PART I. NMR STUDIES OF P-INVERSION IN AND CONFORMATIONAL ANALYSIS OF CIS- AND TRANS-4-TERT-BUTYL-1-PHENYL-PHOSPHORINANES

PART II. CONFORMATIONAL ANALYSIS OF SELECTED 4-PHOSPHORINANONES AND DERIVATIVES

By

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May, 1978

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ACKNOWLEDGMENTS

I express my sincere gratitude to Dr. K. Darrell Berlin for his guidance and friendship throughout the course of this work. A special thank you is due Dr. Otis C. Dermer for his helpful comments and proof-reading the manuscript. I am indebted to the members of Dr. Berlin's research group for their aid and companionship.

Thanks are due to the Chemistry Department at Oklahoma State University, the United States Public Health Service, The Dow Chemical Company, and the Continental Oil Company for financial support.

I thank Professor Dick van der Helm, at The University of Oklahoma, for his expertise in obtaining the X-ray data for this work and Mr. Stan Sigle for his help in obtaining the NMR data.

Thanks are due the entire support staff of the Chemistry Department at the Oklahoma State University for allowing this work to progress as smoothly as possible. A special thank you is due Mrs. Dolores Behrens for typing this manuscript.

Grateful appreciation is extended to the National Science Foundation for financial support to attend the NATO Advanced Study Institute on "Advances in NMR: The Less Receptive Nuclei" in Altavilla Milicia, Sicily, from September 5-18, 1976.

Finally, I thank my parents, James M. and Rita F. Kilkenny, for all their love and understanding.

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INTRODUCTION

Owing to the difference in the primary objectives of the two investigations recorded herein, this dissertation has been divided into two parts. Each is complete and independent of the other, containing its own Historical section, Results and Discussion, Experimental section and Bibliography.

PART I

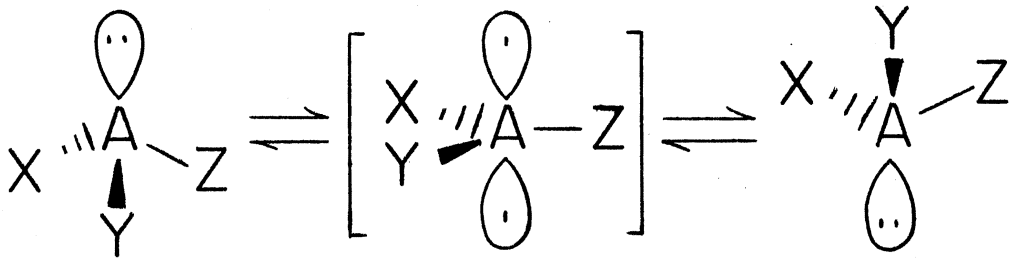
NMR STUDIES OF P-INVERSION IN AND CONFORMATIONAL ANALYSIS OF CIS- AND TRANS-4-TERT-BUTYL-1-PHENYLPHOSPHORINANES

CHAPTER I

HISTORICAL

Pyramidal Inversion

Pyramidal inversion is the process whereby an atom bonded to three groups (pyramidal geometry) and possessing an unshared pair of electrons undergoes an inversion of configuration. An example of pyramidal inversion is indicated in the process of 1 ⇌ 2. The atom undergoing

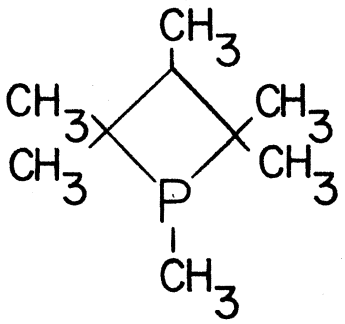


1 2

inversion passes through a transition state in which the bonds to the groups x, y, and z are near sp^2 in character and the lone pair is often pure p. The subject of pyramidal inversion has been discussed particularly in two reviews[26,51] and the determination of the barrier height for pyramidal inversion has been experimentally determined in several cases where A = N, P, and As.[8,19,28,29] The discussion to follow will consider the effects of steric strain (also angular strain)

and electronic delocalization on the barrier to pyramidal inversion.

Substitution of a large group on a pyramidal center sometimes results in steric repulsion between the nonbonded groups. This repulsive force destabilizes the pyramidal ground state relative to the less sterically crowded transition state and consequently lowers the inversion barrier.[26,51] An example of barrier height reduction for pyramidal inversion in a phosphorus system with large steric forces around the central atom was exhibited with phosphetanes 3 and 4.[8] Phosphetane 3 underwent only ca.5% inversion after heating at 162°C for



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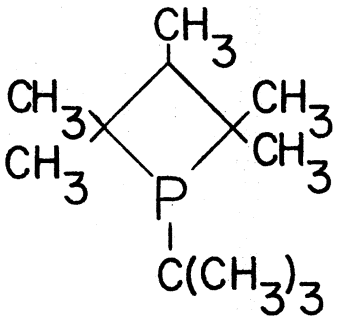

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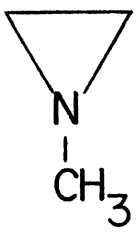
four days, while inversion (ΔH^{*} = ca. 28 kcal/mole; $\Delta G^{*} \approx 31.5$ kcal/mole) in 4 was monitored from 118°C to 157°C.

The effect of angular strain (a decrease in ground state bond angles about the pyramidal atom) is illustrated with the following examples. The barrier to inversion in 1-methylaziridine (5) is



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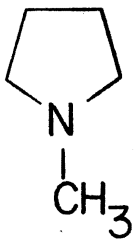

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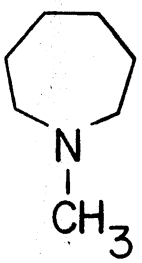

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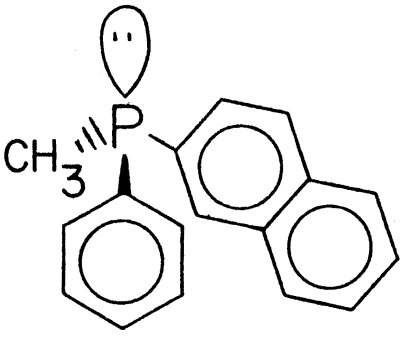
19 kcal/mole.[19] That for 1-methylpyrrolidine (6) is 8 kcal/mole,[30] and that for 1-methylazepane (7) is 7.0 kcal/mole.[30] Therefore, as the endocyclic C-N-C bond angle increases from $60^{\circ} \rightarrow 109^{\circ} \rightarrow 112^{\circ}$, the inversion barrier decreases.

Delocalization of the lone pair at the pyramidal center into an attached π system should lower the inversion barrier by geometrically flattening the ground state pyramid. Such a situation has been investigated for a number of aryl-substituted phosphines.[1] The barrier to pyramidal inversion (29.7 kcal/mole) for methylphenyl(2-naphthyl)-phosphine (8) is ca. 3 kcal/mole lower than that of methylphenyl-



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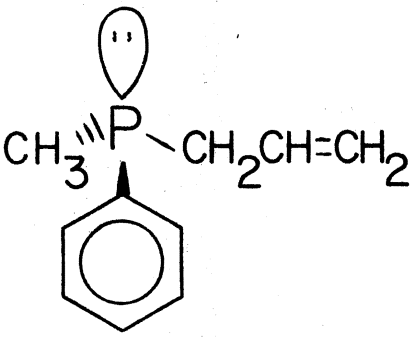

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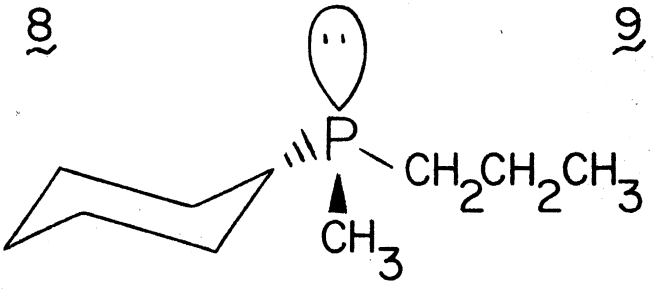

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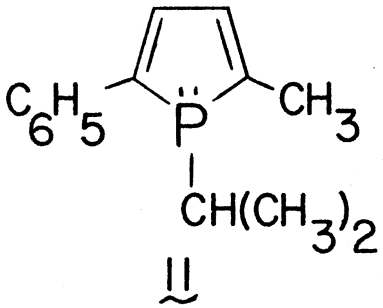
(2-propenyl)phosphine (9) (32.8 kcal/mole) which in turn is ca. 3 kcal/mole lower than that of cyclohexylmethylpropylphosphine (10) (35.6 kcal/mole).[1] Furthermore the barrier height in 2-methyl-5-phenyl-1-isopropylphosphole (11)[10] is only 16 kcal/mole indicating

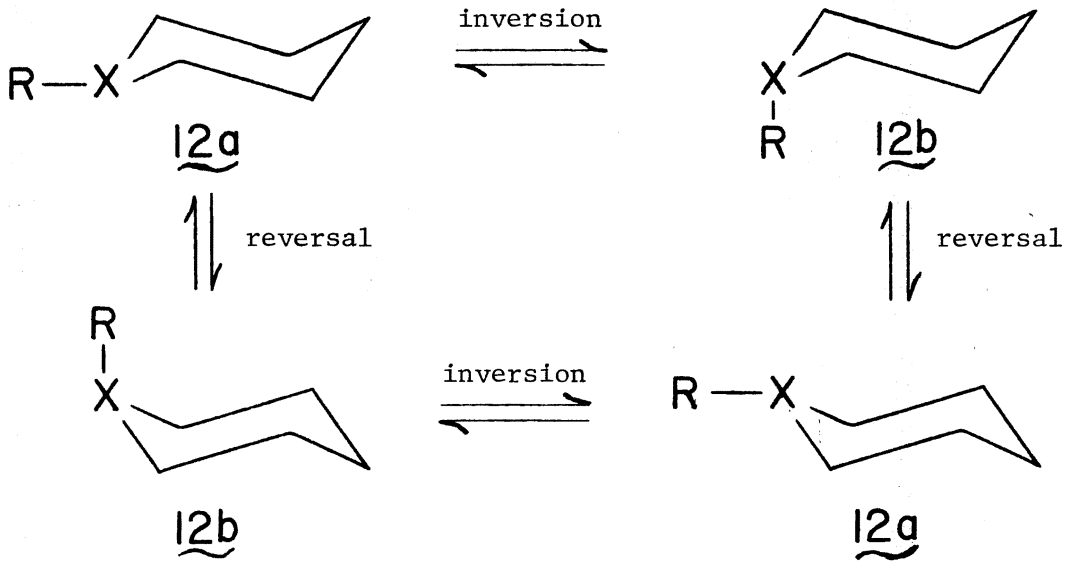


11

that there is effective delocalization of the lone pair of electrons on phosphorus into the π ring system. Also repulsive interactions between the 1-isopropyl group and the 2-methyl and 5-phenyl groups may contribute to the low barrier to inversion in 11.

Pyramidal Inversion vs Ring Reversal

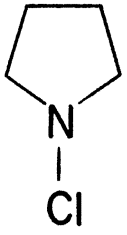
Early in the study of conformational analysis it was recognized that in selected six-membered ring systems both inversion at an atomic center and ring reversal may occur. An example of this phenomenon is



12a 12b 12b 12a

illustrated above. If the functionality R is NMR active (such as ^{1}H, ^{19}F, or ^{31}P), a lone signal should occur for the time-averaged population of 12a and 12b at elevated temperatures. Upon cooling the mixture, either pyramidal inversion or ring reversal may be sufficiently slow on the NMR time scale to permit observation of two signals for R. However, it is often difficult to differentiate pyramidal inversion from ring reversal with only a variable-temperature NMR study.

It was concluded from an NMR study[32] of 1-chloropiperidine (13) and 1-chloropyrrolidine (14) that a cooled ($T<-40^{\circ}C$) solution (H_2CCl_2)



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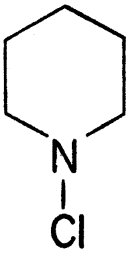

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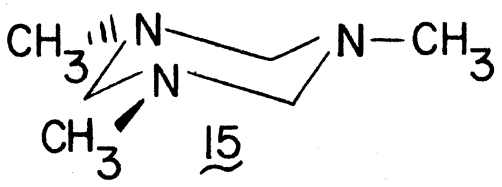
of 13-3,3,5,5-d_4 gave only one AB pattern for the α-protons. However, upon cooling a solution of 14 below $-80^{\circ}C$, a similar lone AB pattern was observed. Complete line-shape analysis of the two systems revealed very close Arrhenius activation energies for nitrogen inversion for 13 (15.9 ± 0.7 kcal/mole) and 14 (13.9 ± 0.7 kcal/mole). This indicated that in 13 inversion of N could not be ruled out (14 was considered incapable of ring reversal).

A similar problem was encountered in the conformational analysis of hexahydro-1,3,5-trimethyl-1,3,5-triazine (HTMT) (15).[20] In the course of a low temperature ^{1}H NMR study of HTMT, an AB quartet at δ 6.854 and a single line at δ 7.763 appeared for the methylene and

methyl protons, respectively. It was argued that a chair form in

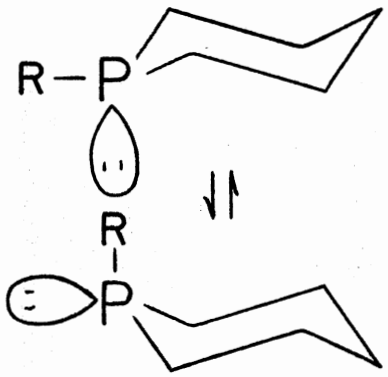


15

which the three methyl groups were all equatorial was the only conformer present to an appreciable extent. To account for these observations, it was concluded that ring reversal occurs simultaneously with pyramidal inversion at one or two nitrogen atoms and that this was preceded or followed by a fast pyramidal inversion of the other nitrogen atoms(s).[20] The above example is not without ambiguities in the arguments and suggests that caution must be taken in conformational analysis of six-membered ring systems in which both ring reversal and pyramidal inversion may occur at similar rates.

Stereochemistry of Phosphorinanes

The phosphorinane ring system 16 possesses unique features which contribute to the developing interest in these phosphorus heterocycles but are not found in the piperidine family 17.[27] Certain inherent structural differences of 16 from 17 more readily permit dynamic studies with the phosphorus analog (e.g. thermodynamic data for the barrier to pyramidal inversion).[26,51] The main differences are: 1) size of the heteroatom (van der Waals radius, N, 1.5 Å vs P, 1.9 Å)[45]; 2) empty d orbitals present in phosphorus; 3) C-P bond longer (ca. 1.83 Å)[7] than C-N bond (1.47 Å);[45] and 4) C-P-C endocyclic bond angle smaller than C-N-C Angle (98° vs 108°).[27,45] These differences, coupled with ^{31}P which possesses a spin of 1/2, and no electric



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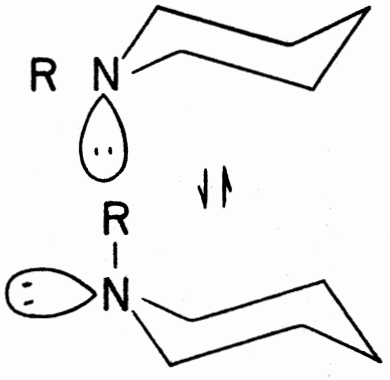

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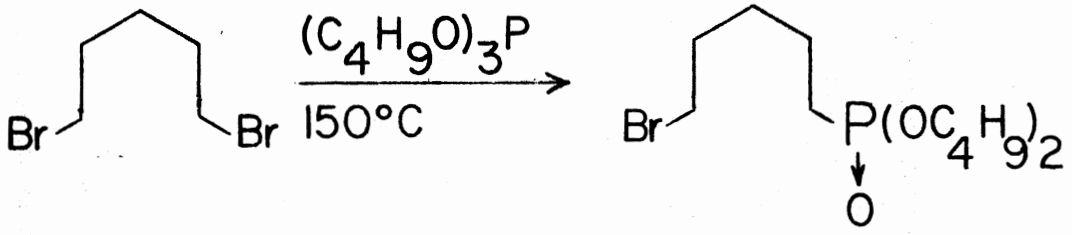
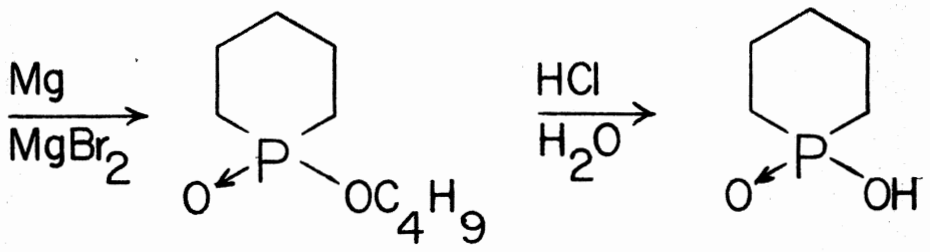
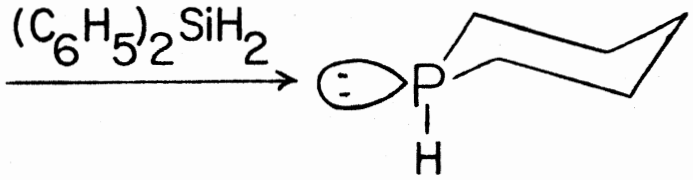
quadrupole moment allow investigations of structural parameters in the phosphorinane system 16 which are more difficultly accessible in the nitrogen analogs even via DNMR methods.

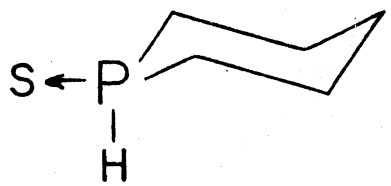






18

Phosphorinane 18, prepared by several methods,[4,31,33,59] one of which is illustrated, apparently exists with the proton axially oriented.[31,33] At -50°C, one-half of the P-H resonance consists of a triplet of triplets due to J_{aa} and J_{ae} (the other half is under the ring protons resonance, $^{1}J_{PH}$ = ca. 200 Hz). Computer simulation (LAOCN3) of the observed spectra gave J_{aa} = 12 Hz and J_{ae} = 2.5 Hz.[31,33] Similarly it was determined that phosphorinane 1-sulfide 19[31] and the corresponding methiodide 20[31] possesses axially oriented P-H bonds.



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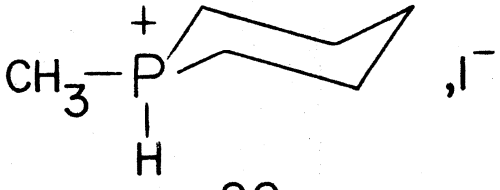
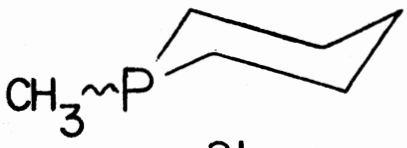


20

However, the experimental evidence in support of the configuration at phosphorus in 20 was somewhat ambiguous.[31]

Quin and co-workers[13,14] have determined the barriers (ΔG^{*}) to ring reversal in 1-methylphosphorinane (21), 1-ethylphosphorinane (22), 1-isopropylphosphorinane (23), and 1-phenylphosphorinane (24) by low temperature ^{1}H and ^{31}P NMR analyses. Lowering the temperature of solutions (vinyl chloride, tetramethylethylene) of these phosphines resulted in the appearance of two signals in the ^{31}P spectrum. The low-field signal was assigned to the conformer with an equatorial P substituent. Accordingly, $\Delta G^{*}_{T_c}$ (T_c = coalescence temperature)



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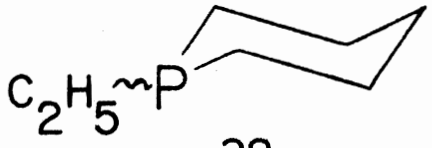

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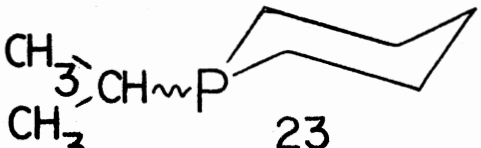

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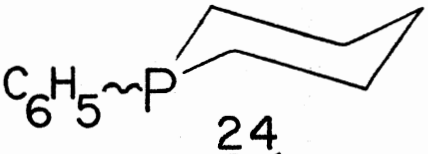

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for ring reversal was calculated to be 8.7 kcal/mole (T_c = 186 K) for 21, 8.4 kcal/mole (T_c = 177 K) for 22, 8.6 kcal/mole (T_c = 169 K) for 23, and 9.3 kcal/mole (T_c = 208 K) for 24.[14] The above values for ΔG^* were obtained using the equation $k_c = \pi\Delta\nu/\sqrt{2}$ [46] [where $\Delta\nu$ is the peak separation at the lower temperature limit] and the Eyring equation. The validity of the above method for calculating $\Delta G^*_{T_c}$ rests on the accuracy of the temperature measurement since a variation of $\pm$ 2°C yields a variance in ΔG^* of ca. 0.1-0.2 kcal/mole.[25] Also errors of 25% in the value of the rate constants at the coalescence temperature yield a variation in ΔG^* of ca. 0.1 kcal/mole.[25]

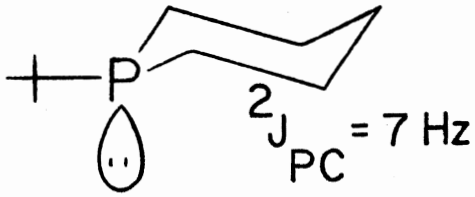
^{31}P NMR analysis of the low temperature ($T<T_c$) spectra of 21-24 gave equilibrium constants which favored the equatorial P substituent.[14] However, extrapolation to room temperature of plots of log K_{eq} vs 1/T showed the predominance of the axial conformer for 21, 22, and 24.[14]

The use of ^{13}C NMR spectroscopy in the conformational analysis of phosphorinanes has received considerable attention.[12,15,49] Of particular importance is the relationship between the $^2J_{^{31}P-^{13}C}$ at C(3,5) and the disposition of the lone pair of electrons on phosphorus.[15] A large dihedral angle between the lone pair of electrons and C(3,5),

such as in 25 (axial-R), results in a small (ca. 0-1 Hz)

(axial - R) **25** (equatorial - R)

$^{2}J_{31_P\text{-}13_C}$ value. Subsequent use was made of the above relationship in the assignment of configuration of P for 21-24 and for 1-tert-butylphosphorinane (26)[12] based on the coupling constants for 27a and



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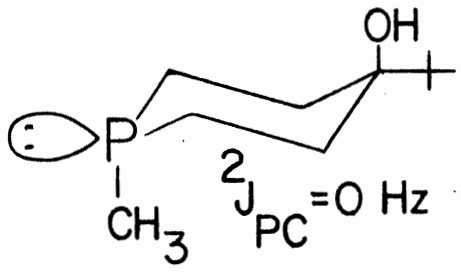
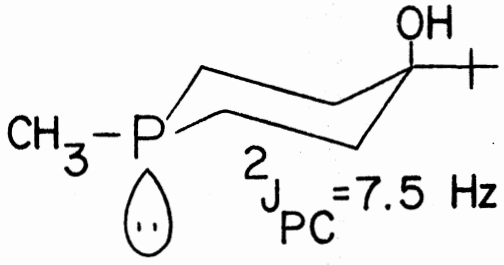


27a

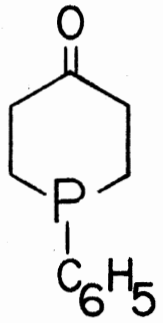


27b

27b with known absolute configuration.[15,44]

Sulfurization of unbiased phosphorinanes has been shown to produce configurations at P with axial sulfur.[12] Phosphorinanes 21-24 and 26 were sulfurized in boiling benzene, a process known to proceed with

retention of configuration.[35] That the configurational isomer with axial sulfur resulted was based upon the shielded signals for C(3,5) in the ^{13}C spectra in comparison to the ^{13}C chemical shifts of C(3,5) in phosphorinanol 1-sulfides of known stereochemical configuration.[49] Fortunately, X-ray crystallographic data have been collected for 1-phenyl-4-phosphorinanone (28),[42] 4,4-dimethoxy-1-phenylphosphorinane (29),[43] trans-4-tert-butyl-1-methyl-4-phosphorinanol (27a),[44] epimeric



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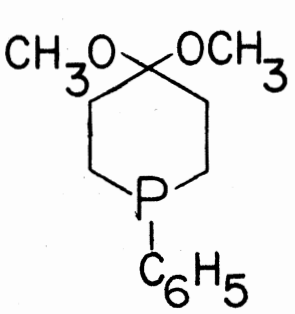

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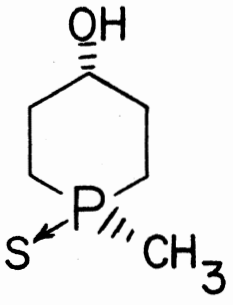

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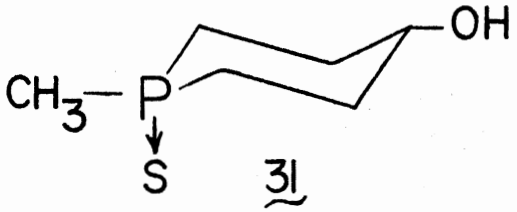

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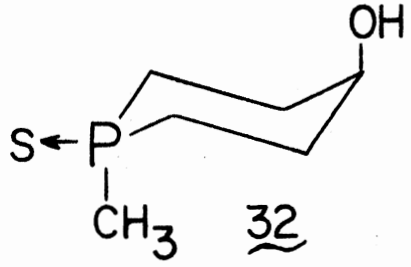

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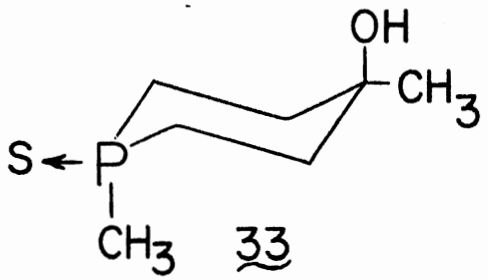

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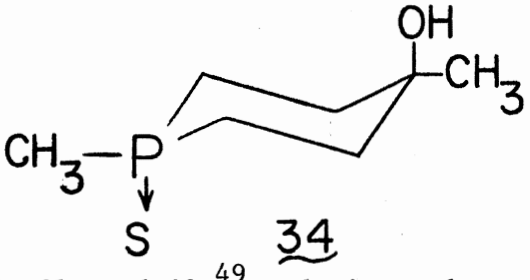


34

1-methyl-4-phosphorinanol 1-sulfides 30, 31, and 32,[49] and cis- and trans-1,4-dimethyl-4-phosphorinanol 1-sulfides 33 and 34.[49]

The phosphorinanes with axial P substituents (nonsulfides), 27a, 28, and 29, possess slightly flattened chair conformations.[42-44] The

ring torsion angles for 27a, 28, and 29 are presented in Table I. A listing of the endocyclic torsion angles for sulfides 30, 31, 32, 33, and 34 is given in Table II.[49]

TABLE I

TORSION ANGLES (°)

	27a	28	29
C(6)-P(1)-C(2)-C(3)	45.3	-44.3	45.2
P(1)-C(2)-C(3)-C(4)	57.7	49.8	57.1
C(2)-C(3)-C(4)-C(5)	59.7	-53.0	61.5

TABLE II

TORSION ANGLES (°)

	30	31	32	33	34
C(6)-P(1)-C(2)-C(3)	45	50	44	45	52
P(1)-C(2)-C(3)-C(4)	56	59	55	56	59
C(2)-C(3)-C(4)-C(5)	64	63	62	61	60

It is interesting to note that in all cases (phosphines and phosphine sulfides) when the alkyl group was axially oriented (27a, 28, 29, 30, 32, and 33), the P(1)-C(2) torsion angle was ca. 45°. In contrast, when sulfur was axially oriented (31 and 34), the P(1)-C(2) torsion angle was ca. 51°.[42-44,49] This may be accounted for by the repulsive forces (electronic) between axial sulfur and the C(3,5) axial hydrogens. This argument was supported by the increased shielding in the ^{13}C NMR spectra at C(3,5) when sulfur was axial compared to that when methyl was axial (154.7 ppm for 33 vs 155.5 ppm for 34).[49]

Experimental Methods for the Determination of Thermodynamic Parameters

Dynamic Nuclear Magnetic Resonance (DNMR)

The theory and application of DNMR to intramolecular rate processes has received considerable attention in the last decade.[3,23,26,51,54-56] Only two uses of DNMR will be discussed herein, that for the study of pyramidal atomic inversion and for the study of ring reversal in six-membered rings.

A classic example of the use of DNMR in the case of pyramidal atomic inversion has been presented recently.[34] 1,1,2,2-Tetraisopropyl-1,2-diphenyldisilane (35) was cleaved with lithium to yield

$$C_6H_5[(CH_3)_2CH]_2SiSi[CH(CH_3)_2]_2C_6H_5 \xrightarrow{2Li} 2\ C_6H_5[(CH_3)_2CH]_2SiLi$$

35 → 36

phenyl-di-isopropylsilyllithium (36). At 35°C in several solvents (hexamethylphosphoramide, diglyme, tetrahydrofuran-d_8, 1,2-dimethoxyethane, benzene-d_6 or 1,4-dioxane), the ^1H NMR spectrum of 36

consisted of two nonequivalent methyl signals, indicative of slow inversion at silicon. Heating a solution (diglyme) of 36 to 185°C revealed no change in the ^{1}H NMR spectrum of the nonequivalent methyl groups. Based on those observations, it was concluded that the barrier to pyramidal inversion at silicon in 36 was greater than ca. 24 kcal/mole.[34]

Cyclohexane has probably been the most widely studied molecule for ring reversal.[3,23] The room temperature ^{1}H NMR spectrum of cyclohexane consists of a single line. Lowering the temperature to ca. -70°C results in two equally intense signals in the proton spectrum. The downfield signal has been assigned to the protons equatorially oriented and the upfield signal to the protons axially oriented. Several methods (e.g. line-shape analysis) have yielded barriers (ΔG^*) to ring reversal of ca. 10 kcal/mole.[3,23]

Infrared and Microwave Spectroscopy

The use of infrared and microwave spectroscopy for the determination of intromolecular rate processes (i.e. pyramidal inversion) has been particularly effective for simple amines.[26,51] As the studies of processes utilizing these techniques have been discussed in detail, these topics may be referred to elsewhere.[26,51]

Classical Kinetics

Classical kinetics has been employed for the determination of the barrier to pyramidal atomic inversion in several instances.[1,8,11,34] The application of classical kinetics is limited to compounds which invert over an accessible temperature range at a convenient rate. Also

the invertomers must be distinguishable as enantiomers or diastereomers and obtainable as a nonequilibrium mixture for best results.

The barrier to pyramidal atomic inversion may be obtained from the Arrhenius equation (Eq. 1)

$$k = Ae^{-E_a/RT} \qquad \text{(Eq. 1)}$$

where k is the rate constant at temperature T, A is the frequency factor, and E_a is the Arrhenius activation energy. Similarly the Eyring equation (Eq. 2)

$$k = \frac{k_B T}{h} e^{-\Delta G^*/RT} \qquad \text{(Eq. 2)}$$

may be employed where k is the rate constant at temperature T in K, k_B is the Boltzmann constant (1.38×10^{-16} erg K^{-1} $mole^{-1}$), h is Planck's constant (6.63×10^{-27} erg sec), and ΔG^* is the Gibbs free energy difference between ground state and transition state.

Errors in the Determination of Thermodynamic Parameters

Only the errors associated with the determination of thermodynamic parameters via classical kinetics will be discussed here. Since the calculation of the first order rate constant (Eq. 3) is directly dependent upon the

$$kt = \ln \frac{[A]}{[B]} \qquad \text{(Eq. 3)}$$

concentration of two species (A and B) at time t, methods to determine those concentrations accurately are extremely important. In utilizing NMR for the determination of the concentration of two distinguishable species (A and B), one relies on the integrated intensity of two or

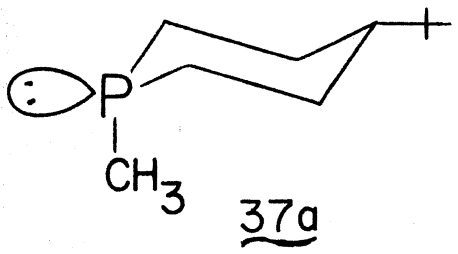
more signals. It follows that the method(s) of integration must be reliable and reproducible. Triangulation, planimetry, cutting and weighing, and digital integration all possess strong and weak points and should be used in conjunction where possible. However, it should be realized that an error in the rate constant of 25% yields an error of only 0.1 kcal/mole in ΔG^*.[25]

Another parameter most difficult to control in NMR analyses is that of temperature. If the data accumulation is performed while the NMR spectrometer is operating at a temperature other than ambient, one must be capable of controlling and monitoring that temperature accurately. It is best with current VT accessories on NMR spectrometers to calibrate the temperature readout device over the entire temperature range to be used. This is easily done by observing the chemical shifts in a standard compound as a function of temperature (e.g. methanol, ethylene glycol).[57] Direct thermometer (or thermocouple) readings before and after sampling and the incorporation of a temperature-sensing device in the sample are other applicable techniques. It is important to realize that if the temperature monitored is near 300 K a variance of $\pm$ 2 K results in ca. 1% variation in ΔG^*.[25]

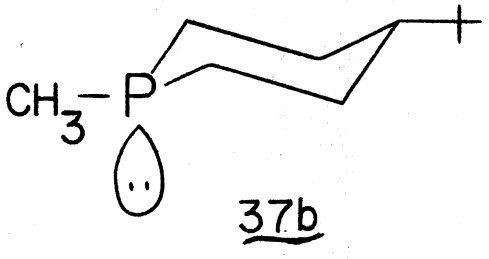
CHAPTER II

RESULTS AND DISCUSSION

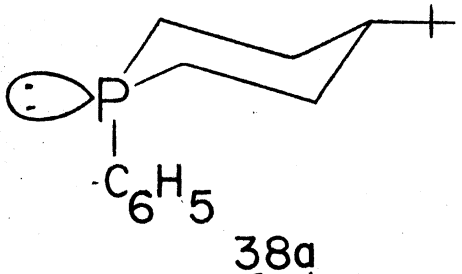
The chemistry of phosphorinanes is a very active area, and there recently appeared in the literature the preparation and tentative stereochemical assignment of cis- and trans-4-tert-butyl-1-methyl-phosphorinane (37a and 37b, respectively) and cis- and trans-4-tert-butyl-1-phenylphosphorinane (38a and 38b, respectively).[39]



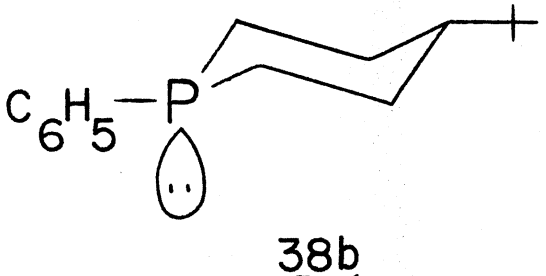
37a



37b



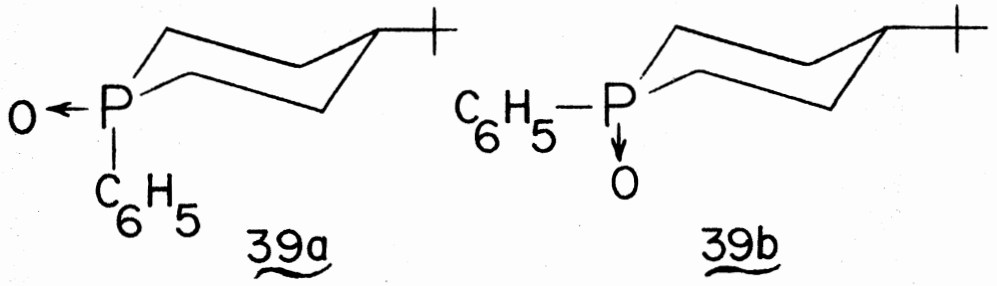
38a



38b

The work in this thesis presents NMR studies which have provided thermodynamic data (ΔG^{*} and ΔG^{o}) for the pyramidal inversion involving 38a $\rightleftharpoons$ 38b. In addition, analyses of the ^{13}C and ^{31}P NMR spectra of phosphines 38a and 38b and their corresponding oxides 39a and 39b have also been recorded. All data support the original stereochemical

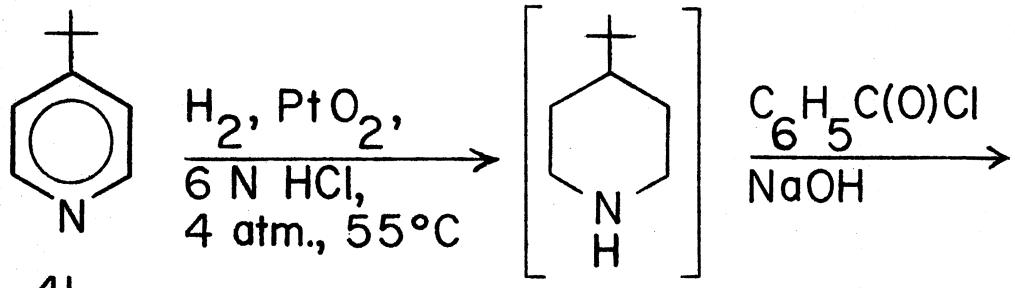
assignments.[39] Also, our work presents a single crystal X-ray crystallographic analysis of oxide 39b which also supports the original structural assignments for the phosphines 38a and 38b.



39a 39b

The preparation of phosphines 38a and 38b have been reported previously[39] but will be discussed here to familarize the reader with the synthetic procedure. The basic starting material for the phosphines was 1,5-dibromo-3-tert-butylpentane (40). Several methods[24,47,52] have been employed and these will be discussed on the basis of ease and reproducibility. The earliest procedure[24] involved utilization of 4-tert-butylpyridine (41). 4-tert-Butylpyridine (41) was catalytically reduced over platinum oxide to give, presumably, a piperidine (not isolated). Benzoylation of this product with benzoyl chloride gave the amide 42 in 90% yield. Cleavage of the amide 42 was effected (von Braun reaction) with PBr_3 and Br_2 to yield, after the appropriate work-up, 40 (40%). The major problems involved in the above procedure are the expense of the platinum oxide catalyst and pyridine 41 and the modest reproducibility of the von Braun cleavage owing to the number of product transfers involved and final steam distillation of dibromide 40.

The second method[52] employed 4-tert-butylcyclohexane (43) as the starting material. Lactonization of ketone 43 was performed



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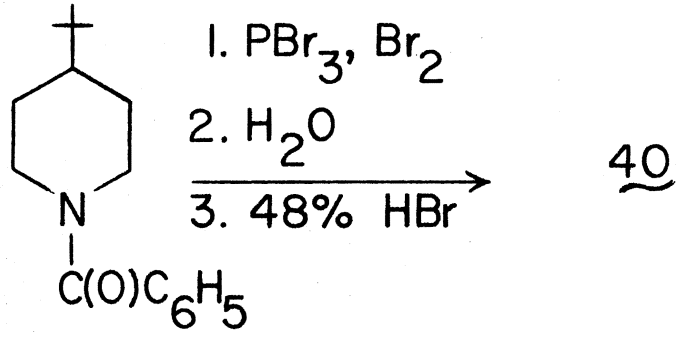
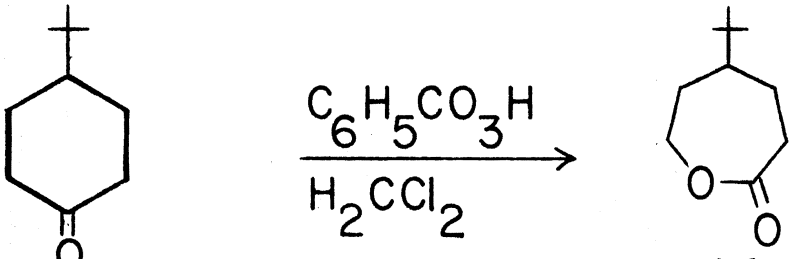
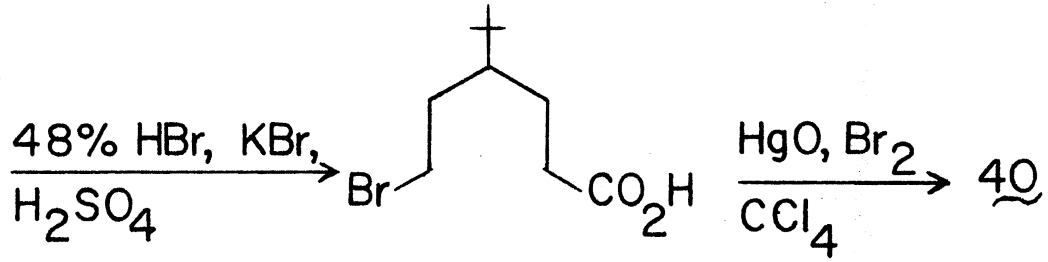


42 → 40



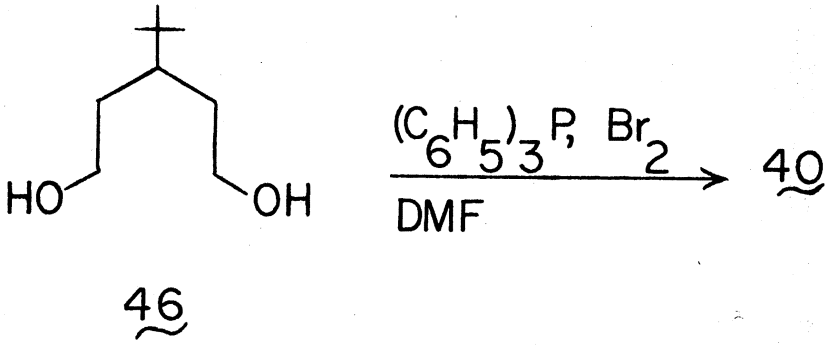
43 → 44



45 → 40

with perbenzoic acid followed by fractional distillation to give the lactone 44 (reported yield 100%).[52] Cleavage of the lactone 44 with 48% HBr-KBr and H_2SO_4 gave bromo acid 45 (83%). The final bromination-decarboxylation (Hunsdiecker reaction) process utilized HgO-Br_2 instead of the usual silver salt-Br_2 to give dibromide 40 (61%) after steam distillation. This method is attractive on the basis of simplicity; however, other workers[39] have been unable to reproduce the reported yields.

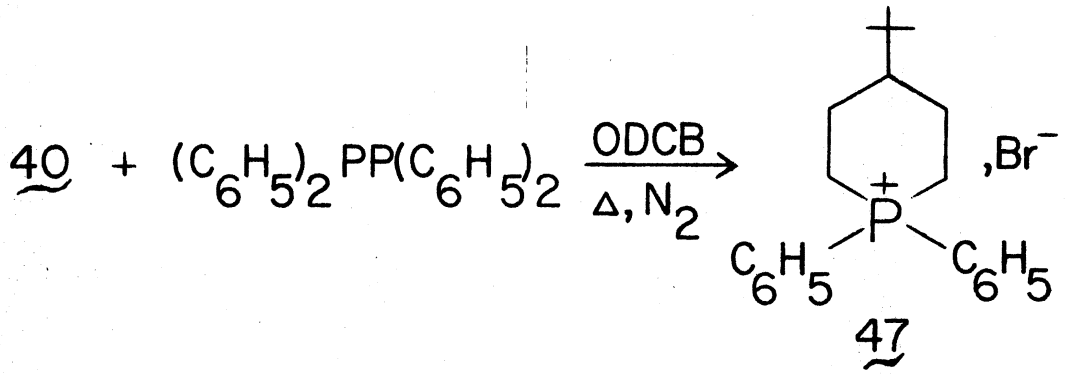
The third method began with 3-tert-butyl-1,5-pentanediol (46).[47]



46

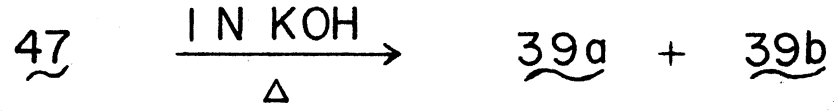
The diol 46 was brominated with dibromotriphenylphosphorane (from triphenylphosphine and Br_2). Hydrolysis and separation of the organic phase followed by vacuum distillation gave 40 (39%). This method appears most attractive on the basis of ease of reactions; however, the number of reaction steps (8) to prepare 46 makes the overall procedure less attractive.

With a method developed by Märkl,[36,39,40] the dibromo compound 40 was cyclized (37%) to 4-tert-butyl-1,1-diphenylphosphorinanium bromide (47) with tetraphenyldiphosphine in boiling 1,2-dichlorobenzene (ODCB). The reaction is believed to proceed via nucleophilic displacement of Br^- by the phosphine with concomitant P-P bond cleavage to



yield a tertiary phosphine. A second nucleophilic displacement of Br^- by the phosphine gave the cyclic salt 47. Since diphenylphosphinous bromide is a side product in the reaction, its role as reagent in the cyclization process has been studied[40] and found to be insignificant.

Base cleavage of the salt 47 gave a mixture of phosphine oxides

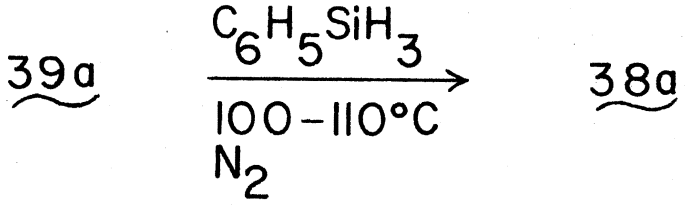


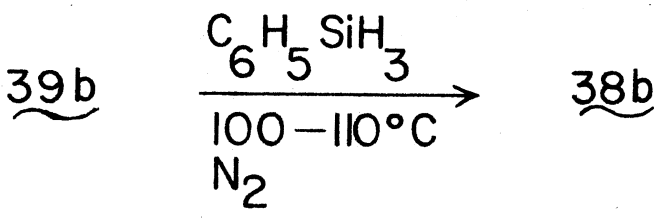
39a and 39b.[39] The composition of the product mixture was rationalized on the basis of product-resembling transition states which tend to favor the diequatorially substituted oxide 39b.[39]

Oxides 39a and 39b were separated via preparative thick-layer chromatography on silica gel plates with acetone as eluent.[39] The separated oxides [39a:R_f = 0.24; 39b:R_f = 0.94] were extracted (Soxhlet) with methanol, and the resulting extracts were then vacuum distilled (Kugelrohr) after rotary evaporation of the solvent.

Preparation of the phosphines 38a and 38b was accomplished by reduction with phenylsilane of the corresponding oxides 39a and 39b.[39]

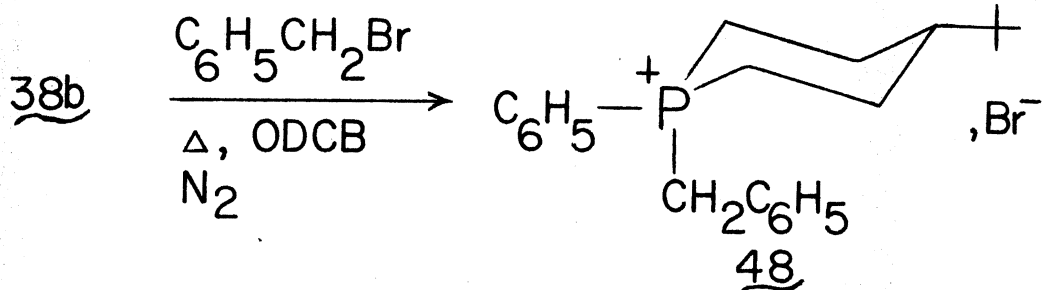
This type of reduction of phosphine oxides is known to proceed stereospecifically with retention of configuration.[38] Freshly distilled





phosphines 38a or 38b were then used directly in the kinetic experiments (discussion to follow).

A simple experiment to check the structure assignments previously reported was conducted with oxide 39b.[39] Oxide 39b was reduced with phenylsilane[38] to the corresponding phosphine 38b. Quaternization



48

of phosphine 38b with benzyl bromide in ODCB at room temperature gave salt 48 (22%) whose physical and spectral properties were identical to those reported previously.[39]

Few reports have appeared[8,10] on the barrier (ΔG^*) to pyramidal atomic inversion in cyclic organophosphorus compounds. It was the intent of this work to determine the barrier (ΔG^*) to inversion at phosphorus in phosphorinanes 38a and 38b. The procedure consisted of dissolving the phosphine 38a or 38b in ODCB at a specified temperature which was maintained at either 417, 437, or 454 K by the appropriate selection of an external boiling liquids [1,1,2,2-tetrachloroethane bp 417 K; 1,3,5-trimethylbenzene, bp 437 K; ODCB, bp 454 K]. Periodically, an aliquot of the phosphine solution was withdrawn and quenched by placement in a cold NMR tube. The ^1H or ^{31}P NMR spectrum was then recorded. The composition of the phosphine mixture was determined by integration of the well separated tert-butyl singlets in the ^1H NMR spectrum or the distinct ^{31}P signals in the ^{31}P NMR spectrum. Data so collected are presented in Tables III-VIII and displayed in Figures 1-3.

The determination of the barrier (ΔG^*) to pyramidal inversion at phosphorus in 38a $\rightleftharpoons$ 38b was by a least-squares fit of the mixture composition data. Data collected up to ca. 10-hr reaction time were used as some decomposition of the phosphines 38a or 38b took place after ca. 10 hr at these elevated temperatures. Also, little change in the mole fraction of 38a or 38b was noticed after ca. 10 hr of reaction time; thus it was assumed that the equilibrium mixture for 38a $\rightleftharpoons$ 38b had been formed. The rate constants so obtained from the least-squares plot of the change in concnetration of 38a (or 38b) with time were averaged for each temperature and subsequently employed in the Eyring equation.[25] A sample calculation of ΔG^* at 437 K follows:

TABLE III

RATE DATA FOR 38a ⇌ 38b AT 417 K (TRIAL 1)

Time (hr)	Mole Fraction	
	38a	38b
0	1.00	0.00
2	0.942	0.058
6	0.783	0.217
19	0.517	0.483

TABLE IV

RATE DATA FOR 38a ⇌ 38b AT 417 K (TRIAL 2)

Time (hr)	Mole Fraction	
	38a	38b
0	1.00	0.00
3.25	0.901	0.098
6.75	0.834	0.166
10.25	0.748	0.252
17.50	0.544	0.456
71.75	0.410	0.589

TABLE V

RATE DATA FOR 38a $\rightleftharpoons$ 38b AT 437 K (TRIAL 1)

Time (hr)	Mole Fraction	
	38a	38b
0	0.394	0.606
1.25	(0.417)*	(0.583)*
2.17	0.339	0.661
4.17	0.314	0.686
10.17	0.265	0.735
13.17	0.297	0.703

* Least reliable point.

