic* methyl groups at C(2,6) should also be instructive regarding the configuration at phosphorus. Interestingly, for **1a** the $^2J_{PC}$ values for the exocyclic methyl groups are remarkedly similar in $DCCl_3$ (30.92 and 8.98 Hz), in C_6D_6 (32.09 and 9.62 Hz), and in pyridine-d_5 (31.63 and 9.63 Hz). However, since an axial CH_3 generally resonates at higher field than an equatorial CH_3 (in cyclohexanes),[12] one would expect a marked difference in $\Delta\delta$ for $CH_{3(a)}$ vs. $CH_{3(e)}$ if an equatorial C_6H_5-P bond existed in the major conformer for **1a**. This is because both equatorial and methyl groups are gauche to the C_6H_5-P bond. In contrast, if the major conformer had an axial C_6H_5-P bond, only the equatorial (and gauche) CH_3 would expectedly be shifted *upfield*, and the $\Delta\delta$ for $CH_{3(a)}$ and $CH_{3(e)}$ should practically disappear. This is observed (δ 31.01 and 30.09), and thus the conformer **1a'** with an axial C_6H_5-P is strongly supported rather than **1a''**.



1a'



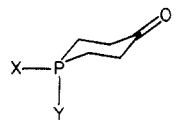
1a''

Courtauld models indicate that a twist conformation such as **3** for the phosphorinanone ring in **1a** may be tolerated. Thus, caution is necessary in the use of the $^2J_{PC}$ values of the exocyclic methyl carbons to assign configurational preference at phosphorus in **1a**.

Although **1a** showed two doublets for the exocyclic methyl carbons as indicated previously, ^{13}C NMR analysis for oxide **1b** and sulfide **1c** displayed one doublet and one singlet each for the methyl carbons in the proton-decoupled spectra (Table I). We tentatively conclude that the larger $^2J_{PCCH_3}$ = 30.92 Hz is for the CH_3 (axial) and the $^2J_{PCCH_3}$ = 8.98 Hz is for CH_3 (equatorial) in **1a'** on the basis of analysis with somewhat related phosphetanes[12c] and phospholenes.[12d] Both full proton-decoupled and nondecoupled ^{13}C spectra were recorded to verify the identity of the carbons. With the assumption that the P=O and P=S groups are axially oriented in **1b** and **1c** (this also assumes that **1a''** is present in low concentrations at equilibrium with **1a'** or that if the latter undergoes oxidation or sulfurization, a ring reversal occurs to give **1b** or **1c**), the ^{13}C chemical shifts and couplings are still different to assign. We tentatively assign signals at 25.07 ($^2J_{PCCH_{3(ax)}}$ = 2.11 Hz) and 25.62 ppm for **1b** and 26.17 and 27.19 ppm ($^2J_{PCCH_{3(ax)}}$ = 1.47 Hz) for **1c** on the basis of the analysis[12d] cited previously. Shielding of the equatorial CH_3 by the P=O group in **1b** may account for the upfield shift observed as compared to the value for the counterpart in the sulfide **1c**. Moreover, the less polar and longer P=S (compared to the P=O bond) would possibly not be expected to exhibit as significant a shielding effect on the CH_3(eq). As an analogy, it could be calculated that in 1-phenyl-4-phosphorinanone 1-oxide and 1-phenyl-4-phosphorinanone 1-sulfide[11a] the angle between the C_6H_5-P bond and the plane P-C(2)-C(6) was 61° and 62.5°, respectively. Then, very probably a similar situation exists, and the phenyl ring with its face exposed toward the CH_3(eq) in **1b** and **1c** is closer in the former compound than in the latter which could cause increased shielding of the CH_3(eq) also. Very surprising was the fact that no ^{31}P-^{13}C coupling was observed for C(3,5) or for the exocyclic methyl carbons at C(2,6) in **1d-f**.

With regard to the diagnostic value of $^2J_{PC(3,5)}$, ketones **4a-d**[11a] have $^2J_{PC(3,5)}$ values which clearly suggest a predominance of a phenyl group *equatorially* situated in **4b-d** but axially positioned in **4a** in $DCCl_3$ on the basis of work with other related systems.[4-11] An X-ray diffraction study

(5) R. P. Welcher and N. E. Day, *J. Org. Chem.*, **27**, 1824 (1962).
(6) G. Markl, D. E. Fischer, and H. Olbrich, *Tetrahedron Lett.*, 645 (1970).
(7) G. Markl and H. Olbrich, *Angew. Chem.*, **78**, 598 (1966).
(8) F. Asinger, A. Saus, and E. Michel, *Monatsh. Chem.*, **99**, 1695 (1968).
(9) S. I. Featherman and L. D. Quin, *Tetrahedron Lett.*, 1955 (1973).
(10) J. J. Breen, S. O. Lee, and L. D. Quin, *J. Org. Chem.*, **40**, 2245 (1975); S. I. Featherman, S. O. Lee and L. D. Quin, *ibid.*, **39**, 2899 (1974).
(11) (a) S. D. Venkataramu, K. D. Berlin, S. E. Ealick, J. R. Baker, S. Nichols and D. van der Helm, *Phosphorus Sulfur*, **7**, 133 (1979); (b) G. D. Macdonell, K. D. Berlin, J. R. Baker, S. E. Ealick, D. van der Helm, and K. L. Marsi, *J. Am. Chem. Soc.*, **100**, 4535 (1978); (c) J. B. Rampal, K. D. Berlin, J. P. Edasery, N. Satyamurthy, and D. van der Helm, *J. Org. Chem.*, following paper in this issue.
(12) (a) D. K. Dalling and D. M. Grant, *J. Am. Chem. Soc.*, **89**, 6612 (1967); (b) E. Bretmaier, "^{13}C NMR Spectroscopy", Verlag Chemie, Weinheim/Bergstr., 1974, Chapter 4; (c) G. A. Gray and S. E. Cremer, *J. Chem. Soc., Chem. Commun.*, 367 (1972); (d) J. J. Breen, S. I. Featherman, L. D. Quin, and R. C. Stocker *ibid.*, 657 (1972).

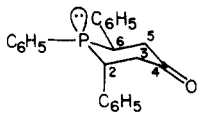


4a, X = lone pair; Y = C_6H_5
b, X = C_6H_5; Y = O
c, X = C_6H_5; Y = S
d, X = C_6H_5; Y = CH_3, I^-

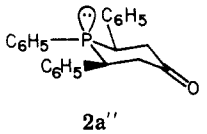
of **4b** and **4c** revealed that this configuration at P was correct in the *solid state*. In biased *cis*- (axial P–C_6H_5) and *trans*-4-*tert*-butyl-1-phenylphosphorinane,[11b] $^2J_{PC(3,5)}$ was 0.0 and 5.1 Hz, respectively, for example. ^{13}C NMR data on **1b–f** therefore could be taken to signify the presence of an axial P–C_6H_5 group with an equatorial P=O (or P=S or P–alkyl) group. However, some ring deformation may be present as a result of nonbonded interactions between the phenyl group (ortho protons) and the axial methyl group at C(2) and C(6) which may effectively negate or greatly reduce P–C couplings to C(3,5) and the methyl carbons. At present, there does not appear to be any intuitively obvious explanation for the lack of $J_{PC(3,5)}$ couplings in **1b–f**.

Defense of system **1b** with P=O (or P=S in **1c** or P–alkyl in **1d–f**) in an equatorial position is *not* easy in view of the findings of others on phosphorinanes and phosphorinanones in which the bond is axial.[4-11] Another point to consider in the ^{13}C NMR spectrum of **1b** is that $\delta_{C(3,5)}$ is *downfield* in this oxide compared to the signal in phosphine **1a**. It has been observed in $DCCl_3$ that the C(3,5) ^{13}C resonance in *cis*-4-*tert*-butyl-1-phenylphosphorinane (axial C_6H_5–P) occurred at 21.32 ppm while *trans*-4-*tert*-butyl-1-phenylphosphorinane 1-oxide (equatorial C_6H_5–P) had $\delta_{C(3,5)}$ downfield at 22.37 ppm.[11] However, the latter displayed a $^2J_{PC(3,5)}$ value of 5.8 Hz, a coupling not observed in **1b–f**. Consequently, the exact orientation of the C_6H_5–P bond in **1b–f** in solution must remain speculative at the moment, but we feel that it is of the equatorial type.