TABLE VI

RATE DATA FOR 38a ⇌ 38b AT 437 K (TRIAL 2)

Time (hr)	Mole Fraction	
	38a	38b
0	1.00	0.00
1.08	0.829	0.171
2	0.763	0.237
4	0.521	0.479
6.83	0.571	0.429
11.1	0.475	0.525
21.42	0.420	0.579

TABLE VII

RATE DATA FOR 38a ⇌ 38b AT 437 K (TRIAL 3)

Time (hr)	Mole Fraction	
	38a	38b
0	0.00	1.00
1	0.061	0.939
2	0.098	0.900
3	0.164	0.836
5	0.229	0.771
11	0.227	0.773
24	0.428	0.572
48	0.474	0.526
72	0.492	0.508

TABLE VIII

RATE DATA FOR 38a ⇌ 38b AT 454 K (TRIAL 1)

Time (hr)	Mole Fraction	
	38a	38b
0	0.602	0.398
1.17	0.561	0.439
3.5	0.392	0.608
8.08	0.331	0.669
17.00	0.311	0.689

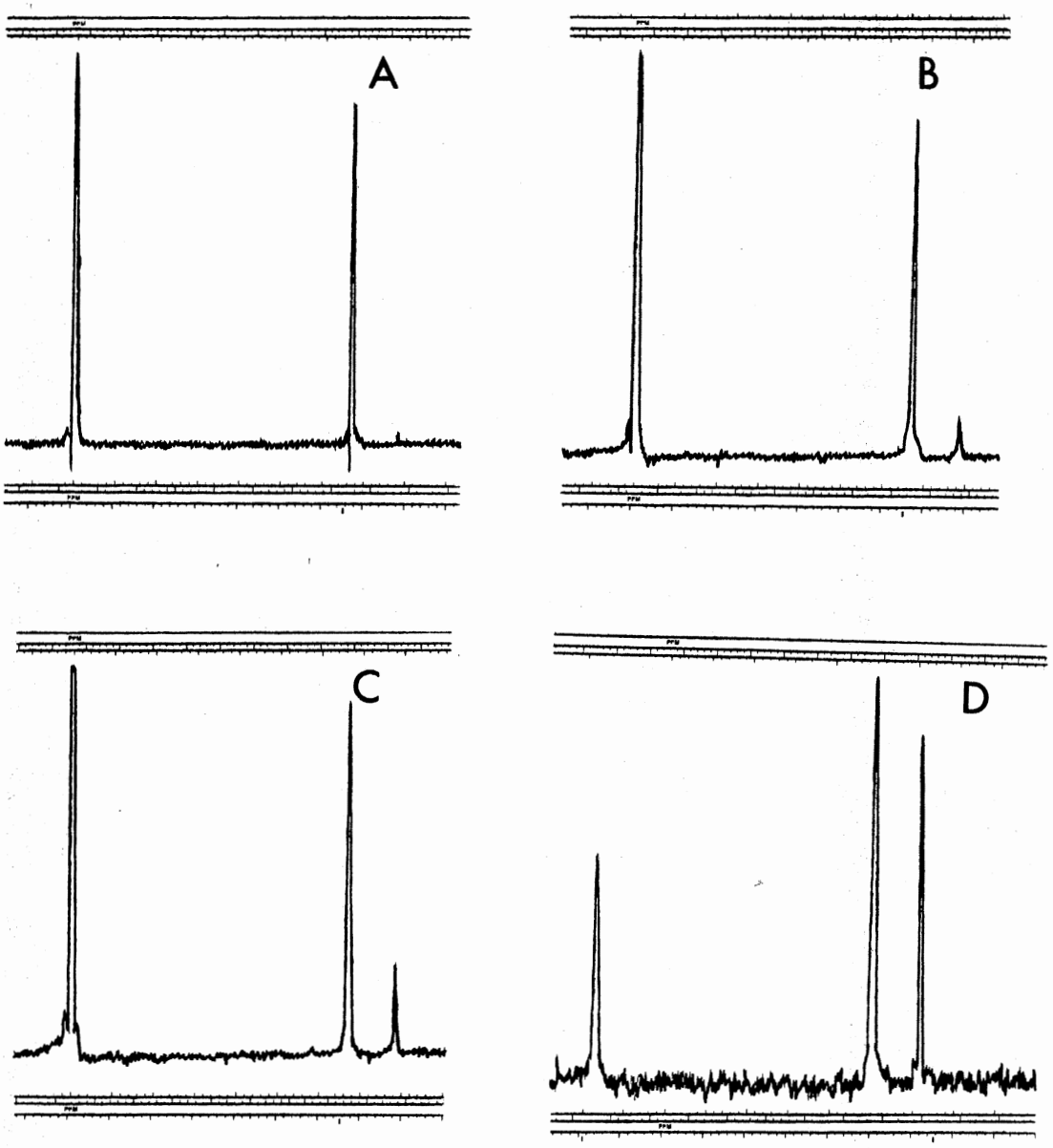


Figure 1. ^{31}P NMR spectra of 38a $\rightleftharpoons$ 38b at 417 K as a function of time (signal at left end is 85% H_3PO_4): A) 38a, t_o; B) t_o + 3.25 hr; C) t_o + 6.75 hr; D) t_o + 10.25 hr [phosphines 38a and 38b].

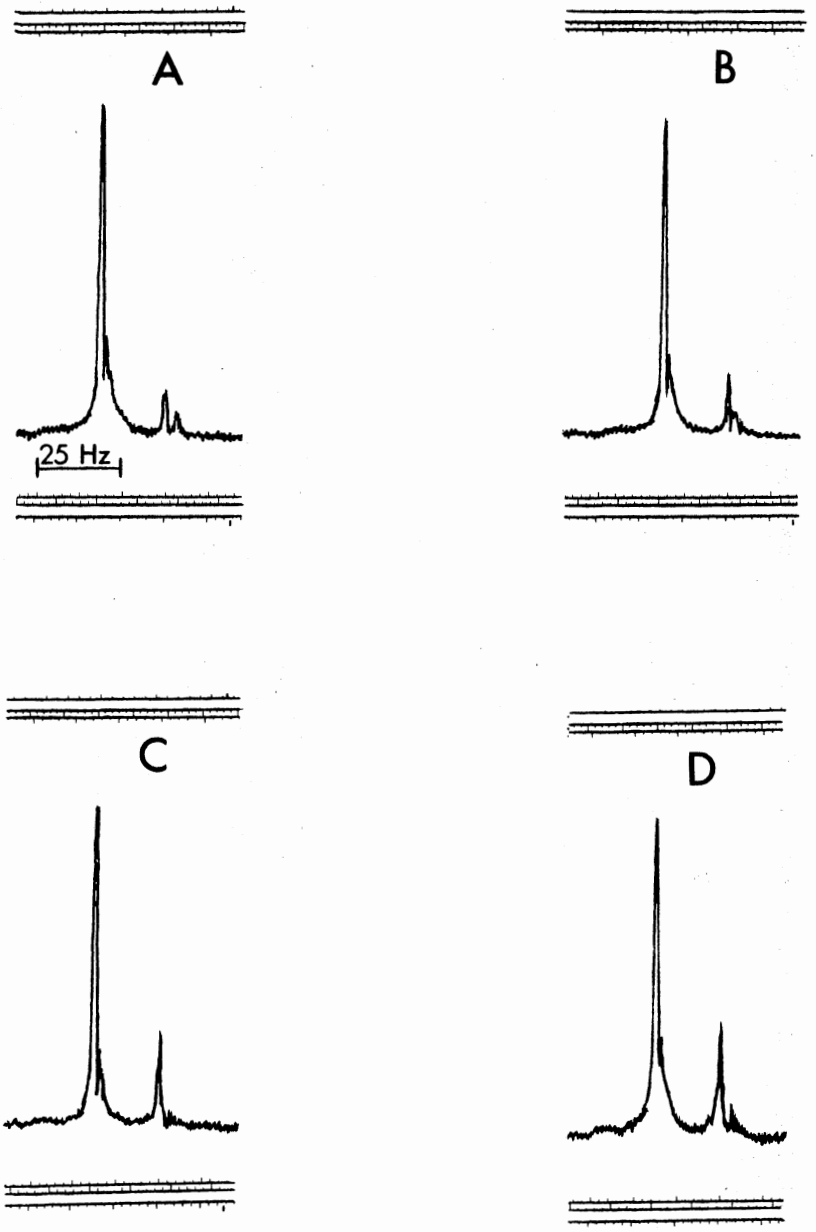


Figure 2. ^{1}H NMR spectra of tert-butyl signal in 38a ⇌ 38b at 437 K as a function of time: A) 38b, t_o + 1 hr; B) t_o + 2 hr; C) t_o + 3 hr; D) t_o + 5 hr.

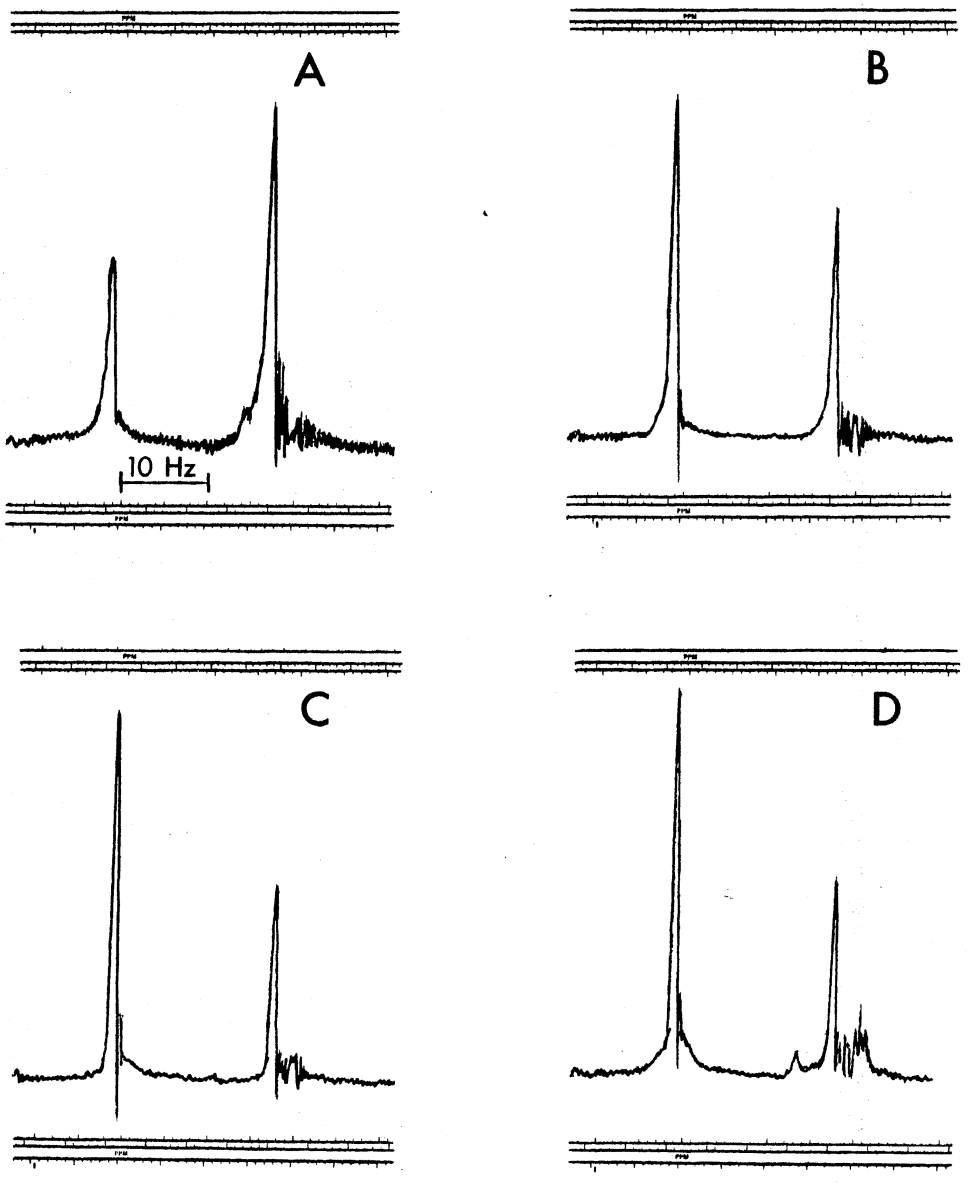


Figure 3. ^{1}H NMR spectra of tert-butyl signal in 38a $\rightleftharpoons$ 38b at 454 K as a function of time: A) t_o; B) t_o + 1.17 hr; C) t_o + 3.5 hr; D) t_o + 8.08 hr.

Average k for 38a $\rightleftharpoons$ 38b at 437 K

$$k = 0.0339\ hr^{-1} = 9.42 \times 10^{-6}\ sec^{-1}$$

$$k = \frac{k_B T}{h} e^{-\Delta G^*/RT}$$

$$9.42 \times 10^{-6}\ sec^{-1} = (2.08 \times 10^{10}\ sec^{-1}\ K^{-1})(437\ K)e^{-\Delta G^*/RT}$$

$$1.04 \times 10^{-18} = e^{-\Delta G^*/RT}$$

$$-41.4 = -G^*/(1.98\ cal\ K^{-1}\ mole^{-1})(437\ K)$$

$$\Delta G^* = 35.9\ kcal\ mole^{-1}$$

The barriers (ΔG^*) to pyramidal inversion at 417 and 454 K were determined in like manner and are given in Table IX.

The barrier (ΔG^*) for inversion in 38a $\rightleftharpoons$ 38b compares to the reported value of ca. 36 kcal mole^{-1} for 3-methyl-1-phenylphospholane (49)[10] and is ca. 4 kcal mole^{-1} higher than that for a number of dialkylphenylphosphines.[1] It is interesting to note that 1,2,2,3,4,-hexamethylphosphetane (50),[8] 1,3-dimethylphospholane (51),[37] and 1-methyl-4-phosphorinanol (52)[50] failed to invert after heating at 162°C

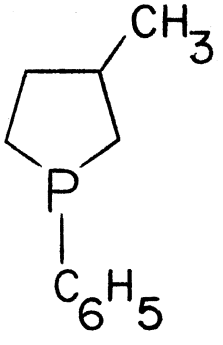


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TABLE IX

BARRIER (ΔG^*) TO PYRAMIDAL INVERSION IN 38a $\rightleftharpoons$ 38b

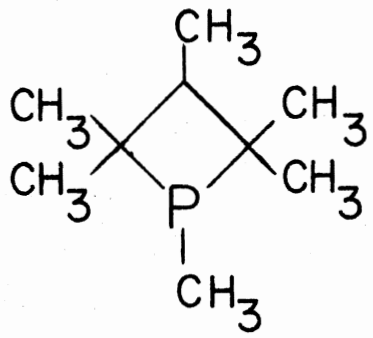
T(K)	k x 10^6 (sec^{-1})	ΔG^* (kcal/mole)
417	6.83*	34.6
437	9.42*	35.9
454	17.1*	36.9

* Using the equation for a first-order reversible process for

$$\ln \frac{[C_{38b}] - K_{eq}[C_{38a}]}{[C_{38b}]_o - K_{eq}[C_{38b}]_o} = -(k_1 + k_2)t$$

38a $\underset{k_2}{\overset{k_1}{\rightleftharpoons}}$ 38b, the values for k are respectively: 0.87, 2.37, and 4.11 x 10^{-5} sec^{-1}.

for 4 days, 150°C for 3 days, and 170°C for 18 days, respectively. Therefore that 38a ⇌ 38b undergoes pyramidal inversion constitutes the first report of a phosphorinane to do so.



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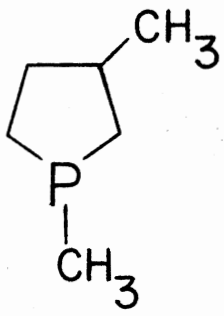

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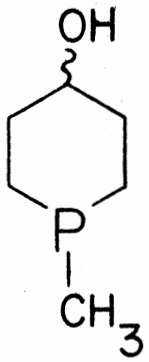
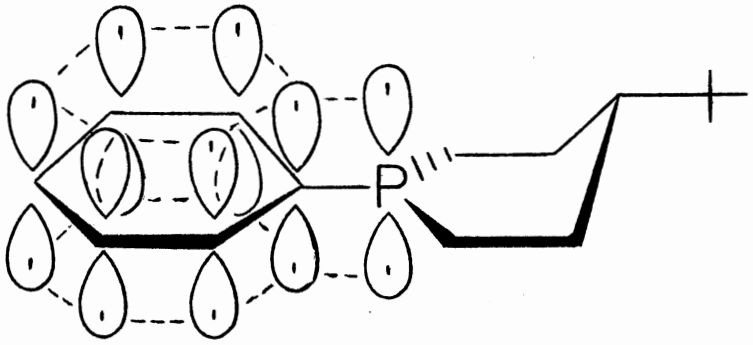


52

From the observations that 49 and 38a (38b) undergo inversion at phosphorus while 50, 51, and 52 do not at approximately the same temperatures, it is reasonable to conclude that the phenyl group on P must influence the development of the transition state in 38a (or 38b) and 49 in a significant manner. It seems likely that there is a decrease in the barrier to pyramidal inversion when a phenyl group is attached to P due to (p-p)π overlap in the transition state. An illustration of this possible effect is given in 53.



53

As stated previously, equilibrium data (mixture composition-mole fraction) were collected for 38a $\rightleftharpoons$ 38b at the three different temperatures (417, 437, and 454 K). Data used in the calculation of ΔG^{o} at the three different temperatures are presented in Table X. The equilibrium constants are in favor of the diequatorially substituted phosphine 38b. Values for ΔG^{o} were then calculated from

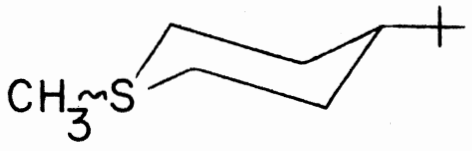
$$- \Delta G^{o} = RT \ln K_{eq}.$$

TABLE X

EQUILIBRIUM DATA FOR 38a $\rightleftharpoons$ 38b

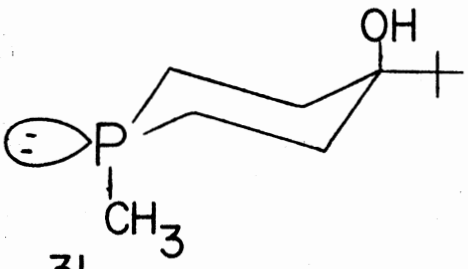
T(K)	K_{eq}	ΔG^{o} (kcal mole^{-1})
417	1.44	-0.30
437	1.38	-0.28
454	1.21	-0.17

In all cases the diequatorially substituted phosphine 38b was favored, which agrees with a report[11] for 4-*tert*-butyl-1-methyl-thianium perchlorate (54), where the equatorial S-methyl group was favored by 0.275 kcal mole^{-1} (ΔG^{o}) at 100°C.

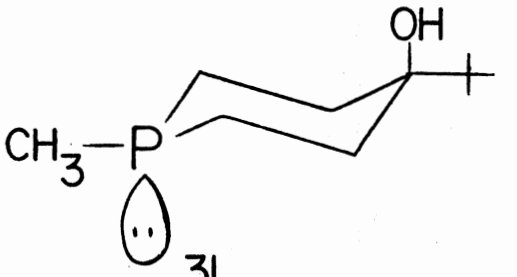


54

The ^{31}P NMR chemical shifts for 38a, 38b, 39a, and 39b have been recorded in Table XI. The ^{31}P NMR data revealed an unusual difference between phosphorinanes 38a and 38b and structurally similar phosphorinanols 27a and 27b reported previously.[50] Chemical shifts of -32.92 and -38.62 ppm (upfield from external reference 85% H_3PO_4) were observed for 38a and 38b, respectively, whereas ^{31}P shifts of -67.3 and -57.7 ppm were recorded for 27a and 27b, respectively. That the ^{31}P



27a



27b

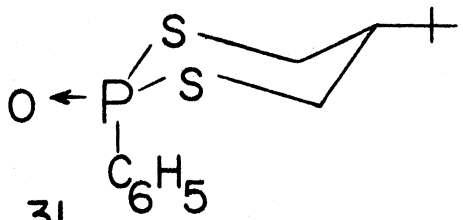
chemical shifts for 38a and 38b were assigned correctly was based on the ^{13}C NMR data (discussion to follow) as well as on a single crystal X-ray crystallographic analysis of oxide 39b (discussion to follow). The latter was reduced with phenylsilane[38] to 38b. A similar observation concerning ^{31}P NMR shifts has recently been made for cis- and trans-2-phenyl-2-oxo-5-tert-butyl-1,3,2,-dithiaphosphorinanes 55a and 55b.[41] These workers suggested that the reversal[14] in ^{31}P chemical shifts may be due to a predominance of a twist conformer

TABLE XI

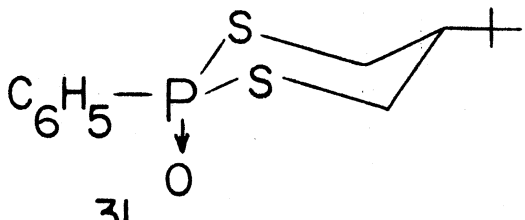
^{31}P CHEMICAL SHIFTS[a]

Cpd.	δ[b] (ppm)
38a	-32.92
38b	-38.62
39a	+29.99
39b	+28.19

[a]Shifts are ±0.02 ppm. Shifts determined on ca. 200 mg samples in 2 ml ODCB. [b]Chemical shifts relative to 85% H_3PO_4. Minus sign indicates shifts upfield from the external standard.

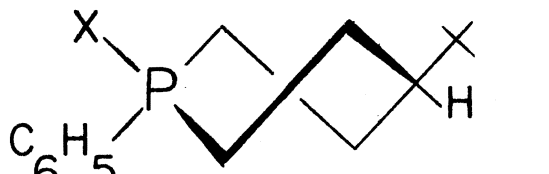


55a



55b

for 55a in solution. Similarly, the small ^{13}C shift differences [between C(2,6) and C(3,5), discussion to follow] of $\Delta\delta$ -0.23 in 38a and $\Delta\delta$ -2.55 ppm in 39a may be the result of a distorted chair or twist conformation since the same atoms in 27a (with known absolute configuration) displayed a ^{13}C chemical shift difference of $\Delta\delta$ +6.06.[15] We conclude that the anomalous ^{31}P chemical shift data for 38a, 38b, 39a, and 39b may result from a geometric deformation of a chair conformation in both 38a and 39a. Also in support of this argument, molecular models (Courtauld) indicate a severe steric interaction between the π orbital of the phenyl group (or ortho hydrogens) with the axial protons at C(3,5) of the phosphorinane ring when phenyl was axial. This interaction could be relieved to some extent in a distorted chair or twist conformation (such as 56) for 38a and 39a. Therefore, we suggest that assignment of configuration at phosphorus in phosphorinanes based on ^{31}P NMR data alone should be done with marked caution.



56

The ^{13}C NMR chemical shifts and ^{31}P-^{13}C coupling constants for phosphines 38a and 38b and the corresponding oxides 39a and 39b are given in Table XII. Shifts for C(2,6) in 38a and 38b reflect a steric compression effect for axial substituents compared to that in cyclohexanes.[9] Also the ^{13}C shifts for C(2,6) in 38a and 38b reflect the same steric compression effect found for 27a and 27b, which have the P substituent in a fixed arrangement of known stereochemical configuration.[15] A decrease in the ^{13}C chemical shift from 25.55 ppm (38b) to 21.55 ppm (38a) was noted in interchanging the position of the lone pair of electrons on phosphorus with a phenyl group (group changed from the equatorial to the axial position with the resultant change in chemical shift being a result of a steric compression effect[9]). This $\Delta\delta$ of -3.60 ppm is smaller than that found by interchanging the lone pair and methyl group ($\Delta\delta$ -5.8 ppm[15]) in 27a to give 27b. However, the ^{13}C spectra for 38a and 38b were taken in $DCCl_3$ and H_2CCL_2 for 27a and 27b; thus the difference in $\Delta\delta$ could be due to solvent effects.[2] It remains speculative that this difference (-3.6 vs -5.8 ppm) was due to a steric effect (phenyl vs methyl) since there also exists some uncertainty in the actual geometry about the phosphorus atoms (particularly in 38a) in solution.

The ^{31}P-^{13}C coupling constant ($^1J_{PC}$) for P-C(2,6) in 38a (11.5 Hz) was essentially the same for 27a (12 Hz) and similar to that found for $^1J_{PC}$ [P-C(2,6)] in 38b (8.9 Hz) and 27b (10 Hz). This suggests the electronic factors affecting $^1J_{PC}$ [P-C(2,6)] in these two compounds do not differ markedly.

The ^{13}C chemical shifts for C(3,5) were apparently indicative of the orientation of the substituent on phosphorus in phosphines 27a and

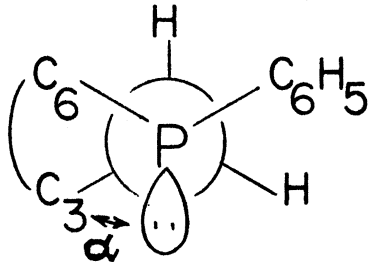
TABLE XII

^{13}C NMR PARAMETERS: CHEMICAL SHIFTS[a] (^{31}P-^{13}C COUPLING CONSTANTS)[b]

	Compounds			
Carbon(s)	38a	38b	39a	39b
2,6	21.55(11.6)	25.55(8.9)	27.58(64.8)	28.69(64.2)
3,5	21.32(s)	24.86(5.1)	25.03(3.8)	22.37(5.8)
4	47.98(s)	48.48(s)	48.06(s)	49.03(s)
7	31.82(s)	31.93(s)	32.72(s)	33.03(s)
8,9,10	26.17(s)	26.70(s)	27.64(s)	27.48(8)
11	137.34(19.4)	140.60(15.6)	130.06(75.0)	133.31(94.9)
12,16	128.82(11.9)	129.40(15.6)	129.63(8.9)	129.95(9.0)
13,15	126.99(s)	126.98(7.6)	128.79(11.1)	128.35(11.1)
14	124.98(s)	126.64(s)	129.45(s)	131.42(s)

[a]Shifts are $\pm$ 0.03 ppm downfield from internal TMS. [b]Coupling constants are $\pm$ 0.7 Hz; s = singlet. [c]See Figure 5 for numbering of positions.

27b.[15] The ^{13}C chemical shift for C(3,5) in 38a (21.32 ppm) was at higher field as compared to that in 38b (24.86 ppm), which reflected the axial orientation of the phenyl group in 38a. The ^{31}P-^{13}C coupling constants ($^2J_{PC}$) of 0 Hz for 38a and 5.1 Hz for 38b are also similar to those reported for 27a (0 Hz) and 27b (7.5 Hz).[15] As discussed for 27a and 27b, these $^2J_{PC}$ values are representative of the disposition of the substituent on phosphorus, i.e., the larger coupling constant ($^2J_{PC}$) corresponds to the conformer where the dihedral angle (α) between the lone pair of electrons on phosphorus and the C(3) [or C(5)] atom is small (see structure 57).[15] Also carbon atoms 4, 7, and 8 (9,10) in 38a and 38b had very similar ^{13}C chemical shifts, probably relfecting minor geometric differences around C(4) in solution.



(equatorial phenyl, 38b)

57

The ^{13}C chemical shifts for the carbon atoms in the phenyl group in 38a and 38b were suggestive of the disposition of that group. For example, in 38a with axial phenyl, C(11) should be shielded compared to C(11) in 38b with equatorial phenyl. This was indeed the case and C(11) in 38a had a ^{13}C shift of 137.3 ppm compared to a value of 140.6 ppm in 38b. However, the ^{13}C signal for C(11) in 38b was nearly the

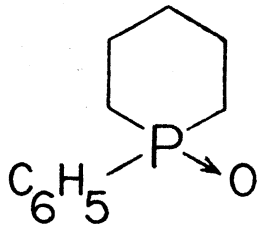
same (140.6 vs 141.3 ppm) as that for the same carbon in 1-phenylphosphorinane (24).[18] This similarity could have arisen from a solvent-induced shift[2] (C_6D_6 vs $DCCl_3$ for 38b) since the axial preference of several exocyclic P substituents in phosphorinanes has been well documented.[27] The ^{31}P-^{13}C coupling constant ($^1J_{PC}$) for C(11) in 38a was 19.1 Hz compared to 15.6 Hz for C(11) in 38b. This reduction in the coupling constant in 38b (presumably becoming less negative[18]) may have been due to a relief in steric strain about phosphorus with equatorial phenyl as compared to 38a with axial phenyl. The same observation was made for C(12,16) in 38b, i.e., $^2J_{PC}$ increased with a decrease in steric strain at phosphorus [$^2J_{PC}$ (38b) = 15.6 Hz vs $^2J_{PC}$ (38a) = 11.9 Hz]. The above conclusions were based on the assumption that $^1J_{PC}$ was negative and $^2J_{PC}$ was positive utilizing data reported for similar compounds.[18]

Phosphine oxides 38a and 39b gave quite interesting ^{13}C NMR results, further delineating the geometric configuration about phosphorus. The ^{13}C chemical shifts for C(2,6) in 39a appeared upfield at 27.58 ppm ($^1J_{PC}$ = 64.8 Hz) compared to the same carbon atoms at 28.69 ppm ($^1J_{PC}$ = 64.2 Hz) in 39b. This small shift difference probably reflects the steric comperession associated with axial phenyl in 39a.[9]

It was interesting to note that atoms C(3,5) in 39b (equatorial phenyl) were more shielded (22.37 vs 25.03 ppm) than C(3,5) in 39a (axial phenyl). These data compare favorably to those reported earlier concerning increased shielding at the γ-carbon (γ to oxygen) ("γ-shielding") caused by the change triethylphosphine→triethylphosphine oxide[17] and γ-shielding accompanying sulfurization of phosphines.[48]

Again carbon atoms 4, 7, and 8(9,10) were quite similar in both 39a and 39b, suggesting that the geometric and electronic environments about these atoms were similar.

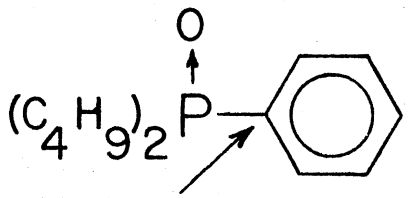
The striking feature found in the ^{13}C NMR spectra of the phenyl carbons [11,12(16), 13(15), and 14] of oxides 39a and 39b was the dramatic difference at C(11) in terms of both ^{13}C chemical shift and ^{31}P-^{13}C coupling constant. The ^{13}C chemical shift for C(11) in 39b of 133.31 ppm was close to the ^{13}C shift for the comparable carbon (134.29 ppm) in simple 1-phenylphosphorinane 1-oxide (58)[18], and



58

the $^{1}J_{PC}$ values were similarly close (94.9 Hz in 39b vs 92.6 Hz in 58), both in $DCCl_3$. This similarity was suggestive of prefential axial orientation of the oxygen atom in 58, an observation reported earlier with similarly substituted phosphorinane 1-sulfides.[12] However, the higher field signal for C(11) in 39a (130.06 vs 133.31 ppm in 39b) and the smaller $^{1}J_{PC}$ value of 75.0 Hz (vs 94.9 Hz for 39b more nearly resembled the same parameters found in dibutylphenylphosphine oxide (59) and 2,2-dimethyl-1-phenylphosphetane 1-oxide (60).[18] Consequently, that the ^{13}C chemical shift for C(11) in 39a and the corresponding $^{1}J_{PC}$ value were only the result of steric factors seems questionable. Interestingly, a small upfield ^{13}C

shift was observed for C(14) in 39a compared to C(14) in 39b (129.45 vs 131.42 ppm, $\Delta\delta$ -1.97).



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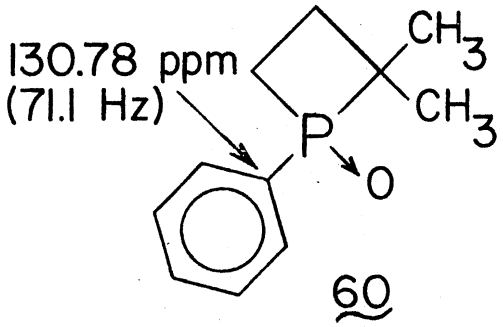

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A single crystal X-ray crystallographic analysis of oxide 39b further supported the ^{31}P and ^{13}C NMR data for phosphines 38a and 38b and oxides 39a and 39b discussed previously. A stereoview of a single molecule of 39b is shown in Figure 4, and the numbering scheme, bond distances, and bond angles are shown in Figure 5. The phosphorinane oxide 39b exists in a chair conformation as can be seen from the torsion angles reported in Table XIII. The tert-butyl and phenyl groups are in equatorial positions with the tert-butyl group staggered with respect to its attachment to the phosphorinane ring. With the exception of the phenyl group, oxide 39b possesses a pseudo mirror plane passing through atoms P(1), C(4), C(7), C(9), C(11) and O(1). The dihedral angle between the pseudo mirror plane and the plane defined by the atoms of the phenyl group is 20.1°. Alternatively, this can be viewed as a rotation of the phenyl group about the P(1)—C(11) bond away from the pseudo mirror plane resulting in a torsion angle O(1)-P(1)-C(11)-C(12) of 19.8°; the related torsion angles as reported in Table XIII.

The rotation (≃20°) of the phenyl group is a result of two close intramolecular contacts. The rotation cannot easily be less than 20°

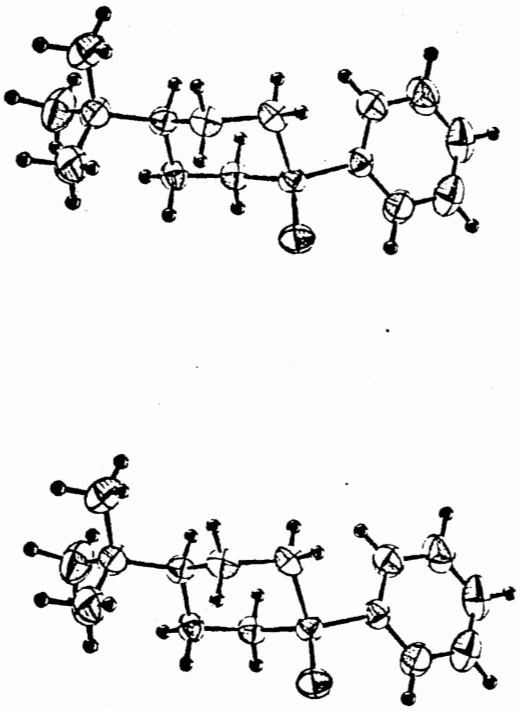


Figure 4. Stereoview of a single molecule of 39b.

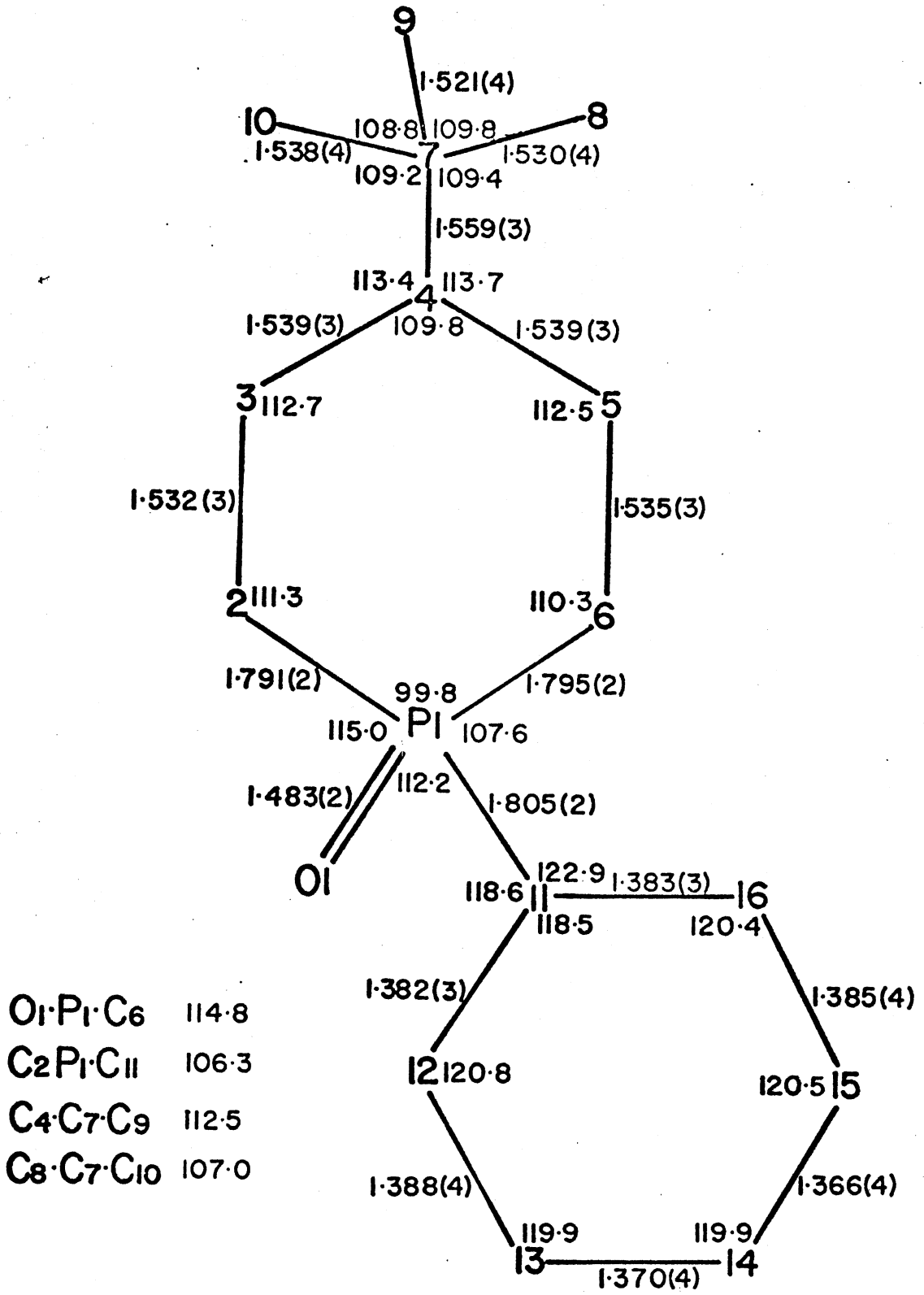


Figure 5. Numbering scheme, bond angles, and bond distances for 39b.

because of a contact between O(1) and H[C(12)] of 2.63 Å and cannot be greater than 20° because of a contact between H[C(6)] and H[C(16)] of 2.19 Å. These contacts result in a high rotational barrier for the phenyl group, and thus produce the observed conformation.

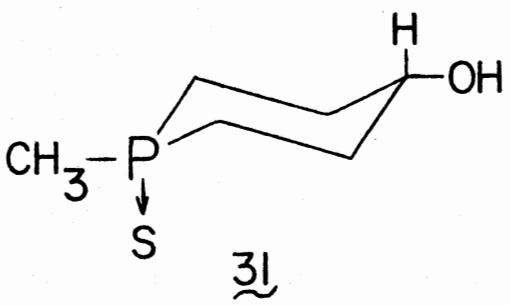
TABLE XIII

TORSION ANGLES FOR 39b

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

When the chair conformation in oxide 39b was compared to the chair conformations in 1-phenyl-4-phosphorinanone (28)[42], 4,4-dimethoxy-1-phenylphosphorinane (29)[43], trans-4-tert-butyl-1-methyl-4-phosphorinanol (27a)[44], and 4-substituted epimeric 1-methyl-4-phosphorinanol 1-sulfides[49] (all with axially oriented alkyl or aryl substituents on phosphorus), it was observed that the magnitudes of all torsion angles were larger for the present structure 39b. The difference is ca. 10° for the P(1)-C(2) type, 5° for the C(2)-C(3) type, and 2° for the

C(3)-C(4) type, indicating that the chair conformations for those phosphorinane structures are flattened with respect to the phosphorinane oxide ring in 39b. However, the average torsion angles in equatorial substituted sulfides 31 and 34[49] are only slightly smaller than those



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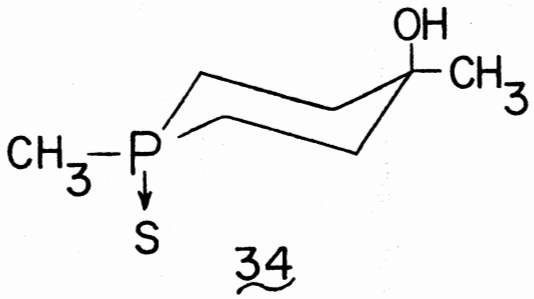

34

in 39b which conceivably results from the presence of sulfur with a larger van der Waals' radius of 1.85 Å compared to oxygen with a radius of 1.40 Å.[45] In addition, the average endocyclic bond angles at a ring C atom in 39b was 3° smaller than the average of the previously reported values for the phosphorinane ring systems. Also the endocyclic bond angle at the P atom was 2° larger. These observations are accountable on the basis of an equatorial phenyl group and the hydridization at phosphorus. The hybridization change on P is probably the main factor for resultant shortening of the P-C bond distances in 39b by 0.03-0.05 Å compared to the comparable bond in 4,4-dimethoxy-1-phenylphosphorinane (29)[43] and 1-phenyl-4-phosphorinanone (28).[42] The observation that the P(1)-C(11) (sp^2) bond length of 1.805(2) Å in 39b was greater than two reported[21,61] P-C(sp^3) bond lengths [average of 1.793 Å] is somewhat unusual. Comparison of the P(1)-C(11) bond length in 39b with that in the salts reported[21,61] may not be entirely legitimate since the angles around P exhibit about 1% variation. Nevertheless, the C_6H_5-P distance compared well with average value of 1.80 Å reported for the P-C(sp^2) bond length for a large number of compounds.[6] Many factors influence

the P-C bond length, e.g., hybridization, charge, valency, and steric factors, resulting in wide variations for these distances in P-C heterocycles; accordingly more observations seem necessary to correlate these factors with bond length.

The electronegativity of the substituents attached to phosphorus influence the P→O bond length. The value of 1.483 Å in 39b is considered normal and can be compared to a value of 1.48 Å determined by electron diffraction of trimethylphosphine oxide.[60] The value of 1.483 Å for P→O bond length in 39b is somewhat larger than the average value of 1.462 Å reported[6] for many compounds having highly electronegative atoms attached to the phosphorus atom.

The average C-C (phenyl) bond length was 1.379 Å, which is only an apparent shortening due to thermal motion, and can be correlated with the distance of the bonding atoms from the center of the molecule. A calculation of intermolecular distances based on final parameters for 39b revealed no unusually short contacts (see Tables XIV and XV). Table XVI contains a listing of observed and calculated structure factor amplitudes.

TABLE XIV

POSITIONAL PARAMETERS ($\times 10^4$) AND ANISOTROPIC TEMPERATURE FACTORS ($\times 10^4$) FOR P, C, AND O ATOMS; ANISOTROPIC THERMAL FACTORS ARE OF THE FORM EXP $[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$; ESTIMATED STANDARD DEVIATION FOR THE LAST DIGIT ARE GIVEN IN PARENTHESES

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	668.1(4)	1095.8(9)	1329.9(3)	421(2)	332(2)	384(2)	-21(2)	86(2)	14(3)
O(1)	488(1)	-1387(2)	1288(1)	626(9)	352(8)	671(11)	-56(7)	123(8)	3(8)
C(2)	44(2)	2635(4)	546(1)	477(11)	456(12)	386(11)	-2(9)	117(8	20(9)
C(3)	-1178(2)	2629(4)	422(1)	462(11)	501(13)	393(11)	1(10)	72(8)	7(9)
C(4)	-1562(2)	3787(4)	1023(1)	432(10)	374(11)	484(11)	-14(9)	113(8)	16(10)
C(5)	-1135(2)	2490(4)	1719(1)	515(12)	479(13)	429(11)	-35(10)	164(9)	12(9)
C(6)	93(2)	2533(4)	1960(1)	496(11)	506(13)	373(11)	-42(10)	105(9)	32(9)
C(7)	-2795(2)	4201(4)	844(1)	485(12)	493(13)	652(14)	36(10	149(10)	-6(12)
C(8)	-3125(2)	5610(5)	167(2)	724(17)	970(23)	754(18)	327(17)	132(14)	189(17)
C(9)	-3432(2)	2007(5)	756(2)	482(13)	659(17)	1259(27)	-87(13)	138(15)	-121(19)
C(10)	-3076(2)	5598(5)	1440(2)	674(16)	725(18)	832(20)	144(14)	293(14)	-53(15)
C(11)	2074(2)	1809(4)	1527(1)	449(10)	437(11)	404(11)	4(9)	61(8)	48(9)
C(12)	2790(2)	207(4)	1403(1)	531(13)	588(15)	690(14)	63(11)	129(11)	38(13)
C(13)	3876(2)	688(5)	1536(2)	496(13)	865(21)	973(22)	134(14)	188(14)	120(18)
C(14)	4252(2)	2757(5)	1803(2)	446(13)	913(21)	883(20)	-72(14)	34(13)	251(17)
C(15)	3552(2)	4358(5)	1926(2)	567(14)	696(18)	886(20)	-157(13)	16(13)	26(16)
C(16)	2465(2)	3905(4)	1784(1)	522(13)	545(14)	723(16)	-58(12)	99(11)	-23(13)

TABLE XV

POSITIONAL PARAMETERS ($\times 10^3$) AND ISOTROPIC TEMPERATURE FACTOR ($Å^2$) FOR HYDROGEN ATOMS: ESTIMATED STANDARD DEVIATION FOR THE LAST DIGIT IS GIVEN IN PARENTHESES

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

TABLE XVI

OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES FOR 39b

F_o = Observed Structure Amplitude

F_c = Calculated Structure Amplitude

h,k,l = general indices (identify each different direction of X-ray radiation)

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC
K=	0 H=-16		4	15	16	18	8	9	24	6	6	4	2	-2*
8	7	7	6	25	27	20	8	8	K=	0 H= -1		6	44	45
4	2	-3*	8	32	-32	22	12	-12	2	29	29	8	6	7
6	4	5	10	30	-31	24	2	-3	4	143	-160	10	28	-29
K=	0 H=-15		12	19	20	K=	0 H= -5		6	37	-38	12	5	-5
2	3	2	14	9	9	2	73	76	8	56	56	14	31	33
4	13	-12	16	12	-13	4	10	10	10	12	-12	16	2	-4*
6	6	6	18	2	-1*	6	40	-42	12	55	-56	18	21	-22
8	13	12	20	13	13	8	8	-8	14	11	-13	20	6	7
10	6	-6	22	2	1*	10	36	36	16	26	26	22	4	4
12	7	-7	K=	0 H=	9	12	2	-2*	18	2	0*	K=	0 H=	4
14	4	4	2	5	-6	14	22	-23	20	5	-5	0	6	-7
K=	0 H=-14		4	31	31	16	6	5	22	10	10	2	27	-28
2	6	-6	6	20	19	18	18	18	24	4	4	4	2	-2*
4	7	-6	8	44	-44	20	2	3*	K=	0 H=	0	6	39	40
6	11	10	10	5	-4	22	11	-12	2	13	-12	8	7	6
8	2	1*	12	17	17	24	2	2*	4	129	-142	10	37	-37
10	11	-10	14	14	-15	K=	0 H= -4		6	90	93	12	6	7
12	4	-5	16	2	-2*	2	10	11	8	2	3*	14	33	35
14	7	8	18	13	13	4	2	-3	10	25	-25	16	2	-2*
16	2	1*	20	9	9	6	54	-55	12	20	-22	18	10	-11
K=	0 H=-13		22	2	-2*	8	17	-16	14	11	11	20	10	10
2	10	-10	K=	0 H=	-8	10	45	45	16	15	16	K=	0 H=	5
4	2	-2*	2	2	0*	12	13	-14	18	14	-15	0	19	-20
6	16	16	4	28	29	14	22	-22	20	2	0*	2	116	-118
8	5	5	6	2	1*	16	18	18	22	11	11	4	20	21
10	14	-13	8	37	-38	18	5	5	K=	0 H=	1	6	33	32
12	2	0*	10	9	9	20	7	-7	0	86	95	8	43	-43
14	10	9	12	8	8	22	6	-5	2	6	-6	10	14	-15
16	2	-2*	14	26	-28	24	4	4	4	60	62	12	12	11
18	5	-5	16	9	-9	K=	0 H= -3		6	27	27	14	9	9
K=	0 H=-12		18	18	18	2	65	66	8	2	1*	16	2	-4*
2	10	-11	20	8	9	4	27	-27	10	26	-25	18	2	-1*
4	2	-1*	22	6	-6	6	36	-37	12	20	-21	20	13	14
6	9	9	K=	0 H=	-7	8	3	0	14	20	20	K=	0 H=	6
8	11	-11	2	20	20	10	25	25	16	8	7	0	9	-9
10	3	3	4	30	31	12	30	-31	18	10	-10	2	55	-55
12	6	6	6	7	-7	14	4	5	20	3	3	4	49	49
14	2	1*	8	30	-30	16	43	43	22	7	7	6	12	-12
16	4	5	10	20	20	18	2	-1*	K=	0 H=	2	8	36	-37
18	4	-5	12	11	12	20	11	-11	0	10	-10	10	5	6
20	6	5	14	28	-28	22	2	0*	2	28	-27	12	8	8
K=	0 H=-11		16	12	-12	24	4	5	4	38	-37	14	2	0*
2	16	-15	18	11	11	K=	0 H= -2		6	42	41	16	8	-8
4	14	13	20	7	7	2	7	-8	8	2	3*	18	5	5
6	2	-1*	22	9	-9	4	48	49	10	37	-36	K=	0 H=	7
8	24	-25	K=	0 H=	-6	6	66	-68	12	9	-9	0	6	6
10	6	-7	2	108	111	8	4	4	14	12	13	2	10	9
12	2	2*	4	23	25	10	27	27	16	2	-3*	4	20	22
14	11	12	6	39	-40	12	64	-65	18	13	-14	6	11	-10
16	2	-1*	8	3	1	14	8	-8	20	2	2*	8	26	-26
18	12	-12	10	34	34	16	51	52	22	6	6	10	5	5
20	12	12	12	3	-1	18	10	10	K=	0 H=	3	12	12	13
K=	0 H=-10		14	10	-11	20	9	-9	0	105	112	14	4	-4
2	15	-15	16	2	-1*	22	3	4	2	40	-41	16	4	-4

TABLE XVI (Continued)

L	FO	FC
18	6	6
K=	0 H=	8
0	8	-9
2	4	-3
4	28	28
6	10	-11
8	41	-41
10	6	6
12	9	10
14	7	-8
16	2	-2*
K=	0 H=	9
0	10	-10
2	11	12
4	32	34
6	10	-10
8	25	-25
10	6	6
12	2	0*
14	8	-9
16	1	-2*
K=	0 H=	10
0	5	-4
2	18	18
4	10	10
6	7	-7
8	5	4
10	7	7
12	2	-4*
14	4	-4
K=	0 H=	11
0	4	-1
2	12	12
4	5	-6
6	10	-9
8	2	0*
10	7	7
12	2	0*
K=	0 H=	12
0	2	2*
2	9	9
4	3	4
6	13	-13
8	2	0*
10	9	9
K=	0 H=	13
0	4	3
2	10	10
4	8	-8
6	10	-10
8	12	12
K=	0 H=	14
0	13	13
2	2	2*
4	11	-11
6	9	-8
K=	0 H=	15
0	9	9
2	1	1*
K=	1 H=	-15
1	6	6
2	9	-9
3	6	-6
4	2	-1*
5	2	-2*
6	9	8
7	5	5
8	5	-6
9	2	-1*
10	8	-7
11	5	-6
12	3	3
13	1	2*
K=	1 H=	-14
1	3	2
2	8	-7
3	6	-6
4	3	3
5	2	1*
6	4	4
7	11	10
8	6	-5
9	2	-2*
10	4	-4
11	8	-8
12	3	3
13	3	3
14	4	5
15	6	6
16	4	-4
K=	1 H=	-13
1	7	-7
2	2	-1*
3	11	-11
4	6	6
5	8	8
6	5	5
7	5	4
8	4	-4
9	7	-7
10	3	-3
11	3	-1
12	3	4
13	5	5
14	4	3
15	3	3
16	3	-3
17	5	-5
18	1	1*
K=	1 H=	-12
1	12	-12
2	10	-10
3	3	-1
4	7	8
5	8	8
6	3	-2
7	2	-1*
8	2	-1*
9	9	-8
10	7	7
11	5	-5
12	2	-1*
13	7	8
14	3	4
15	2	3*
16	3	-3
17	6	-6
18	2	-1*
19	3	-2
K=	1 H=	-11
1	2	1*
2	2	-1*
3	4	-4
4	2	1*
5	7	7
6	11	-11
7	18	19
8	2	1*
9	8	-8
10	4	5
11	9	-10
12	5	6
13	10	10
14	9	9
15	4	3
16	8	-8
17	6	-6
18	2	1*
19	2	1*
20	8	8
21	4	5
K=	1 H=	-10
1	20	-21
2	5	-5
3	16	-16
4	11	12
5	21	21
6	9	-10
7	4	-1
8	17	-17
9	12	-12
10	14	14
11	13	13
12	11	12
13	8	8
14	2	1*
15	10	-10
16	3	1
17	6	-6
18	4	5
19	8	8
20	2	2*
21	6	6
K=	1 H=	9
1	26	-27
2	11	-12
3	15	15
4	15	17
5	11	12
6	26	-28
7	33	-33
8	21	-21
9	9	-10
10	19	20
11	21	21
12	2	2*
13	9	9
14	2	0*
15	15	-16
16	9	10
17	8	-8
18	4	5
19	9	9
20	3	-2
21	2	2*
22	4	-4
K=	1 H=	-8
1	7	7
2	6	-5
3	32	32
4	10	10
5	5	6
6	23	-23
7	11	-12
8	20	-20
9	10	-11
10	8	8
11	11	11
12	6	-5
13	11	11
14	2	-1*
15	8	-9
16	12	13
17	2	-3*
18	6	6
19	6	6
20	4	-4
21	2	-1*
22	3	-2
23	5	-5
K=	1 H=	-7
1	20	-20
2	2	2
3	16	16
4	5	6
5	17	16
6	20	-20
7	17	-18
8	3	3
9	2	-2*
10	6	6
11	18	18
12	17	-17
13	2	-3*
14	2	1*
15	10	-10
16	11	12
17	6	7
18	4	4
19	8	8
20	3	-3
21	3	-3
22	2	-2*
23	2	-3*
K=	1 H=	-6
1	27	-27
2	2	0*
3	25	25
4	30	-30
5	9	-9
6	5	-6
7	37	-37
8	10	10
9	8	9
10	5	-5
11	19	19
12	2	-3*
13	9	-10
14	2	1*
15	16	-17
16	2	0*
17	7	7
18	7	7
19	7	7
20	5	-4
21	7	-7
22	5	-5
23	3	-3
K=	1 H=	-5
1	38	39
2	9	-9
3	29	31
4	6	5
5	16	-16
6	4	-4

TABLE XVI (Continued)

L	FO	FC
7	10	-11
8	14	-13
9	15	17
10	4	4
11	13	13
12	2	0*
13	13	-13
14	2	-2*
15	7	-8
16	2	0*
17	11	11
18	2	3*
19	2	2*
20	6	-6
21	10	-10
22	5	-6
23	2	-3*
24	4	5
K=	1	H= -4
1	34	34
2	24	25
3	30	30
4	13	13
5	39	-39
6	17	-17
7	4	-4
8	34	34
9	57	57
10	9	8
11	2	1*
12	14	-13
13	28	-28
14	14	14
15	7	6
16	3	-1
17	19	20
18	7	-7
19	2	1*
20	2	-2*
21	9	-9
22	3	-3
23	3	1
24	1	1*
K=	1	H= -3
1	19	19
2	10	-11
3	7	-6
4	22	-24
5	73	-75
6	40	-38
7	2	-1*
8	30	31
9	37	36
10	22	21
11	2	-3*
12	2	-2*
13	18	-19
14	26	26
15	7	-8
16	2	1*
17	11	12
18	14	-14
19	2	1*
20	2	-1*
21	8	-7
22	2	0*
23	4	4
24	1	-1*
K=	1	H= -2
1	73	76
2	1	-2*
3	18	-18
4	3	-2
5	12	-12
6	65	-66
7	4	-4
8	5	5
9	9	9
10	12	-12
11	17	16
12	2	-3*
13	16	-15
14	39	39
15	2	-2*
16	2	2*
17	8	8
18	13	-13
19	11	-11
20	2	2*
21	6	-5
22	2	-2*
23	7	7
24	4	-5
K=	1	H= -1
1	74	80
2	75	-80
3	35	35
4	17	-17
5	43	-42
6	30	32
7	3	2
8	4	-4
9	53	53
10	22	-23
11	22	-22
12	5	5
13	16	-16
14	23	23
15	32	33
16	4	3
17	3	5
18	2	-3*
19	17	-17
20	5	5
21	2	0*
22	3	-3
23	8	8
K=	1	H= 0
1	8	-9
2	130	-150
3	45	-45
4	25	25
5	51	-53
6	44	-45
7	61	62
8	18	-19
9	2	0*
10	28	27
11	51	-51
12	2	1*
13	6	6
14	10	11
15	18	18
16	3	3
17	2	-2*
18	3	2
19	9	-9
20	7	7
21	2	1*
22	2	-2*
23	5	6
K=	1	H= 1
0	5	-5
1	14	-14
2	5	4
3	95	-97
4	4	4
5	38	38
6	65	-66
7	59	59
8	28	-27
9	23	-24
10	2	-1*
11	18	-17
12	7	7
13	5	5
14	3	3
15	5	4
16	2	-4*
17	5	-5
18	7	7
19	8	-8
20	4	4
21	2	2*
22	2	-1*
23	3	3
K=	1	H= 2
0	44	45
1	27	27
2	17	-18
3	38	-39
4	14	15
5	2	1
6	2	2*
7	37	37
8	23	-23
9	13	11
10	2	-1*
11	14	-15
12	4	4
13	8	8
14	4	-3
15	14	15
16	7	-8
17	5	-6
18	4	3
19	6	-7
20	4	4
21	5	5
22	2	-2*
K=	1	H= 3
0	15	14
1	21	-21
2	13	13
3	27	-27
4	6	-5
5	2	-1
6	13	-13
7	18	20
8	6	5
9	12	-13
10	2	1*
11	14	-15
12	10	11
13	9	9
14	2	3*
15	7	8
16	15	-15
17	6	-5
18	4	4
19	3	-3
20	3	4
21	6	7
K=	1	H= 4
0	5	5
1	37	-38
2	11	11
3	28	-29
4	2	2
5	29	29
6	7	-7
7	14	14
8	12	-11
9	18	-18
10	2	3*
11	8	-9
12	15	16
13	11	11
14	2	-1*
15	2	-1*
16	10	-11
17	15	-15
18	6	5
19	3	2
20	2	-1*
21	9	9
K=	1	H= 5
0	56	-56
1	18	-18
2	7	-7
3	10	-10
4	21	22
5	26	25
6	20	-20
7	11	11
8	5	4
9	20	-21
10	11	11
11	4	5
12	2	1*
13	24	24
14	2	2*
15	8	-8
16	4	-4
17	14	-14
18	5	5
19	6	6
20	3	-3
K=	1	H= 6
0	39	-38
1	23	-23
2	7	8
3	18	19
4	13	-13
5	24	24
6	24	-24
7	16	-16
8	21	22
9	25	-25
10	12	12
11	15	15
12	2	-1*
13	10	10
14	2	3*
15	7	-7

TABLE XVI (Continued)

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC
16	4	3	11	12	12	5	6	-6	12	2	3*	9	4	-4
17	2	0*	12	3	-3	6	8	8	13	5	5	10	5	-5
18	6	6	13	2	-2*	7	2	-1*	14	4	2	11	7	7
19	2	2*	14	4	4	8	6	6	15	6	-6	12	8	7
K=	1	H= 7	15	7	-6	K=	1	H= 14	16	4	-4	13	7	-7
0	5	-6	16	3	4	0	5	-4	17	6	-6	14	9	8
1	34	-35	K=	1	H= 10	1	6	5	K=	2	H=-12	15	10	-10
2	2	-1*	0	7	7	2	10	-11	1	6	-5	16	10	-10
3	9	9	1	7	9	3	2	-3*	2	2	2*	17	6	6
4	13	-14	2	3	2	4	2	-2*	3	8	7	18	3	-4
5	27	27	3	9	9	5	3	-4	4	2	2*	19	8	8
6	26	-27	4	2	-4*	6	3	3	5	3	3	20	2	-2*
7	13	-13	5	4	-4	K=	1	H= 15	6	2	3*	21	6	-6
8	11	12	6	2	-4*	0	5	-4	7	2	-1*	K=	2	H= 9
9	12	-12	7	12	-11	1	5	5	8	8	9	1	2	-4*
10	15	15	8	2	2*	2	4	-4	9	5	-5	2	7	7
11	4	5	9	2	2*	K=	2	H=-15	10	2	-1*	3	14	14
12	7	-7	10	4	-5	1	4	-4	11	6	5	4	6	5
13	2	-2*	11	6	6	2	4	-3	12	2	0*	5	10	-9
14	4	3	12	3	-3	3	7	-7	13	8	8	6	3	-1
15	5	-4	13	5	-6	4	2	0*	14	2	-1*	7	3	-2
16	9	9	14	3	3	5	5	5	15	6	-6	8	18	18
17	2	-1*	K=	1	H= 11	6	2	-2*	16	4	-4	9	18	19
18	2	3	0	5	5	7	4	4	17	5	-5	10	7	6
K=	1	H= 8	1	2	-1*	8	2	1*	18	2	1*	11	8	8
0	3	-2	2	7	-8	9	3	-3	K=	2	H=-11	12	2	1*
1	25	-25	3	7	7	10	4	4	1	4	-4	13	11	-12
2	5	-5	4	4	-5	11	1	0*	2	6	-5	14	5	5
3	8	8	5	2	-1*	K=	2	H=-14	3	4	4	15	11	-11
4	13	-14	6	3	4	1	5	-6	4	7	-7	16	2	-2*
5	12	12	7	4	-5	2	4	-3	5	13	14	17	7	7
6	23	-24	8	4	2	3	2	-2*	6	2	3*	18	2	-1*
7	2	-3*	9	5	6	4	2	-3*	7	9	-9	19	5	6
8	9	9	10	3	-3	5	7	7	8	9	9	20	3	-2
9	2	2*	11	3	3	6	4	-4	9	13	-13	21	5	-5
10	7	8	12	2	-3*	7	2	-2*	10	2	-2*	K=	2	H= -8
11	6	7	K=	1	H= 12	8	2	2*	11	9	10	1	22	23
12	6	-7	0	6	7	9	8	-8	12	4	5	2	18	-17
13	2	2*	1	9	9	10	2	0*	13	5	5	3	14	14
14	3	4	2	2	-3*	11	3	3	14	3	3	4	7	-7
15	7	-8	3	9	9	12	2	-1*	15	6	-5	5	19	-19
16	4	4	4	6	-6	13	6	5	16	10	-10	6	15	-16
17	1	-1*	5	10	-10	14	2	2	17	2	1*	7	13	-14
K=	1	H= 9	6	2	1*	K=	2	H=-13	18	2	-2*	8	11	11
0	17	18	7	3	-3	1	13	-13	19	3	4	9	15	16
1	4	4	8	8	8	2	2	-1*	20	2	-2*	10	14	14
2	4	-4	9	7	7	3	2	4*	K=	2	H=-10	11	17	17
3	20	21	10	5	-5	4	2	-3*	1	23	-25	12	2	1*
4	12	-12	11	2	2	5	12	11	2	4	-4	13	10	-10
5	10	-10	K=	1	H= 13	6	5	4	3	14	14	14	4	4
6	14	-14	0	2	3*	7	5	-6	4	8	8	15	6	-6
7	12	-13	1	8	8	8	2	1*	5	19	20	16	4	-1
8	2	2*	2	4	-3	9	9	-8	6	2	2*	17	9	10
9	4	5	3	2	2*	10	8	-8	7	14	-14	18	3	-3
10	4	2	4	5	-5	11	3	3	8	5	5	19	2	0*

TABLE XVI (Continued)

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC
20	3	0	5	15	-15	12	2	0*	19	3	4	1	44	-46
21	6	-6	6	24	-24	13	5	-6	20	9	-9	2	1	-2*
22	2	-1*	7	5	6	14	2	5*	21	11	11	3	15	15
K=	2	H= -7	8	2	1*	15	7	8	22	2	-3*	4	2	1*
1	13	13	9	13	13	16	9	-9	23	1	-1*	5	10	10
2	10	-10	10	15	14	17	2	1*	K=	2	H= 0	6	20	-20
3	19	21	11	5	-5	18	5	-5	0	21	-21	7	4	-3
4	3	-3	12	3	-1	19	8	-8	1	6	-6	8	4	3
5	8	-8	13	5	-4	20	4	-4	2	6	-6	9	3	-3
6	11	-11	14	12	-12	21	4	3	3	14	-14	10	4	-5
7	17	-19	15	10	11	22	2	-1*	4	24	-24	11	5	5
8	2	-2*	16	4	-1	23	4	4	5	30	29	12	2	-2*
9	9	9	17	4	4	K=	2	H= -2	6	4	5	13	5	5
10	7	-6	18	7	8	1	31	31	7	2	0*	14	2	2*
11	6	6	19	9	-9	2	6	7	8	41	41	15	6	-5
12	11	11	20	6	-6	3	18	-18	9	54	-54	16	3	0
13	14	-14	21	2	-2*	4	8	-7	10	6	6	17	4	-4
14	7	7	22	2	1*	5	3	-2	11	10	10	18	2	0*
15	2	0*	23	8	8	6	2	0*	12	2	0*	19	6	5
16	6	-7	K=	2	H= -4	7	25	25	13	20	21	20	2	-1*
17	10	9	1	5	6	8	32	32	14	13	13	21	2	3*
18	2	0*	2	25	25	9	22	22	15	13	-13	K=	2	H= 3
19	3	-4	3	9	8	10	4	-3	16	2	-2*	0	23	23
20	2	-1*	4	17	-17	11	11	-10	17	12	-11	1	20	-20
21	4	-4	5	12	-12	12	10	10	18	8	-8	2	23	-23
22	2	-2*	6	6	-6	13	6	-5	19	2	2*	3	2	3
K=	2	H= -6	7	7	8	14	2	1*	20	4	-4	4	18	-18
1	12	12	8	6	6	15	13	14	21	4	4	5	3	0
2	7	-7	9	2	2*	16	13	-14	22	2	1*	6	23	22
3	2	1*	10	11	-11	17	9	-9	K=	2	H= 1	7	15	-15
4	9	8	11	19	-18	18	5	4	0	53	-53	8	4	4
5	10	-10	12	5	5	19	5	-5	1	7	-7	9	11	-11
6	10	10	13	5	-5	20	7	-6	2	18	-19	10	6	-6
7	10	9	14	8	-8	21	12	12	3	20	19	11	9	10
8	9	-9	15	13	14	22	6	-6	4	4	-4	12	8	9
9	9	9	16	6	-8	23	2	1*	5	48	47	13	2	2*
10	2	1*	17	6	6	K=	2	H= -1	6	24	-24	14	2	-2*
11	7	-8	18	2	2*	1	3	-3	7	7	-7	15	10	-10
12	9	9	19	10	-10	2	15	15	8	6	7	16	6	-5
13	9	-8	20	9	-9	3	6	5	9	17	-17	17	2	-2*
14	6	-6	21	2	-2*	4	14	-14	10	8	8	18	2	1*
15	2	4*	22	2	2*	5	17	-16	11	8	8	19	8	7
16	3	2	23	8	8	6	7	-7	12	8	8	20	2	-1*
17	2	2*	K=	2	H= -3	7	4	4	13	4	4	21	2	0*
18	6	6	1	5	4	8	21	19	14	9	9	K=	2	H= 4
19	4	-5	2	10	10	9	2	-2*	15	2	-1*	0	1	-1*
20	3	-4	3	34	-35	10	6	6	16	4	3	1	22	22
21	2	-2*	4	3	-3	11	9	-10	17	6	-6	2	4	-5
22	2	0*	5	4	4	12	2	4*	18	3	-2	3	16	17
23	3	3	6	34	34	13	19	19	19	2	1*	4	6	5
K=	2	H= -5	7	37	36	14	4	-5	20	4	-3	5	2	1*
1	16	17	8	24	24	15	2	1*	21	4	5	6	2	0*
2	14	-13	9	8	-8	16	4	-4	22	2	3*	7	4	-3
3	9	8	10	10	-10	17	19	-19	K=	2	H= 2	8	7	-5
4	11	11	11	22	-22	18	2	-1*	0	60	-60	9	2	-2*

TABLE XVI (Continued)

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC
10	2	-1*	2	21	21	3	11	-11	1	2	1*	12	7	7
11	7	7	3	24	25	4	11	-11	2	6	-6	13	4	-4
12	9	9	4	15	-15	5	2	-4*	3	3	3	14	13	-13
13	2	0*	5	15	-14	6	9	-9	4	3	0	15	3	3
14	2	-2*	6	2	-3*	7	5	4	5	4	-3	16	11	-11
15	12	-12	7	11	-10	8	10	10	6	9	9	17	3	2
16	2	-3*	8	24	24	9	5	5	7	2	-1*	18	6	7
17	4	3	9	8	8	10	4	3	8	2	0*	K=	3	H=-10
18	2	1*	10	2	-1*	11	5	-6	9	5	5	1	7	7
19	11	12	11	2	-5*	12	2	1*	10	7	-7	2	22	22
20	3	-3	12	6	7	13	5	-5	11	2	2*	3	2	3*
K=	2	H= 5	13	6	-6	K=	2	H= 11	K=	3	H=-13	4	5	6
0	29	-29	14	5	6	0	2	-1*	1	6	6	5	5	-5
1	2	3*	15	2	3*	1	5	6	2	9	-8	6	6	-5
2	11	11	16	6	-8	2	2	-1*	3	5	4	7	2	-2*
3	9	10	17	2	3	3	2	-2*	4	7	6	8	5	-4
4	6	5	K=	2	H= 8	4	2	-3*	5	6	-6	9	2	3*
5	2	-2*	0	17	-17	5	7	-7	6	6	6	10	6	7
6	12	12	1	15	15	6	2	-2*	7	4	-4	11	2	-3*
7	11	-11	2	2	-1*	7	10	10	8	9	-9	12	12	12
8	6	-5	3	7	7	8	2	-2*	9	4	4	13	4	-5
9	9	9	4	3	-3	9	7	7	10	2	-1	14	13	-14
10	11	-11	5	9	-9	10	2	0*	11	3	3	15	5	6
11	21	21	6	8	9	11	8	-7	12	8	8	16	9	-9
12	6	7	7	12	12	12	1	-1*	13	3	-2	17	5	5
13	11	-11	8	2	-2*	K=	2	H= 12	14	2	-2*	18	6	6
14	8	-8	9	9	9	0	2	-3*	K=	3	H=-12	19	4	-4
15	15	-15	10	3	-3	1	8	7	1	6	6	K=	3	H= 9
16	7	-7	11	6	-7	2	2	0*	2	2	-2*	1	2	1*
17	11	11	12	11	11	3	13	-12	3	3	3	2	23	25
18	2	2*	13	7	-7	4	2	0*	4	11	10	3	2	1*
19	7	8	14	2	-2*	5	6	-5	5	5	-5	4	10	11
K=	2	H= 6	15	4	4	6	2	1*	6	2	2*	5	6	-7
0	8	-8	16	4	-4	7	9	9	7	5	-4	6	4	-3
1	8	8	K=	2	H= 9	8	2	1*	8	12	-12	7	5	3
2	2	-1*	0	27	-28	9	2	1*	9	2	3*	8	9	-10
3	17	17	1	14	13	10	2	-2	10	2	-1*	9	5	6
4	2	5*	2	9	-8	K=	2	H= 13	11	2	3*	10	4	5
5	19	-19	3	18	-19	0	7	6	12	5	4	11	12	-11
6	13	14	4	12	12	1	2	0*	13	4	-5	12	5	5
7	31	-32	5	11	-12	2	2	2*	14	8	-8	13	8	-8
8	11	11	6	7	-6	3	8	-8	15	2	-2*	14	12	-13
9	15	15	7	10	10	4	3	-2	16	2	-2*	15	8	8
10	5	5	8	4	3	5	3	3	K=	3	H=-11	16	2	-1*
11	16	16	9	8	8	6	5	5	1	8	8	17	4	4
12	2	3*	10	10	10	7	4	4	2	2	0*	18	5	5
13	15	-15	11	6	-5	K=	2	H= 14	3	2	0*	19	5	-5
14	6	-7	12	2	1*	0	2	-1*	4	7	7	20	4	-5
15	4	-4	13	7	-8	1	3	-3	5	8	-8	K=	3	H= -8
16	7	-7	14	3	-3	2	3	3	6	5	6	1	18	18
17	5	6	15	3	3	3	4	-4	7	2	0*	2	10	10
18	2	-2	K=	2	H= 10	4	1	0*	8	6	-6	3	19	-19
K=	2	H= 7	0	7	-7	K=	2	H= 15	9	6	6	4	13	14
0	10	-11	1	8	7	0	1	-1*	10	2	-2*	5	11	-12
1	23	24	2	11	11	K=	3	H=-14	11	2	-2*	6	2	1*

TABLE XVI (Continued)

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC
7	22	22	18	2	0*	5	22	22	14	3	3	1	23	23
8	7	8	19	2	1*	6	3	4	15	9	-9	2	16	14
9	4	4	20	8	-8	7	11	10	16	4	-4	3	38	37
10	2	3*	21	2	2	8	3	4	17	3	3	4	4	4
11	15	-16	K=	3	H= -5	9	27	-27	18	10	-10	5	5	-5
12	7	-6	1	5	-4	10	9	-9	19	9	9	6	20	20
13	4	-3	2	10	9	11	8	-9	20	2	2*	7	20	-20
14	10	-11	3	12	-13	12	5	-5	21	2	-1*	8	12	-12
15	9	9	4	13	-13	13	16	16	K=	3	H= 0	9	4	3
16	2	-2*	5	7	8	14	5	5	1	20	-20	10	9	-9
17	2	0*	6	3	-4	15	2	0*	2	13	-13	11	8	9
18	2	4*	7	6	7	16	3	3	3	17	17	12	19	18
19	5	-6	8	10	10	17	11	-10	4	8	8	13	4	-2
20	4	-4	9	13	-14	18	8	-7	5	13	13	14	2	0*
21	3	2	10	2	-2*	19	4	4	6	38	38	15	2	-3*
K=	3	H= -7	11	2	1*	20	2	0*	7	21	-21	16	13	-12
1	10	11	12	15	-15	21	6	6	8	11	12	17	2	2*
2	25	26	13	7	8	22	12	12	9	5	-5	18	2	0*
3	21	-22	14	9	-8	K=	3	H= -2	10	9	-10	19	4	4
4	13	-13	15	2	2*	1	40	-39	11	14	14	20	7	7
5	2	4*	16	13	13	2	12	11	12	4	5	K=	3	H= 3
6	7	-7	17	2	-6*	3	11	-11	13	6	-5	0	29	-29
7	16	16	18	3	0	4	7	-7	14	2	1*	1	2	-1*
8	24	25	19	3	-4	5	32	31	15	10	-10	2	6	-5
9	2	-1*	20	6	-6	6	30	30	16	10	-11	3	14	14
10	13	13	21	3	4	7	9	-9	17	2	2*	4	32	32
11	11	-12	22	6	6	8	10	-10	18	4	-5	5	7	-8
12	6	-6	K=	3	H= -4	9	24	-25	19	5	5	6	7	7
13	2	2*	1	4	-5	10	32	-32	20	7	7	7	8	-8
14	9	-8	2	2	0*	11	10	10	21	2	1*	8	16	-15
15	10	10	3	2	-1*	12	2	3*	K=	3	H= 1	9	2	4*
16	6	6	4	28	-29	13	13	13	0	33	-33	10	13	13
17	4	-4	5	11	11	14	4	-3	1	7	-7	11	4	3
18	2	2*	6	13	14	15	9	-9	2	5	3	12	12	12
19	2	-3*	7	2	2*	16	2	-2*	3	30	29	13	5	-6
20	7	-7	8	13	13	17	7	-6	4	3	3	14	8	-9
21	4	4	9	13	-14	18	6	-6	5	2	2*	15	5	-4
K=	3	H= -6	10	2	0*	19	9	9	6	3	4	16	2	-2*
1	18	-18	11	9	-9	20	5	-5	7	28	-29	17	5	5
2	18	18	12	12	-13	21	3	2	8	2	0*	18	4	4
3	11	-12	13	10	11	22	10	10	9	3	0	19	3	2
4	12	-13	14	2	-4*	K=	3	H= -1	10	2	-3*	20	6	6
5	9	10	15	11	11	1	15	-15	11	16	16	K=	3	H= 4
6	15	-15	16	11	12	2	10	-11	12	13	13	0	38	-38
7	8	9	17	8	-8	3	26	26	13	2	-1*	1	6	6
8	12	12	18	8	-8	4	7	-7	14	2	-2*	2	7	7
9	8	-9	19	4	-3	5	14	14	15	7	-9	3	2	0*
10	15	14	20	3	-2	6	60	60	16	15	-14	4	15	15
11	8	-7	21	7	7	7	19	-20	17	2	-2*	5	5	-5
12	12	-12	22	12	13	8	2	3*	18	3	-4	6	19	-19
13	7	7	K=	3	H= -3	9	11	-11	19	5	5	7	8	-8
14	6	-5	1	35	-35	10	30	-30	20	7	7	8	16	-17
15	2	0*	2	8	7	11	11	11	21	1	0*	9	4	4
16	16	15	3	12	-12	12	2	-1*	K=	3	H= 2	10	15	15
17	6	-6	4	8	-7	13	4	4	0	4	-4	11	9	8

TABLE XVI (Continued)

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC
12	8	7	7	6	7	12	3	-3	11	4	4	18	2	-2*
13	9	-9	8	4	5	K=	3 H=	11	12	6	-6	K=	4 H=	-8
14	12	-12	9	3	3	0	5	5	13	3	3	1	9	9
15	3	-3	10	7	6	1	2	2*	K=	4 H=	-11	2	14	15
16	2	0*	11	6	-6	2	4	-5	1	4	-3	3	4	-5
17	8	8	12	2	-2*	3	6	-6	2	6	6	4	13	-14
18	3	3	13	2	-1*	4	6	-6	3	4	5	5	5	-5
19	2	-1*	14	18	-18	5	4	3	4	6	-7	6	2	2*
K=	3 H=	5	15	5	4	6	2	1*	5	3	3	7	2	-1*
0	3	2	16	3	2	7	10	10	6	7	-7	8	11	11
1	12	12	K=	3 H=	8	8	4	3	7	5	-4	9	2	2*
2	13	12	0	20	21	9	3	-3	8	4	4	10	11	-11
3	13	14	1	13	12	10	3	-1	9	2	-2*	11	6	6
4	14	16	2	11	11	K=	3 H=	12	10	6	6	12	14	-14
5	10	-11	3	8	-8	0	10	10	11	6	6	13	3	-1
6	7	-6	4	2	0*	1	4	-5	12	11	-11	14	6	6
7	9	-9	5	3	3	2	4	-4	13	2	1*	15	3	-2
8	24	-25	6	7	-7	3	9	-9	14	5	-6	16	7	7
9	17	18	7	6	6	4	6	-5	15	2	-1*	17	4	4
10	6	6	8	2	-2*	5	4	4	K=	4 H=	-10	18	6	-6
11	2	1*	9	2	-3*	6	7	8	1	10	-10	19	1	2*
12	2	2*	10	13	13	7	4	4	2	2	3*	K=	4 H=	-7
13	11	-11	11	6	-5	8	1	2*	3	5	5	1	6	-6
14	13	-13	12	7	-7	K=	3 H=	13	4	14	-14	2	4	-4
15	5	5	13	3	3	0	3	4	5	2	1*	3	7	7
16	2	3*	14	12	-12	1	4	-4	6	4	-3	4	18	-18
17	7	8	15	3	3	2	8	-8	7	11	-11	5	4	-5
18	4	5	K=	3 H=	9	3	2	-2*	8	3	2	6	25	26
K=	3 H=	6	0	7	7	4	2	-1*	9	2	2*	7	15	-16
0	3	-4	1	2	-3*	5	1	2*	10	4	4	8	9	8
1	19	19	2	30	31	K=	3 H=	14	11	4	5	9	5	4
2	24	25	3	2	-4*	0	4	4	12	10	-10	10	21	-23
3	5	4	4	6	-7	1	2	-3*	13	2	-3*	11	2	4*
4	12	11	5	4	2	K=	4 H=	-13	14	8	-9	12	8	-8
5	28	-29	6	3	-3	1	5	-5	15	2	-1*	13	7	-6
6	2	0*	7	2	2*	2	5	5	16	10	11	14	10	10
7	2	2*	8	18	18	3	3	-4	17	2	2	15	2	-1*
8	4	4	9	2	-2*	4	6	6	K=	4 H=	9	16	2	3*
9	16	17	10	2	-1*	5	5	4	1	8	7	17	6	6
10	2	3*	11	3	-2	6	7	-7	2	5	6	18	8	-9
11	7	-7	12	8	-9	7	2	-1*	3	6	6	19	2	1*
12	8	-9	13	2	-1*	8	2	-3	4	12	-12	K=	4 H=	-6
13	8	-8	K=	3 H=	10	9	5	-4	5	13	-13	1	11	10
14	12	-12	0	8	8	10	7	7	6	5	-5	2	20	-21
15	4	4	1	2	1*	K=	4 H=	-12	7	2	2*	3	4	5
16	4	5	2	6	5	1	2	-1*	8	2	2*	4	8	-8
17	4	4	3	2	-4*	2	10	9	9	6	6	5	9	-9
K=	3 H=	7	4	15	-14	3	4	4	10	4	4	6	27	28
0	13	14	5	2	-2*	4	2	-1*	11	3	-3	7	4	4
1	29	31	6	10	10	5	2	1*	12	12	-12	8	2	4*
2	15	15	7	2	2*	6	9	-9	13	2	1*	9	4	5
3	15	-15	8	10	10	7	3	-3	14	4	-4	10	19	-19
4	16	-17	9	2	1*	8	2	1*	15	2	-1*	11	5	-6
5	16	-17	10	2	-2	9	2	-1*	16	10	10	12	4	-5
6	7	7	11	6	-6	10	8	7	17	2	0*	13	7	-7

TABLE XVI (Continued)

L	FO	FC
14	14	14
15	2	1*
16	2	1*
17	5	5
18	11	-11
19	3	-2
20	3	3
K=	4 H=	-5
1	14	15
2	22	-22
3	4	-5
4	2	0*
5	11	-11
6	21	21
7	7	7
8	2	0*
9	19	19
10	15	-15
11	4	-4
12	4	-4
13	7	-8
14	15	15
15	9	8
16	2	2*
17	2	1*
18	10	-10
19	6	-6
20	4	5
K=	4 H=	-4
1	12	12
2	29	-29
3	6	-7
4	2	4*
5	18	-18
6	17	17
7	7	7
8	2	-3*
9	4	4
10	12	-12
11	10	-10
12	2	-1*
13	6	6
14	15	15
15	6	7
16	2	-1*
17	2	-3*
18	8	-8
19	3	-3
20	10	11
K=	4 H=	-3
1	3	4
2	27	-28
3	19	-20
4	5	6
5	13	14
6	16	16
7	15	16
8	21	-21
9	18	-18
10	12	-12
11	6	-6
12	15	15
13	5	5
14	8	9
15	2	1*
16	8	-9
17	2	1*
18	2	-2*
19	2	-2*
20	14	14
K=	4 H=	-2
1	15	-15
2	23	-24
3	12	-13
4	29	30
5	5	6
6	8	8
7	9	9
8	46	-47
9	12	12
10	2	-1*
11	4	-2
12	19	19
13	2	-2*
14	3	-2
15	6	6
16	8	-7
17	2	0*
18	2	0*
19	2	-3*
20	12	12
K=	4 H=	-1
1	4	-4
2	7	-7
3	8	-9
4	42	42
5	16	-16
6	2	-3*
7	2	-1*
8	44	-44
9	2	2*
10	2	2*
11	4	-3
12	14	14
13	9	9
14	6	-5
15	6	6
16	6	-6
17	4	-3
18	3	3
19	3	-3
20	8	-8
K=	4 H=	2
0	17	-17
1	6	-6
2	4	3
3	6	-6
4	35	35
5	12	12
6	3	2
7	2	1*
8	34	-35
9	21	-21
10	3	-1
11	6	-7
12	9	9
13	11	10
14	8	-8
15	2	3*
16	4	-4
17	5	-5
18	7	8
19	2	0
K=	4 H=	1
0	18	-18
1	6	-7
2	14	13
3	11	-11
4	24	24
5	14	15
6	4	-3
7	11	11
8	20	-20
9	6	-5
10	7	6
11	3	-3
12	5	5
13	6	7
14	15	-15
15	2	0*
16	6	-6
17	3	-4
18	10	11
19	3	3
K=	4 H=	2
0	2	-3*
1	11	-12
2	25	26
3	6	-6
4	12	12
5	5	6
6	16	-16
7	7	-7
8	10	-11
9	2	-5*
10	20	20
11	6	7
12	2	2*
13	7	7
14	18	-18
15	5	-5
16	2	0*
17	4	-3
18	10	10
K=	4 H=	3
0	2	1*
1	11	-12
2	31	31
3	11	12
4	8	9
5	11	13
6	26	-26
7	15	-15
8	2	2*
9	12	-13
10	24	24
11	8	8
12	7	-8
13	2	2*
14	10	-9
15	6	-6
16	5	6
17	2	0*
18	6	6
K=	4 H=	4
0	2	-1*
1	2	-4*
2	27	28
3	11	12
4	5	-5
5	8	9
6	25	-26
7	4	-4
8	9	8
9	2	3*
10	15	16
11	4	4
12	8	-8
13	2	-1*
14	3	-4
15	2	-1*
16	5	5
17	2	0*
K=	4 H=	5
0	6	7
1	2	-1*
2	21	21
3	10	10
4	6	-7
5	8	-8
6	23	-25
7	5	-4
8	4	2
9	8	7
10	13	13
11	6	5
12	9	-8
13	2	1*
14	2	-2*
15	2	-2*
16	8	9
K=	4 H=	6
0	18	19
1	2	4*
2	14	15
3	2	1*
4	10	-9
5	4	-4
6	12	-13
7	8	-8
8	4	4
9	3	-1
10	5	4
11	7	6
12	13	-13
13	2	-1*
14	3	3
15	3	-3
K=	4 H=	7
0	24	25
1	2	-2*
2	7	-7
3	2	2*
4	12	-12
5	4	2
6	2	0*
7	6	-5
8	5	5
9	2	2*
10	4	-3
11	3	3
12	16	-16
13	2	1*
14	3	3
K=	4 H=	8
0	22	23
1	3	2
2	8	-9
3	9	8
4	14	-14
5	7	-7
6	2	2*
7	3	-3
8	6	7
9	5	5

TABLE XVI (Continued)

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC
10	7	-7	10	1	0*	9	8	8	11	3	-1	12	4	-3
11	2	3*	K=	5	H=-10	10	2	2*	12	2	-2*	13	5	4
12	12	-12	1	7	7	11	12	-11	13	13	13	14	6	6
13	1	-2*	2	2	-2*	12	2	3*	14	7	7	15	12	-11
K=	4	H= 9	3	2	3*	13	3	1	15	3	-3	16	3	4
0	26	27	4	2	-2*	14	2	0*	16	2	-3*	17	3	-3
1	6	7	5	6	-7	15	10	9	17	10	-10	K=	5	H= 0
2	3	-3	6	4	-4	16	2	-1*	K=	5	H= -3	1	4	-3
3	2	-2*	7	4	4	K=	5	H= -6	1	20	-21	2	10	-10
4	10	-11	8	2	1*	1	4	5	2	11	-11	3	5	7
5	7	-8	9	8	8	2	2	0*	3	2	-2*	4	4	2
6	10	9	10	3	4	3	13	-13	4	2	-1*	5	4	3
7	3	-2	11	5	-5	4	4	4	5	26	27	6	12	-12
8	3	3	12	2	-2*	5	3	-3	6	5	-4	7	13	-13
9	6	5	13	2	-2*	6	6	-6	7	4	-4	8	2	-2*
10	6	-7	K=	5	H= 9	7	11	12	8	4	4	9	2	-4*
11	2	-1*	1	7	8	8	6	-6	9	16	-17	10	6	6
K=	4	H= 10	2	5	-5	9	3	-4	10	7	7	11	17	17
0	16	17	3	7	-7	10	2	1*	11	3	4	12	2	-1*
1	6	5	4	2	-2*	11	10	-10	12	2	2*	13	6	6
2	6	-6	5	8	-8	12	2	1*	13	11	11	14	5	6
3	5	-5	6	8	-8	13	7	7	14	5	5	15	11	-11
4	4	-4	7	10	11	14	3	2	15	2	0*	16	4	4
5	6	-6	8	2	0*	15	8	8	16	2	-1*	17	3	-2
6	7	7	9	5	4	16	2	-1*	17	8	-8	K=	5	H= 1
7	2	2*	10	3	4	17	5	-5	K=	5	H= -2	0	3	-2
8	2	1*	11	4	-5	K=	5	H= -5	1	26	-27	1	11	-11
9	3	3	12	5	-5	1	5	-4	2	4	-5	2	3	-3
K=	4	H= 11	13	2	-2*	2	2	-2*	3	13	13	3	21	21
0	7	7	14	5	5	3	10	-11	4	4	4	4	2	0*
1	7	7	K=	5	H= -8	4	3	3	5	20	21	5	10	10
2	8	-7	1	4	3	5	7	7	6	17	-17	6	10	-9
3	2	-1*	2	9	-10	6	2	0*	7	3	-1	7	20	-21
4	2	-2*	3	13	-13	7	12	12	8	2	0*	8	7	-8
5	2	-2*	4	5	-5	8	2	-1*	9	9	-9	9	2	-3*
6	7	7	5	4	-4	9	9	-10	10	8	9	10	4	-3
7	4	4	6	2	0*	10	5	-6	11	2	1*	11	18	17
K=	4	H= 12	7	9	9	11	10	-9	12	2	-2*	12	2	0*
0	2	-1*	8	3	-4	12	2	-1*	13	7	7	13	2	0*
1	2	-2*	9	7	7	13	10	10	14	4	3	14	4	3
2	7	-7	10	4	-3	14	2	3*	15	6	-5	15	9	-10
3	3	-3	11	5	-5	15	2	3*	16	3	2	16	2	2*
4	6	6	12	2	1*	16	2	-2	17	4	-4	17	3	3
K=	4	H= 13	13	6	-7	17	8	-8	K=	5	H= -1	K=	5	H= 2
0	8	-8	14	2	2*	K=	5	H= -4	1	17	-17	0	13	12
K=	5	H=-11	15	6	7	1	9	-10	2	4	-5	1	12	-12
1	8	9	K=	5	H= -7	2	3	-2	3	2	-1*	2	12	-12
2	5	-4	1	2	3*	3	18	-18	4	5	-5	3	23	24
3	4	4	2	5	-5	4	5	-7	5	8	8	4	2	1*
4	3	-1	3	12	-13	5	16	16	6	8	-7	5	5	-5
5	7	-7	4	2	-1*	6	6	6	7	2	0*	6	7	7
6	2	-2*	5	9	-10	7	12	12	8	2	3*	7	20	-20
7	3	-3	6	2	0*	8	11	11	9	2	-3*	8	6	-6
8	3	3	7	13	13	9	17	-17	10	4	4	9	9	9
9	6	7	8	5	-7	10	4	-4	11	11	11	10	7	-6

TABLE XVI (Continued)

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC
11	12	13	0	5	-5	0	2	1*	8	2	1*	4	3	5
12	2	-1*	1	12	12	1	5	-4	9	4	-3	5	2	1*
13	7	-7	2	2	0*	2	2	-3*	10	5	-5	6	3	-1
14	3	3	3	4	-3	K=	6	H= 9	11	7	6	7	2	0*
15	7	-7	4	3	1	1	2	2*	12	2	1*	8	4	4
16	2	1*	5	13	-13	2	2	1*	13	2	2*	9	3	3
K=	5	H= 3	6	3	-4	3	4	-5	K=	6	H= -4	10	2	2*
0	2	0*	7	4	4	4	2	-2*	1	7	-7	11	2	-1*
1	15	16	8	6	6	5	4	4	2	5	-5	12	4	4
2	7	-6	9	12	12	6	5	-5	3	9	8	13	7	-7
3	14	15	10	2	-1*	7	6	6	4	2	-1*	14	3	3
4	4	3	11	4	-4	K=	6	H= -8	5	5	6	K=	6	H= 0
5	16	-17	12	2	3*	1	2	-2*	6	8	9	0	18	-19
6	2	2*	K=	5	H= 7	2	3	3	7	10	-11	1	2	0*
7	9	-10	0	11	-11	3	5	-3	8	3	2	2	2	0*
8	6	6	1	13	13	4	2	-1*	9	2	-2*	3	2	-1*
9	10	10	2	8	-7	5	6	7	10	7	-8	4	2	4*
10	2	-3*	3	4	-3	6	5	-4	11	6	7	5	2	0*
11	4	4	4	2	1*	7	5	4	12	2	2*	6	2	-3*
12	2	-2*	5	11	-11	8	6	6	13	2	-1*	7	2	1*
13	7	-8	6	2	-4*	9	4	-3	14	3	2	8	5	5
14	3	4	7	10	9	10	2	2*	K=	6	H= -3	9	5	5
15	2	-2*	8	2	-2*	K=	6	H= -7	1	5	-5	10	2	1*
K=	5	H= 4	9	9	8	1	8	-9	2	8	-7	11	2	2*
0	2	-3*	10	2	0*	2	2	-3*	3	11	12	12	4	3
1	16	16	11	5	-5	3	3	-2	4	3	2	13	8	-8
2	2	-1*	K=	5	H= 8	4	4	-4	5	2	2*	K=	6	H= 1
3	7	7	0	7	-8	5	8	8	6	7	7	0	10	-10
4	6	-6	1	8	8	6	2	-1*	7	8	-8	1	9	8
5	8	-9	2	8	-8	7	5	6	8	2	1*	2	4	-5
6	2	-1*	3	10	-9	8	6	7	9	3	-2	3	5	4
7	2	0*	4	5	5	9	5	-5	10	3	-4	4	2	0*
8	3	5	5	4	-4	10	2	1*	11	5	5	5	8	-7
9	9	9	6	5	-6	11	4	-4	12	6	6	6	2	-1*
10	2	-1*	7	7	8	K=	6	H= -6	13	2	0*	7	2	0*
11	3	-2	8	6	-6	1	6	-6	14	2	-2*	8	2	-1*
12	2	2*	9	2	1*	2	8	-8	K=	6	H= -2	9	11	12
13	7	-7	K=	5	H= 9	3	7	-7	1	7	6	10	2	3*
14	2	1*	0	3	-3	4	5	-5	2	3	3	11	2	-1*
K=	5	H= 5	1	4	-4	5	6	5	3	11	11	12	6	6
0	2	2*	2	2	-1*	6	2	1*	4	2	1*	13	7	-8
1	9	9	3	7	-8	7	6	6	5	2	0*	K=	6	H= 2
2	3	-2	4	4	3	8	2	2*	6	2	2*	0	7	-7
3	3	-1	5	2	2*	9	6	-5	7	6	-5	1	12	12
4	2	-1*	6	5	-5	10	3	-2	8	4	2	2	2	1*
5	10	-9	7	5	5	11	2	2*	9	2	0*	3	2	0*
6	2	-2*	8	1	-1*	12	2	1	10	2	-1*	4	5	6
7	2	4*	K=	5	H= 10	K=	6	H= -5	11	4	3	5	14	-13
8	2	2*	0	2	-2*	1	2	-1*	12	7	7	6	8	-9
9	11	11	1	4	-4	2	2	-2*	13	4	-3	7	7	7
10	2	1*	2	3	-3	3	2	-1*	14	2	0*	8	2	-3*
11	2	-2*	3	8	-8	4	3	-3	K=	6	H= -1	9	8	8
12	2	2*	4	3	-1	5	4	4	1	2	1*	10	8	9
13	9	-9	5	3	3	6	3	3	2	2	3*	11	5	-5
K=	5	H= 6	K=	5	H= 11	7	2	-3*	3	6	6	12	3	2

TABLE XVI (Continued)

L	FO	FC
K=	6 H=	3
0	7	-7
1	10	9
2	9	9
3	10	-9
4	3	0
5	5	-4
6	8	-8
7	5	4
8	4	3
9	2	-1*
10	4	4
11	2	-2*
12	2	-2*
K=	6 H=	4
0	2	2*
1	2	2*
2	2	2*
3	2	-3*
4	5	-5
5	2	3*
6	3	1
7	4	4
8	4	4
9	3	-3
10	2	0*
11	5	-6
K=	6 H=	5

L	FO	FC
0	5	5
1	2	-4*
2	5	5
3	2	-4*
4	6	-6
5	4	3
6	2	1*
7	7	7
8	6	7
9	3	-4
K=	6 H=	6
0	4	3
1	4	-3
2	5	6
3	7	-7
4	5	-5
5	2	3*
6	3	3
7	6	6
8	4	5
K=	6 H=	7
0	3	-3
1	2	-1*
2	3	-1
3	5	-5
4	2	-2*
5	7	7
6	4	3

L	FO	FC
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1	5	-6
2	3	-2
3	2	0*
4	4	-5
K=	6 H=	9
0	1	0*
K=	7 H=	-5
1	2	-1*
2	4	-4
3	2	1*
K=	7 H=	-4
1	5	5
2	2	-2*
3	2	-1*
4	8	9
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K=	7 H=	-3
1	7	7
2	3	3
3	2	-1*
4	7	7
5	4	-4
6	3	-2
7	2	0*
K=	7 H=	-2

L	FO	FC
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2	9	9
3	2	1*
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5	4	-4
6	5	-5
7	2	-3*
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4	2	-1*
5	4	-4
6	4	-4
7	2	0*
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5	2	-1*
6	4	-3
7	2	2*
K=	7 H=	1
0	2	-2
1	2	2*
2	11	11
3	2	-1*

L	FO	FC
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5	2	0*
6	4	-4
7	2	3*
K=	7 H=	2
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1	2	0*
2	7	7
3	3	-4
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6	2	-2*
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3	2	-2*
K=	7 H=	5
0	10	10

CHAPTER III

EXPERIMENTAL

General Data

Melting points were obtained on a Thomas-Hoover melting point apparatus and are uncorrected. The ^{1}H, ^{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 MHz with tetramethylsilane (TMS) as internal standard for ^{1}H NMR, at 25.2 MHz with TMS as internal standard for ^{13}C NMR, and at 40.5 MHz with 85% H_3PO_4 as external standard for ^{31}P NMR. Infrared spectral data were obtained on a Beckmann IR-5A unit. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

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 1,5-Dibromo-3-tert-butylpentane (40) from 4-tert-Butylpyridine (41)[24]

To 48.9 g (0.362 mole) of pyridine 41 (Aldrich Chemical Company, Inc.) dissolved in 60 ml of 6 N HCl was added 2 g of 85% PtO_2. The mixture was hydrogenated on a Parr hydrogenation apparatus at 55 psig

and ca. 60°C until hydrogen uptake ceased. A small amount of white solid had formed during the hydrogenation, and this was dissolved in H_2O. The reaction mixture was filtered and transferred to a 1-ℓ,3-necked, round-bottom flask fitted with a mechanical stirrer and addition funnel. The stirred mixture was cooled to 0°C (ice) and 75 g (1.87 mole) of NaOH pellets were then added all at once. After stirring for 0.5 hr, benzoyl chloride (50.7 g, 0.362 mole) was added dropwise over a 1-hr period. The reaction mixture was stirred overnight, and the resulting solid was filtered and washed (H_2O). Air drying of the solid followed by vacuum drying gave 81.26 g (82%) of 1-benzoyl-4-tert-butylpiperidine (42) which was used in the next step.

Phosphorus tribromide (45 g, 0.166 mole) was added dropwise to 40 g (0.163 mole) of amide 42 over a 45-min period. After stirring for 2 hr, the mixture was cooled (ice) to 0°C and 41 g (0.256 mole) of Br_2 was added dropwise over a 45-min period. The resultant dark oil was allowed to stand for two days. Distillation of the oil at 20 mm up to 150°C gave a distillate (≈50 ml) which was poured onto 100 ml of ice. The hydrolyzed mixture was stirred for 1 hr and then extracted with 3 x 50-ml portions of $HCCl_3$. The $HCCl_3$ was removed (rotary evaporation), and to the residual oil was added 75 ml of 48% HBr. The solution was then boiled for 3 hr followed by steam distillation until no oil formed in the condenser. The distillate was extracted with petroleum ether (≈300 ml) and the extracts were combined and dried ($CaCl_2$). Filtration and removal of the petroleum ether (rotary evaporation) gave an oil which was distilled under reduced pressure to yield 8.68 g (18.6%) of 40, bp 94-96°C/0.6 mm [lit[24] bp 87-88°C/0.7 mm].

Preparation of 40 from 4-tert-Butylcyclohexanone (43)[52]

Ketone 43 (25 g, 0.162 mole, Columbia Organic Chemicals Co., Inc., m.p. 47-49°C) and 85% m-chloroperbenzoic acid (36.25 g, 0.18 mole, Aldrich Chemical Company, Inc., m.p. 92-94°C dec) were added to 500 ml of 1,2-dichloroethane (DCE) in a 1-ℓ, round-bottom flask fitted with a magnetic stirrer, condenser, and $CaCl_2$ drying tube. After the exothermic reaction had subsided, the mixture was boiled for 6 hr and cooled. A solid had formed upon cooling which was filtered out and washed with 50 ml of DCE. The filtrate was shaken with 200 ml of saturated aqueous $NaHCO_3$ and the aqueous phase separated. The organic phase was washed with 200 ml of H_2O and subsequently separated. Solvent removal (rotary evaporation) gave an oil which was steam distilled until no odor of unreacted 42 was present in the distillate. The residue was extracted with 3 x 100 ml portions of ether and then the extracts were combined and dried ($MgSO_4$). Filtration and removal of the ether by rotary evaporation gave 17.0 g (61%) of 5-tert-butyl-2-oxepanone (44) which was used as such in the next step.

Concentrated H_2SO_4 (18 ml) was slowly added to a cooled (0°C) mixture of KBr (6 g) and 48% HBr (93 ml) in a 500-ml, 3-necked, round-bottom flask to which was attached an immersion thermometer, magnetic stirrer, and condenser. Lactone 44 (17.0 g, 0.1 mole) was then added, and the reaction mixture was stirred at room temperature for 12 hr and then heated at 100°C for 12 hr. The dark brown solution allowed to cool 250 ml of H_2O was then added. The solution was extracted with 4 x 200-ml portions of ether which were then combined and dried

($MgSO_4$). Filtration and removal of the ether by rotary evaporation gave an oil which was distilled at reduced pressure to yield 19.5 g (78%) of 6-bromo-4-tert-butylhexanoic acid (45), bp 140°C/0.3 mm [lit[52] bp 133-143°C/4 mm].

Mercuric oxide (15 g, 0.07 mole) was placed in a 500-ml, 3-necked, round-bottom flask fitted with a mechanical stirrer, addition funnel, Soxhlet extractor (containing 50 g of Linde 3A molecular sieve), condenser, and N_2 inlet. The HgO was covered with 50 ml of freshly distilled CCl_4 (from $CaCl_2$) and dried via extracting of any residual water with CCl_4 which was passed through molecular sieve (Linde 3A) for 1 hr. Acid 45 (22 g, 0.088 mole) and Br_2 (17.5 g, 0.11 mole) in 50 ml of CCl_4 were added dropwise to the boiling reaction mixture over a 2-hr period. After the addition was complete, boiling was continued for 1 hr and the flask was allowed to cool. The molecular sieve was washed with 50 ml of CCl_4 and the reaction mixture, plus washings, were filtered and washed with 2 x 100 ml of 2% NaOH and 100 ml of H_2O. Drying ($CaCl_2$) of the organic solution followed by evaporation of the CCl_4 (rotary evaporation) gave a residual oil which was vacuum distilled to give 14.74 g (56%) of 1,5-dibromo-3-tert-butylpentane (40), bp 83-93°C/0.15 mm [lit[52] bp 87-88°C/0.7 mm].

Additional experiments to prepare 40 by the above procedure unaccountably resulted in yields of only 10-20%.

Preparation of 40 from 3-tert-Butyl-1,5-pentanediol (46)[47]

Diol 46 (4.0 g, 0.025 mole) and freshly recrystallized (hexane) triphenylphosphine (13.1 g, 0.05 mole) were dissolved in 50 ml of dry

DMF in a 100-ml, 3-necked, round-bottom flask fitted with a magnetic stirrer, addition funnel, condenser, and N_2 inlet. Bromine (ca. 8 g, 0.05 mole) was added dropwise, under N_2 (the temperature being maintained below 55°C) until an orange-yellow color persisted. The reaction mixture was stirred an additional 15 min and was then distilled at 0.5 mm up to 90°C. The distillate (≈35 ml) was poured onto 100 ml of H_2O and the bottom oily layer separated. The aqueous phase was extracted with 2 x 75-ml portions of ether and combined with the first layer. Drying ($MgSO_4$) of the organic solution followed by filtration and removal of the ether (rotary evaporation) gave an oil which was distilled at reduced pressure to yield 2.7 g (39%) of 40, bp 93°C/0.8 mm [lit[24] bp 87-88°C/0.7 mm].

Preparation of 4-tert-Butyl-1,1-diphenyl-phosphorinanium Bromide (47)[39]

To 250 ml of boiling ODCB in a 500-ml, 3-necked, round-bottom flask fitted with a magnetic stirrer, addition funnel, and condenser was added dropwise, over a 1-hr period, under N_2, dibromide 40 (7.73 g, 0.027 mole) and tetraphenyldiphosphine [50 ml, 0.27 M in ODCB, 0.0135 mole, Pressure Chemical Company (as a solid)]. After the addition was complete, ca. 150 ml of ODCB was distilled off, under N_2, and the reaction mixture was allowed to cool (to room temperature) and to stand overnight. The resultant solid (A) was filtered off and washed with 50 ml of ODCB. Approximately 100 ml more of ODCB was distilled (atmospheric pressure) from the filtrate, and the resulting solution was again allowed to cool and stand overnight. A solid (B) formed which was filtered off and washed with 5 ml of ODCB. The solids (A and B) were

combined and dried over P_2O_5 at 80°C/5 mm to yield 1.95 g (37%) of 47, mp >300°C [lit[39] mp 316.5-318.5°C dec]. The ^1H NMR spectra of 47 thus prepared was identical to that previously reported;[39] ^{31}P NMR ($DCCl_3$) +41.9 ppm.