Although formation of a 1,2,6-triphenyl-4-phosphorinanone (**2a**) has been reported,[5] no record exists which has defined the exact structure of this phosphine. In our hands, initial ^1H and ^{13}C NMR examination of the reaction mixture which produces phosphine **2a** suggested the presence of two isomers. Several recrystallizations from H_3CCN, with considerable care to avoid oxidation, gave a pure isomer which we suggest is **2a′**. The other isomer



2a′

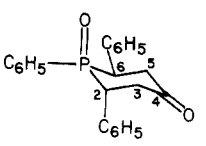


2a″

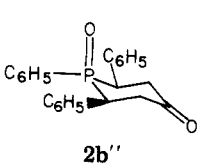
is believed to be **2a″** which could be isolated in very low yields after repeated crystallizations but was contaminated with traces of **2a′**. That **2a′** is the correct structure of the major product rests on the following observations. The ^{13}C NMR chemical shifts and J_{P-C} coupling values (Table I) for **2a–c** suggest a *trans arrangement* for the phenyl groups at C(2,6). If the arrangement was syn, two signals [a doublet in each case for C(2,6) and C(3,5)] would be expected regardless of the configuration at phosphorus. This was observed in the ^{13}C spectrum for **2a″** which was contaminated with **2a′**. This assumes that C(2) and C(6) as well as C(3) and C(5) would be magnetically equivalent in **2a″**, respectively, and that the energy barrier for epimerization at phosphorus would be high.[11b] Also assumed is that there is no large dissymmetry imposed on the system by a skewed C_6H_5–P bond. Since the pure **2a′** had only one ^{31}P NMR signal and could be converted cleanly to oxide **2b** or sulfide **2c**, the homogeneity of **2a′** in solution seems assured. The $^2J_{PC(3,5)}$ values (2.79 and 7.98 Hz) for **2a′** in $DCCl_3$ are somewhat abnormal and suggest that some crowding may exist at phosphorus around the *equatorial* C_6H_5–P bond, perhaps to enlarge the C–P–C_6H_5 angle. Stereochemical diagnosis has been possible via analysis of the $^2J_{PC(3,5)}$ parameter in several isomeric phosphorinane systems but in no case have there been substituents at C(2) and C(6).[9,11] An examination of **2a′** (slightly contamined presumably with **2a″**) in C_6D_6 (Table I) gave similar ^{13}C spectral data to those found in $DCCl_3$.

Signal assignments for C(2) and C(6) in **2a′** are based on the supposition that the γ_a shielding effect of the C_6H_5–C(2) bond on the resonance of C(6) is greater than any β-deshielding effects.[11c] An upfield shift for a ring carbon γ to an axial *C*-methyl group (compared to the shift for a carbon γ to an equatorial *C*-methyl group) arising from a compression effect has been noted in cyclohexanes.[12] Noteworthy is the fact that in *r*-2,*trans*-6-diphenyl-4-thianone the ^{13}C signal for C(2,6) occurs[13] at 43.78 ppm, sharply upfield from that in the cis isomer (48.15 ppm) which has both C_6H_5–C bonds in equatorial positions. This value for the *trans*-thianone is, of course, an average since undoubtedly it undergoes ring reversal at room temperature, but nevertheless it clearly demonstrates the shielding characteristics imposed by an axial C_6H_5–C bond on a γ ring carbon.

Air oxidation of a dioxane solution of pure **2a′** gave pure oxide **2b′** after 20 days. Oxidation of slightly impure **2a′** with H_2O_2[14] in the cold (0 °C) gave two oxides as indicated by ^{31}P NMR analysis, the second oxide presumably being **2b″** which has also thwarted all efforts at purification.



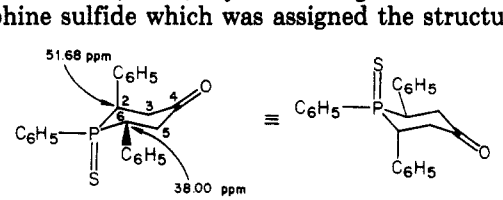
2b′



2b″

However, pure **2b′** (Table I) has ^{13}C NMR signals at 46.43 and 38.19 ppm for C(2) and C(6), respectively, with reasonable coupling constants.[11a] This assumes that the shielding effect on C(6) by the axial C_6H_5–P bond at C(2) is significant[11,12] and is reminiscent of the thianone system cited previously.[13] The resonance at 42.65 ppm ($^2J_{PC(3)}$ = 4.27 Hz) in **2b′** is taken to be supportive of an *axial* P=O group shielding more than an axial phenyl group.[11] Therefore the signal at 45.05 ppm ($^2J_{PC(3)}$ = 4.57 Hz) should be C(5). Again, the $^3J_{PC(4)}$ value of 6.44 Hz is not unreasonable in phosphorinanones.[10,11a]

Sulfurization (in boiling benzene) of **2a′** afforded, after recrystallization, one (only one ^{31}P signal was observed) phosphine sulfide which was assigned the structure **2c′**



2c′

(13) K. Ramalingam, K. D. Berlin, N. Satyamurthy, and R. Sivakumar, *J. Org. Chem.*, 44, 471 (1979).

(14) Oxidation of tertiary phosphines with H_2O_2 is known to proceed stereospecifically with retention of configuration at phosphorus. H. R. Hays and D. J. Peterson, "Organic Phosphorus Compounds", Vol. 3, G. M. Kosolapoff and L. Maier, Eds., Interscience, New York, 1972, Chapter 6, p 344 and references cited therein.

Table I. ^{13}C NMR Chemical Shifts[a] and ^{31}P-^{13}C Coupling Constants[b] for Substituted 4-Phosphorinanones

compd	carbon atom 2,6	3,5	4	CH_3 (ax)	CH_3 (eq)	Ar C[l]
1a	35.17 (18.32)	52.90 (2.53)	211.11	31.01 (30.92)	30.09 (8.98)	c
1a[d]	34.93 (19.04)	52.81 (2.82)	208.76	31.01 (32.09)	30.10 (9.62)	c
1a[e]	34.93 (18.78)	52.68 (3.49)	209.83	30.97 (31.63)	30.07 (9.63)	c
1b	37.84 (60.38)	53.57	206.26 (8.09)	25.62	25.07 (2.11)	C(α) *127.86* (84.80), C(β) *132.40* (7.92), C(γ) *128.26* (10.89), C(δ) *131.79* (2.25)
1c	39.39 (43.34)	53.52	205.50 (7.35)	26.17	27.19 (1.47)	C(α) *127.72* (76.15), C(β) *133.27* (8.44), C(γ) *128.23* (11.01), C(δ) *131.52* (2.94)
1d[f,g]	33.71 (40.43)	50.92	203.65 (7.35)	25.62	25.62	C(α) *115.77* (74.25), C(β) *133.44* (8.58), C(γ) *129.62* (11.68), C(δ) *134.41* (2.86)
1e[f,h]	34.47 (37.63)	51.65	203.49 (7.35)	26.78[i]	23.35[i]	C(α) *114.10* (71.37), C(β) *133.92* (7.88), C(γ) *130.03* (11.56), C(δ) *134.38* (2.38)
1f[f,j]	35.07 (36.80)	51.56	203.56 (6.44)	26.54[i]	25.44[i]	c
2a′	38.80 (23.47), 36.32 (16.19)	42.68 (2.79), 46.14 (7.98)	209.70			c
2a′[k]	38.93 (24.16), 36.80 (17.04)	42.76 (2.21), 46.04 (7.42)	207.59			c
2b′	46.43 (56.66), 38.19 (60.34)	42.65 (4.27), 45.05 (4.57)	207.14 (6.44)			c
2c′	51.68 (41.83), 38.00 (44.85)	43.02 (2.95), 44.95 (2.89)	207.16 (5.45)			c

[a] All samples were ca. 100 mg in $DCCl_3$ except where noted. Shifts are in parts per million (+0.1 ppm) from internal Me_4Si. [b] ^{31}P-^{13}C coupling constants (given in parentheses) in hertz (+0.4 Hz). [c] The signals for Ar C were complex and could not be assigned unequivocally. [d] In hexadeuteriobenzene a small amount of presumably 1a″ was detected also. [e] In pyridine-d_5. [f] In Me_2SO-d_6. [g] The ^{13}C signal for CH_3-P in the methiodide occurs at −0.96 ppm (48.41 Hz). [h] The ^{13}C signals for CH_3CH_2P in the ethiodide occur at 7.07 (6.49 Hz) and 7.83 (44.96 Hz) ppm, respectively. [i] Signal assignments may be reversed. [j] The ^{13}C signal for $C_6H_5CH_2P$ in the benziodide occurs at 20.93 ppm (42.86 Hz). [k] In C_6D_6. [l] The average value of the two signals of the doublet is italic.

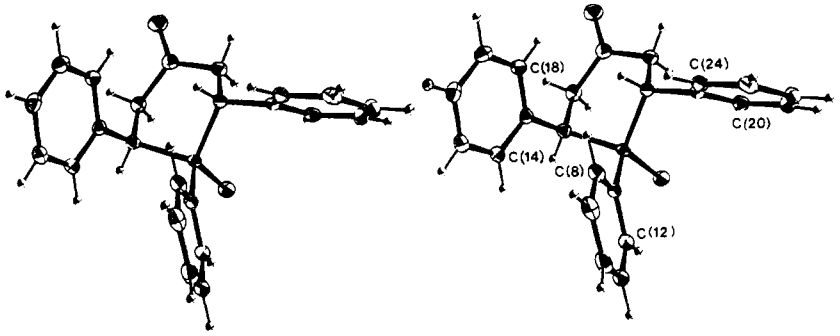
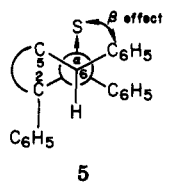


Figure 1. Stereoview of the single molecule (Johnson)[38] of **2c′**.