Preparation of cis- and trans-4-tert-Butyl-1-phenylphosphorinane 1-Oxides, (39a) and (39b)[39]

To 38 ml of 1 N KOH was added 30 g (7.7 mmole) of salt 47. The reaction mixture was boiled 44 hr and allowed to cool. After cooling, 9 KOH pellets (Mallinckrodt-Analytical Reagent; 0.85 g) were added and the mixture was extracted with 6 x 25-ml portions of $HCCl_3$. The extracts were combined and dried ($MgSO_4$). Rotary evaporation of the $HCCl_3$ and air drying of the resultant oil gave a solid which was dried in vacuo (110°C/5 mm) over P_2O_5 to yield 1.76 g (91.4%) of 39a and 39b, mp 102-121°C [lit[39] mp 131-145°C]. The composition of the mixture was estimated by integration of the tert-butyl signals in the ^1H NMR spectrum to contain 39a (34%) and 39b (66%).

Separation of cis- and trans-4-tert-Butyl-1-phenylphosphorinane 1-Oxides, (39a) and (39b)[39]

A mixture (840 mg) of oxides 39a and 39b were spotted (acetone solution ≈1.5 ml) onto two 8-inch x 8-inch, 2-mm-thick silica gel (Brinkmann Silica Gel 60 PF-254) plates. The plates were placed in an elution chamber and eluted with reagent-grade acetone. After elution and drying, the plates were developed in an iodine vapor

chamber and the spots were marked (39a: R_f 0.24; 39b: R_f 0.94). After sublimation of the iodine, the spots were scraped and oxides 39a and 39b were extracted (Soxhlet) separately for 36 hr with methanol. Rotary evaporation of the methanol from the individual samples gave oils for 39a and 39b which were distilled (Kugelrohr) under reduced pressure to give 39a (bp 180-190°C/0.5 mm, mp 110-135°C) and 39b (bp 180-190°C/0.5 mm, mp 158-159°C) (total recovery: 568 mg, 67.5%) [lit[39] 39a mp 88.5-95°C and 39b mp 160-161°C]; 39a: IR (KBr) ν 2925, 1428 (P-C_6H_5), 1165 (P→O), 1112 (P-C_6H_5), 813, 696 cm^{-1}; ^1H NMR ($DCCl_3$) δ 0.81 [s, $C(C\underline{H}_3)_3$, 9 H], 0.81-146 [m, ring H, 3 H], 1.60-2.80 [m, ring H, 6 H], 7.41-7.86 [ArH, 5 H]; ^{31}P NMR (ODCB) + 30.62 ppm (see Plates V-VII). 39b: IR(KBr) ν 2925, 1435 (P-C_6H_5), 1177 (P→O), 1115 (P-C_6H_5), 807, 696 cm^{-1}; ^1H NMR ($DCCl_3$) δ 0.94 [s, $C(C\underline{H}_3)_3$, 9 H], 0.94-1.36 [m, ring H, 1 H], 1.46-2.52 [m, ring H, 8 H], 7.34-7.92 [m, ArH, 5 H]; ^{31}P NMR (ODCB) +28.19 ppm (see Plates VII-X). See Table XII for the ^{13}C NMR parameters for 39a and 39b.

Preparation of cis- and trans-4-tert-Butyl-1-phenylphosphorinanes (38a) and (38b)[39]

In preparation for a typical kinetic experiment ca. 200 mg (0.8 mmole) of oxide 39a or 39b was heated on an oil bath with excess (ca. 2 ml) of phenylsilane at 100-110°C for 2 hr under N_2 in a 10-ml round-bottom flask equipped with a magnetic stirrer and condenser. The reaction mixture was allowed to cool and was transferred to a Kuglerohr distillation apparatus under N_2. The phosphine 38a or 39b was distilled under reduced pressure (0.1 mm) at 100-120°C. The distilled phosphine 38a or 38b was then dissolved in 10 ml of degassed ODCB and used as

such for the NMR measurements. The ^{1}H NMR spectra of 38a and 38b prepared herein were identical to those reported previously (see Plates I-IV).[39]

^{31}P NMR Spectral Measurements

Freshly distilled phosphorinanes 38a or 38b were dissolved in 10 ml of degassed ODCB and transferred under N_2 to a coaxial vessel equipped with a septum inlet to the inner chamber and a ground glass joint to which was attached a condenser and N_2 inlet. In the outer vessel was placed an appropriate liquid (1,1,2,2-tetrachloroethane, bp 144°C; 1,3,5-trimethylbenzene, bp 164°C; or ODCB, bp 181°C) and a condenser. The liquids were maintained at their boiling point, which was monitored (thermometer) throughout the experiment. At regular intervals, a 1.5-ml aliquot was withdrawn and placed in the inner tube of a Wilmad 12-mm coaxial NMR tube along with a 1-mm sealed capillary of 85% H_3PO_4. In the outer portion of the NMR tube was placed D_2O as the lock source. The ^{31}P spectra were obtained using gated broad-band proton decoupling with a 40s delay between pulses to minimize effects of a nuclear Overhauser enhancement and unequal relaxation times. The composition of the mixture was then determined by several integrations of the ^{31}P signals for 38a and 38b which were then averaged.

Preparation of trans-1-Benzyl-4-tert-butyl-1-phenylphosphorinanium Bromide (48)[39]

Oxide 39b (175 mg, 0.7 mmole) was heated on an oil bath at 100-110°C for 3 hr under N_2 with ca. 1 ml of phenylsilane in a 10-ml,

round-bottom flask equipped with a magnetic stirrer and condenser. The reaction mixture was allowed to cool to room temperature and then distilled (Kugelrohr) under reduced pressure (0.03 mm) at 100-110°C. Phosphine 38b was then dissolved in 2 ml of ODCB and excess (ca. 1 ml) of benzyl bromide was added. The reaction mixture was allowed to stand at room temperature overnight. The solid that formed was filtered off and washed with 3 ml of benzene. Recrystallization from ethanol/ethyl acetate (1:1) gave 61 mg (22%) of 48, mp 271-272°C [lit[39] mp 268-279°C]. The ^{1}H NMR spectrum of 48 prepared herein was identical to that reported previously.[39]

Structure Determination of trans-4-tert-Butyl-1-phenylphosphoriane 1-Oxide (39b)

Crystals of 39b were obtained by slow evaporation of a refrigerated solution in acetone and water in a 2:1 ratio. The crystal selected for data collection was clear and blocky, having dimensions of 0.138 x 0.121 x 0.242 mm. The crystal data are: $C_{15}H_{23}PO$; M.W. = 250.31; monoclinic; space group = $P2_1/c$; a = 12.8680(7) Å; b = 5.9065(3) Å; c = 10.5011(9) Å; β = 104.102(4)°; V = 1437.51 Å^3; Z = 4; ρ_{calc} = 1.156, ρ_{obs} = 1.152 g/cm^3; nickel-filtered CuKα radiation: λ = 1.54051 Å for 2θ data and λ = 1.54178 Å for intensity data; all data collected at room temperature, using a Nonius CAD-4 automatic diffractometer. The least-square cell parameters were determined from the +2θ and -2θ values of 52 reflections distributed throughout reciprocal space. The observed density was measured by the flotation method using a mixture of toluene and carbon tetrachloride.

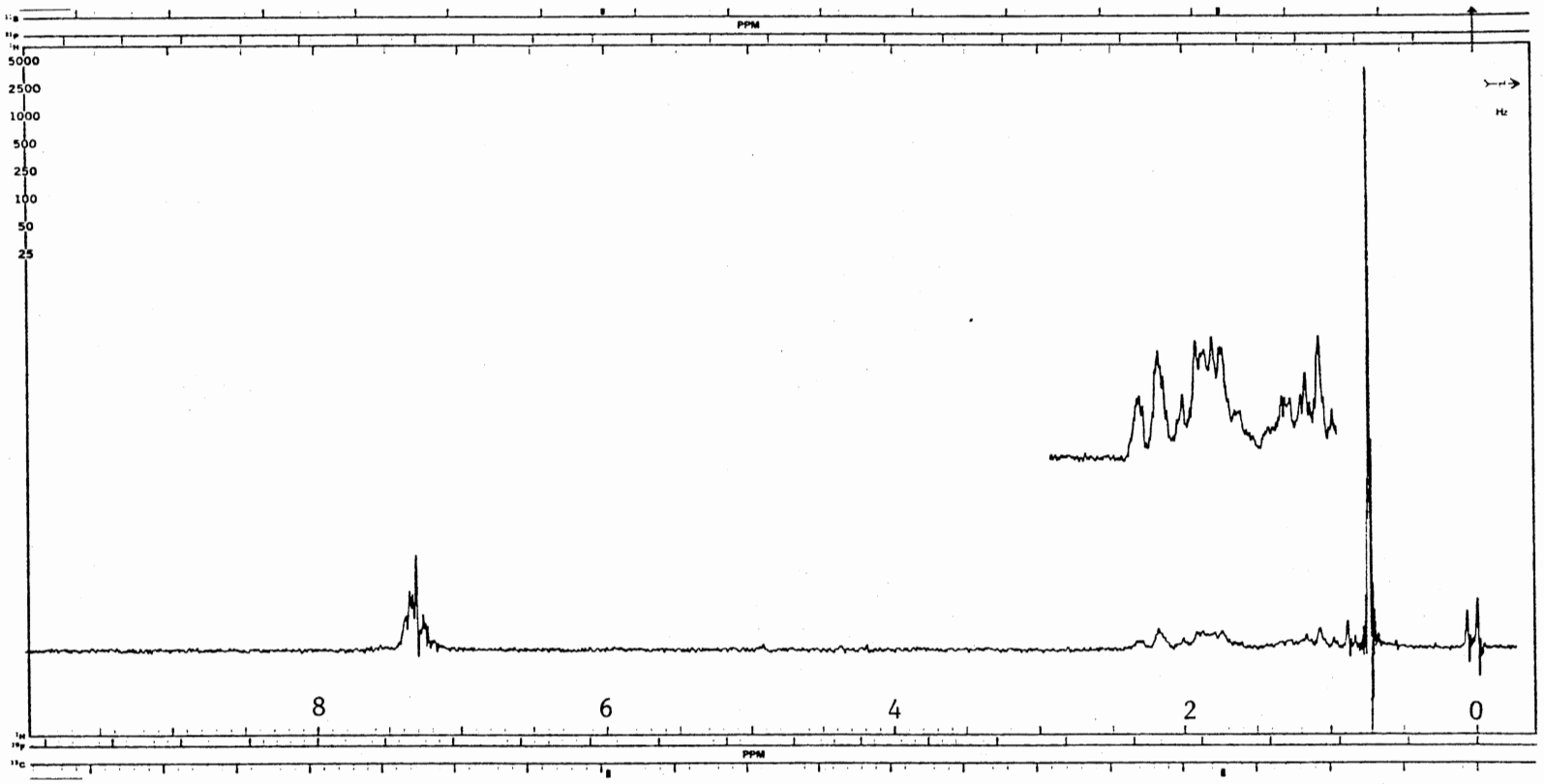
The intensities of all 2960 unique reflections with θ less than 75^{o} were measured using the θ-2θ scan technique. The scan width used was calculated for each reflection by the formula $\Delta\theta = (0.9 + (0.09) \tan \theta)$. A horizontal receiving aperture with variable width (width (mm) = 5 + (0.5) tan θ) and fixed height of 6 mm was positioned 173 mm from the crystal. The maximum scan time used was 60 seconds with 2/3 of the time used for scanning the peak (P), and 1/6 each for each of the low θ (RH) backgrounds. A standard reflection was monitored every 25 reflections, and over the period of data collection, its intensity decreased by 3%. The monitor reflection was used to bring all intensities on a common relative scale. Three reflections were used to check the orientation of the crystal every 100 reflections, and a new orientation matrix was calculated when a deviation larger than 0.1^{o} was observed.

There were 677 reflections whose intensities could not be distinguished from the background. All reflections meeting this criterion ($I < 2(T)^{\frac{1}{2}}$ where $T = P + 2(RH + LH)$) were assigned intensities of $T^{\frac{1}{2}}$ for further data analysis. Lorentz, polarization, and absorption corrections ($\mu = 15.331\ cm^{-1}$) were applied to the data. A Gaussian integration was employed to correct for absorption,[5] using 216 sampling points.

The structure was solved by the combined use of MULTAN[16] and a sharpened Patterson synthesis. The structure was refined using block-diagonal least-squares calculations. After several cycles of refinement a difference Fourier synthesis revealed the positions of all hydrogen atoms, which were included in the refinement procedure. The

refinement was considered completed when all shifts were less than 1/2 their standard deviations. The final R-value (= $\Sigma||F_c|| / \Sigma|kF_o|$) for all 2960 reflections was 0.067. Each structure amplitude was assigned an individual weight.[58] The mean values of $\omega_F \Delta F^2$ calculated for various ranges of $|F_o|$ were constant, thus validating the weighting scheme used (see Table XVI). A final difference Fourier map showed negative peaks of -0.33 and -0.28 $e\text{Å}^{-3}$ corresponding to the P(1) and O(1) positions, respectively. The largest positive peak in the map was 0.20 $e\text{Å}^{-3}$ at approximately halfway between P(1) and C(10). Atomic scattering factors for P, O, and C atoms were taken from the "International Tables for X-ray Crystallography"[22] while those for H atoms were taken from Stewart, Davidson and Simpson.[53]

PLATE I



^{1}H NMR Spectrum of cis-4-tert-Butyl-1-phenylphosphorinane (38a)

Solvent. . . . . $DCCl_3$ S.F. . . . 100.1 MHz F.B. . . . 20 Hz R.F. . . .55dB

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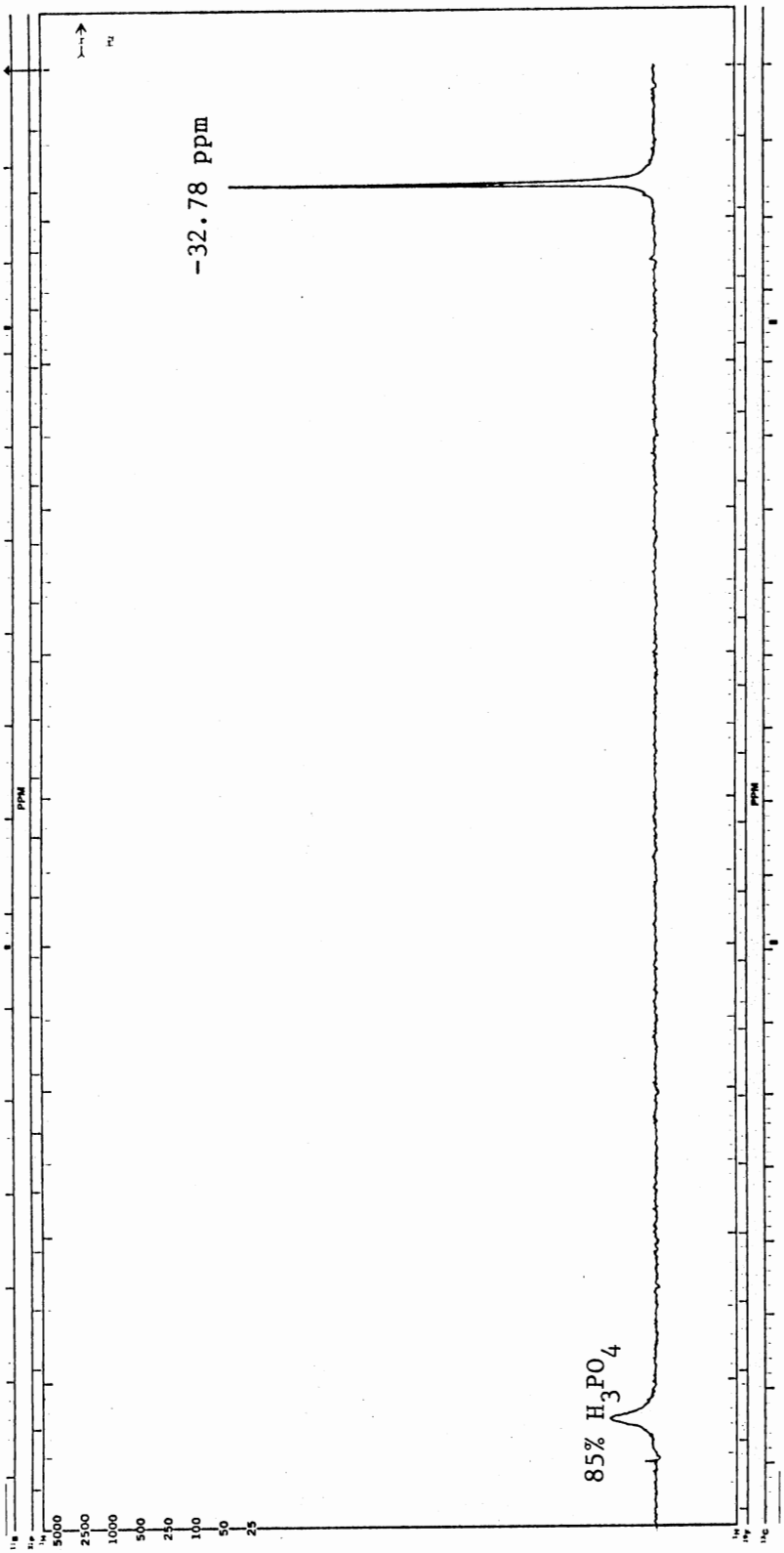
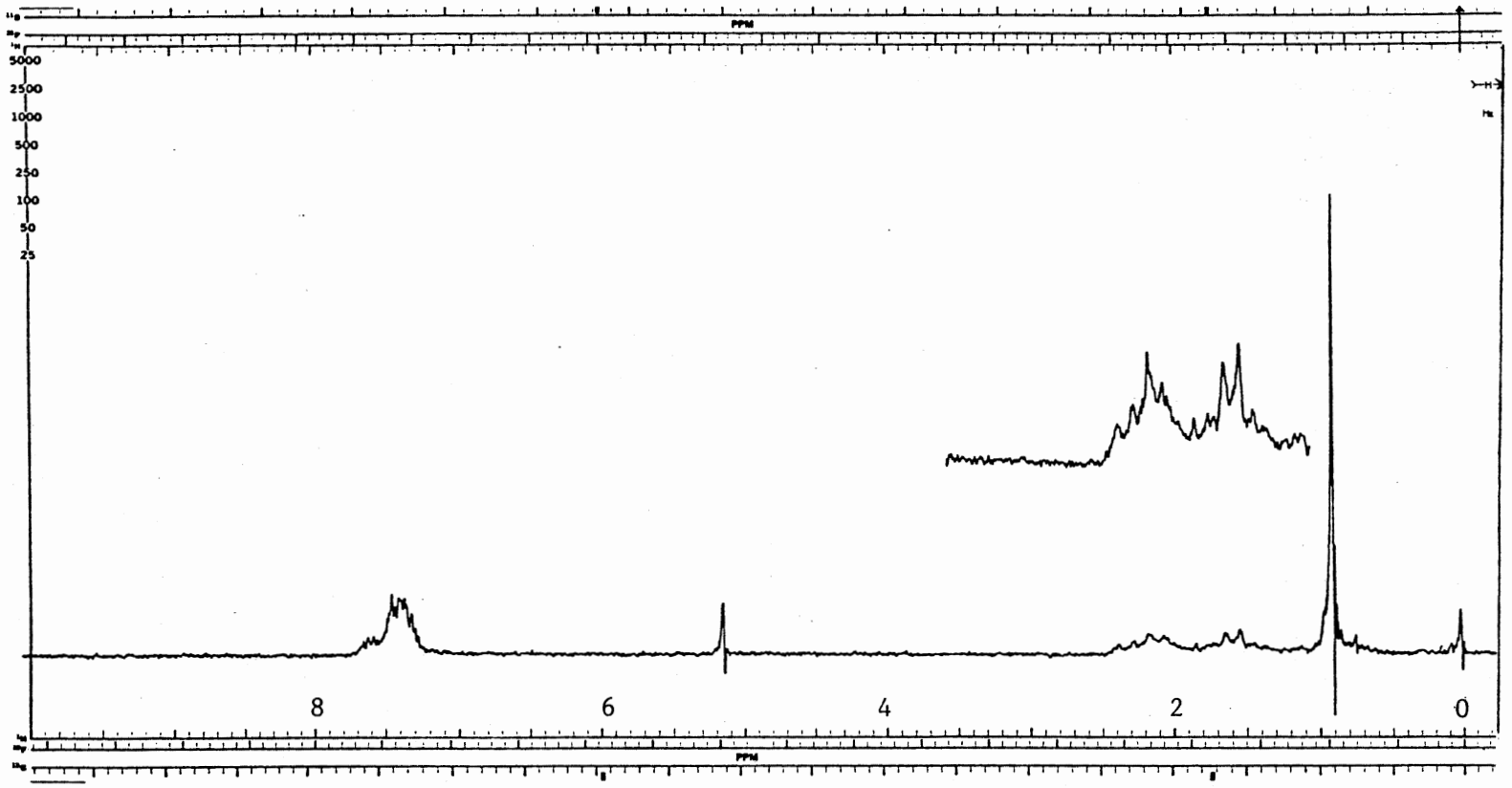
PLATE II



^{31}P NMR Spectrum of 38a ($DCCl_3$)

PLATE III

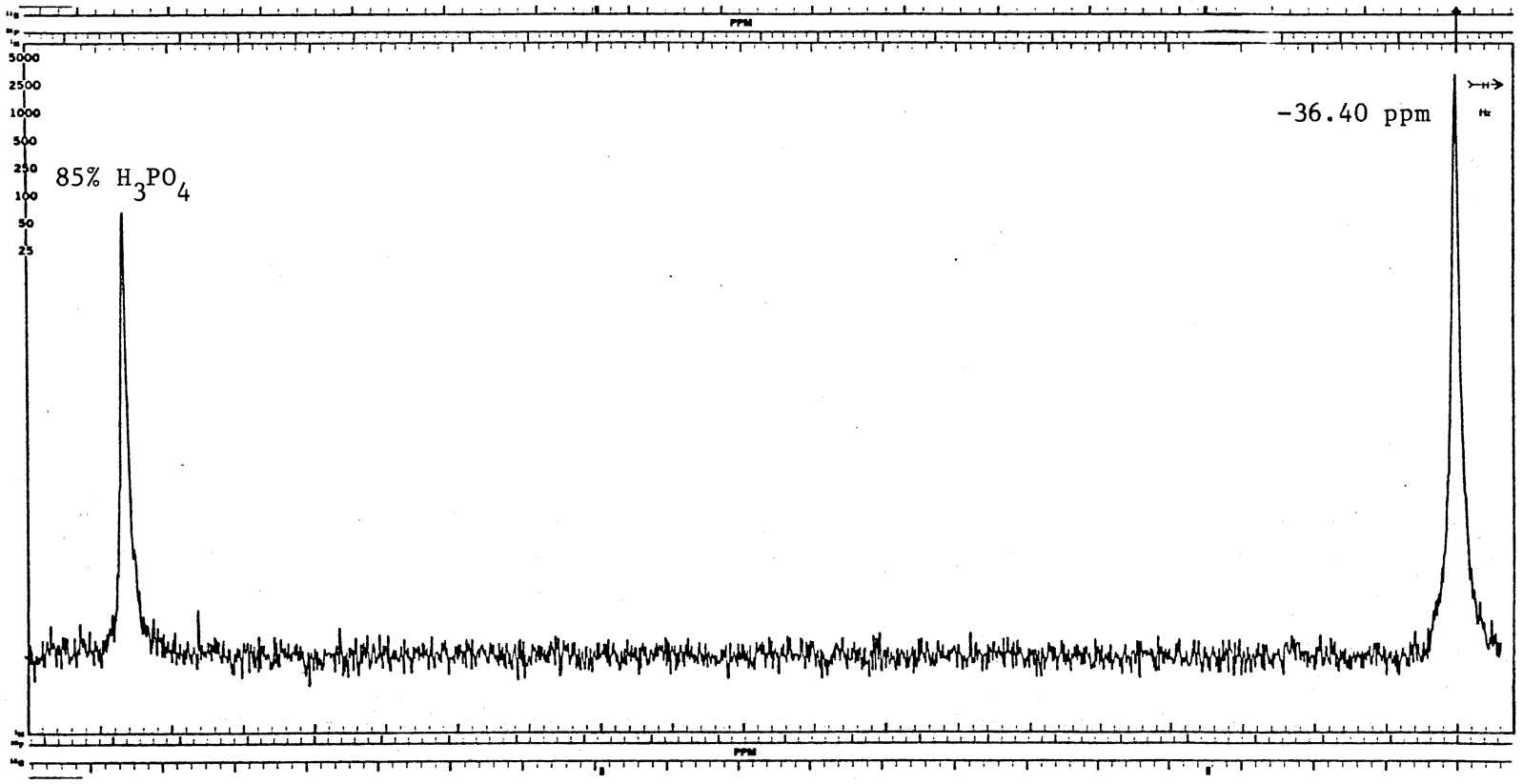


^{1}H NMR Spectrum of trans-4-tert-Butyl-1-phenylphosphorinane (38b)

Solvent. . . . . $DCCl_3$ S.F. . . 100.1 MHz F.B. . . . 20 Hz R.F. . . .100dB

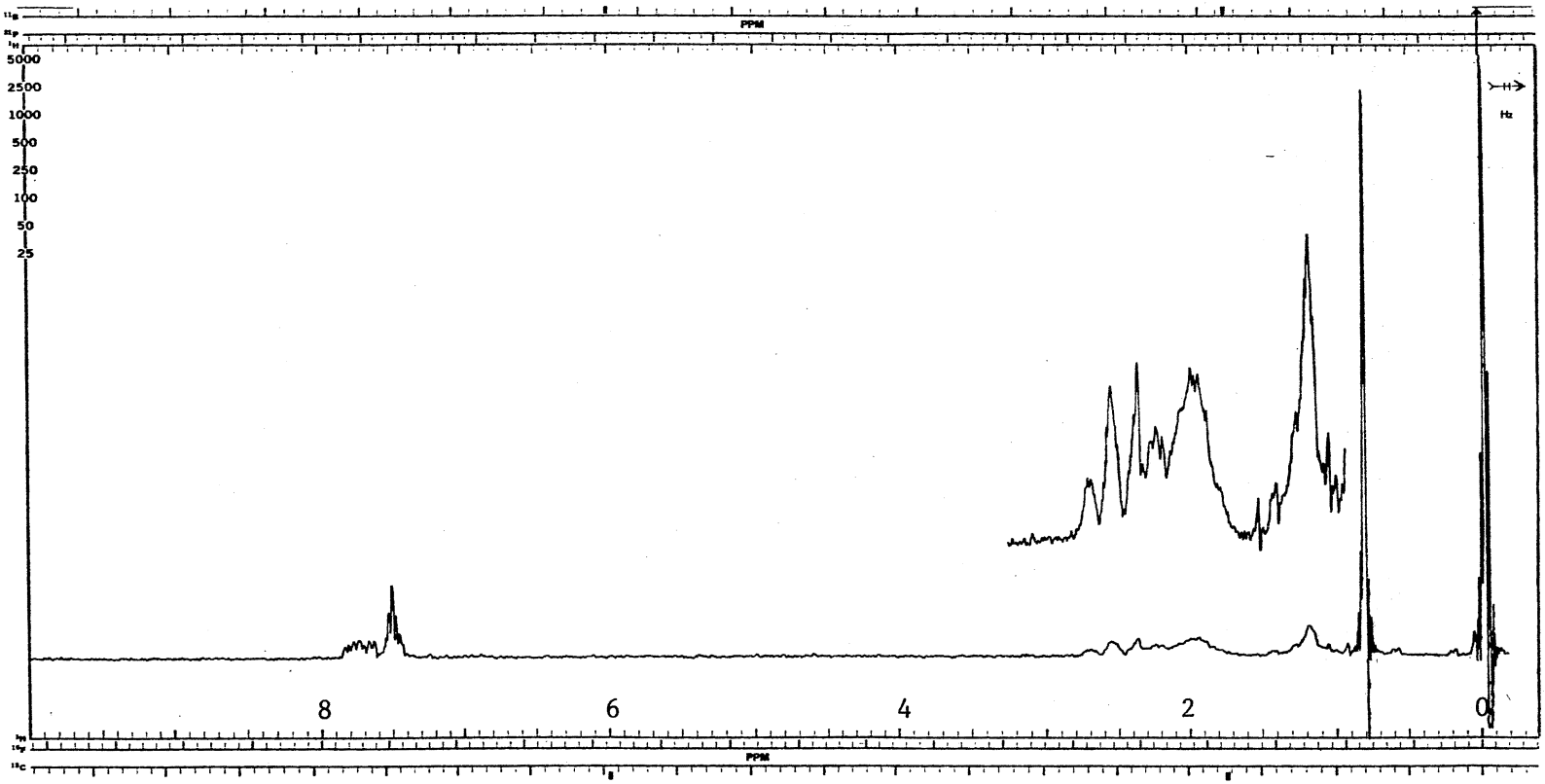
S.W. . . . . 1000 Hz S.T. . . 250 sec. S.O. . . .85570 Hz S.A. . . . 1.25 Lock. . . ^{2}H

PLATE IV



^{31}P NMR Spectrum of 38b ($DCCl_3$)

PLATE V



^{1}H NMR Spectrum of cis-4-tert-Butyl-1-phenylphosphorinane 1-Oxide (39a)

Solvent. . . . . $DCCl_3$ S.F. . . 100.1 MHz F.B. . . . 2.0 Hz R.F. . . .59dB

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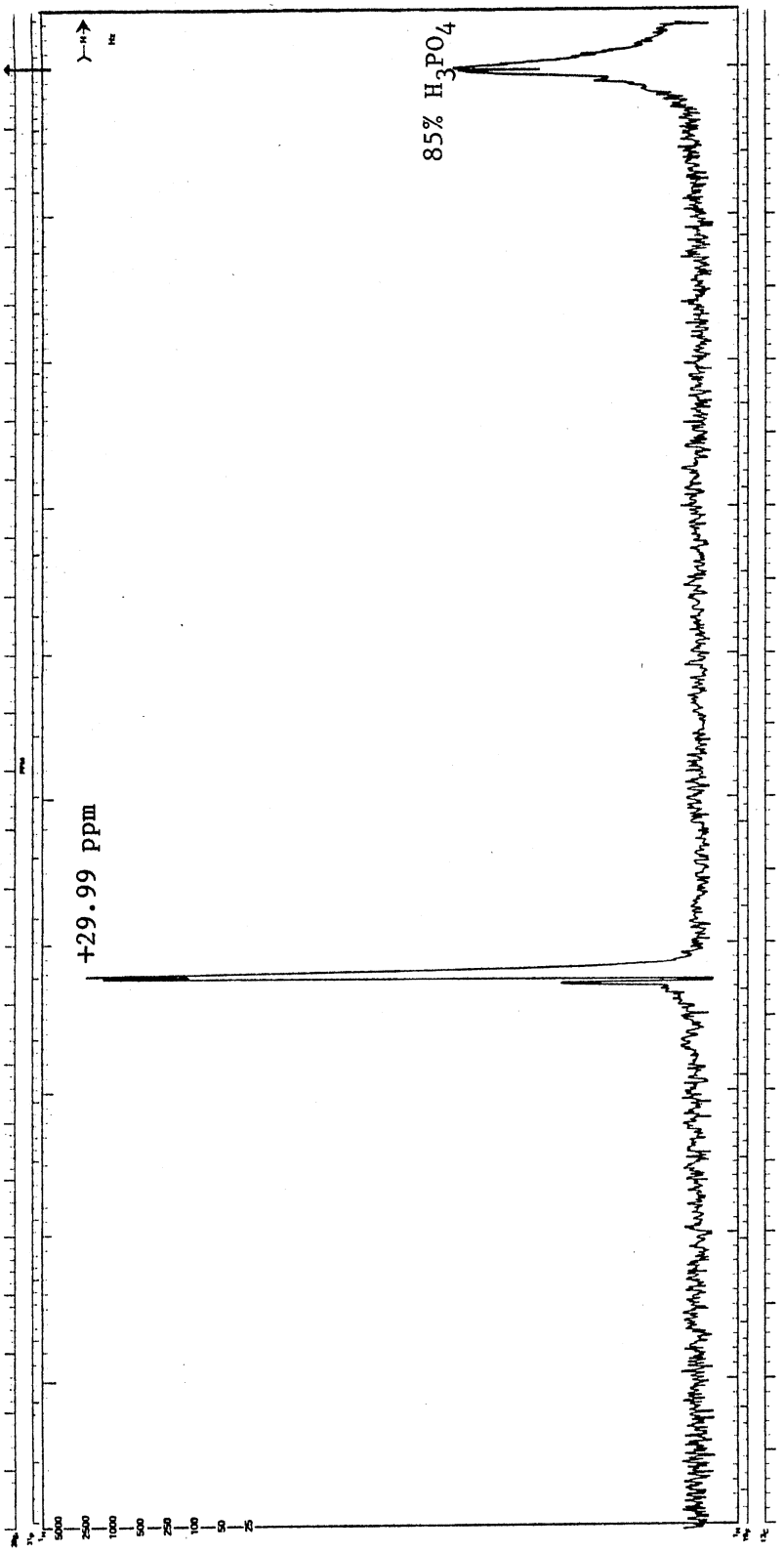
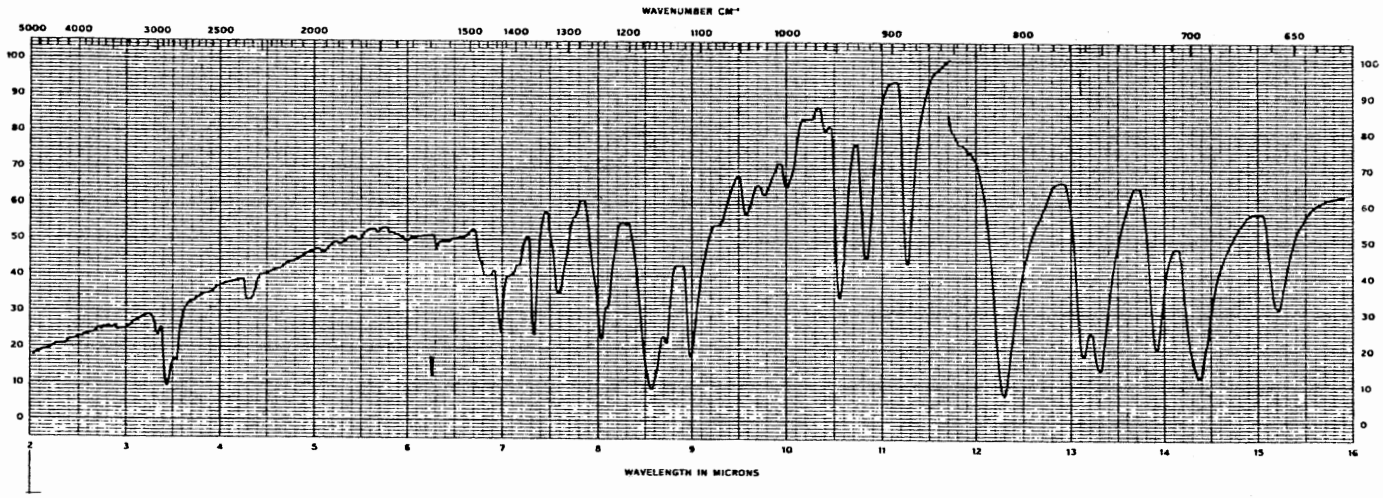
PLATE VI



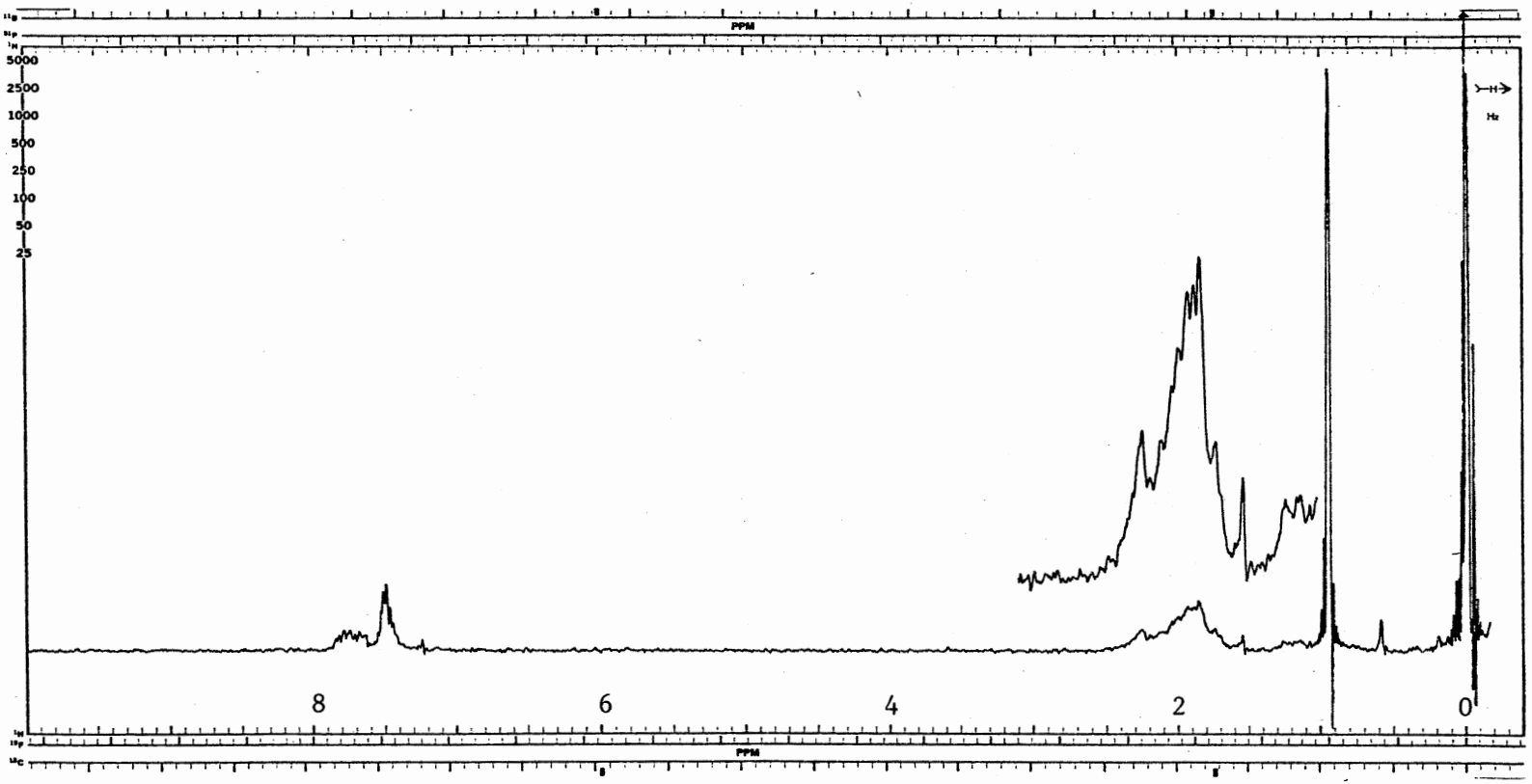
^{31}P NMR Spectrum of 39a in ODCB

PLATE VII



IR Spectrum of cis-4-tert-Butyl-1-phenylphosphorinane 1-Oxide (39a), KBr Pellet

PLATE VIII

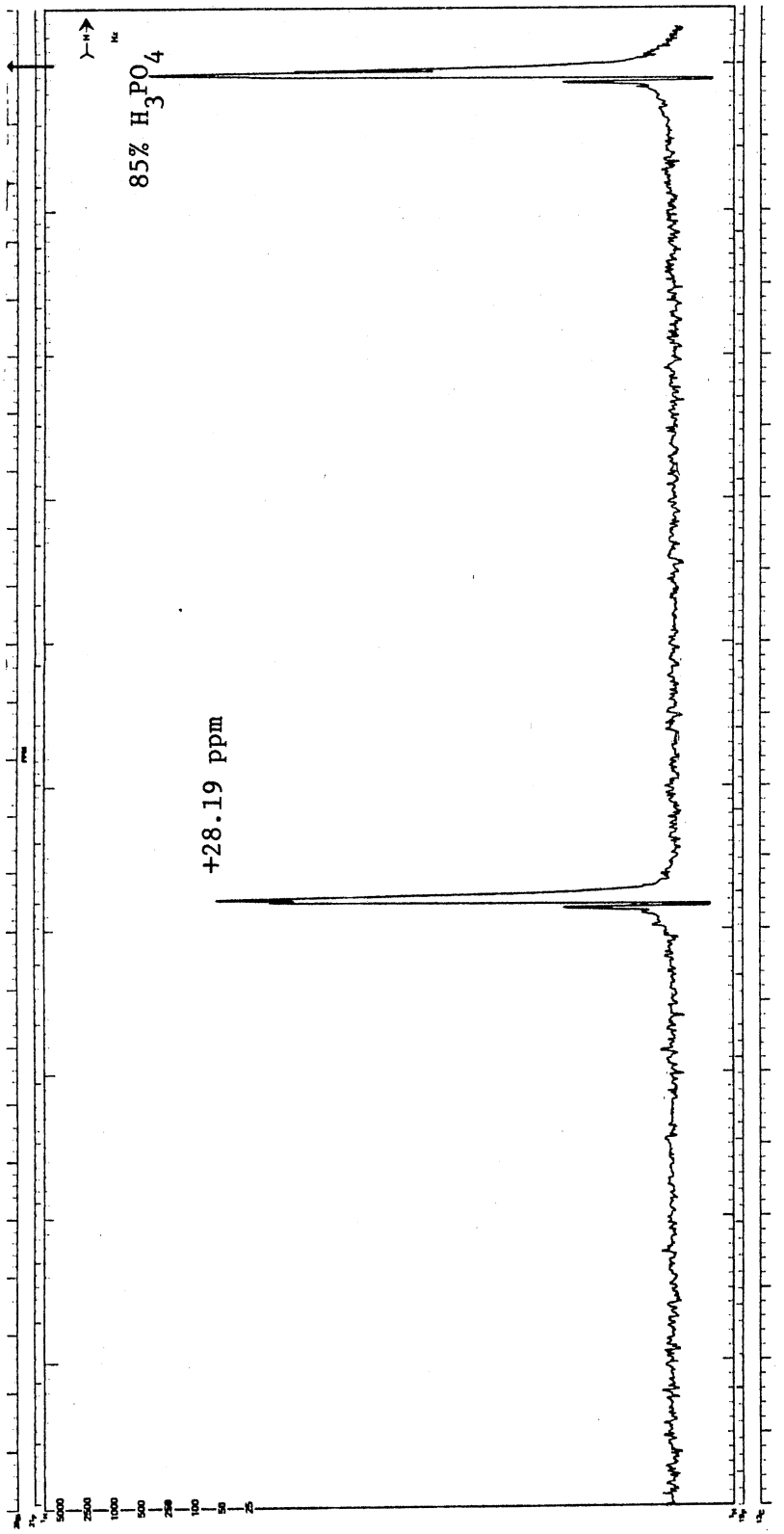


^{1}H NMR Spectrum of trans-4-tert-Butyl-1-phenylphosphorinane 1-Oxide (39b)

Solvent. . . . . $DCCl_3$ S.F. . . 100.1 MHz F.B. . . . 2.0 Hz R.F. . . .70dB

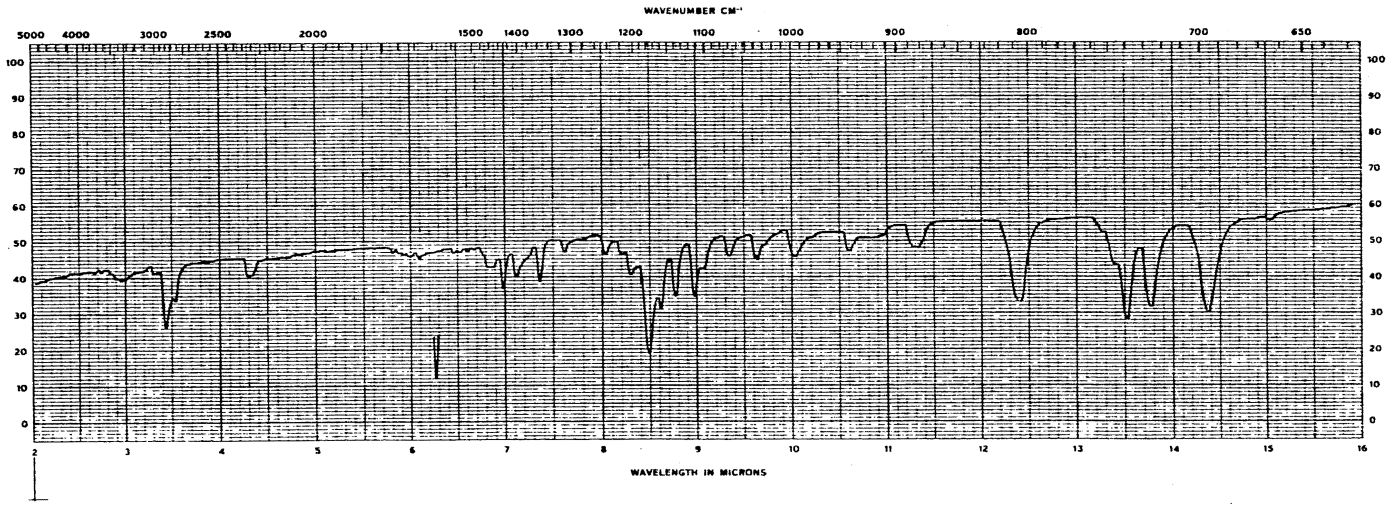
S.W. . . . . 1000 Hz S.T. . . 250 sec. S.O. . . .83701 Hz S.A. . . .1.25 Lock. . . ^{2}H

PLATE IX



^{31}P NMR Spectrum of 39b in ODCB

PLATE X



IR Spectrum of trans-4-tert-Butyl-1-phenylphosphorinane 1-Oxide (39b), KBr Pellet

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PART II

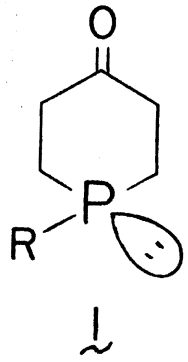
CONFORMATIONAL ANALYSIS OF SELECTED 4-PHOSPHORINANONES AND DERIVATIVES

CHAPTER I

HISTORICAL

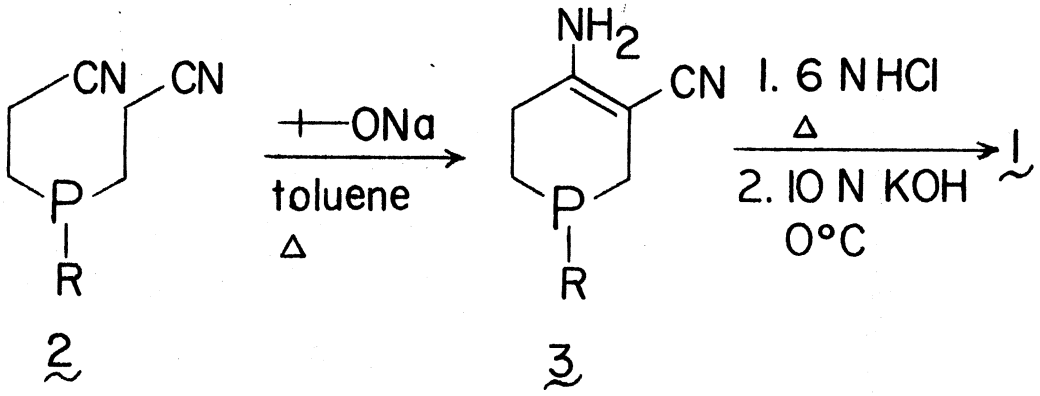
Phosphorinanones—Preparations, Reactions, Properties

Phosphorinanones[18,29,33,58] 1 have proven to be a class of organophosphorus compounds in which lively interest has been maintained since their initial synthesis.[60] The classic preparation consisted of a



1

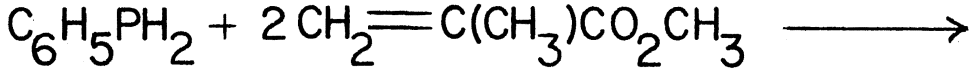
Thorpe condensation of a P-substituted bis(2-cyanoethyl)phosphine 2 followed by hydrolysis of the amino nitrile 3 with concomitant decarboxylation to yield the 4-phosphorinanone 1.[60] Certain phosphorinanones 1 ($R = C_2H_5$, C_6H_5) have been characterized through the preparation of the corresponding semicarbazones and methiodides. A later report[54] furnished a modified procedure for the synthesis of phosphorinanone 1 ($R = C_6H_5$) involving rapid addition of 10 N KOH to the acidic reaction mixture (final step) and ether extraction of the crude phosphorinanone 1 ($R = C_6H_5$) after the solution was extremely basic. Combination of the

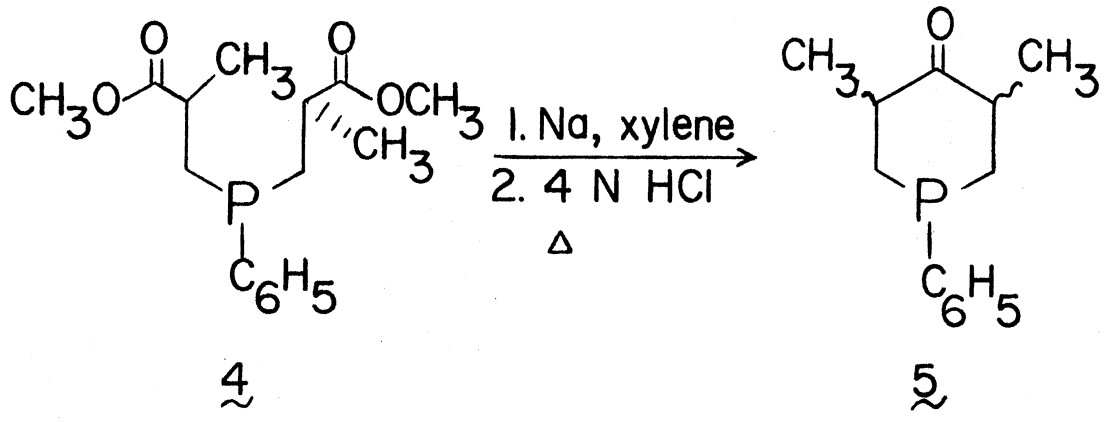


R = C_2H_5, C_6H_5

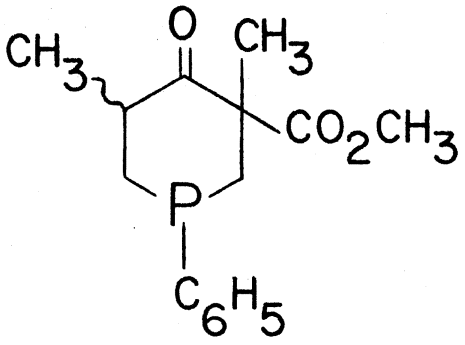
ether extracts followed by an aqueous wash and vacuum distillation gave the desired phosphorinanone 1 (R = C_6H_5) in good yield (68%).[25,54]

A related synthetic approach to members of 1 was realized when phenylphosphine was condensed with methyl methacrylate to yield bis-(2-methoxycarbonylpropyl)phenylphosphine (4).[6] Cyclization of phosphine





4 with Na in boiling xylene followed by acidic hydrolysis and decarboxylation of the resulting initial product gave the phosphorinanone 5 (17.8%).[6] Phosphorinanone 5 could be oxidized, sulfurized, or selenized. These derivatives, along with 5, were subjected to ^{1}H NMR analysis to ascertain if several major conformations existed in solution and to determine the equilibrium concentrations of the most populous conformers.[6] A second report[4] has appeared on the preparation of phosphorinanone 5; it included the isolation (albeit crude) of the β-keto ester 6 (51%).