(based on previous arguments and similar ^{13}C parameters reported for 1-phenyl-4-phosphorinanone 1-sulfide).[15] The X-ray diffraction analysis of solid **2c′** will be discussed shortly, and it confirmed the structure. The ^{13}C signal at 38.00 ppm ($^1J_{PC(2)}$ = 44.85 Hz) was tentatively assigned to the C(6) carbon atom bearing an equatorially oriented phenyl group with only a small gauche deshielding effect by the C_6H_5-P group (as in **5**) but a larger shielding effect



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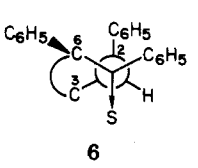

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by the C_6H_5-C(2) bond. Another argument could be made that the signal was for C(2) on the basis of a smaller deshielding effect by the attached axial phenyl group (shown in **5**) and a larger deshielding of C(6) by the phenyl group (on P shown in **6**) which is not wholly unreasonable.[15]

Infrared Spectral Data. Infrared C=O absorptions for **1a–f** and **2a–c** were between 1680 and 1710 cm^{-1} on KBr pellets (Table II). The C=O stretching frequencies for the compounds presented herein agreed well with those previously reported for **4a** (1695 cm^{-1}),[16] 1-ethyl-4-phosphorinanone (1715 cm^{-1}),[16] and 2-phenyl-3-methyl-2-phosphabicyclo[4.4.0]decan-5-one (**7**, 1700 cm^{-1}),[17] as well as with the corresponding oxide (1705 cm^{-1}), methiodide (1710 cm^{-1}), and benzchloride (1720 cm^{-1}).[17] Infrared absorptions assigned to the P-C_6H_5 bond[18] (1430–1455 and

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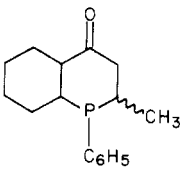

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1103–1117 cm^{-1}) were also clearly in evidence for **1a–f** and **2a–c**. Absorptions for P=O and P=S were also recorded (**1b**, P=O, 1176 cm^{-1}; **2b′**, P=O, 1175 cm^{-1}). However, only meager information regarding structural features based on P=O and P=S infrared absorptions has been presented[18-20] for systems of known configuration, and this precluded any conformational assignments.

^{1}H NMR Spectral Data. The ^{1}H NMR data (Table II) for **1a–f** and **2a–c** could not all be obtained in the same solvent due to the insolubility of the salts **1d–f** in $DCCl_3$. Therefore ^{1}H NMR spectra for **1a–c** and **2a–c** were obtained in $DCCl_3$, and ^{1}H NMR spectra for **1d–f** were obtained in Me_2SO-d_6. Phosphine **1a** gave rise to two doublets (CH_3) in the ^{1}H NMR spectrum at δ 0.93 ($^3J_{PCCH}$ = 11 Hz) and 1.32 ($^3J_{PCCH}$ = 18 Hz). On the basis of the ^{13}C chemical shifts and ^{31}P–^{13}C coupling constants for the exocyclic methyl carbons in **1a** [30.09 ppm ($^2J_{PCC}$ = 8.98 Hz) and 31.01 ppm ($^2J_{PCC}$ = 30.92 Hz)], one might surmise that the signal at 31.01 ppm was for *axial* H_3C. This is supported also by the known deshielding of such methyl protons in cyclohexanes and larger $^3J_{HCCH}$ values in such systems compared to that of an equatorially situated methyl group.[21] Thus the equatorial methyl group is assigned the upfield doublet by assuming that the P–C_6H_5 group is axially oriented. Thus, this could place the equatorial methyl groups in the shielding cone of the phenyl ring in conformer **1a′**. However, evidence is not totally unequivocal so as to permit a completely tenable analysis.

Double-resonance experiments (^{1}H [^{31}P]) simplified the ^{1}H NMR spectrum of **1a′** and clearly indicated an A_2B_2X pattern for the H(3,5) axial and equatorial protons. Since two different $^3J_{PCCH}$ values were apparent (2 and 6 Hz) for the H(3,5) protons, it seems reasonable that these values could be assigned to the axial and equatorial protons of the A_2B_2X pattern. Previous work[21-26] has suggested a "Karplus type" relationship for $^3J_{PCH}$ in phosphonates and phosphonous dihalides. In this relationship, the portion of the A_2B_2 spectrum at highest magnetic field would correspond to the equatorial H(3,5) protons. Also, in comparison, replacement of α-protons with methyl groups causes shielding of equatorial protons in cyclohexanes[25] which supports our assignments. Therefore, in **1a-f** (except **1c**), the high-field portion of the A_2B_2X spectrum was assigned to the equatorial H(3,5) protons.

The ^{1}H NMR spectrum of **1c** revealed a multiplet for the H(3,5) protons between δ 2.48 and 3.41. Irradiation of the ^{31}P signal caused this multiplet to collapse to a broad ($W_{1/2}$ = 4 Hz) singlet at δ 2.94. This implies the ^{1}H–^{1}H geminal coupling is small for the conformer in $DCCl_3$. Recording the ^{1}H NMR spectrum of **1c** in acetone-d_6 revealed a doublet of AB portions, one between δ 2.46 and 2.90 and the other between δ 3.18 and 3.44. Irradiation of the ^{31}P signal of **1c** caused the low-field portion to collapse to an *AB spectrum* with $^2J_{HCH}$ = 14 Hz while the high-field portion was an extremely complex multiplet between δ 2.46 and 2.94. Further analysis revealed $^3J_{PCCH}$ values of 24 and 6 Hz for the high-field and low-field signals, respectively. A rational conclusion would be that the high-field multiplet [equatorial (3,5) protons], after ^{31}P irradiation, could be the result of long range ^{1}H–^{1}H coupling or possibly a preferred solute–solvent orientation particularly in acetone-d_6.

The ^{1}H spectra of **2a–c** revealed no immediately apparent ^{31}P–^{1}H coupling at both the H(2,6) and H(3,5) protons. However, addition of 1 drop of 40% NaOD in D_2O to a saturated acetone-d_6 solution of **2a** led to an observation of coupling [$^2J_{PC(2,6)H}$] after deuterium exchange at C(3,5). After the reaction mixture had been allowed to stand at room temperature for 19 h, the ^{1}H NMR spectrum exhibited two doublets at δ 3.92 ($^2J_{PCH}$ = 12 Hz) and 4.09 ($^2J_{PCH}$ = 6 Hz). Again the assignment of these H(2,6) proton signals was based on previous work[26] in which a relationship for the dihedral angle between the phosphorus lone pair and the α-protons has been established in simple acyclic and aliphatic systems. Consequently, the upfield doublet with the larger coupling constant was assigned to the H(6) axial proton.[11c]

^{31}P NMR Spectral Data. ^{31}P signals for **1a–f** and **2a–c** are listed in Table II. The deshielded signal for **1a** (–16.05 ppm) compared to that for 1-phenyl-4-phosphorinanone (–39.3 ppm)[27] is probably the result of β deshielding[27] by the four C(2,6) methyl groups with each methyl group contributing ca. +6 ppm to the ^{31}P chemical shift. This deshielded signal for **1a** is in accord with similar observations of β deshielding for a number of phosphorus compounds.[28] Unfortunately, little ^{31}P NMR data is available on the derivatives of 1-phenyl-4-phosphorinanone to test the validity of the above observed shielding differences for the other phosphorinanones (**1b–f**) presented herein. Noticeably, the ^{31}P signals for salts **1d–f** occur over a range of ca. 2 ppm, indicating that the electronic and geometric environments are similar in **1d–f**.

Again the ^{31}P NMR spectra of **2a–c** afforded interesting observations. For example, pure **2a′** gave one signal at –6.04 ppm (Table II), but the slightly crude sample gave, in addition, a very small signal at –2.85 ppm, apparently for **2a″**. The latter does not agree with data for a majority of isomeric, six-membered, phosphorus-containing ring systems in which the equatorial isomer has the most *downfield* ^{31}P signal.[29] We feel this observation supports our contentions that **2a″** has one equatorial C_6H_5–P bond and differs from **2a′** only in that the former has two equatorial C_6H_5–C(2,6) bonds. Large bulky groups near or on phosphorus may reverse the order and this has been predicted.[29] Since it has been possible to isolate **2a** and **2b** in pure form, we feel the assignments are more defensible. Nevertheless, caution is needed on the assignment of the conformation via the shift of the ^{31}P signal. A reversal of shift has been recorded for *cis*- and *trans*-4-*tert*-butyl-1-phenylphosphorinane.[11b] That is, cis isomer (axial P–C_6H_5) had the ^{31}P signal at lowest field. In our

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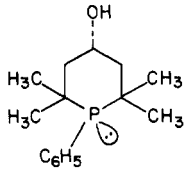
Table II. Spectral Data for 4-Phosphorinanones 1a-f and 2a

compd	IR (KBr;[a] selected bands), cm^{-1}	^1H NMR shifts, δ [b]	^{31}P NMR shifts, δ [c]
1a	2900, 1680, 1435, 1290, 1187, 748, 698	0.93 (d, J_{PCCH} = 11 Hz, CH_3, 6 H), 1.32 (d, J_{PCCH} = 18 Hz, CH_3, 6 H), 2.12 (dd, J_{HCH} = 14 Hz, J_{PCCH} = 6 Hz, CH_a, 2 H), 2.93 (dd, J_{HCH} = 14 Hz, J_{PCH} = 2 Hz, CH_e, 2 H), 7.32-7.86 (m, Ar H, 5 H)	-16.05
1b	2940, 1700, 1442, 1176, 1104, 757, 713	1.23 (d, J_{PCCH} = 14 Hz, CH_3, 6 H), 1.30 (d, J_{PCCH} = 14 Hz, CH_3, 6 H), 2.61 (dd, J_{HCH} = 13 Hz, J_{PCCH} = 13 Hz, CH_a, 2 H), 2.99 (dd, J_{HCH} = 13 Hz, J_{PCCH} = 13 Hz, CH_e, 2 H), 7.46-7.64 (m, Ar H, 3 H), 7.82-8.08 (m, Ar H, 2 H)	41.21
1c	2850, 1690, 1430, 1092, 867, 718, 697	1.08 (d, J_{PCCH} = 16 Hz, CH_3, 6 H), 1.44 (d, J_{PCCH} = 16 Hz, CH_3, 6 H), 2.48-3.41 (m, J_{HCH} < 2 Hz, CH_2, 4 H), 7.58-7.79 (m, Ar H, 3 H), 8.37-8.60 (m, Ar H, 2 H)	64.42
1d	2850, 1700, 1435, 1206, 1105, 907, 748	1.18 (d, J_{PCCH} = 16 Hz, CH_3, 6 H), 1.41 (d, J_{PCCH} = 15 Hz, CH_3, 6 H), 2.60 (d, J_{PCH} = 14 Hz, CH_3, 3 H), 2.85 (dd, J_{HCCH} = 14 Hz, J_{PCCH} = 14 Hz, CH_a, 2 H), 3.27 (dd, J_{HCCH} = 14 Hz, J_{PCCH} = 14 Hz, CH_e, 2 H), 7.66-7.96 (m, Ar H, 3 H), 7.98-8.26 (m, Ar H, 2 H)	35.27
1e	2850, 1710, 1435, 1195, 1110, 753, 697	0.84-1.64 (m, CH_3, 3 H), 1.16 (d, J_{PCCH} = 16 Hz, CH_3, 6 H), 1.51 (d, J_{PCCH} = 14 Hz, CH_3, 6 H), 2.72 (dd, J_{HCCH} = 16 Hz, J_{PCCH} = 16 Hz, CH_a, 2 H), 3.00-3.50 (m, J_{HCH} = 7 Hz, CH_2, 2 H), 3.25 (dd, J_{HCH} = 16 Hz, J_{PCCH} = 16 Hz, CH_e, 2 H), 7.64-8.28 (m, Ar H, 5 H)	37.39
1f	2850, 1700, 1445, 1207, 1103, 843, 697	1.02 (d, J_{PCCH} = 16 Hz, CH_3, 6 H), 1.56 (d, J_{PCCH} = 16 Hz, CH_3, 6 H), 2.83 (dd, J_{HCCH} = 14 Hz, J_{PCCH} = 22 Hz, CH_a, 2 H), 3.25 (dd, J_{HCCH} = 14 Hz, J_{PCCH} = 18 Hz, CH_e, 2 H), 5.02 (d, J_{PCH} = 13 Hz, CH_2, 2 H), 7.18-7.52 (m, Ar H, 5 H), 7.70-8.08 (m, Ar H, 3 H), 8.38-8.72 (m, Ar H, 2 H)	35.21
2a'	2960, 1690, 1430, 1237, 1138, 905, 696	2.44-3.35 (m, CH_2, 4 H), 3.60-4.05 (m, CH, 2 H), 6.68-6.84 (m, Ar H, 2 H), 6.84-7.40 (m, Ar H, 13 H)	-6.04
2b'	3000, 1700, 1435, 1175, 1117, 847, 698	2.80-3.45 (m, CH, 2 H), 3.48-4.10 (m, CH_2, 4 H), 6.74-6.96 (m, Ar H, 2 H), 6.98-7.44 (m, Ar H, 13 H)	33.91
2c'	3000, 1700, 1445, 1225, 1105, 800, 694	2.74-3.40 (m, CH, 2 H), 3.68-4.40 (m, CH_2, 4 H), 6.76-6.96 (m, Ar H, 2 H), 7.00-7.46 (m, Ar H, 13 H)	47.92

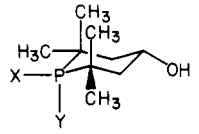
[a] The spectra were obtained on samples (2 mg) with KBr (200 mg) pellets. [b] Spectra were obtained in $DCCl_3$ solution, except for 1d-f (Me_2SO-d_6), of each compound with tetramethylsilane as an internal standard; peak positions quoted in the case of doublets are measured from the approximate center, and relative peak areas are given as whole numbers. [c] The spectra were obtained on samples (ca. 200 mg) in $DCCl_3$ solution (2 mL), except for 1d-f (ca. 200 mg in 2 mL of Me_2SO-d_6), with 85% H_3PO_4 as an external standard. A positive value indicates peak position downfield from the standard.

case, the isomer difference results from substitution at carbon rather than at phosphorus.

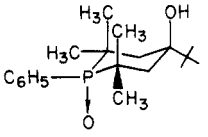
Lithium Aluminium Hydride Reduction of 1a. Reaction of a THF solution of **1a** with $LiAlH_4$, followed by aqueous hydrolysis and the appropriate workup, did not afford a crystalline material in our hands. However, the resulting viscous oil (**8a**) resisted all attempts at purification and was easily oxidized to a complex mixture. ^1H NMR analysis of crude **8a** showed a broad multiplet at δ 3.82–4.24 for the H(4) proton in the ^1H NMR spectrum as possibly due to the alcohol with equatorially oriented hydroxyl group. Although one broad signal appeared at -8.07 ppm for the ^{31}P nucleus in **8a**, the data must be considered tentative since the crude phosphine could not be purified. However, oxidation, sulfurization, and quaternization (benzyl bromide) of **8a** afforded isomerically pure solids **8b–d**, respectively. Again the isomer formed in each case probably possesses an equatorial hydroxyl group on the basis of the broad multiplet for the proton H(4) in the ^1H NMR spectrum. Interestingly, the signals for C(4) in crude **8a** and **8b–d** occurred at 62.21, 64.07 (^3J = 5.94 Hz), 64.83 (^3J = 5.12 Hz), and 62.77 ppm (^3J = 5.84 Hz), respectively. In the sulfur analogue *cis*-2,6-*trans*-2,6-tetramethylthian-*r*-4-ol (equatorial C–OH bond) the ^{13}C resonance for C(4) appeared at 65.48 ppm.[13,30] The infrared spectra of **8a–d** show strong absorptions at 1030–1052 cm^{-1} for the C–O stretch, indicative of an equatorially oriented hydroxyl group.[20] Also, absorptions between 1428–1442 and 1092–1105 cm^{-1} were recorded for **8b–d** and **9**, supportive of the P–C_6H_5 bond.[18]



8a



8b, X = C_6H_5; Y = O
c, X = C_6H_5; Y = S
d, X = C_6H_5; Y = $H_2CC_6H_5$ Br^-



9

Reaction of **1a** with *tert*-butyllithium, followed by oxidation, afforded **9** with the proposed stereochemistry, as illustrated. The assignment rests on the shielded ^{13}C chemical shifts for **9** (compared to those of **1b** and **8b**) and the singlet for the protons of the $(CH_3)_3C$ group in the ^1H NMR at δ 1.06 (compared to that of δ 0.94 for *trans*-4-*tert*-butyl-1-phenylphosphorinane 1-oxide whose structure is known with certainty from X-ray crystallographic data).[11b] The ^{13}C NMR spectral data (Table III) and the lone ^{31}P NMR signal (Table IV) support the structure for **9**.