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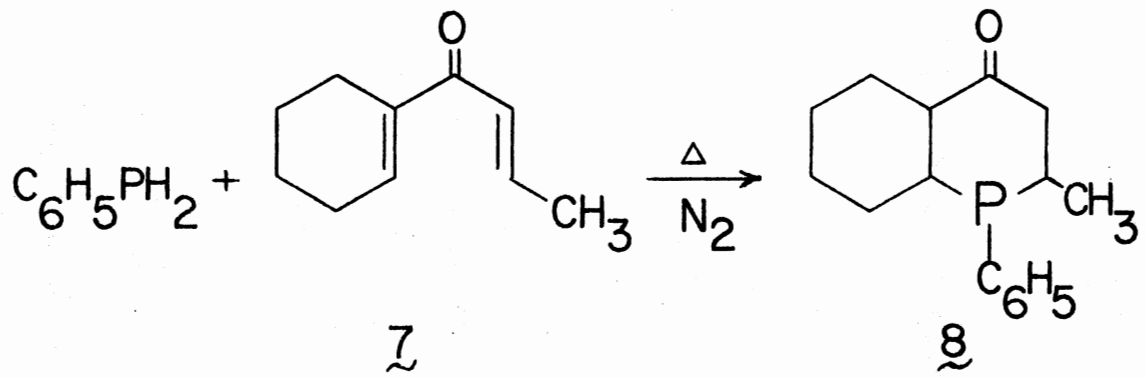
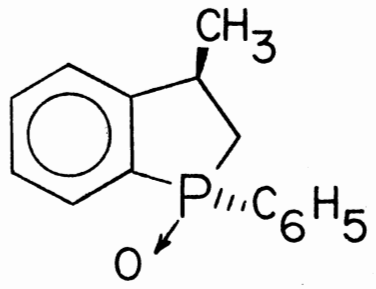
With the intent to prepare phosphasteroids,[31] phenylphosphine was condensed with cyclohexenyl propenyl ketone 7 to give 3-methyl-2-pheny-2-phosphabicyclo[4.4.0]decan-5-one (8). The authors suggested a trans configuration for the methyl and P-phenyl groups in the corresponding P-oxide based on ^{1}H NMR analysis of the downfield shift (0.5 ppm) of the methylene protons on the carbon atom adjacent to the carbonyl group. A comparison was made with the same protons in phosphine 8 in which these protons were less deshielded by the lone pair of electrons on phosphorus.[31]

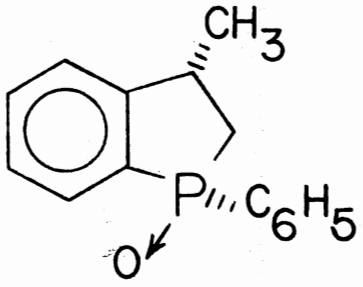


7 8

Support of the above observation with structurally related phosphindolines[8] 9a and 9b and phospholanes[9] 10a and 10b has appeared and suggests that the phosphoryl group (P→O) deshields the C(3) methyl



9a



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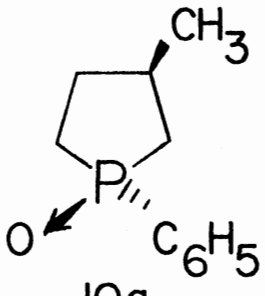

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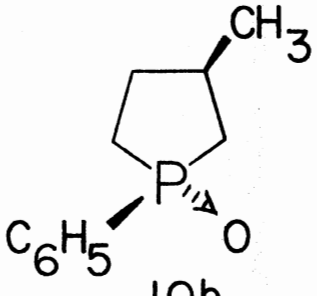
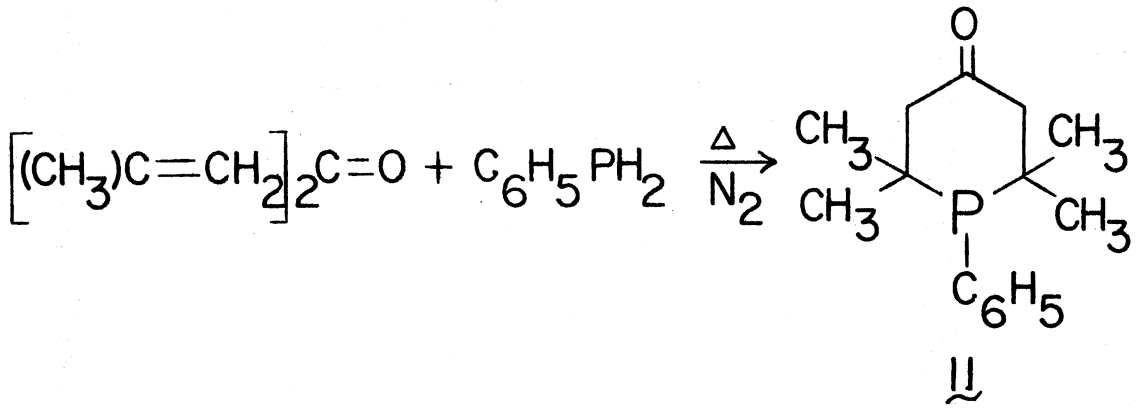


10b

more than the P-phenyl function. For 9a the ^{1}H NMR signal for the C(3) methyl group appeared at δ 1.54, and that same group in 9b had a ^{1}H NMR resonance at δ 1.45.[8] Similarly, 10a (with a syn arrangement of P→O and C(3)-methyl) had a ^{1}H NMR signal for the C(3)-methyl protons at δ 1.23 compared to a ^{1}H NMR signal for those same protons in 10b at δ 0.78.[8]

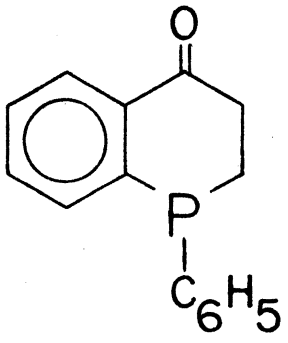
The entire stereochemical relationship rests on the X-ray analysis of cis-1-iodomethyl-1-phenylphospholanium iodide.[23]

A second synthetic method for the preparation of 4-phosphorinanones has utilized a Michael addition of primary phosphines to substituted α,β-unsaturated ketones.[4,59] An example is illustrated with the preparation of 2,2,6,6-tetramethyl-1-phenyl-4-phosphorinanone (11).[30] The general utility of the above process for the preparation



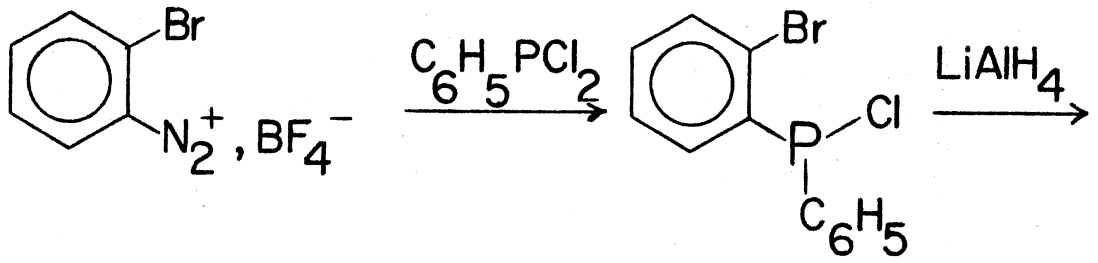
11

of a variety of P-substituted and ring-substituted 4-phosphorinanones has been discussed in a U.S. patent.[59]

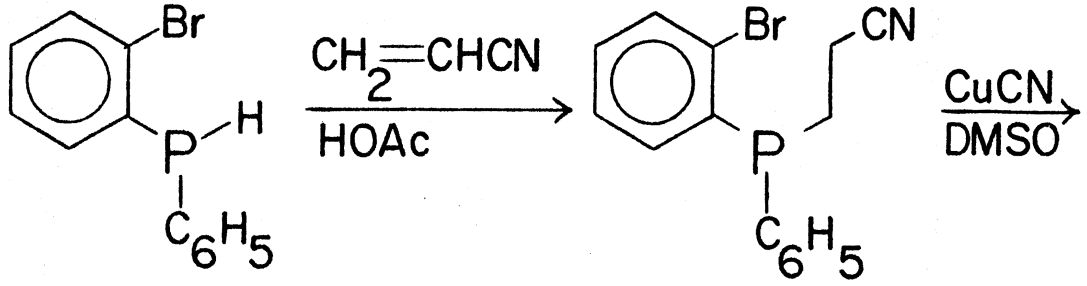


12

Another Thorpe-type condensation has been employed in the synthesis of 1,2,3,4-tetrahydro-4-oxo-1-phenylphosphinoline (12).[24] Condensation of phenylphosphonous dichloride with 2-bromophenyldiazonium tetrafluoroborate 13 gave the phosphinous chloride 14 (18.6%).



13 14



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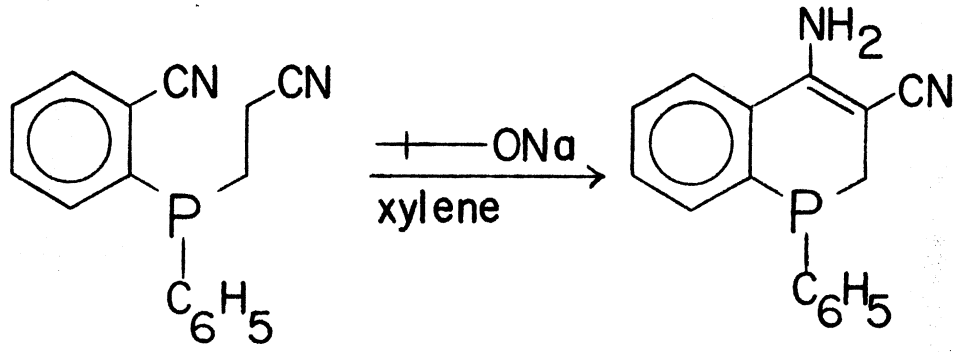

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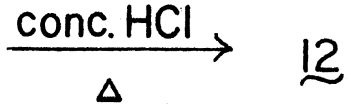
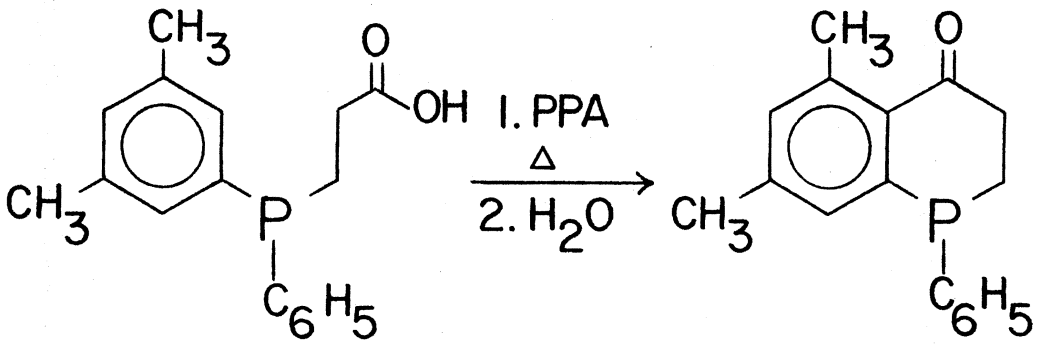


12

Reduction of 14 to the secondary phosphine 15 (82%) was accomplished with $LiAlH_4$ in ether. Cyanoethylation of 15 in acetic acid gave phosphine 16 (88%) which was condensed with CuCN to give 17 (not isolated). The latter was cyclized to amino nitrile 18 which was hydrolyzed-decarboxylated with conc. HCl and gave keto-phosphine 21 (last step 55%). Keto-phosphine 12 was characterized as its phenylsemicarbazone, methoperchlorate, and P-oxide.[24]

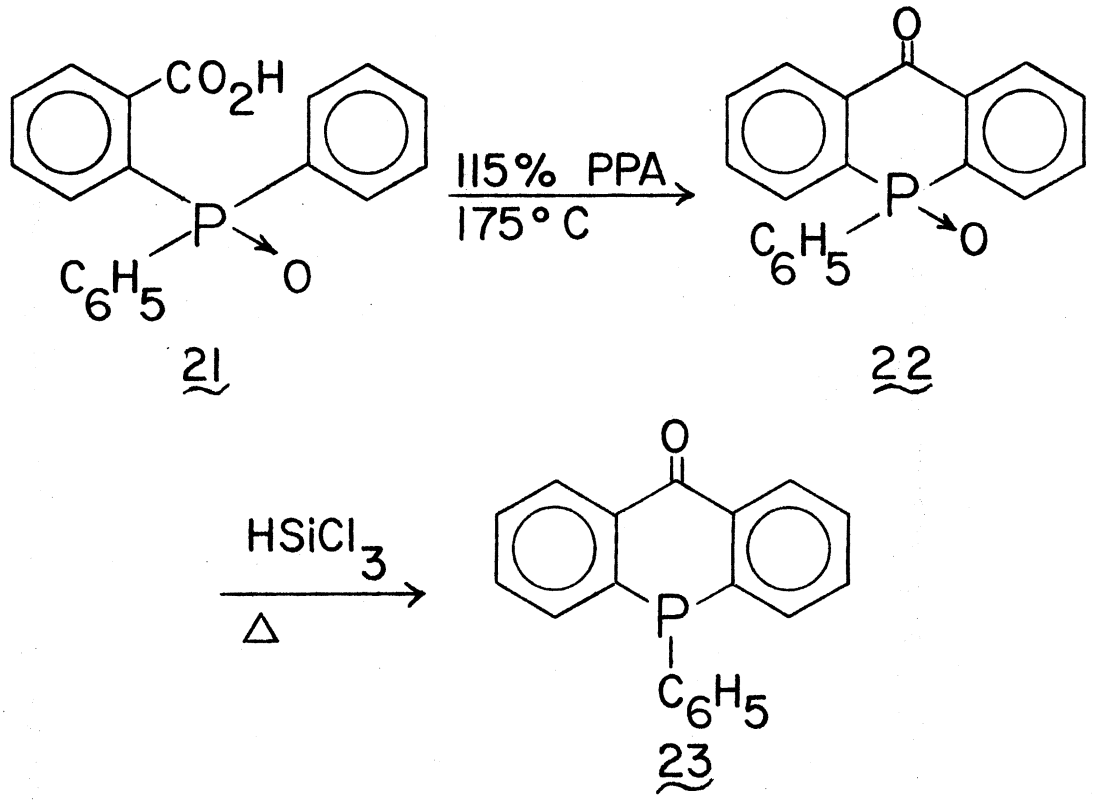
Polyphosphoric acid (PPA) has been used in the cyclization of



19 20

(2-carboxyethyl)(2,4-dimethylphenyl)phenylphosphine (19) to 1,2,3,4-tetrahydro-5,7-dimethyl-4-oxo-1-phenylphosphinoline (20), albeit in "very small yield".[24] Similarly, PPA proved a successful reagent in the conversion of oxide 21 to 5,10-dihydro-5-oxo-5-phenylacridophosphin-10-one (22), the immediate precursor of phosphine 23.[10,52] Removal of phosphoryl oxygen from 22 was accomplished with $HSiCl_3$ to give keto-phosphine 23 (90%).[10]

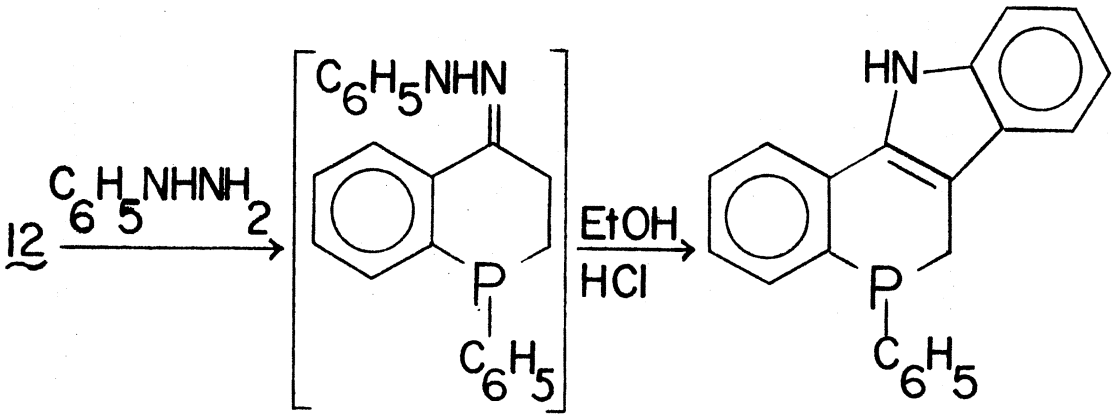
A most striking observation is that the few previously cited procedures for the preparation of 4-phosphorinanones are all that could



be found in the literature. Possibly the relatively moderate yields of desired product and simple reaction conditions via the Thorpe condensation[4,6,24,54,60] and Michael addition[31,59] have resulted in a state of complacency about developing better synthetic methods.

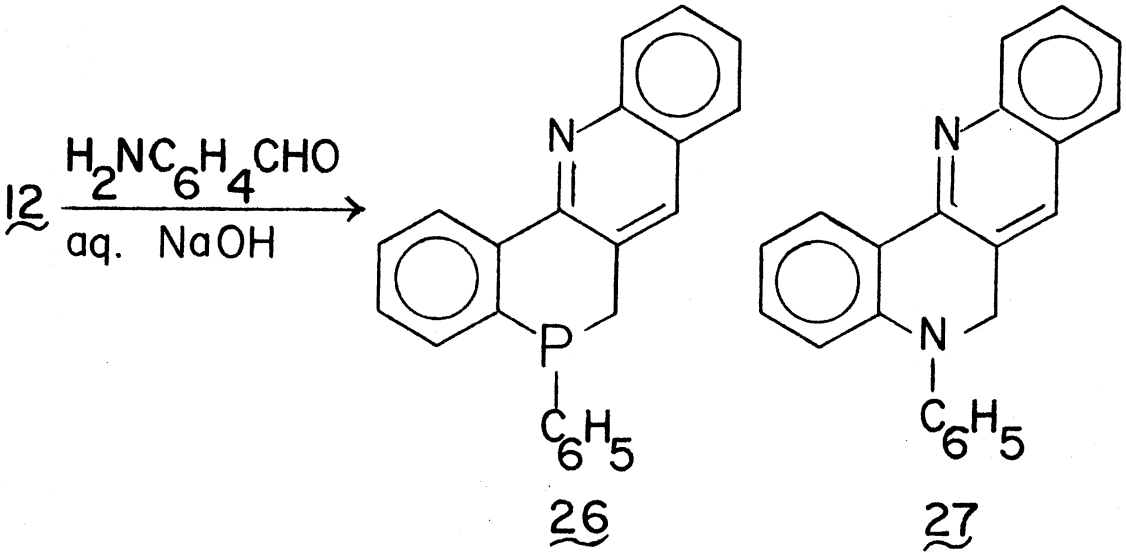
Obviously the most important reactions to date with 4-phosphorinanones 1 consist of additions to the carbonyl group and of attack at trivalent phosphorus (e.g., oxidation, sulfurization, and quaternization). A few examples of each will be included in the following discussion.

Concurrently with the preparation of phosphinoline 12,[24] Gallagher and Mann undertook the synthesis of polycyclic carbon-phosphorus (C-P) heterocycles 24 and 25.[26] Phosphinoline 12 condensed with phenylhydrazine to give the corresponding hydrazone 24. Cyclization of 24 in a



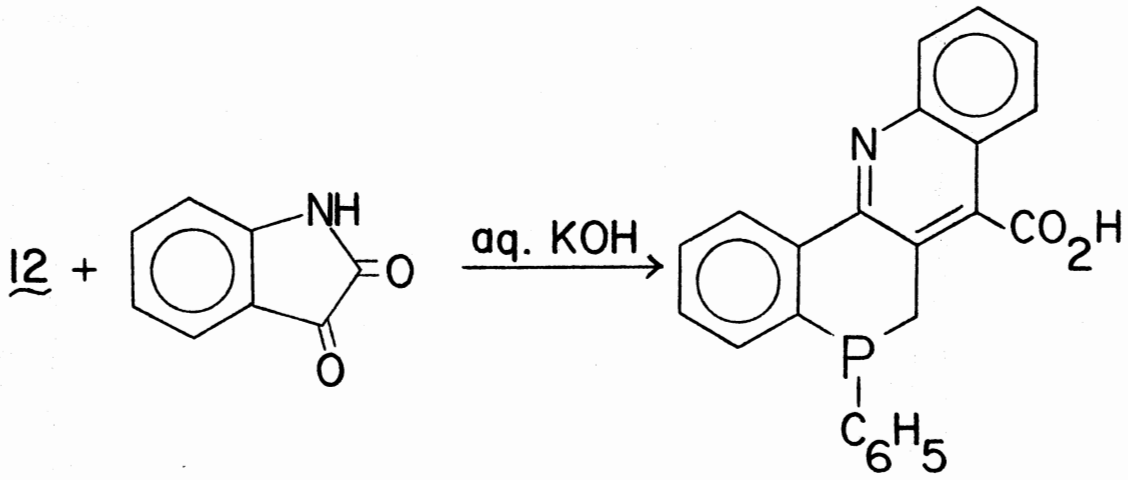
24 25

Fischer reaction with C_2H_5OH/HCl gave the indole derivative 25 (37%).[26] The indicated structure for 25 was supported by a N-H stretch at 3470 cm^{-1} in the infrared spectra. Phosphine 25 was characterized via its methiodide, mp 205-206°C.[26] Similarly, 12 condensed with 2-amino-benzaldehyde in aqueous NaOH and formed the quinoline derivative 26



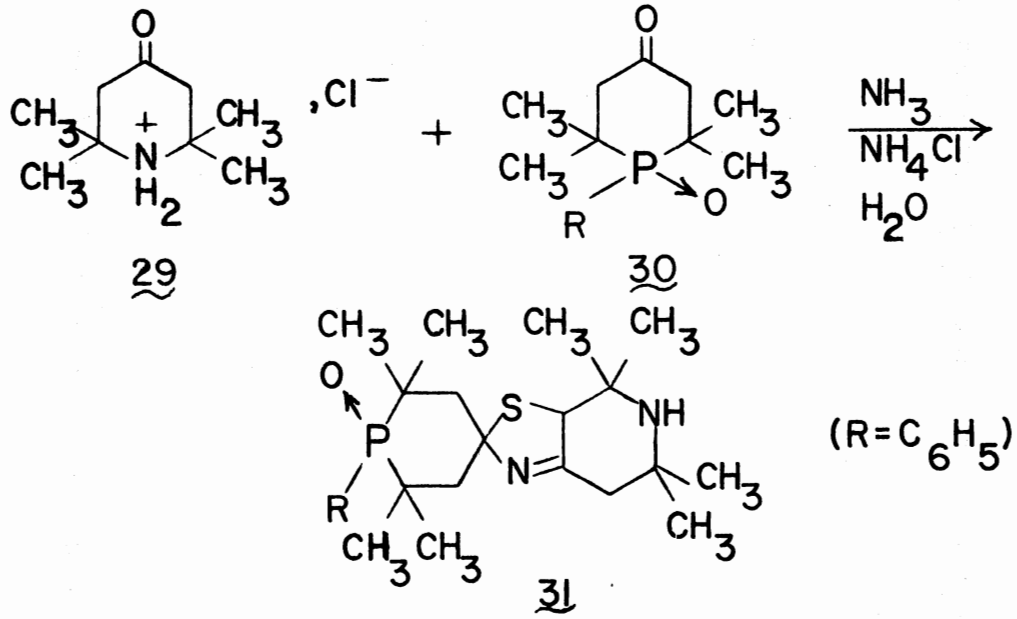
26 27

(89%).[26] The authors indicated that the ^{1}H NMR spectrum of 26 was quite complex and could not be simply interpreted. However, the ultraviolet spectrum of 26 (in C_2H_5OH) was nearly identical to that of its structurally similar nitrogen analog 27.[26] Condensation of 12 with isatin in 80% aqueous potassium hydroxide gave the carboxyphosphine 28 (46%).[26] Preparation of the benzylthiouronium salt of 28 gave two crystalline solids, mp 138.5-139.5°C and mp 212.5-213.5°C.[26] No rationale was



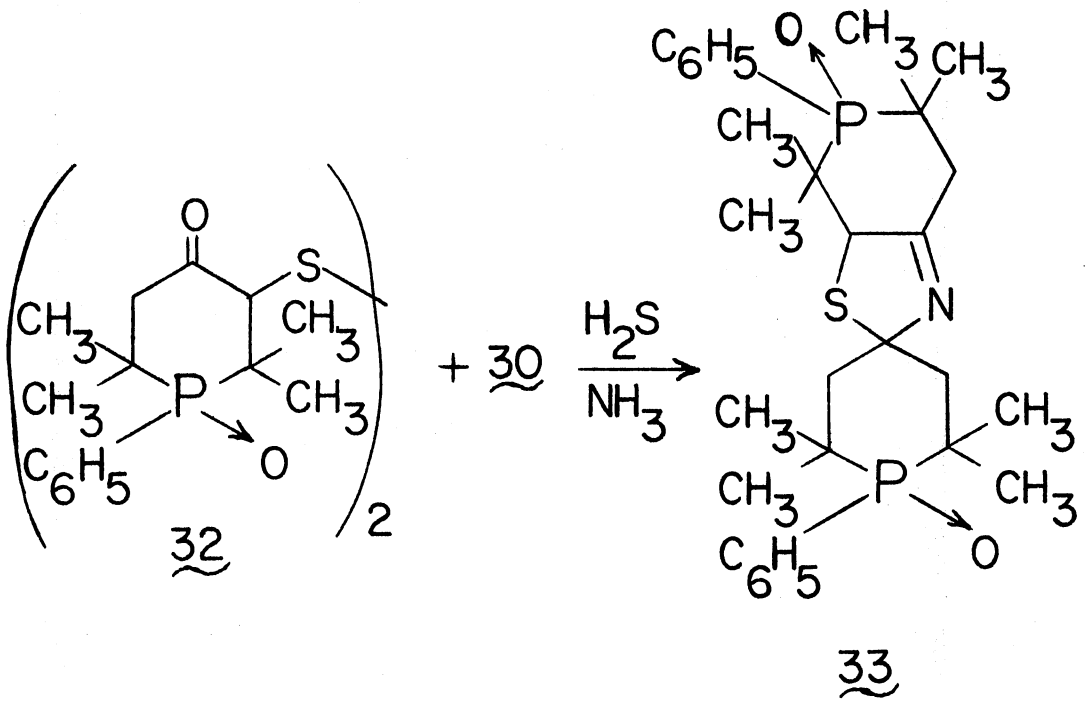
28

given for this observation; however, the salts could differ in their configuration at phosphorus.

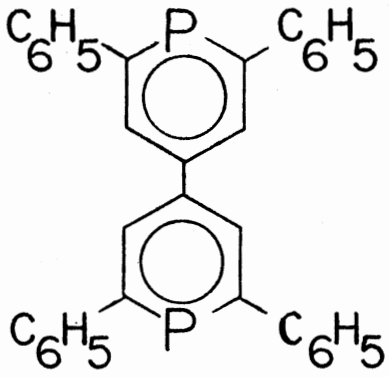


29 30 31

Interestingly, piperidonium chloride 29 and ketone 30 gave the novel Δ^3-thiazoline derivative 31 [61% (X = O); 41% (S = S)].[3] Unfortunately, no spectral data were given for 31, but the elemental analyses agreed quite well with the calculated values. Likewise, bis-oxide 32 reacted with ketone 30 (X = O) to give another Δ^3-thiazoline 33 (34%).[3]

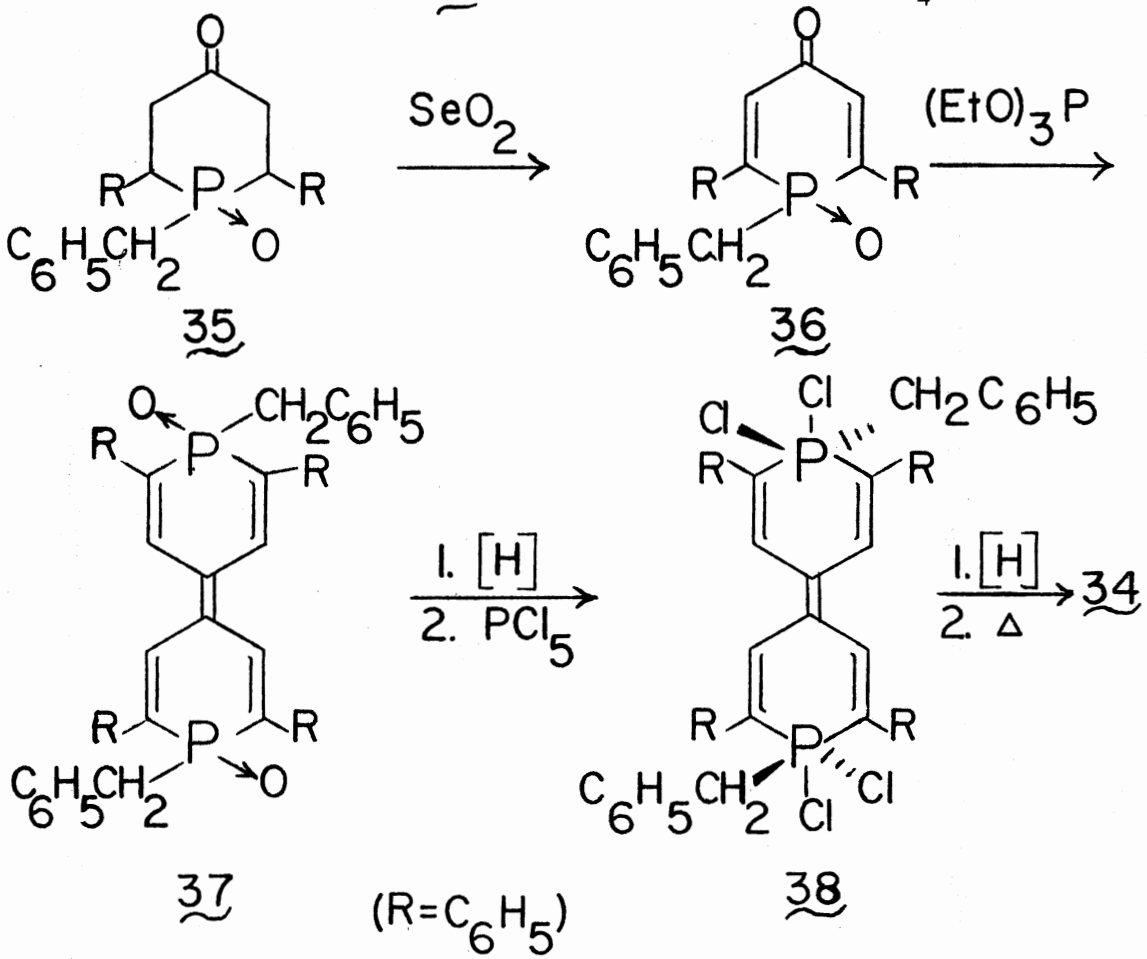


Attempts in the preparation of potentially aromatic C-P heterocycles has led to the synthesis of a bis-phosphorin 34.[41] Dehydrogenation with SeO_2 of oxide 35 followed by dimerization (via deoxygenation) with triethyl phosphite gave the bis-oxide 37 (80%). The

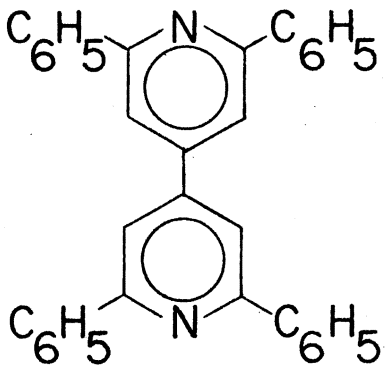


34

^{1}H NMR spectrum of 37 exhibited a doublet at δ 3.12 ($^2J_{PCH}$ = 18.5 Hz) for the benzylic protons and a singlet at δ 7.63 for the vinylic protons. Reduction of oxide 37 with phenylsilane and $LiAlH_4$ followed by

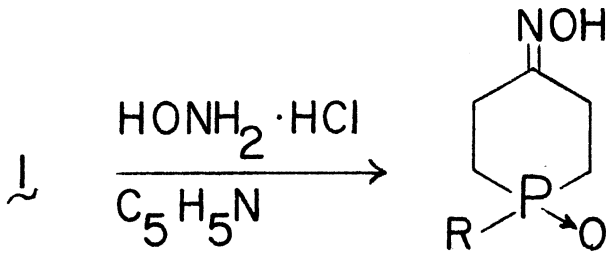


chlorination of the product gave the bis-phosphorane 38. Dechlorination of 38 was accomplished with phenylsilane followed by debenzylation at 350°C and resulted in 34 (mp 236-238°C).[41] The ^{1}H NMR spectrum of 34 exhibited a doublet at δ 8.23 ($^{3}J_{PCCH}$ = 5.5 Hz), which supported the aromatic-like structure for 34. Similarly, the ultraviolet spectrum of 34 exhibited absorptions at 328 and 280 nm which compared well to those found for 2,2',6,6'-tetraphenyl-4,4'-bipyridyl (39) at 317 and 246 nm.[41]



39

A rather surprising observation was made in the attempted preparation of oximes of 4-phosphorinanones 1 (R = CH_3, C_2H_5).[44] For example, reaction of 1 with hydroxylamine hydrochloride in pyridine did not



R = CH_3, C_2H_5 40

give the simple phosphine oxime but rather the corresponding oxide 40 was isolated (25%, R = CH_3; 65%, R = C_2H_5).[44] Hydroxylamine was also found to oxidize tertiary phosphines which did not contain a carbonyl group. The authors suggested that the phosphine reduced hydroxylamine

to ammonia; however, no attempts were made to prove this hypothesis.[44]

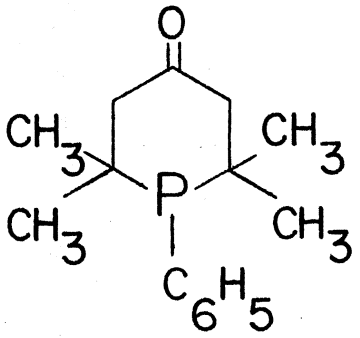
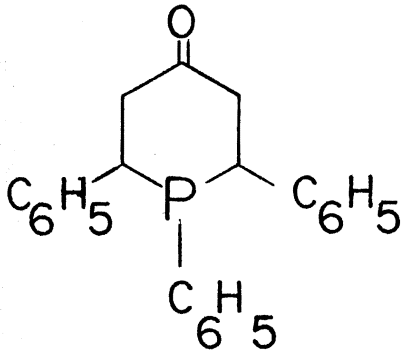
For the most part, chemical and physical properties of 4-phosphorinanones 1 have not been investigated. One report listed pK_a values of a few derivatives of 1; in general, the cyclic phosphines were less basic than acyclic tertiary phosphines (see Table I).[55,59]

To date, only one 4-phosphorinanone 1, where R = C_6H_5, has been analyzed by X-ray crystallography.[45,58] Phosphorinanone 1 (R = C_6H_5) exists in a flattened chair conformation with the phenyl group <u>axially</u> oriented. Steric stain between the phenyl group and H(3,5) axial protons may, in part, be relieved by a 0.29-Å displacement of the phosphorus atom from the plane defined by the phenyl group carbon atoms. The exocyclic C-P-C bond angle for 1 (R = C_6H_5) was determined to be <u>ca</u>. 103° which compared remarkably well to the 103° for triphenylphosphine.[16] However, the P-C (phenyl) bond distance in 1 (R = C_6H_5) was 1.838 Å compared to 1.828 Å for triphenylphosphine.[16] This increase in bond length may also, in part, relieve the steric crowding about phosphorus in 1 (R = C_6H_5).

Two derivatives of 1 (R = C_6H_5) have also been examined in the solid state.[57] A striking difference is that the oxide and sulfide of 1 (R = C_6H_5) have the phenyl group in the <u>equatorial</u> position in the crystal. The P-C (phenyl) bond distance for the oxide of 1 (R = C_6H_5) was determined to be 1.799 Å and 1.802 Å was found for the C-P length in the sulfide of 1 (R = C_6H_5). This shortening of the P-C (phenyl) bond length compared to that in the phosphine could result from a reduced electronegativity of phosphorus when oxidized or sulfurized. Also the C-P-C exocyclic bond angle is <u>ca</u>. 5° larger in the oxide and sulfide of 1 (R = C_6H_5) than in the phosphine 1 (R = C_6H_5).[57]

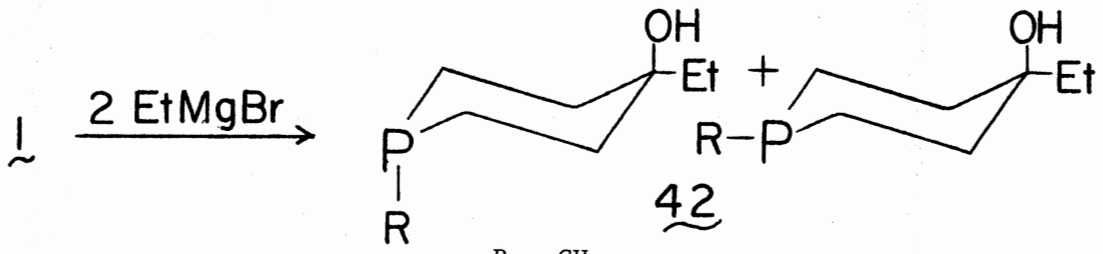
TABLE I

pK_a VALUES OF SELECTED PHOSPHINES

Phosphine	pK_a
 II	4.61[59]
 III	1.85[59]
$C_6H_5P(C_2H_5)_2$	6.25[55]
$(C_2H_5)_3P$	8.69[55]
$(C_6H_5)_3P$	2.73[55]
$C_6H_5P(CH_2CH_2CN)_2$	3.20[55]

Stereochemistry and Energetics of Six-Membered P-Ring Systems

One of the first observations of geometrical isomerism in six-membered, phosphorus-containing ring compounds was made on 4-ethyl-1-methyl-4-phosphorinanol (42).[51] The reaction of two equivalents of ethylmagnesium bromide with 1 (R = CH_3) gave a mixture of alcohols 42

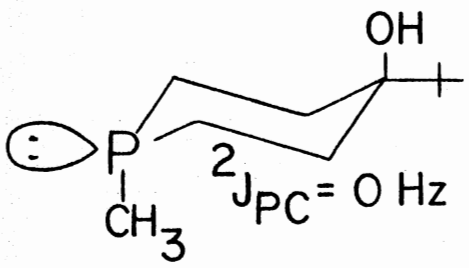


R = CH_3

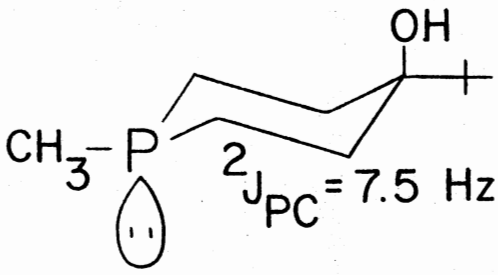
in a ratio of 1:1.33. Separation was effected by fractional distillation and both alcohols were identified via the preparation of isomeric benzoperchlorates.[51] Further investigations of alcohols 42 led the same authors to suggest a difference in configuration at P instead of the carbinol carbon.[53] Nearly identical C-O stretching frequencies (1100 and 1105 cm^{-1}) were noted in the infrared spectra of alcohols 42 which suggested identical configurations at C(4). Also, the ^1H NMR spectra of alcohols 42 exhibited two P-CH_3 doublets at δ 0.95 ($^2J_{PCH}$ = 2.5 Hz) and δ 0.91 ($^2J_{PCH}$ = 3.8 Hz) which supported the assignment of alcohols 42 as differing only in configuration at P.[53]

Recently, ^{13}C NMR analysis for a number of 4-phosphorinanones appeared in the literature.[9] A small ^{31}P-^{13}C coupling constant of 2 Hz was noted for the C(3,5) carbon atoms in 1 (R = CH_3); this was taken to indicate an appreciable concentration of the phosphine with axial methyl in $HCCl_3$. This observation was based on previous ^{13}C NMR

assignments[22] for isomeric 4-tert-butyl-1-methyl-4-phosphorinanols 43a and 43b of known[21,47] stereochemical configuration.

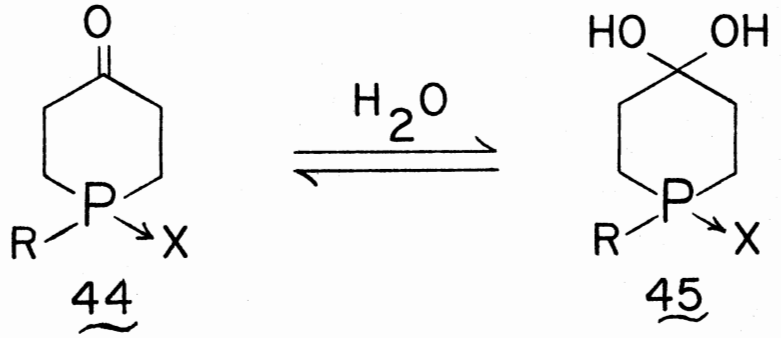


43a



43b

Upon dissolving oxides or sulfides 44 in H_2O, a signal in the ^{13}C NMR spectrum appeared at ca. 96 ppm which was suggested to represent



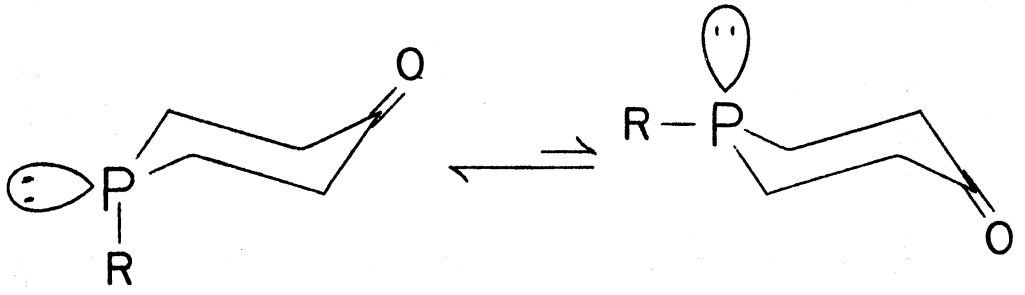
44 ⇌ 45

R = CH_3, C_2H_5

X = O, S

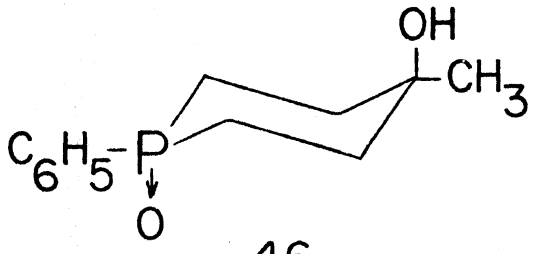
the hydrated C(4) carbon atom as in 45.[9] The dramatic chemical shift difference (ca. -110 ppm) for the hydrated C(4) carbon atom compared to the nonhydrated C(4) carbon atom was not without precedent.[30] Also, the carbonyl form 44 and the hydrated form 45 exhibited different signals in the ^{31}P NMR spectra and equilibrium compositions could be obtained from H_2O solutions containing 5-10% CH_3OH at 30°C.[9]

^{13}C NMR data have also been found useful in the assignment of configuration at phosphorus in derivatives of 1-phenyl-4-phosphorinanone (1, R = C_6H_5).[57] A $^2J_{PC(3,5)}$ value of 1.23 Hz for 1 (R = C_6H_5) suggests

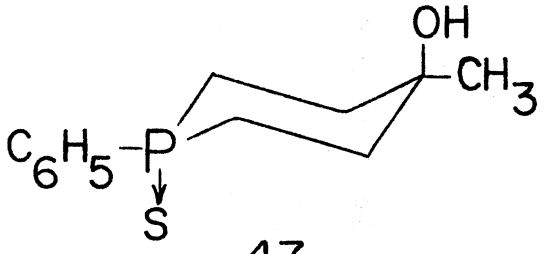


1 (R = C_6H_5)

a predominance of the 4-phosphorinanone with axial phenyl in $DCCl_3$ in view of the observation that $^2J_{PC(3,5)}$ = 0 Hz for 43a.[22] However, $^2J_{PC(3,5)}$ values of 5.89 Hz and 5.31 Hz were recorded for the oxide 46 and sulfide 47, respectively. This observation was consistent with an

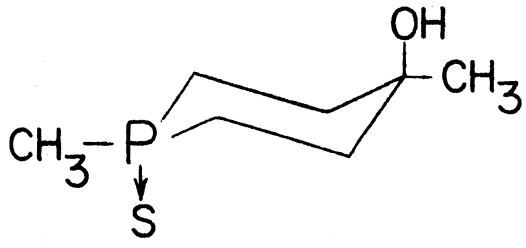


46

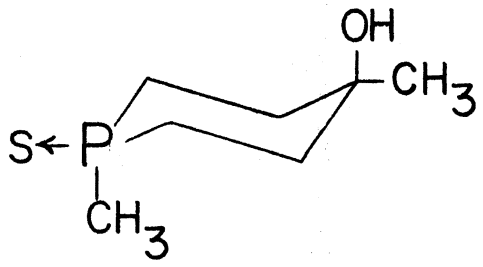


47

axial preference for sulfur as noted in other six-membered P-ring systems.[20,50] Previous work[50] implied that when sulfur was axially oriented in 1,4-dimethyl-4-phosphorinanol 1-sulfide (48a) there were



48a

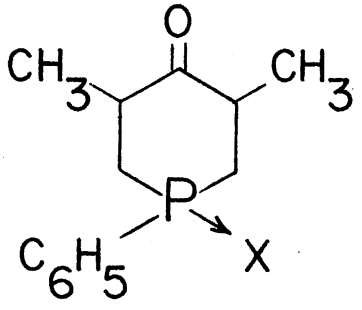


48b

displayed shielded ^{13}C NMR signals for the C(3,5) carbons atoms. Larger ^{31}P-^{13}C coupling constants were also recorded compared to those for similar carbons in 48b.

Little other work has been recorded on conformational analysis of 4-phosphorinanones. However, there is a report on the epimerization and equilibration at carbons C(3,5) in 3,5-dimethyl-1-phenyl-4-phosphorinanone (5) and certain derivatives.[6] For example, in the synthesis of the sulfide and selenide of 5, two configurational isomers were produced.[16] A chair form was suggested by the authors for the six-membered ring with both methyls equatorially disposed (cis). Therefore, the two isomers were considered epimeric at phosphorus. However, only one isomer was isolated after oxidation of 5 with 50% H_2O_2 in chloroform, but a second component was observed by TLC. No explanation was presented for the difference in reactions $R_3P \longrightarrow R_3P{\rightarrow}S$ (or $R_3P{\rightarrow}Se$) vs $R_3P{\rightarrow}O \longrightarrow R_3P{\rightarrow}O$.

Equilibration of 5, 49, 50 and 51 was accomplished by addition



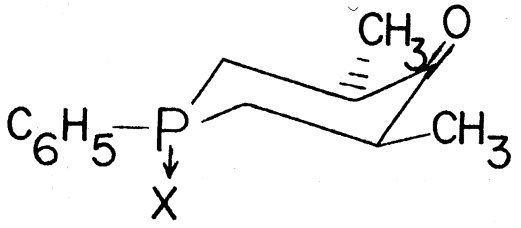
49: X = O

50: X = S

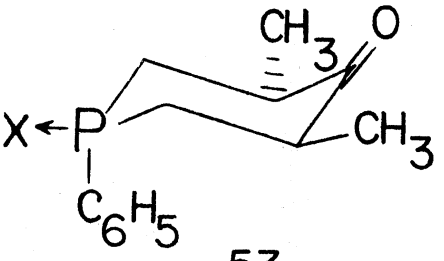
51: X = Se

of NaOD to D_2O:dioxane solutions.[6] Deuteration occurred simultaneously at C(3,5), which greatly reduced the complexity of the ^1H NMR spectra

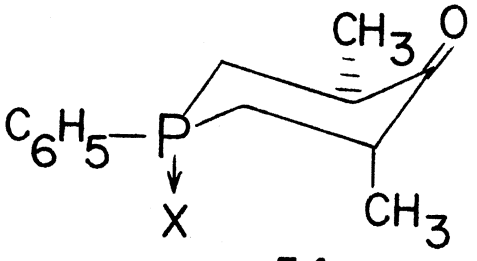
in the quilibration measurements. Equilibration of 49, 50, and 51 with NaOD gave three signals in the ^{1}H NMR spectra which corresponded to three different conformations. The major component 52 in all three cases (X = O, S, Se) was the configurational isomer with diequatorial methyl groups



52



53

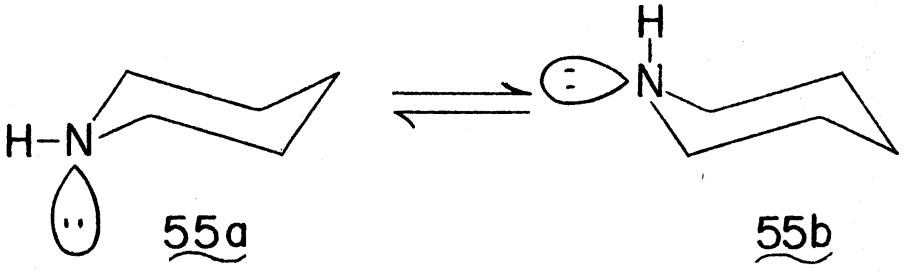


54

X = O, S, Se

(cis) and equatorial phenyl group, followed in concentration by 53 and 54, respectively. The 4-phosphorinanone 5, after equilibration with NaOD, yielded similar results as did its derivatives 49, 50, and 51. However, the configurational isomer 53 with diequatorial C(3,5) methyl groups and an axial phenyl group was judged to be of highest concentration in the equilibration mixture. In summary, the authors noted that the substituent on phosphorus in 5 (i.e. lone pair of electrons, O, S, or Se) had little effect on the equilibration data.[6]

Since relatively little information is known concerning the energetics of ring reversal in 4-phosphorinanones 1, the brief discussion to follow will be focused on a few nitrogen-, sulfur-, and saturated phosphorus-containing systems. Apparently, the first six-membered heterocycle to be studied was piperidine (55a $\rightleftharpoons$ 55b).[34,36] Determination of the barrier (E_a) to ring reversal for 55a $\rightleftharpoons$ 55b



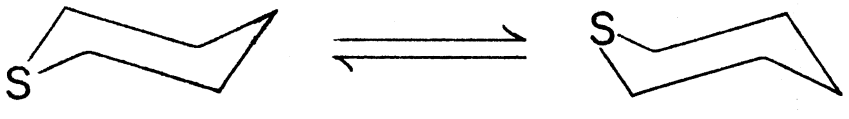
55a 55b

over the temperature range -50 to -80°C by complete line-shape analysis of the ^{1}H NMR spectrum gave E_a = 14.5 ± 0.5 kcal/mole.[36] Similar experiments were performed with 1-methylpiperidine and a value of ca. 14 kcal/mole was calculated for the barrier (E_a) to ring reversal.[36]

Recently, a report[2] appeared on the determination of the barrier (ΔG^*) to pyramidal inversion in piperidine. Low-temperature (-100 to -172°C) ^{13}C NMR analysis of piperidine indicated that below -142°C two distinct ^{13}C signals for carbons C(3,5) were apparent. Absolute rate theory provided a value of 6.1 ± 0.2 kcal/mole for this barrier to pyramidal inversion on nitrogen. High-resolution (251 MHz) ^{1}H NMR analysis of piperidine at T < -150°C indicated an equatorial preference for the proton on nitrogen. Observation of a 1:2:1 triplet for the C(2,6) protons in the low-temperature ^{1}H NMR spectra supported the

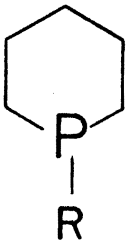
assignment since the axial-equatorial and equatorial-equatorial NH—C(2,6) H coupling constants should be nonresolvable.[2]

The barrier (ΔG^*) to ring reversal in thiane 56a $\rightleftharpoons$ 56b has been experimentally determined to be ca. 90 kcal/mole at -93°C.[35,37]



56a 56b

Several P-substituted phosphorinanes 57 have been examined by low-temperature ^{31}P NMR spectroscopy and the barriers (ΔG^*) to ring reversal in these systems were determined.[21] When R = CH_3, ΔG^* for



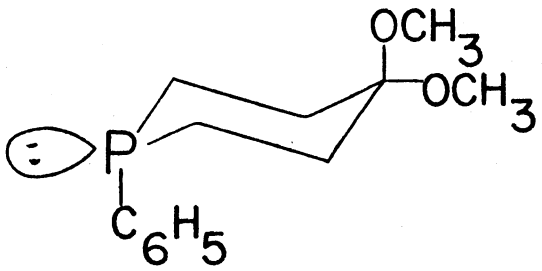
57

R = CH_3, C_2H_5, C_6H_5

ring reversal was found to be 8.7 kcal/mole at -87°C (T_c). Similarly when R = C_2H_5, ΔG^* was 8.4 kcal/mole at -96°C (T_c), and, when R = C_6H_5, ΔG^* was 9.3 kcal/mole at -65°C (T_c).[21] It should be noted that the barriers (ΔG^*) to ring reversal in the phosphorinanes 57 are lower than those of the piperidines which may be due, in part, to the increased size of P vs N and the increased bond length (to minimize

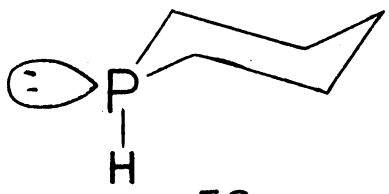
nonbonded repulsive interactions) of C-P vs C-N (C-P bond length, 1.83 $\overset{o}{A}$[13]; C-N bond length 1.47 $\overset{o}{A}$[48]).