Single-Crystal Analysis of 1-*r*,*cis*-2(a),*trans*-6(e)-Triphenylphosphorinan-4-one 1-Sulfide (2c'). A stereoview of a single molecule of 1,2,6-triphenyl-4-phosphorinanone 1-sulfide (**2c'**) is shown in Figure 1. The heterocyclic ring is in a chair conformation in which the P=S and C_6H_5–C(2) bonds are axial and the C_6H_5–C(6) and C_6H_5–P bonds are equatorial. The numbering scheme and bond distances are shown in Figure 2, and bond angles and relevant torsion angles are given in Figure 3. The two P–C(sp^3) bond distances are 1.853 [P(1)–C(2)] and 1.840 Å [P(1)–C(6)]. Values of these bond distances in 4-*tert*-butyl-1-phenylphosphorinane 1-oxide (**10**)[11b] are 1.791 and 1.795 Å, and in 1-phenyl-4-phosphorinanone 1-sulfide[11a]

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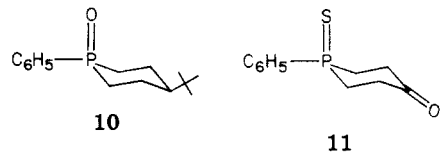

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(11) they are 1.818 and 1.814 Å, respectively. The significant elongation of these two P–C bonds in compound **2c′** are probably due to intramolecular crowding caused by the substituents on P(1), C(2), and C(6). The P=S bond length is 1.957 Å. This is 1.949 Å in 11 and 1.950 Å in triphenylphosphine sulfide.[31] The C–C bond lengths in the heterocyclic ring are as expected. The bond angles at C(2) and C(6) are close to those expected for a tetrahedral configuration, but the angles at C(3) and C(5) are significantly larger (118.3 and 115.1°). This is similar to the values of bond angles found in 11. The (C2)–P(1)–C(6) angle is 100.4° which is very close to the angle found in 11 (99.8°). The P(1)–C(sp^2) bond length is 1.805 Å. This is slightly shorter than the average P–C value of 1.817 Å in 11.

The six-membered ring exists in a chair conformation as can be seen from the torsion angles (Figure 3). The endocyclic torsion angles about P(1)–C(2) and C(6)–P(1) are 58.0 and −61.9° (57.9 and −57.2° in 11). The torsion angles about C(2)–C(3) and C(5)–C(6) are −52.0 and 58.5° (−59.2 and 56.8° in 11).

Torsion angles about C(3)–C(4) and C(4)–C(5) are 44.6 and −47.4°. These are about 8–10° less than those found in 11. The relative orientation of the phenyl rings with respect to the six-membered ring may be described by the torsion angles about the respective P–C and C–C bonds (Figure 3). The dihedral angles between the plane through P(1), C(2), and C(6) and the phenyl rings are 78.5, 72.9, and 70.8°, respectively (Table V). Atoms P(1), S(25), C(4), O(26), and C(7) are planar, and the planes of the phenyl rings through C(7)–C(12) and C(13)–C(18) are approximately parallel to this plane while the plane through C(19)–C(24) makes an angle of 65°. The conformation of the phenyl groups is determined by a number of intramolecular distances which are listed in Table VI, and it appears unlikely that either of the three groups can freely rotate. Calculation of the $H(6)_a$–C(13) [ipso carbon in the phenyl group at C(2)–C_6H_5] distance gave a result of 2.89 Å which supports our contention that rotation around the latter bond would be difficult. Interestingly, the dihedral angle between $H(5)_e$ and C=O was determined to be 13 ± 1.5° which is near that of the biased 4-*tert*-butylcyclohexan-4-one.[32] Also, calculations of the P–C(2)–$H(2)_e$ and P–C(6)–$H(6)_a$ angles gave values of 104.1 ± 1.0 and 104.5 ± 1.0°, respectively.

Positional parameters are found in Tables VII and VIII (supplementary material).

Experimental Section

General Data. Melting points were obtained on a Thomas-Hoover melting point apparatus and are uncorrected. The ^1H, ^{13}C, and ^{31}P NMR data were obtained on a Varian XL-100(15) NMR spectrometer equipped with a Nicolet TT-100 PFT accessory operating at 100.1 M Hz with tetramethylsilane (Me_4Si) as internal standard for ^1H NMR, at 25.2 M Hz with Me_4Si as internal standard for ^{13}C NMR analysis, and at 40.5 MHz with 85% H_3PO_4 as external standard for ^{31}P NMR analysis. The ^{13}C NMR spectra were obtained operating in the FT mode utilizing broad-band proton decoupling or with no decoupling. The ^{31}P NMR spectra of **1a–f**, **8a–d**, and **9** were obtained in the CW mode and those of **2a–c** in the FT mode utilizing broad-band proton decoupling for **2a–c**. Infrared spectral data were obtained on a Beckman IR-5A unit. Elemental analyses were performed by Galbraith Laboratories.

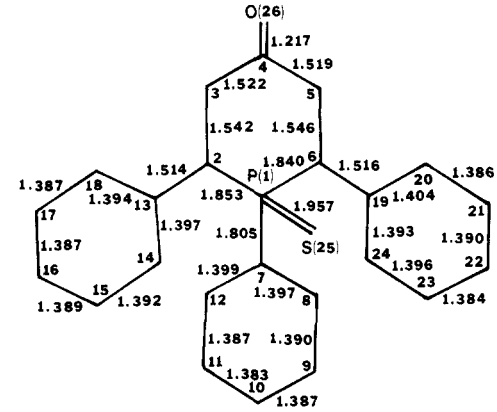

Figure 2. Numbering scheme and bond distances. Standard deviations are 0.002 Å.

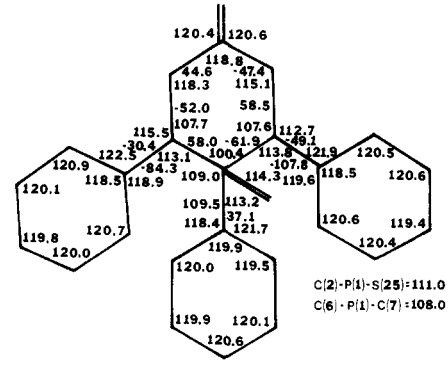

Figure 3. Bond angles and torsion angles. Standard deviations of the bond angles are 0.1°.

Starting Materials. Reagents (commercially available) were purified before use as necessary. Solvents used were reagent grade and were dried over sodium where required.

Preparation of 2,2,6,6-Tetramethyl-1-phenyl-4-phosphorinanone (1a).[5] In a 25-mL flask equipped with a condenser and N_2 inlet were placed 3.5 g (0.0254 mol) of 2,6-dimethylhepta-2,5-dien-4-one (City Chemical Corp., bp 196–198 °C) and 2.75 g (0.025 mol) of phenylphosphine (Pressure Chemical Co.). The reaction mixture was heated at 120 °C for 6 h under N_2 and was allowed to cool to room temperature (~1 h). The resulting solid distilled at 105–120 °C (0.3 mm) to give 4.53 g (72.5%) of ketone **1a**, mp 91–92 °C.

The 2,4-dinitrophenylhydrazone of **1a** was prepared in the following manner. To a methanol solution (5 mL) of 0.073 g (0.37 mmol) of 2,4-dinitrophenylhydrazine were added 1 mL of H_2O and 0.5 mL of concentrated H_2SO_4. Ketone **1a** (0.091 g, 0.37 mmol) was then added, and the reaction mixture was warmed on a steam bath for 15 min. The reaction mixture was then allowed to cool to room temperature, resulting in the formation of a solid. Vacuum filtration of the solid followed by recrystallization (twice) from methanol gave 41 mg (26.1%) of the 2,4-dinitrophenylhydrazone of **1a**: mp 153–154 °C; IR (KBr) 3280 (NH), 1610 (C=N), 1580 (C=N), 1410 (PC_6H_5), 1335, 1137 (PC_6H_5), 922, 833, 743, 696 cm^{-1}.

Anal. Calcd for $C_{21}H_{25}N_4OP$: N, 13.03; P, 7.23. Found: N, 12.97; P, 7.27.

Preparation of 2,2,6,6-Tetramethyl-1-phenyl-4-phosphorinanone 1-Oxide (1b).[8] Ketone **1a** (2.48 g, 0.01 mol) was dissolved in 25 mL of acetone in a 50-mL, round-bottomed flask. To the solution was added dropwise, at 0 °C (ice bath) with stirring, 2.6 g (0.02 mol) of 30% H_2O_2 (Mallinckrodt, analytical reagent). The reaction mixture was stirred at room temperature for 24 h and was then diluted with 25 mL of saturated NaCl solution. The diluted reaction mixture was then extracted with $HCCl_3$ (3 × 40 mL). The $HCCl_3$ extracts were combined and washed with 25 mL of saturated aqueous $Fe(NH_4)_2(SO_4)_2$ solution.

(32) A. Lectard, A. Lichanot, F. Metras, J. Gaultier, and C. Hauw, *Cryst. Struct. Commun.*, 4, 527 (1975).

Table III. ^{13}C NMR Chemical Shifts[a] and ^{31}P–^{13}C Coupling Constants[b] for Substituted 4-Phosphorinanols

compd	carbon atoms					
	2,6	3,5	4	CH_3 (ax)	CH_3 (eq)	Ar C[d]
8b	35.05 (61.02), 35.05 (61.02)	47.32, 47.32	64.07 (5.94)	26.00 (2.15)[c]	24.97 (1.50)[c]	C(α) *127.23* (78.81), C(β) *133.55* (7.49), C(γ) *127.70* (10.83), C(δ) *131.41* (2.04)
8c	36.99 (43.39), 36.99 (43.39)	46.89, 46.89	64.83 (5.12)	28.53[c]	26.52[c]	C(α) *125.92* (70.89), C(β) *134.62* (8.25), C(γ) *127.59* (10.95), C(δ) *131.34* (2.95)
8d[e,f]	33.14 (35.39), 33.14 (35.39)	44.90	62.77 (5.84)	27.19[c]	26.76[c]	*g*
9[h]	32.63 (61.09), 32.63 (61.09)	44.47	76.36 (7.33)	28.35[c]	26.52[c]	C(α) *131.13* (82.27), C(β) *131.60* (7.41), C(γ) *128.09* (10.23), C(δ) *130.89* (2.81)

[a] All samples were ca. 200 mg in $DCCl_3$ except where noted. Chemical shifts in parts per million (+0.1 ppm) downfield from Me_4Si. [b] ^{31}P–^{13}C coupling constants (given in parentheses) in Hz (±0.4 Hz). [c] Signals maybe reversed. [d] The average value of the two signals of the doublet is italic. [e] In Me_2SO-d_6. [f] The ^{13}C signal of the benziodide of $C_6H_5CH_3P$ occurs at 22.02 ppm (41.02 Hz). [g] ^{13}C signals for Ar C were complex. Only C(α) could be detected at 116.07 ppm (67.62 Hz). [h] The ^{13}C signals for the $(CH_3)_3C$ group occur at 39.31 and 25.21 ppm, respectively.

Table IV. Spectral Data for 4-Phosphorinanols 8a-d and 9

compd	IR (KBr;[a] selected bands), cm^{-1}	^1H NMR shifts, δ[b]	^{31}P NMR shifts, δ[c]
8b	3280, 1435, 1142, 1100, 1052, 754, 701	1.08 (d, J_{PCCH} = 13 Hz, CH_3, 6 H), 1.46 (d, J_{PCCH} = 15 Hz, CH_3, 6 H), 1.64–2.48 (m, CH_2, 4 H), 3.80–4.26 (m, CHO and OH, 2 H), 7.28–7.64 (m, Ar H, 3 H), 7.72–8.00 (m, Ar H, 2 H)	41.59
8c	3270, 1436, 1092, 1030, 746. 670	1.22 (d, J_{PCCH} = 17 Hz, CH_3, 6 H), 1.56 (d, J_{PCCH} = 14 Hz, CH_3, 6 H), 1.68 (s, OH, 1 H), 1.68–2.62 (m, CH_2, 4 H), 3.94–4.32 (m, CHO, 1 H), 7.36–7.62 (m, Ar H, 3 H), 8.02–8.32 (m, Ar H, 2 H)	62.53
8d	3220, 1428, 1103, 1046, 773, 754, 697	1.20 (d, J_{PCCH} = 15 Hz, CH_3, 6 H), 1.58 (d, J_{PCCH} = 15 Hz, CH_3, 6 H), 1.90–2.30 (m, CH_2, 4 H), 3.32 (s, OH, 1 H), 4.00–4.30 (m, CHO, 1 H), 4.57 (d, J_{PCH} = 14 Hz, C_6H_5 CH_2, 2 H), 7.08–7.40 (m, Ar H, 5 H), 7.60–8.02 (m, Ar H, 3 H), 8.08–8.36 (m, Ar H, 2 H)	34.68
9	3320, 1442, 1150, 1105, 1070, 713, 699	0.91 (d, J_{PCCH} = 14 Hz, CH_3, 6 H), 1.06 (s, $C(CH_3)$, 9 H), 1.58 (d, J_{PCCH} = 12 Hz, CH_3, 6 H), 1.78–2.24 (m, CH_2, HO, 5 H), 7.40–7.62 (m, Ar H, 3 H), 7.74–7.98 (m, Ar H, 2 H)	46.77

[a] The spectra were obtained on samples (2 mg) with KBr (200 mg) pellets. [b] Spectra were obtained in $DCCl_3$ solution, except 8d (Me_2SO_6), of each compound with tetramethylsilane as an internal standard; the peak positions quoted in the case of doublets are measured from the approximate center, and relative peak areas are given as whole numbers. [c] The spectra were obtained on samples (ca. 200 mg) in $DCCl_3$ solution (2 mL), except 8d (ca. 200 mg in 2 mL of Me_2SO-d_6), with 85% H_3PO_4 as an external standard. A positive value indicates a peak position downfield from the standard.

Table V. Dihedral Angles (in Degrees) between Planes in 2c′

A. Dihedral Angles between the Best Plane through the Six-Membered Heterocyclic Ring and the Planes of the Phenyl Rings

plane through C(7)-C(12)	72.3
plane through C(13)-C(18)	88.6
plane through C(19)-C(24)	77.4

B. Dihedral Angles between the Plane through P(1), C(2), and C(6) and the Planes of the Phenyl Rings

plane through C(7)-C(12)	78.5
plane through C(13)-C(18)	72.9
plane through C(19)-C(24)	70.8

C. Dihedral Angles between the Plane through P(1), C(4), O(26), S(25), and C(7) and the Phenyl Rings

plane through C(7)-C(12)	0
plane through C(13)-C(18)	17
plane through C(19)-C(24)	65

Table VI. Intramolecular Contacts (in Angstroms) of Phenyl Groups in 2c′

H(8)···C(13)	2.92	C(18)···H(31)	2.97
H(8)···H(6)	2.38	C(18)···H(6)	2.79
H(12)···S(25)	2.76	H(14)···H(2)	2.40
H(14)···H(2)	2.40	H(20)···C(5)	2.85
H(18)···C(3)	2.69	H(20)···H(51)	2.43
H(18)···C(4)	2.52	C(20)···H(51)	2.92
H(18)···O(26)	2.81	H(24)···H(6)	2.31

The $HCCl_3$ layer was separated and dried ($MgSO_4$). The solution was filtered, and the $HCCl_3$ was removed by rotary evaporation. Dissolution of the resulting oil was achieved with the minimum amount of hot xylene, and the solution was then filtered. When the filtrate was allowed to stand at 0 °C overnight, white needles formed and were filtered. The crystals were dried [P_2O_5, 110 °C (5 mm)] to give 1.4 g (53%) of **1b**, mp 207–208 °C (lit.[8] mp 212–213 °C).

Preparation of 2,2,6,6-Tetramethyl-1-phenyl-4-phosphorinanone 1-Sulfide (1c).[5,8] A solution of ketone **1a** (2.48 g, 0.01 mol) and sulfur (0.64 g, 0.02 mol) dissolved in 25 mL of benzene was placed in a 50-mL flask fitted with a condenser and magnetic stirrer. The reaction mixture was gently boiled for 3 h and filtered hot. The volume was reduced to ca. 10 mL (by evaporation on a steam bath), and 10 mL of petroleum ether (bp 35–60 °C) was added. After the mixture had been allowed to stand at 0 °C overnight, a solid formed and was filtered and dried [P_2O_5, 110 °C (5 mm)] to give 1.98 g (70.5%) of mp 129–132 °C. A small portion was recrystallized from methanol; mp 138–139 °C (lit.[5] mp 138.5–139 °C).

Preparation of 1,1,1,6,6-Pentamethyl-1-phenyl-4-phosphorinanonium Iodide (1d).[5] Ketone **1a** (6.0 g, 0.0142 mol) and CH_3I (7.0 g, 0.0483 mol) were dissolved in 35 mL of ether, and the reaction mixture was allowed to stand at 0 °C with periodic swirling for 4 days. A resulting solid was filtered and washed with ether to give 6.3 g (65.3%) of **1d**. A small portion

was recrystallized from CH_3CN; mp 229–230 °C (lit.[5] mp 229–230 °C).

Preparation of 1-Ethyl-2,2,6,6-tetramethyl-1-phenyl-4-phosphorinanonium Iodide (1e). Ketone **1a** (10 g, 0.0403 mol) and ethyl iodide (7 g, 0.045 mol) dissolved in 50 mL of benzene were placed in a 100-mL, round-bottom flask fitted with a condenser, magnetic stirrer, and N_2 inlet. The reaction mixture was gently boiled for 24 h to give a white solid. The solid was filtered, washed with portions of ether (2 × 25 mL), and air-dried to give 11.87 g (73%) of **1e**, mp 240–243 °C. An analytical sample was obtained by recrystallization from CH_3CN; mp 247 °C dec.

Anal. Calcd for $C_{17}H_{22}IOP$: C, 50.50; H, 6.48; P, 7.66. Found: C, 50.74; H, 6.58; P, 7.09.

Preparation of 1-Benzyl-2,2,6,6-tetramethyl-1-phenyl-4-phosphorinanonium Bromide (1f). Ketone **1a** (2.48 g, 0.01 mol) and benzyl bromide (2.00 g, 0.0117 mol) dissolved in 15 mL of benzene were placed in a 25-mL flask fitted with condensor, magnetic stirrer, and N_2 inlet. The reaction mixture was gently boiled for 12 h. A resulting solid was filtered and washed (ether). Recrystallization (CH_3CN) gave 2.26 g (54%) of **1f**, mp 233–235 °C.

Anal. Calcd for $C_{22}H_{28}BrOP$: C, 61.92; H, 6.93; P, 7.60. Found: C, 61.85; H, 6.84; P, 7.51.