Of particular interest in the conformational analysis of phosphorinanes has been the determination of the configurational preference of an alkyl or aryl group attached to phosphorus. In the majority of cases studied, the P-substituent has preferred an axial position at room temperature.[21] Support of this is presented in the X-ray crystallographic analysis of 1-phenyl-4-phosphorinanone (1, R = C_6H_5)[45] and 4,4-dimethoxy-1-phenylphosphorinane (58)[46] where the phenyl groups occupy exclusively the axial positions. However, at low temperatures



58

a predominance of the configurational isomer with an equatorially oriented P-substituent was noted for phosphorinanes 57 (R = CH_3, C_2H_5, and C_6H_5) via a ^{31}P NMR analysis.[21] The above results suggest there is little energy cost in minor geometric deformations (e.g. puckering, flattening[45,46]) of phosphorinanes when the P-substituent is axially oriented.



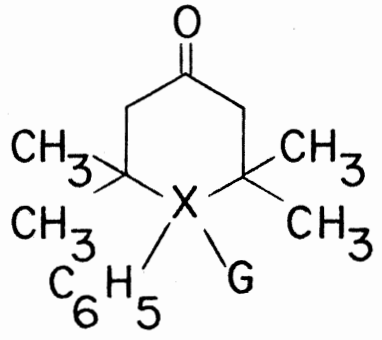
59

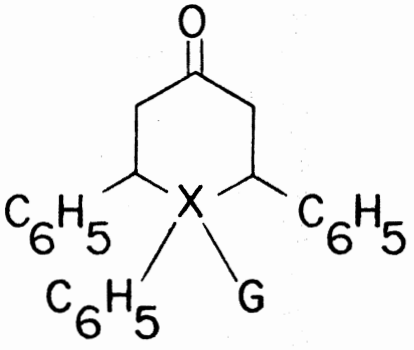
An axial preference for the proton on phosphorus has been determined for phosphorinane 59 via low-temperature ^{1}H NMR spectroscopy. At -50°C the multiplicity of the ^{1}H NMR signal for P-H consists of a triplet of triplets with $J_{HPCH_{ax}}$ = 12 Hz and oriented, the ^{1}H NMR spectra should consist of a quintet since $J_{HPCH_{ax}} \cong J_{HPCH_{eq}}$.[38,39]

CHAPTER II

RESULTS AND DISCUSSION

The chemistry and conformation analysis of six-membered cyclic heterocycles containing phosphorus as the heteroatom is an area of active interest.[13,33,58] Herein we report the synthesis of new derivatives of 11a and 41a and conformational analysis, via ^{1}H, ^{13}C, and ^{31}P NMR examination, and configurational preferences of groups which are





11a: X = P; G = lone pair

11b: X = P; G = O

11c: X = P; G = S

11d: X = P^{+}; G = CH_3, I^{-}

11e: X = P^{+}; G = C_2H_5, I^{-}

11f: X = P^{+}; G = $C_6H_5CH_2$, Br^{-}

41a: X = P; G = lone pair

41b: X = P; G = O

41c: X = P; G = S

attached to phosphorus or are located at C(2,6) and C(4) [See Tables II and III]. A few of the compounds to be discussed have previously

TABLE II

^{13}C NMR CHEMICAL SHIFTS[a] (^{31}P-^{13}C COUPLING CONSTANTS)[b] FOR SUBSTITUTED 4-PHOSPHORINANONES 11a-f AND 41a-c

Carbon	Compound						
	11a	11a[c]	11b	11c	11d[d]	11e[d]	11f[d]
2,6	35.2(18.3)	34.9(19.0)	37.9(60.9)	39.7(25.8)	33.7(40.4)	34.5(37.6)	35.1(36.8)
3,5	52.9(3.0)	52.8(7.8)	53.6	53.8	50.9	51.7	51.6
4	211.1	208.8	206.4	205.9(6.8)	203.7(7.4)	203.5(7.4)	203.5(6.5)
ax-me	30.8(44.3)	30.8(44.9)	25.7	27.4	25.6	26.8	26.6
eq-me	30.3(4.3)	30.3(2.2)	25.1	26.4	25.6	25.4	25.4
Ph-1[e]	135.5(23.5)	135.9(23.6)	128.0(83.9)	127.9(65.6)	115.8(74.2)	114.1(71.4)	115.5(69.2)
Ph-2[e]	128.9(29.6)	129.1(18.3)	132.1(16.2)	133.5(8.3)	133.5(8.6)	133.9(7.9)	134.9(10.9)
Ph-3[e]	128.2(8.7)	128.2(8.7)	128.3	128.4(11.0)	129.6(11.7)	130.0(11.6)	129.8(18.4)
Ph-4[e]	128.0	127.8	132.4	131.7(2.8)	134.4(2.9)	134.4(2.4)	134.8
CH_2						7.8(46.0)	20.9(43.3)
CH_3					-1.0(48.4)	8.0(6.5)	
Bz-1[f]							128.5(30.0)
Bz-2[f]							130.0(3.7)
Bz-3[f]							129.9
Bz-4[f]							128.7

TABLE II (Continued)

Carbon	Compound						
	41a	41a'	41a[c]	41a'[c]	41b	41b'	41c'
2,6	36.4(16.3)	36.4(16.3)	36.8(17.0)	48.6(14.6)	38.2(60.4)	46.5(56.6)	51.6(41.8)
	38.9(22.9)	38.9(22.9)	38.9(23.7)	44.8(13.3)	45.0(60.5)	40.5(60.5)	38.0(44.8)
3,5	42.7(2.9)	44.9(13.2)	42.8(2.7)	42.8(2.7)	42.7(4.3)	42.7(4.3)	45.0(2.9)
	46.2(8.1)	48.6(14.0)	46.1(7.9)	46.1(7.9)	45.2(4.7)	45.2(4.7)	43.0(3.0)
4	509.7	207.7(11.5)	207.6	205.5	205.7(2.8)	207.2(6.2)	207.1(5.4)

[a]All samples were ca. 200 mg in $DCCl_3$ except where noted. Chemical shifts are in ppm (±0.1) downfield from internal tetramethylsilane (TMS).

[b]^{31}P-^{13}C coupling constants are in Hz (±0.4).

[c]In hexadeuteriobenzene (C_6D_6).

[d]In hexadeuteriodimethyl sulfoxide (DMSO-d_6).

[e]Ph-1 signifies the carbon attached to phosphorus, Ph-2 = ortho carbons, Ph-3 = meta carbons, and Ph-4 = para carbon.

[f]Bz-1 signifies the carbon attached to the methylene group, Bz-2 = ortho carbons, Bz-3 = meta carbons, and Bz-4 = para carbon.

TABLE III

SPECTRAL DATA FOR SUBSTITUTED 4-PHOSPHORINANONES 11a-f AND 41a-c

Cpd	IR Absorption Spectra in KBr,[a] Selected Bands, cm^{-1}	^1H NMR Spectral Assignments Chemical Shifts, δ[b]	^{31}P NMR, δ[c]
11a	2900,1680,1435,1290, 1187,478,698	0.93[d(J_{PCCH}=11 Hz), CH_3, 6 H] 1.32[d(J_{PCCH}=18 Hz), CH_3, 6 H] 2.12[d of d(J_{HCH}=14 Hz,J_{PCCH}=6 Hz), CH_a, 2 H] 2.93[d of d(J_{HCH}=14 Hz,J_{PCH}=2 Hz, CH_e, 2 H] 7.32-7.86[m, ArH, 5 H]	-16.05
11b	2940,1700,1442,1176, 1104,757,713	1.19[d(J_{PCCH}=8 Hz), CH_3, 6 H] 1.32[d(J_{PCCH}=7 Hz), CH_3, 6 H] 2.61[d of d(J_{HCH}=13 Hz,J_{PCCH}=13 Hz), CH_a, 2 H] 2.99[d of d(J_{HCH}=13 Hz,J_{PCCH}=13 Hz), CH_e, 2 H] 7.46-7.64[m, ArH, 3 H] 7.82-8.08[m, ArH, 2 H]	+41.21
11c	2850,1690,1430,1092 867,718,697	1.14[d(J_{PCCH}=16 Hz), CH_3, 6 H] 1.44[d(J_{PCCH}=16 Hz), CH_3, 6 H] 2.56-3.22[m(J_{HCH}<2 Hz), CH_2, 4 H] 7.40-7.68[m, ArH, 3 H] 8.12-8.44[m, ArH, 2 H]	+64.42

TABLE III (Continued)

Cpd	IR Absorption Spectra in KBr,[a] Selected Bands, cm^{-1}	^1H NMR Spectral Assignments Chemical Shifts, δ[b]	^{31}P NMR, δ[c]
11d	2850,1700,1435,1206 1105,907,748	1.18[d(J_{PCCH}=16 Hz), $C\underline{H}_3$, 6 H] 1.41[d(J_{PCCH}=15 Hz), $C\underline{H}_3$, 6 H] 2.60[d(J_{PCH}=14 Hz), $C\underline{H}_3$, 3 H] 2.85[d of d(J_{HCH}=14 Hz,J_{PCCH}=14 Hz), $C\underline{H}_a$, 2 H] 3.27[d of d(J_{HCH}=14 Hz,J_{PCCH}=14 Hz), $C\underline{H}_e$, 2 H] 7.27-7.96[m, Ar$\underline{H}$, 3 H] 7.98-8.26[m, Ar$\underline{H}$, 2 H]	+35.27
11e	2850,1710,1435,1195 1110,753,697	0.84-1.64[m, $C\underline{H}_3$, 3 H] 1.16[d(J_{PCCH}=16 Hz) $C\underline{H}_3$, 6 H] 1.51[d(J_{PCCH}=14 Hz) $C\underline{H}_3$, 6 H] 2.72[d of d(J_{HCH}=16 Hz,J_{PCCH}=16 Hz) $C\underline{H}_a$, 2 H] 3.00-3.50[m(J_{HCCH}=7 Hz), $C\underline{H}_2$, 2 H] 3.25[d of d(J_{HCH}=16 Hz,J_{PCCH}=16 Hz), $C\underline{H}_e$, 2 H] 7.64-8.28[m, Ar$\underline{H}$, 5 H]	+37.39

TABLE III (Continued)

Cpd	IR Absorption Spectra in KBr,[a] Selected Bands, cm^{-1}	^1H NMR Spectral Assignments Chemical Shifts, δ[b]	^{31}P NMR, δ[c]
11f	2850,1700,1445,1207	1.02[d(J_{PCCH}=16 Hz) $C\underline{H}_3$, 6 H]	+35.21
	1103,843,697	2.56[d(J_{PCCH}=16 Hz) $C\underline{H}_3$, 6 H]	
		2.83[d of d(J_{HCH}=Hz,J_{PCCH}=22 Hz), $C\underline{H}_a$, 2 H]	
		3.13[d of d(J_{HCH}=14 Hz,J_{PCCH}=18 Hz), $C\underline{H}_e$, 2 H]	
		4.91[d(J_{PCH}=13 Hz) $C\underline{H}_2$, 2 H]	
		7.18-7.52[m, Ar$\underline{H}$, 5 H]	
		7.70-8.08[m, Ar$\underline{H}$, 3 H]	
		8.38-8.72[m, Ar$\underline{H}$, 2 H]	
41a	2960,1690,1430,1237	2.80-3.48[m, $C\underline{H}_2$, 4 H]	- 6.20
(41a')	1138,905,696	3.64-4.06[m, C$\underline{H}$, 2 H]	- 3.37
		6.68-6.84[m, Ar$\underline{H}$, 2 H]	
		6.94-7.40[m, Ar$\underline{H}$, 13 H]	
41b	3000,1700,1435,1175	2.70-3.40[m, C$\underline{H}$, 2 H]	+32.21
(41b')	1117,847,698	3.44-4.08[m, $C\underline{H}_2$, 2 H]	+33.95
		6.76-6.96[m, Ar$\underline{H}$, 2 H]	
		6.98-7.44[m, Ar$\underline{H}$, 13 H]	

TABLE III (Continued)

Cpd	IR Absorption Spectra in KBr,[a] Selected Bands, cm^{-1}	^1H NMR Spectral Assignments Chemical Shifts, δ[b]	^{31}P NMR, δ[c]
41c'	3000,1700,1445,1225	2.74-3.40[m, C<u>H</u>, 2 H]	+47.92
	1105,800,694	2.68-4.40[m, C<u>H</u>$_2$, 2 H]	
		6.76-6.96[m, Ar<u>H</u>, 2 H]	
		7.00-7.46[m, Ar<u>H</u>, 13 H]	

[a]The spectra were obtained on samples (2 mg) with KBr (200 mg) pellets.

[b]Spectra obtained in $DCCl_3$ solution, except 11d-f (DMSO-d_6), of each compound with tetramethylsilane (TMS) as 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.

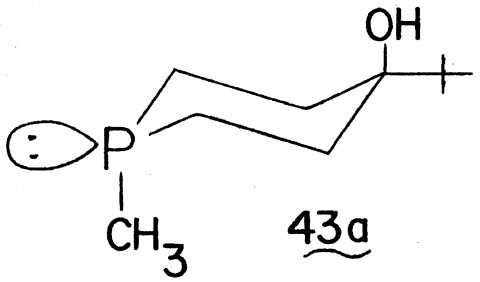
[c]The spectra were obtained on samples (ca. 200 mg) in $DCCl_3$ solution (2 ml), except 11d-f (ca. 200 mg, 2 ml DMSO-d_6), with 85% H_3PO_4 as external standard. A positive sign indicates peak position downfield from standard.

been synthesized although there is a void of definitive conclusions for the geometry of these systems in solution.[3,41,43,59]

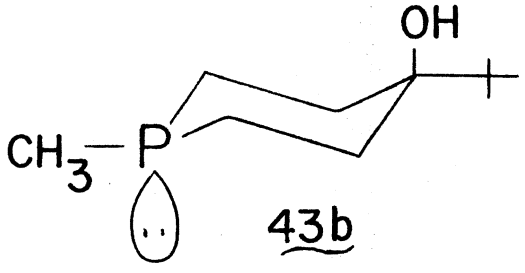
Slightly modified procedures[3,41,59] gave 11a-d and 41a, the physical properties of which agreed with published values. The syntheses of 11e-f and 41b-d were accomplished via techniques of a similar nature.

^{13}C NMR Spectral Parameters

Quite novel ^{13}C chemical shifts and ^{31}P-^{13}C coupling values were recorded for 11a-f and 41a-c. 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 11a-f. It has been stated that the magnitude of $^{2}J_{PC(3,5)}$ for several six-membered phosphorus-containing heterocycles can be employed for the determination of the configuration at phosphorus.[9,22] For example, the $^{2}J_{PC(3,5)}$ value in 43a is 0 Hz and for 43b the $^{2}J_{PC(3,5)}$



43a

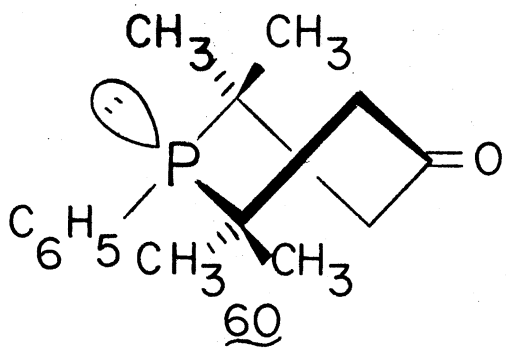


43b

value is 7.5 Hz in H_2CCl_2.[22] For 11a in $DCCl_3$, a $^{2}J_{PC(3,5)}$ value of 3.0 Hz was recorded while a $^{2}J_{PC(3,5)}$ value of 7.8 Hz was found in C_6D_6. Therefore, it might be argued that in $DCCl_3$ 11a exists with the P-phenyl group predominately in an axial orientation and in C_6D_6 the opposite is true. However, the $^{2}J_{PC}$ values for the exocyclic methyl

groups at C(2,6) should also be instructive regarding the configuration at phosphorus for the same reasons given above. In contrast, for 11a, the $^{2}J_{PC}$ values for the exocyclic methyl groups are quite similar in both $DCCl_3$ (44.3 and 4.3 Hz) and C_6D_6 (44.9 and 2.2 Hz). Thus, it is difficult to suggest a predominate configuration at phosphorus for 11a based only on the $^{31}P-^{13}C$ coupling constants involving C(3,5) or the exocyclic methyl groups at C(2,6).

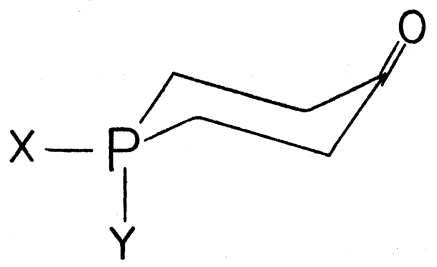
Courtauld models indicate that a twist conformation such as 60, for the phosphorinanone ring in 11a may be tolerated. If such exists, caution may be necessary in the use of $^{2}J_{PC}$ values to assign



60

configurational preference at phosphorus in 11a. Also, no $^{31}P-^{13}C$ coupling was observed for C(3,5) or for the exocyclic methyl carbons at C(2,6) in 11b-f. However, for ketones 1a-d,[57] the $^{2}J_{PC(3,5)}$ values clearly suggest a predominance of group distributions as shown (in $DCCl_3$) based on work in other related systems.[9,22]

^{13}C chemical shifts and $^{31}P-^{13}C$ coupling constants (Table I) for 41a-c suggest a trans arrangement of the phenyl groups at C(2,6). If the arrangement at C(2,6) was cis, only one ^{13}C signal should be observed for C(2,6) and only one signal for C(3,5) since these atoms would presumably be magnetically identical, regardless of the configuration at phosphorus. This, of course, assumes no dissymmetry imposed



1a: X = lone pair; Y = C_6H_5

1b: X = C_6H_5; Y = O

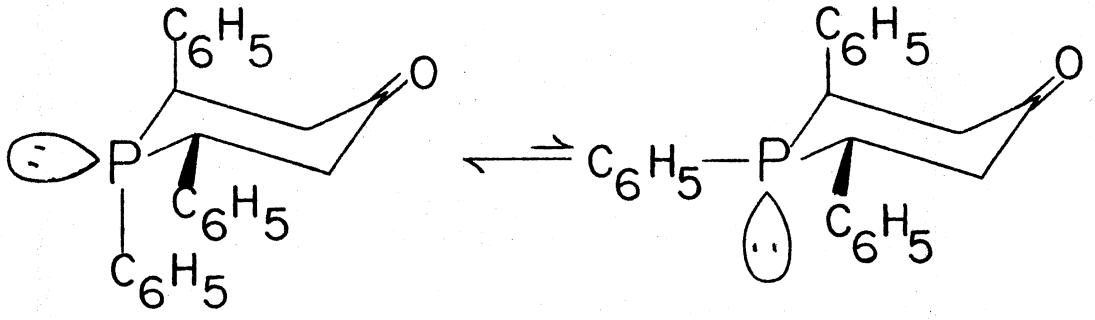
1c: X = C_6H_5; Y = S

1d: X = C_6H_5; Y = CH_3, I^-

on the system by a skewed P-C_6H_5 bond. The $^2J_{PC(3,5)}$ values (2.9 and 8.1 Hz) for 41a do suggest a predominance of configurational isomer with axial P-phenyl. This follows from the observation that the $^2J_{PC(3,5)}$ couplings have been shown to be dependent upon the configuration at phosphorus in isomeric 4-tert-butyl-1-phenyl-4-phosphorinanols 43a and 43b of known stereochemistry.[22] It could also be argued that the position for the ^{13}C signal for C(2,6) at 36.4 ppm ($^oJ_{PC(2,6)}$ = 16.3 Hz) in 41a is due to a carbon atom with an equatorial phenyl group since steric compression between the axial P-phenyl and equatorial phenyl-C(2,6) should shield that carbon compared to the C(2,6) carbon with axial phenyl. Similar arguments concerning shielding at carbon due to a steric compression effect have been noted for cyclohexanes.[15]

It was interesting to note that apparently 41a crystallized in only one form. However, in solution two phosphines with different

^{13}C chemical shifts and ^{31}P-^{13}C coupling constants, as well as two distinct ^{31}P NMR signals (Table II), were apparent. Based upon the relative intensity of thw ^{31}P signals, the ratio was 1.00:1.56 at 37°C. We attribute these observations to an equilibrium biased in favor of 41a in solution. In support of the two configurational isomers

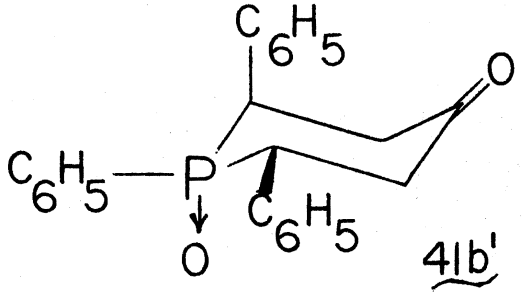


41a ⇌ 41a'

being epimeric at phosphorus was the observation of two new signals for C(3,5) at 44.9 ppm ($^2J_{PC(3,5)}$ = 13.2 Hz) and 48.6 ppm ($^2J_{PC(3,5)}$ = 14.0 Hz) and no new ^{13}C signals for C(2,6). These new C(3,5) signals for 41a' were deshielded (2.2 and 2.4 ppm) compared to those signals of the major isomer 41a; these facts were in accord with a similar observation for isomeric 4-tert-butyl-1-methyl-4-phosphorinanols 43a and 43b.[22] Also the larger $^2J_{PC(3,5)}$ values support an equatorial P-phenyl group, assuming that a smaller dihedral between the phosphorus lone pair and the C(3,5) carbons corresponds to a larger $^2J_{PC(3,5)}$ value.[22]

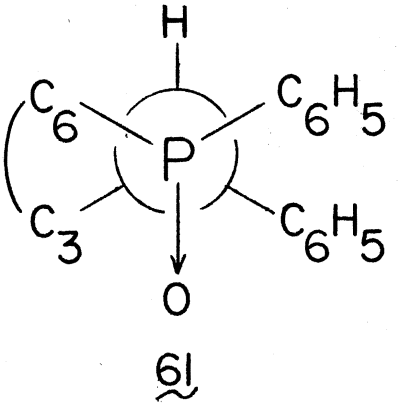
Oxidation of 41a (and 41a') with H_2O_2[27] in the cold (0°C) resulted in formation of apparently two oxides 41b ⇌ 41b' in a ratio of 1:1.2. This is strong evidence for a dynamic system 41a ⇌ 41a'. Based on the ^{13}C chemical shifts and ^{31}P-^{13}C coupling constants for

C(4) in 1-methyl- and 1-ethyl-4-phosphorinanone 1-oxides[9] and 1-phenyl-4-phosphorinanone 1-oxide,[57] the C(4) signal at 207.2 ppm ($^{3}J_{PC(4)}$ = 6.2 Hz) was assigned to the configurational isomer (41b') with axial

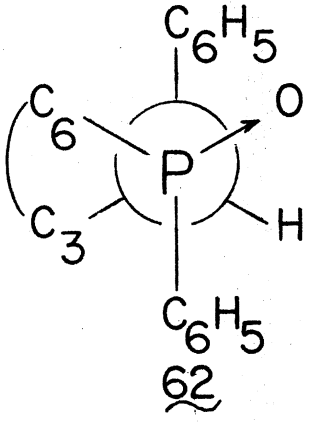


41b'

P→O. It is conceivable that the C(2,6) signal at 46.5 ppm ($^{1}J_{PC(2,6)}$ = 56.6 Hz) corresponds to the C(2,6) atom with equatorially oriented phenyl and equatorial P-phenyl, which results in the most deshielded signal compared to similarly substituted cyclohexanes.[15] Similarly, the signal at 38.2 ppm ($^{1}J_{PC(2,6)}$ = 60.4 ppm) could represent the C(2,6) bearing the axial phenyl group in the axial P-phenyl isomer. Newman formulas for these arrangements are illustrated in 61 and 62. Accordingly the C(3,5) signal at 45.2 ppm ($^{2}J_{PC(3,5)}$ = 4.7 Hz) should



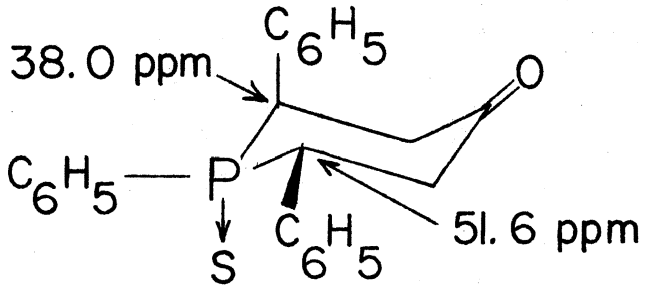
61



62

correspond to 41b', with axial phosphoryl oxygen deshielding C(3,5) more than axial phenyl group.[9,57] Since the signal intensities of ^{13}C resonances at 42.7 and 4.52 ppm in the spectrum of the oxides were equal and since four C(3,5) signals were observed for 41a $\rightleftharpoons$ 41a', it is not possible to determine absolutely whether these two different C(3,5) signals are for the same carbon atoms in different isomers [42.7 ppm for C(3,5) in 41b; 45.2 ppm for C(3,5) in 41b' or vice versa] or represent two different ^{13}C signals for C(3,5) in 41b and 41b' which possess identical chemical shifts for the two isomers. Our assessment is that the signals are for different carbon atoms based on analogy with 41a and 41a'.

Sulfurization (in boiling benzene) afforded only one isomeric P-sulfide assigned the structure 41c' (based on previous arguments and similar ^{13}C parameters observed for 1-phenyl-4-phosphorinanone 1-sulfide[57]). The ^{13}C signal at 51.6 ppm ($^{1}J_{PC(2,6)}$ = 41.8 Hz) was assigned to the C(2,6) carbon atom bearing an equatorially oriented phenyl group (as per 41b').



41c'

Infrared Spectral Data

Infrared C=O absorptions for 11a-f and 41a-c occurred between 1680 and 1710 cm^{-1} in KBr pellets. The C=O stretching frequencies for the compounds presented herein agreed well with those previously reported for 1a (1695 cm^{-1}),[60] 1-ethyl-4-phosphorinanone (1715 cm^{-1})[60] and 2-phenyl-3-methyl-2-phosphabicyclo[4.4.0]decan-5-one (8) (1700 cm^{-1}),[31] as well as with the corresponding oxide (1705 cm^{-1}), methiodide (1710 cm^{-1}), and benzochloride (1720 cm^{-1}).[31] Infrared absorptions assigned to the P-phenyl bond (1430-1445 cm^{-1} and 1103-1117 cm^{-1})[56] were also clearly in evidence for 11a-f and 41a-c. Absorptions for P→O and P→S were also recorded on solids [11b: P→O, 1176 cm^{-1}; 41b (or 41b'): P→O, 1175 cm^{-1}]. However, only meager information regarding structural features based on P→O and P→S infrared absorption has been presented[14,56] for systems of known configuration and this precluded any conformational assignments in our systems.

^{1}H NMR Spectral Data

The ^{1}H NMR data for 11a-f and 41a-c could not be obtained in the same solvent, unfortunately, due to the limited solubility of the salts 11d-f in many solvents. Therefore, ^{1}H NMR spectra for 11a-c and 41a-c were obtained in $DCCl_3$ and ^{1}H NMR spectra for 11d-f were obtained in DMSO-d_6. Phosphine 11a gave rise to two CH_3 doublets in the ^{1}H NMR spectrum at δ 0.93 ($^3J_{PCCH}$ = 11 Hz) and δ 1.32 ($^3J_{PCCH}$ = 18 Hz). Based on the ^{13}C chemical shifts and ^{31}P-^{13}C coupling constants for the exocyclic methyl carbons in 11a [30.3 ppm ($^2J_{PCC}$ =

4.34 Hz) and 30.8 ppm ($^2J_{PCC}$ = 44.30 Hz)], one might initially surmise the P-phenyl group to be predominately equatorial for reasons cited previously. However, molecular models (Courtauld) indicate severe steric strain in 11a if a chair conformation existed. Such strain could be relieved somewhat if the phosphorinanone ring adopted a twist form as in 60. It is tempting to assign the equatorial methyl carbon at C(2,6) to the upfield CH_3 doublet by assuming the P-phenyl group is axially oriented. Thus, this could place the equatorial methyl groups in reasonably close proximity to the shielding cone of the phenyl ring. However, evidence is not totally unequivocal to permit assignment of a conformation to the phosphorinanone ring in solution and a configuration at phosphorus; thus the argument must be considered tentative.

Double resonance experiments (^1H $\{^{31}P\}$) simplified the ^1H NMR spectrum of 11a and clearly indicate an A_2B_2X pattern for the H(3,5) axial and equatorial protons. Since two different $^3J_{PCCH}$ values were apparent (2 Hz 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[5,7,19] has suggested a "Karplus type" relationship for $^3J_{PCCH}$ in phosphonates and phosphonous dihalides. In this relationship, the portion of the A_2B_2X 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,[8] which supports our assignments. Therefore, in 11a-f (except 11c), the high-field portion of the A_2B_2X spectrum was tentatively assigned to the equatorial H(3,5) protons.

The ^{1}H NMR spectrum of 11c revealed a multiplet for the protons at C(3,5) between δ 2.56-3.22. 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 H-H geminal coupling is small for the conformer in $DCCl_3$. Recording the ^{1}H NMR spectrum of 11c in acetone-d_6 revealed a doublet of AB portions, one between δ 2.46-2.90 and the other between δ 3.18-3.44. Irradiation of the ^{31}P signal of 11c caused the low-field portion to collapse to an AB spectrum with $^{2}J_{HCH}$ = 14 Hz while the high-field portion was an extremely complex multiplet between δ 2.46-2.94. Further analysis revealed $^{3}J_{PCCH}$ values of 24 Hz and 6 Hz for the high-field and low-field signals, respectively. A rational conclusion would be that the high-field multiplet [equatorial H(3,5) protons], after ^{31}P irradiation, could be the result, in part, of long range ^{1}H-^{1}H coupling or more likely a preferred solute-solvent orientation particularly in acetone-d_6.

The ^{1}H NMR spectra of 41a-c revealed no immediately apparent ^{31}P-^{1}H coupling with both the H(2,6) and H(3,5) protons. However, addition of one drop of 40% NaOD in D_2O to a saturated acetone-d_6 of 41a led to an observation of coupling [$^{2}J_{PC(2,6)H}$] after deuterium exchange for H(3,5). When the reaction mixture had been at room temperature for 19 hr, the ^{1}H NMR spectrum of 41a exhibited two doublets at δ 3.92 ($^{2}J_{PCH}$ = 12 Hz) and δ 4.09 ($^{2}J_{PCH}$ = 6 Hz). Again the assignment of these signals for H(2,6) proton was based on previous work[1] in which a relationship for the dihedral angle between the phosphorus lone pair and α-protons has been established in simple acyclic and alicyclic systems. Consequently, the upfield doublet with the larger

coupling constant was assigned to the axial protons at C(2,6).

^{31}P NMR Spectral Data

^{31}P signals for 11a-f and 41a-c are listed in Table II. The deshielded signal for 11a (-16.05 ppm), compared to 1-phenyl-4-phosphorinanone (-39.3 ppm),[54] is probably the result of β-deshielding[49] by the four C(2,6) methyl carbons with each methyl group contributing ca. +6 ppm to the ^{31}P chemical shift. This deshielded signal for 11a is in accord with similar observations of β-deshielding for a number of phosphorus compounds.[49] Unfortunately, little ^{31}P NMR data is available on the derivatives of 1-phenyl-4-phosphorinanone to test the validity of the postulate for shielding differences in the other phosphorinanones (11b-f) presented herein. Noticeably, the ^{31}P signals for salts 11d-f occur over a range of ca. 2 ppm, suggesting that the electronic and geometric environments are similar but not identical in 11d-f.

Again, the ^{31}P NMR spectra of 41a-c afforded interesting observations. For example, phosphine 41a', based on chemical shifts and relative signal intensities in both the ^{1}H and ^{13}C spectra, was assigned the downfield ^{31}P signal at -3.37 ppm. This agrees with data for a majority of isomeric six-membered phosphorus-containing ring systems in which the equatorial isomer has the more downfield ^{31}P signal.[21] Therefore the signals for isomeric oxides are assigned accordingly: 41b: + 32.21 ppm; 41b' + 33.95 ppm.

Low-temperature ^{31}P NMR experiments were attempted with 11a. However, cooling a solution (CCl_3F) of 11a to -140°C revealed only one

^{31}P signal. Therefore the barrier (ΔG^*) to ring reversal in 11a must be lower than ca. 6 kcal/mole. [The value for ΔG^* was determined by assuming that the peak separation at the lower temperature limit would be ca. 100 Hz[21] and calculated from:

$$k_c = \Delta\nu\pi/\sqrt{2}$$

$$k_c = \frac{k_B T}{h} e^{-\Delta G^*/RT} \;] \; .$$

The validity of the short-form equation for relating k_c to $\Delta\nu$ has been assessed.[32]

Lithium Aluminum Hydride Reduction of 11a

Reaction of a THF solution of 11a with $LiAlH_4$, followed by aqueous hydrolysis and the appropriate work-up, has not afforded to date a crystalline material in our hands.[59] ^1H NMR, ^{13}C NMR, and ^{31}P NMR data (Tables III and IV) were obtained on the resulting viscous oil 63a which seemingly was only one isomer in solution. This isomer was identified by the broad multiplet at δ 3.82-4.24 for the axial proton on C(4) in the ^1H NMR spectrum. This supports an alcohol with equatorially oriented hydroxyl group. Also, only two doublets for the protons of the methyl group attached at C(2,6) were apparent, suggestive of only one conformer in solution. Oxidation, sulfurization, and quaternization (benzyl bromide) of 63a afforded isomerically pure products 63b, 63c, and 63d, respectively. Again the isomer formed in each case possessed an equatorial hydroxyl group, based on the broad multiplet for the proton on C(4) in the ^1H NMR spectrum.

TABLE IV

^{13}C NMR CHEMICAL SHIFTS[a] (^{31}P-^{13}C COUPLING CONSTANTS)[b] FOR SUBSTITUTED 4-PHOSPHORINANOLS 63a-d AND 64

Carbon	63a	63b	63c	63d[c]	64
2,6	31.9(16.1)	35.1(61.1)	37.0(43.4)	33.1(28.8)	32.6(61.1)
3,5	50.9(11.8)	47.3	46.9	44.9	44.5
4	62.2	64.1(5.9)	64.9(5.1)	62.7(5.8)	76.4(7.3)
ax-CH_3	32.3(30.2)	26.0(2.2)	28.5	27.2	28.4
eq-CH_3	26.3(5.1)	25.0(1.5)	26.5	26.8	26.5
Ph-1[d]	126.9(22.8)	127.2(78.8)	126.0(70.9)	116.1(67.6)	131.1(82.3)
Ph-2[d]	128.7(33.7)	122.4(7.5)	134.6(8.3)	134.4(7.4)	131.6(7.4)
Ph-3[d]	127.7(20.0)	127.7(10.8)	127.6(11.0)	130.0(8.9)	128.1(10.2)
Ph-4[d]	127.6	131.4(2.0)	131.3(3.0)	134.2	130.9(2.8)
CH_2				22.0(41.0)	
7					39.3
8,9,10					25.2

[a]All samples were ca. 200 mg in $DCCl_3$ except where noted. Chemical shifts in ppm (±0.1) downfield from internal tetramethylsilane (TMS).

[b]^{31}P-^{13}C coupling constants in Hz (±0.4).

[c]In hexadeuteriodimethyl sulfoxide (DMSO-d_6). ^{13}C NMR chemical shifts (^{31}P-^{13}C coupling constants for benzyl carbons in 63d are: 128.2(22.0 Hz), 130.0, 129.4, and 128.6 ppm.

[d]Ph-1 signifies the carbon attached to phosphorus, Ph-2 = ortho carbons, Ph-3 = meta carbons, and Ph-4 = para carbon.

TABLE V

SPECTRAL DATA FOR SUBSTITUTED 4-PHOSPHORINANOLS 63a-d AND 64

Cpd	IR Absorption Spectra in KBr,[a] Selected Bonds, cm^{-1}	^1H NMR Spectral Assignments, Chemical Shifts, δ[b]	^{31}P NMR, δ[c]
63a		0.68-2.42[m, CH_2, 4 H, O<u>H</u>, 1H] 1.08[d(J_{PCCH}=19 Hz), C<u>H</u>$_3$, 6 H] 1.36[d(J_{PCCH}=4 Hz), C<u>H</u>$_3$, 6 H] 3.82-4.24[m, C<u>H</u>-O, 1 H] 7.08-8.12[m, Ar<u>H</u>, 5 H]	- 8.57
63b	3280,1435,1142,1100, 1052,754,701	1.08[d(J_{PCCH}=13 Hz), C<u>H</u>$_3$, 6 H] 1.46[d(J_{PCCH}=15 Hz), C<u>H</u>$_3$, 6 H] 1.64-2.48[m, C<u>H</u>$_2$, 4 H] 3.80-4.26[m, C<u>H</u>-O, 1 H, O<u>H</u>, 1 H] 7.28-7.64[m, ArH, 3 H] 7.72-8.00[m, Ar<u>H</u>, 3 H]	+41.59
63c	3270,1436,1092,1030 746,670	1.22[d(J_{PCCH}=17 Hz), C<u>H</u>$_3$, 6 H] 1.56[d(J_{PCCH}=14 Hz), C<u>H</u>$_3$, 6 H] 1.68[S, O<u>H</u>, 1 H] 1.68-2.62[m, C<u>H</u>$_2$, 4 H]	+62.53

TABLE V (Continued)

Cpd	IR Absorption Spectra in KBr,[a] Selected Bonds, cm^{-1}	^1H NMR Spectral Assignments, Chemical Shifts, δ[b]	^{31}P NMR, δ[c]
63c (Con't)		3.94-4.32[m, C<u>H</u>-O, 1 H] 7.36-7.62[m, Ar<u>H</u>, 3 H] 8.02-8.32[m, Ar<u>H</u>, 2 H]	
63d	3220,1428,1103,1046, 773,754,697	1.20[d(J_{PCCH}=15 Hz), C<u>H</u>$_3$, 6 H] 1.58[d(J_{PCCH}=15 Hz), C<u>H</u>$_3$, 6 H] 1.96-2.26[m, C<u>H</u>$_2$, 4 H] 4.00-4.30[m, C<u>H</u>-O, 1 H] 4.57[d(J_{PCH}=14 Hz), C<u>H</u>$_2$, 2 H] 5.16[d(J =4 Hz), O<u>H</u>, 1 H] 7.08-7.40[m, Ar<u>H</u>, 5 H] 7.60-8.02[m, Ar<u>H</u>, 3 H] 8.08-8.36[m, Ar<u>H</u>, 2 H]	+34.68
64	3320,1442,11501105 1070,713,699	0.91[d(J_{PCCH}=14 Hz), C<u>H</u>$_3$, 6 H] 1.06[S, C(C<u>H</u>$_3$)$_3$, 9 H] 1.58[d(J_{PCCH}=12 Hz), C<u>H</u>$_3$, 6 H] 1.78-2.24[m, C<u>H</u>$_2$, C<u>H</u>-O, 5 H] 2.12[S, O<u>H</u>, 1 H]	+46.77

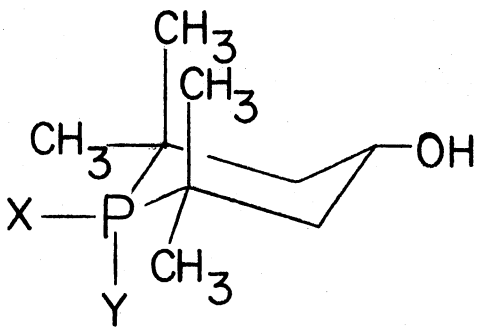
TABLE V (Continued)

Cpd	IR Absorption Spectra in KBr,[a] Selected Bonds, cm^{-1}	^1H NMR Spectral Assignments, Chemical Shifts, δ[b]	^{31}P NMR, δ[c]
64 (Con't)		7.40-7.62[m, ArH, 3 H] 7.74-7.98[m, ArH, 2 H]	

[a] The spectra were obtained on samples (2 mg) with KBr (200 mg) pellets.

[b] Spectra obtained in $DCCl_3$ solution, except 63d (DMSO-d_6), of each compound with tetramethylsilane (TMS) as 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 63d (ca. 200 mg, 2 ml DMSO-d_6), with 85% H_3PO_4 as external standard. A positive sign indicates peak position downfield from standard.



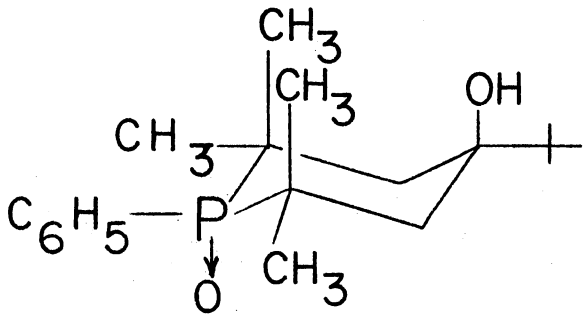
63a: X = C_6H_5; Y = lone pair

63b: X = C_6H_5; Y = O

63c: X = C_6H_5; Y = S

63d: X = C_6H_5; Y = $C_6H_5CH_2$, Br^-

Reaction of 11a with tert-butyllithium, followed by oxidation, afforded 64 with the proposed stereochemistry as illustrated. The

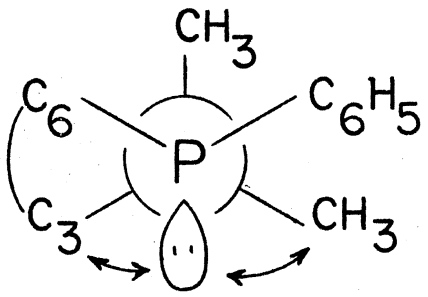


64

assignment rests on the shielded ^{13}C chemical shifts for 64 (as compared to 63a) and the tert-butyl singlet in the ^{1}H 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[40]).

Support for the assignment of an equatorial P-C_6H_5 in 63a follows from the ^{13}C NMR data. As previously cited,[22] the configuration

at phosphorus in certain systems has been assigned from the $^{3}J_{PC(3,5)}$ values. In the case of 64, the $^{3}J_{PC(3,5)}$ value of 11.79 Hz is even larger than the corresponding value (7.5 Hz) in 4-tert-butyl-1-methyl-4-phosphorinanol (43b) of known configuration.[22] It has been suggested that a small dihedral angle between the phosphorus lone pair and a carbon atom two bonds removed should yield a large $^{2}J_{PCC}$ value.[22] The Newman formula for 64 aids in visualizing the effect at C(3,5) with axial orientation of the phosphorus lone pair. These assignments must, however, remain somewhat tentative in view of some uncertainty as to the actual geometry of the precursor (11a) for 63a.



The infrared spectra of 63a-d show strong absorptions at 1030-1052 cm^{-1} for the C-O stretch, indicative of an equatorially oriented hydroxyl group.[11] Also, absorptions between 1428-1442 cm^{-1} and 1092-1105 cm^{-1} were recorded for 63b-d and 64 and were supportive of the presence of the P-phenyl bond.[56]

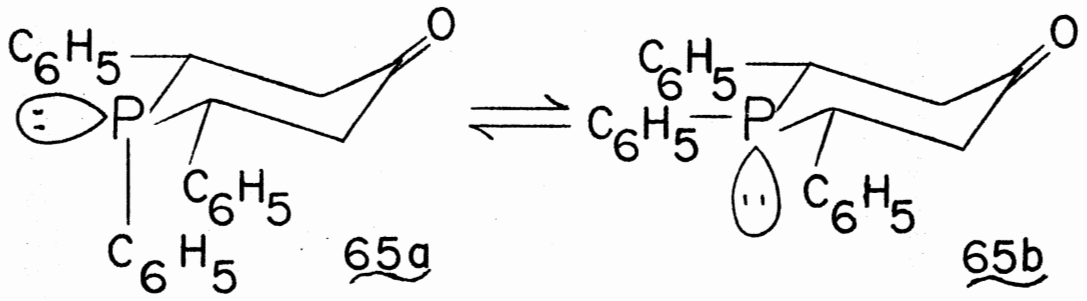
^{31}P NMR data for 63a-d and 64 are listed in Table V. A value of -8.57 ppm was recorded for 63a, which differs by +7.48 ppm from its immediate precursor 11a. One rationale may be that the change in hybridization at C(4) in going from 11a→63a markedly influences the

^{31}P signal for 63a. However, very little change was noted in the ^{31}P NMR signals for the tetracoordinate derivatives of 63a (63b-d) compared to the similarly substituted tetracoordinate derivatives of 11a (11b-d). Therefore, it remains difficult to attribute the remarkable differences in the ^{31}P signals for 11a and 63a to only a change in hybridization at C(4).

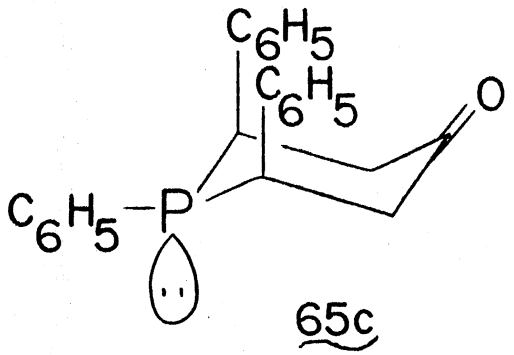
Herein, we have attempted to derive useful conformational data from an intensive study of the ^{1}H, ^{13}C, and ^{31}P NMR parameters of several 4-phosphorinanones and derivatives. Notabley, there is difficulty in attempting to utilize $^{2}J_{PC(3,5)}$ values for conformational assignment[22] in 4-phosphorinanones which also possess gem-dimethyl groups at C(2) and C(6). The preferred configuration of phenyl groups attached to C(2,6) in the 4-phosphorinanones studied appears to be trans on the basis of different ^{13}C NMR signals for all the ring carbon atoms. Finally, a change in hybridization at C(4) [$sp^2 \rightarrow sp^3$] in converting the 4-phosphorinanones to the corresponding 4-phosphorinanols seems to have a marked influence on the ^{31}P chemical shift in trivalent phosphines. However, many more derivatives should be examined carefully to verify this.

In summary, with the tetramethyl analogs 11a, cooling to -140°C did not show two ^{31}P peaks. Then, we assume that ring reversal may be found for all members of this family. If a twist conformer exists for the members of 11, one might not observe two signals for ^{31}P even at low temperature assuming rapid ring adjustment between one or more twist forms which provide a similar environment about P. Whether or not such a theory holds for all members of 11 must await testing. Since the triphenyl-substituted phosphorinanone 41a (41a')

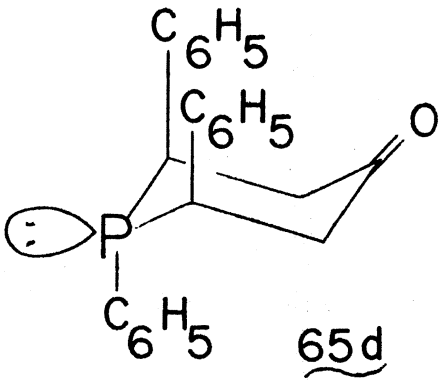
displayed two ^{31}P NMR signals ($DCCl_3$ or C_6D_6) at room temperature (37^oC), there is implied that a ring reversal process is in operation. This is supported by the isolation of only one product 41a (41a') in high yield (82%). Of course, a P-inversion could give the same result but such processes have been reported to have ΔG^* values usually exceeding 25 kcal/mole in simple cyclic phosphines [see K. Mislow, Trans. N.Y. Acad. Sci., 35, 227(1973) and Part I of this thesis]. Oxidation of 41a (41a') gives a mixture (in solution) of oxides but only one oxide 41b (or 41b') has been isolated to date. Pure oxides 41b (or 41b') in $DCCl_3$ gave two ^{31}P signals, implying a ring reversal. Quite possibly, comparison of the ^{31}P spectrum of the crude oxidation mixture would reveal identical ^{31}P signals as found when 41b (or 41b') was placed in $DCCl_3$. One can imagine that perhaps the barrier would be high for the ring reversal for converting 65a or 65b to the ring reversal



products 65c and 65d, respectively, because of severe 2,6-interactions of axial phenyl groups. We might assume also the P-inversion barrier for 65a $\rightleftharpoons$ 65b would be high. Surprisingly, Courtauld models could only be constructed for 65b and the phosphorinanone ring appeared slightly twisted. This suggests that preparation of 65a (and 65b) might require special conditions. Interestingly, only one phosphine



65c



65d

of 1,2,6-triphenyl-4-phosphorinanone has ever been reported. Our sample (mp 175-176°C--our 41a) assigned the trans arrangement has been submitted to Professor D. van der Helm at Oklahoma University for X-ray analysis. The same situation persists for oxide 41b (41b') but only ^{31}P signal is available for the sulfide 41c'. This suggests a steric factor imposed by the S atom may restrict ring reversal but cooling experiments might reveal if ring reversal is fast at room temperature if two signals appeared.

Suggestions for Further Work

In view of the work presented herein, a complete ^{13}C NMR study of ring-substituted 4-phosphorinanones seems necessary to determine whether $^{2}J_{PC(3,5)}$ values can be used without hesitation in the assignment of the configuration at phosphorus. Of particular interest should be those 4-phosphorinanones with various alkyl groups attached to phosphorus (e.g., CH_3, C_2H_5, $CH(CH_3)_2$, $C(CH_3)_3$, etc.) and differing in the degree and type of substitution at C(2) and C(6).

An in-depth study via ^{31}P NMR of the factors influencing the ^{31}P chemical shift of 4-substituted phosphorinanes with changes in the

hybridization at C(4) and the type of substitutents there attached (e.g. H, R, OH, =C< , =O, =N-, etc.) would be informative. From this study experimental evidence could be derived in support of an electric field effect[9] associated with the phosphorus atom or geometric contributions to the ^{31}P chemical shift with changes in the conformation of the six-membered ring.

Current interest in the biological activity of organophosphorus heterocycles is attested to by the voluminous amount of reports concerning these compounds.[58] The incorporation of the carbonyl moiety in these heterocycles "opens the door" for a variety of chemical reactions. Annelations, Reformatsky reactions, and condensations, to name a few, could yield heterocyclic products with active functionalities as well as hydrophilic and lipophilic characteristics. Thus, this area of heterocyclic and medicinal chemistry appears boundless and only requires the imagination and persistent efforts of chemists and biochemists.

CHAPTER III

EXPERIMENTAL

General Data

Melting points were obtained on a Thomas-Hoover melting point apparatus and were uncorrected. The ^{1}H, ^{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 MHz with tetramethylsilant (TMS) as internal standard for ^{1}H NMR, at 25.2 MHz with TMS as internal standard for ^{13}C NMR, and at 40.5 MHz with 85% H_3PO_4 as external standard for ^{31}P NMR. The ^{13}C NMR spectra were obtained operating in the FT mode utilizing broad-band proton decoupling. The ^{31}P NMR spectra of 11a-f, 63a-d, and 64 were obtained in the CW mode and those of 41a-d in the FT mode utilizing broad-band proton decoupling for 41a-d. Infrared spectral data were obtained on a Beckmann IR-5A unit. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

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 (11a)[59]

In a 25-ml, round-bottom flask equipped with a condenser and N_2 inlet were placed 3.5 g (0.0254 mole) of 2,6-dimethylhepta-2,5-dien-4-one (City Chemical Corp., bp 196-198°C) and 2.75 g (0.025 mole) of phenylphosphine (Pressure Chemical Company). The reaction mixture was heated at 120°C for 6 hr under N_2 and allowed to cool to room temperature (≃1 hr). The resulting solid distilled at 105-120°C/0.3 mm to give 4.53 g (72.5%) of ketone 11a, mp 91-92°C [lit[59] bp 130-140°C/0.5 mm, mp 91-92°C].