Preparation of Bis(hydroxymethyl)phenylphosphine.[33] Paraformaldehyde (5 g, 0.166 mol) and phenylphosphine (10 g, 0.091 mol) were placed in a 50-mL flask equipped with a condenser, magnetic stirrer, and N_2 inlet. After the reaction mixture was warmed to 110 ± 5 °C (oil bath), it was maintained at that temperature for 4 h. The reaction mixture was allowed to cool to room temperature (~1 h) and was then distilled at 105–110 °C (0.3 mm) to give 10.0 g (71%) of bis(hydroxymethyl)-phenylphosphine [lit.[33] bp 93–96 °C (0.1–0.15 mm)].

Preparation of 1,2,6-Triphenyl-4-phosphorinanone (2a').[20] Bis(hydroxymethyl)phenylphosphine (1.97 g, 0.0116 mol) and dibenzalactone (2.70 g, 0.0116 mol; mp 113 °C; City Chemical Corp.) were dissolved in 25 mL of dry pyridine and placed in a 50-mL flask equipped with a condenser, magnetic stirrer, and N_2 inlet. The reaction mixture was gently boiled for 4 h, during which time paraformaldehyde collected in the condenser. After the reaction mixture had cooled to room temperature, pyridine was removed on a rotary evaporator. The resulting orange solid was dissolved in a minimum amount of hot CH_3CN; the solution was filtered and allowed to cool to room temperature, during which time pale yellow needles precipitated. After ca. 3 h, the solid was filtered and dried to give 3.25 g (82%) of **2a'**. The yellow solid was suspended in 25 mL of ether (with stirring), was filtered, and was recrystallized from hot CH_3CN to give pure **2a'** (mp 171–172 °C) as white needles (lit.[6] mp 176–177 °C.

The mother liquors were concentrated to give a orange solid which became bright yellow after being washed with ether. Repeated recrystallizations (H_3CCN) gave a solid melting at 172–175 °C. The obviously crude **2a''** was found to be contaminated with **2a'** which resisted all attempts at removal. A ^{13}C NMR spectrum ($DCCl_3$) of the crude **2a''** revealed signals at 44.84 [$^1J_{PC}$ = 13.23 Hz, C(2,6)], 48.59 [$^2J_{PC}$ = 14.02, C(3,5)], and 207.67 ppm [$^3J_{PC}$ = 1.48 Hz, C(4)] which are in agreement with the all equatorially substituted **2a''**. The reported[6] melting range of 176–177 °C we feel was for a mixture of **2a'** and **2a''**.

The 2,4-dinitrophenylhydrazone of **2a'** was prepared in the following manner. To a methanol solution (5 mL) of 0.05 g (0.252 mmol) of 2,4-dinitrophenylhydrazine were added 1 mL of H_2O and 0.5 mL of concentrated H_2SO_4. Ketone **2a'** (0.05 g, 0.15 mmol) was then added, and the reaction mixture was warmed on a steam bath for 15 min. Cooling to room temperature afforded a solid which was filtered out and dried (P_2O_5) at 60 °C (5 mm) to yield 66 mg (91%) of the 2,4-dinitrophenylhydrazone of **2a'**. Recrystallization (ethyl acetate) gave a more pure sample of the 2,4-DNP of **2a'**: mp 250 °C; IR (KBr) 3220 (NH), 1610 (C=N), 1590 (C=N), 1420 (PC_6H_5), 1337, 830, 766, 697 cm^{-1}.

Anal. Calcd for $C_{29}H_{25}N_4O_4P$: N, 10.68; P, 5.91. Found: N, 10.25; P, 5.80.

Preparation of 1,2,6-Triphenyl-4-phosphorinanone 1-Oxide (2b'). A solution of pure **2a'** (0.035 g, 0.1 mmol) in dioxane (2.3 mL) was allowed to stand at room temperature exposed to the atmosphere for 20 days. Evaporation of the solvent produced a white solid which was recrystallized (C_2H_5OH) and melted at 253–254 °C; yield 0.015 g (41.6%).

Anal. Calcd for $C_{23}H_{21}OP$: C, 76.65; H, 5.87; P, 8.59. Found: C, 76.59; H, 5.92; P, 8.58.

Oxidation of very slightly impure **2a'** with 30% H_2O_2 in acetone gave a modest yield (46.2%) of **2b'** and a small amount of presumably **2b''** as evidenced by ^{31}P NMR signals at 33.91 (major) and 32.21 ppm (minor).

Preparation of 1,2,6-Triphenyl-4-phosphorinanone 1-Sulfide (2c'). Ketone **2a** (2.0 g, 5.78 mmol) and sulfur (0.2 g, 6.25 mol) were dissolved in 25 mL of benzene and placed in a 50-mL flask fitted with a condenser, magnetic stirrer, and N_2 inlet. The reaction mixture was gently boiled (4 h) and was then allowed to cool to room temperature. The benzene was removed by rotary evaporation to give a solid which recrystallized from benzene–ethanol (1:1) to yield 0.78 g (35.6%) of **2c**, mp 240–242 °C.

Anal. Calcd for $C_{23}H_{23}OPS$: C, 73.38; H, 5.62; P, 8.23. Found: C, 73.51; H, 5.68; P, 8.14.

Preparation of 2,2,6,6-Tetramethyl-1-phenyl-4-phosphorinanol (8a).[5] To a slurry of 0.38 g (0.01 mol) of $LiAlH_4$ in 20 mL of dry THF in a 100-mL flask equipped with a magnetic stirrer, condenser, addition funnel, and N_2 inlet was added dropwise, over a 1-h period, 1.24 g (5 mmol) of **1a** in 25 mL of dry THF. After the addition was completed, the reaction mixture was gently boiled for 8 h, cooled with ice to 0 °C, and then hydrolyzed with 5 mL of H_2O. The solution was dried ($MgSO_4$) and filtered, and the volume was reduced to ca. 10 mL on a rotary evaporator. The remaining solvent was removed at 60 °C (0.5 mm) for 15 min and then at room temperature (0.5 mm) for 1 h. The resulting viscous oil (crude **8a**) dissolved in $DCCl_3$ was used for a rough NMR analysis: ^1H ($DCCl_3$) δ 1.08 (d, $^3J_{PCCH}$ = 19 Hz, CH_3), 1.36 (d, $^3J_{PCCH}$ = 4 Hz, CH_3), 3.80–4.24 (m, HCO, 1 H), 7.30–8.00 (m, ArH, 5 H); ^{13}C NMR 31.92 [$^1J_{PC}$ = 16.09, C(2,6)], 50.92 [$^2J_{PC}$ = 11.79, C(3,5)], 62.21 ppm [C(4)]. The signals for the methyl carbons and aromatic carbons were very complex and could not be distinguished; the ^{31}P NMR ($DCCl_3$) showed a signal at −8.07 ppm.

Preparation of 2,2,6,6-Tetramethyl-1-phenyl-4-phosphorinanol 1-Oxide (8b). Lithium aluminum hydride (1.52 g, 0.04 mol) was added slowly to 100 mL of freshly distilled tetrahydrofuran (distilled from $LiAlH_4$) in a 500-mL flask equipped with a condenser, addition funnel, mechanical stirrer, and N_2 inlet. Ketone **1a** was dissolved in 125 mL of THF and added dropwise (addition time ca. 2 h) to the slurry. After the addition was complete, the reaction mixture was gently boiled for 3 h and subsequently cooled to 0 °C (ice). The cooled reaction mixture was hydrolyzed by the dropwise addition (**Caution!**) of H_2O. The hydrolyzed mixture was extracted with ether (3 × 100 mL), and the ether layers were combined and dried ($MgSO_4$). After the solution was filtered, the ether was removed by rotary evaporation followed by exposure for 15 min to a higher vacuum (0.5 mm). The resulting oil was dissolved in 150 mL of acetone, and the solution was poured into a 300-mL flask equipped with a condenser and magnetic stirrer. The acetone solution was cooled (ice) to 0 °C, and 5.0 g (0.044 mol) of 30% H_2O_2 was added dropwise. After the reaction mixture was allowed to warm to room temperature, it was stirred for 12 h; this was followed by a period of 12 h in which the mixture was boiled gently. When the reaction mixture had cooled to room temperature, 100 mL of saturated aqueous NaCl was added, and the mixture was extracted (3 × 50 mL of $HCCl_3$). The $HCCl_3$ extracts were combined and washed with 50 mL of a saturated aqueous $Fe(NH_4)_2(SO_4)_2$ solution and then dried ($MgSO_4$). The $HCCl_3$ solution was filtered, and the $HCCl_3$ was removed by rotary evaporation to give 4.43 g (83%) of crude **8b** as an oil. Pure **8b** was obtained by trituration of the crude oil with acetone, followed by recrystallization (acetone). An analytical sample of **8b** had a melting point of 198–200 °C.

Anal. Calcd for $C_{15}H_{23}O_2P$: C, 67.65; H, 8.71; P, 11.63. Found: C, 67.92; H, 8.90; P, 11.71.

Preparation of 2,2,6,6-Tetramethyl-1-phenyl-4-phosphorinanol 1-Sulfide (8c). To 0.76 g (0.02 mol) of $LiAlH_4$ and 25 mL of dry THF in a 100-mL flask equipped with a condenser, mechanical stirrer, addition funnel, and N_2 inlet was added dropwise (ca. 2 h) ketone **1a** (1.24 g, 5 mmol) dissolved in 25 mL

(33) H. Hellmann, J. Bader, H. Birkner, and O. Schumacher, *Justus Liebigs Ann. Chem.*, **659**, 49 (1962).

of dry THF. After the addition was complete, the reaction mixture was gently boiled for 4 h. The reaction mixture was cooled (ice) to 0 °C and hydrolyzed (**Caution!**) with 5 mL of H_2O. The mixture was then dried ($MgSO_4$) and filtered. After the filter cake was washed with 50 mL of benzene, 0.16 g (5 mmol) of sulfur was added. The reaction mixture was gently boiled for 4 h and then allowed to cool to room temperature. Removal of the solvent by rotary evaporation gave an oil which was dissolved in 2 mL of hot methanol. The hot methanol solution was passed through a Pasteur pipet packed with neutral aluminum (ca. 1 g, Brinkmann, aluminum oxide 90, active). Solvent was evaporated from the eluants by rotary evaporation, and the resulting oil was covered with 25 mL of petroleum ether (bp 35–60 °C). After the mixture was allowed to stand 48 h at 0 °C, a white solid was formed, filtered off, and air-dried to give 0.81 g (57.5%) of crude **8c**, mp 114–123 °C. An analytical sample was prepared by recrystallization (hot CH_3OH); mp 142–143 °C.

Anal. Calcd for $C_{15}H_{23}OPS$: C, 63.80; H, 8.21; P, 10.97. Found: C, 63.90; H, 8.22; P, 10.90.

Preparation of 1-Benzyl-2,2,6,6-tetramethyl-1-phenyl-4-phosphorinanolium Bromide (8d). The crude alcohol **8a** prepared from 4.96 g (0.02 mol) of **1a** and 1.52 g (0.04 mol) of $LiAlH_4$ was used immediately to prepare **8d**. Oily **8a** was dissolved in 50 mL of benzene and placed in a 200-mL flask equipped with a magnetic stirrer, condenser, and N_2 inlet. To this was added 3.42 g (0.02 mol) of benzyl bromide, and the reaction mixture was gently boiled for 4 h. The solvent was removed by rotary evaporation, and the resulting oil was covered with 150 mL of ether. This mixture was then boiled for 6 h, and the solid which formed was removed by vacuum filtration and air-dried to give 3.12 g (38.5%) of **8d**. Recrystallization (CH_3CN) afforded 1.49 g of **8d**, mp 260 °C dec. An analytical sample of **8d** was obtained by repeated recrystallization (methanol–ethyl acetate, 1:10); mp 260–261 °C.

Anal. Calcd for $C_{22}H_{30}BrOP$: C, 62.71; H, 7.13; P, 7.35; Br, 19.00. Found: C, 62.74; H, 7.43; P, 7.32; Br, 18.68.

Preparation of 4-*tert*-Butyl-2,2,6,6-tetramethyl-1-phenyl-4-phosphorinanol 1-Oxide (9). To 43 mL (0.069 mol, 1.6 M in pentane) of *tert*-butyllithium in a 500-mL flask equipped with an additional funnel, condenser, mechanical stirrer, and N_2 inlet was added dropwise ketone **1a** (6.7 g, 0.027 mol) over a 1-h period. After the addition, the reaction mixture was gently boiled (24 h) and was then allowed to cool to 0 °C (ice). To the cold mixture was slowly added 50 mL of H_2O (**Caution!**). The organic layer was then separated, and the aqueous layer was extracted (3 × 100 mL of ether). The organic phases were combined and dried ($MgSO_4$). The dried solution was filtered, and the solvents were evaporated. A resulting oil was distilled (Kugelrohr) under reduced pressure to give 6.3 g (76.5%) of an oil, bp 140 °C (0.5 mm). The oil was dissolved in 50 mL of acetone to which was slowly added ca. 5 mL of 30% H_2O_2. After the acetone solution was stirred at room temperature (12 h), 20 mL of H_2O was added. The reaction mixture was extracted (3 × 50 mL of $HCCl_3$), and these extracts were combined and dried ($MgSO_4$). Filtration and solvent removal (rotary evaporation) gave an oil which, when triturated with acetone, solidified. Recrystallization (acetone) gave pure **9**, mp 201–202 °C.

Anal. Calcd for $C_{19}H_{31}O_2P$: C, 70.78; H, 9.69; P, 9.61. Found: C, 71.03; H, 9.92; P, 9.57.

X-ray Analysis. A suitable crystal of size 0.59 × 0.51 × 0.26 mm was chosen for data collection. Crystallographic data and all integrated intensities were collected on a Nonius CAD-4 automatic diffractometer equipped with Enraf-Nonius cold-stream cooling device. The crystal data are as follows: $C_{23}H_{21}OPS$; mol wt 376.46; triclinic; space group $P\bar{1}$; a = 9.600 (5) Å, b = 10.219 (7) Å, c = 10.490 (4) Å, α = 103.02 (3)°, β = 109.77 (2)°, γ = 76.29 (3)°, V = 928.87 Å^3 (at −135 °C); Z = 2; Mo Kα_1 radiation, λ = 0.709 26 Å, for 2θ data and Mo K$\bar{\alpha}$ radiation, λ = 0.710 69 Å, for intensity data; at 25 °C a = 9.700 (1) Å, b = 10.273 (1) Å, c = 10.643 (1) Å, α = 103.029 (5)°, β = 110.227 (5)°, γ = 76.245 (5)°, V = 954.65 Å^3, D_{calcd} = 1.310 g/cm^3, and D_{obsd} = 1.315 g/cm^3. The least-squares cell parameters were determined from the $+2\theta$ and -2θ values of 48 reflections distributed throughout reciprocal space. The density was measured by the flotation method with a mixture of hexane and carbon tetrachloride.

The intensities of 3826 reflections comprising all unique data with $2\theta \leq 53°$ were collected at −135 °C, with the θ–2θ scan technique, a variable scan width of $(1 + 0.2 \tan \theta)°$, and a variable aperture width of $(4 + 0.86 \tan \theta)$ mm. A maximum of 50 s was spent on each reflection with $^2/_3$ of the time for scanning the peak and $^1/_6$ of the time for scanning each of the left and right backgrounds. Intensities of three monitor reflections, measured after every 3000 s of X-ray exposure time, showed a maximum variation of ±3%, and appropriate scaling was done for this variation. The orientation matrix was checked after every 300 measurements. Intensities of 308 reflections were considered indistinguishable from the background on the basis that the net intensity was less than $2\sigma(I)$. Lorentz and polarization corrections were applied to the data, but no absorption correction was made. An experimental weight, based on counting statistics,[34] was assigned to each structure amplitude.

The structure was solved by direct methods using the computer program MULTAN,[35] and all nonhydrogen atoms were located from the E map. A block-diagonal, least-squares program was used for refinement, and after several cycles of isotropic refinement the hydrogen atoms were located from a difference Fourier map. The structure was further refined with anisotropic thermal parameters for nonhydrogen atoms and isotropic temperature factors for hydrogen atoms. The final R value, defined as $R = (\sum||kF_o| - |F_c||)/\sum|kF_o|$, was 0.030 for 3475 reflections (0.035 for all reflections). At this stage a final difference Fourier map showed a maximum electron density of 0.3 e Å^{-3} around the phosphorus atom. Values of atomic scattering factors for P, S, C, and O atoms were taken from the literature,[36] while those for H atoms were taken from Stewart, Davidson, and Simpson.[37]

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Registry No. 1a, 13887-05-3; **1a** DNP, 76156-69-9; **1b**, 21230-89-7; **1c**, 1216-38-2; **1d**, 76156-70-2; **1e**, 76156-71-3; **1f**, 76156-72-4; **2a′**, 76189-76-9; **2a′** DNP, 76156-73-5; **2a″**, 76189-77-0; **2b′**, 76156-74-6; **2b″**, 76189-78-1; **2c′**, 76156-75-7; **8a**, 76156-76-8; **8b**, 76156-77-9; **8c**, 76156-78-0; **8d**, 76156-79-1; **9**, 76156-80-4; 2,6-dimethylhepta-2,5-dien-4-one, 504-20-1; phenylphosphine, 638-21-1; methyl iodide, 74-88-0; ethyl iodide, 75-03-6; benzyl bromide, 100-39-0; bis(hydroxymethyl)phenylphosphine, 3127-08-0; paraformaldehyde, 30525-89-4; dibenzalactone, 5396-91-8; *tert*-butyllithium, 594-19-4.

Supplementary Material Available: Table VII, positional and anisotropic thermal parameters for **2c′**; Table VIII, positional parameters and temperature factors for the hydrogen atoms in **2c′** (2 pages). Ordering information is given on any current masthead page.

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