IR, ^1H, ^{13}C, and ^{31}P NMR data for 11a are listed in Tables II and III. The IR and ^1H NMR spectra of 11a are illustrated in Plates I and II, respectively.

The 2,4-dinitrophenylhydrazone of 11a was prepared in the following manner. To a methanol solution (5 ml) of 0.073 g (0.37 mmole) of 2,4-dinitrophenylhydrazine was added 1 ml of H_2O and 0.5 ml of conc. H_2SO_4. Ketone 11a (0.091 g, 0.37 mmole) 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 mixture followed by recrystallization of the solid obtained (twice) from methanol gave 41 mg (26.1%) of the 2,4-dinitrophenylhydrazone of 11a, mp 153-154°C. IR (KBr) ν 3280 (N-H), 1610 (C=N), 1580 (C=N), 1410 (P-C_6H_5), 1335, 1137 (P-C_6H_5), 922, 833, 743, 696 cm^{-1}.

Anal. Calcd. for $C_{21}H_{25}N_4O_4P$: 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 (11b)[3]

Ketone 11a (2.48 g, 0.01 mole) was dissolved in 25 ml of acetone in a 50-ml round-bottom flask. To the solution was added dropwise, with stirring, 2.6 g (0.02 mole) of 30% H_2O_2 (Mallinckrodt, Analytical Reagent). The reaction mixture was stirred at room temperature for 24 hr and was diluted with 25 ml of satd. aqueous NaCl solution. The diluted reaction mixture was then extracted with 3 x 40 ml of $HCCl_3$. The $HCCl_3$ extracts were combined and washed with 25 ml of satd. aqueous $Fe(NH_4)_2(SO_4)_2$ solution. 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, which was then filtered. When the filtrate was allowed to stand at 0^oC overnight, white needles formed and were filtered off. The crystals were dried (P_2O_5; 100^oC/5 mm) to give 1.4 g (53%) of 11b, mp 207-208^oC [lit[3] mp 212-213^oC].

IR, ^1H, ^{13}C, and ^{31}P NMR data for 11b are listed in Tables II and III. The IR and ^1H NMR spectra of 11b are illustrated in Plates III and IV, respectively.

Preparation of 2,2,6,6-Tetramethyl-1-phenyl-4-phosphorinanone 1-Sulfide (11c)[3,59]

Ketone 11a (2.48 g, 0.01 mole) and sulfur (0.64 g, 0.02 mole) dissolved in 25 ml of benzene were placed in a 50-ml, round-bottom flask fitted with a condenser and magnetic stirrer. The reaction mixture was gently boiled for 3 hr and filtered hot. The volume was

reduced to ca. 10 ml (by evaporation on a steam bath) and 10 ml of petroleum ether was added. After the mixture was allowed to stand at $0^{o}C$ overnight, a solid formed and was dried (P_2O_5; $110^{o}C/5$ mm) to give 1.98 g of 11c (70.5%), mp 129-132°C. A small portion was recrystallized from methanol, mp 138-139°C [lit[59] mp 138.5-139°C].

IR, ^{1}H, ^{13}C, and ^{31}P NMR data for 11c are listed in Tables II and III. The IR and ^{1}H NMR spectra of 11c are illustrated in Plates V and VI, respectively.

Preparation of 1,2,2,6,6-Pentamethyl-1-phenyl-4-phosphorinanonium Iodide (11d)[59]

Ketone 11a (6.0 g, 0.0242 mole) and CH_3I (7.0 g, 00483 moles) were dissolved in 35 ml of ether, and the reaction mixture was allowed to stand at $0^{o}C$ with periodic swirling for four days. A resulting solid was filtered and washed with ether to give 6.3 g (65.3%) of 11d. A small portion was recrystallized from CH_3CN, mp 229-230°C [lit[59] mp 229-230°C].

IR, ^{1}H, ^{13}C, and ^{31}P NMR data for 11d are listed in Tables II and III. The infrared and ^{1}H NMR spectra of 11d are illustrated in Plates VII and VIII, respectively.

Preparation of 1-Ethyl-2,2,6,6-tetramethyl-1-phenyl-4-phosphorinanonium Iodide (11e)

Ketone 11a (10 g, 0.0403 mole) and ethyl iodide (7 g, 0.045 mole) 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 hr to give a white solid.

The solid was filtered off, washed with 2 x 25 ml portions of ether, and air dried to give 11.87 g (73%) of 11c, mp 240-243°C. An analytical sample was obtained by recrystallization from CH_3CN, mp 247°C dec.

IR, ^1H, ^{13}C, and ^{31}P NMR data for 11e are listed in Tables II and III. The IR and ^1H NMR spectra of 11e are illustrated in Plates IX and X, respectively.

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 (11f)

Ketone 11a (2.48 g, 0.01 mole) and benzyl bromide (2.00 g, 0.0117 mole) dissolved in 15 ml of benzene were placed in a 25-ml, round-bottom flask fitted with a condenser, magnetic stirrer and N_2 inlet. The reaction mixture was gently boiled for 12 hr. A resulting solid was filtered out and washed (ether). Recrystallization (CH_3CN) gave 2.26 g (54%) of 11f, mp 233-235°C.

IR, ^1H, ^{13}C, and ^{31}P NMR data for 11f are listed in Tables II and III. The IR and ^1H NMR spectra of 11f are illustrated in Plates XI and XII, respectively.

Anal. Calcd. for $C_{22}H_{28}BrOP$: C, 6192; H, 6.93; P, 7.60.
Found: C, 61.85; H, 6.84; P, 7.51.

Preparation of Bis(hydroxymethyl)-phenylphosphine[28]

Paraformaldehyde (5 g, 0.166 mole) and phenylphosphine (10 g,

0.091 mole) were placed in a 50-ml, round-bottom 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 hr. The reaction mixture was allowed to cool to room temperature (~1 hr) and was then distilled at 105-100°C/0.3 mm to give 10.06 g (71%) of bis(hydroxymethyl)phenylphosphine, [lit[28] bp 93-96°C/0.1-0.15 mm].

Preparation of 1,2,6-Triphenyl-4-phosphorinanone (41a)[41,59]

Bis(hydroxymethyl)phenylphosphine (1.97 g, 0.0116 mole) and dibenzalacetone (2.70 g, 0.0116 moel, mp 113°C, City Chemical Corp.) was dissolved in 25 ml of dry pyridine and placed in a 50-ml, round-bottom flask equipped with a condenser, magnetic stirrer, and N_2 inlet. The reaction mixture was gently boiled for 4 hr during which time paraformaldehyde collected in the condenser. After the reaction mixture was allowed to cool to room temperature, pyridine was removed on a rotary evaporator. The resulting orange solid was dissolved in the 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 hr, the solid was filtered off and dried to give 3.25 g (82%) of 41a. The yellow solid was stirred with 25 ml of ether, filtered off, and recrystallized from hot CH_3CN to give pure 41a, mp 175-176°C, as white needles [lit[41] mp 176-177°C].

IR, ^1H, ^{13}C, and ^{31}P NMR data for 41a are listed in Tables II and III. The IR and ^1H NMR spectra of 41a are illustrated in Plates XIII and XIV, respectively.

The 2,4-dinitrophenylhydrazone of 41a was prepared in the following manner. To a methanol solution (5 ml) of 0.05 g (0.252 mmole) of 2,4-dinitrophenylhydrazone was added 1 ml of H_2O and 0.5 ml of conc. H_2SO_4. Ketone 41a (0.05 g, 0.15 mmole) 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 41a. Recrystallization (ethyl acetate) gave a sample, mp 250°C dec. Further attempts (fractional recrystallization, tlc) to purify the 2,4-DNP of 41a were moderately successful as implied from the analysis.

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

Found: N, 10.25; P, 5.80.

The semicarbazone of 41a was prepared (76.3%) by standard techniques and had mp 283-285°C [lit[59] mp > 270°C].

Preparation of 1,2,6-Triphenyl-4-phosphorinanone 1-Oxides (41b and 41b')

To phosphine 41a (2.0 g, 5.83 mmole) dissolved in 40 ml of acetone in a 100-ml, round-bottom flask equipped with a condenser and magnetic stirrer was added 2.0 g (17.49 mmole) of 30 H_2O_2 dropwise at 0°C (ice bath). After the addition was complete, the reaction mixture was gently boiled for 24 hr. After the mixture cooled to room temperature, 50 ml of satd. aqueous NaCl was added. The mixture was extracted with 2 x 50 ml of $HCCl_3$; the extracts were combined and washed with a satd. aqueous $Fe(NH_4)_2(SO_4)_2$ solution and then with H_2O. The $HCCL_3$ layer was dried ($MgSO_4$) and filtered, and the $HCCL_3$ was evaporated by rotary evaporation. The resulting

solid was recrystallized from benzene:ethanol (1:1) to yield 970 mg (46.2%) of 41b and 41b', mp 258-259°C.

IR, ^{1}H, ^{13}C, and ^{31}P NMR data for 41b is listed in Tables II and III. IR and ^{1}H NMR spectra of 41b are illustrated in Plates XV and XVI, respectively.

Anal. Calcd. for $C_{23}H_{21}O_2P$: C, 76.65; H, 5.87; P, 8.59.

Found: C, 76.59; H, 5.92; P, 8.58.

Preparation of 1,2,6-Triphenyl-4-phosphorinanone 1-Sulfide (41c')

Ketone 41a (2.0 g, 5.83 mmole) and sulfur (0.2 g, 6.25 mmole) were dissolved in 25 ml of benzene and placed in a 50-ml, round-bottom flask fitted with a condenser, magnetic stirrer and N_2 inlet. The reaction mixture was gently boiled 4 hr 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 41c', mp 235-237°C.

IR, ^{1}H, ^{13}C, and ^{31}P NMR data for 41c' are listed in Tables II and III. The IR and ^{1}H NMR spectra of 41c' are illustrated in Plates XVII and XVIII, respectively.

Anal. Calcd. for $C_{23}H_{21}OPS$: 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 (63a)[59]

To a slurry of 0.38 g (0.01 mole) of $LiAlH_4$ in 20 ml of dry THF in a 100-ml, round-bottom flask equipped with a magnetic stirrer,

condenser, addition funnel and N_2 inlet was added dropwise over a 1-hr period 1.24 g (5 mmole) of 11a in 25 ml of dry THF. After the addition was complete, the reaction mixture was gently boiled for cooled (ice bath) to $0^{o}C$, and then was hydrolyzed (caution!) slowly 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 $60^{o}C/0.5$ mm for 15 min and then at room temperature/ 0.5 mm for 1 hr. The resulting viscous oil was dissolved in 8 ml of $DCCl_3$ under N_2 and aliquots were withdrawn to obtain the ^{1}H, ^{13}C, and ^{31}P NMR data presented in Tables IV and V. The ^{1}H NMR of 63a is illustrated in Plate XIX.

Preparation of 2,2,6,6-Tetramethyl-1-phenyl-4-phosphorinanol 1-Oxide (63b)

Lithium aluminum hydride (1.52 g, 0.04 mole) was added slowly to 100 ml of freshly distilled tetrahydrofuran (distilled from $LiAlH_4$ in a 500-ml, round-bottom flask equipped with a condenser, addition funnel, mechanical stirrer and N_2 inlet. Ketone 11a was dissolved in 125 ml of THF and added dropwise (addition time ca. 2 hr) to the $LiAlH_4$ slurry. After the addition was complete, the reaction mixture was gently boiled for 3 hr and subsequently cooled to $0^{o}C$ (ice bath). The cooled reaction mixture was hydrolyzed by the dropwise addition (caution!) of H_2). The hydrolyzed mixture was extracted with 3 x 100 ml of ether, 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, round-bottom flask equipped with a condenser and magnetic stirrer. The acetone solution was cooled (ice bath) to 0°C, and 5.0 g (0.044 mole) of 30% H_2O_2 was added dropwise. After the reaction mixture was allowed to warm to room temperature, it was stirred for 12 hr; this was followed by a period of 12 hr in which the mixture was boiled gently. When the reaction mixture had cooled to room temperature, 100 ml of satd. aqueous NaCl was added and the mixture was extracted with 3 x 50 ml portions of $HCCl_3$. The $HCCl_3$ extracts were combined, washed with 50 ml of a satd. aqueous $Fe(NH_4)_2(SO_4)_2$ solution, and then dried ($MgSO_4$). The $HCCl_3$ solution was filtered, and the solvent was removed by rotary evaporation to give 4.43 g (83%) of crude 63b as an oil. Pure 63b was obtained by trituration of the crude oil with acetone, followed by recrystallization (acetone). An analytical sample of 63b had a mp 198-200°C.

IR, ^1H NMR, ^{13}C NMR, and ^{31}P NMR data for 63b are listed in Tables IV and V. The IR and ^1H NMR spectra of 63b are illustrated in Plates XX and XXI, respectively.

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 (63c)

To 0.76 g (0.02 moles) of $LiAlH_4$ and 25 ml of dry THF in a 100-ml, round-bottom flask equipped with a condenser, mechanical stirrer, addition funnel, and N_2 inlet was added dropwise (ca. 2 hr)

ketone 11a (1.24 g, 5 mmole) dissolved in 25 ml of dry THF. After the addition was complete, the reaction mixture was gently boiled for 4 hr. The reaction mixture was cooled (ice bath) 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 mg-atom) of sulfur was added. The reaction mixture was gently boiled for 4 hr and 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 pipette packed with neutral alumina (ca. 1 g, Brinkmann, Aluminium Oxide 90 active). Solvent was evaporated by rotary evaporation and the resulting oil was covered with 25 ml of petroleum ether (bp 35-60°C). After standing 48 hr at 0°C a white solid formed and was filtered off and air dried to give 0.81 g (57.5%) of crude 63c, mp 114-123°C. An analytical sample of 63c was prepared by recrystallization (hot CH_3OH), mp 142-143°C.

IR, ^1H NMR, ^{13}C NMR and ^{31}P NMR data for 63c are listed in Tables IV and V. The IR and ^1H NMR spectra of 63c are illustrated in Plates XXII and XXIII, respectively.

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 (63d)

The crude alcohol 63a prepared from 4.96 g (0.02 mole) of 11a and 1.52 g (0.04 mole) of $LiAlH_4$ was used as such to prepare 63d.

Oily 63a was dissolved in 50 ml of benzene and placed in a 200-ml, round-bottom flask equipped with a magnetic stirrer, condenser, and N_2 inlet. To this was added 3.42 g (0.02 mole) of benzyl bromide and the reaction mixture was gently boiled for 4 hr. 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 hr, and the solid which formed was removed by vacuum filtration and air dried to give 3.12 g (38.5%) of 63d. Recrystallization (CH_3CN) afforded 1.49 g of 63d, mp 260°C dec.

IR, ^1H, ^{13}C, and ^{31}P NMR data for 63d are listed in Tables IV and V, also the IR and ^1H NMR spectra of 63d are illustrated in Plates XXIV and XXV. A solid sample of 63d was obtained by repeated recrystallization (methanol:ethyl acetate, 1:10), mp 256.5-257.5°C but repeated tlc and elemental analysis showed a small impurity.

Anal. Calcd. for $C_{22}H_{30}BrOP$: C, 62.71; H, 7.18; P, 7.35.

Found: C, 63.57; H, 7.47; P, 7.32.

Preparation of 4-tert-Butyl-2,2,6,6-tetramethyl-1-phenyl-4-phosphorinanol 1-Oxide (64)

To 43 ml (0.069 mole, 1.6 m in pentane) of tert-butylithium in a 500-ml, round-bottom flask, equipped with an addition funnel, condenser, mechanical stirrer, and N_2 inlet was added dropwise ketone 11a (6.7 g, 0.027 mole) over a 1-hr period. After the additon, the reaction mixture was gently boiled 24 hr 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

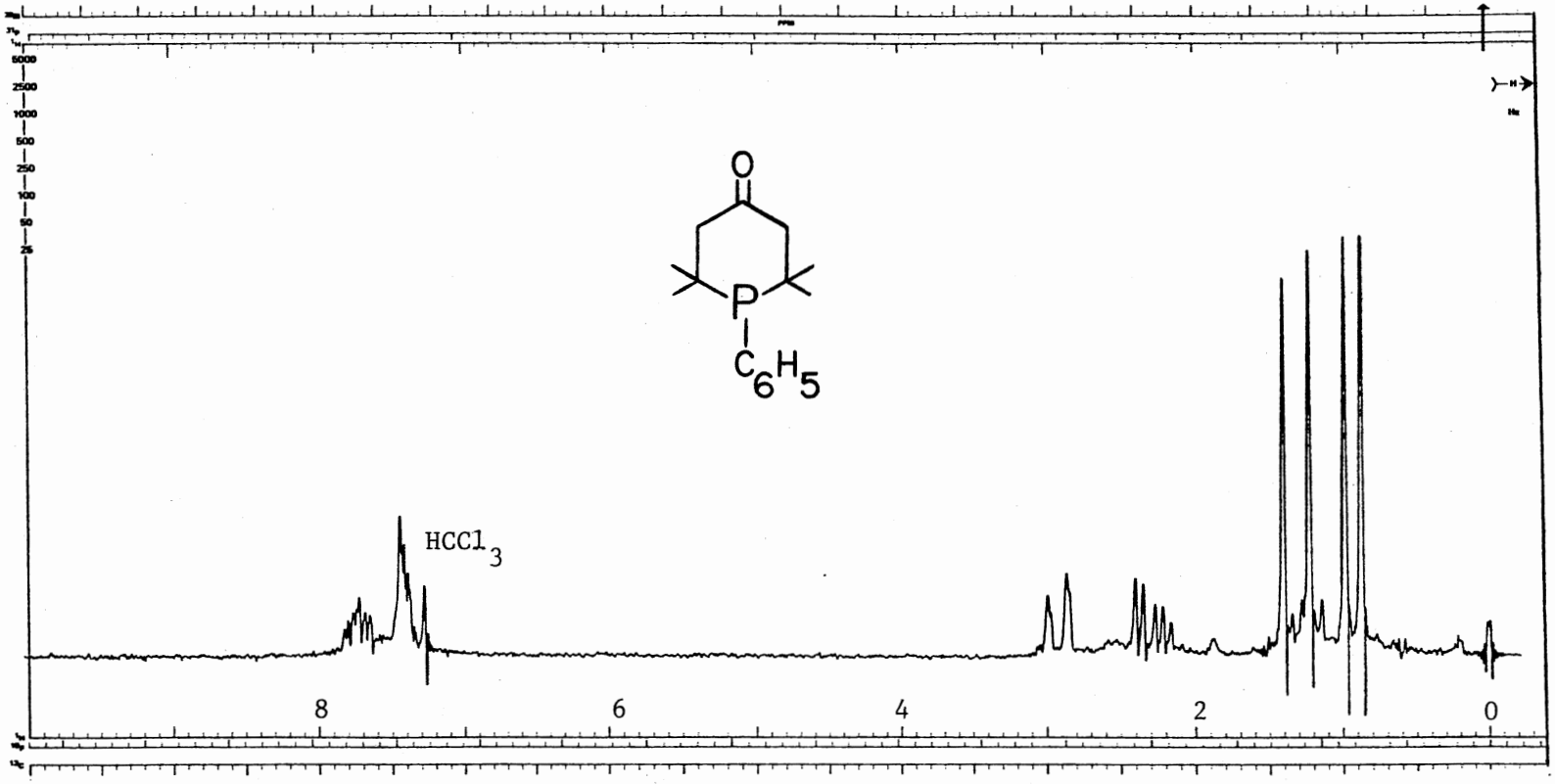
layer was extracted with 3 x 100 ml ether. The organic phases were combined and dried ($MgSO_4$). The dried solution was filtered and the solvents were removed by rotary evaporation. A resulting oil was distilled (Kugelrohr) under reduced pressure to give 63 g (76.5%) of an oil, bp 140°C/0.5 mm. The 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 had stirred at room temperature for 12 hr, 20 ml of H_2O was added. The reaction mixture was extracted with 3 x 50 ml of $HCCl_3$ and the 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 64, mp 201-202°C.

IR, ^1H, ^{13}C, and ^{31}P NMR data for 64 are listed in Tables IV and V. The IR and ^1H NMR spectra of 64 are illustrated in Plates XXVI and XXVII, respectively.

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.

PLATE I

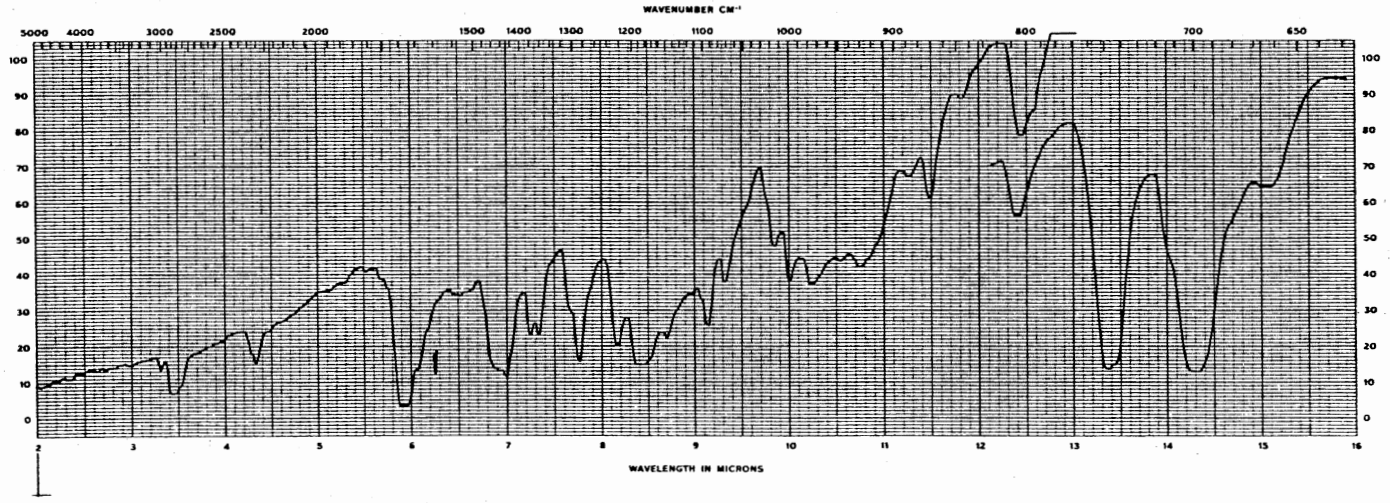


^1H NMR Spectrum of 2,2,6,6-Tetramethyl-1-phenyl-4-phosphorinanone (11a)

Solvent . . . . . .$DCCl_3$ S.F. . . .100.1 MHz F.B. . . . 2.0 Hz R.F. . . .60db

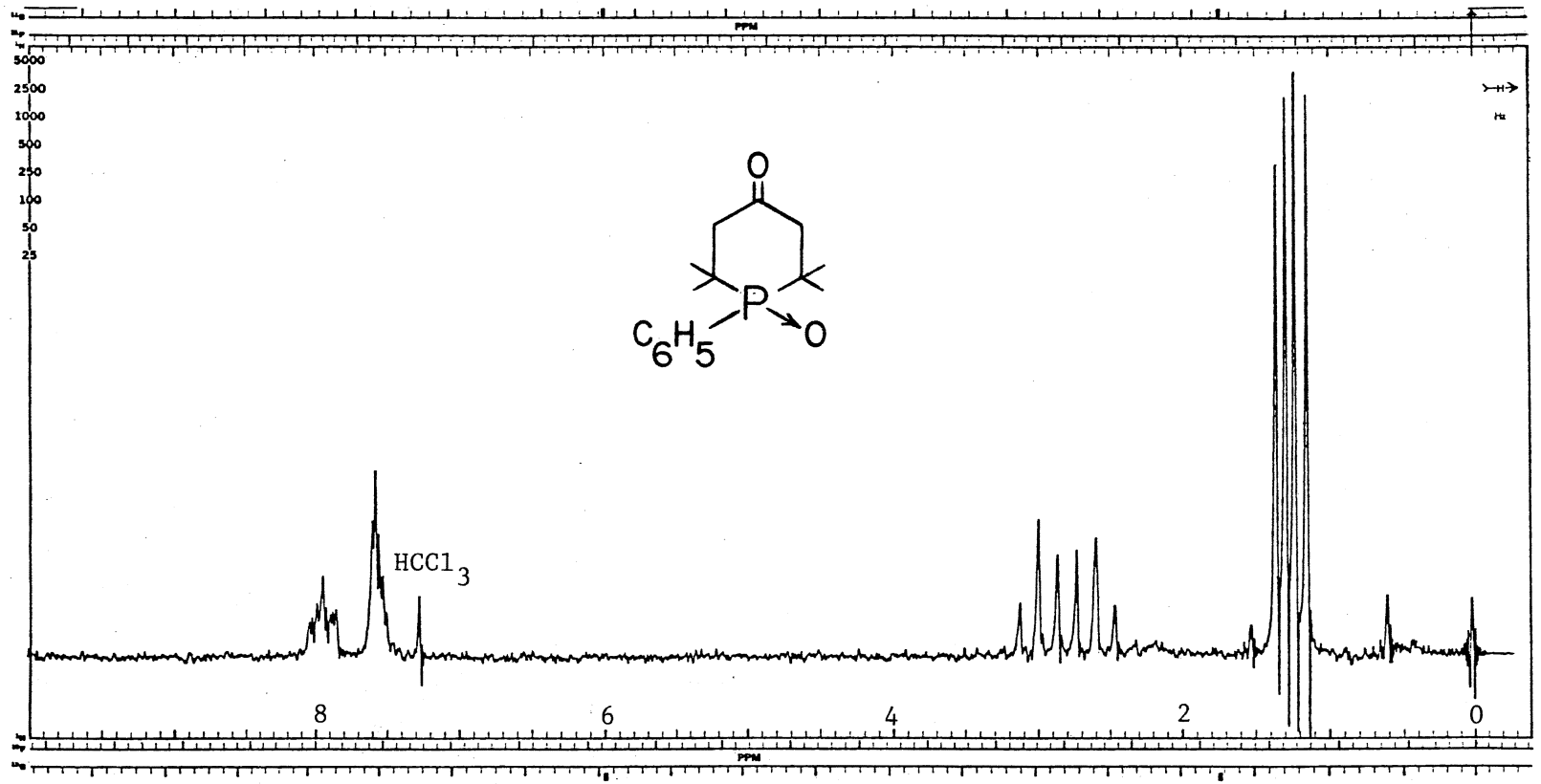
S. W. . . . . .1000 Hz S.T. . . . .250 sec. S.O. . . .8370 Hz S.A. . . . 1.6 Lock. . .^1H

PLATE II



IR Spectrum of 11a, KBr Pellet

PLATE III

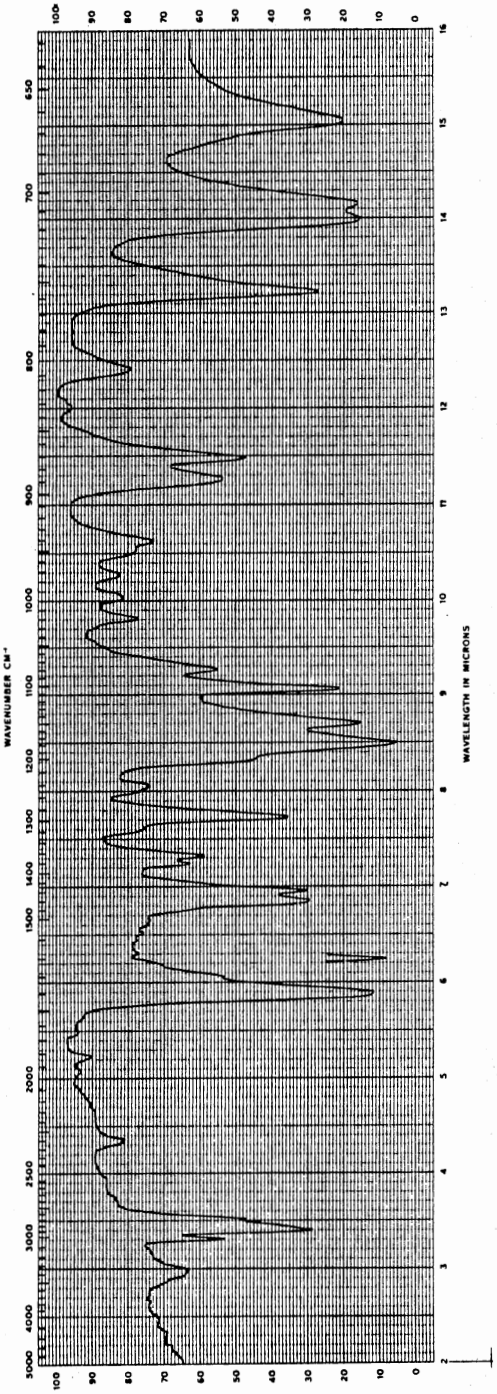


^1H NMR Spectrum of 2,2,6,6-Tetramethyl-1-phenyl-4-phosphorinanone 1-Oxide (11b)

Solvent. . . . . $DCCl_3$ S.F. . . .100.1 MHz F.B. . . 2.0 Hz R.F. 60dB

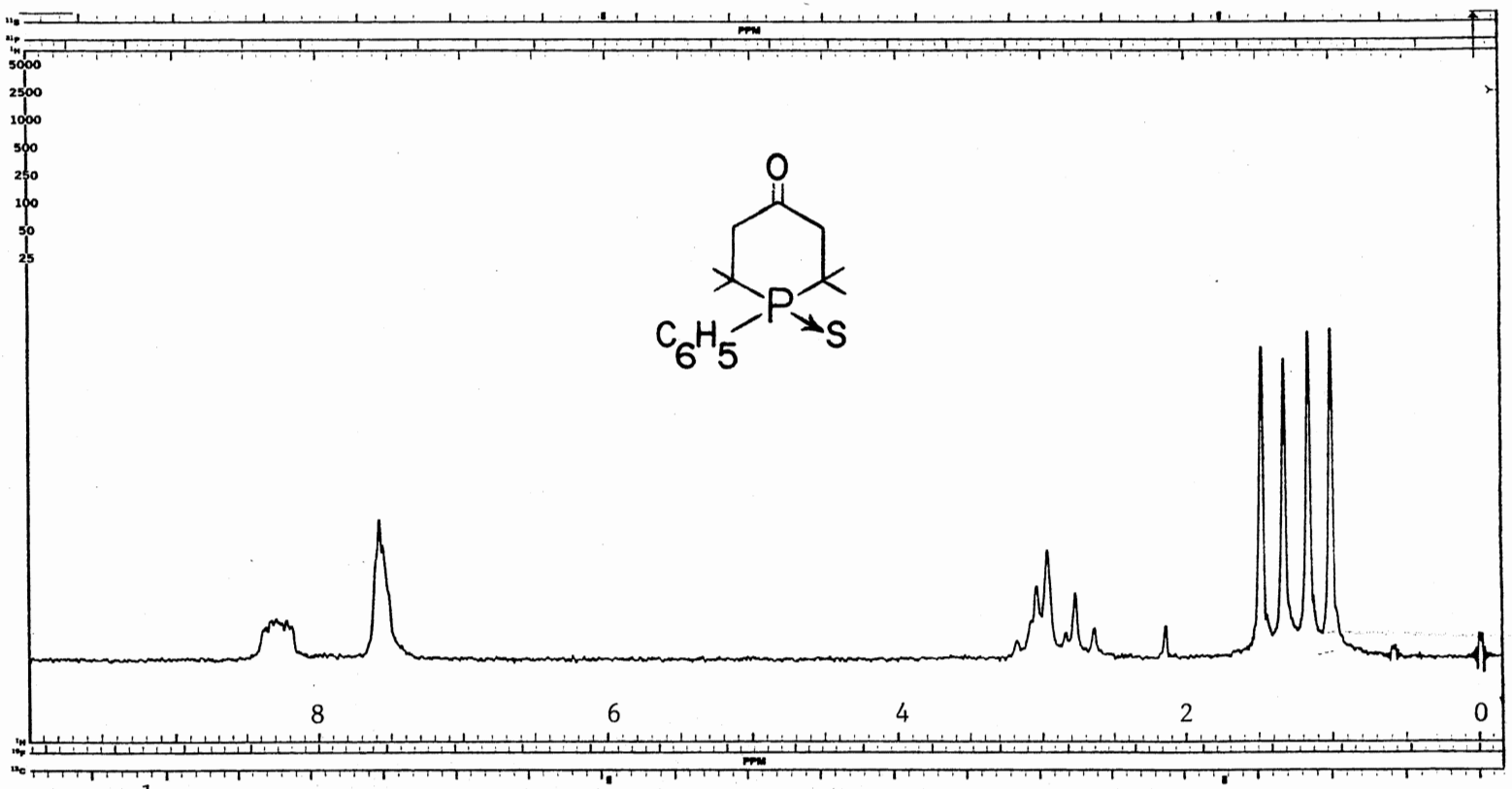
S.W. . . . . 1000 Hz S.T. . . . 250 sec. S.O. . .83701 Hz S.A. . . . 3.2 Lock. . . ^1H

PLATE IV



IR Spectrum of 11b, KBr Pellet

PLATE V

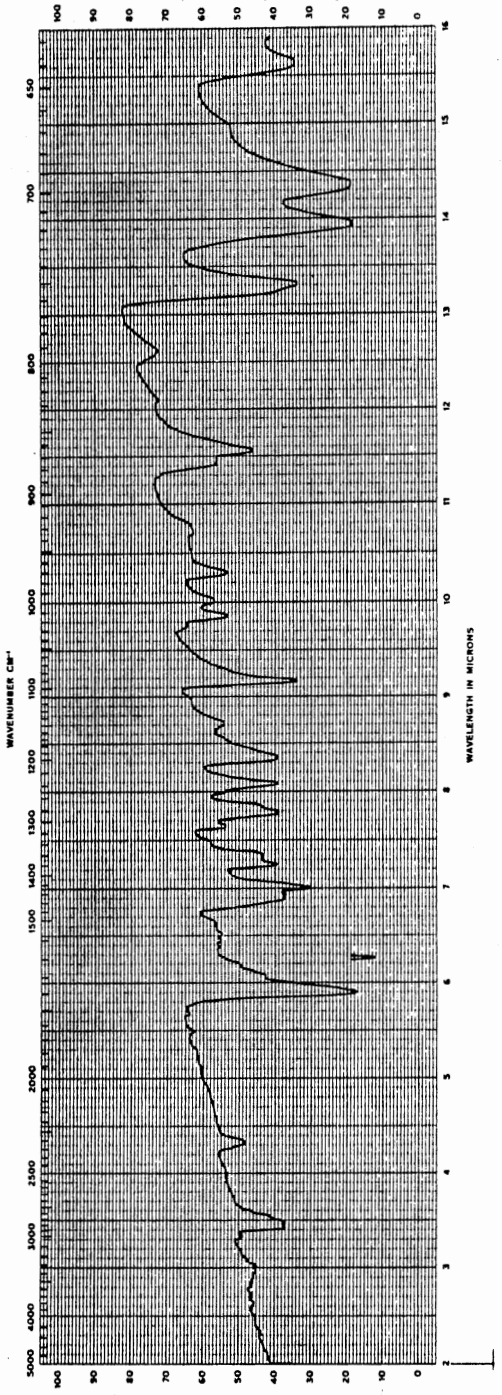


^1H NMR Spectrum of 2,2,6,6-Tetramethyl-1-phenyl-4-phosphorinanone 1-Sulfide (11c)

Solvent. . . . . $DCCl_3$ S.F. . . .100.1 MHz F.B. . . . 2.0 Hz R.F. . . .45dB

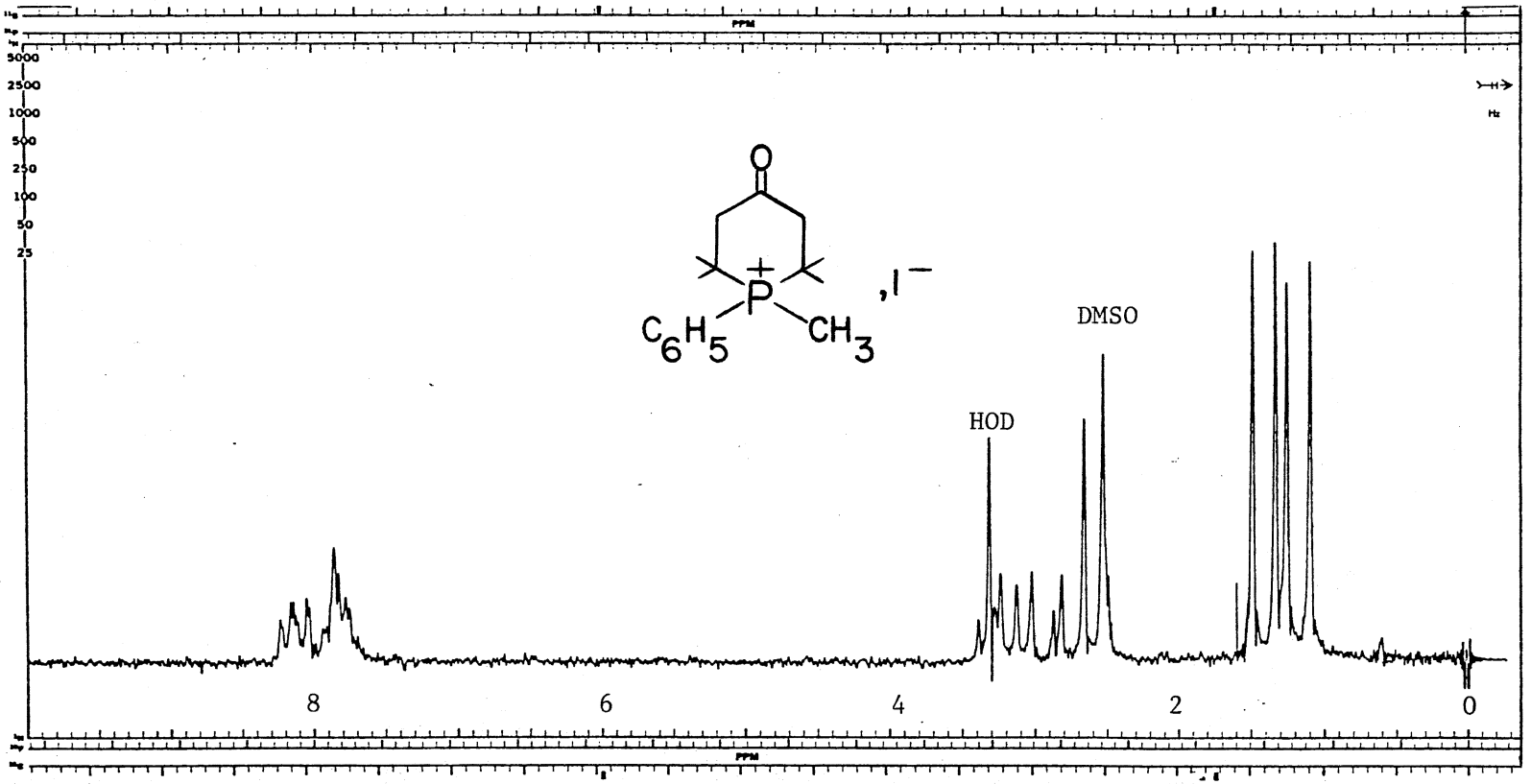
S.W. . . . . 1000 Hz S.T. . . . 250 sec. S.O. . . .83701 Hz S.H. . . . 2.0 Lock. . . ^1H

PLATE VI



IR Spectrum of 11c, KBr Pellet

PLATE VII

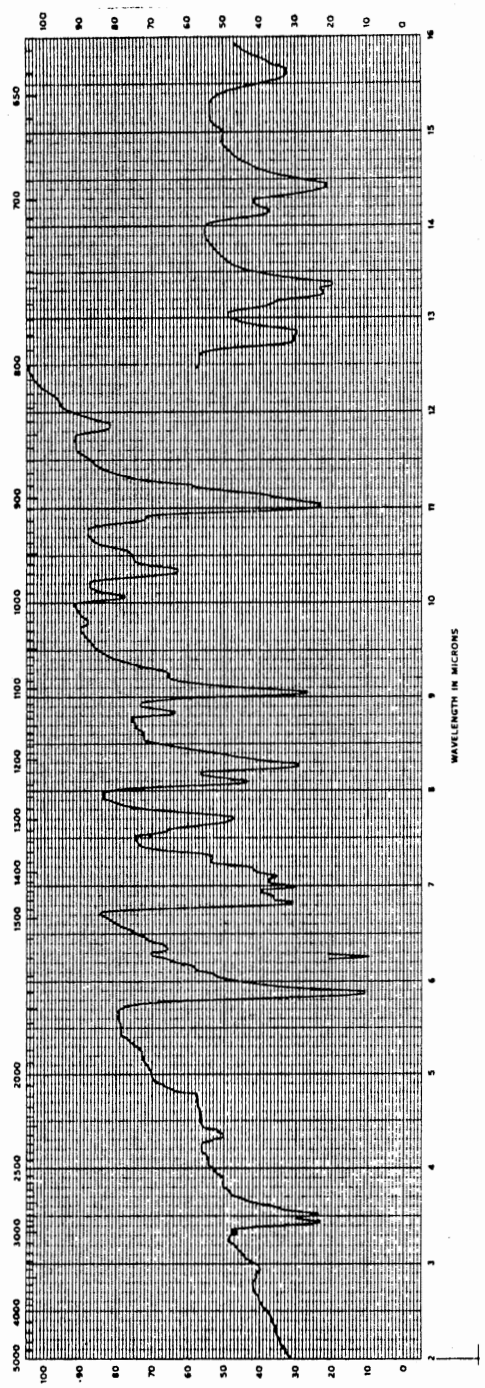


^{1}H NMR Spectrum of 1,2,2,6,6-Pentamethyl-1-phenyl-4-phosphorinanonium Iodide (11d)

Solvent. . . . DMSO-d_6 S.F. . . .100.1 MHz F.B. . . . 2.0 Hz R.F. . . .65dB

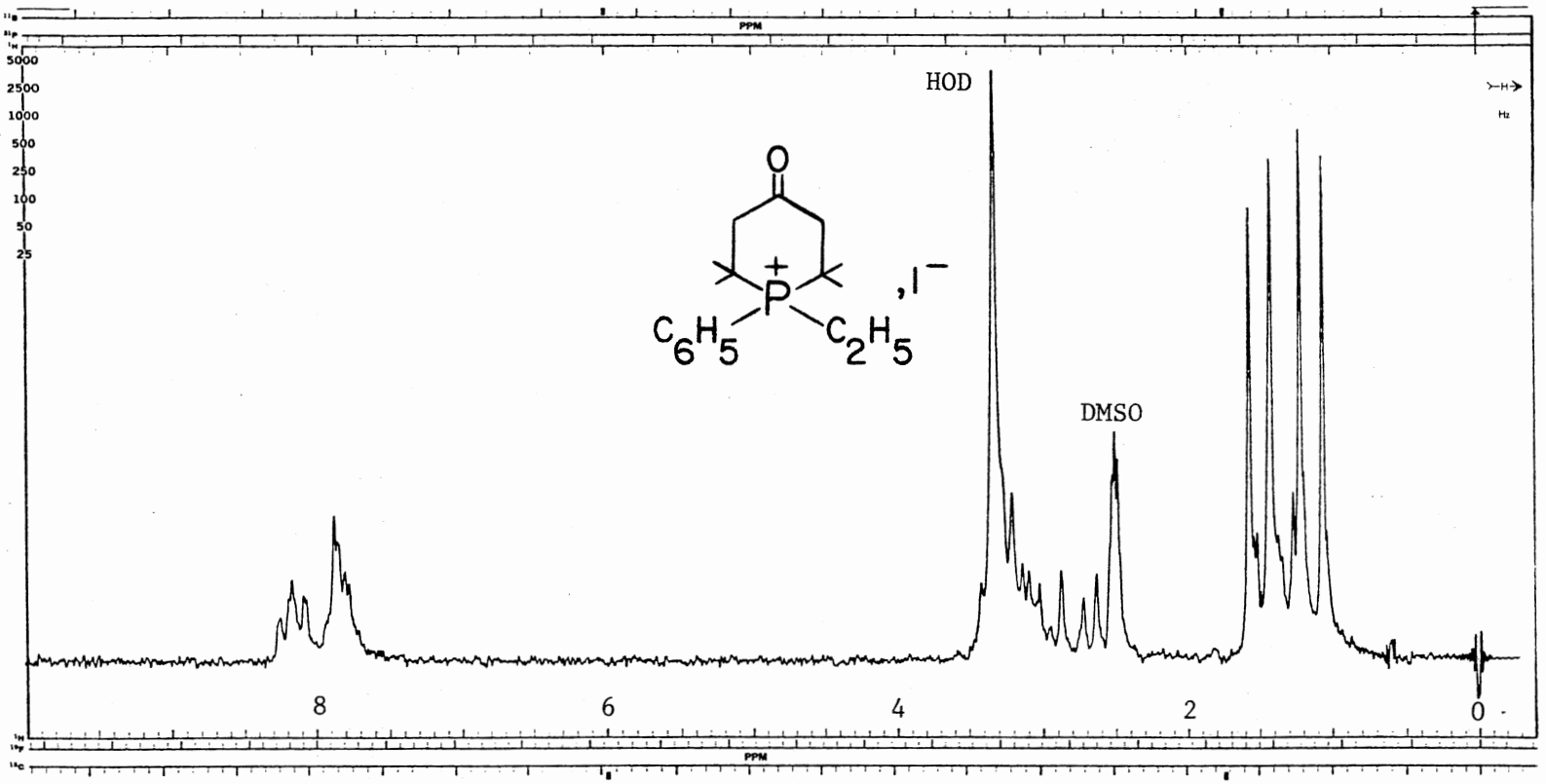
S.W. . . . . 1000 Hz S.T. . . . 250 sec. S.O. . . .83701 Hz S.A. . . . 3.2 Lock. . .^{1}H

PLATE VIII



IR Spectrum of 11d, KBr Pellet

PLATE IX

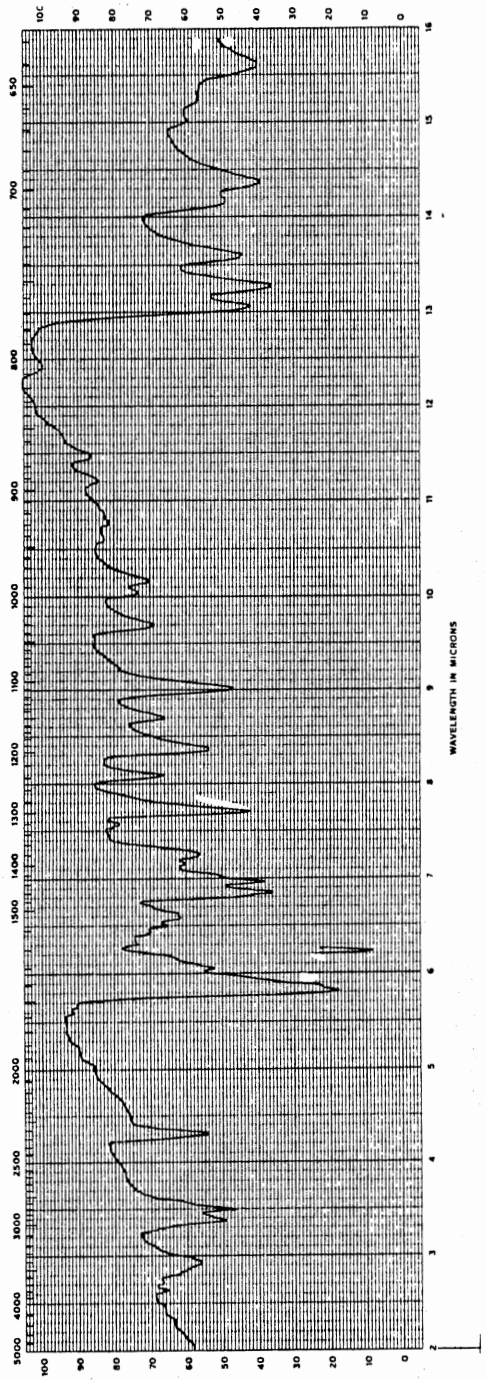


^{1}H NMR Spectrum of 1-Ethyl-2,2,6,6-tetramethyl-1-phenyl-4-phosphorinanonium Iodide (11e)

Solvent. . . . DMSO-d_6 S.F. . . .100.1 MHz F.B. . . . 2.0 Hz R.F. . . .68dB

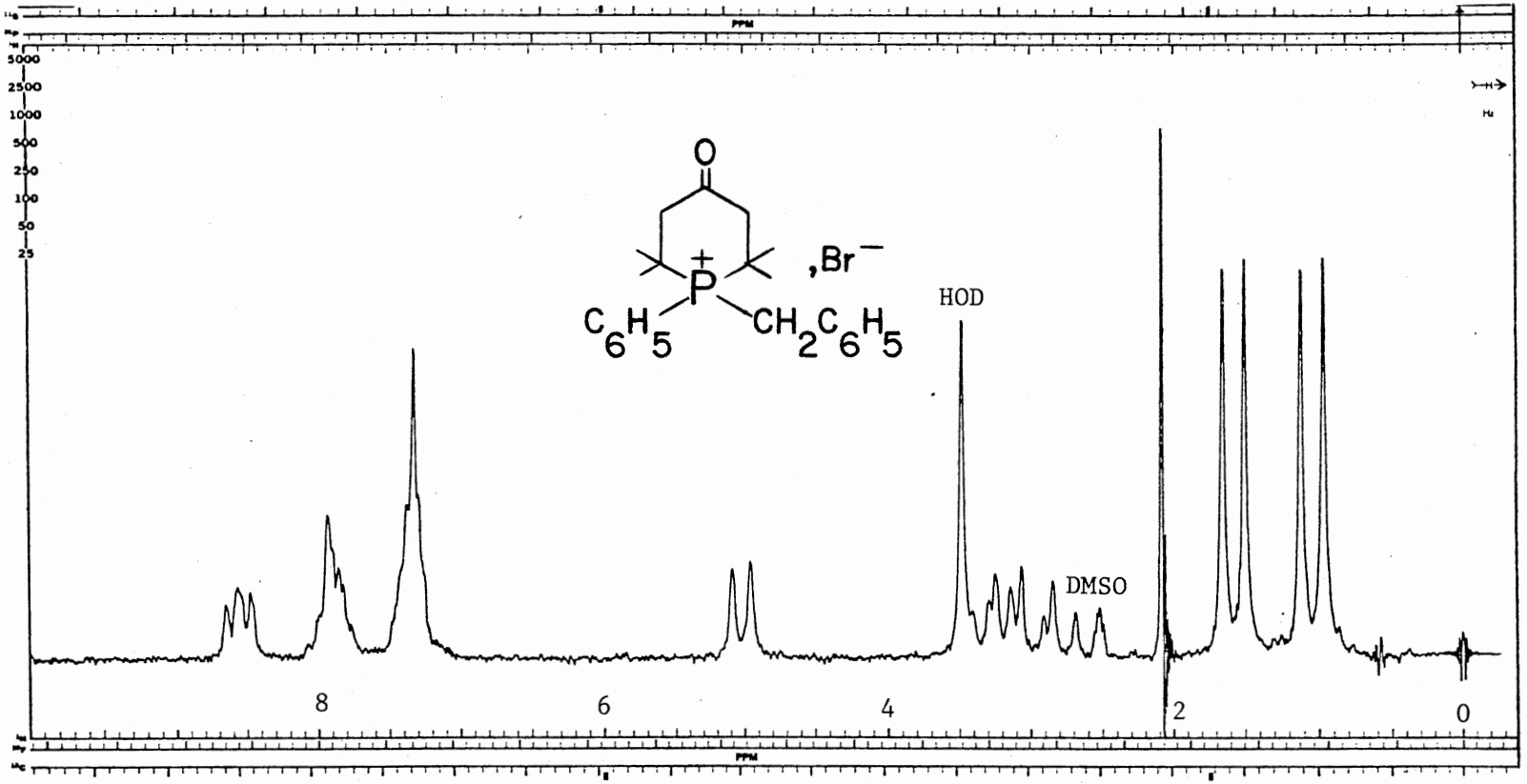
S.W. . . . . 1000 Hz S.T. . . . 250 sec. S.O. . . .83701 Hz S.A. . . . 3.2 Lock. . .^{1}H

PLATE X



IR Spectrum 11e, KBr Pellet

PLATE XI

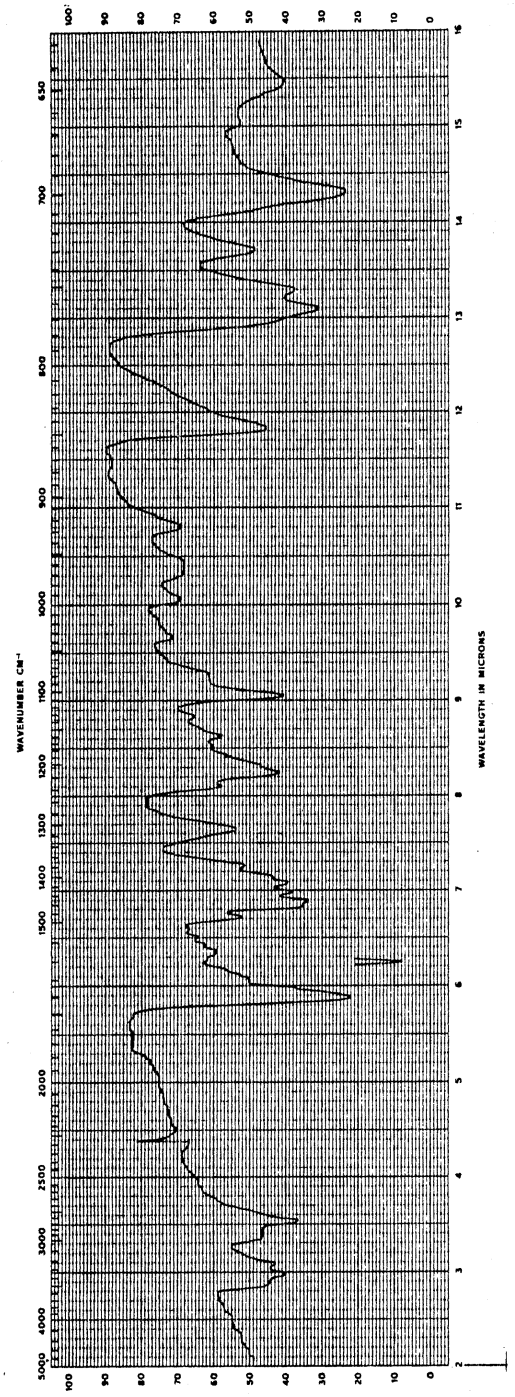


^{1}H NMR Spectrum of 1-Benzyl-2,2,6,6-tetramethyl-1-phenyl-4-phosphorinanonium Bromide (11f)

Solvent. . . . .DMSO-d_6 S.F. . . .100.1 MHz F.B. . . . 2.0 Hz R.F. . . .55dB

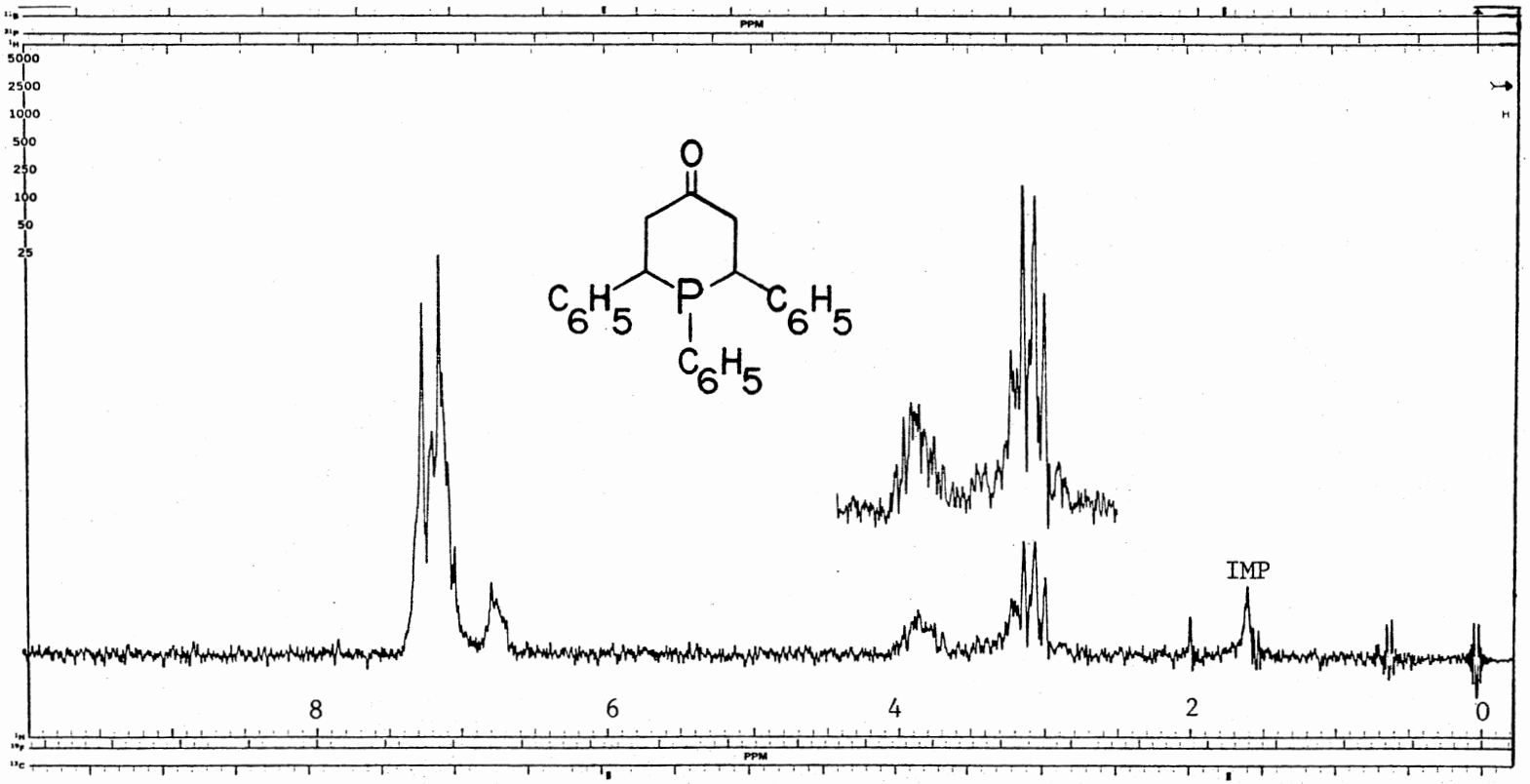
S.W. . . . . 1000 Hz S.T. . . . 250 sec. S.O. . . .83701 Hz S.A. . . . 3.2 Lock. . .^{1}H

PLATE XII



IR Spectrum of 11f, KBr Pellet

PLATE XIII

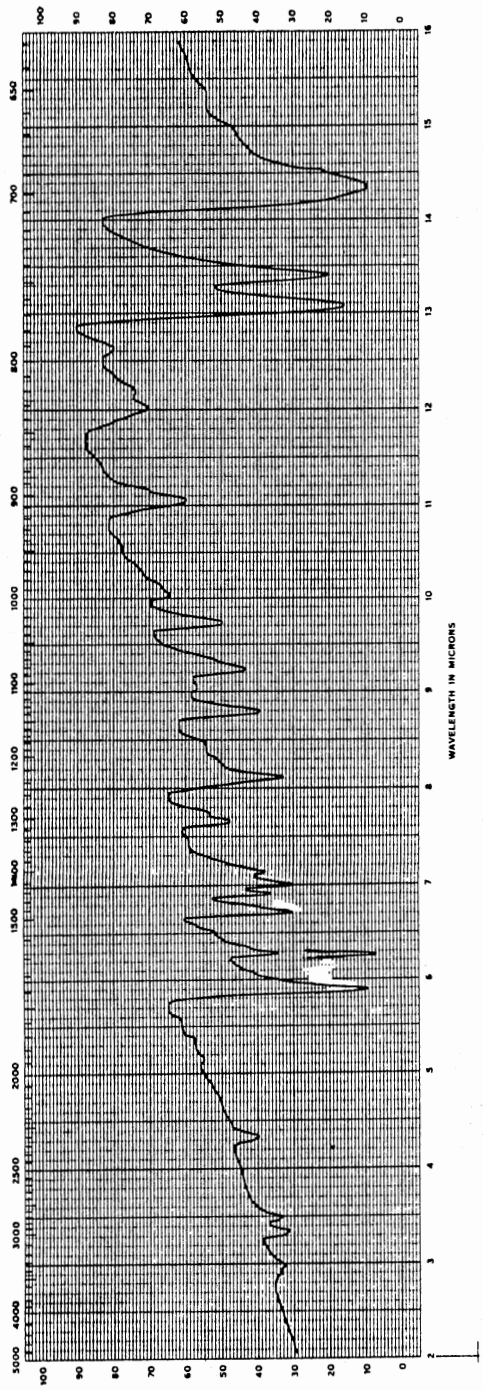


^1H NMR Spectrum of 1,2,6-Triphenyl-4-phosphorinanone (41a and 41a')

Solvent. . . . . .$DCCl_3$ S.F. . . .100.1 MHz F.B. . . . 2.0 Hz R.F. . . .60dB

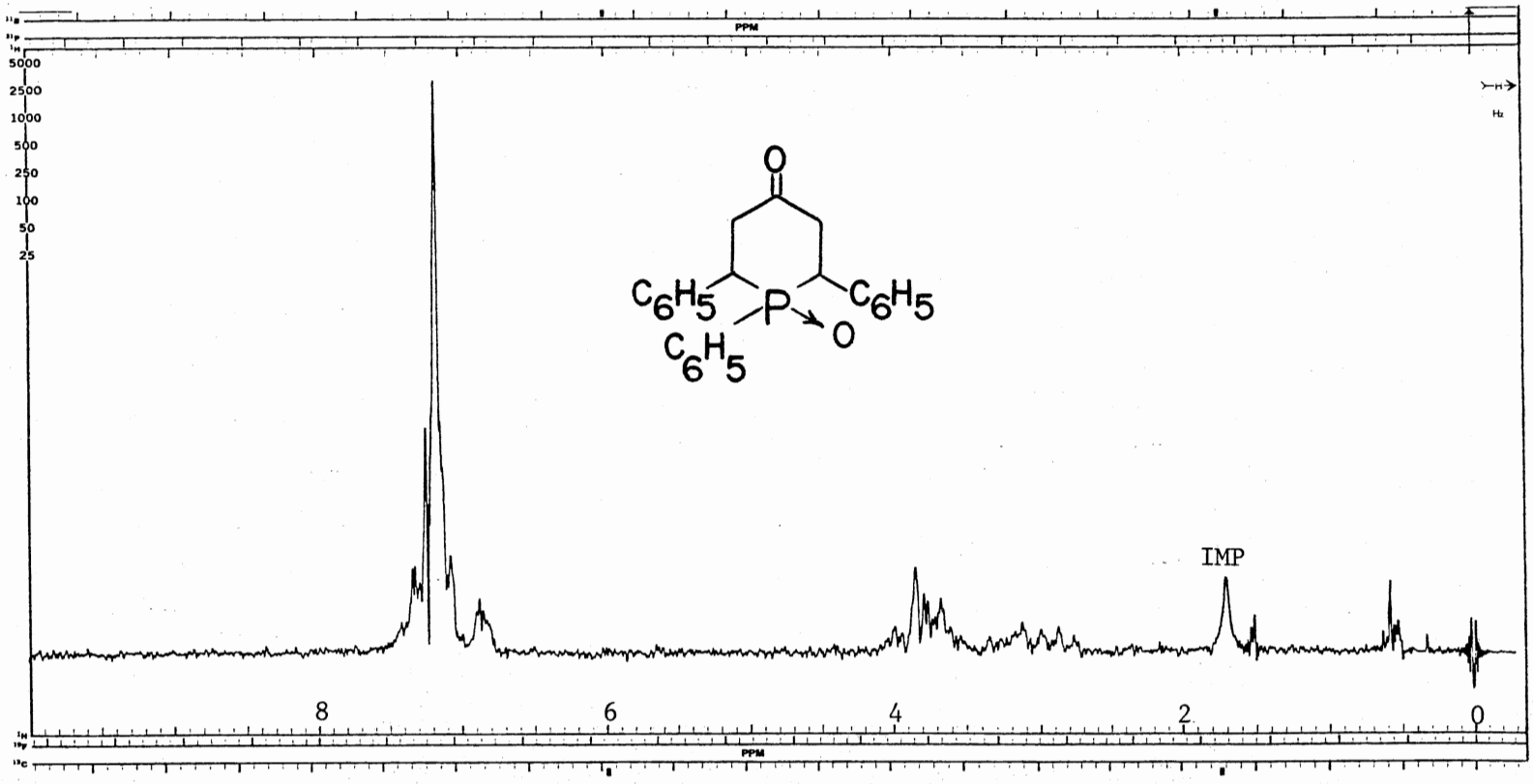
S.W. . . . . .1000 Hz S.T. . . . 250 sec. S.O. . . .83701 Hz S.A. . . . 5.0 Lock. . .^1H

PLATE XIV



IR Spectrum of 41a and 41a', KBr Pellet

PLATE XV

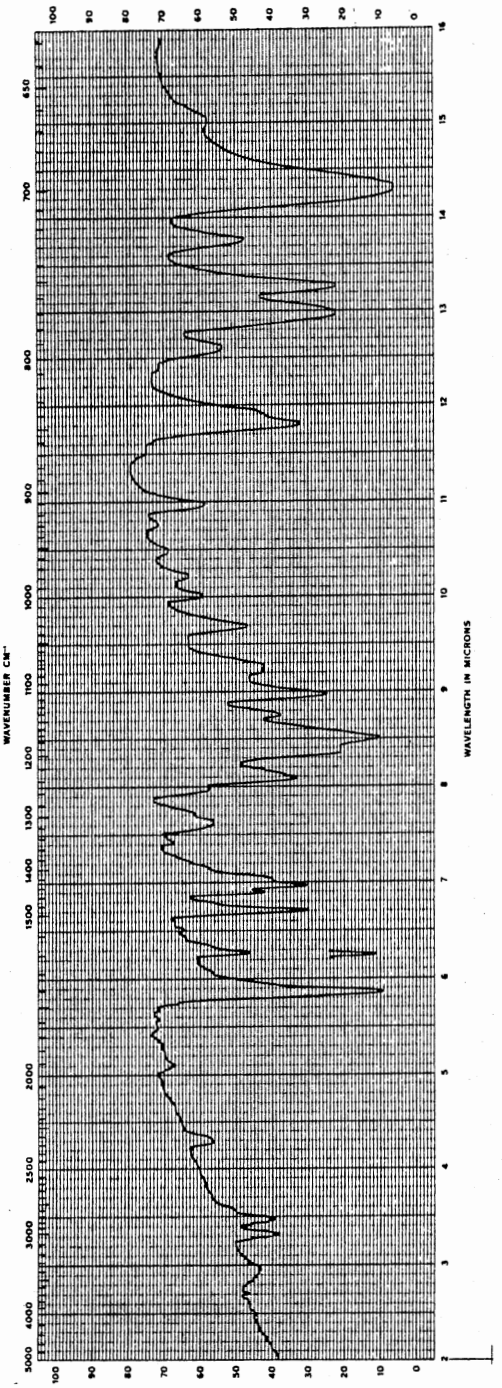


^{1}H NMR Spectrum of 1,2,6-Triphenyl-4-phosphorinanone 1-Oxide (41b and 41b')

Solvent. . . . .$DCCl_3$ S.F. . . .100.1 MHz F.B. . . . 2.0 Hz R.F. . . .68dB

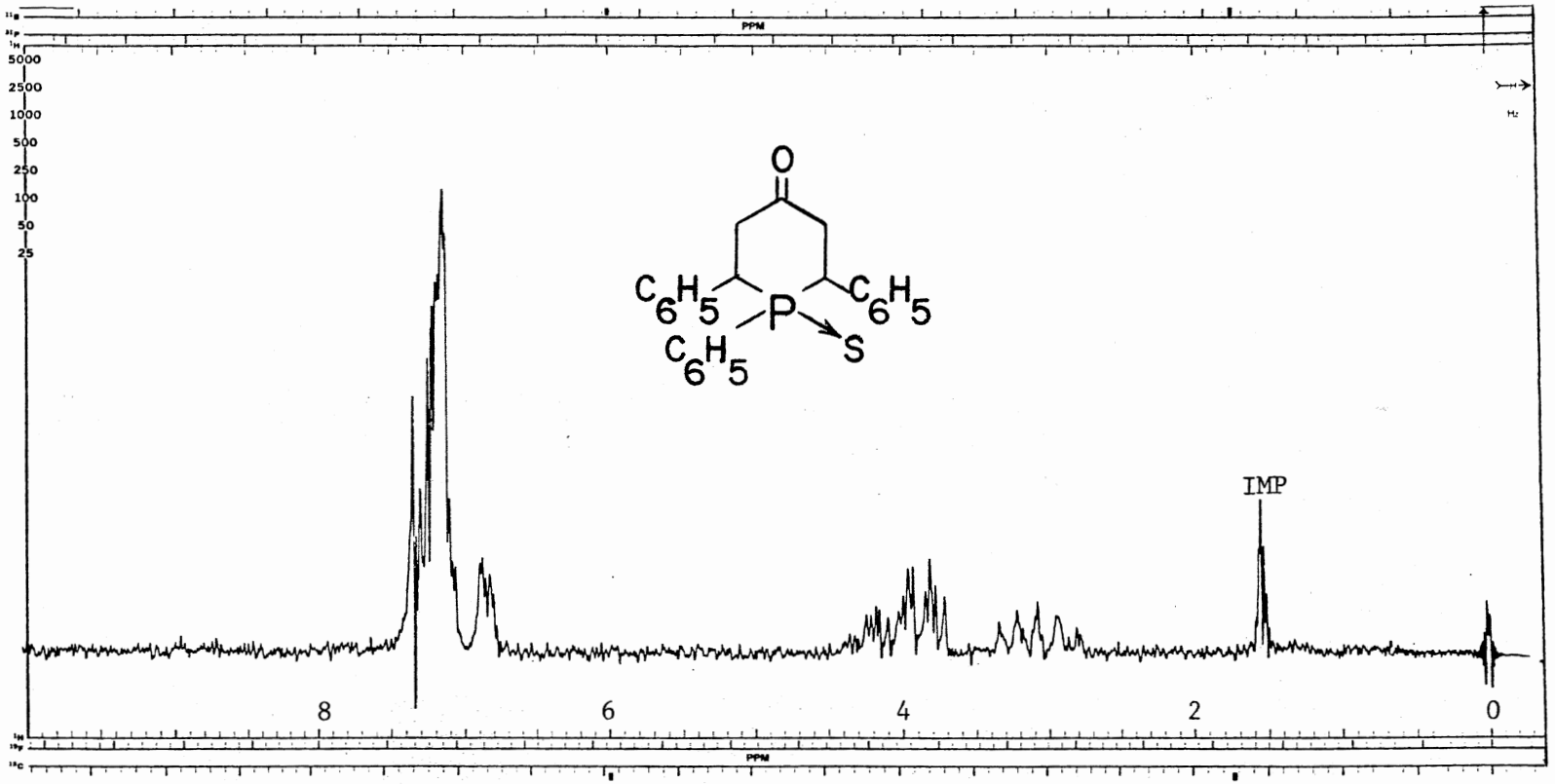
S.W. . . . . .1000 Hz S.T. . . . 250 sec. S.O. . . .83701 Hz S.A. . . . 3.2 Lock. . .^{1}H

PLATE XVI



IR Spectrum of 41b and 41b', KBr Pellet

PLATE XVII

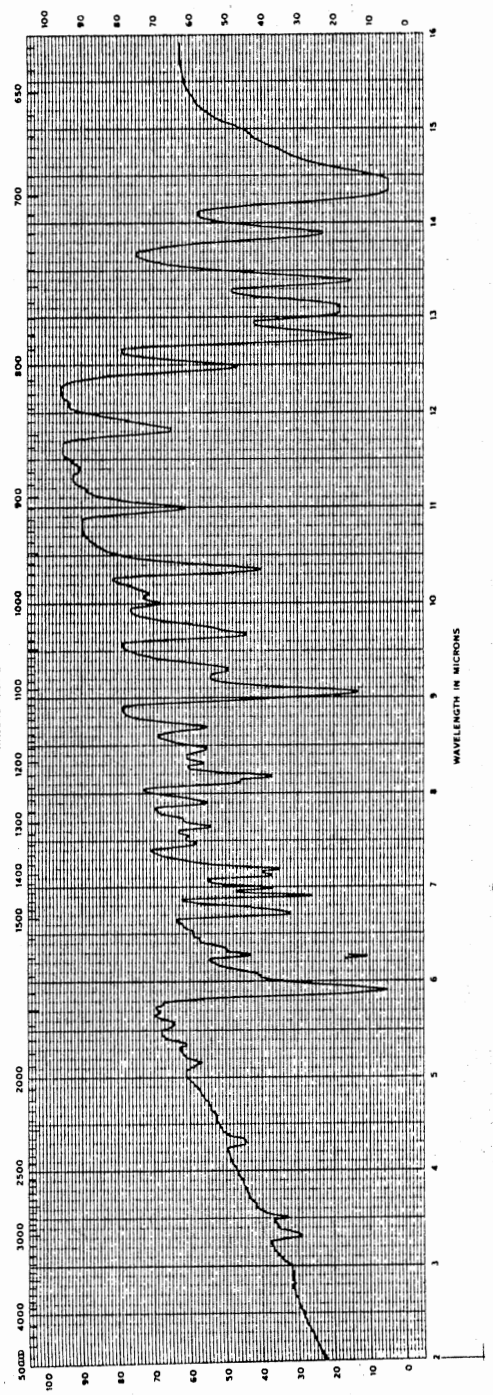


^{1}H NMR Spectrum of 1,2,6-Triphenyl-4-phosphorinanone 1-Sulfide (41c')

Solvent. . . . .$DCCl_3$ S.F. . . .100.1 MHz F.B. . . . 2.0 Hz R.F. . . .65dB

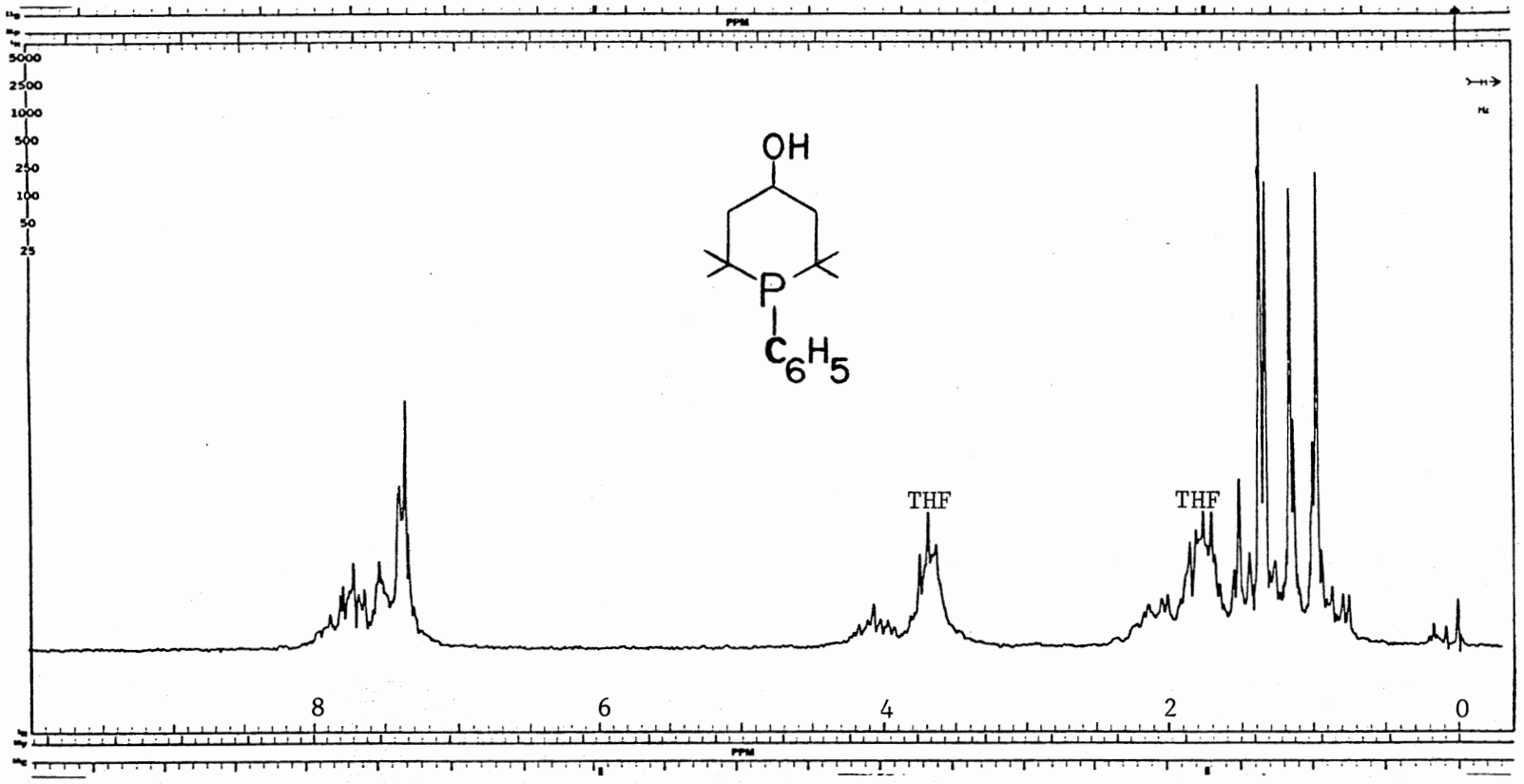
S.W. . . . . .1000 Hz S.T. . . . 250 sec. S.O. . . .83701 Hz S.A. . . . 3.2 Lock. . .^{1}H

PLATE XVIII



IR Spectrum of 41c', KBr Pellet

PLATE XIX

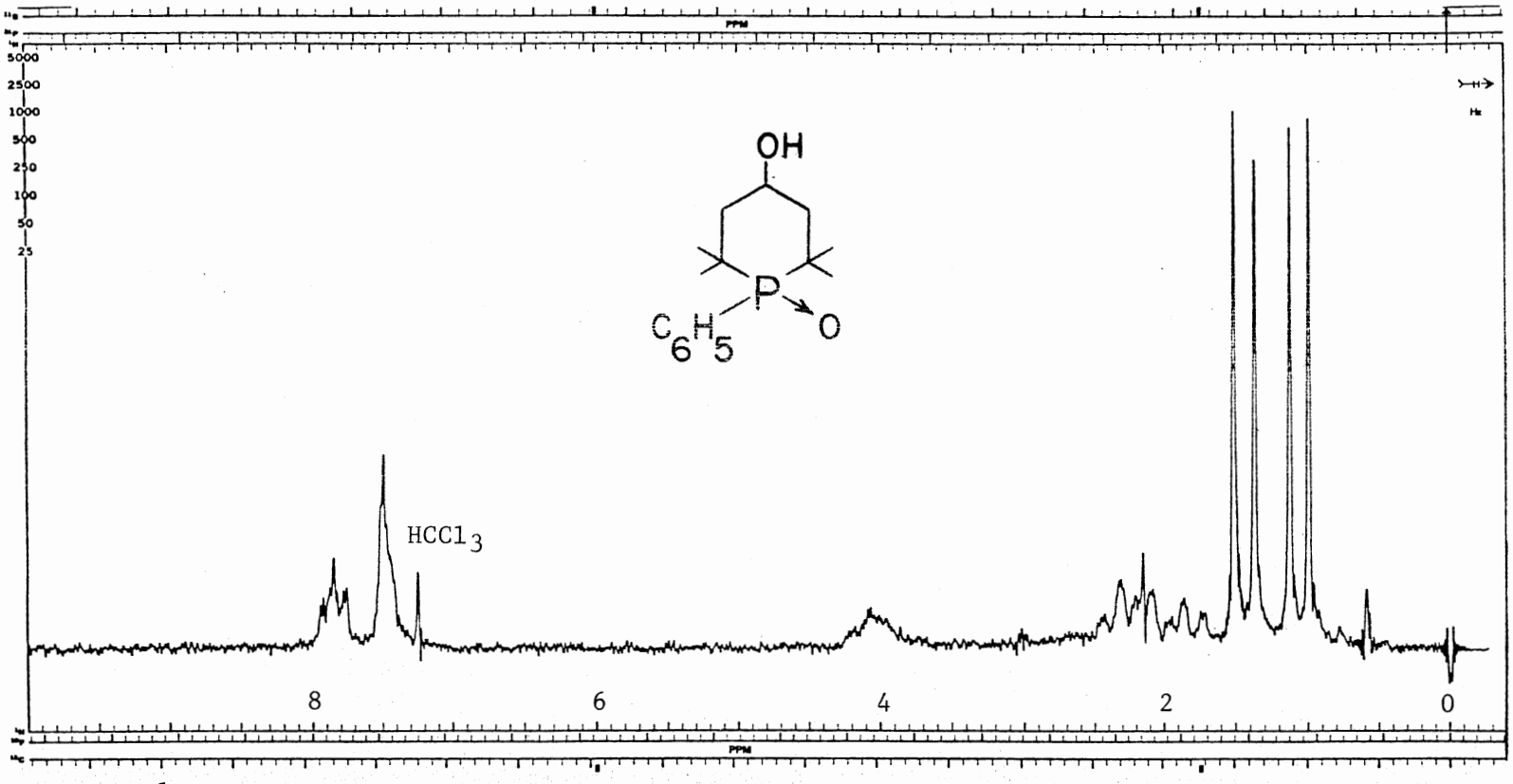


^{1}H NMR Spectrum of 2,2,6,6-Tetramethyl-1-phenyl-4-phosphorinanol (63a)

Solvent. . . . .$DCCl_3$ S.F. . . .100.1 MHz F.B. . . . 2.0 Hz R.F. . . .100dB

S.W. . . . . .1000 Hz S.T. . . . 250 sec. S.O. . . .85771 Hz S.A. . . . 1.0 Lock. . .^{2}H

PLATE XX

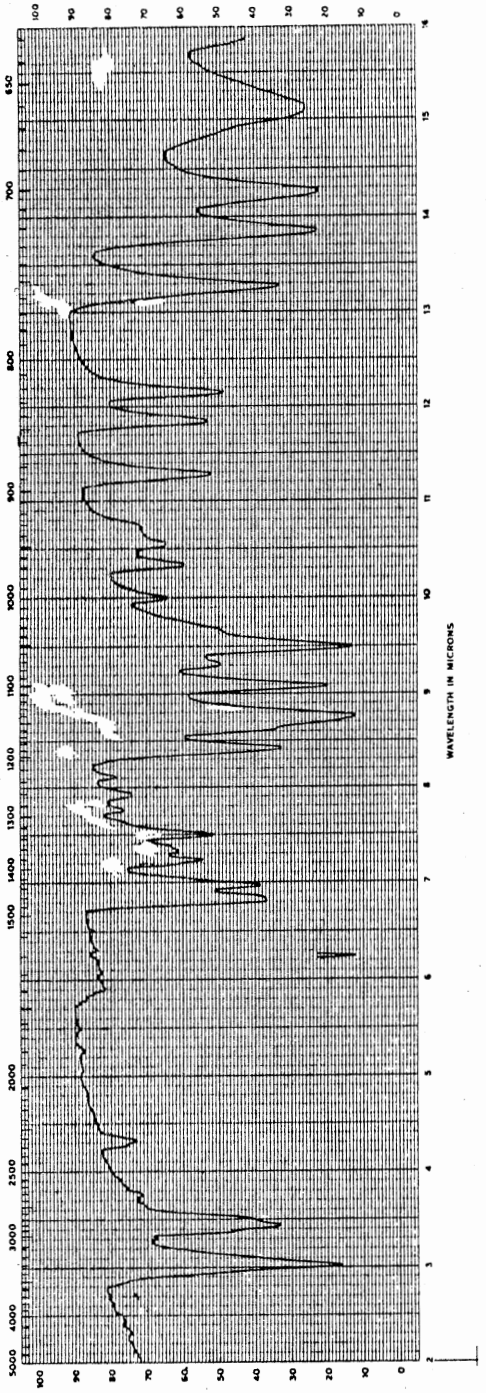


^1H NMR Spectrum of 2,2,6,6-Tetramethyl-1-phenyl-4-phosphorinanol 1-Oxide (63b)

Solvent. . . . .$DCCl_3$ S.F. . . .100.1 MHz F.B. . . . 2.0 Hz R.F. . . .60dB

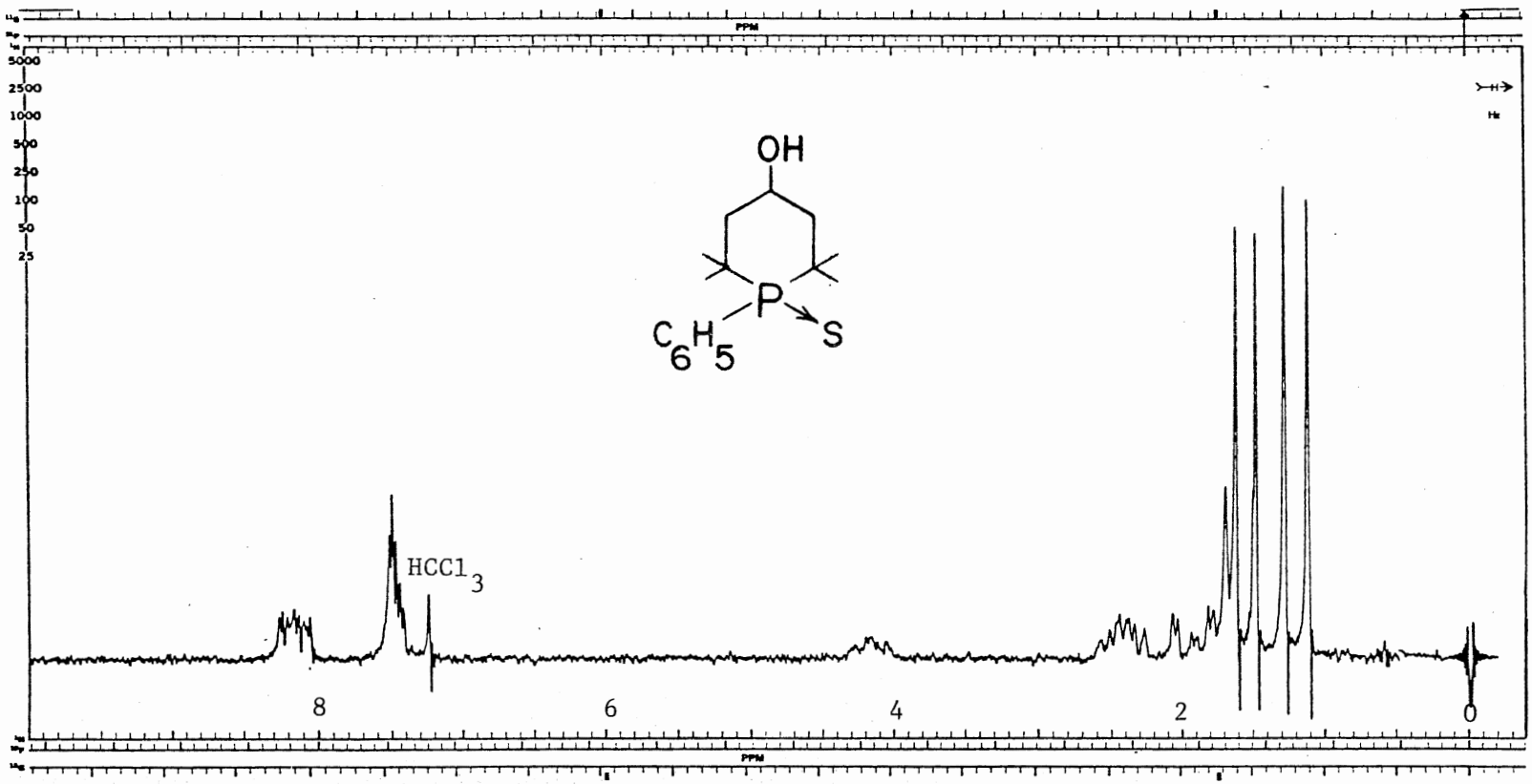
S.W. . . . . .1000 Hz S.T. . . . 250 sec. S.O. . . .87091 Hz S.A. . . . 3.2 Lock. . .^1H

PLATE XXI



IR Spectrum of 63b, KBr Pellet

PLATE XXII

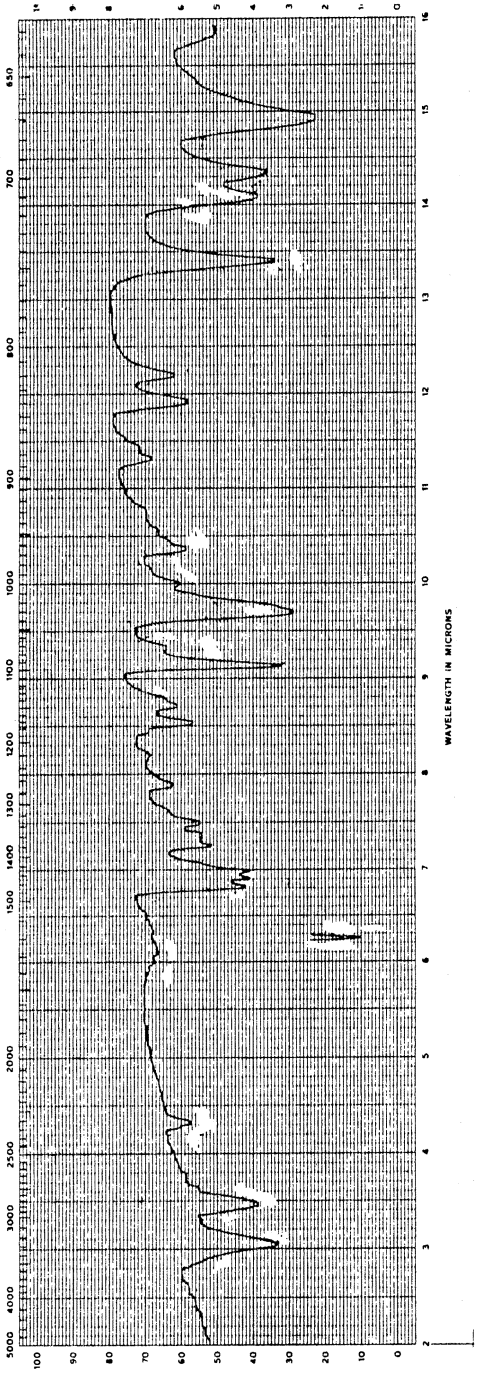


^1H NMR Spectrum of 2,2,6,6-Tetramethyl-1-phenyl-4-phosphorinanol 1-Sulfide (63c)

Solvent. . . . .$DCCl_3$ S.F. . . .100.1 MHz F.B. . . . 2.0 Hz R.F. . . .60dB

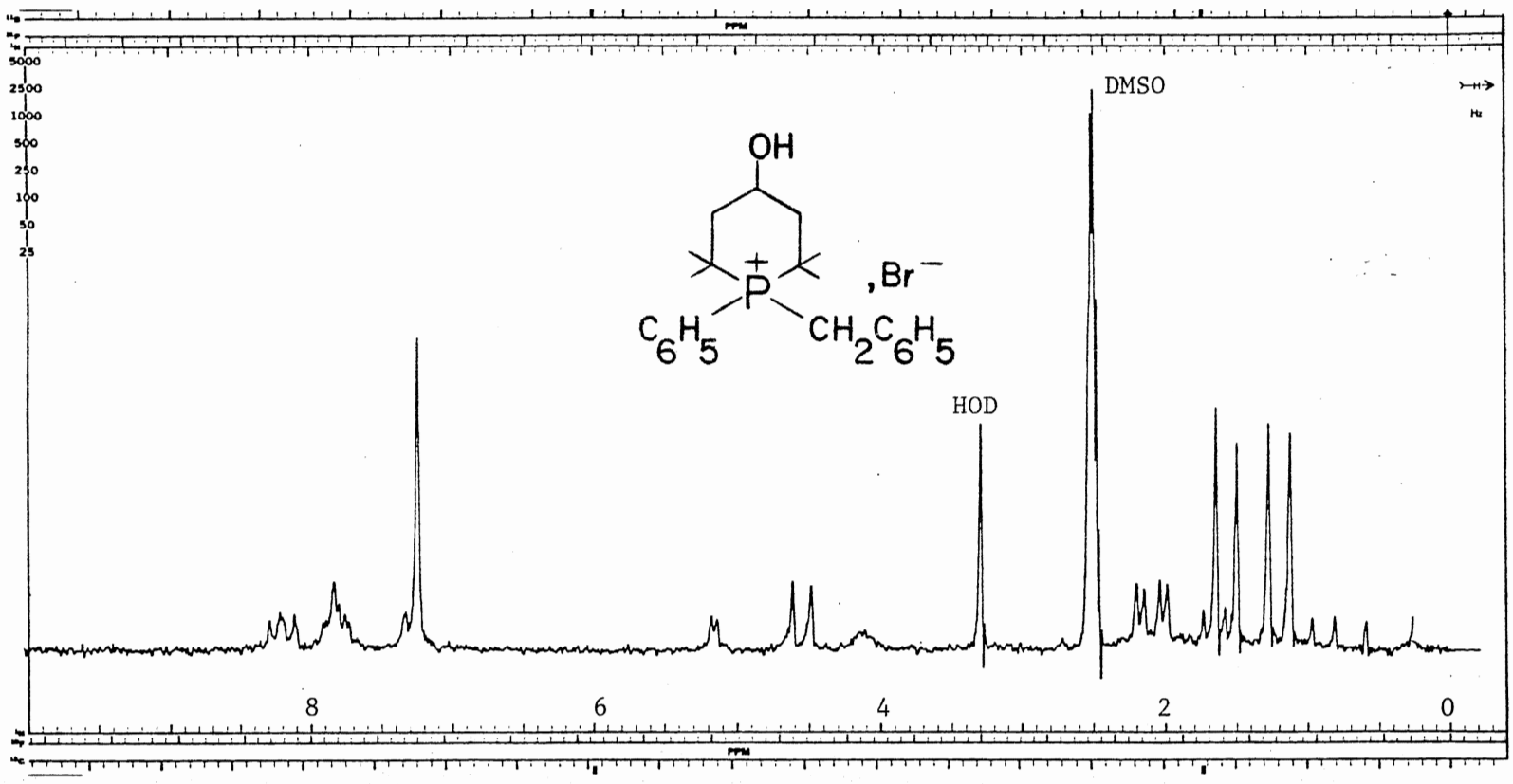
S.W. . . . . .1000 Hz S.T. . . . 250 sec. S.O. . . .83701 Hz S.A. . . . 2.5 Lock. . .^1H

PLATE XXIII



IR Spectrum of 63c, KBr Pellet

PLATE XXIV

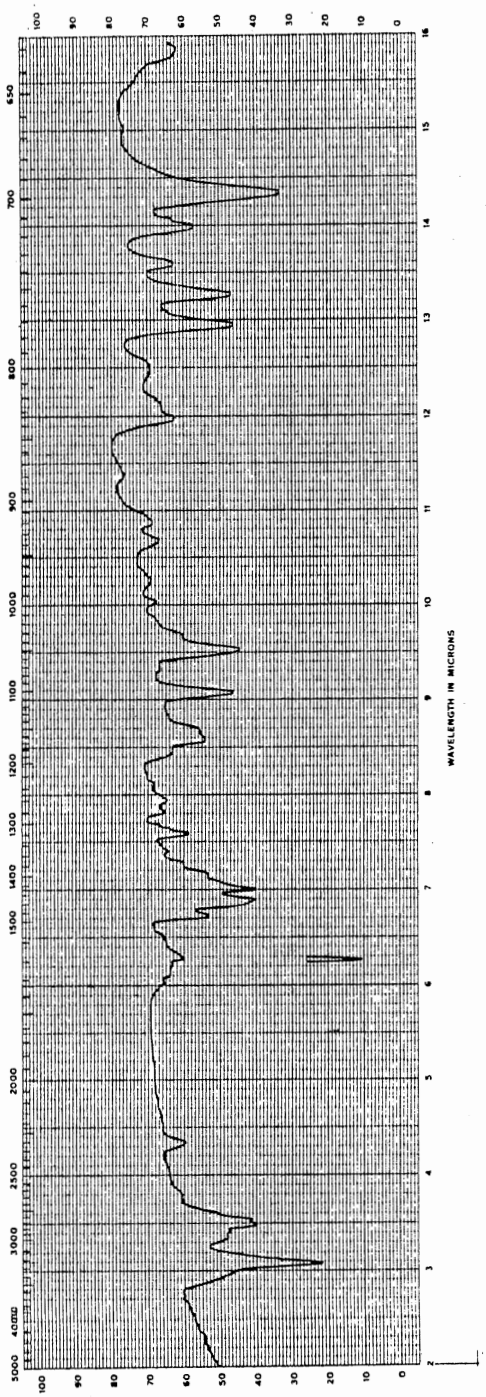


^{1}H NMR Spectrum of 1-Benzyl-2,2,6,6-tetramethyl-1-phenyl-4-phosphorinanolium Bromide (63d)

Solvent. . . . .DMSO-d_6 S.F. . . .100.1 MHz F.B. . . . 2.0 Hz R.F. . . .65dB

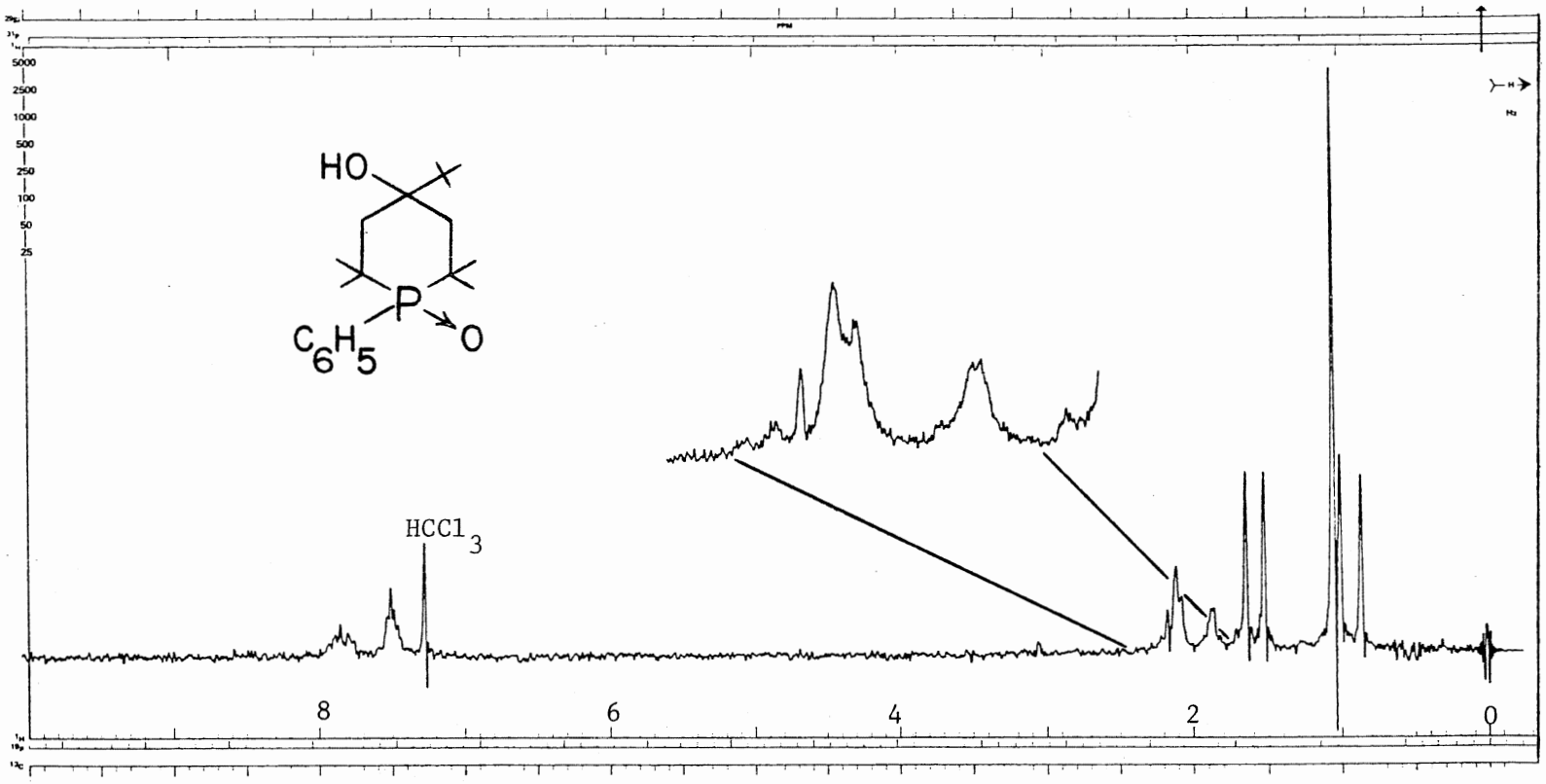
S.W. . . . . 1000 Hz S.T. . . . 250 sec. S.O. . . . .37801 Hz S.A. . . .5 Lock. . .^{1}H

PLATE XXV



IR Spectrum of 63d, KBr Pellet

PLATE XXVI

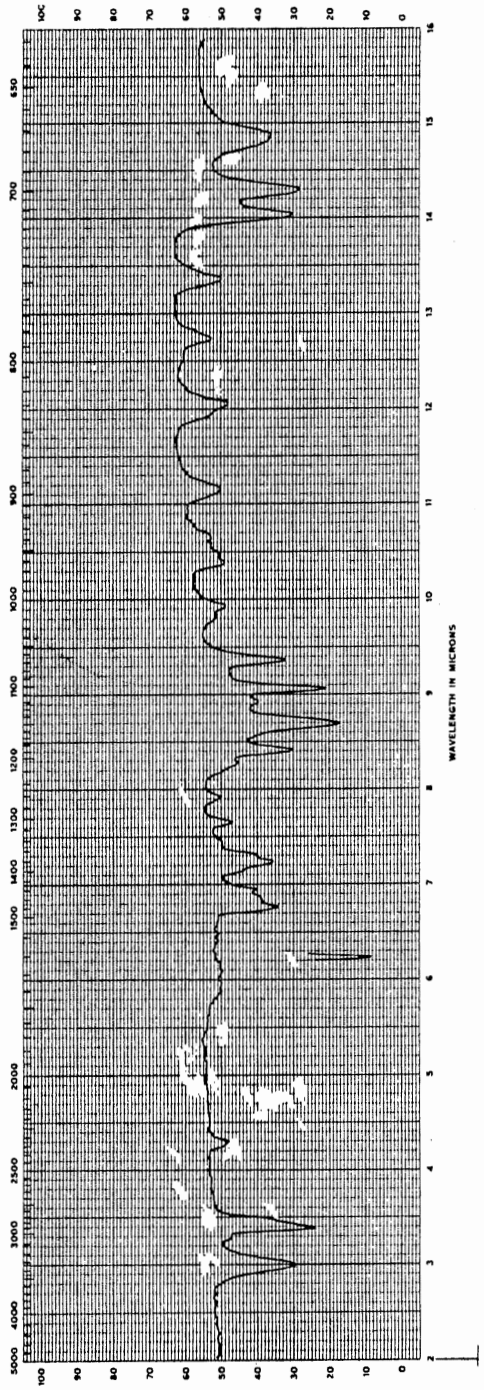


^1H NMR Spectrum of 4-tert-Butyl-2,2,6,6-tetramethyl-1-phenyl-4-phosphorinanol 1-Oxide (64)

Solvent. . . . .$DCCl_3$ S.F. . . .100.1 MHz F.B. . . . 2.0 Hz R.F. . . .62dB

S.W. . . . . .1000 Hz S.T. . . . 250 sec. S.O. . . .83701 Hz S.A. . . . 3.2 Lock. . .^1H

PLATE XXVII



IR Spectrum of 64, KBr Pellet

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Part II. CONFORMATIONAL ANALYSIS OF SELECTED 4-PHOSPHORINANONES AND DERIVATIVES

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